Stratospheric Chemistry

Environmental Chemistry, vanLoon & Duffy – Chapter 3

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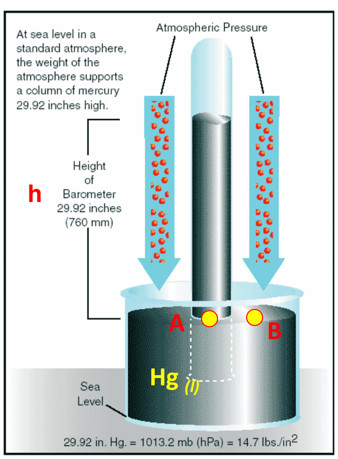
Atmospheric Pressure

The atmospheric pressure is the weight exerted by the overhead atmosphere on a unit area of surface.

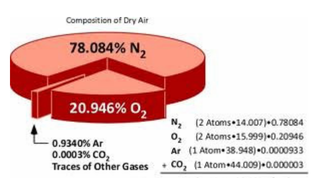


Mercury Barometer

$$P_A = \rho_{Hg} g h$$

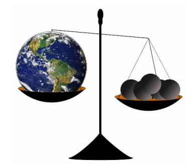
$$1\,mm\,Hg = 1\,Torr$$

$$1\,Torr = 133.32\,Pa$$



Mass of the Atmosphere

$$P_0 = \frac{m_a g}{4\pi R^2} \Rightarrow m_a = \frac{4\pi R^2 P_0}{g}$$

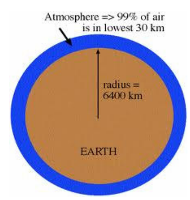


P_0 the global mean pressure at the surface,

P_0=101325 Pa.

R=6400 km, the earth radius

g=9.8 m/s^2, acceleration of gravity



Result: $m_a = 5.2 \times 10^{18}$ kg

Barometric Law

$$P_{tot}(Pa) \approx 10^{\left(5 - \frac{x}{15500}\right)}$$

$$x = \text{Height above sealevel in m}$$

$$P_h = P^0 e^{\left(-\frac{\overline{M}_a g h}{RT}\right)}$$

Better algorithm

Where

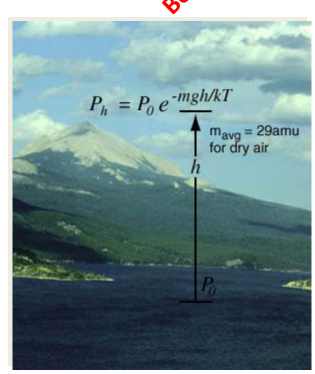
$\overline{M}_a$: *the average molecular weight of air,* ***29 g mol^{-1}***

g: acceleration of gravity, 9.81 m s^{-2}

R: gas constant, 8.314 J mol^{-1} K^{-1}

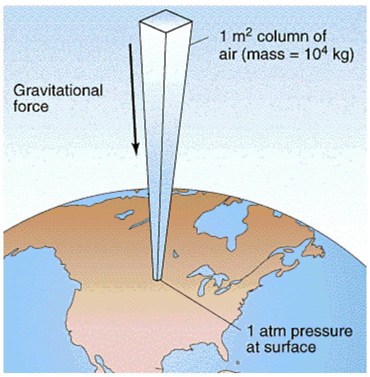
T: temperature in K

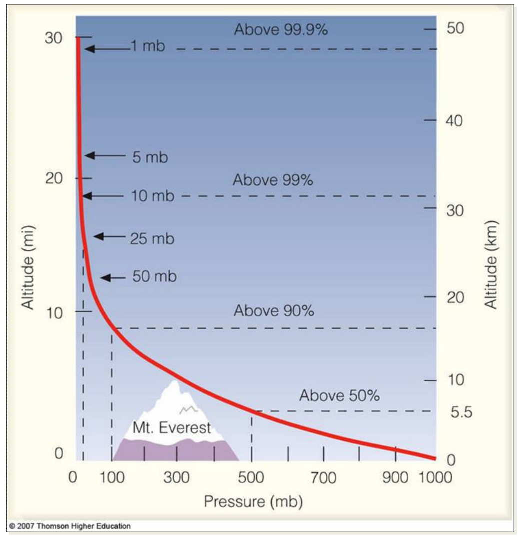
h: altitude in km



Pressure and Altitude

$$P_h = P^0 e^{\left(-\frac{\overline{M}_a g h}{RT}\right)}$$





Units of Pressure

- International System of Units: Pascal (N/m^2)
- Hectopascal (hPa)
- mm Hg or Torr
- Millibar (mbar)
- psi (lb/in^2)

1 atm = 1.01325×10^5 Pascal (Pa) = 1.01325×10^3 hPa

1 atm = 760 mm Hg = 760 Torr

1 atm = 1013.25 mbar

1 Torr = 133.32 Pa

1 atm = 14. 7 psi

Units of Pressure

	Pa = N/m²	bar	mbar	µbar = dyn/cm²	Torr = mm Hg	micron µ = mTorr	atm	at	mm WS	psi = lbf/inch²	psf = lbf/ft²
Pa	1	$1 \cdot 10^{-5}$	$1 \cdot 10^{-2}$	10	$7.5 \cdot 10^{-3}$	7.5	$9.87 \cdot 10^{-6}$	$1.02 \cdot 10^{-5}$	0.102	$1.45 \cdot 10^{-4}$	$2.09 \cdot 10^{-2}$
bar	$1 \cdot 10^{5}$	1	$1 \cdot 10^{-3}$	$1 \cdot 10^{6}$	750	$7.5 \cdot 10^{5}$	0.987	1.02	$1.02 \cdot 10^{4}$	14.5	$2.09 \cdot 10^{3}$
mbar	100	$1 \cdot 10^{-3}$	1	1,000	0.75	750	$9.87 \cdot 10^{-4}$	$1.02 \cdot 10^{-3}$	10.2	$1.45 \cdot 10^{-2}$	2.09
µbar	0.1	$1 \cdot 10^{-6}$	$1 \cdot 10^{-3}$	1	$7.5 \cdot 10^{-4}$	0.75	$9.87 \cdot 10^{-7}$	$1.02 \cdot 10^{-6}$	$1.02 \cdot 10^{-2}$	$1.45 \cdot 10^{-5}$	$2.09 \cdot 10^{-3}$
Torr	$1.33 \cdot 10^{2}$	$1.33 \cdot 10^{-3}$	1.33	1,330	1	1,000	$1.32 \cdot 10^{-3}$	$1.36 \cdot 10^{-3}$	13.6	$1.93 \cdot 10^{-2}$	2.78
micron	0.133	$1.33 \cdot 10^{-6}$	$1.33 \cdot 10^{-3}$	1.33	$1 \cdot 10^{-3}$	1	$1.32 \cdot 10^{-6}$	$1.36 \cdot 10^{-6}$	$1.36 \cdot 10^{-2}$	$1.93 \cdot 10^{-5}$	$2.78 \cdot 10^{-3}$
atm	$1.01 \cdot 10^{5}$	1.013	1,013	$1.01 \cdot 10^{6}$	760	$7.6 \cdot 10^{5}$	1	1.03	$1.03 \cdot 10^{4}$	14.7	$2.12 \cdot 10^{3}$
at	$9.81 \cdot 10^{4}$	0.981	981	$9.81 \cdot 10^{5}$	735.6	$7.36 \cdot 10^{5}$	0.968	1	$1 \cdot 10^{-4}$	14.2	$2.04 \cdot 10^{3}$
mm WC	9.81	$9.81 \cdot 10^{-5}$	$9.81 \cdot 10^{-2}$	98.1	$7.36 \cdot 10^{-2}$	73.6	$9.68 \cdot 10^{-5}$	$1 \cdot 10^{-4}$	1	$1.42 \cdot 10^{-3}$	0.204
psi	$6.89 \cdot 10^{3}$	$6.89 \cdot 10^{-2}$	68.9	$6.89 \cdot 10^{4}$	51.71	$5.17 \cdot 10^{4}$	$6.8 \cdot 10^{-2}$	$7.02 \cdot 10^{-2}$	702	1	144
psf	47.8	$4.78 \cdot 10^{-4}$	0.478	478	0.359	359	$4.72 \cdot 10^{-4}$	$4.87 \cdot 10^{-4}$	4.87	$6.94 \cdot 10^{-3}$	1

What fraction of total atmospheric mass is in the troposphere?

