This material is for reference only. Points present in the slides are only for assistance and their elaboration are present in book. Examination questions will be in depth and can be solved by following text book only.

INTRODUCTION TO ENVIRONMENTAL CHEMISTRY

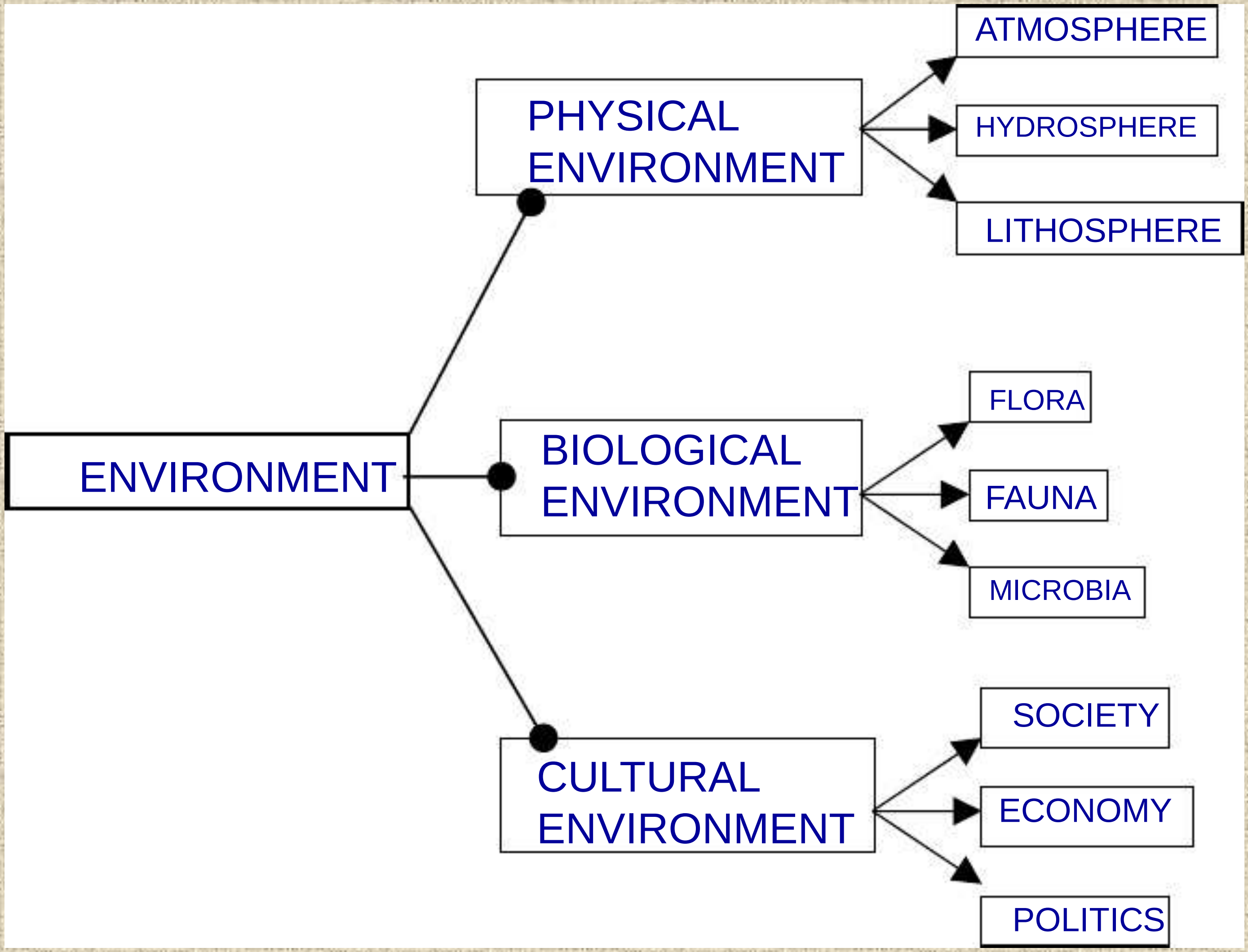
Environment

The word environment is derived from the French word "environ".

Environment is what surrounds us !!

It is the sum total of all social, economical , biological , physical and chemical factors which constitute the surroundings of humans, who are both the creators and moulders of the environment.

