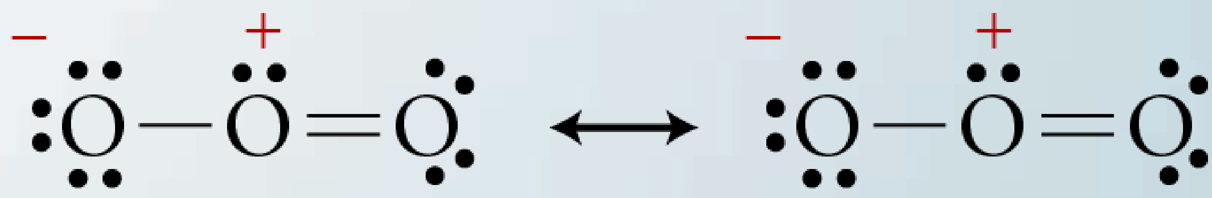
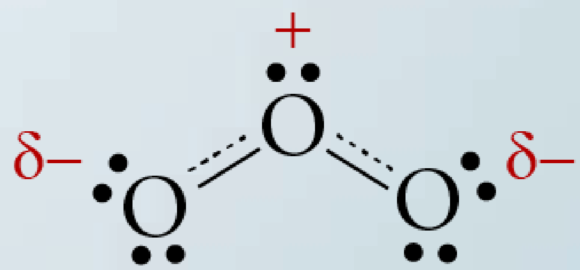
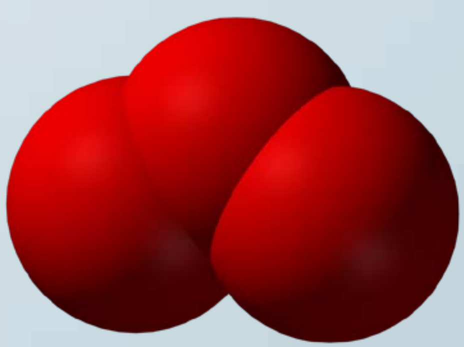
IPOL 512

Ozone

Ozone, O_3







Ozone Information

- Less stable than O_2, breaking down with a half life of about 30 minutes in the lower atmosphere.

  $$2O_3 \rightarrow 3O_2$$

- Ozone's odor is sharp, similar to that of chlorine.
- Ozone is a powerful oxidizing agent
  - Has many industrial and consumer applications related to oxidation.
    - Used to sanitize hot tubs
    - Used in industry to bleach waxes, oils, and textiles.
  - Strong respiratory irritant that can lead to shortness of breath, chest pain when inhaling, wheezing, and coughing
  - Damages rubber and plastics, leading to premature deterioration of products made with these materials.
  - Ozone damages plants.

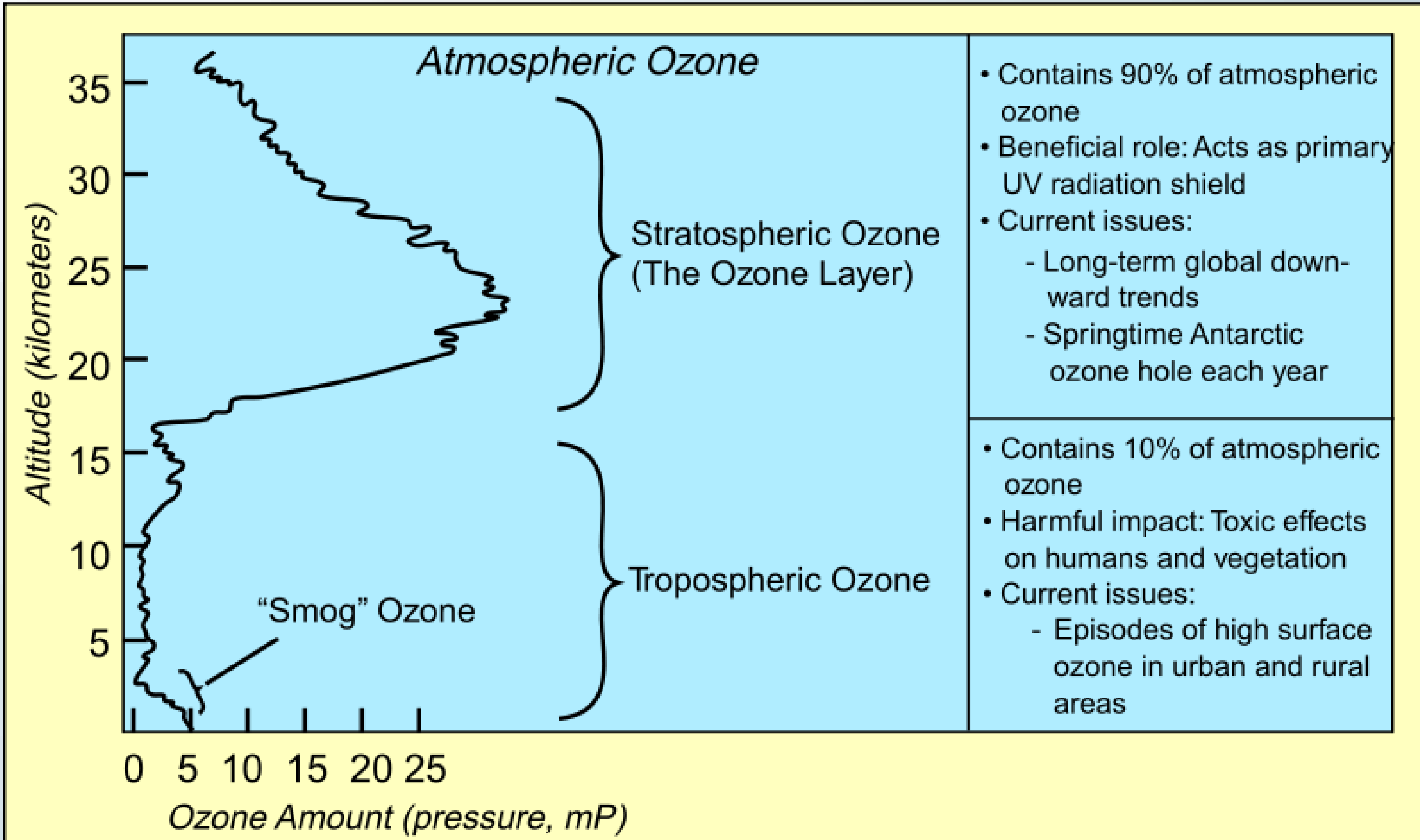
Ozone Information

- Ozone layer prevents damaging ultraviolet radiant energy from reaching the Earth's surface, preventing damage to both plants and animals.
- Ozone is also a greenhouse gas.

Vertical Distribution of Ozone

- Distribution of O_3 in the atmosphere is non-uniform.
  - Mean lifetime of O_3 molecules between formation and destruction is short compared to atmospheric mixing times, so different formation rates at different altitudes cannot be evened out by mixing.
- Vertical distribution: >90% of O_3 is in stratosphere, <10% in troposphere.
- Human activities tend to
  - Decrease O_3 concentrations in the stratosphere, increasing penetration of damaging UV radiation to Earth's surface
  - Increase O_3 concentrations near the surface, aggravating damage to organisms.
- Therefore, we are decreasing ozone where it is good for us and increasing it where it is bad for us.

Ozone in the Atmosphere



Ozone Formation in Troposphere

- Highest concentrations found in large industrial cities with lots of cars and lots of sun.