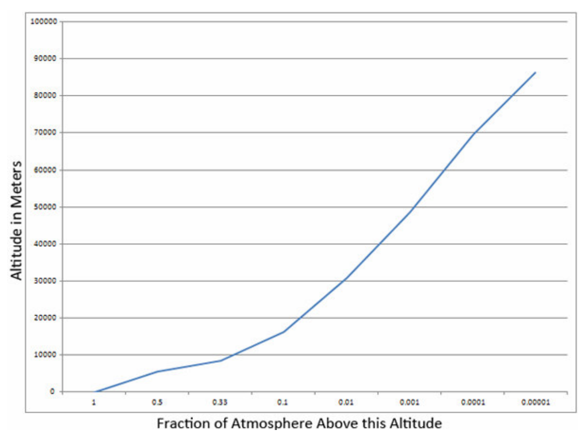
The troposphere contains all of the atmospheric mass except for the fraction: $P_{tropopause}/P_{surface}$ that lie above the tropopause.

$$F_{trop} = 1 - \frac{P_{tropopause}}{P_{surface}}$$

$P_{tropopause}$ = 100 hPa

$P_{surface}$ = 1000 hPa

Result: F_{trop} =0.90



How did the knowledge of atmospheric processes evolve?

Back to chemistry

"for their work in atmospheric chemistry, particularly concerning the formation and decomposition of ozone"

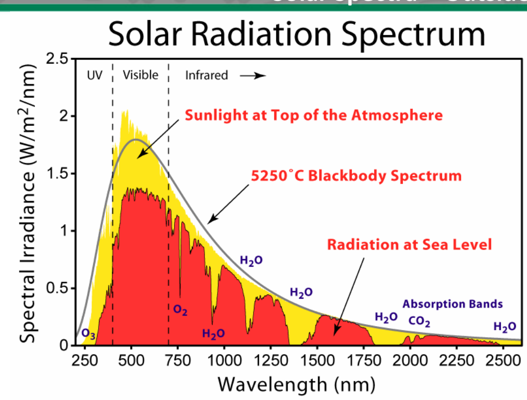
Unprecedented examples of good Science but many others supplied valuable results

Paul J. Cruzen

Mario J. Molina

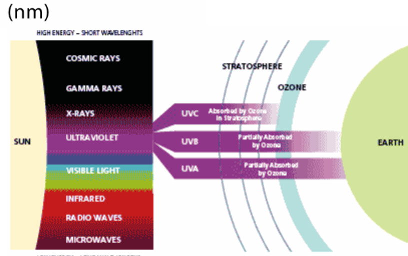
F. Sherwood Rowland

Solar Spectra - Outside & Inside

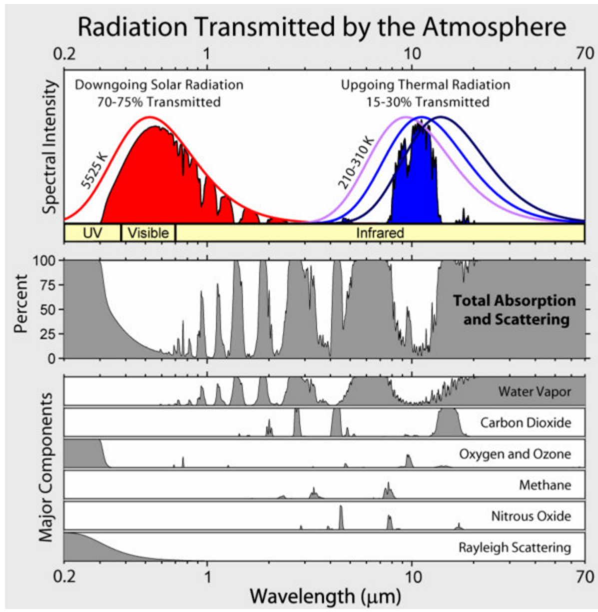


ENERGY DISTRIBUTION

100 - 300 nm	**10 %**	**UV**
300 - 800 nm	**45 %**	**Visible**
800 – 5000 nm	**45 %**	**IR**



Solar Spectra - Outside & Inside



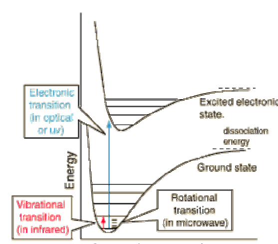
Energy Transitions

Gas molecules absorb radiation by increasing internal energy:

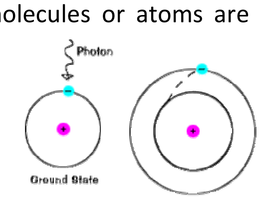
Internal energy ≡ electronic, vibrational, & rotational states.

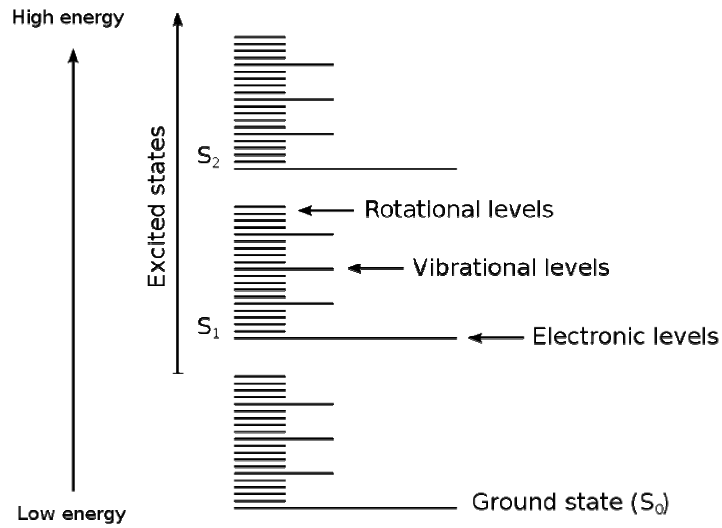
Energy requirements

- *Electronic transitions* ≡ UV (< 0.4 μm)
- *Vibrational transitions* ≡ Near-IR (0.7 < 20 μm)
- *Rotational transitions* ≡ Far-IR (> 20 μm)



Photochemical reactions occur typically when molecules or atoms are in an electronically excited state marked as X*.





Molecular energy levels

Higher energy levels of molecules are at discrete displacements from ground-state energy level.

Quantum requirement

Each molecule undergoing photochemical change absorbs one photon, the energy of which is exactly equal to the difference in energy between the ground-state energy level and one of the higher energy levels of the molecule.

Consequences of quantum requirement

Absorption of light by a molecule is wavelength dependent because energy of a photon is wavelength dependent.

