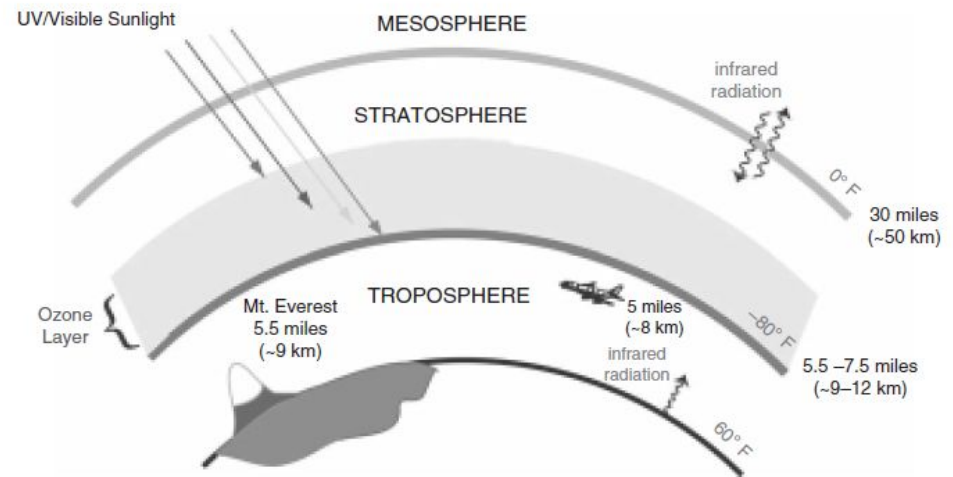


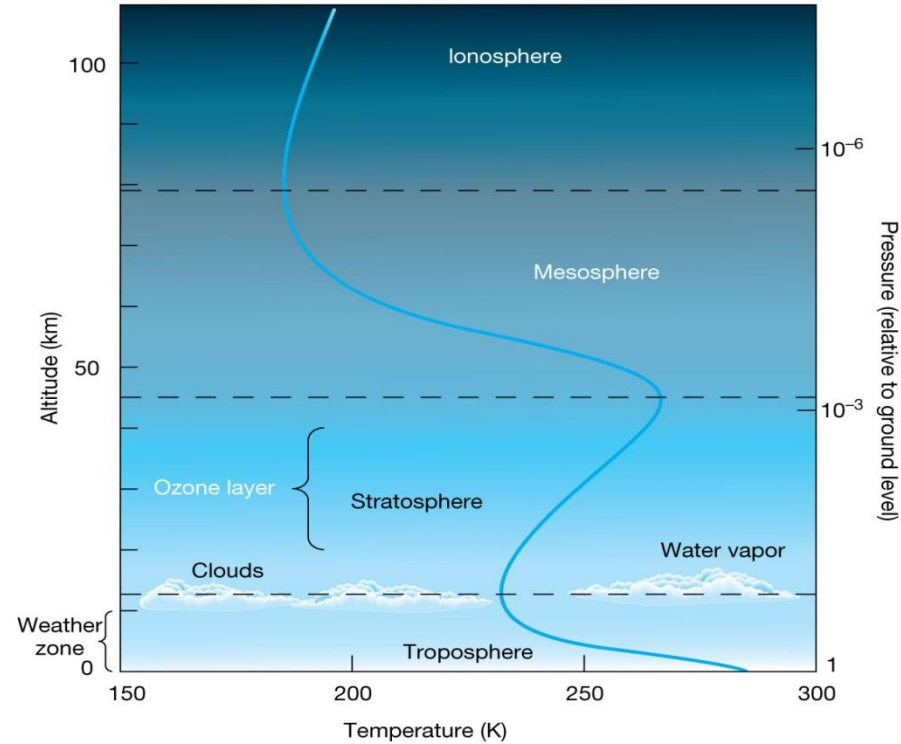
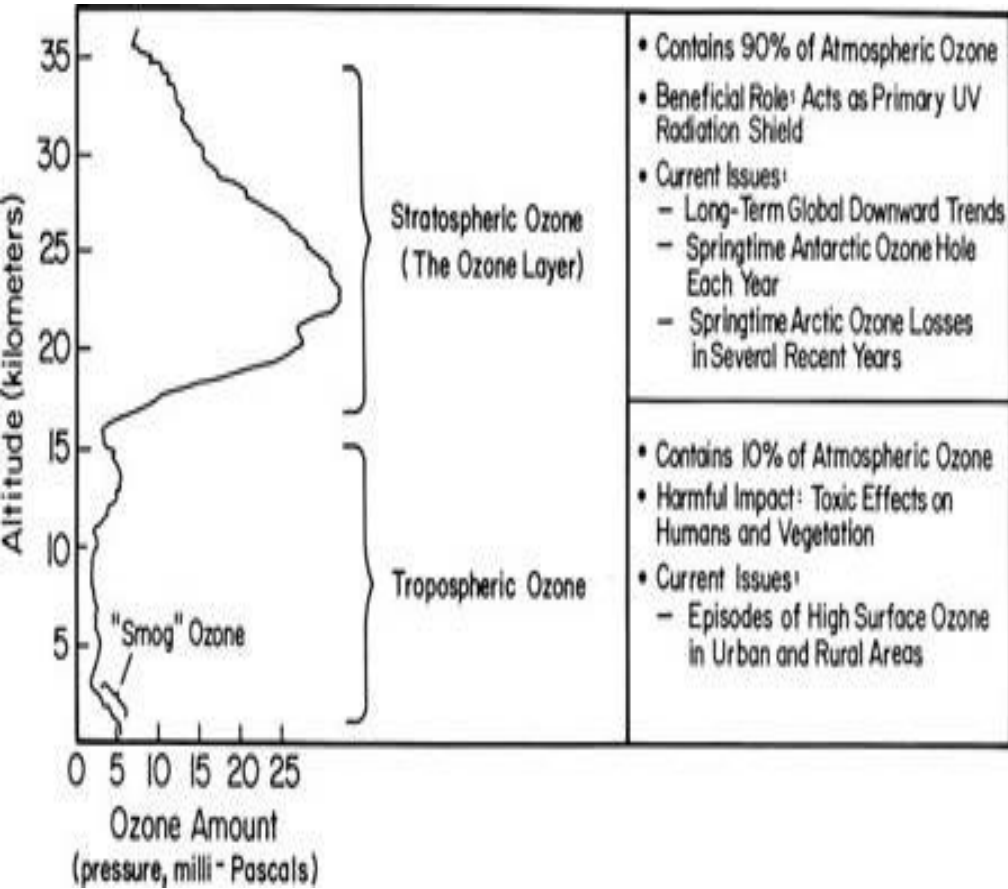
Ozone depletion



Regions of the atmosphere. Credit: NOAA OAR ESRL

Basic information

- The stratospheric ozone layer began to form soon after the onset of oxygen producing photosynthesis, about 2.3 billion years ago (b.y.a.).
- Absorption of ultraviolet (UV) radiation by ozone is responsible for the temperature inversion that defines the present day stratosphere.
- This absorption is critical for preventing UV radiation from reaching the surface of the Earth, where it can harm life.



Basic information

- A measure of the quantity of ozone in the air is the ozone column abundance, which is the sum of all ozone molecules above a square centimeter of surface between the ground and the top of the atmosphere. When this number is divided by $2.7 * 10^{16}$, the result is the column abundance in **Dobson units** (DUs).
- Thus, 1 DU is equivalent to $2.7 * 10^{16}$ molecules of ozone per square centimeter of surface.
- In 2000, the globally averaged column abundance of ozone from 90°S to 90°N was 293.4 DU. This column abundance contains the same number of molecules as a column of air 2.93-mm high at 1 atm of pressure and 273 K (near-surface conditions).