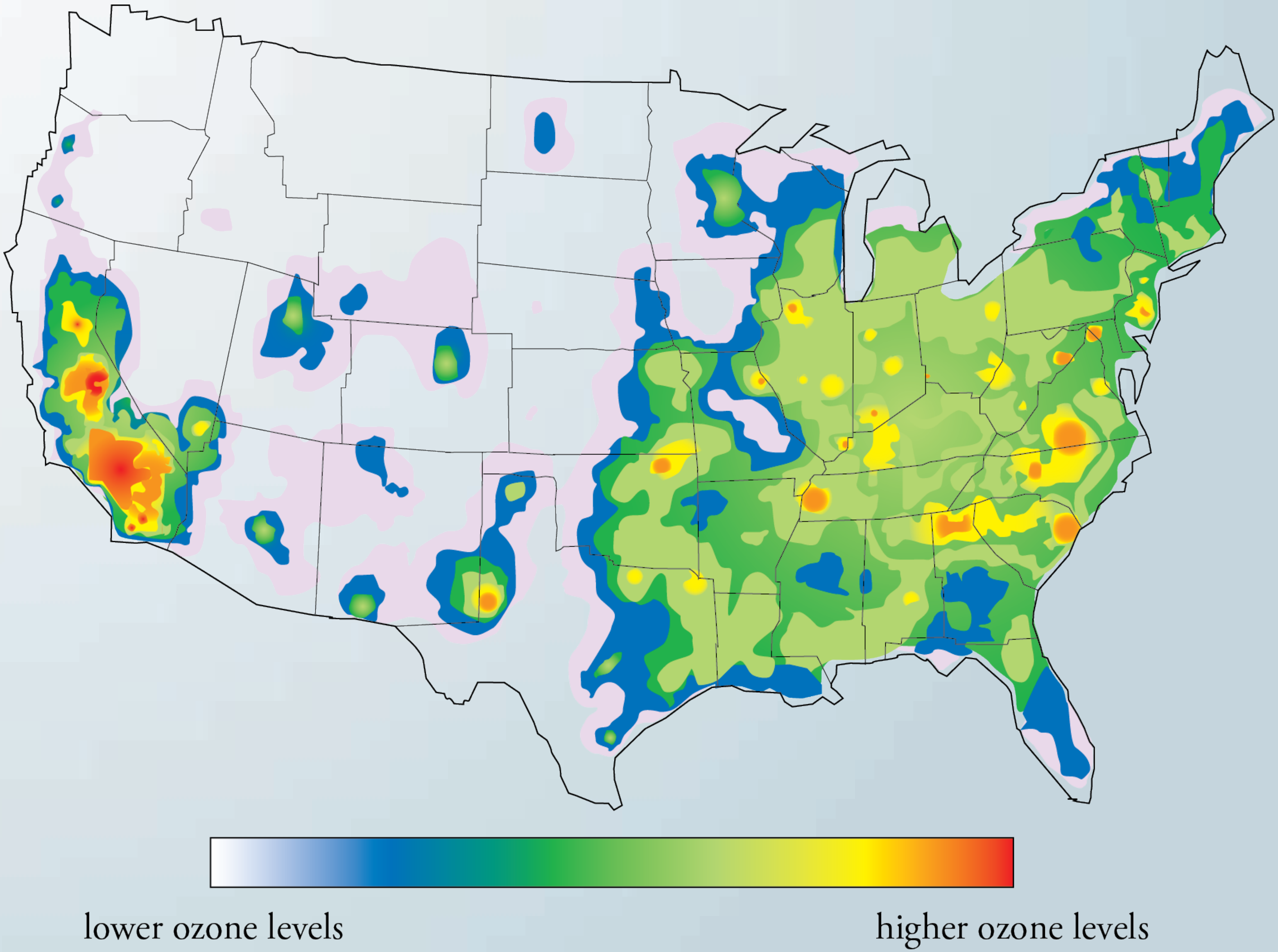
$$N_2(g) + O_2(g) \rightarrow 2NO(g)$$

$$2NO(g) + O_2(g) \rightarrow 2NO_2(g)$$

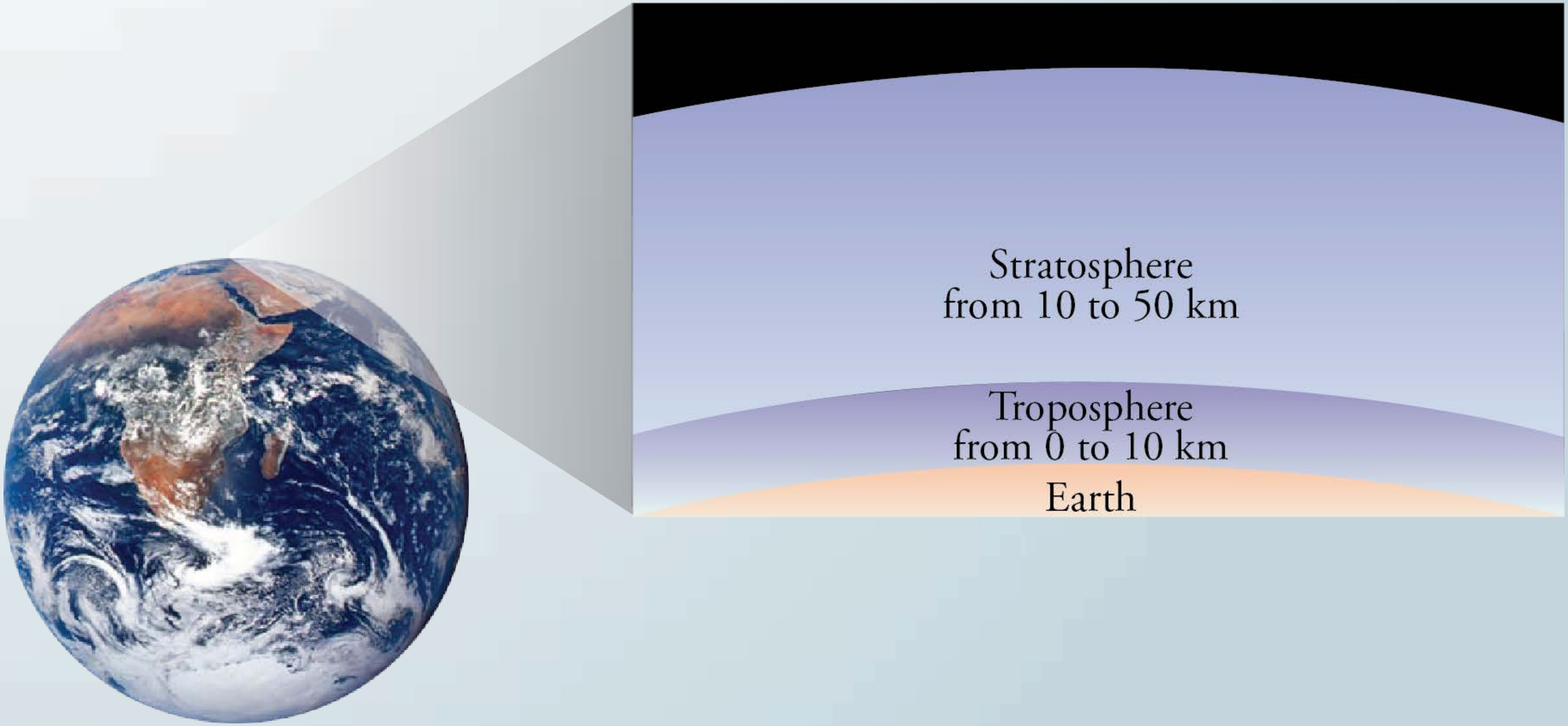
$$NO_2(g) \xrightarrow{\lambda < 400\ \text{nm}} NO(g) + O(g)$$

$$O(g) + O_2(g) \rightarrow O_3(g)$$

National Ozone Concentrations

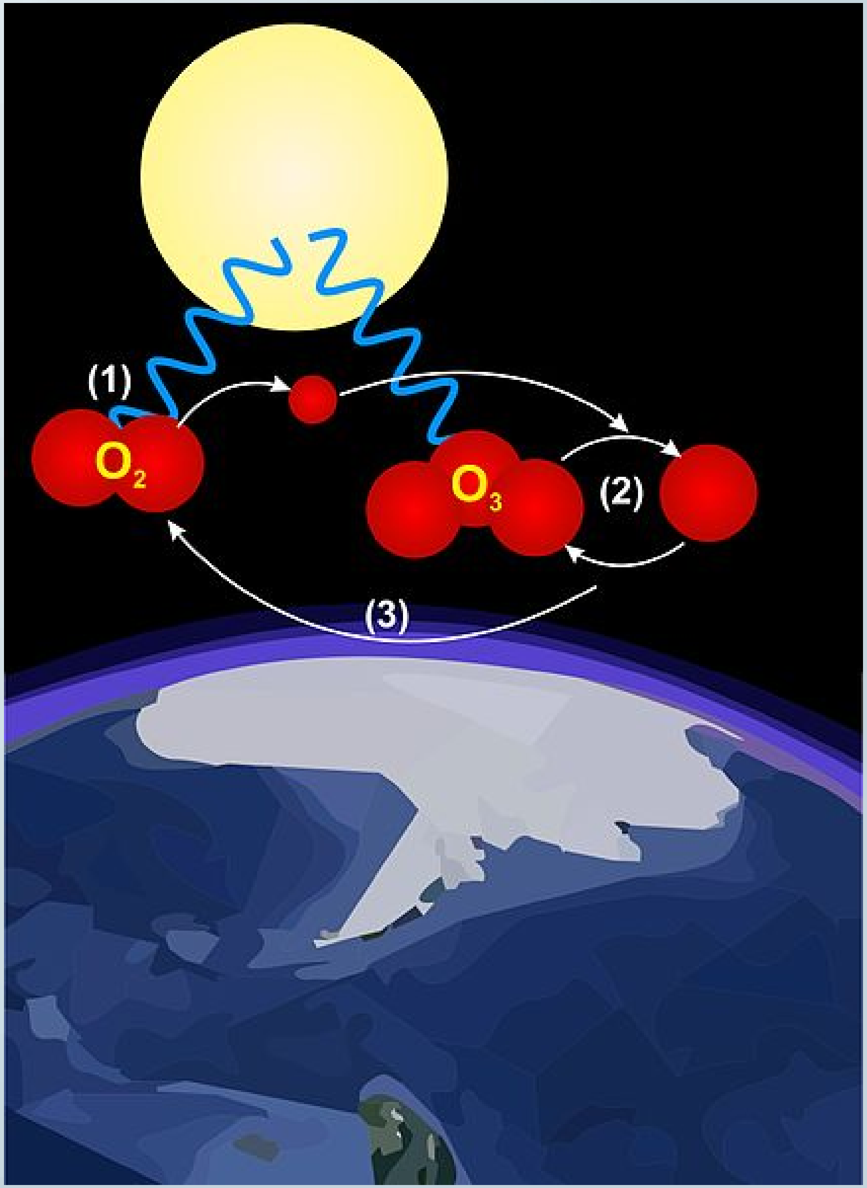


The Earth’s Atmosphere



Ozone-Oxygen (Chapman) Cycle

- 400 Gt O_3 produced per day.
- Global mass of ozone is about 3000 Gt, meaning the Sun produces about 12% of the ozone layer each day.
- 1930 Sydney Chapman suggested a cycle for the production and destruction of ozone.



O_2-O_3 Cycle in the Stratosphere

- Mostly made by

  O_2 + photon $\rightarrow$ 2O

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

  M represents third body, such as an N_2 molecule, that carries off the excess energy of the reaction.

- Destroyed by

  O_3 + photon $\rightarrow$ O + O_2

  O + O_3 $\rightarrow$ $2O_2$

Photon Energy, Wavelength, and Frequency

$$\varepsilon = h\nu$$

$$c = \lambda\nu$$

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

$$\varepsilon = \frac{hc}{\lambda}$$

$$\lambda = \frac{hc}{\varepsilon}$$

ε = energy of photon

h = Planck's constant = 6.626×10^{-34} J•s

c = velocity of light = 2.9979×10^{8} m/s

ν = frequency

λ = wavelength

Photon Energy O_2 to 2O

- What is the maximum wavelength in nanometers required to photo-dissociate one molecule of O_2?

O_2 + photon $\rightarrow$ O + O ΔE = 495 kJ/mol

Photon Energy O_2 to 2O

- What is the maximum wavelength in nanometers required to photo-dissociate one molecule of O_2?