Energy Transitions

- Absorption of light leads to excited molecule

  AB + hν → AB*

- Primary photochemical processes

  Ionization: AB* → $AB^+ + e^-$

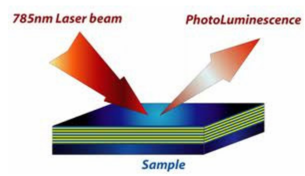
  Luminescence: AB* → AB + hν

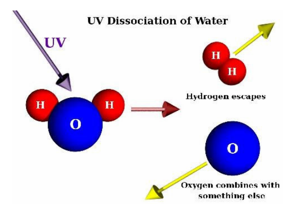
  Intermolecular energy transfer: AB*+CD → AB+CD*

  Quenching: AB* + M → AB + M

  Dissociation: AB* → A + B

  Reaction: AB* + E → C + D





Photochemistry - Examples

- Photochemical reactions – breaking a bond

  N_2 + hν → 2 N ΔH_r= 945 kJ/mol λ ≤126 nm

  O_2 + hν → 2 O ΔH_r= 498 kJ/mol λ ≤ 240 nm

- Photochemical reactions – Ionization

  N_2 + hν → $N_2^+ + e^-$ ΔH_r= 1500 kJ/mol λ ≤ 80 nm

  O + hν → $O^+ + e^-$ ΔH_r= 1310 kJ/mol λ ≤ 91 nm

- Photochemical dissociation into an excited state

  O_3 + hν → O_2*+ O* λ range 230-320 nm

- Quenching of an excited state

  O* + M → O + M + kinetic energy

Photochemistry - Examples

- Photochemical formation of radicals

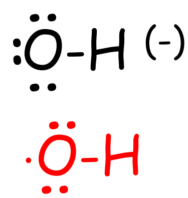
$$O^* + H_2O \rightarrow 2\ \cdot OH$$

These chemical species are very reactive oxidizing reagents

$\cdot OH + CO \rightarrow CO_2 + \cdot H$

$\cdot H + O_2 + M \rightarrow HOO\cdot + M$

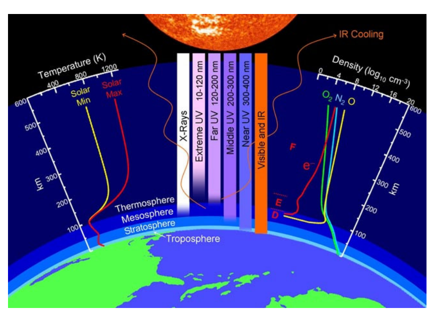
.....



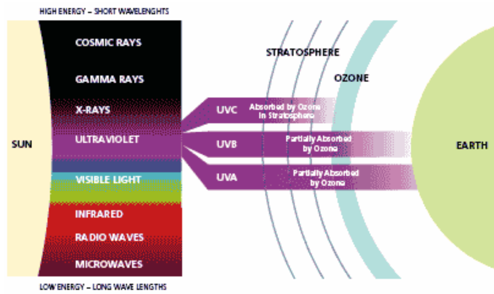
Don't confuse $\cdot OH$ with OH^- in water!

UV Absorption

- Thermospheric and Mesospheric photochemistry
  Absorption of all kind of short wavelength <200nm.
- Stratospheric photochemistry
  ~100% absorption of UV<315 nm.
  Electronic transitions of O_2 and O_3 in the stratosphere.
- Tropospheric photochemistry
  Absorption of UV<400 nm.
- And on the beach?
  Absorption of the remaining radiation.

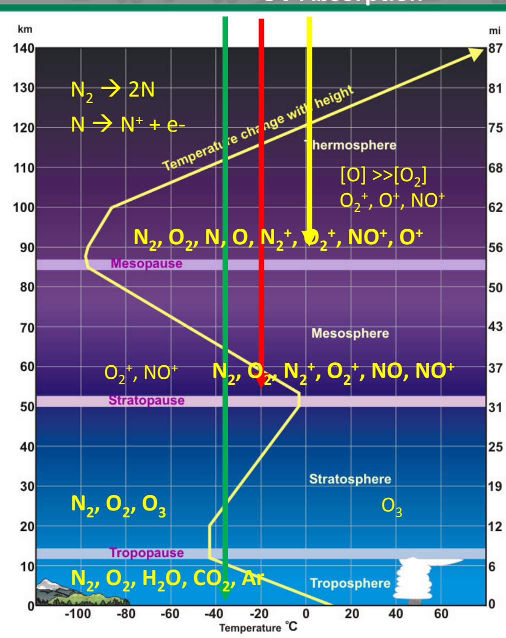


UV Absorption



Name	Abbreviation	Wavelength (nm)	Energy per photon
Ultraviolet A	UVA	400 nm–315 nm	3.10–3.94 eV
Ultraviolet B	UVB	315 nm–280 nm	3.94–4.43 eV
Ultraviolet C	UVC	280 nm–100 nm	4.43–12.4 eV

UV Absorption



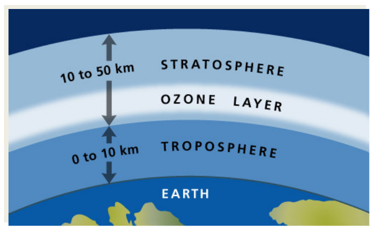
Individual Processes: Ozone & Ozone Hole

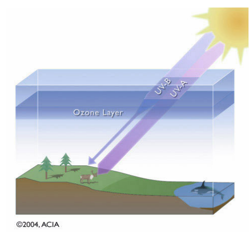
The Ozone Layer *(Definition by NASA)*

"The ozone layer" refers to the ozone within stratosphere, where over 90% of the earth's ozone resides.

Ozone is an irritating, corrosive, colorless gas with a smell something like burning electrical wiring.

Each molecule of ozone has three oxygen atoms and is produced when oxygen molecules (O_2) are broken up by energetic electrons or high energy radiation.



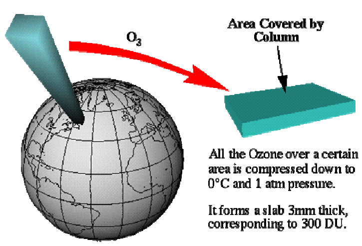


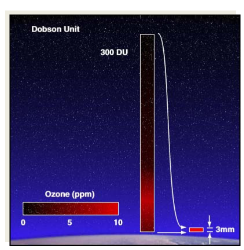
The Ozone Hole

Ozone – O_3 a gas present in small conc. throughout the atmosphere.

Total overhead amount expressed in terms of *Dobson Units.*

1DU = 0.01 mm thickness of O_3 when brought to ground level (1 atm) at 0°C

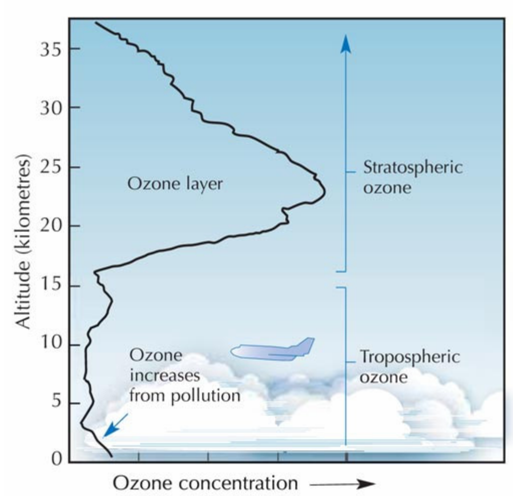




Normal amount is 350 DU at temperate latitudes (thus, a layer of only 3.5 mm thickness keeps away all the UV-radiation).

Ozone Formation: Chapman Theory

Chapman theory describes how sunlight converts the various forms of oxygen from one to another, explains why the highest contents of ozone occur in the layer between 15 and 50 km, termed the ozone layer



Photochemical O_3 - Ozone Formation: Chapman Theory

Both synthesis and decomposition of ozone in the stratosphere may be described in terms of chemistry involving only oxygen-containing species.