UV portion of the solar spectrum is divided into far- and near-UV wavelengths

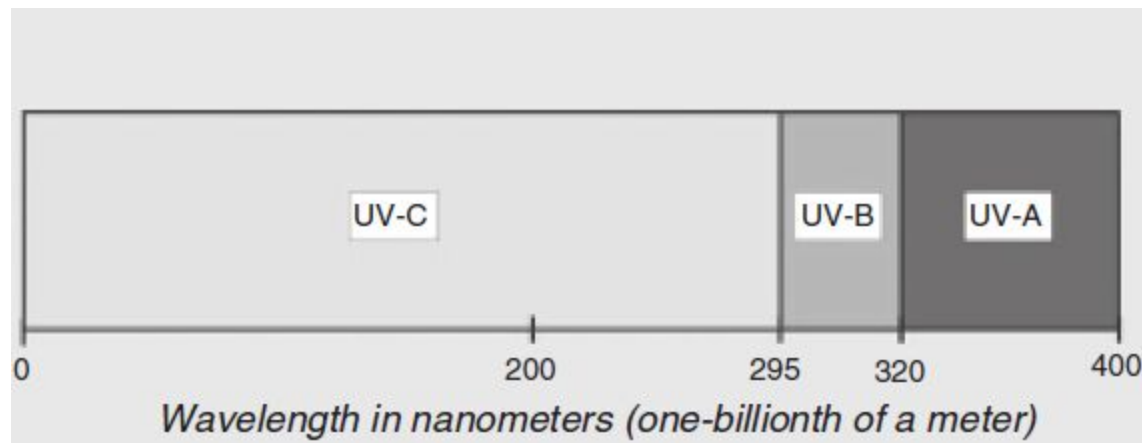
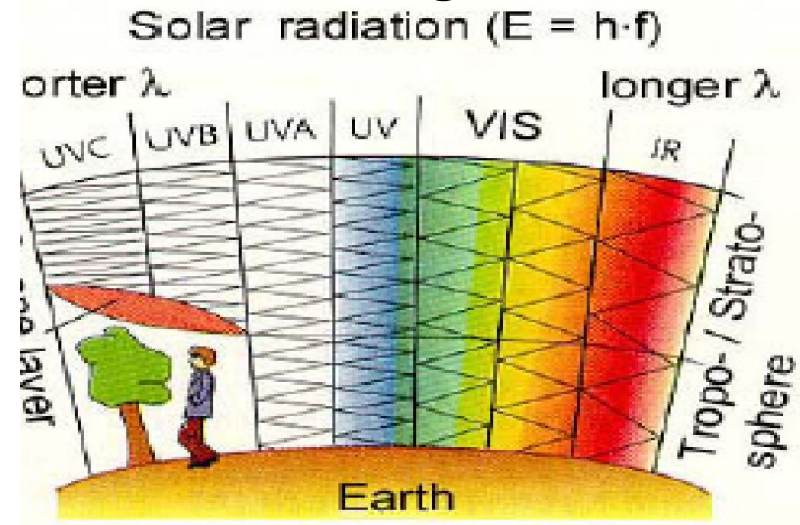
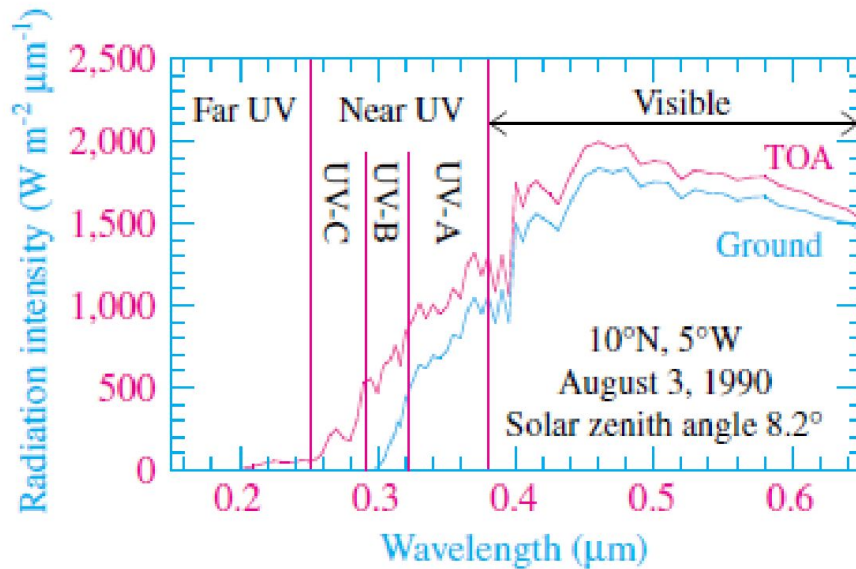
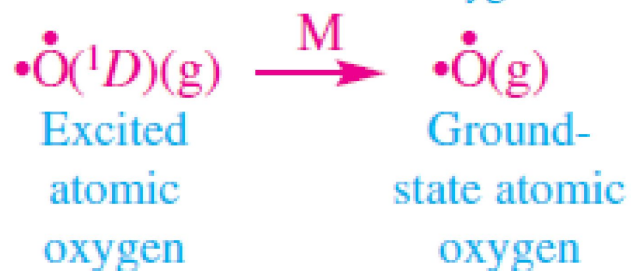
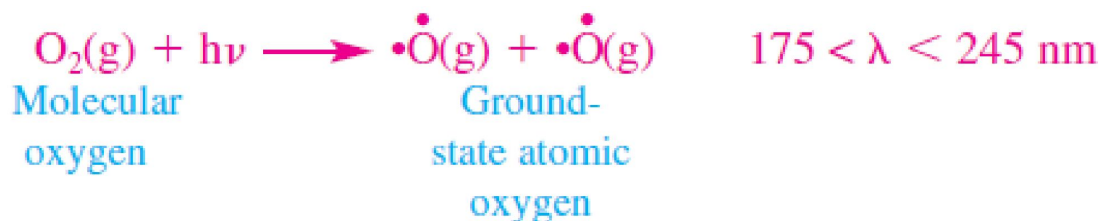
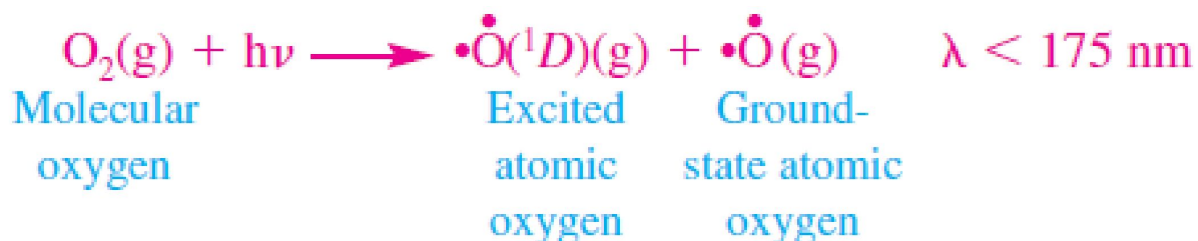


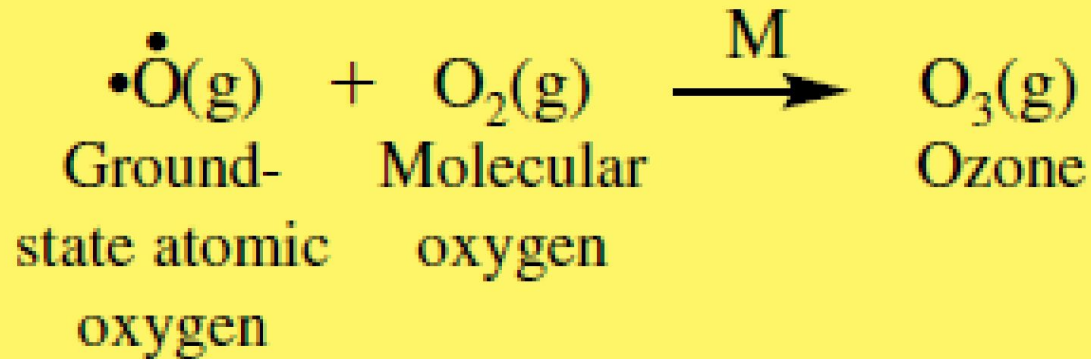
Table 11.1. Summary of Major Absorbers of UV Radiation

Name of Spectrum	Wavelengths (μm)	Dominant Absorbers	Location of Absorption
Far-UV	0.01–0.25	$\text{N}_2(\text{g})$ $\text{O}_2(\text{g})$	Thermosphere, mesosphere Thermosphere, mesosphere, stratosphere
Near-UV			
UV-C	0.25–0.29	$\text{O}_3(\text{g})$	Stratosphere
UV-B	0.29–0.32	$\text{O}_3(\text{g})$ Particulate components	Stratosphere, troposphere Polluted troposphere
UV-A	0.32–0.38	$\text{NO}_2(\text{g})$ Particulate components	Polluted troposphere Polluted troposphere

The chemistry of the natural ozone layer



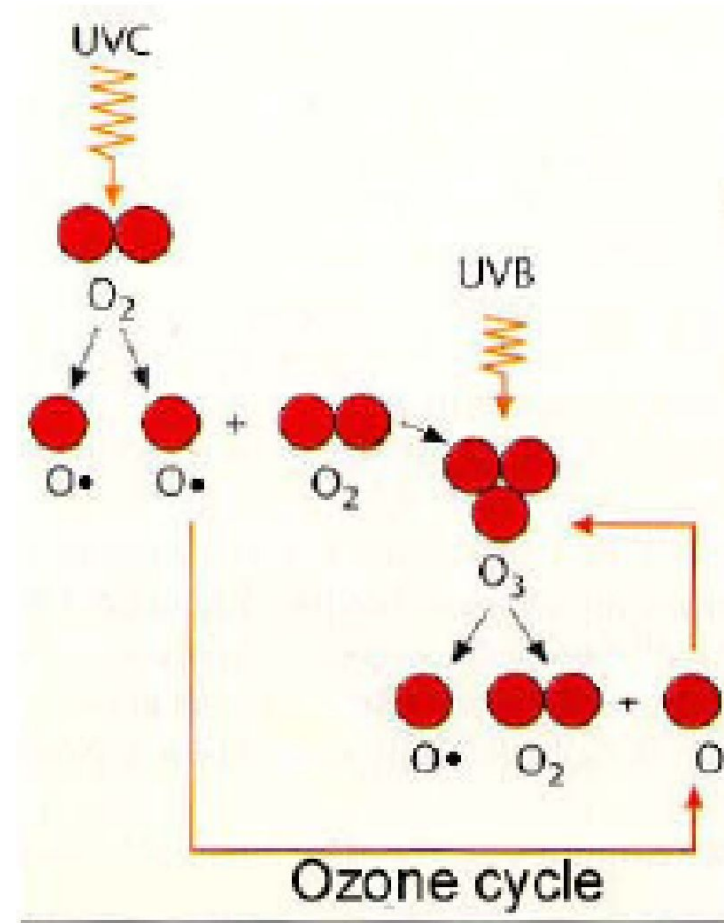
The chemistry of the natural ozone layer (Ozone forms by)



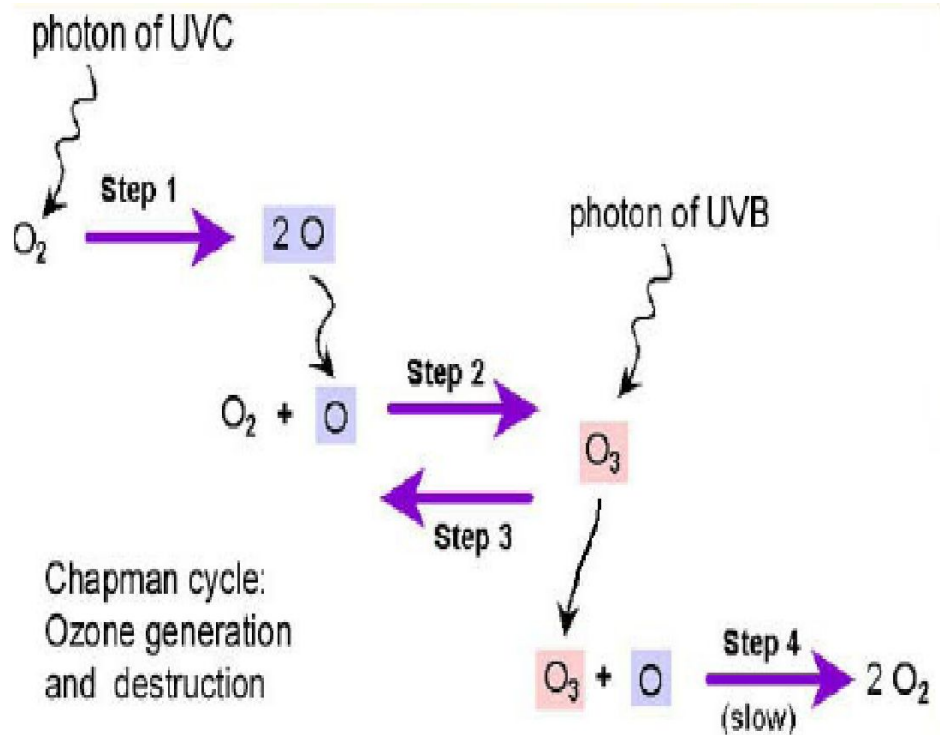
Chapman cycle



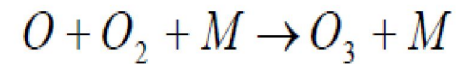
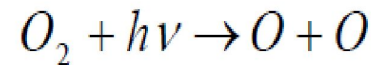
Sidney Chapman (1888–1970)



