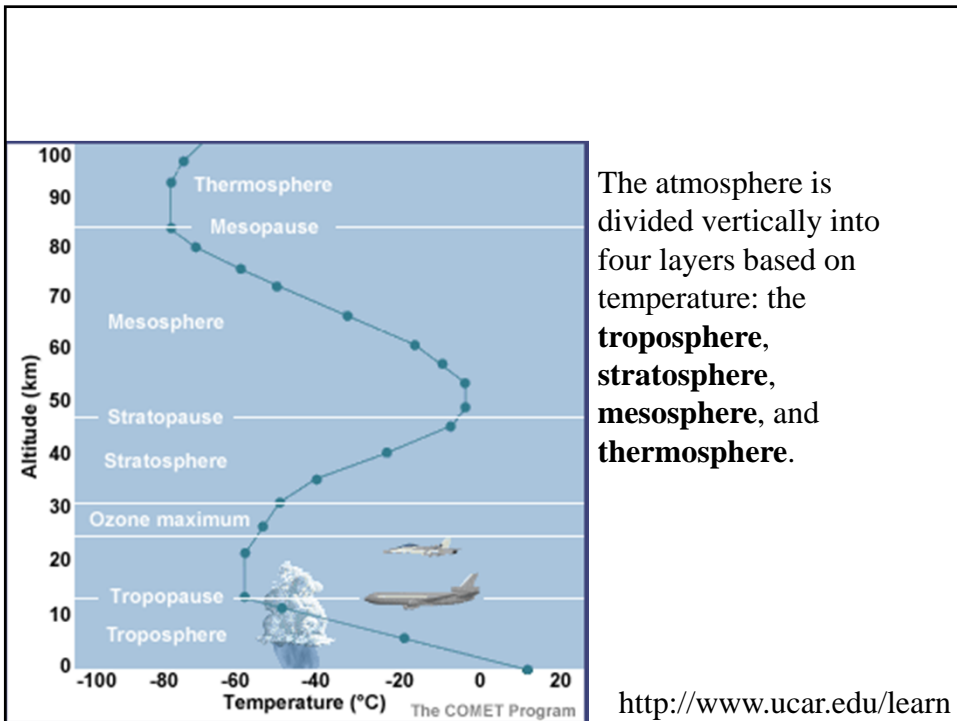
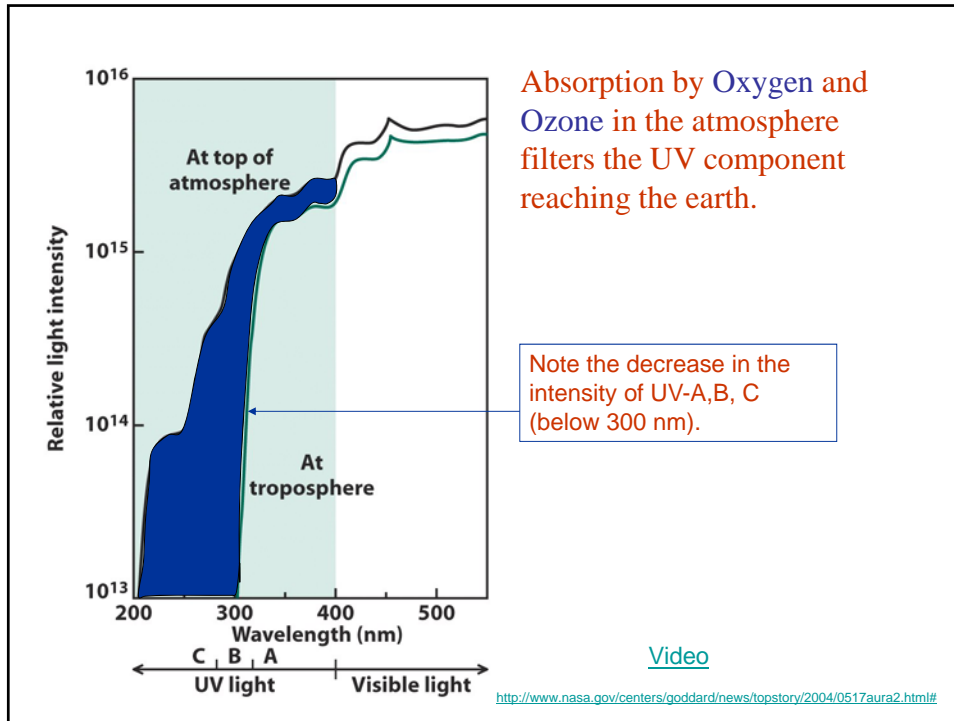
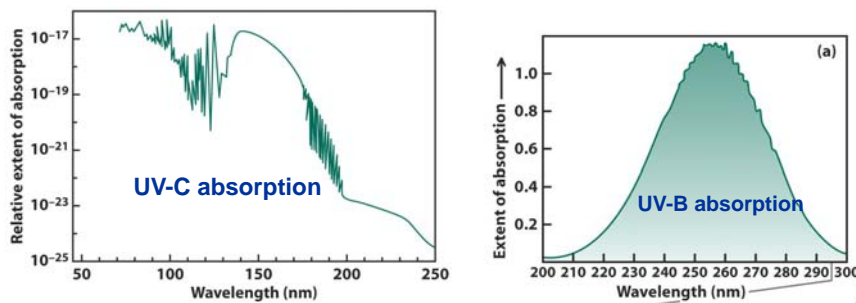