This was first described by Chapman and involves 4 fundamental reactions.

There is a lot of bright light at an altitude of 15 km:

Now we need all the terms that we studied recently

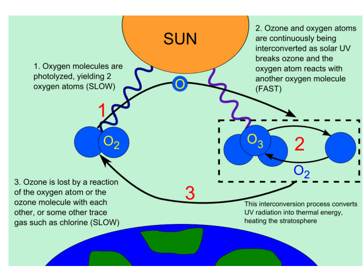
photon energy

activation energy

catalyst

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

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

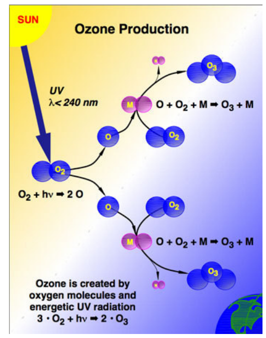


Photochemical O_3 - Ozone Formation: Chapman Theory

Formation of Ozone - Reaction step 1 - slow

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

$\Delta H_{reac} = 2\ \Delta H_f(O_{(g)}) - \Delta H_f\ (O_{2(g)}) = 498$ kJ/mol ($\lambda = 240$ nm)



Formation of Ozone - Reaction step 2 - fast

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

$\Delta H_{reac} = \Delta H_f(O_{3(g)}) - \Delta H_f\ (O_{2(g)}) - \Delta H_f(O_{(g)}) = -106$ kJ/mol

M is kind of a catalyst, a neutral third body, an O_2 or N_2 molecule.

Photochemical O_3 - Ozone Destruction: Chapman Theory

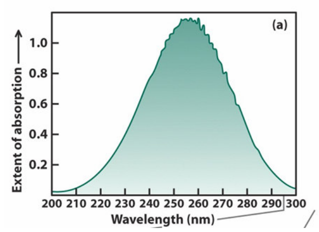
Photochemical dissociation:

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

$\Delta H_{reac} = \Delta H_f\ (O_{2(g)}) + \Delta H_f(O_{(g)}) - \Delta H_f(O_{3(g)})$
= 106 kJ/mol

equivalent to λ=1125 nm

but Ozone absorbs UV-light



Thus the reaction doesn't proceed that way, it leads to two molecules in an excited state:

$O_3 + h\nu \rightarrow O_2^* + O^*$

$\Delta H_{reac} = \Delta H_f\ (O_{2(g)}) + E_e(O_2) + \Delta H_f(O_{(g)}) + E_e(O) - \Delta H_f(O_{3(g)}) = 387$ kJ/mol

equivalent to λ= 308nm

Photochemical O_3 - Ozone Destruction: Chapman Theory

Decomposition of Ozone – reaction 2 - slow

$O + O_3 \rightarrow O_2 + O_2$

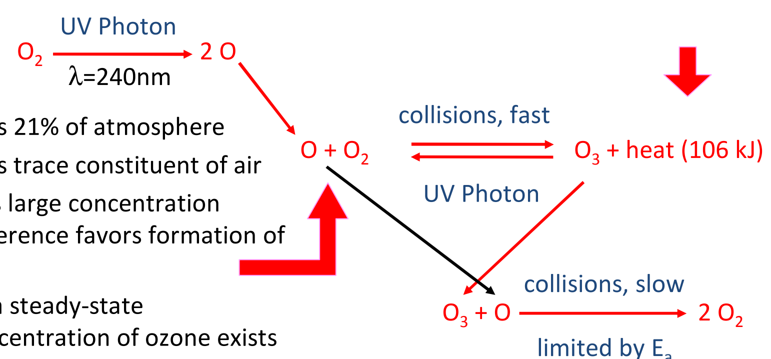
ΔH_{reac}= - 392 kJ/mol

The reactions of formation and destruction are controlled by radiation intensity and availability of O_2-molecules:

- Radiation increases with the altitude
- availability of O_2-molecules decreases with the altitude

Explains a Steady State of the Stratospheric Ozone

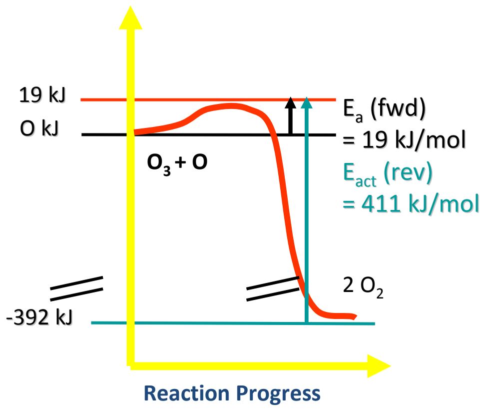
- Heat generated by this reaction warms stratosphere
- Warmer air lies above cooler air
- Slow vertical mixing in this atmospheric layer.
- Hence, air is stratified in the stratosphere



- O_2 is 21% of atmosphere
- O_3 is trace constituent of air
- This large concentration difference favors formation of O_3
- So a steady-state concentration of ozone exists based on *Chapman* Cycle

Arrhenius equation relates *k*, *T*, E_a, and orientation

$$k = Ae^{\frac{-E_a}{RT}}$$



A Key reaction in the upper atmosphere is

O_3 (g) + O (g) ↔ 2O_2 (g)

The E_a (fwd) is 19 kJ, and the ΔH_{rxn} as written is -392 kJ.

A reaction energy diagram for this reaction with the calculated E_a(rev) is shown.

In the previous section, we have seen that there are “natural” photochemical and chemical processes that lead to the continuous formation and destruction of ozone in the stratosphere.

The balance between these processes would result in a steady-state situation with a well-defined and stable ozone layer.

BUT !!!!!! oxygen-only chemistry does not explain the present situation.

Some chemicals (natural and anthropogenic) are involved in the destruction of the ozone. These chemicals are released in the troposphere and then move up into the stratosphere and take part in the catalytic ozone-consuming processes.

$X + O_3 \rightarrow XO + O_2$

$XO + O \rightarrow X + O_2$

Net: $O + O_3 \rightarrow 2\ O_2$

X is a free radical (odd electron species):
- HO_x which includes •H, •OH, and HOO•
- NO_x which includes •NO and •NO_2
- ClO_x which includes •Cl and ClO•

Depending on altitude and the mixing ratio, each of these species has varying ability to destroy ozone.

High stratosphere (near the stratopause), HO_x account for 70% of the ozone.

Lower in the stratosphere (~30 Km), NO_x catalytic decomposition cycle dominates.

Near the tropopause, NO_x account for 70% of the ozone destruction.

Mechanism I

Occurs in mid- and upper stratosphere

$X + O_3 \rightarrow XO + O_2$

$XO + O \rightarrow X + O_2$

Net: $O + O_3 \rightarrow 2\ O_2$

Mechanism II

Occurs in low stratosphere

$X + O_3 \rightarrow XO + O_2$

$X' + O_3 \rightarrow X'O + O_2$

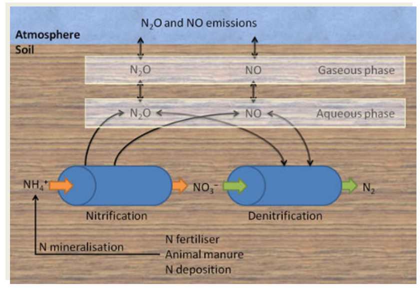
$XO + X'O \rightarrow X + X' + O_2$

Net: $2\ O_3 \rightarrow 3\ O_2$

X is a free radical (odd electron species) and can be NO•, Cl•, OH•, Br• & (not O•)

Ozone Destruction Catalysts : NOx Cycle

In 1970, *Paul Crutzen* showed that the nitrogen oxides NO and NO_2 react catalytically (without themselves being consumed) with ozone, thus accelerating the rate of reduction of the ozone content.