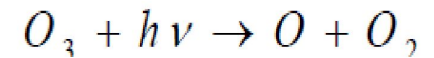
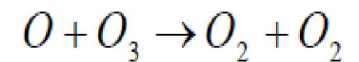
Chapman cycle



Production:



Loss:



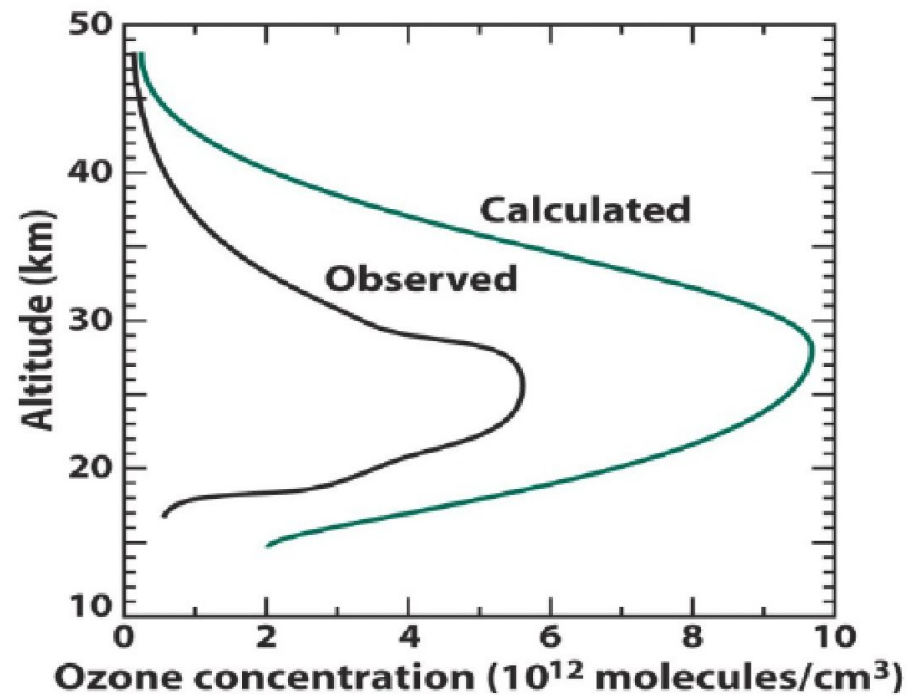
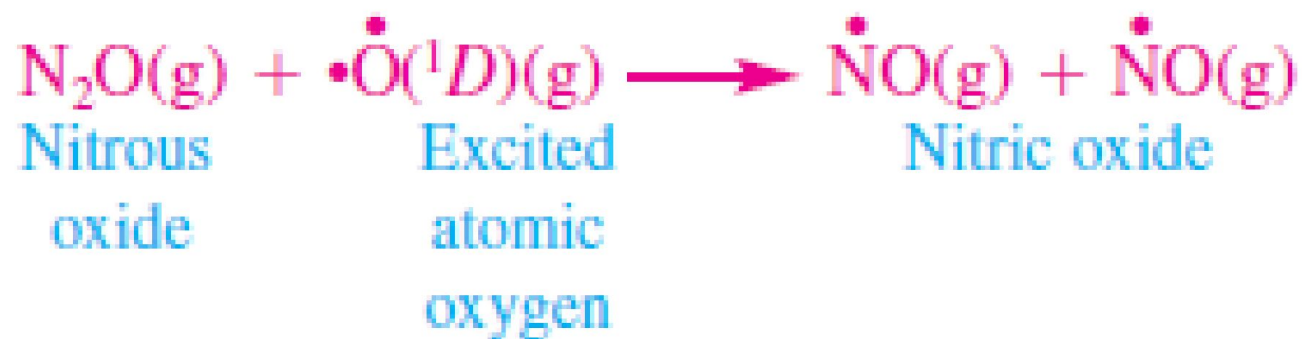


Figure 1.14

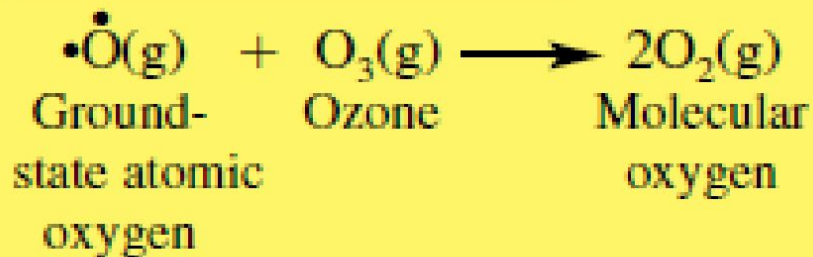
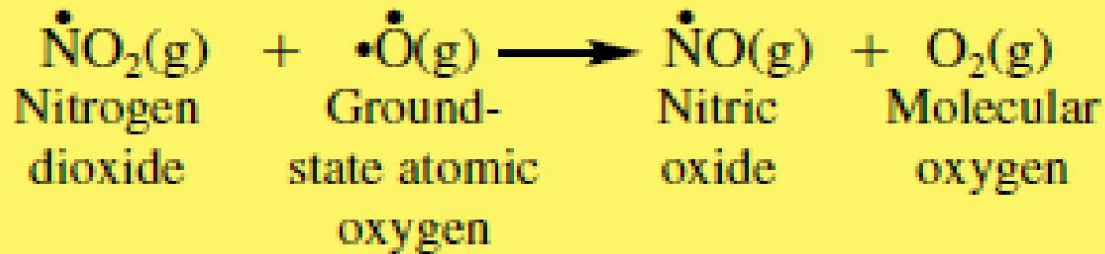
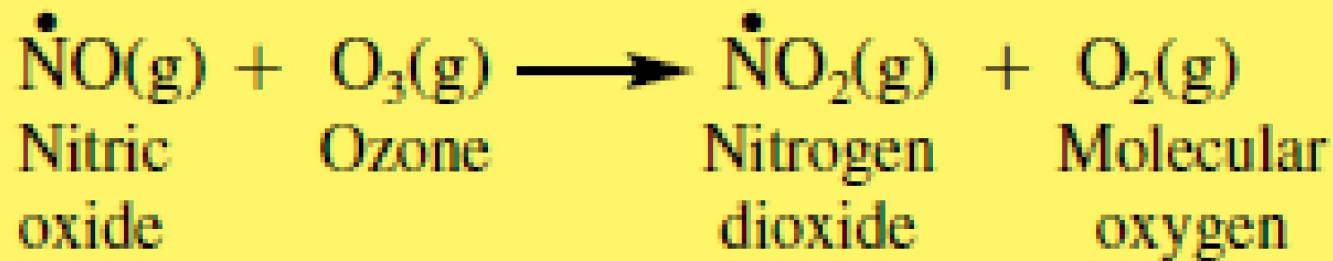
Effects of Nitrogen on the Natural Ozone Layer

- Oxides of nitrogen [$\text{NO}(\text{g})$ and $\text{NO}_2(\text{g})$] naturally destroy ozone, primarily in the upper stratosphere, helping shape the vertical profile of the ozone layer.
- In the troposphere, the major sources of nitric oxide (NO) are surface emissions and lightning.
- The major source of $\text{NO}(\text{g})$ in the stratosphere is transport from the troposphere and the breakdown of **nitrous oxide** [$\text{N}_2\text{O}(\text{g})$] (laughing gas), a colorless gas emitted during denitrification by anaerobic bacteria in soils. It is also emitted by bacteria in fertilizers, sewage, and the oceans and during biomass burning, automobile combustion, aircraft combustion, nylon manufacturing, and the use of spray cans.

$\text{N}_2\text{O}(\text{g})$ produces nitric oxide by



Nitric oxide naturally reduces ozone in the upper stratosphere by

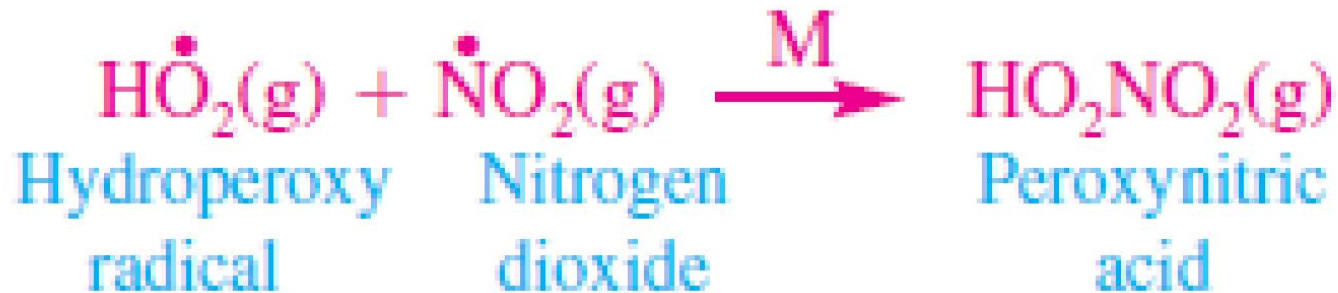
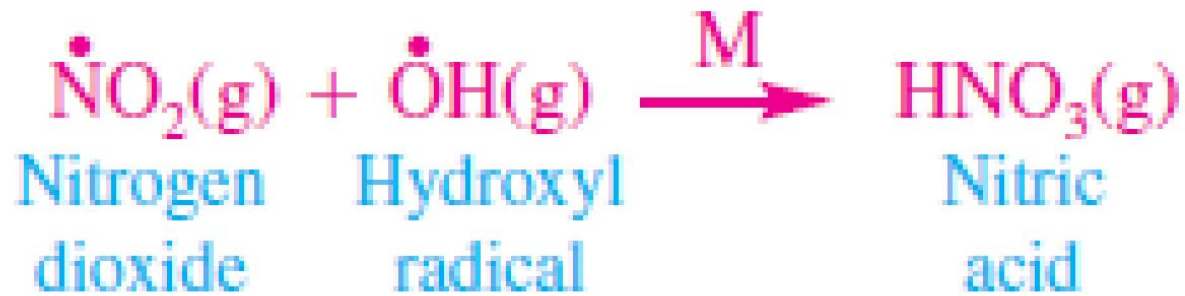


(net process)