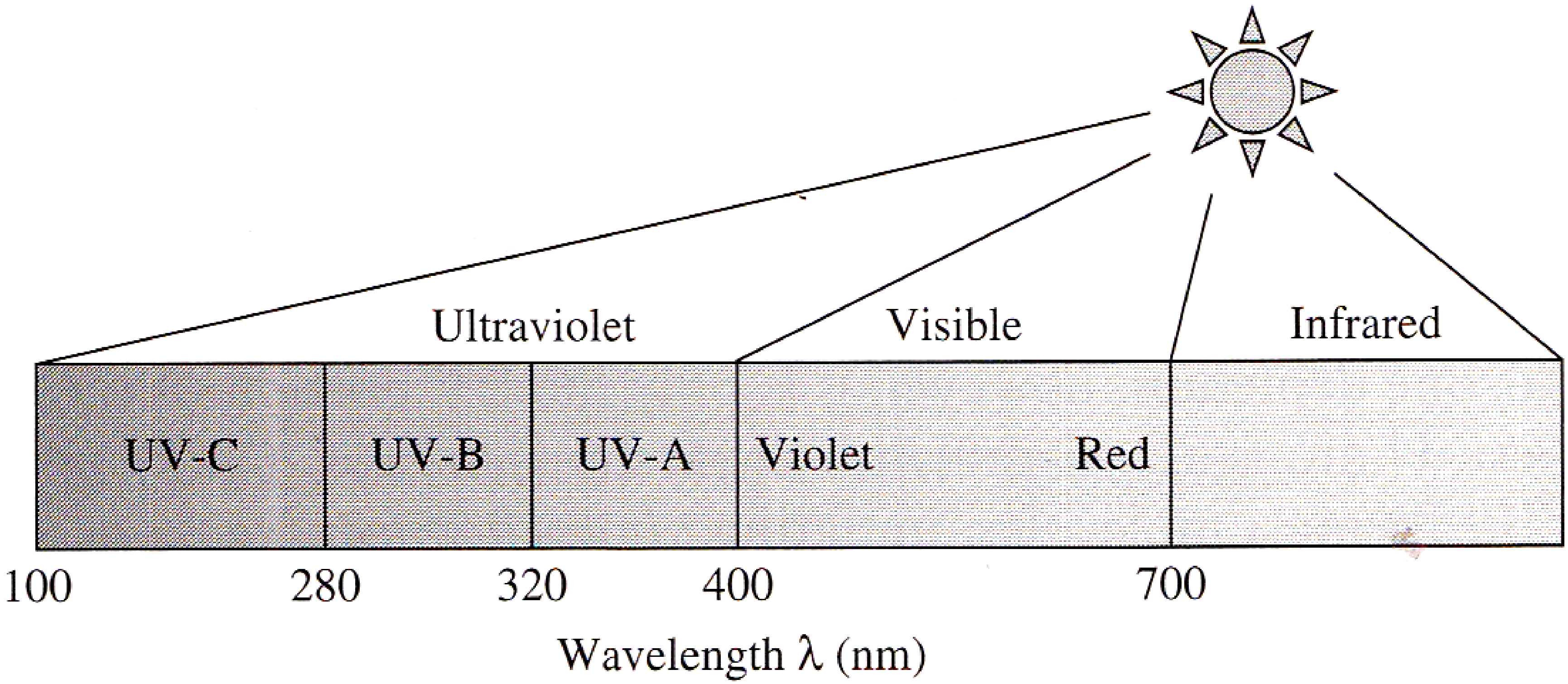
O_2 + photon $\rightarrow$ O + O $\Delta E = 495$ kJ/mol O_2

$$\frac{?\,\text{J}}{\text{photon}} = \left(\frac{495\ \text{kJ}}{1\ \text{mol}}\right)\left(\frac{10^3\ \text{J}}{1\ \text{kJ}}\right)\left(\frac{1\ \text{mol}}{6.022 \times 10^{23}\ \text{molecules}}\right)\left(\frac{1\ \text{molecule}}{1\ \text{photon}}\right)$$

$$= 8.22 \times 10^{-19}\ \text{J/photon}$$

$$\lambda = \frac{hc}{\varepsilon} = \frac{6.626 \times 10^{-34}\ \text{J}\bullet\text{s}\ 2.9979 \times 10^{8}\ \text{m/s}}{8.22 \times 10^{-19}\ \text{J}}\left(\frac{10^9\ \text{nm}}{1\ \text{m}}\right) = \mathbf{242\ nm}$$

Solar UV, visible, and IR ranges



Masters & Ela, 3rd ed.

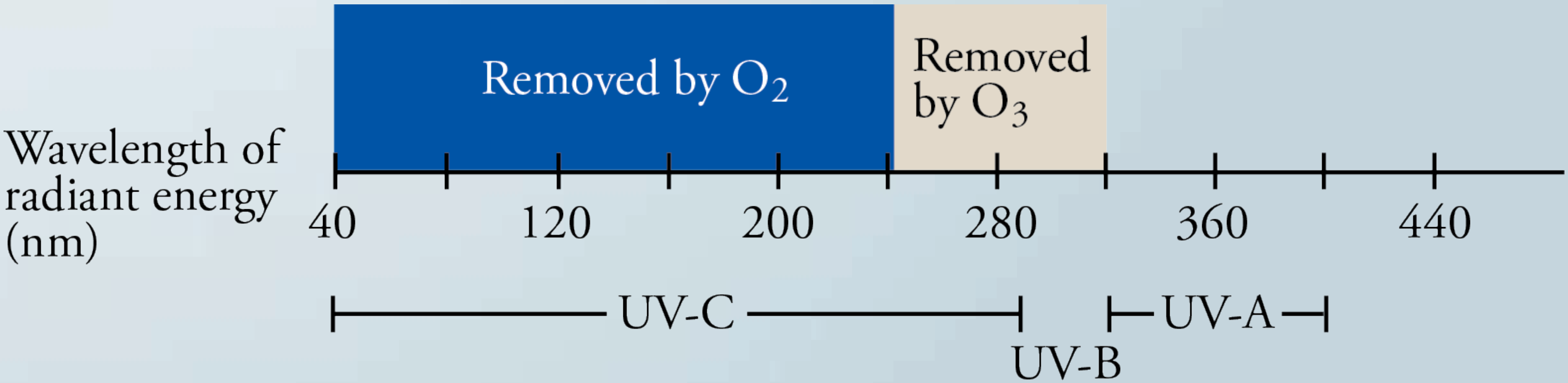
Ultraviolet Radiation

- **UV-A** 320-400 nm
  - reaches the surface of the Earth
- **UV-B** 280-320 nm
  - 10% of UV-B reaches the surface of Earth
- **UV-C** 100-280 nm
  - mostly removed in upper atmosphere

Removal of UV in Stratosphere

$$O_2(g) \xrightarrow{\text{UV with } \lambda < 242 \text{ nm}} 2O(g)$$

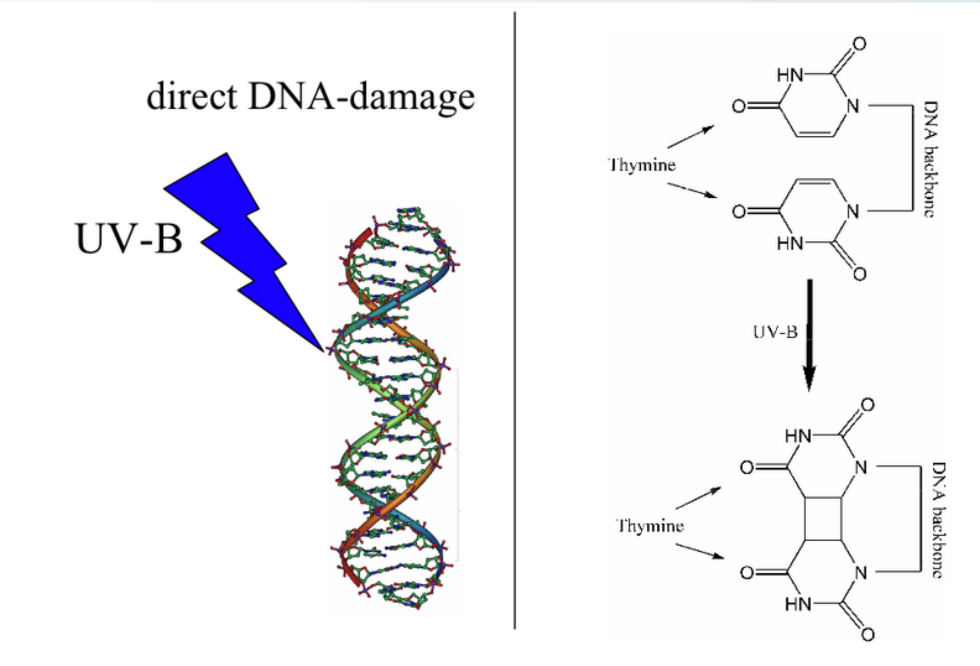
$$O_3(g) \xrightarrow{\text{UV with } \lambda \text{ from 240 to 320 nm}} O(g) + O_2(g)$$

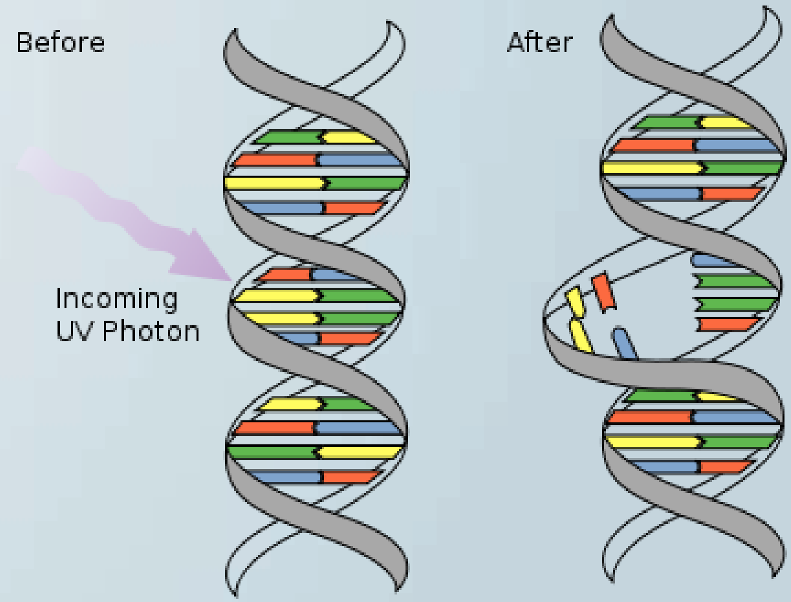


UV and Health

- UV-A, UV-B, and UV-C can all damage collagen fibers and accelerate aging of the skin.
- UVB facilitates the production of Vitamin D_3.
- Both UV-A and UV-B destroy vitamin A in skin.
- UV-A creates mostly free radicals. The damage caused by free radicals is called indirect DNA damage.
- UV-B and UV-C can cause direct DNA damage that can lead to a variety of problems, including cancer.