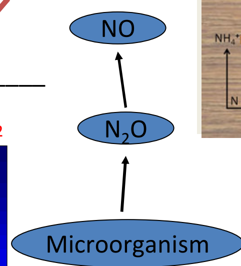
$NO + O_3 \rightarrow NO_2 + O_2$

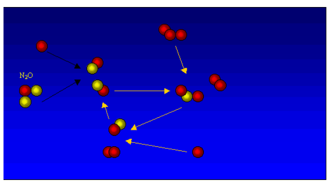
$NO_2 + O \rightarrow NO + O_2$

$O_3 + \text{UV-light} \rightarrow O_2 + O$

____

Net result: $2\ O_3 \rightarrow 3\ O_2$





Ozone Destruction Catalysts : NOx Cycle

NO is generated via the following reactions depending on the altitude:

Rxn 1 (altitudes > 30 Km):

$N_2 + h\nu\ (\lambda < 126\ nm) \rightarrow N(^4S) + N(^2D)$

$N(^4S) + O_2 \rightarrow NO + O$

N*

Rxn 2 (altitudes < 30 Km):

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

O*

$O(^1D)$ excited state atomic oxygen

$N(^2D)$: electronically excited N* (2s+1=2)

$N(^4S)$: ground state N resulting in another natural source of nitric acid that can take part in the catalytic process according the usual pattern. (2s+1=4)

This set of catalytic reactions depends on the availability of a source of hydrogen to combine with the plentiful supply of oxygen throughout the stratosphere.

The most important sources are Water or Methane.

At the tropopause, the water is in the form of ice and thus do not cross the boundary into the stratosphere. Thus the stratosphere is a relatively dry portion of the atmosphere.

Methane does not freeze out, thus some of it will go to the stratosphere. In the upper part of the stratosphere, hydrogen will be taken out from the methane through some photochemical reactions involving oxygen species. Thus water is formed in the stratosphere.

•OH radicals are generated by either one of these reactions:

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

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

$O(^3P) \equiv O$

$O(^1D) \equiv O^*$

$$\bullet OH + O_3 \rightarrow HOO\bullet + O_2$$

$$HOO\bullet + O \rightarrow \bullet OH + O_2$$

Net: $O + O_3 \rightarrow 2\ O_2$

$$\bullet H + O_3 \rightarrow \bullet HO + O_2$$

$$HO\bullet + O \rightarrow \bullet H + O_2$$

Net: $O + O_3 \rightarrow 2\ O_2$

Chlorine and chlorine-containing radicals (•Cl and •ClO, and their bromine analogues) are the most reactive of all the stratospheric species that catalyze ozone destruction.

Sources:

-Natural: Methyl chloride (CH_3Cl) produced and released by biological reactions throughout the oceans and in much amount from the burning of vegetation and volcanic emissions.

$$CH_3Cl + h\nu \rightarrow \bullet CH_3 + \bullet Cl$$

Not all ocean-derived methyl chloride reaches the stratosphere. They are removed at lower altitudes by reaction with hydroxyl radicals:

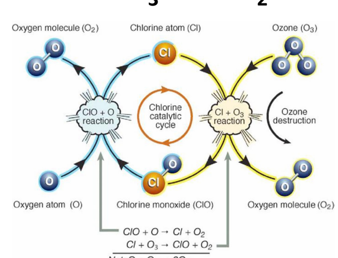
$$CH_3Cl + \bullet OH \rightarrow \bullet CH_2Cl + H_2O$$

Hydrochloric acid (HCl) release from volcanoes and chloride ions arising from the sea-salt spray are eliminated from the atmosphere by rain before reaching the stratosphere.

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

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

Net: $O + O_3 \rightarrow 2\ O_2$



$$HOO\bullet + ClO\bullet \rightarrow HOCl + O_2$$

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

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

$$\bullet OH + O_3 \rightarrow HOO\bullet + O_2$$

Net: $2O_3 \rightarrow 3\ O_2$

Br can also replace Cl in this mechanism

Ozone Destruction Catalysts : ClOx Cycle

BrO• + ClO• → •Br + •Cl + O_2

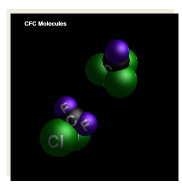
•Br + O_3 → BrO• + O_2

•Cl + O_3 → ClO• + O_2

Net: $2O_3$ → 3 O_2

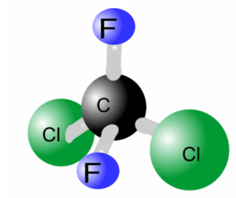
Chlorofluorocarbons (CFCs)

- CFCs is the abbreviated form of ChloroFluoroCarbons, a collective name given to a series of compounds containing chlorine, fluorine and carbon atoms. Examples: $CFCl_3$, CF_2Cl_2, and $CF_2ClCFCl_2$.



- Related names
  - HCFCs: Hydrochloroflorocarbons, halocarbons containing hydrogen atoms in addition to chlorine, fluorine and carbon atoms.
  - HFCs: hydroflorocarbons, halocarbons containing atoms of hydrogen in addition to fluorine and carbon atoms.
  - Perhalocarbons: halocarbons in which every available carbon bond contains a haloatom.
  - Halons: bromine-containing halocarbons, especially used as fire extinguishing agents.

Chlorofluorocarbons (CFCs)



CFC-XYZ

1) Z = number of fluorine atoms.
2) Y =1 + number of hydrogen atoms.
3) X = number of carbon atoms -1
   When X=0 (i.e., only one carbon compound), it is omitted.
4) The number of chlorine atoms in the compound is found by subtracting the sum of fluorine and hydrogen atoms from the total number of atoms that can be connected to the carbon atoms.
5) Examples:
   - CCl_2F_2 (CFC-12, refrigerant)
   - CCl_3F (CFC-11, blowing agent)
   - $CHClF_2$ (CFC-22, refrigerant, blowing agent)
   - $C_2Cl_2F_4$ (CFC-114)

CFCs are biologically and chemically inert in the troposphere.

Chlorofluorocarbons (CFCs)

Sources of Cl·: Photolysis of Cl-containing compounds

$$CFCl_3 + h\nu\ (185\text{-}210nm) \rightarrow \bullet CFCl_2 + \bullet Cl$$

$$CF_2Cl_2 + h\nu\ (185\text{-}210nm) \rightarrow \bullet CF_2Cl + \bullet Cl$$

Subsequent reactions of $\bullet CFCl_2$ and $\bullet CF_2Cl \rightarrow$ more Cl atoms

The principal Cl-containing species are:

CF_2Cl_2, $CFCl_3$, $CFCl_2$, CF_2Cl, CCl_4, CH_3CCl_3, CF_2HCl, CH_3Cl

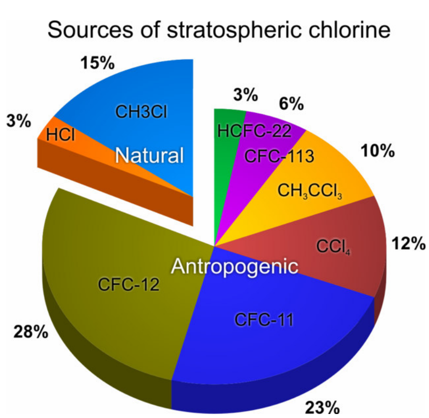
Sources for Cl-containing compounds (need to be long-lived in the troposphere)

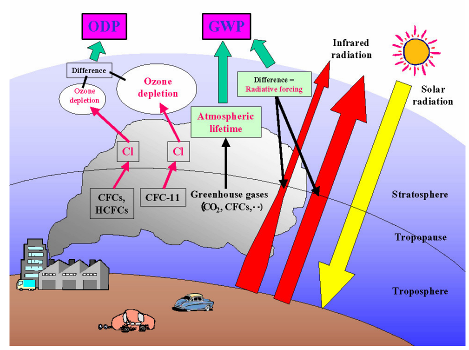
- Man-made: e.g. CFCs
- Natural: e.g. methyl chloride from biomass burning and volcanoes.