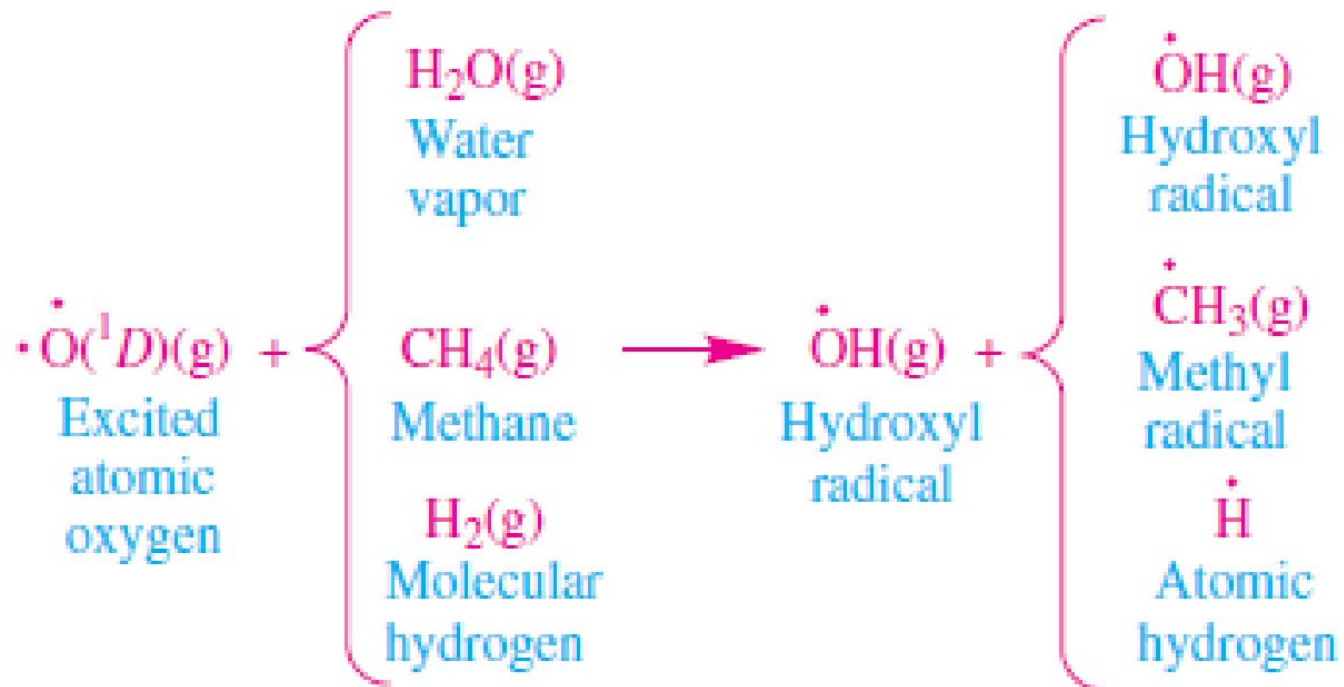
Effects of Nitrogen on the Natural Ozone Layer

- This sequence is called a **catalytic ozone destruction cycle** because the species causing the $O_3(g)$ loss, $NO(g)$, is recycled.
- This particular cycle is the **$NO_x(g)$ catalytic ozone destruction cycle**, where $NO_x(g)$: $NO(g)$ $NO_2(g)$, and $NO(g)$ is the catalyst.
- The number of times the cycle is executed before $NO_x(g)$ is removed from the cycle by reaction with another gas is the **chain length**. In the upper stratosphere, the chain length of this cycle is about 10^5 . Thus, 10^5 molecules of $O_3(g)$ are destroyed before one $NO_x(g)$ molecule is removed from the cycle.
- In the lower stratosphere, the chain length decreases to near 10.

Major loss processes are the formation of nitric acid and peroxyntic acid by the reactions



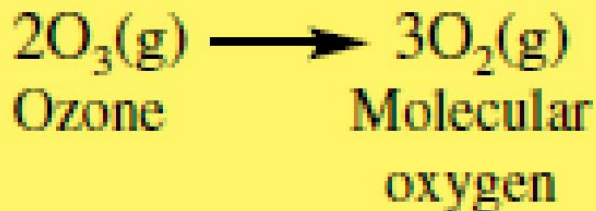
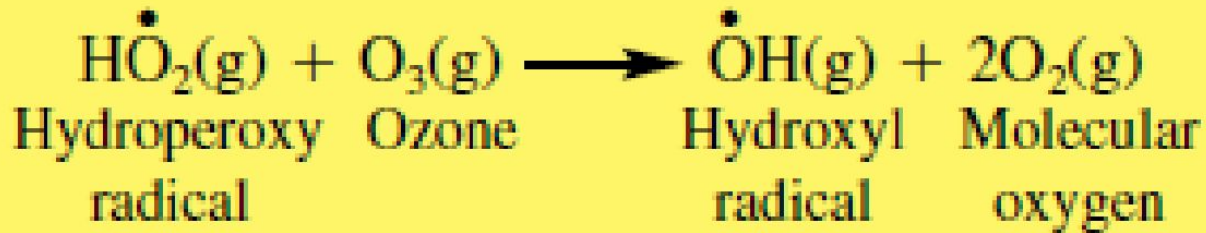
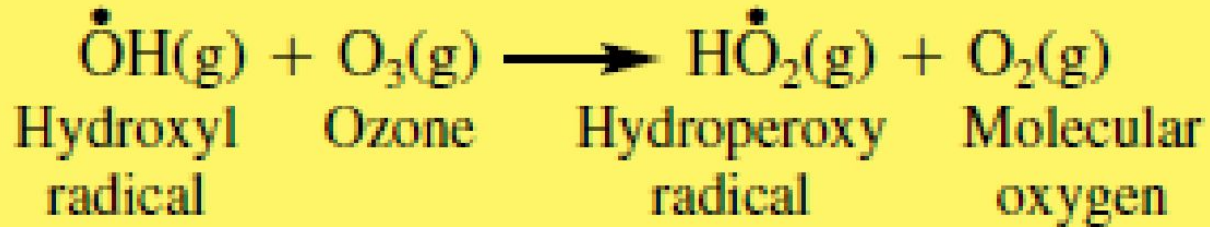
Effects of Hydrogen on the Natural Ozone Layer



Effects of Hydrogen on the Natural Ozone Layer

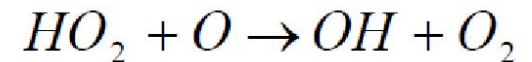
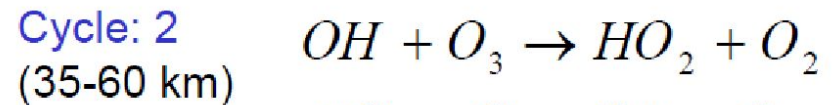
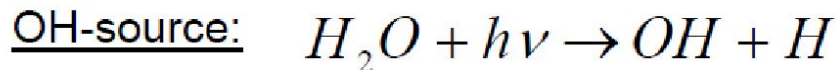
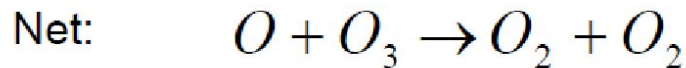
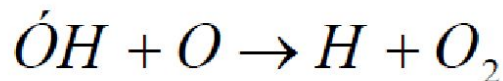
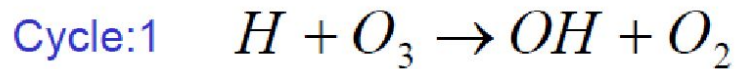
- The hydroxyl radical participates in an **HOx(g) catalytic ozone destruction cycle**, where $\cdot\text{HO}_x(\text{g}) = \cdot\text{OH}(\text{g}) + \cdot\text{HO}_2(\text{g})$. $\cdot\text{HO}_x(\text{g})$ catalytic cycles are important in the lower stratosphere.

The most effective $\cdot\text{HOx}(\text{g})$ cycle, which has a chain length in the lower stratosphere of 1 to 40

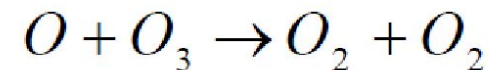


(net process)

Effects of Hydrogen on the Natural Ozone Layer



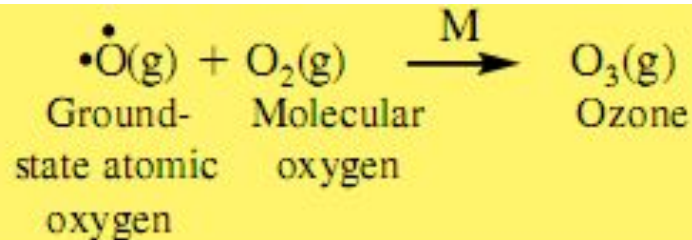
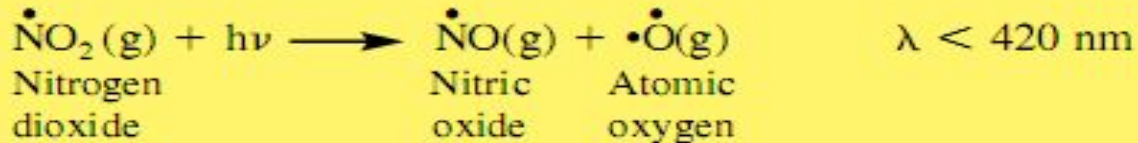
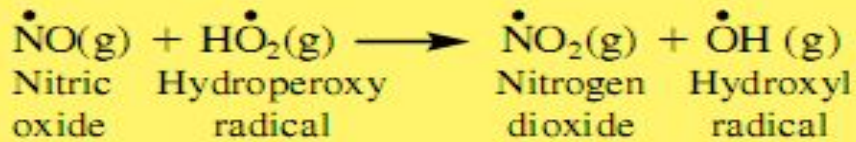
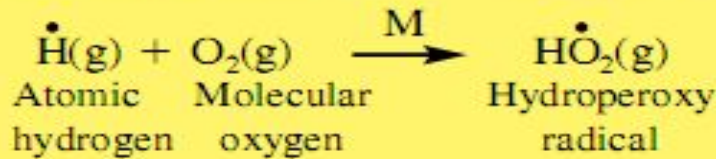
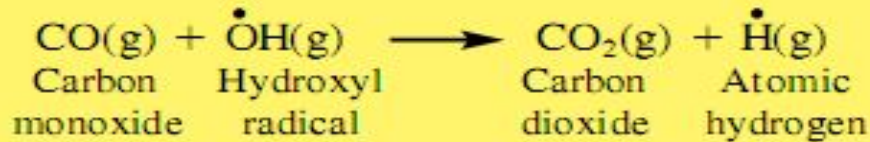
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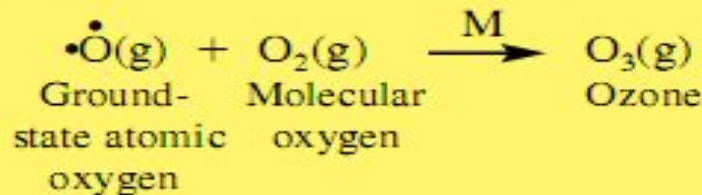
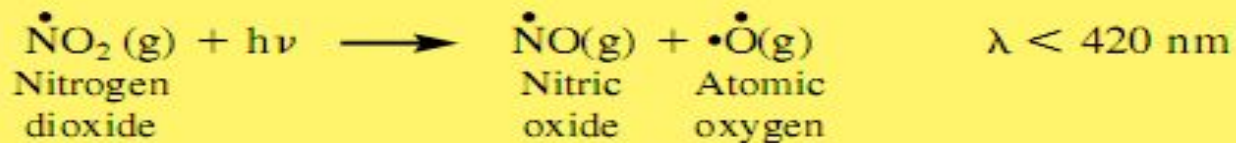
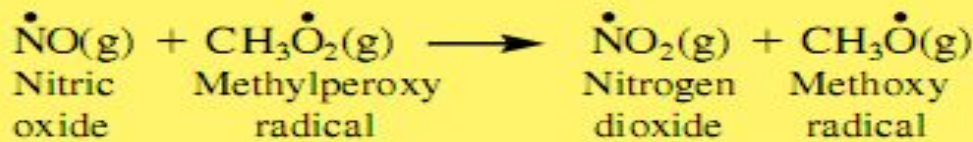
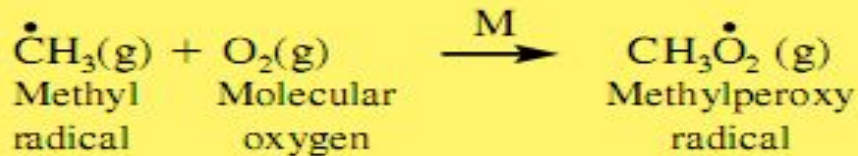
H₂O-source in the stratosphere:

(Oxidation of CH₄, not direct injection of H₂O from troposphere)

Effects of Carbon on the Natural Ozone Layer (CO)



Effects of Carbon on the Natural Ozone Layer (CH₄)

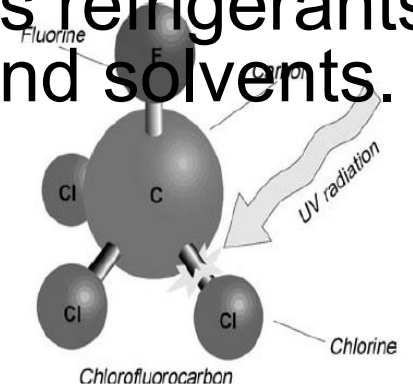


Changes on a Global Scale

- Between 1979 and 2000, the global stratospheric ozone column abundance decreased by approximately 3.5 percent (from 304.0 to 293.4 DU).
- Unusual decreases in global ozone occurred following the El Chichyn (Mexico) volcanic eruption in April 1982, and the Mount Pinatubo (Philippines) eruption in June 1991.
- These eruption injected particles into the stratosphere. On the surfaces of these particles, chemical reactions involving chlorine took place that contributed to ozone loss. Over time, however, the concentration of these particles decreased, and the global ozone layer partially recovered. Because volcanic particles were responsible for only temporarily ozone losses, the net loss of ozone over the globe from 1979 to 2000 was still about 3.5 percent. The decrease between 60°S and 60°N was 2.5 percent (298.08 to 290.68 DU), that between 60°N and 90°N was 7.0 percent (370.35 to 344.29 DU), and that between 60°S and 90°S was 14.3 percent (335.20 to 287.23 DU).

CFCs and Related Compounds

- The compounds that play the most important role in reducing stratospheric ozone are **chlorofluorocarbons (CFCs)**.
- CFCs are gases formed synthetically by replacing all hydrogen atoms in methane [$\text{CH}_4(\text{g})$] or ethane [$\text{C}_2\text{H}_6(\text{g})$] with chlorine and/or fluorine atoms.
- They are also commonly known by the DuPont brand name **Freon**.
- Many CFCs have been widely used as refrigerants, propellants (in aerosol applications), and solvents.

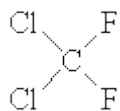
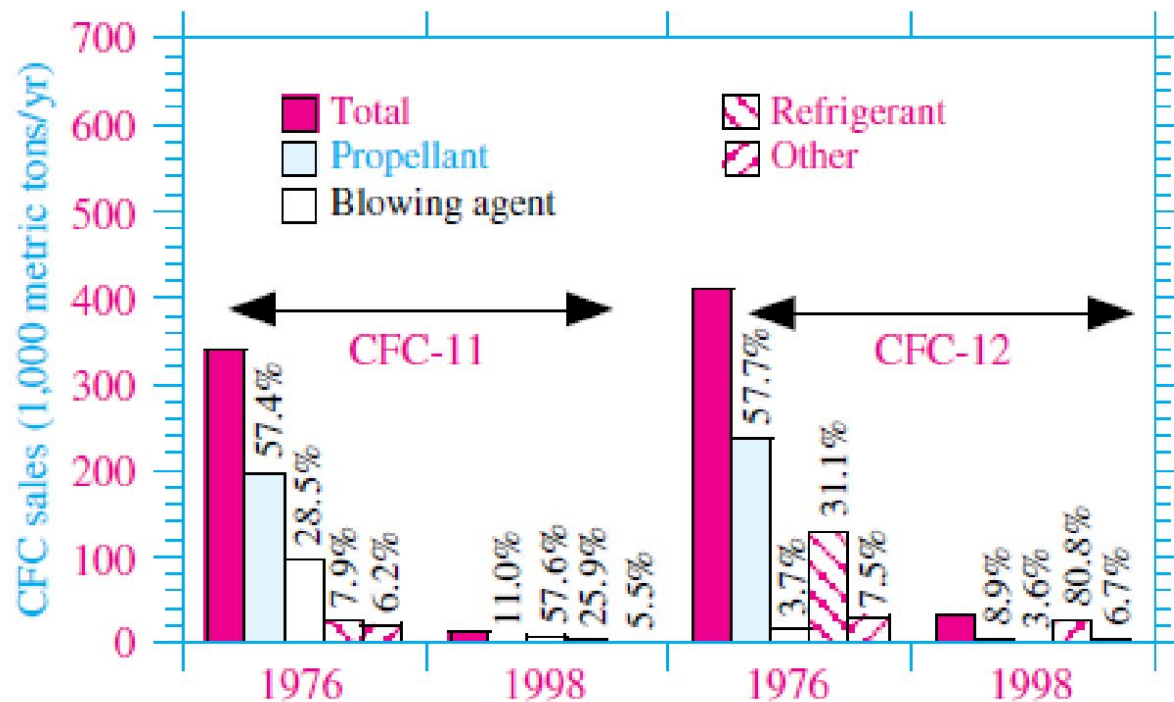


CFCs and Related Compounds

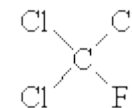
- These compounds are non-flammable, tasteless and odourless, and chemically stable.
- Their other important property is their volatility, having boiling points close to zero degrees Centigrade.
- These physical properties make them ideal for use as refrigerant gases in air conditioners, freezers and refrigerators. Their low boiling points also make them ideal for blowing agents for foam plastics, allowing the foam to expand as the liquid CFC boils.

Chemical Formula	Trade Name	Chemical Name	Tropospheric Mixing Ratio (pptv)	Estimated Overall Atmospheric Lifetime (yrs)
CHLOROCARBONS AND CHLORINE COMPOUNDS				
Chlorofluorocarbons (CFCs)				
CFCl ₃ (g)	CFC-11	Trichlorofluoromethane	270	45
CF ₂ Cl ₂ (g)	CFC-12	Dichlorodifluoromethane	550	100
CFCl ₂ CF ₂ Cl(g)	CFC-113	1-Fluorodichloro, 2-difluorochloroethane	70	85
CF ₂ ClCF ₂ Cl(g)	CFC-114		15	220
CF ₂ ClCF ₃ (g)	CFC-115		5	550
Hydrochlorofluorocarbons (HCFCs)				
CF ₂ ClH(g)	HCFC-22	Chlorodifluoromethane	130	11.8
CH ₃ CFCl ₂ (g)	HCFC-141b		6	9.2
CH ₃ CF ₂ Cl(g)	HCFC-142b	2-Difluorochloroethane	8	18.5
Other Chlorocarbons				
CCl ₄ (g)		Carbon tetrachloride	100	35
CH ₃ CCl ₃ (g)		Methyl chloroform	90	4.8
CH ₃ Cl(g)		Methyl chloride	610	1.3
Other Chlorinated Compounds				
HCl(g)		Hydrochloric acid	10–1,000	<1
BROMOCARBONS				
Halons				
CF ₃ Br(g)	H-1301	Trifluorobromomethane	2	65
CF ₂ ClBr(g)	H-1211	Difluorochlorobromomethane	2	11
CF ₂ BrCF ₂ Br	H-2402	1-Difluorobromo, 2-difluorobromoethane	1.5	22–30

CFCs and Related Compounds



CFC 11



CFC 12

Atmospheric lifetimes and ozone depletion potentials of selected ozone-depleting gases

Chlorine gases	Atmospheric lifetime (years)	Ozone depleting potential (ODP)
CFC-12 (Freon)	100	1
CFC-11	45	1
Carbon tetrachloride	26	0.73
HCFCs	1–26	0.02–0.12
Bromine gases		
Halon-1301	65	16
Halon-1211	16	7.1
Methyl bromide	0.7	0.51

Other Chlorine Compounds

- **Hydrochlorofluorocarbons (HCFCs)** are another subset of chlorocarbons. The hydrogen atom allows HCFCs to be broken down in the troposphere by reaction with $\cdot\text{OH}(\text{g})$. Because HCFCs break down more readily than do CFCs, a smaller percentage of emitted HCFCs than CFCs reaches the stratosphere.
- Other chlorocarbons include **carbon tetrachloride** [$\text{CCl}_4(\text{g})$], **methyl chloroform** [$\text{CH}_3\text{CCl}_3(\text{g})$], and **methyl chloride** [$\text{CH}_3\text{Cl}(\text{g})$]. Carbon tetrachloride is used as an intermediate in the production of CFCs and HCFCs and as a solvent and grain fumigant.
- Another chlorine-containing gas in the troposphere is **hydrochloric acid** [$\text{HCl}(\text{g})$]. $\text{HCl}(\text{g})$ has larger natural than anthropogenic sources. Natural sources include evaporation of chloride from sea-spray and volcanic emissions.