## The Ozone Chemistry





### Absorption of UV light by Oxygen and Ozone



Ozone effectively absorbs the most energetic ultraviolet light, known as UV-C and UV-B, which causes biological damage

## Review:

UV Photons are energetic and can induce chemical reactions in biological and environmental systems.

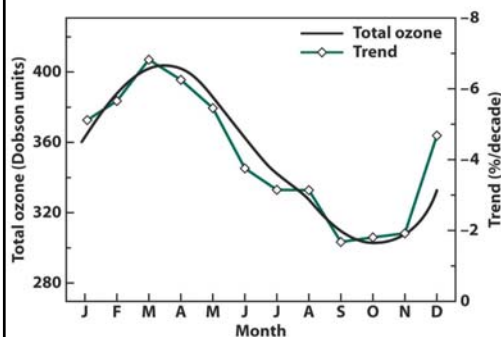
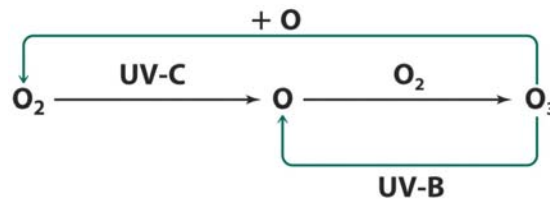
Energy of photons

$$E \text{ (kJ/mole)} = hc/\lambda = 119627/\lambda \quad E \text{ (eV)} = 1240/\lambda$$

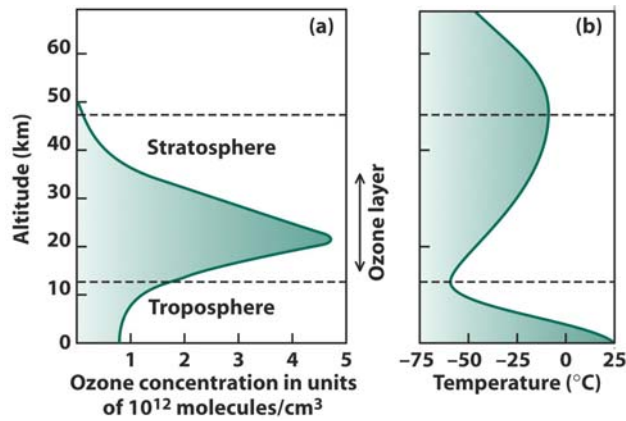
Oxygen and Ozone as a Natural UV-C-Filter