Chlorofluorocarbons (CFCs)

Compound	(CFC No.)	Lifetime (yr)	Conc. (ppbv)
$CFCl_3$	11	70	0.8
CF_2Cl_2	12	110	1.0
CHF_2Cl_2	22	25	
$CF_2ClCFCl_2$	113	90	0.2
CH_3CCl_3		<10	0.5
CCl_4		10	0.6
CH_3Cl	natural		0.6

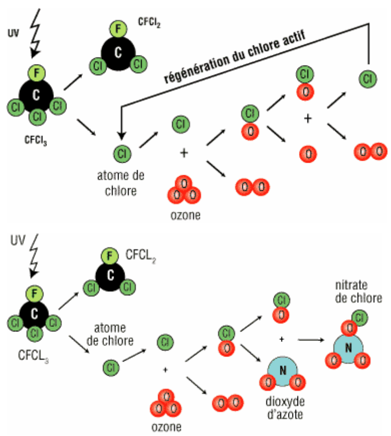
Chlorofluorocarbons (CFCs)

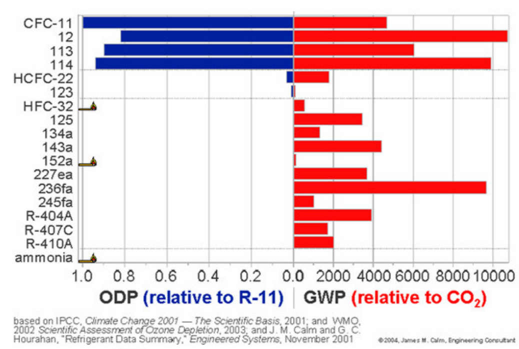




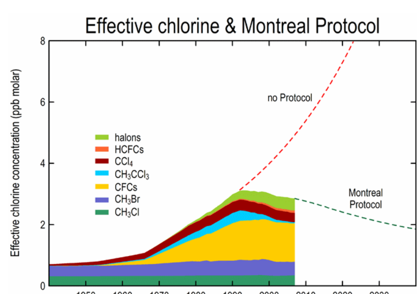
Chlorofluorocarbons (CFCs)

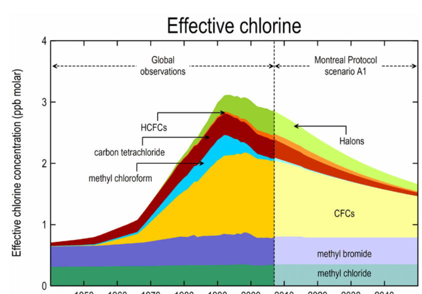
$$\textbf{ODP} = \frac{\text{Long-term impact on ozone from a known mass of a specific chemical}}{\text{Long-term impact on ozone from the same mass of CFC-11}}$$

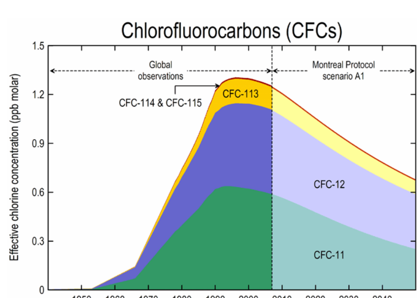


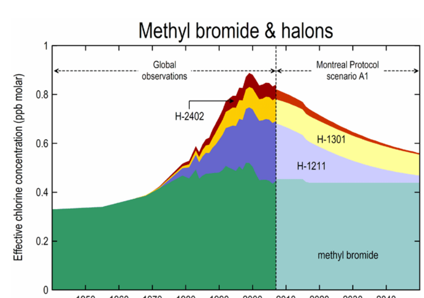


Chlorofluorocarbons (CFCs)

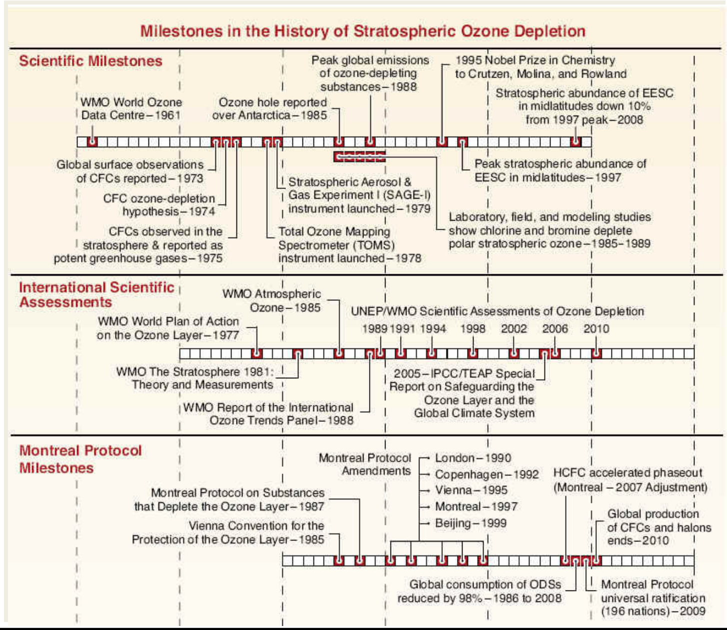








Chlorofluorocarbons (CFCs)



Chlorofluorocarbons (CFCs)

More Facts:

•Rate of O_3 formation depends upon $[O_2]$, $[O_3]$, & UV-light intensity at a given altitude.

•Rate of O_3 destruction is more complex. It depends upon $[O_3]$ x sunlight Intensity x [X].

•Each •Cl can destroy as many as 10,000 O_3 molecules.

•Besides •Cl there are many other catalytic compounds.

•When above opposing rates are equal, then a steady state is reached and $[O_3]$ is constant.

Null (do nothing) cycles interconvert the species X and XO while effecting no net odd oxygen removal.

Null cycles involving nitrogen oxides are:

$$NO + O_3 \rightarrow NO_2 + O_2$$

$$NO_2 + h\nu \rightarrow NO + O$$

$$\mathbf{O_3 + h\nu \rightarrow O + O_2}$$

This sequence compete with the catalytic NOx cycle and is important only during daytime as it requires near-ultraviolet radiation for the photolytic step.

O_3 is rapidly formed according to

$$\mathbf{O + O_2 + M \rightarrow O_3 + M}$$

Another reaction involving NO_2 results in production of NO3 and the establishment of another null cycle:

$$NO_2 + O_3 \rightarrow NO_3 + O_2$$

$$NO_3 + h\nu \rightarrow NO_2 + O$$

$$\mathbf{O_3 + h\nu \rightarrow O + O_2}$$

Other Reactions Involving Stratospheric Ozone: Holding Cycles

In addition to taking part in the null cycle, some of the NO3 reacts in a three-body process to produce N_2O_5:

$$NO + O_3 \rightarrow NO_2 + O_2$$

$$NO_2 + O_3 \rightarrow NO_3 + O_2$$

$$\left\{\begin{array}{l} NO_3 + NO_2 + M \rightarrow N_2O_5 + M \\ N_2O_5 + h\nu \rightarrow NO_2 + NO_3 \end{array}\right.$$

N_2O_5 acts as a relatively stable reservoir of NO_x, and is itself not a catalyst for ozone destruction.