Bromine Compounds

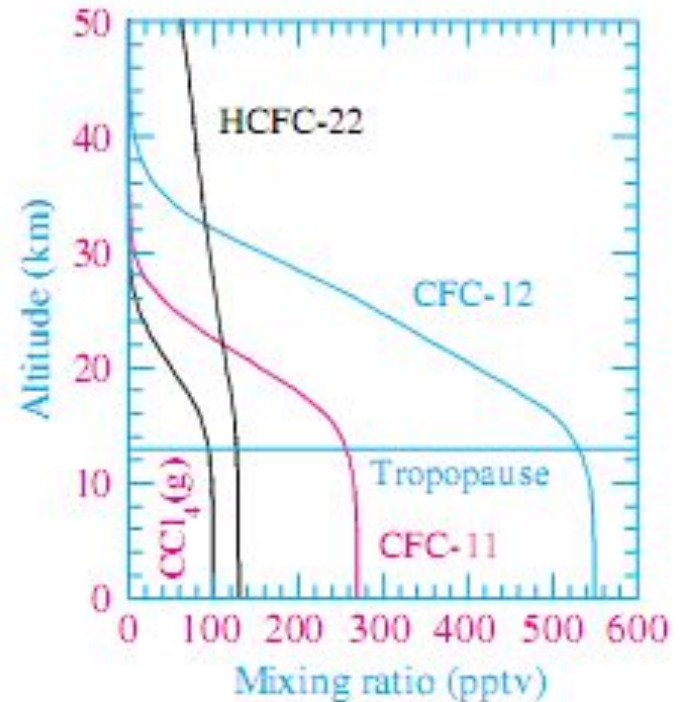
- The primary source of stratospheric bromine is **methyl bromide** [$\text{CH}_3\text{Br}(\text{g})$], which is produced biogenically in the oceans and emitted as a soil fumigant.
- Other sources of bromine are a group of synthetically produced compounds termed **Halons**, which are used in fire extinguishers and as fumigants. The most common Halons are **H-1301** [$\text{CF}_3\text{Br}(\text{g})$], **H-1211** [$\text{CF}_2\text{ClBr}(\text{g})$], and **H-2402** [$\text{CF}_2\text{BrCF}_2\text{Br}(\text{g})$]. Methyl bromide and Halons are **bromocarbons** because they contain both bromine and carbon.

Fluorine Compounds

- Compounds that contain hydrogen, fluorine, and carbon but not chlorine or bromine are **hydrofluorocarbons** (HFCs). HFCs were produced in abundance only recently as a replacement for CFCs and HCFCs.
- Unfortunately, because they absorb thermal-IR radiation, HFCs will enhance global warming if their use increases. The most abundantly emitted HFC to date has been **HFC-134a** [$\text{CH}_2\text{FCF}_3(\text{g})$]. Related to HFCs are **perfluorocarbons** (PFCs), such as perfluoroethane [$\text{C}_2\text{F}_6(\text{g})$], and **sulfur hexafluoride** [$\text{SF}_6(\text{g})$].

Lifetimes and Mixing Ratios of Chlorinated Compounds

- Once emitted, CFCs take about one year to mix up to the tropopause. Because they are chemically unreactive and cannot be broken down by solar wavelengths that reach the troposphere, CFCs are not removed chemically from the troposphere. Instead, they become well mixed in the troposphere and slowly penetrate to the stratosphere. Today, the tropospheric mixing ratios of CFC-11 and CFC-12, the two most abundant CFCs, are about 270 and 550 pptv, respectively.

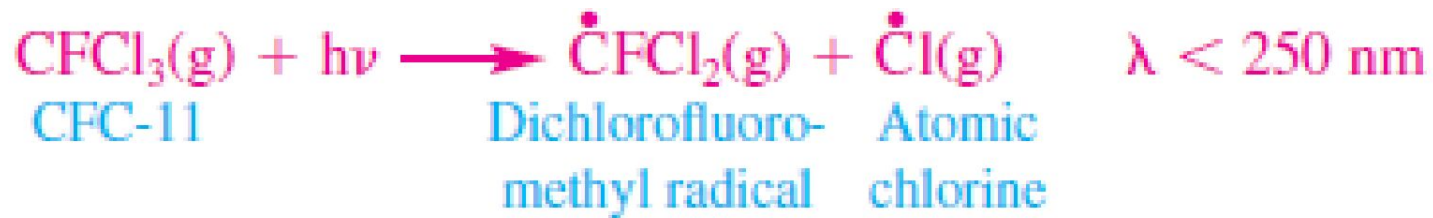


Variation of CFC-11, CFC-12, HCFC-22, and CCl₄(g) with altitude at 30°N latitude. Smoothed and scaled from Jackman et al. (1996) to present-day near surface mixing ratios.

Lifetimes of CFCs

- Because the stratosphere is one large temperature inversion, vertical transport of ozone through it is slow. About 10 Mt of chlorine in the form of CFCs reside in the troposphere, and the transfer rate of CFC-chlorine from the troposphere to the middle stratosphere is about 0.1 Mt per year. In this simplified scenario, the average time required for the transfer of a CFC molecule from the troposphere to the middle stratosphere is about 100 years.

Lifetimes of CFCs



In sum, the limiting factor in CFC decomposition in the stratosphere is not transported from the surface to the tropopause or photochemical breakdown in the stratosphere, but transported from the tropopause to the middle stratosphere.

Lifetimes of Non-CFCs

- Lifetimes of non-CFC chlorinated compounds are often shorter than are those of CFCs.
- The lifetimes of $\text{CCl}_4(\text{g})$ between emission and chemical destruction is about 35 years,

HCFC-22(g) – 12 years ,

$\text{CH}_2\text{Cl}_2(\text{g})$ – 5 years,

$\text{CH}_3\text{Cl}(\text{g})$ – 1.3 years,

$\text{HCl}(\text{g})$ less than 0.1 year.

- Non-CFCs generally have shorter lifetimes than do CFCs because they react faster with $\cdot\text{OH}(\text{g})$ than do CFCs and are often more water soluble than are CFCs.

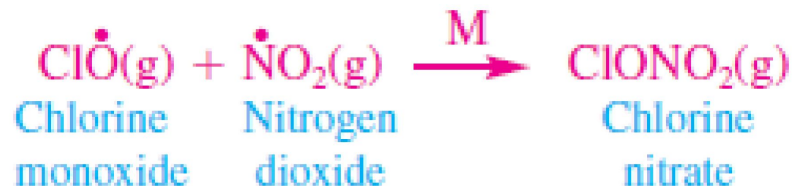
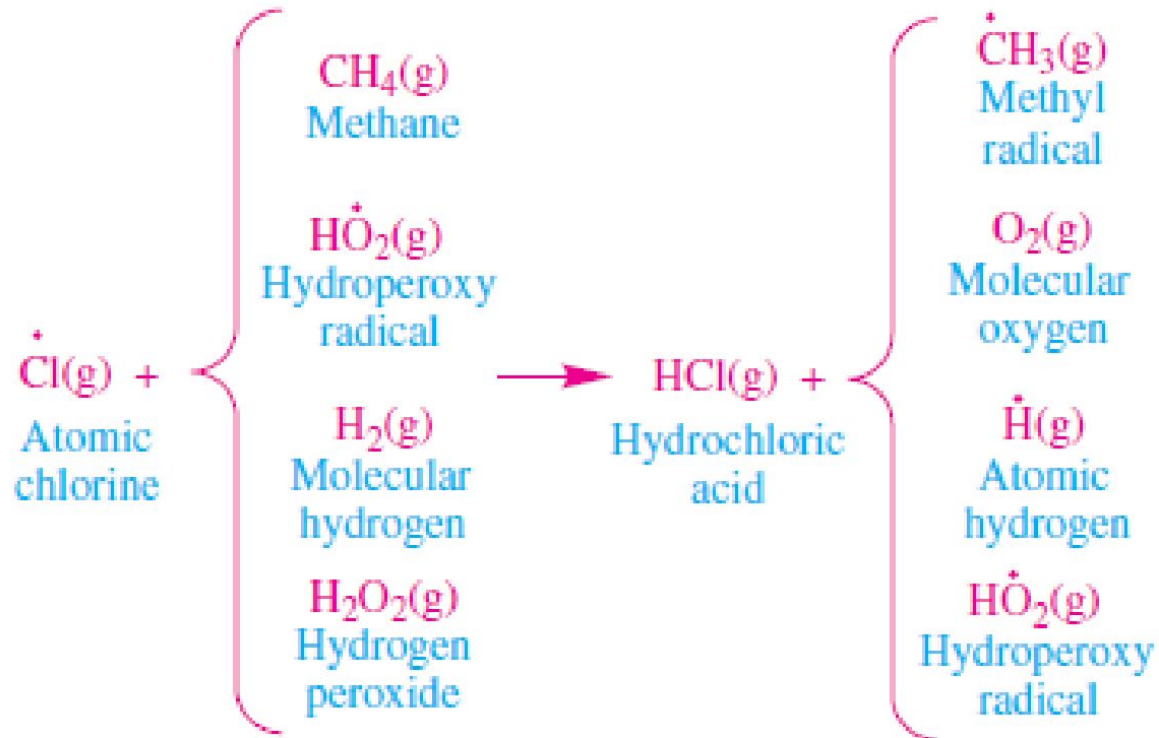
Lifetimes of Non-CFCs

- The benefit of a shorter lifetime for a chlorine-containing compounds is that, if breakdown occurs in the troposphere, the chlorine released can be converted to HCl(g), which is highly soluble and can be removed readily by rainout.
- Because the stratosphere does not contain clouds, except for ice-containing clouds that form seasonally over the poles, HCl(g) cannot be removed from the stratosphere by rainout.
- Some non-CFCs, such as HCFC-22, photolyze slower than do CFCs, so once HCFC- 22 reaches the middle stratosphere, its concentration builds up there to a greater extent than do concentrations of several CFCs

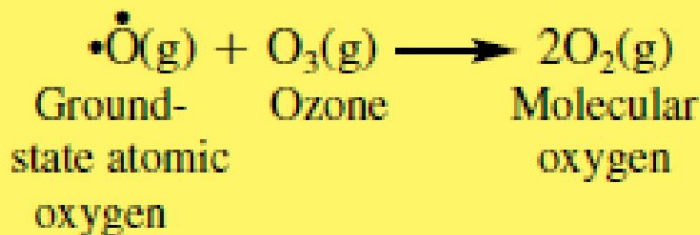
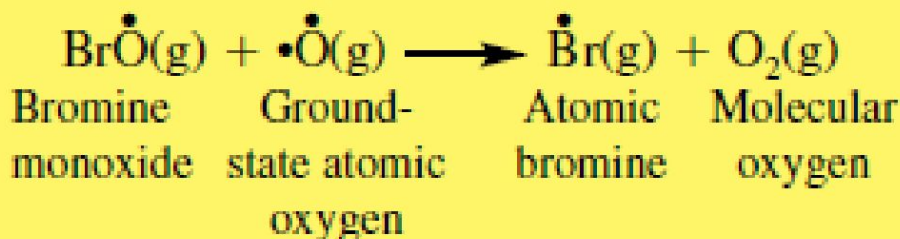
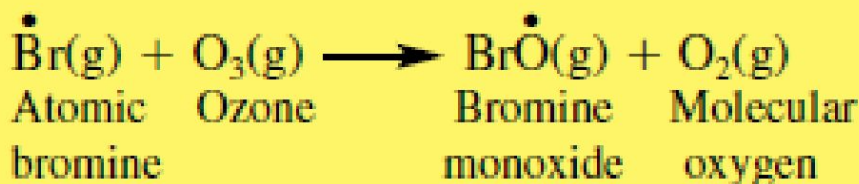
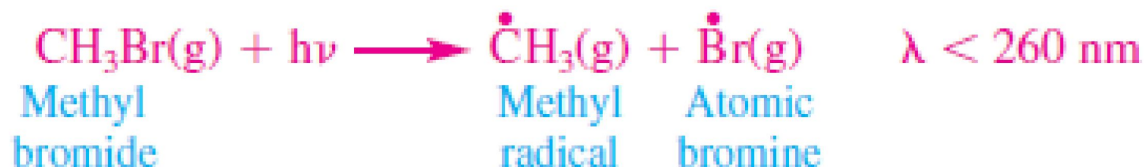
Emissions of Chlorine Compounds to the Stratosphere