## Creation of Ozone in the Stratosphere

### Creation of Ozone in the Stratosphere



Ozone is constantly being formed in the earth's atmosphere by the action of the sun's ultraviolet radiation on oxygen molecules. Ultraviolet light splits the molecules apart by breaking the bonds between the atoms. A highly reactive free oxygen atom then collides with another oxygen molecule to form an ozone molecule. Because ozone is unstable, ultraviolet light quickly breaks it up, and the process begins again.



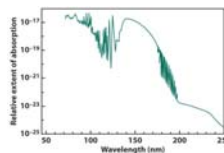
About 90% of the ozone in the earth's atmosphere

In the troposphere, the ground-level or "bad" ozone is an air pollutant that damages human health, vegetation, and many common materials. It is a key ingredient of urban smog. In the stratosphere, we find the "good" ozone that protects life on earth from the harmful effects of the sun's ultraviolet rays.

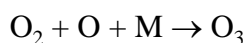
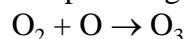
Chapman theory describes how sunlight converts the various forms of oxygen from one to another, explains why the highest content of ozone occur in the layer between 15 and 50 km, termed the ozone layer

## Creation of Ozone in Stratosphere

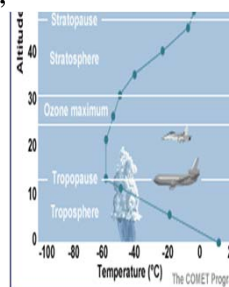
Above stratosphere most of the oxygen absorbs UV-C and exists as O atoms



Because of the high concentration of O<sub>2</sub> in stratosphere, any O atom present gets converted to O<sub>3</sub>



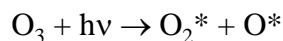
A third molecule M (N<sub>2</sub> or H<sub>2</sub>O) facilitates as a heat energy carrier.



Because of the temperature inversion **vertical mixing** of air is a slow process in stratosphere than in troposphere.

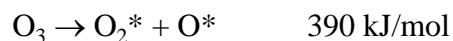
## Destruction of Ozone in Stratosphere

Ozone absorbs UV light below 320 nm and undergoes dissociation



Both O<sub>2</sub> and O produced via UV photon are in the excited state

Determine the longest wavelength that is needed for the dissociation of O<sub>3</sub>



$$\lambda = 119627 \text{ kJ nm mol}^{-1} / 390 \text{ kJ mol}^{-1} = 307 \text{ nm}$$

## The Steady State Analysis

Rate of change of an intermediate = Rate of formation - rate of destruction



$$\text{Rate of change of B} = k_1[A] - k_2[C]$$

At Steady State the rate of change ( $d[B]/dt$ ) is zero

$\therefore$  Rate of formation - Rate of destruction = 0

Or Rate of formation = Rate of destruction

In the above example,

$$k_1[A] = k_2[C] \quad \text{or} \quad [A]/[C] = k_2/k_1$$

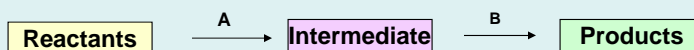
What is the difference between an equilibrium and steady state?

### Equilibrium System (A=B)



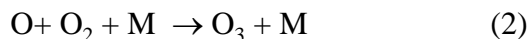
An equilibrium system is a closed system in which the forward and backward reactions occur at the same time and at equal rates.

### Steady State (A=B)



A steady state is an open system in which an intermediate is formed and destroyed at the same rate in separate reactions.