It makes up 5 to 10% of the total NO_x.

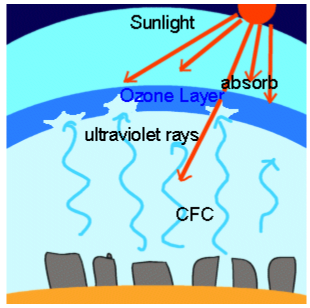
Other Reactions Involving Stratospheric Ozone: Holding Cycles

- $NO_3 + NO_2 + M \rightarrow N_2O_5 + M$
- $Cl\bullet + CH_4 \rightarrow \bullet CH_3 + HCl$
- $OH\bullet + \bullet NO_2 + M \rightarrow HNO_3 + M$
- $HO_2\bullet + \bullet NO_2 + M \rightarrow HO_2NO_2$ (pernitric acid) + M
- $ClO\bullet + HO_2\bullet \rightarrow HOCl$ (hypochlorous acid) + O_2
- $ClO\bullet + \bullet NO_2 \rightarrow ClONO_2$ (chlorine nitrate) + M

Reservoir being formed and destroyed → but due to relatively long lifetime, at any given time a portion of active species is sequested in reservoir species.

Unexpected conversion to active species has large consequences

Antarctic and Arctic “Ozone Hole” Formation

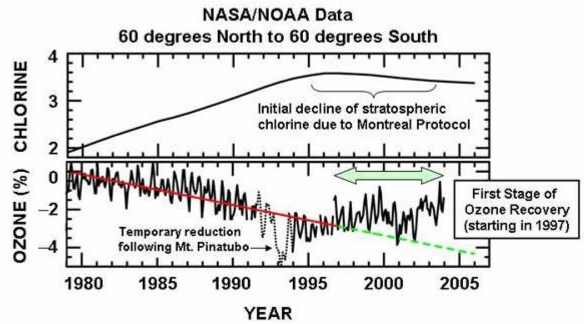


Antarctic and Arctic “Ozone Hole” Formation

The Antarctic ozone hole was discovered in 1985 by British scientists Joseph Farman, Brian Gardiner, and Jonathan Shanklin of the British Antarctic Survey.

The ozone "hole" is really a reduction in concentrations of ozone high above the earth in the stratosphere. The ozone hole is defined geographically as the area wherein the total ozone amount is less than 220 Dobson Units. The ozone hole has steadily grown in size (up to 27 million sq. km.) and length of existence (from August through early December) over the past two decades.

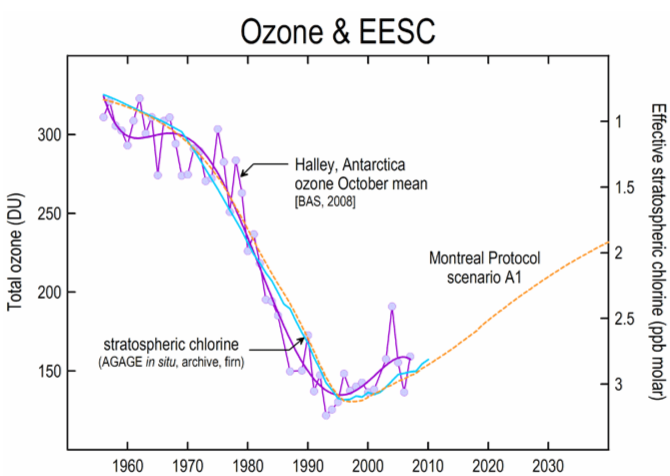
Antarctic and Arctic "Ozone Hole" Formation



NASA/NOAA satellite data showing the rise in stratospheric chlorine and corresponding decline in ozone layer thickness from 1979 to 1997. As stratospheric chlorine declined in response to enactment of the Montreal Protocol, the first stage of ozone recovery began.

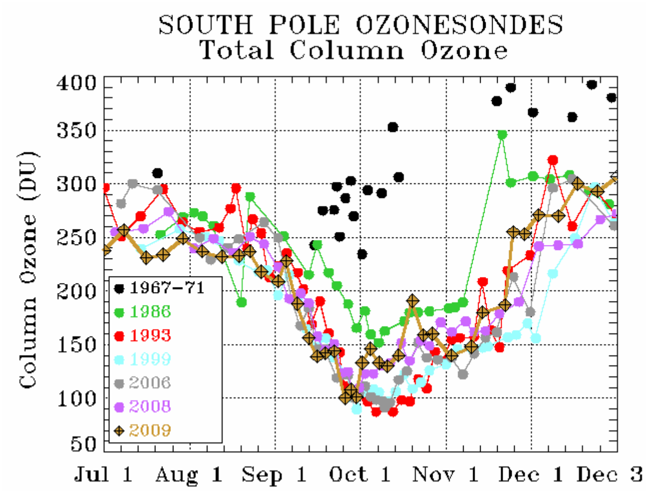
The Montreal Protocol stipulates that the production and consumption of compounds that deplete ozone in the stratosphere--chlorofluorocarbons (CFCs), halons, carbon tetrachloride, and methyl chloroform--are to be phased out by 2000 (2005 for methyl chloroform).

Antarctic and Arctic "Ozone Hole" Formation

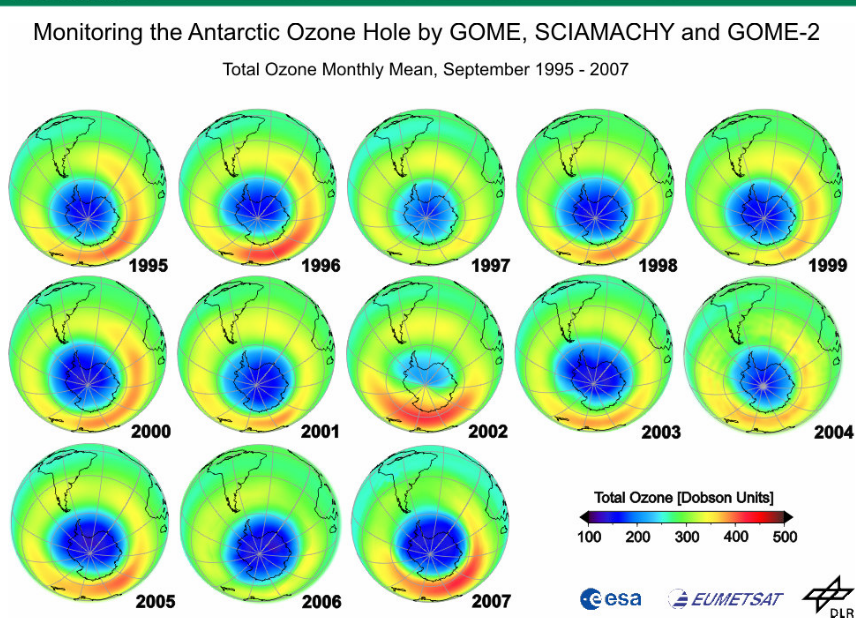


Consistency of ground- and satellite-based measurements of total ozone trends over Antarctica.