Trade Name or Chemical Name	Chemical Formula	Contribution to Stratospheric Emissions (Percent)
Anthropogenic Sources		
CFC-12	$\text{CF}_2\text{Cl}_2(\text{g})$	28
CFC-11	$\text{CFCl}_3(\text{g})$	23
Carbon tetrachloride	$\text{CCl}_4(\text{g})$	12
Methyl chloroform	$\text{CH}_3\text{CCl}_3(\text{g})$	10
CFC-113	$\text{CFCl}_2\text{CF}_2\text{Cl}(\text{g})$	6
HCFC-22	$\text{CF}_2\text{ClH}(\text{g})$	3
Natural Sources		
Methyl chloride	$\text{CH}_3\text{Cl}(\text{g})$	15
Hydrochloric acid	$\text{HCl}(\text{g})$	3
Total		100
Source: WMO (1995).		

Catalytic Ozone Destruction by Chlorine

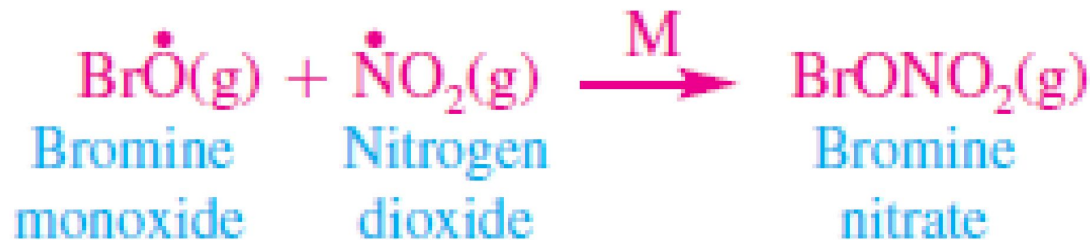
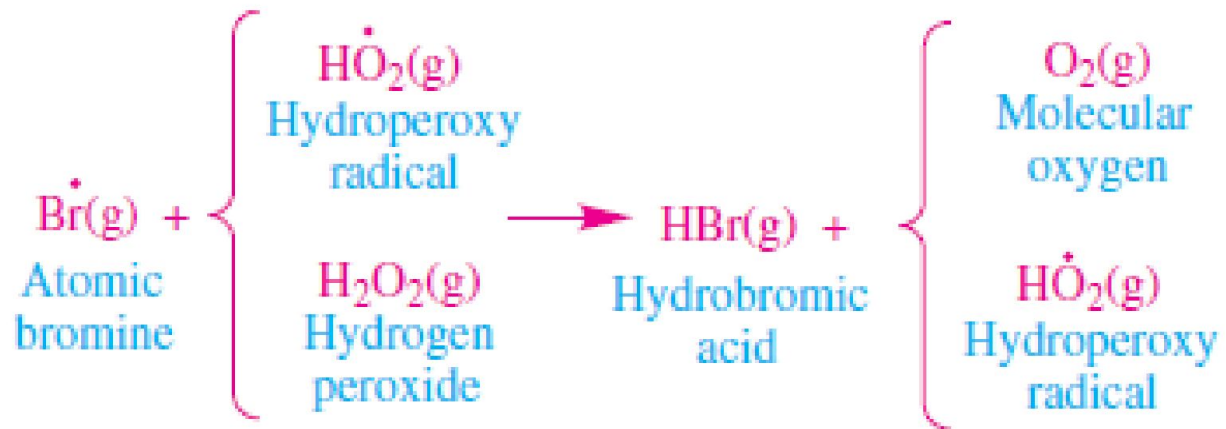


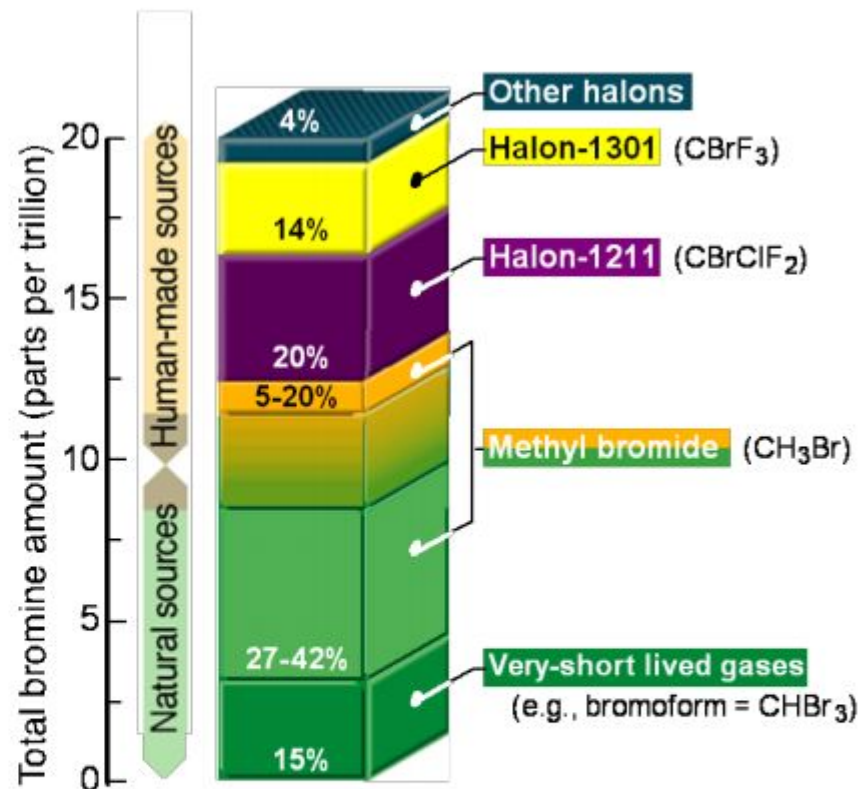
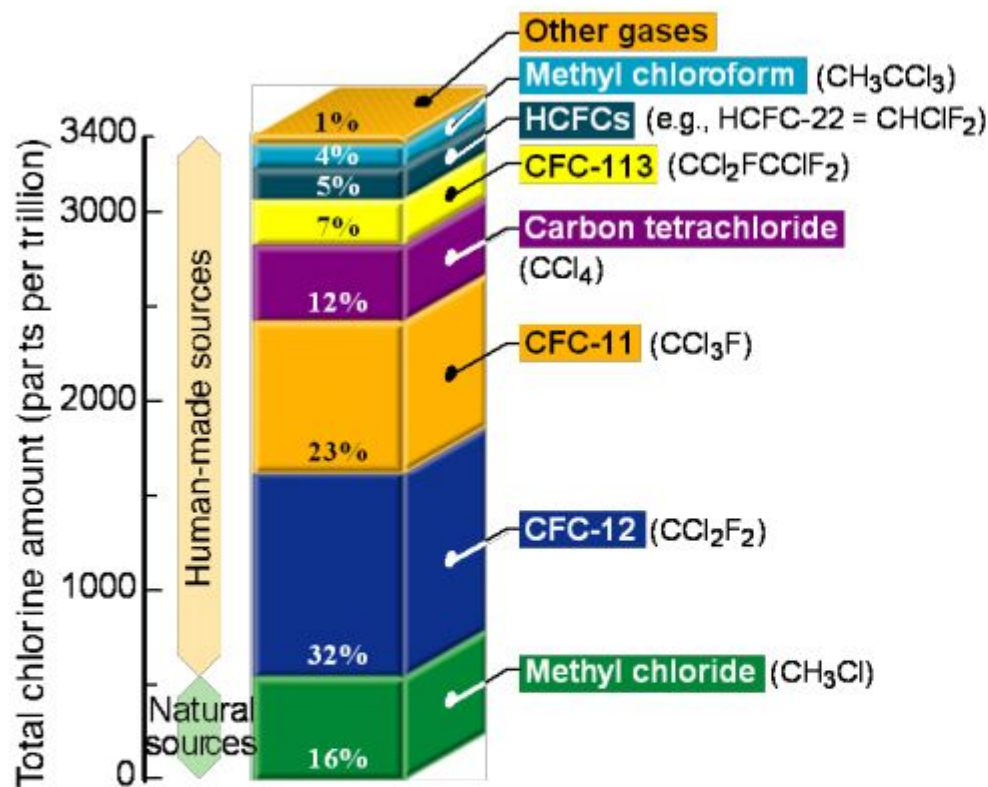
Catalytic Ozone Destruction by Bromine



(net process)

Catalytic Ozone Destruction by Bromine





- Cl is much more abundant than Br
- Br is about 50 times more effective at O_3 destruction

Effects on Humans

Increases in UV-B radiation have potential to affect

- the skin,
- eyes,
- immune system of humans.

Effects on Skin

- The severity of effects of UV-B radiation on skin depends on skin pigmentation.
- UV-B effects on human skin include sunburn (erythema), photoaging of the skin, and skin cancer.

Effects on Eyes

- With respect to the eye, the **cornea**, which covers the iris and the lens, is the tissue most susceptible to UV-B damage.
- The most common eye problem associated with UV-B exposure is **photokeratitis** or “**snowblindness**,” an inflammation or reddening of the eyeball. Other symptoms include a feeling of severe pain, tearing, avoidance of light, and twitching.
- The most expensive eye-related disease associated with UV-B radiation is **cataract**, a degenerative loss in the transparency of the lens that frequently results in blindness unless the damaged lens is removed. Worldwide, cataract is the leading cause of blindness. More severe, but less widespread, eye-related diseases are squamous cell carcinoma, which affects the cornea, and **ocular melanoma**, which affects the iris and related tissues.