Classification of Environment



Types of Environment :

Natural Environment

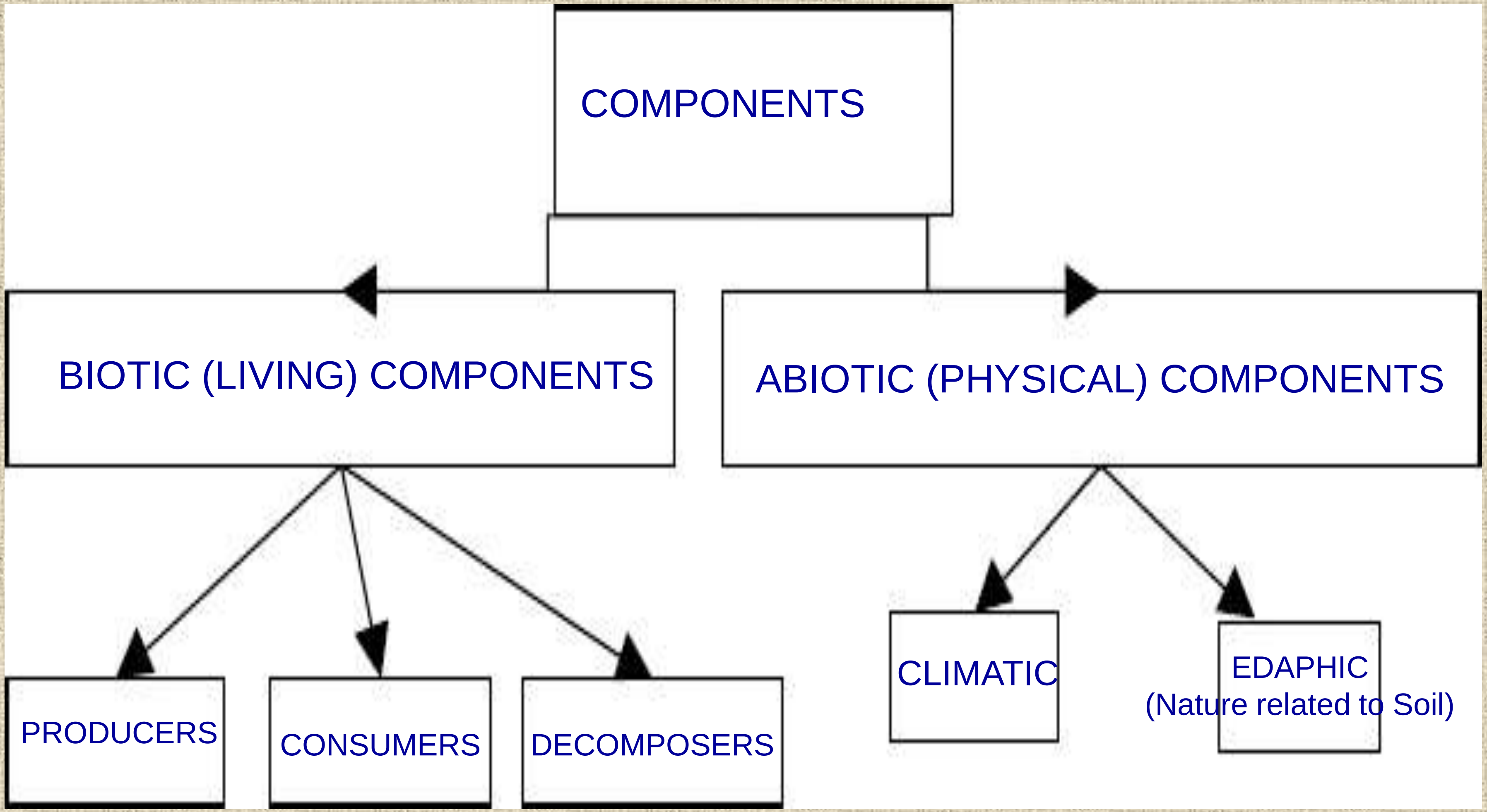
Components such as air, water, soil, land, forest, wildlife, flora , fauna, etc. constitute the **Natural Environment**

Man - Made Environment (Anthropogenic Environment)