Antarctic and Arctic "Ozone Hole" Formation



Antarctic and Arctic "Ozone Hole" Formation



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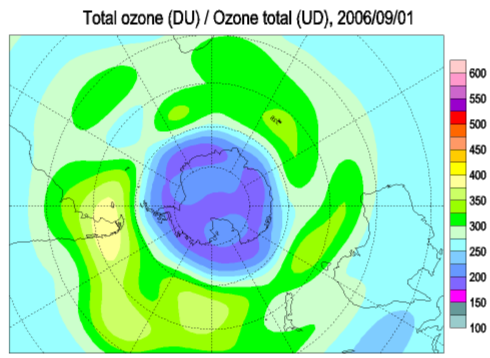
Antarctic and Arctic “Ozone Hole” Formation



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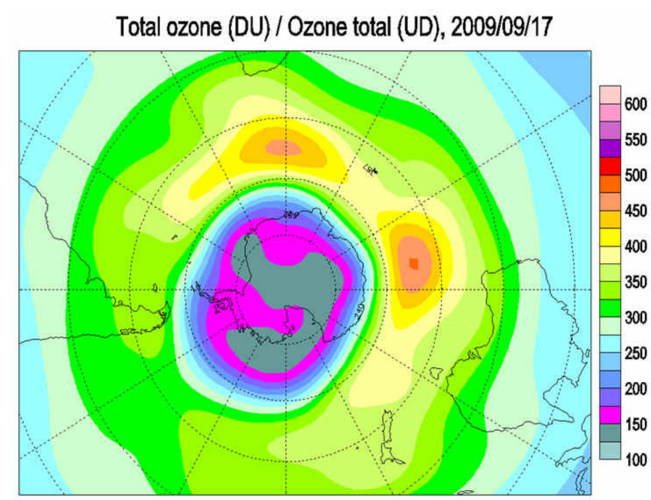
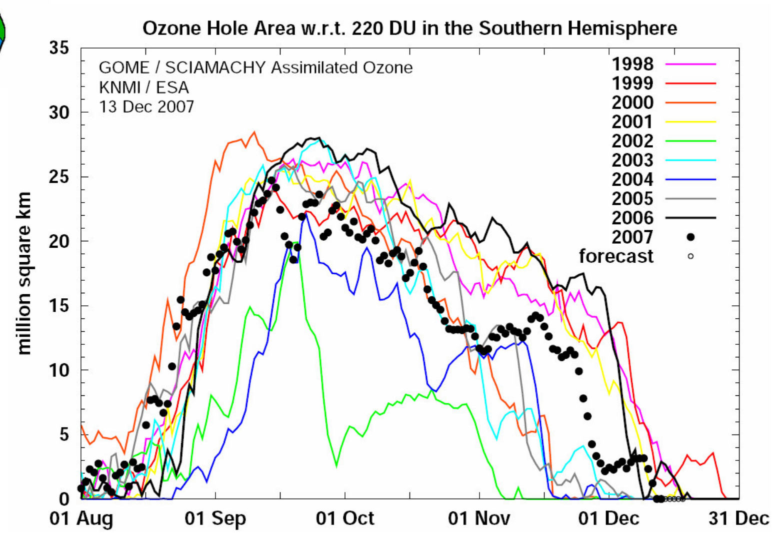
Antarctic and Arctic “Ozone Hole” Formation



In 2009, the ozone hole reached its 10th largest measured size since careful measurements began in 1979.The daily maximum ozone hole area for 2009 was 24 million km^2 on 17 September.

Antarctic and Arctic "Ozone Hole" Formation

Hole in the Ozone Layer?



Antarctic and Arctic "Ozone Hole" Formation

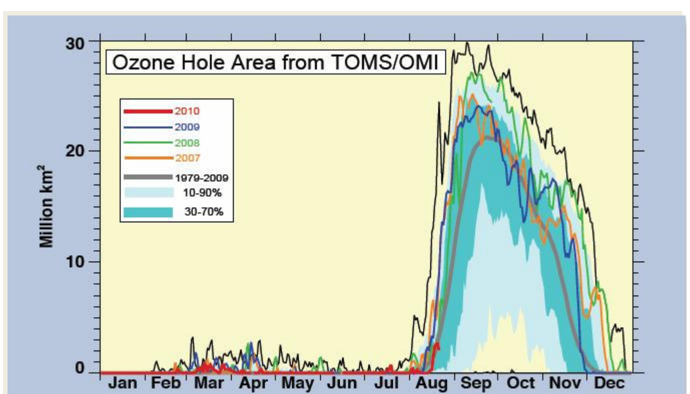
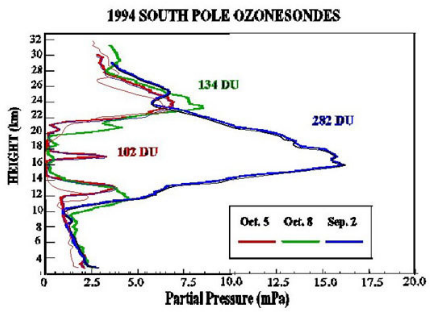


Figure 10. Area (millions of km^2) where the total ozone column is less than 220 Dobson units. 2010 is showed in red (until 17 August). 2009 is shown in blue, 2008 in green and 2007 in orange. The smooth grey line is the 1979-2009 average. The dark green-blue shaded area represents the 30th to 70th percentiles and the light green-blue shaded area represents the 10th and 90th percentiles for the time period 1979-2009. The plot is adapted from a plot downloaded from the NASA Ozonewatch web site and is based on data from the OMI instrument on AURA and various TOMS instruments.

Antarctic and Arctic “Ozone Hole” Formation

Antarctic Ozone Measurements vs Altitude



Ozone partial pressure (mPA) profiles at the South Pole, measured by balloon- borne ozonesondes. The profile on 2 September 1994, before depletion began, is compared with profiles for 5 October and 8 October 1994, during the minimum ozone period.

(from NOAA/CMDL home page http://www.cmdl.noaa.gov)

- Strong depletion between 12 and 20 km.
- Gas phase chemistry predicted decrease near 40 km.

Antarctic and Arctic “Ozone Hole” Formation

During the long dark winter and due to polar low T as well as the rotation of Earth, a giant Vortex is created which can be considered as a self-contained chemical reactor in which important and unique chemical processes occur.

Inside the reactor, stratospheric clouds form as a result of exceptionally low temperatures that exist under conditions of no sunlight.

Polar Stratospheric Clouds (PSCs)

Type I

- believed to consist of nitric acid trihydrate (NAT) ($HNO_3.3H_2O$)
- exist at T of about 193 K (Arctic)
- particle diameters ~1 µm

Type II (less common)

- consist of ice particles
- condense at T of about 187 K (Antarctic)
- grow to diameters 10^+µm

Antarctic and Arctic “Ozone Hole” Formation

Antarctic and Arctic “Ozone Hole” Formation

Within the vortex, accumulated gases-reservoir chlorine- and nitrogen-containing species also exist.

During the winter, on the surface of these PSCs, the following heterogeneous reactions take place:

$HCl + ClONO_2 \rightarrow HNO_3 + Cl_2$

$H_2O + ClONO_2 \rightarrow HOCl + HNO_3$

$HOCl + HCl \rightarrow Cl_2 + H_2O$

In late October, the solar radiation provides energy for photolysis:

$Cl_2 + hv \rightarrow 2 \bullet Cl$

$HOCl + hv \rightarrow \bullet Cl + \bullet OH$

Antarctic and Arctic "Ozone Hole" Formation

This situation persists until the air temperature rises, causing the vortex to break up and the PSC to dissipate.

The presence of atomic oxygen is unnecessary for depletion to occur through a type II mechanism:

$2\ \bullet Cl + 2O_3 \rightarrow 2ClO\bullet + 2O_2$

$ClO\bullet + ClO\bullet \rightarrow ClOOCl$

$ClOOCl + h\nu \rightarrow ClOO\bullet + \bullet Cl$

$ClOO\bullet \rightarrow \bullet Cl + O_2$

Here X = X' = Cl

Antarctic and Arctic "Ozone Hole" Formation