**Steady State Analysis for Ozone in the Atmosphere:  
Chapman Mechanism**



Since O is consumed or formed in all the reactions we can assume that it is in the steady state

$$\text{Rate of change of O} = 2(\text{rate1}) - \text{rate2} + \text{rate3} - \text{rate4} = 0 \quad (\text{A})$$

Similarly,

$$\text{Rate of change of O}_3 = \text{rate2} - \text{rate3} - \text{rate4} = 0 \quad (\text{B})$$

$$(\text{A}) + (\text{B}): \quad 2(\text{rate1}) - 2(\text{rate4}) = 0$$

By expressing rate in terms of rate constant and concentration

$$2k_1[\text{O}_2] - 2k_4[\text{O}_3][\text{O}] = 0$$

$$\text{OR} \quad [\text{O}_3][\text{O}] = k_1[\text{O}_2]/k_4 \quad (\text{C})$$

**From previous analysis,**

$$2(\text{rate1}) - \text{rate2} + \text{rate3} - \text{rate4} = 0 \quad (\text{A})$$

$$\text{Rate of change of O}_3 = \text{rate2} - \text{rate3} - \text{rate4} = 0 \quad (\text{B})$$

$$[\text{O}_3][\text{O}] = k_1[\text{O}_2]/k_4 \quad (\text{C})$$

$$(\text{A}) - (\text{B}): \quad 2\text{rate1} - 2\text{rate2} + 2\text{rate3} = 0$$

$$\text{or} \quad \text{rate3} = \text{rate2} - \text{rate1}$$

since  $\text{rate1} \ll \text{rate2}$  and  $\text{rate3}$ , we can neglect the term

$$\text{rate3} = \text{rate2}$$

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

$$\text{or} \quad [\text{O}_3]/[\text{O}] = k_2[\text{O}_2][\text{M}]/k_3 \quad (\text{D})$$

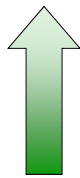
$$(\text{C}) \times (\text{D}): \quad [\text{O}_3]^2 = [\text{O}_2]^2[\text{M}]k_1k_2/k_3k_4$$

$$\text{or} \quad [\text{O}_3]/[\text{O}_2] = [\text{M}]^{0.5}(k_1k_2/k_3k_4)^{0.5} \quad (\text{E})$$

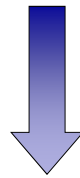
**At Steady State,  $[O_3]_{ss}/[O_2]_{ss} = [M]^{0.5}(k_1k_2/k_3k_4)^{0.5}$  (E)**

The steady state ratio of O<sub>3</sub> to O<sub>2</sub> depend on

- square root of air density
- proportional to square root of product of k<sub>1</sub> & k<sub>2</sub> corresponding to O and O<sub>3</sub> production
- inversely proportional to square root of product of k<sub>3</sub> & k<sub>4</sub>
- based on experimental values of k and M, maximum [O<sub>3</sub>] is of the order of 10<sup>-4</sup> M



M decreases with increasing altitude



Absorption of UV-C (and k<sub>1</sub>) decreases with decreasing altitude

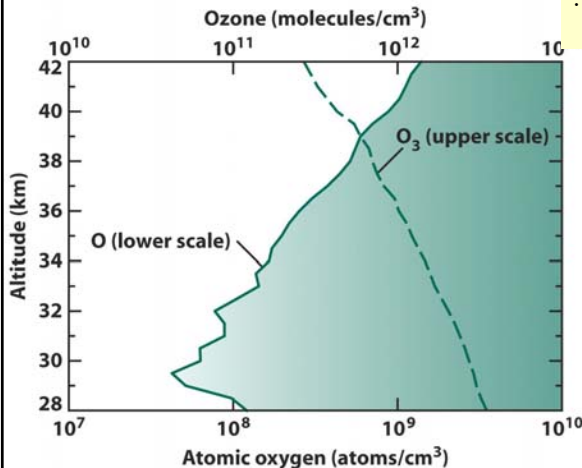
Peak concentration of ozone is expected at altitude of ~40 km  
(Actual peak is observed at 25 km because of the movement of O<sub>3</sub> downwards)