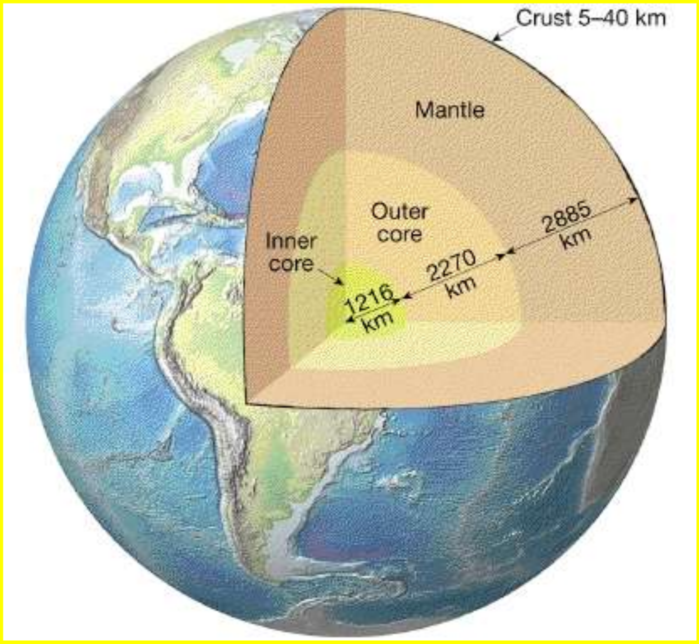
Alteration of the natural environment to serve specific uses by the human beings. For eg agricultural field is an anthropogenic environment and so are the gardens and aquaculture farms.

- Components of Environment as per British literature
  - components are classified in terms of biotic and abiotic based upon life.
  - The biotic components are further listed as producers, consumers and decomposers and the abiotic components are classified as climatic (water, air) and edaphic (land).
  - It is from this component system that the study of structure of ecosystem was evolved.

Components of Environment



- Components of Environment as per American literature
  - the components of environment are listed as
  - 1. Hydrosphere (Water)
  - 2. Atmosphere (Air)
  - 3. Lithosphere (Land)
  - 4. Biosphere (Flora/Fauna/Microbes)
  - 5. Anthrosphere (man made things)



Realms of the earth:

Lithosphere

Atmosphere

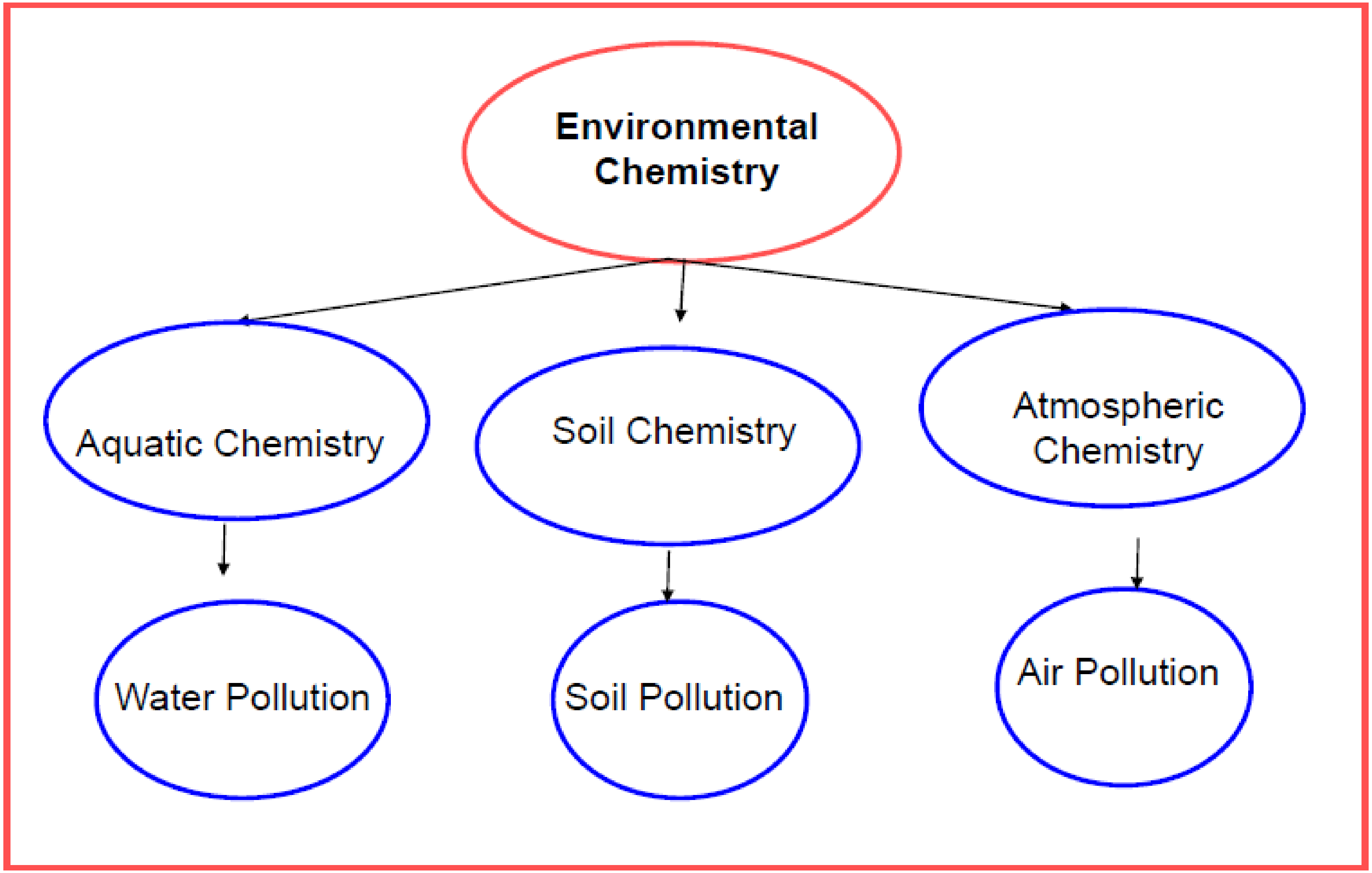
Hydrosphere

Biosphere

Anthrosphere

Chemistry, the science that deals with the properties, composition, and structure of substances (defined as elements and compounds), the transformations