Direct DNA Damage by UV-B





UV photons harm DNA molecules in different ways. In one common way, adjacent thymine bases bond with each other, instead of across the "ladder". This "thymine dimer" makes a bulge, and the DNA molecule does not function properly.

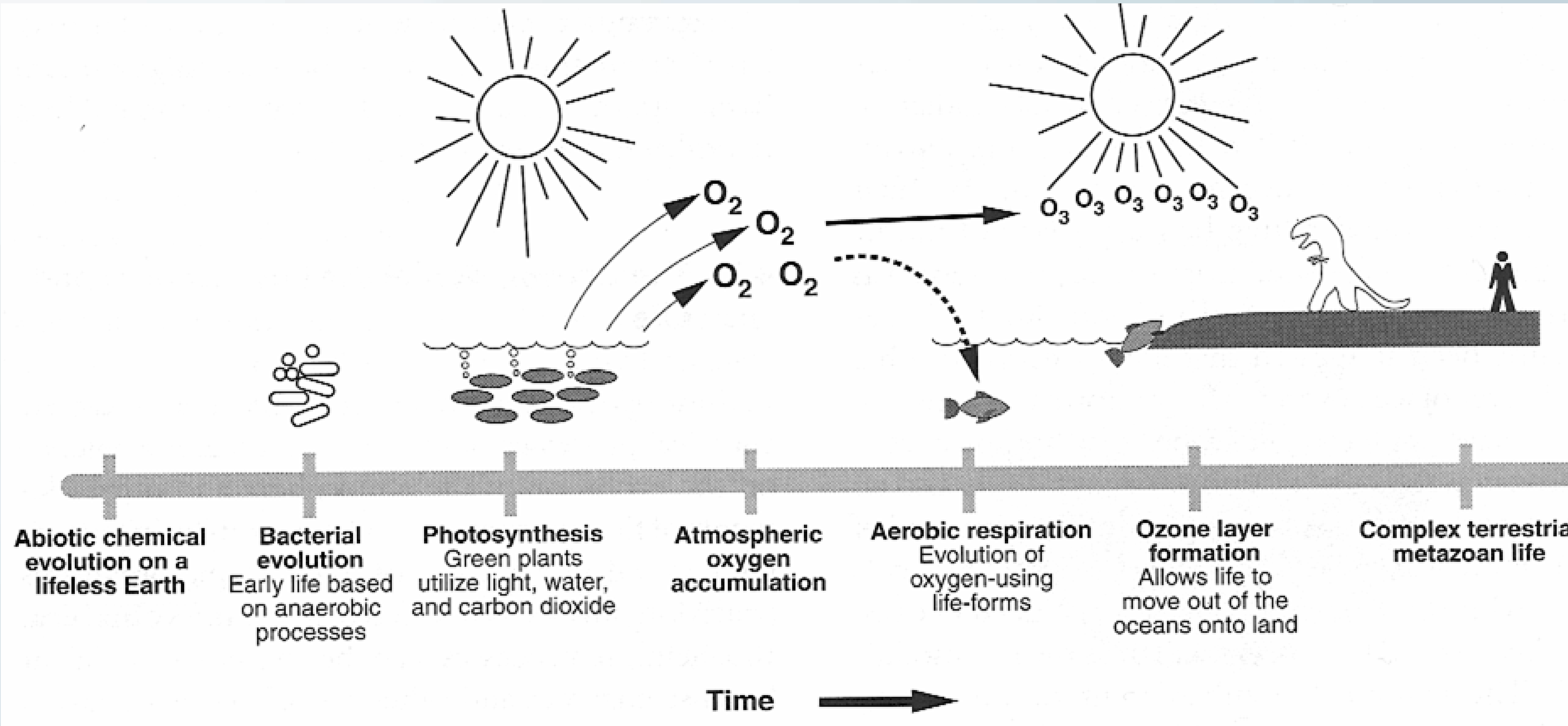
Other Effects of UV

- An increase of UV radiation would affect crops.
- A number of economically important species of plants, such as rice, depend on cyanobacteria residing on their roots for the retention of nitrogen. Cyanobacteria are sensitive to UV light and would be affected by its increase.

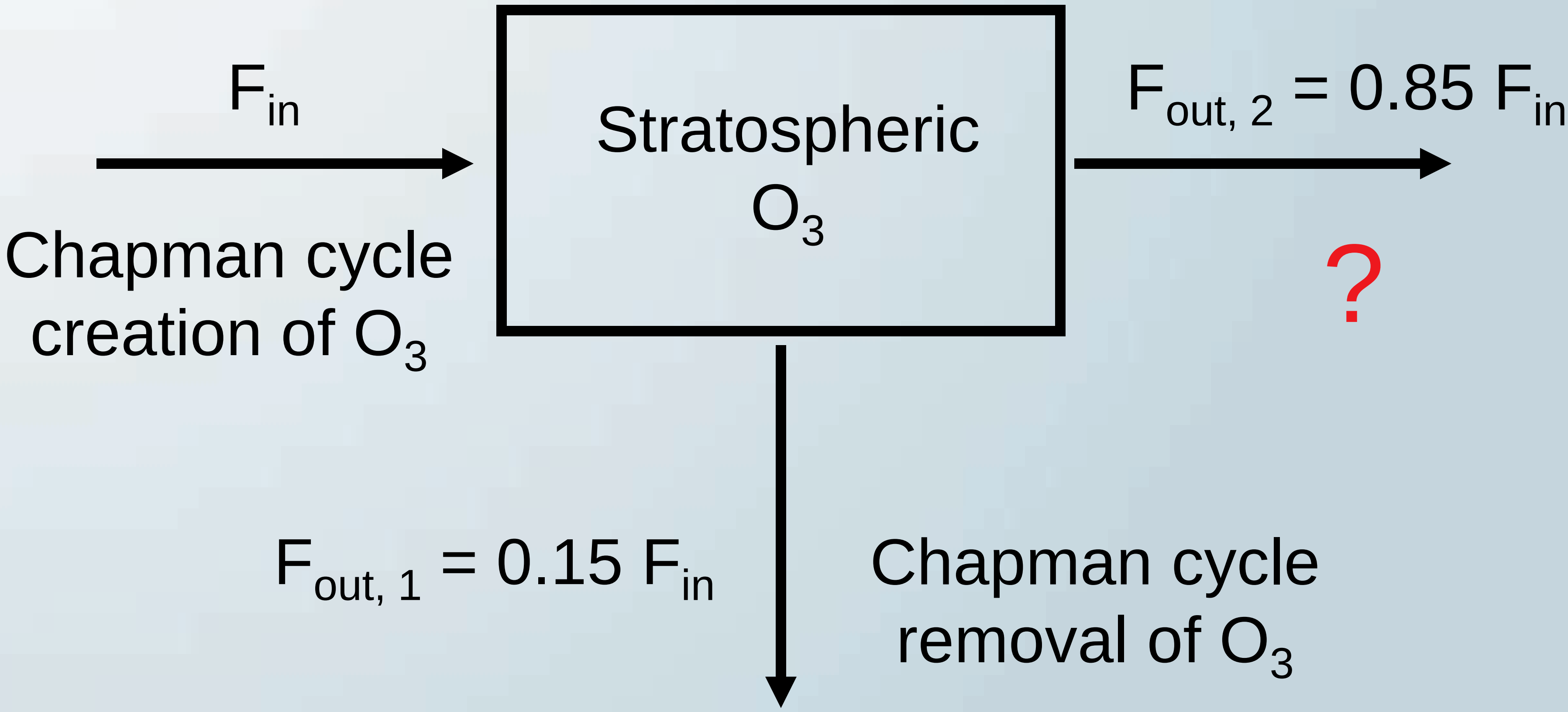
Another Example - UV-B and DNA

- UV-B excites DNA molecules in skin cells, causing covalent bonds to form between adjacent cytosine bases. When DNA polymerase comes along to replicate this strand of DNA, it reads "AA" and not the original "CC". This causes the DNA replication mechanism to add a "TT" on the growing strand.
- This mutation can result in cancerous growths, and is known as a "classical C-T mutation". The mutations caused by the direct DNA damage carry a UV signature mutation that is commonly seen in skin cancers.

Evolution of Life



1930s Mystery: Where Does the O_3 Go?



Free Radical Catalytic Chain Reactions

Catalyst = a substance that speeds a chemical reaction without being permanently altered itself.