**Concentration of Atomic Oxygen**

**From (E) and (C)**

**$[O]_{ss} = (k_1k_3/k_2k_4)^{0.5} / [M]^{0.5}$**

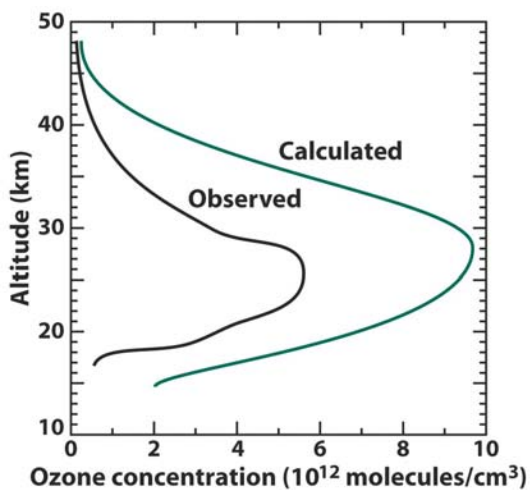
- [O]<sub>ss</sub> increases with increasing altitude as [M] declines
- k<sub>1</sub> and k<sub>3</sub> increase with altitude
- ∴ O atoms dominate over O<sub>3</sub> at higher altitudes (> 50 km).



Concentration of atomic oxygen and ozone versus altitude



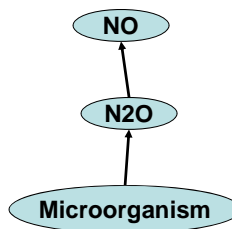
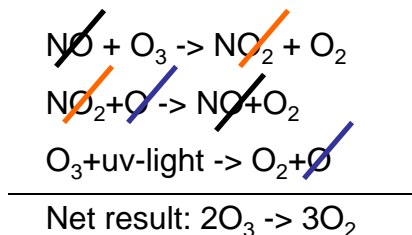
Comparison of stratosphere ozone concentration as a function of altitude



The actual destruction of ozone is more than the prediction

The Chapman theory, however, overestimates the ozone contents. Thus, there must be other chemical reactions contributing to the reduction of the ozone content.

In 1970, Paul Crutzen showed that the nitrogen oxides NO and NO<sub>2</sub> react catalytically (without themselves being consumed) with ozone, thus accelerating the rate of reduction of the ozone content.



Note NO acts as a catalyst and requires O atom for regeneration—referred as Mechanism I

## Two important chemistry contributions leading to the discovery of the link between Freon and ozone depletion

- James Lovelock (England) had developed a highly sensitive device of measuring extremely low organic gas contents in the atmosphere, the electron capture detector. Using this he could now demonstrate that the exclusively man-made, chemically inert, CFC gases had already spread globally throughout the atmosphere.
- Richard Stolarski and Ralph Cicerone (USA) had shown that free chlorine atoms in the atmosphere can decompose ozone catalytically in similar ways as nitrogen oxides do.

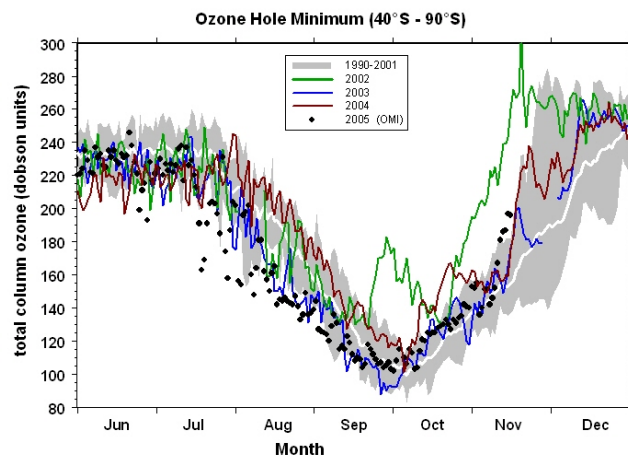
## Spray cans and refrigerators damage the ozone layer

- In 1974, Molina and Rowland proposed in their *Nature* article that the chemically inert CFC could gradually be transported up to the ozone layer, there to be met by such intensive ultra-violet light that they would be separated into their constituents, notably chlorine atoms.
- They calculated that if human use of CFC gases was to continue at an unaltered rate the ozone layer would be depleted by many percent after some decades.