they undergo, and the energy that is released or absorbed during these processes

Illustration of Environmental Chemistry definition



Importance of Environmental Chemistry

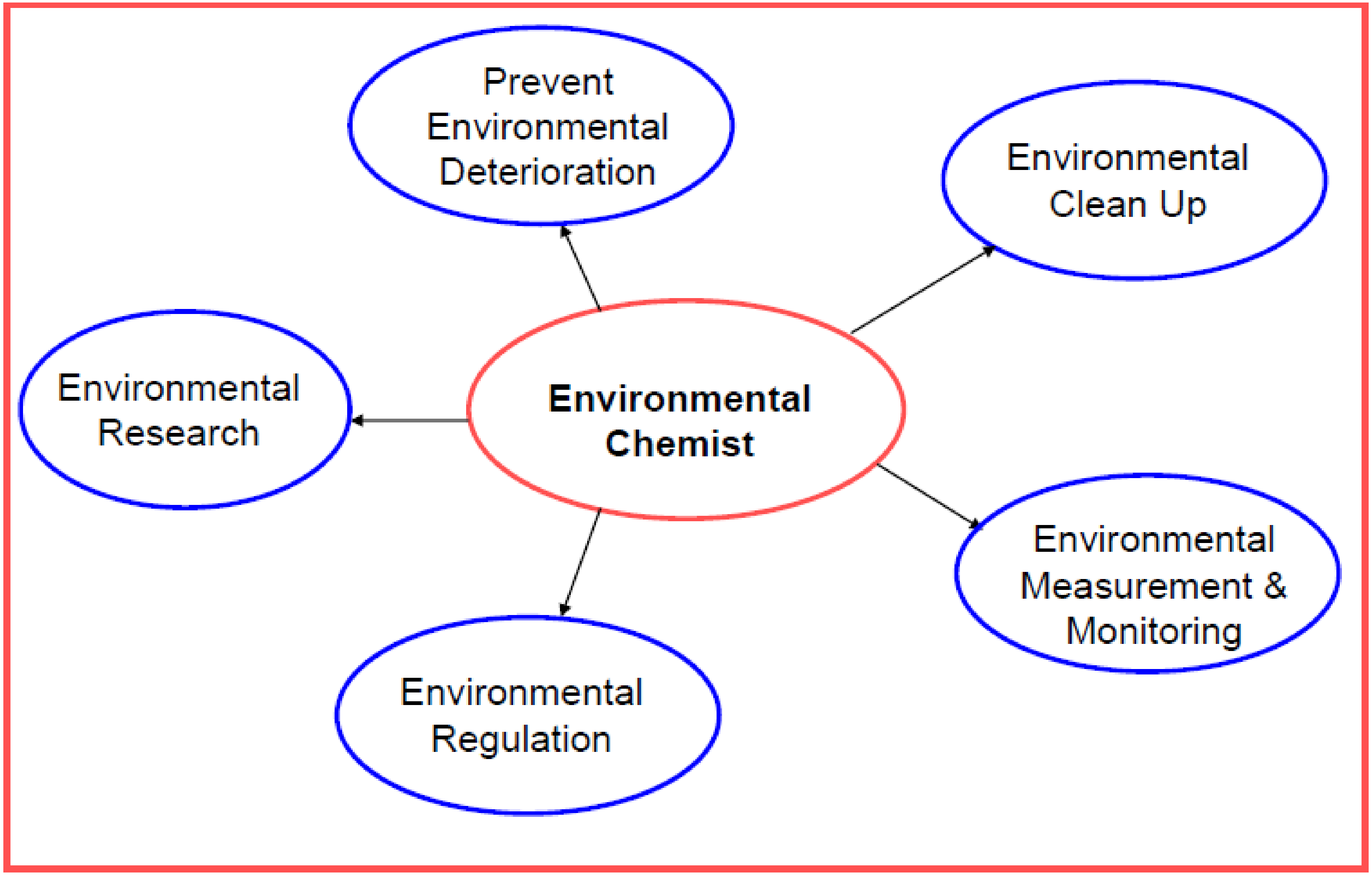
To get basic knowledge of our surroundings.