Effects on the Immune System

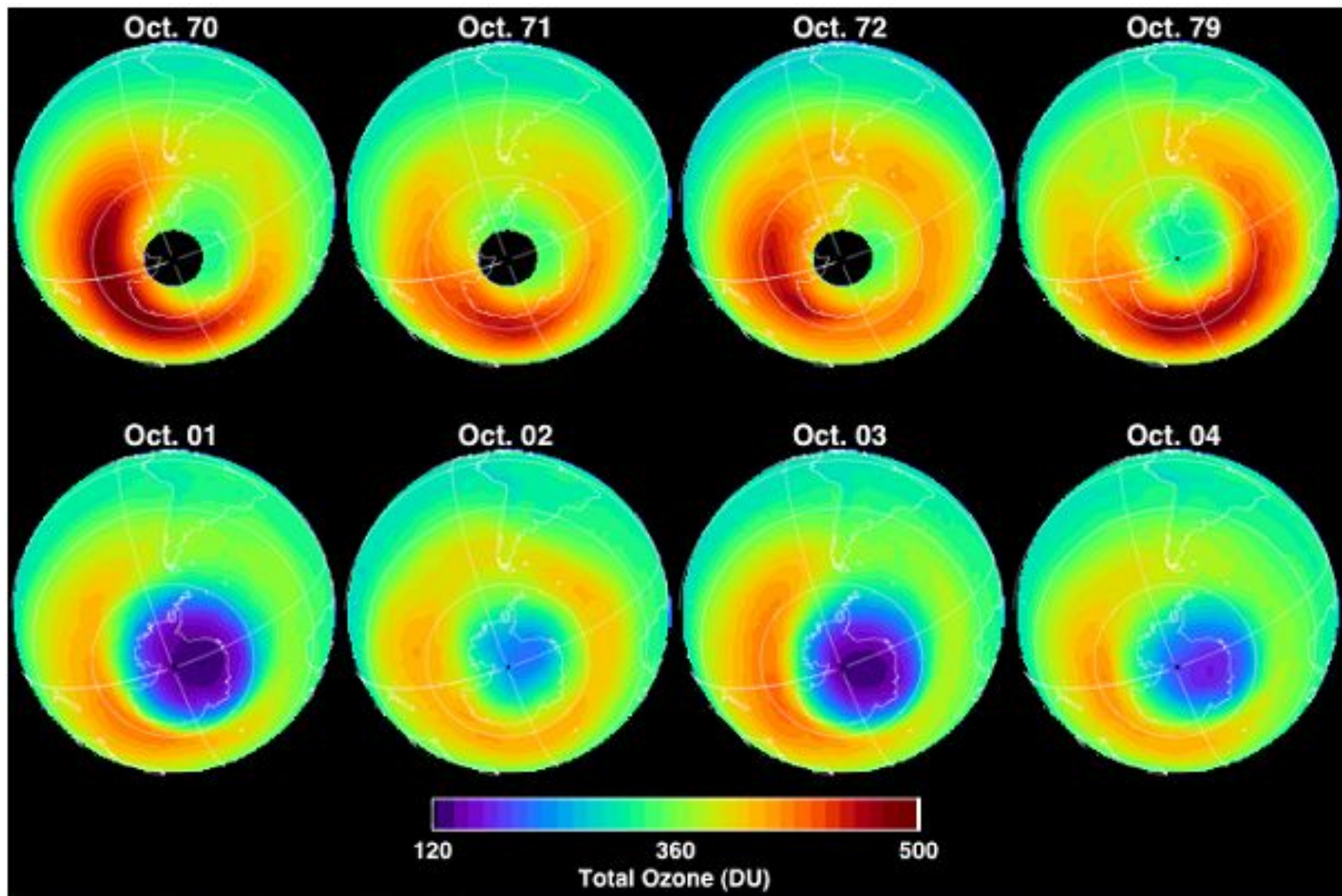
- Enhanced UV-B radiation has been linked to suppression of these cells, reducing resistance to certain tumors and infections. Suppressed immune responses to UV-B have been reported for herpes, tuberculosis, leprosy, trichinella, candidiasis, leishmaniasis, listeriosis, and Lyme disease.

Effects on the Global Carbon and Nitrogen Cycles

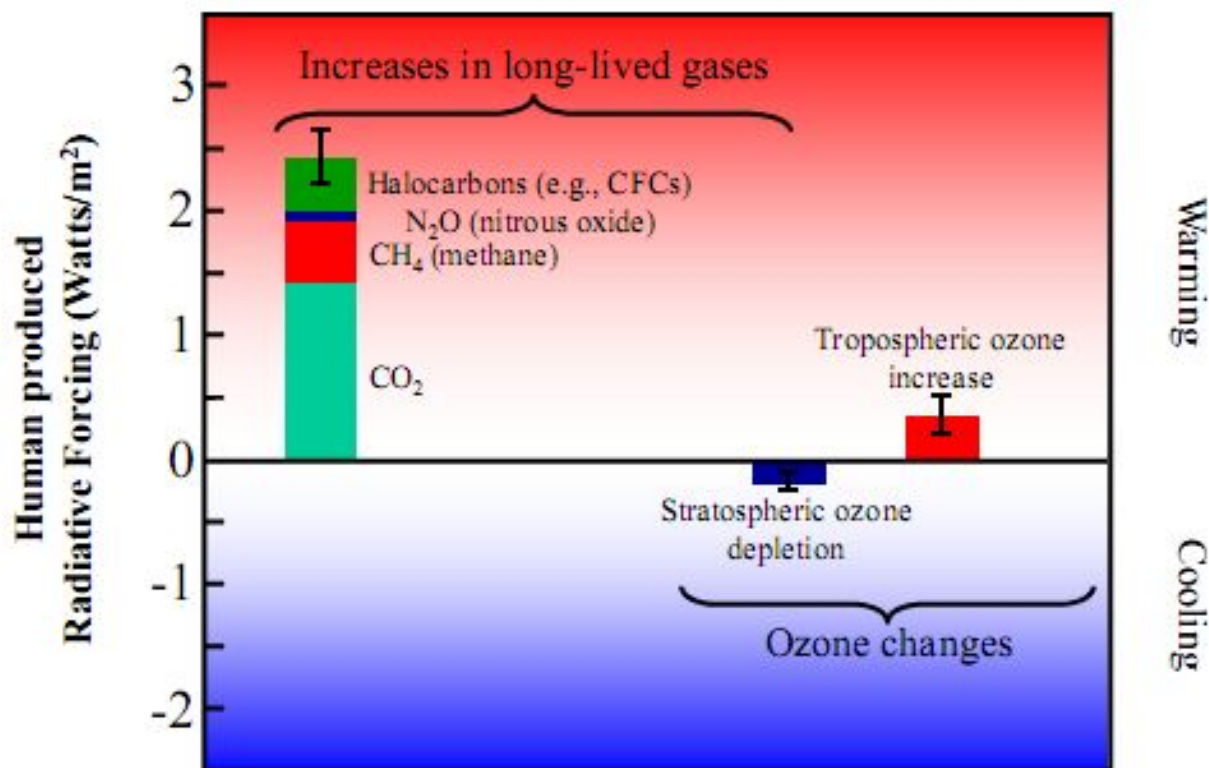
- Changes in UV-B radiation affect the global carbon and nitrogen cycles.
- UV-B damages phytoplankton, reducing their consumption of carbon dioxide gas [CO₂(g)].
- UV-B also enhances photodegradation (breakdown by light) of dead plant material, increasing release of CO₂(g) back to the air. UV-B enhances the release of carbon monoxide gas [CO(g)] from charred vegetation. With respect to the nitrogen cycle, UV-B affects the rate of nitrogen fixation by cyanobacteria.

Effects on Tropospheric Ozone

- Increases in UV-B radiation increase photolysis rates of UV-B absorbing gases, such as ozone, nitrogen dioxide, formaldehyde, hydrogen peroxide, acetaldehyde, and acetone.
- Increases in photolysis rates of nitrogen dioxide, formaldehyde, and acetaldehyde enhance rates of free-tropospheric ozone formation.
- Whereas reductions in stratospheric ozone increase UV-B radiation reaching the free troposphere, increases in aerosol loadings in urban air can either decrease or increase UV-B radiation. Reductions in UV-B in polluted air depress ozone formation; increases in UV-B have the opposite effect.



Ozone and climate change



Ozone change is not a primary cause of climate change.

- Ozone depleting substances contribute to climate change.
- Ozone changes causes a climate response that is generally larger than the Halocarbon response.
- Climate change may seriously impact ozone levels.

Arctic stratospheric ozone

- A great deal of scientific effort has gone into understanding the physical and chemical processes contributing to the Antarctic ozone hole. Less is known about processes of Arctic ozone depletion because, while similar in its general climate, the Arctic does not form a distinct seasonal ozone hole. This
- is primarily due to the instability of the Arctic polar vortex, a consequence of larger land masses in the northern middle hemisphere than in the southern middle hemisphere.

Total column ozone measurement

Toronto data-base St. no.	Year measurements started	Location name	Location country	Latitude, °N	Longitude, ° (negative, if west)
5	1957	Dikson Island	Russia	73.50	80.23
18	1957	Alert	Canada	82.50	-62.30
24	1957	Resolute	Canada	74.72	-94.98
42	1957	St. Petersburg	Russia	59.97	30.30
43	1952	Lerwick	UK	60.13	-1.18
51	1952	Reykjavik	Iceland	64.13	-21.90
52	1943	Tromsø	Norway	69.65	18.95
89	1990	Ny-Ålesund, Svalbard	Norway	78.93	11.88
105	1963	Fairbanks	USA	64.82	-147.87
114	1974	Heiss Island	Russia	80.62	58.10
117	1961	Murmansk	Russia	68.97	33.05
118	1962	Nagaev	Russia	59.58	150.78
123	1973	Yakutsk	Russia	62.08	129.75
129	1973	Pechora	Russia	65.12	57.10
140	1990	Thule	Greenland	76.52	-68.76
142	1973	Igarka	Russia	67.47	86.57
144	1973	Markovo	Russia	64.68	170.42
145	1974	Olenek	Russia	68.50	112.43
148	1973	Vitim	Russia	59.45	112.58
150	1974	Mansijsk	Russia	60.97	69.07
165	1946	Oslo	Norway	59.91	10.72
186	1975	Tiksi	Russia	71.58	128.92
189	1970	Hornsund, Svalbard	Norway	77.00	15.55

<http://www.woudc.org/data/explore.php?lang=en>

Total column ozone levels have been measured for the past several decades in or near the Arctic. Despite their importance for scientific research and long-term monitoring, many of these stations are under threat of being shut down due to budget considerations.

The data from these stations are available from the World Ozone and UV Data Center in Toronto, Canada.

Effects of increased ultraviolet radiation in Arctic

- *Cold climate and low sun make polar life extra vulnerable*
- *Shrubs grow more slowly*
- *Lake life is often stressed by high UV*
- *Marine plants are inhibited by extra radiation*
- *Sunlight can damage zooplankton and fish*
- *Cycling of carbon may change*
- *Plastics will degrade faster*