Joe Farman and his colleagues revealed a dramatic and unpredicted decline in stratospheric ozone in perhaps the most unexpected region of the globe - over the Antarctic in spring, and Farman suggested that it was due to gases emitted into the atmosphere by Man.

Farman, J. C.;Gardiner, B. G.;Shanklin, J. D., *Large Losses of Total Ozone in Antarctica Reveal Seasonal Clox/Nox Interaction.* **Nature**, 1985, 315, 207-210.

Using measurements of the total amount of ozone in a column of atmosphere above the BAS Halley Bay base at 76°S, dating back to the International Geophysical Year in 1957, Joe Farman showed that a dramatic decline in springtime ozone over the entire Antarctic continent had taken place, starting in the late 1970s, reaching. ~30% by 1985.



## Chlorofluorocarbons

Chlorofluorocarbons or CFCs (also known as Freon) are non-toxic, non-flammable and non-carcinogenic. They contain fluorine atoms, carbon atoms and chlorine atoms. The 5 main CFCs include



- CFC-11 (trichlorofluoromethane -  $\text{CFCl}_3$ ),
- CFC-12 (dichloro-difluoromethane -  $\text{CF}_2\text{Cl}_2$ ),
- CFC-113 (trichloro-trifluoroethane -  $\text{C}_2\text{F}_3\text{Cl}_3$ ),
- CFC-114 (dichloro-tetrafluoroethane -  $\text{C}_2\text{F}_4\text{Cl}_2$ ), and
- CFC-115 (chloropentafluoroethane -  $\text{C}_2\text{F}_5\text{Cl}$ ).

CFCs have a lifetime in the atmosphere of about 20 to 100 years, and consequently one free chlorine atom from a CFC molecule can do a lot of damage, destroying ozone molecules for a long time. Although emissions of CFCs around the developed world have largely ceased due to international control agreements, the damage to the stratospheric [ozone layer](#) will continue well into the 21st century.

<http://www.ace.mmu.ac.uk>

[ozone-depleting substances](#) (CFCs, HCFCs, HBFCs, and halons) are numbered according to a system devised several decades ago and now used worldwide.

It provides very complex information about molecular structure and also easily distinguishes among various classes of chemicals.

For example, it is not intuitive that 1,1-dichloro-1-fluoroethane ( $\text{CFCl}_2\text{-CH}_3$ ) is an ozone-depleting substance. The designation HCFC-141b, in contrast, immediately conveys its ozone-depleting nature while concisely describing its structure.

Prefix	Meaning	Atoms in the Molecule
CFC	chlorofluorocarbon	Cl, F, C
HCFC	hydrochlorofluorocarbon	H, Cl, F, C
HBFC	hydrobromofluorocarbon	H, Br, F, C
HFC	hydrofluorocarbon	H, F, C

[www.epa.gov/ozone/defns.html](http://www.epa.gov/ozone/defns.html)

The prefix describes what kinds of atoms are in a particular molecule, the next step is to calculate the number of each type of atom. The key to the code is to add 90 to the number; the result shows the number of C, H, and F atoms. For HCFC-141b:

$$141 + 90 = 231$$

#C #H #F

One more piece of information is needed to decipher the number of Cl atoms. All of these chemicals are saturated; that is, they contain only single bonds. The number of bonds available in a carbon-based molecule is  $2n(\text{C}) + 2$ . Thus, for HCFC-141b, which has  $n=2$  carbon atoms, there are 6 bonds. Cl atoms occupy bonds remaining after the F and H atoms.