To develop skills for identifying and solving environmental problems in our surroundings.

To maintain ecological balance and to strive to achieve sustainable development.

To educate people for their duties towards environmental protection.

The Mission of Environmental Chemist



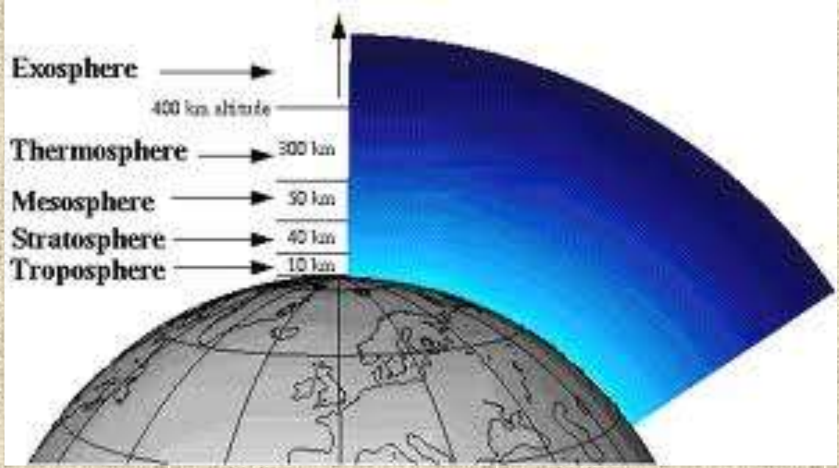
Environment

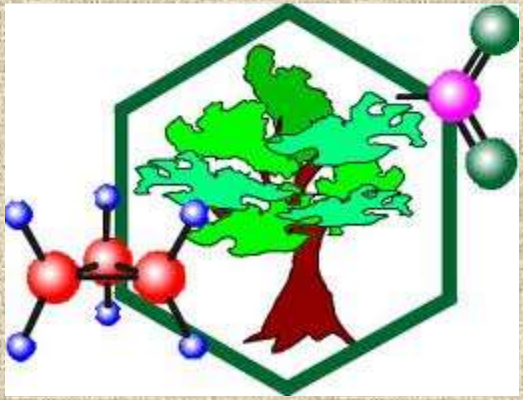
Atmosphere

Electromagnetic Spectrum

Concentration units in atmosphere

Absorption and emission spectra

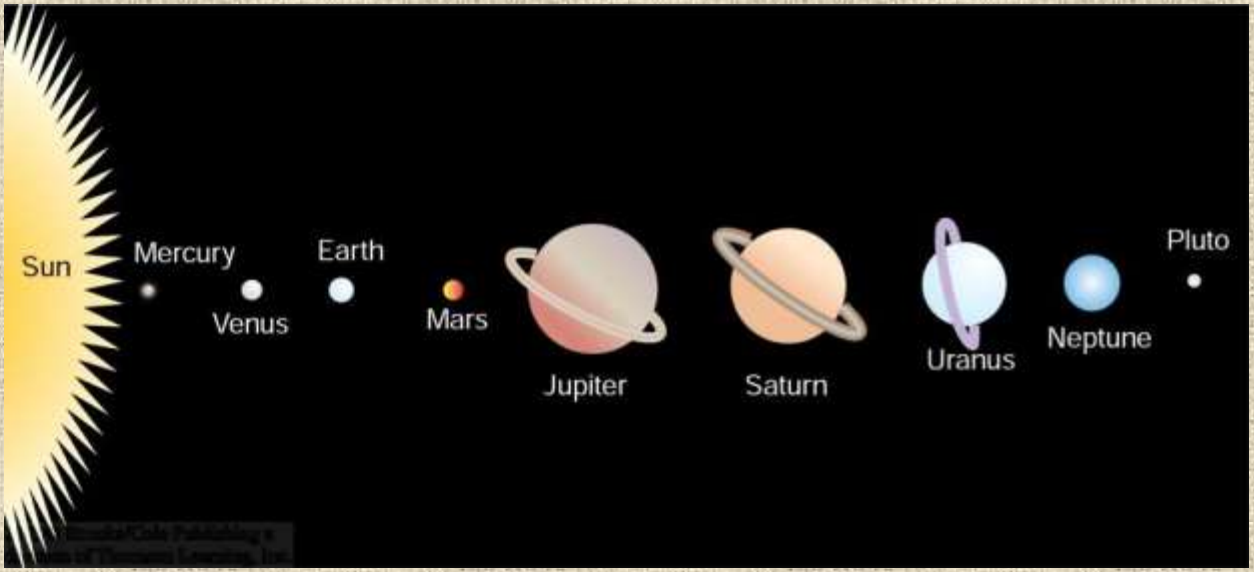




Following discussion focuses on:

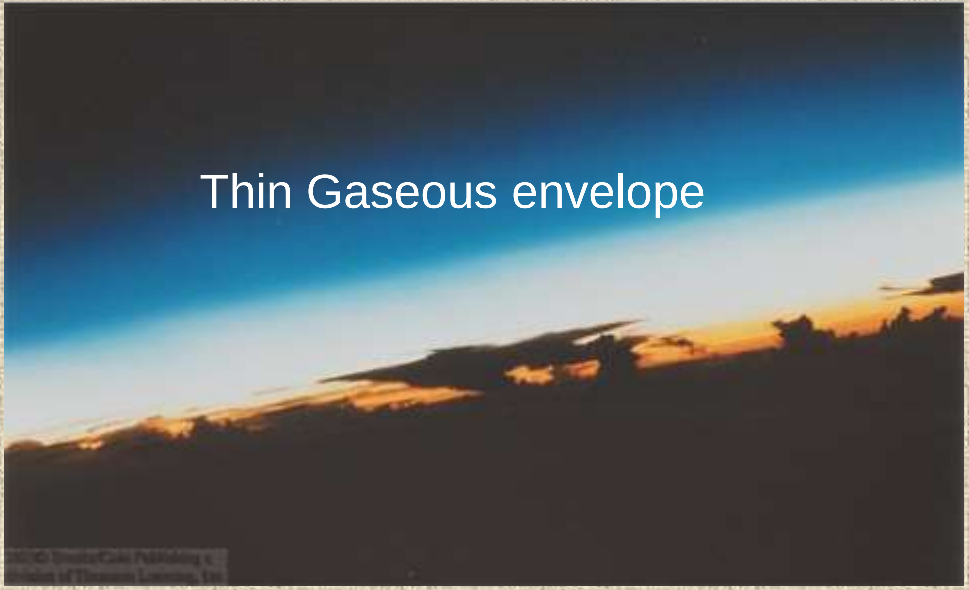
1. Gases in Earth's atmosphere
2. Vertical structure of atmospheric pressure & temperature
3. Types of weather & climate in the atmosphere
4. Concentration units
5. Electromagnetic spectrum

Solar Energy as Radiation



Nearly 150 million kilometers separate the sun and earth, yet solar radiation drives earth's weather.

Earth's Atmosphere



99% of atmospheric gases, including water vapor, extend only 30 kilometer (km) above earth's surface. Most of our weather, however, occurs within the first 10 to 15 km.