Atmospheric gases = the most abundant species have an even number of electrons, e.g. N_2, O_2, Ar, CO_2, H_2O, O_3

Free Radical = species with odd number of electrons, e.g. HO_X•, ClO_X•, NO_X•, BrO_X•, and CH_3O_X•

- Act as catalysts for chain reactions in destroying O_3

Generic Free Radical Chain Reaction

$R\bullet + O_3 \rightarrow ZO\bullet + O_2$

$ZO\bullet + O \rightarrow Z\bullet + O_2$

(Net) $O + O_3 \rightarrow 2\,O_2$

$Z\bullet$ = free radical

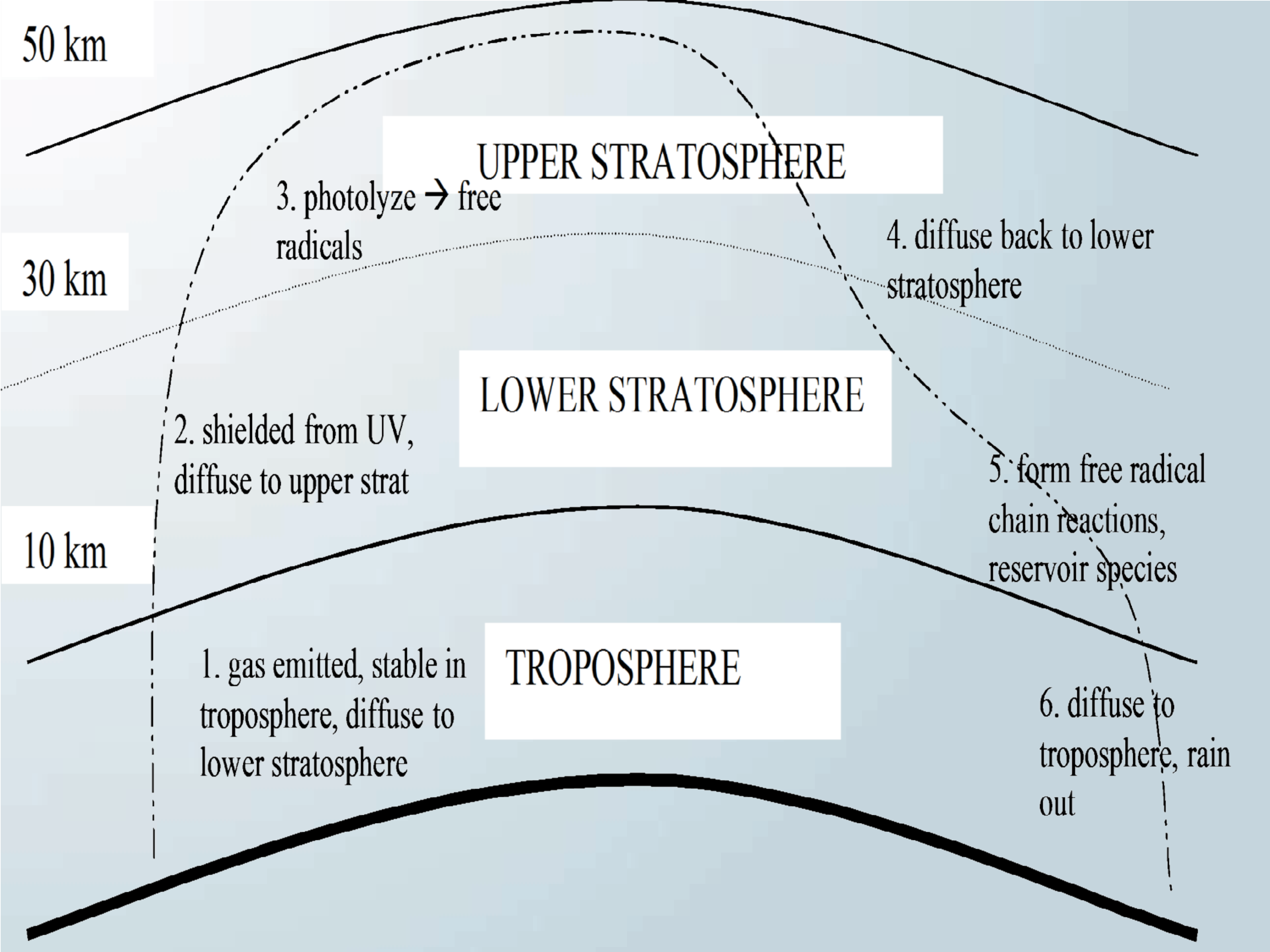
$HO_X\bullet$ such as $H\bullet$, $OH\bullet$, $HO_2\bullet$

$ClO_X\bullet$ such as $Cl\bullet$, $ClO\bullet$, $ClO_2\bullet$

$NO_X\bullet$ such as $NO\bullet$, $NO_2\bullet$

$BrO_X\bullet$

$CH_3O_X\bullet$


50 km
30 km
10 km
UPPER STRATOSPHERE
LOWER STRATOSPHERE
TROPOSPHERE
1. gas emitted, stable in troposphere, diffuse to lower stratosphere
2. shielded from UV, diffuse to upper strat
3. photolyze → free radicals
4. diffuse back to lower stratosphere
5. form free radical chain reactions, reservoir species
6. diffuse to troposphere, rain out

EXAMPLE: N_2O

- N_2O emitted at surface is not very reactive, eventually diffuses into stratosphere, where:

$$N_2O + h\nu \rightarrow N_2 + O \quad \text{(80\% of time)}$$
$$N_2O + h\nu \rightarrow NO + N \quad \text{(20\% of time)}$$

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

(Net) $O + O_3 \rightarrow 2\,O_2$

- Note: NO emitted at surface is too reactive, short residence time, can't make it to stratosphere. But N_2O can.

Example: CH_3Cl (methyl chloride)

- CH_3Cl originates in kelp beds in the ocean, not highly reactive, some diffuses into stratosphere

$$CH_3Cl + h\nu \rightarrow CH_3 + Cl \quad \text{(two odd species!!!)}$$

- 1 Cl molecule → catalyzes destruction of ~10^4 O_3 molecules

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

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

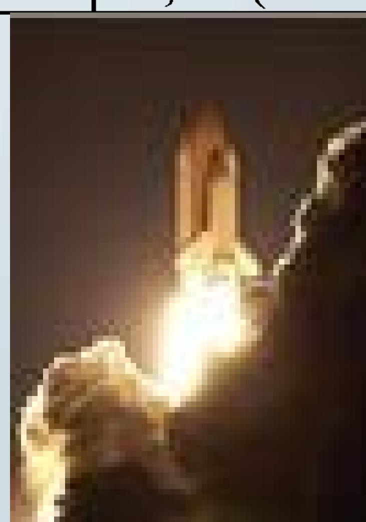
$$\text{(Net)} \quad O + O_3 \rightarrow 3\,O_2$$

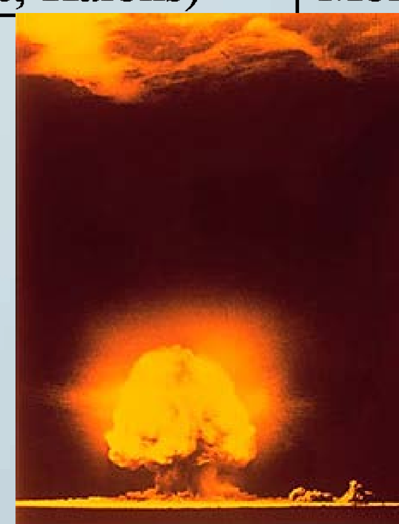
- interference reactions ↓ reservoir species ↘

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

HUMAN IMPACTS ON STRATOSPHERIC OZONE

ANTHROPOGENIC SOURCE	FREE RADICAL ADDED TO STRATOSPHERE	SCIENTIST RAISING CONCERN, YEAR
Supersonic Transports	OH, NO (from combustion)	Harold Johnston, 1970
Fertilizers	NO (from N_2O)	
Gasoline Additives	Br (from EDB - $(CH_2)_2Br_2$)	
Solid Fuel Rockets	Cl (from NH_4ClO_4 oxidizer)	
Nuclear Weapons	NO (from atmospheric testing)	
Refrigerants & Propellants	Cl, Br (from CFCs, Halons)	Molina & Rowland, 1974





Chlorofluorocarbons (CFCs)

- CFC-11 $CFCl_3$
  - average lifetime in atmosphere is ≈50 years
- CFC-12 CF_2Cl_2
  - average lifetime in atmosphere is ≈102 years
- Very stable, nontoxic, and can be liquefied with minimal pressure
- Used as propellants in aerosol cans, solvents, blowing agents for foams, coolant in refrigerators, and other uses.