∴ HCFC-141b has 2C, 3H, 1F, and 2Cl: **HCFC-141b = C<sub>2</sub>H<sub>3</sub>FCl<sub>2</sub>**

Notice that the HCFC designation (hydro chloro fluoro carbon) is a good double-check on the decoding; this molecule does, indeed, contain H, Cl, F, and C. The "b" at the end describes how these atoms are arranged; different "isomers" contain the same atoms, but they are arranged differently. The letter designation for isomers.

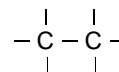
Deduce the formula for the compounds with following code numbers  
12, 113, 123, 134

a. 12     $90+12= 102$     C=1, H=0, and F= 2, (∴ Cl=2) → CF<sub>2</sub>Cl<sub>2</sub>



b. 113     $90+113= 203$     C=2, H=0, and F= 3, (∴ Cl=3) → C<sub>2</sub>F<sub>3</sub>Cl<sub>3</sub>

c. 123     $90+123= 213$     C=2, H=1, and F= 3, (∴ Cl=2) → C<sub>2</sub>HF<sub>3</sub>Cl<sub>2</sub>



d. 134     $90+134= 224$     C=2, H=2, and F= 4, (∴ Cl=0) → C<sub>2</sub>H<sub>2</sub>F<sub>4</sub>

### Other Ozone Depleting Substances

#### CCl<sub>4</sub> (Carbon tetrachloride)

Used as dry cleaning solvent

#### CH<sub>3</sub>-CCl<sub>3</sub> (methyl chloroform)

Cleaning agent for metals

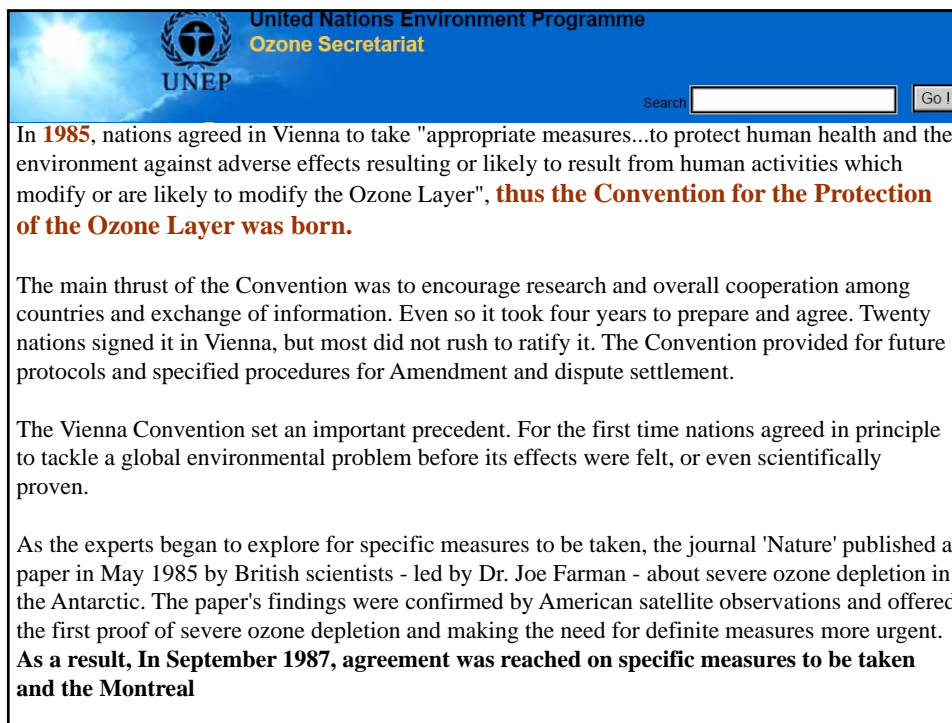
#### Halons

Bromine containing hydrogen free substances such as CF<sub>3</sub>Br and CF<sub>2</sub>BrCl used

Methyl bromide is used as a pesticide, fumigate crops (40% of world use is in the US)

They rise to stratosphere and decompose to produce Br\* – an efficient catalyst X' for O<sub>3</sub> depletion

Developing countries have agreed to reduce consumption, but not complete elimination  
Meantime China & Korea have increased their production!