Atmosphere of Earth

Composition of Atmosphere

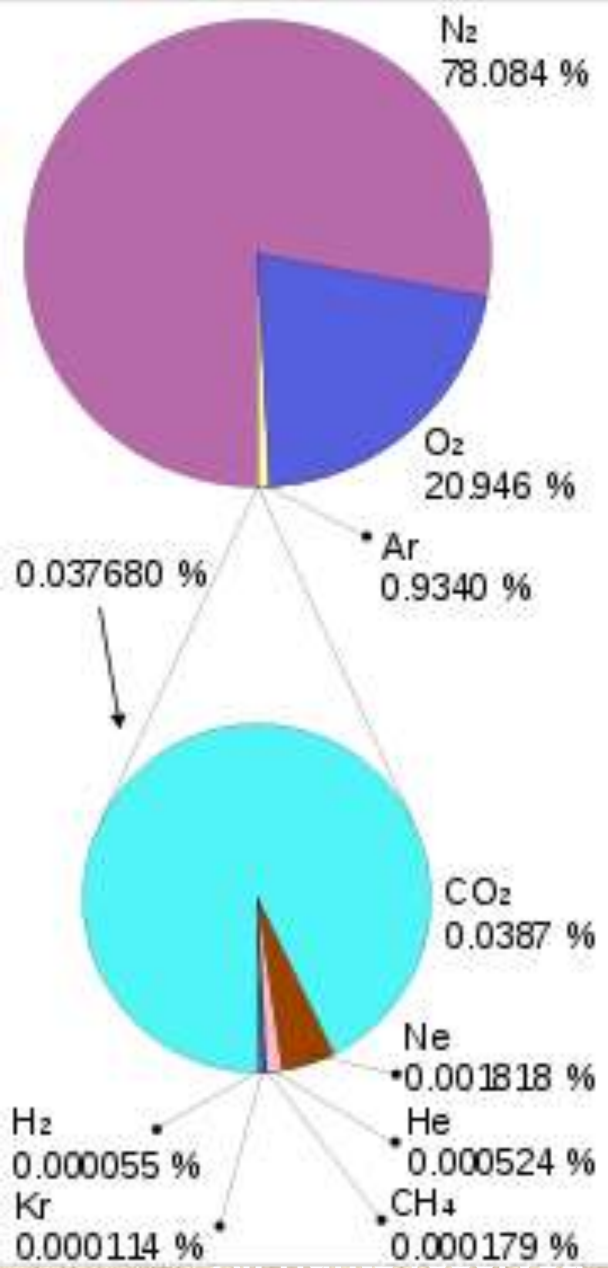
Nitrogen - 78%

Oxygen - 21%

Water Vapor – 0 to 4%

Carbon Dioxide - 0.037%

Other gases make up the rest



- A layer of gases surrounding the planet Earth that is retained by Earth's gravity
- **Air** is the atmosphere used in breathing and photosynthesis.

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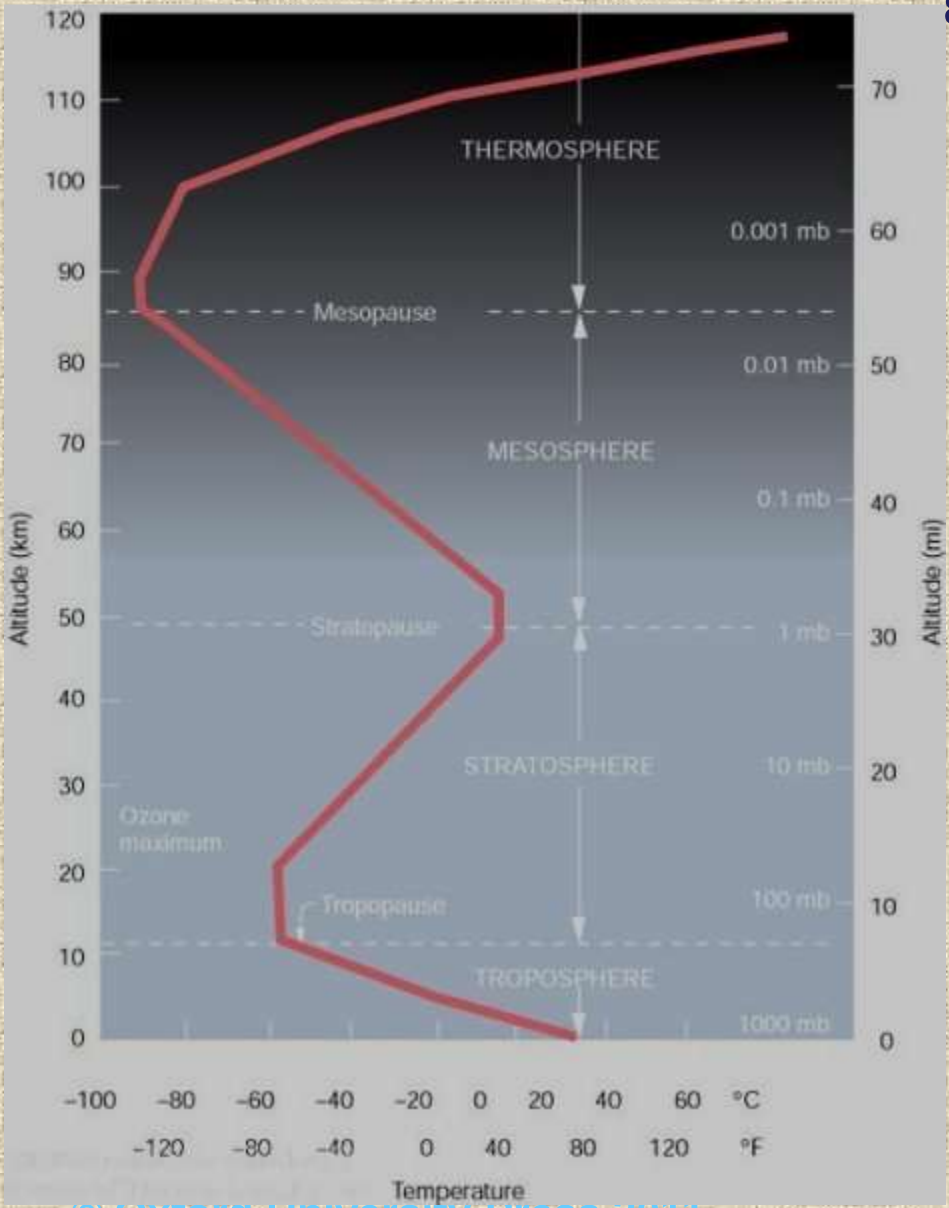
Layers of Atmosphere