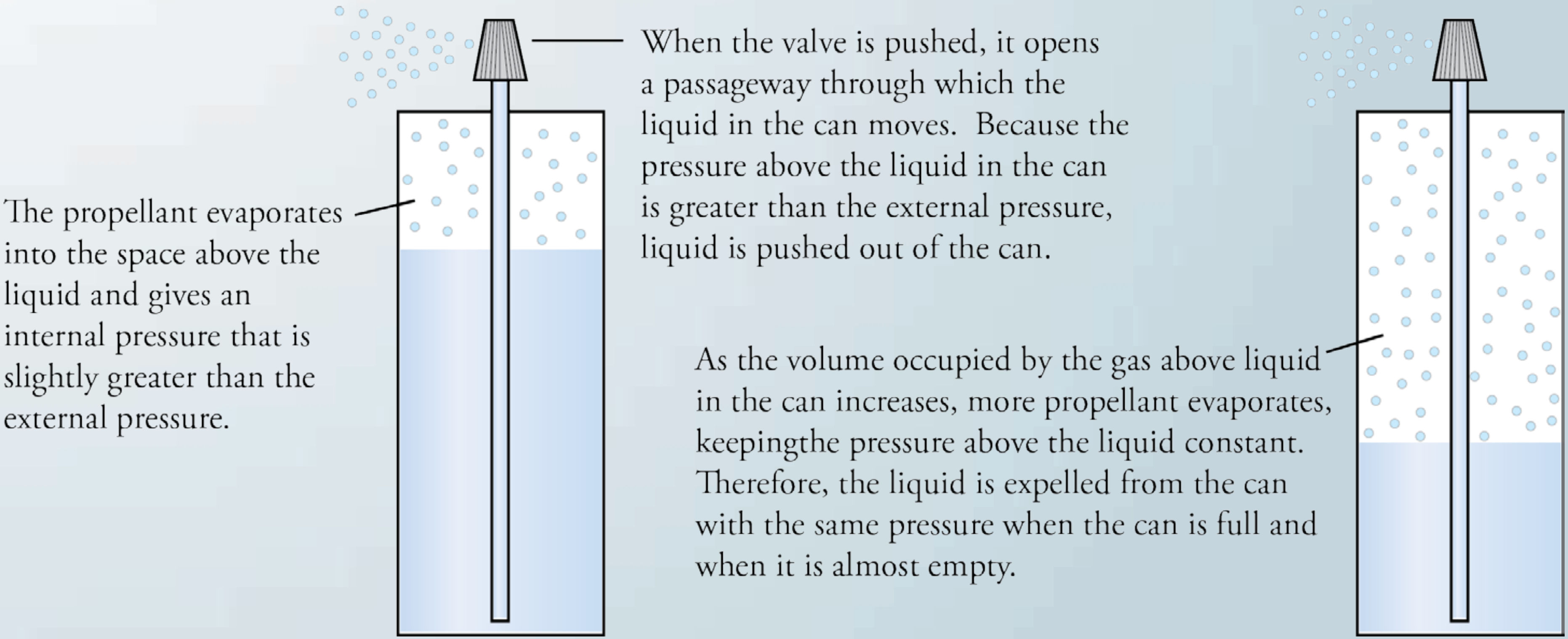
Hydrochlorofluorocarbons - HCFC-22

- Chlorodifluoromethane, (HCF_2Cl) or difluoromonochloromethane (HCFC-22, or R-22) is a hydrochlorofluorocarbon (HCFC).
- Being phased out in developed countries due to the compound's ozone depletion potential (ODP) and high global warming potential (GWP)
- Use continues to increase because of high demand in developing countries.
  - Worldwide production 2008 about 800 Gg per year, up from about 450 Gg per year in 1998, with most production in developing countries.
  - Air conditioning sales are growing 20% annually in India and China.

CFC and HCFC Numbering System

- The rightmost value indicates the number of fluorine atoms.
- The next value to the left is the number of hydrogen atoms *plus* 1.
- The next value to the left is the number of carbon atoms *less* one (zeroes are not stated).
- Remaining atoms are chlorine.

Aerosol Can Propellants



Refrigeration

- The refrigerant is a substance that is a gas at normal pressures but one that can be converted into a liquid at slightly greater than normal pressures.
- Outside the refrigerator, gas is compressed to liquid. Increased attractions leads to increased stability, lower PE, and the release of energy into the room.
- Inside the refrigerator, the liquid is allowed to form a gas. Decreased attractions leads to decreased stability, higher PE, and energy is absorbed. This decreases the temperature inside the refrigerator.

CFC Threat to Ozone (1974)
Mario Molina and F. Sherwood Rowland

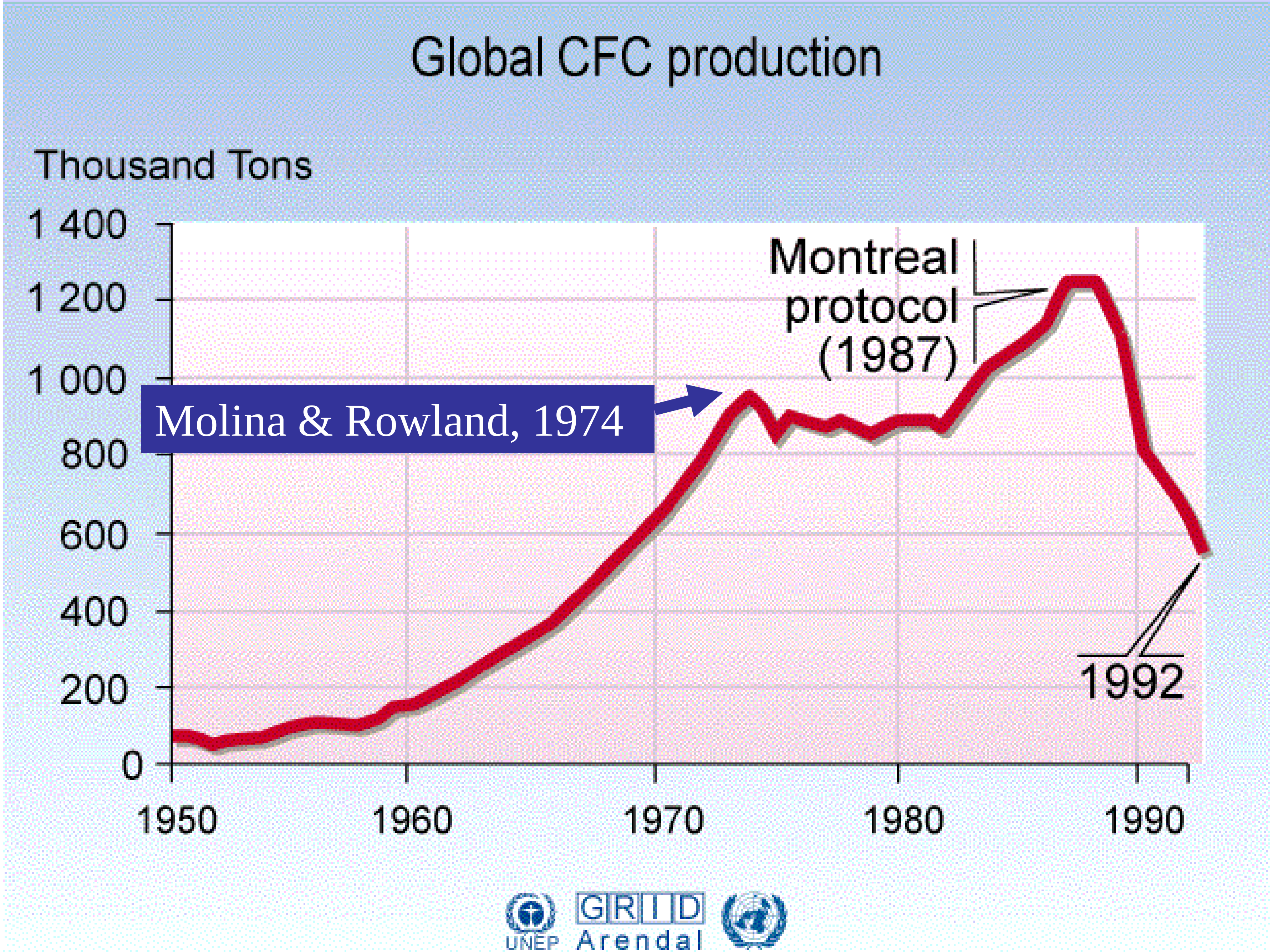
$$CF_2Cl_2(g) \xrightarrow{\lambda < 215\ \text{nm}} CF_2Cl(g) + Cl(g)$$

$$Cl(g) + O_3(g) \rightarrow ClO(g) + O_2(g)$$

$$ClO(g) + O(g) \rightarrow Cl(g) + O_2(g)$$

net reaction

$$O_3(g) + O(g) \xrightarrow{\text{Cl catalyst}} 2O_2(g)$$



http://www.grida.no/graphicslib/detail/global-cfc-production_83db#/

Another Possible Mechanism for the CFC Threat to Ozone

$$CF_2Cl_2(g) \xrightarrow{\lambda < 215\ \text{nm}} CF_2Cl(g) + Cl(g)$$

$$2Cl(g) + 2O_3(g) \rightarrow 2ClO(g) + 2O_2(g)$$

$$2ClO(g) \rightarrow ClOOCl(g)$$

$$ClOOCl(g) \rightarrow ClOO(g) + Cl(g)$$

$$ClOO(g) \rightarrow Cl(g) + O_2(g)$$

net reaction

$$2O_3(g) \xrightarrow{\text{Cl catalyst}} 3O_2(g)$$

Summary

- Ozone in the troposphere is a dangerous pollutant.
- Stratospheric ozone absorbs solar UV-B and some UV-C, protecting life on earth.
- Photolytic destruction of ozone absorbs UV-C and UV-B, accounts for ~15% of ozone removal
- Natural catalytic destruction by free radicals accounts for ~85% of ozone removal. In catalytic destruction, one molecule can catalyze loss of 10,000 - 100,000 molecules of ozone.
- The historic source of free radicals is stable compounds from the troposphere that become “radicalized” once they reach the stratosphere.
- Cl & Br free radicals, created by photolytic action from anthropogenic CFCs and other stable, long-lived ODSs destroy ozone by catalytic action.

CFC and HCFC Alternatives

- R-410A, sold under the trademarked names Puron, EcoFluor R410, Genetron R410A, and AZ-20, is a mixture of difluoromethane (CH_2F_2, called R-32) and pentafluoroethane (CHF_2CF_3, called R-125) is used as a refrigerant in air conditioning applications.
- Does not contribute to ozone depletion.
- However, it has a high global warming potential (1725 times the effect of carbon dioxide), similar to that of R-22.