United Nations Environment Programme  
Ozone Secretariat  
UNEP

Search  Go!

In **1985**, nations agreed in Vienna to take "appropriate measures...to protect human health and the environment against adverse effects resulting or likely to result from human activities which modify or are likely to modify the Ozone Layer", **thus the Convention for the Protection of the Ozone Layer was born.**

The main thrust of the Convention was to encourage research and overall cooperation among countries and exchange of information. Even so it took four years to prepare and agree. Twenty nations signed it in Vienna, but most did not rush to ratify it. The Convention provided for future protocols and specified procedures for Amendment and dispute settlement.

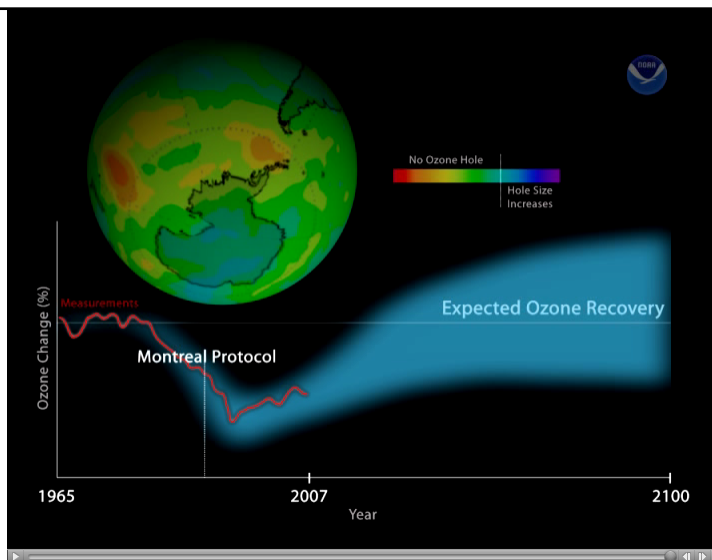
The Vienna Convention set an important precedent. For the first time nations agreed in principle to tackle a global environmental problem before its effects were felt, or even scientifically proven.

As the experts began to explore for specific measures to be taken, the journal 'Nature' published a paper in May 1985 by British scientists - led by Dr. Joe Farman - about severe ozone depletion in the Antarctic. The paper's findings were confirmed by American satellite observations and offered the first proof of severe ozone depletion and making the need for definite measures more urgent. **As a result, In September 1987, agreement was reached on specific measures to be taken and the Montreal**

## 1987: Ozone agreement reached in Montreal

<http://www.cbc.ca/archives/categories/environment/environmental-protection/environmental-protection-general/ozone-agreement-reached-in-montreal.html>

- In 1985, 49 countries met in Vienna to first discuss the protection of the ozone layer
- With the signing of the Montreal Protocol, two years later, 24 of these countries agreed to reduce the production and consumption of Chlorofluorocarbons (CFCs) by 50 per cent by 1999.
- The Protocol came into force on January 1st, 1989, when 29 countries and the European Economic Community (EEC), representing approximately 82 per cent of world consumption, had ratified it.



[http://nnvl.noaa.gov/Media/Ozone/MontrealProtocolGraph\\_compressed.mov](http://nnvl.noaa.gov/Media/Ozone/MontrealProtocolGraph_compressed.mov)

**off the mark**.com by Mark Parisi

JEEPERS! IT'S GETTING PRETTY THIN...  
MAYBE IF I COMB SOME OZONE FROM  
HERE...