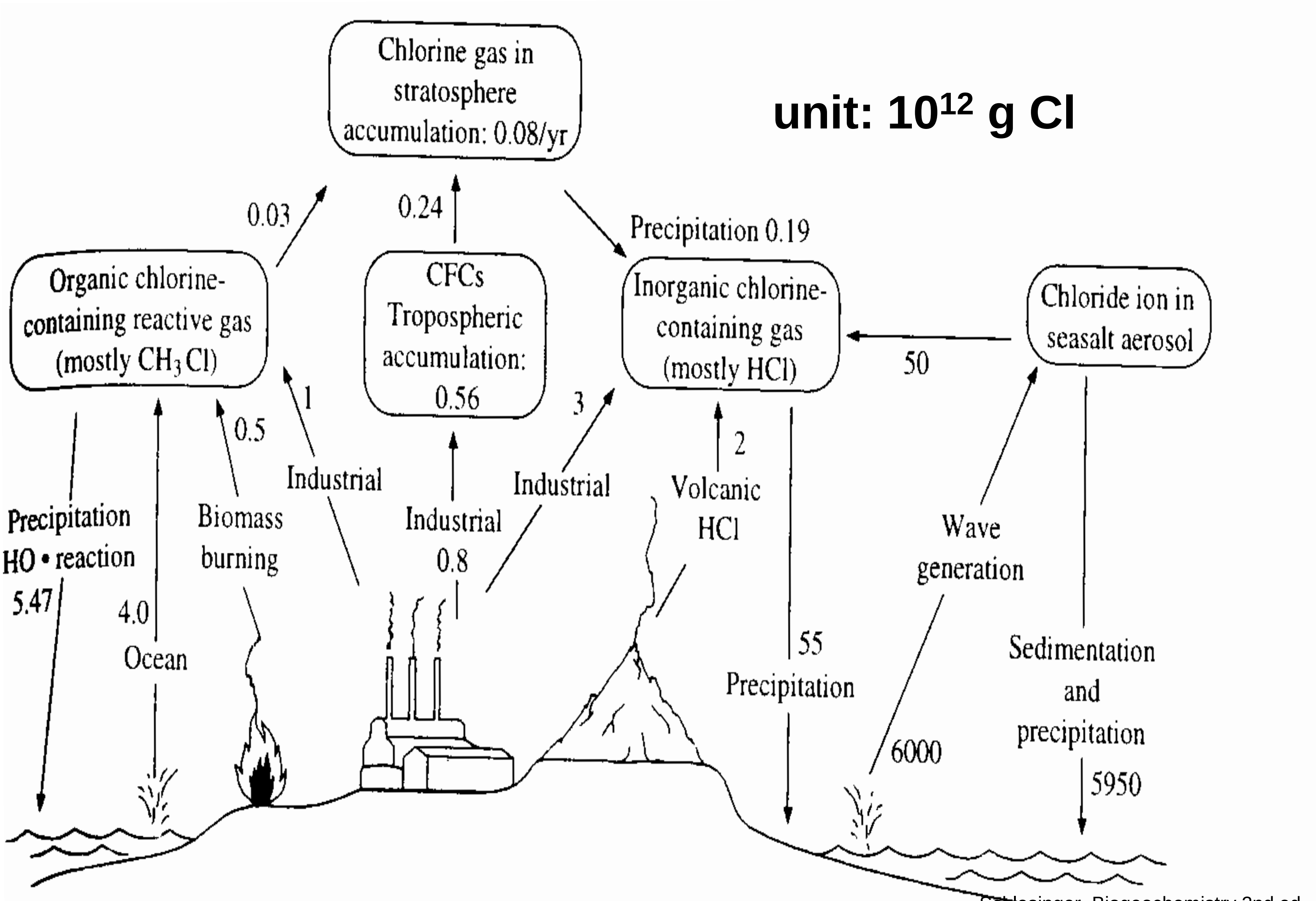
HFC-23

- In the production of HCFC-22, a side reaction forms fluoroform, CHF_3, (HFC-23), which has a GWP of over 11,000.
- Companies that make HCFC-22 can earn carbon credits, which can be sold for a significant profit, by destroying the HFC-23.
  - Cost of destroying HFC-23 is about 1/100 to money derived from selling carbon credits.
- Creates an incentive to increase production of HCFC-22, which contributes to global warming and depletes the ozone layer.
- The high output keeps the prices of the coolant gas low, discouraging air-conditioning companies from switching to less-damaging alternative gases.

Carbon Credits and GWP

- A **carbon credit** is a tradable certificate or permit representing the right to emit one metric ton of carbon dioxide or the mass of another greenhouse gas with a carbon dioxide equivalent (tCO_2e) equivalent to one metric ton of carbon dioxide.
- The **carbon dioxide equivalency** for a gas is obtained by multiplying the mass and the global warming potential (GWP) of the gas. For example, the GWP for methane over 100 years is 25 and for nitrous oxide 298. The following units are commonly used:
  - By the UN climate change panel IPCC: billion metric tons of CO_2 equivalent ($GtCO_2eq$).
  - In industry: million metric tons of carbon dioxide equivalents (MMTCDE).
  - For vehicles: g of carbon dioxide equivalents/km (gCDE/km).

Global Chlorine Budget



Schlesinger, Biogeochemistry 2nd ed

Dobson Unit, DU

- The **Dobson unit** (DU) is a unit of measurement of the density of a column of a trace gas in the Earth's atmosphere.
- One Dobson unit refers to a layer of gas that would be 10 µm thick under standard temperature and pressure (273.15 K and 100 kPa).
- 300 DU of ozone brought down to the surface of the Earth at 0 C° would occupy a layer only 3 mm thick.

Using Dobson Units

Example: Find the moles per cm^2 and molecules per cm^2 in one Dobson Unit of an ideal gas:

Using Dobson Units

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$$PV = nRT = P(A \cdot h)$$

$$\frac{n}{A} = \frac{Ph}{RT} = \frac{100\ \text{kPa}\ (10\ \mu\text{m})}{8.314\ \frac{\text{L}\cdot\text{atm}}{\text{K}\cdot\text{mol}}\ 273.15\ \text{K}} \left(\frac{10^3\ \text{L}}{1\ \text{m}^3}\right)\left(\frac{1\ \text{m}}{10^2\ \text{cm}}\right)^3\left(\frac{1\ \text{m}}{10^6\ \mu\text{m}}\right)\left(\frac{10^2\ \text{cm}}{1\ \text{m}}\right)$$

$$= \mathbf{4.403 \times 10^{-8}\ mol/cm^2} \left(\frac{6.022 \times 10^{23}\ \text{molecules}}{1\ \text{mol}}\right) = \mathbf{2.652 \times 10^{16}\ molecules/cm^2}$$

Ozone Concentrations

The peak concentration of ozone in the stratosphere (25 km) is about 5×10^{12} molecules/cm^3. Convert this into micrograms ozone per cubic meter.

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$$\frac{?\ \mu g}{m^3} = \frac{5 \times 10^{12}\ \text{molecules}}{cm^3}\left(\frac{10^2\ cm}{1\ m}\right)^3\left(\frac{1\ \text{mol}\ O_3}{6.022 \times 10^{23}\ \text{molecules}}\right)\left(\frac{47.9982\ g\ O_3}{1\ \text{mol}\ O_3}\right)\left(\frac{10^6\ \mu g}{1\ g}\right)$$

$$\approx \mathbf{400\ \mu g/m^3}$$

Ozone Concentrations

The global average ozone column density is about 7×10^{18} molecules/cm^2. Convert this into Dobson units.

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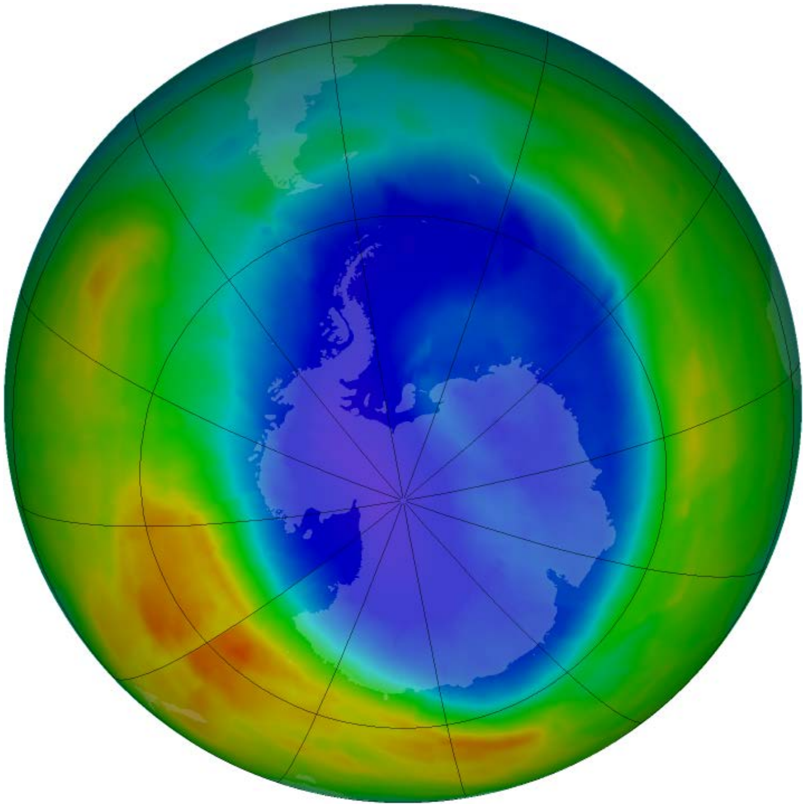
$$? \text{ DU} = \frac{7 \times 10^{18} \cancel{\text{molecules}}}{\cancel{\text{cm}^2}} \left(\frac{\cancel{\text{cm}^2} \cdot \text{DU}}{2.652 \times 10^{16} \cancel{\text{molecules}}} \right) = 264 \text{ DU} \approx \mathbf{300\ DU}$$

Other Ozone Concentrations

- Background near-surface concentrations about 30-80 $\mu g/m^3$
- Polluted near-surface air about 100-300 $\mu g/m^3$

Antarctic Ozone Hole

- An area of the Antarctic stratosphere in which the recent ozone levels have dropped to as low as 33% of their pre-1975 values.
- Occurs during the Antarctic spring, from September to early December
- Over 50% of the lower stratospheric ozone is destroyed during the Antarctic spring.



http://ozonewatch.gsfc.nasa.gov/

Polar Vortex

- Ring of high winds around the polar region that effectively isolates the Antarctic atmosphere from the rest of the atmosphere during the winter and early spring.
- The air stays over the Antarctic throughout the winter, in the complete dark, without mixing with warmer air from lower latitudes, and becomes extremely cold.

Polar Stratospheric Clouds

- PSCs are clouds made of tiny particles of water ice and frozen acid. These particles become the basis for chemical reactions that provide surfaces for chemical reactions that lead to ozone destruction.

Reservoir Compounds

- Most of the chlorine in the stratosphere resides in reservoir compounds, such as hydrochloric acid, HCl, and chlorine nitrate, $ClONO_2$.
- During the Antarctic winter and spring, reactions on the surface of the polar stratospheric cloud particles convert reservoir compounds into Cl_2 and HOCl.

$$ClONO_2(g) + HCl(s) \rightarrow Cl_2(g) + HNO_3(s)$$

$$ClONO_2(g) + H_2O(s) \rightarrow HOCl(g) + HNO_3(s)$$

$$HOCl(g) + HCl(s) \rightarrow Cl_2(g) + H_2O(s)$$

Liberation of Cl

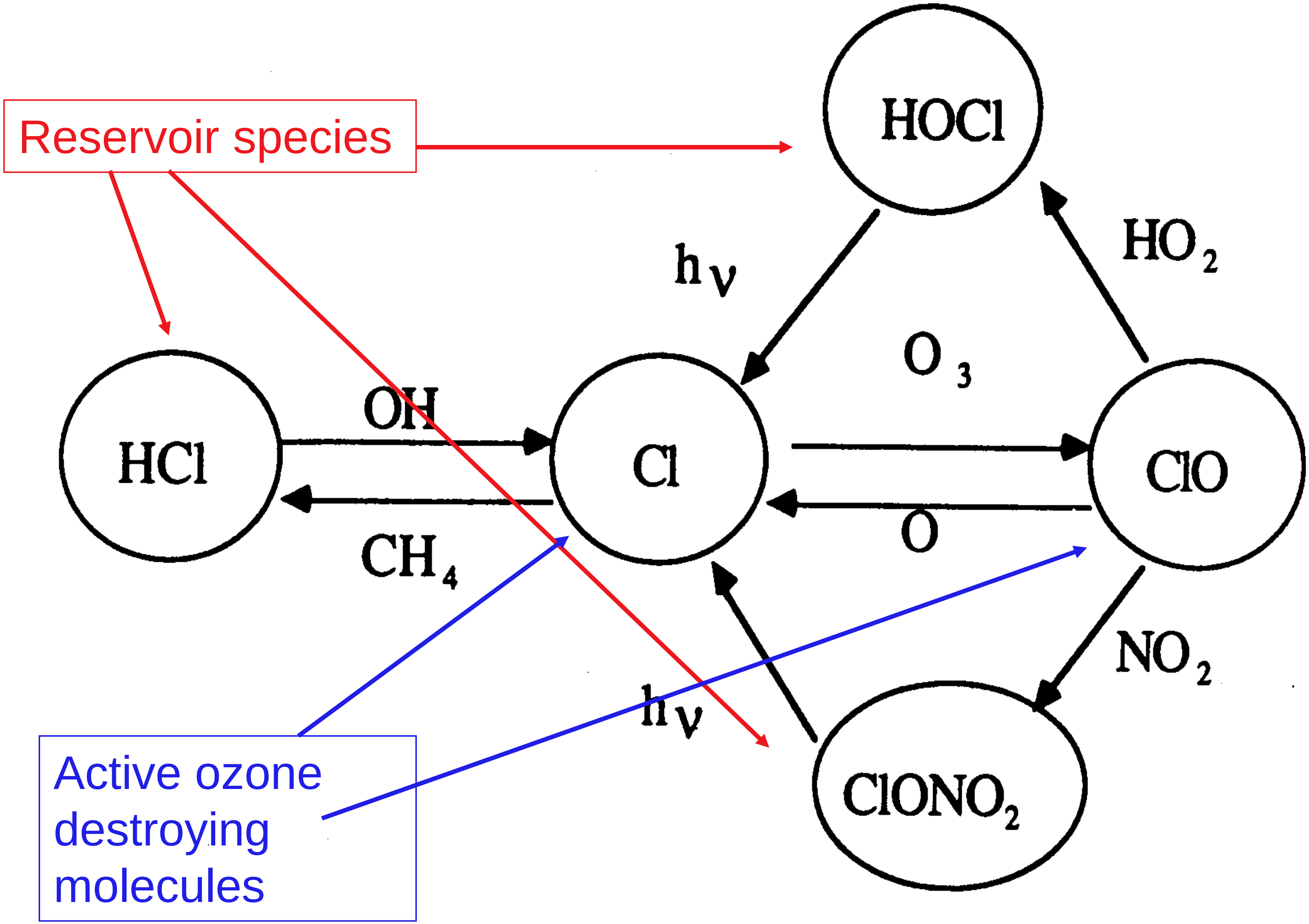
- Radiant energy liberates chlorine atoms, Cl.

$$HOCl(g) \xrightarrow{\text{radiant energy}} Cl(g) + OH(g)$$

$$Cl_2(g) \xrightarrow{\text{radiant energy}} 2Cl(g)$$

- The reactions above take place in spring when there is light.
- Ozone hole closes near end of spring due to
  - Increased temperature breaks up the vortex
  - Ozone-rich air moves in
  - PSCs broken up

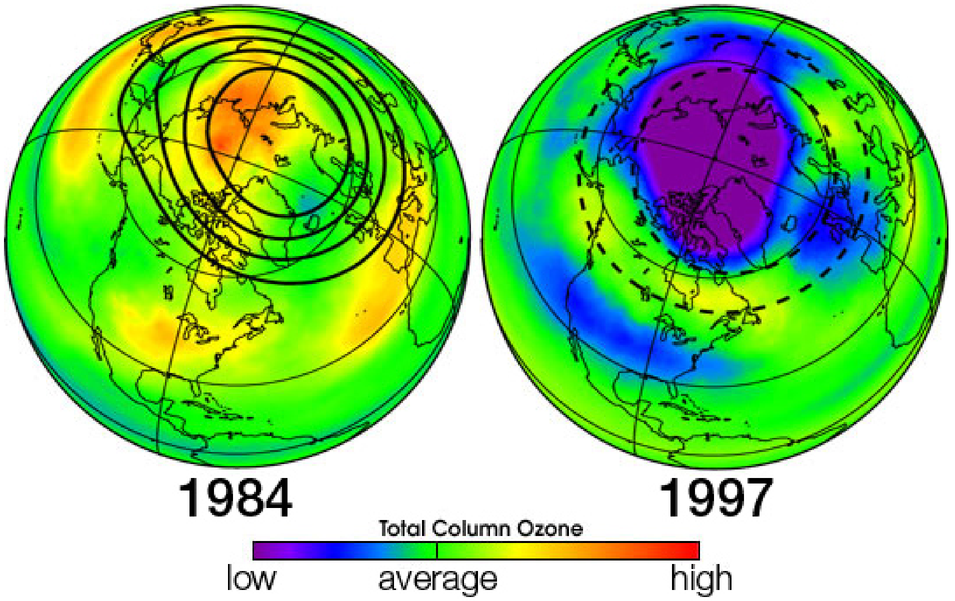
Reservoir Species Reactions



Seinfeld

Artic Ozone Hole

- Appeared in 1990s, depletion ~25% max, less area and shorter duration than Antarctic
- Different weather patterns due to north-south polar asymmetries → no strong polar vortex
- Severity highly dependent on weather → more severe in cold winters



Montreal Protocol

- The **Montreal Protocol on Substances that Deplete the Ozone Layer** (a protocol to the Vienna Convention for the Protection of the Ozone Layer)
- An international treaty designed to protect the ozone layer by phasing out the production of numerous substances believed to be responsible for ozone depletion.
- Opened for signature on September 16, 1987, and entered into force on January 1, 1989
- Seven revisions to tighten restrictions and shorten timeline

Montreal Protocol

- Permitted chlorofluoroalkane uses are medicinal only.
- On September 21, 2007, approximately 200 countries agreed to accelerate the elimination of hydrochlorofluorocarbons entirely by 2020 in a United Nations-sponsored Montreal summit.
  - Developing nations were given until 2030.
  - Many nations, such as the United States and China, who had previously resisted such efforts, agreed with the accelerated phase out schedule.

Montreal Protocol

- It is believed that if the international agreement is adhered to, the ozone layer is expected to recover by 2050.
- Ratified by 197 states and the European Union making them the most widely ratified treaties in United Nations history.
- Due to its widespread adoption and implementation it has been hailed as an example of exceptional international co-operation, with Kofi Annan quoted as saying that "*perhaps the single most successful international agreement to date has been the Montreal Protocol*".

Ozone Depleting Substances

ODS = ozone depleting substance → > 100

http://www.epa.gov/ozone/science/ods/index.html

ODP = ozone depletion potential → CFC-11 = 1

EESC = "effective equivalent stratospheric chlorine" converts other free radicals (e.g. Br) into Cl equivalent

CFC = (C, F, Cl) refrigerants, propellants, solvents, cleaning agents, foaming agents (Styrofoam)

Halons = (some F → Br) fire retardants, highest ODP

HCFC = (H, C, F, Cl) CFC substitutes, more reactive in troposphere, short residence time

HFC = (H, F, C, no Cl or Br) CFC substitutes, ODP = 0

Chlorocarbons = (C, H, Cl) cleaning agents

UN Environmental Programme Ozone Secretariat

http://ozone.unep.org/new_site/en/index.php

http://ozone.unep.org/new_site/en/historical_meetings.php

http://ozone.unep.org/new_site/en/resources.php?pt_id=3

http://ozone.unep.org/Publications/MP_Handbook/MP-Handbook-2012.pdf

Summary

- Ozone in the troposphere is a dangerous pollutant.
- Stratospheric ozone absorbs solar UVB, protecting life on earth.
- Cl & Br free radicals, created by photolytic action from anthropogenic CFCs and other stable, long-lived ODSs destroy ozone by catalytic action.
- The Antarctic ozone hole results from enhanced catalytic destruction due to heterogeneous chemistry on particulates and ice.

Summary

- Ozone damage is causing and will cause health impacts.
- Stratospheric ozone will repair itself by about 2050 if we strictly implement the Montreal Protocol.
- The Montreal Protocol represents a victory of environmental science and international cooperation over short-sightedness and disinformation.

For Reflection and Discussion

- Why was it possible to reach a wide-ranging international agreement to limit ozone-depleting substances within just a few years of emergence of scientific understanding of the threat?
- Why is the case of greenhouse gases and climate change more difficult?

Ozone Depletion vs Climate Change

- Scientific prediction of problem
- Scientific observation supports prediction
- International concern over consequences
- UN-based framework convention
- UN-based protocol requires action
- National governments implement agreement
- Emissions and threat are reduced

WHY THE BIG DIFFERENCE IN OUTCOMES?