8 layers are defined by constant trends in average air temperature (which changes with pressure and radiation), where the outer exosphere is not shown.

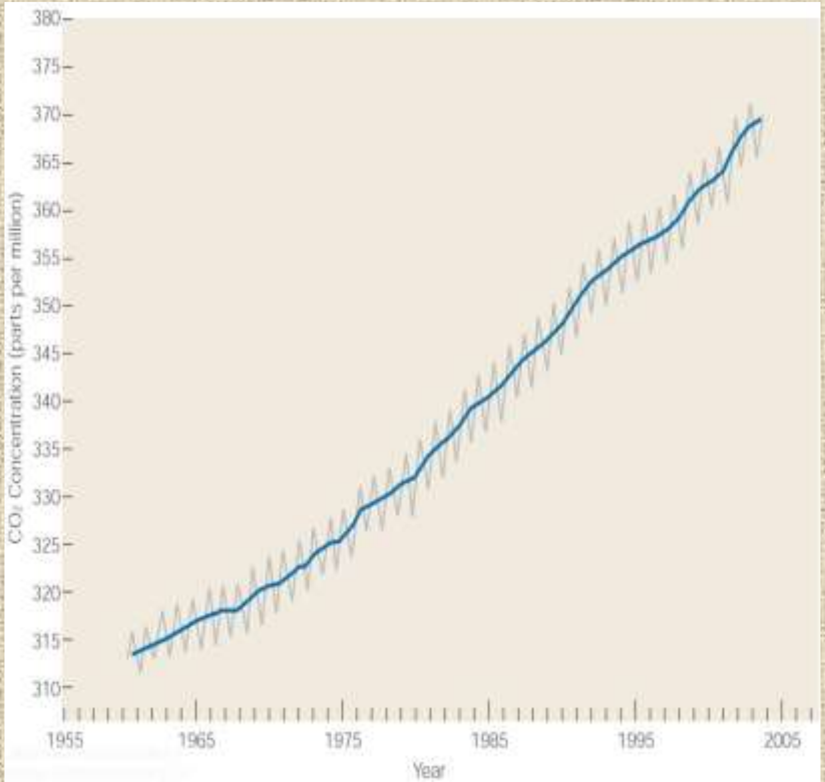
1. Troposphere
2. Tropopause
3. Stratosphere
4. Stratopause
5. Mesosphere
6. Mesopause
7. Thermosphere
8. Exosphere

Troposphere: extends from ground level to about 15 kilometers altitude and contains 85% of the atmosphere's mass

Stratosphere: the portion of the atmosphere from approximately 15 to 50 kilometers

The **ozone layer** mainly exists in stratospheres

Variable & Increasing Gases



- ✓ Nitrogen and oxygen concentrations experience little change, but carbon dioxide, methane, nitrous oxides, and chlorofluorocarbons are greenhouse gases experiencing discernable increases in concentration. CO2 has risen more than 18% since 1958.

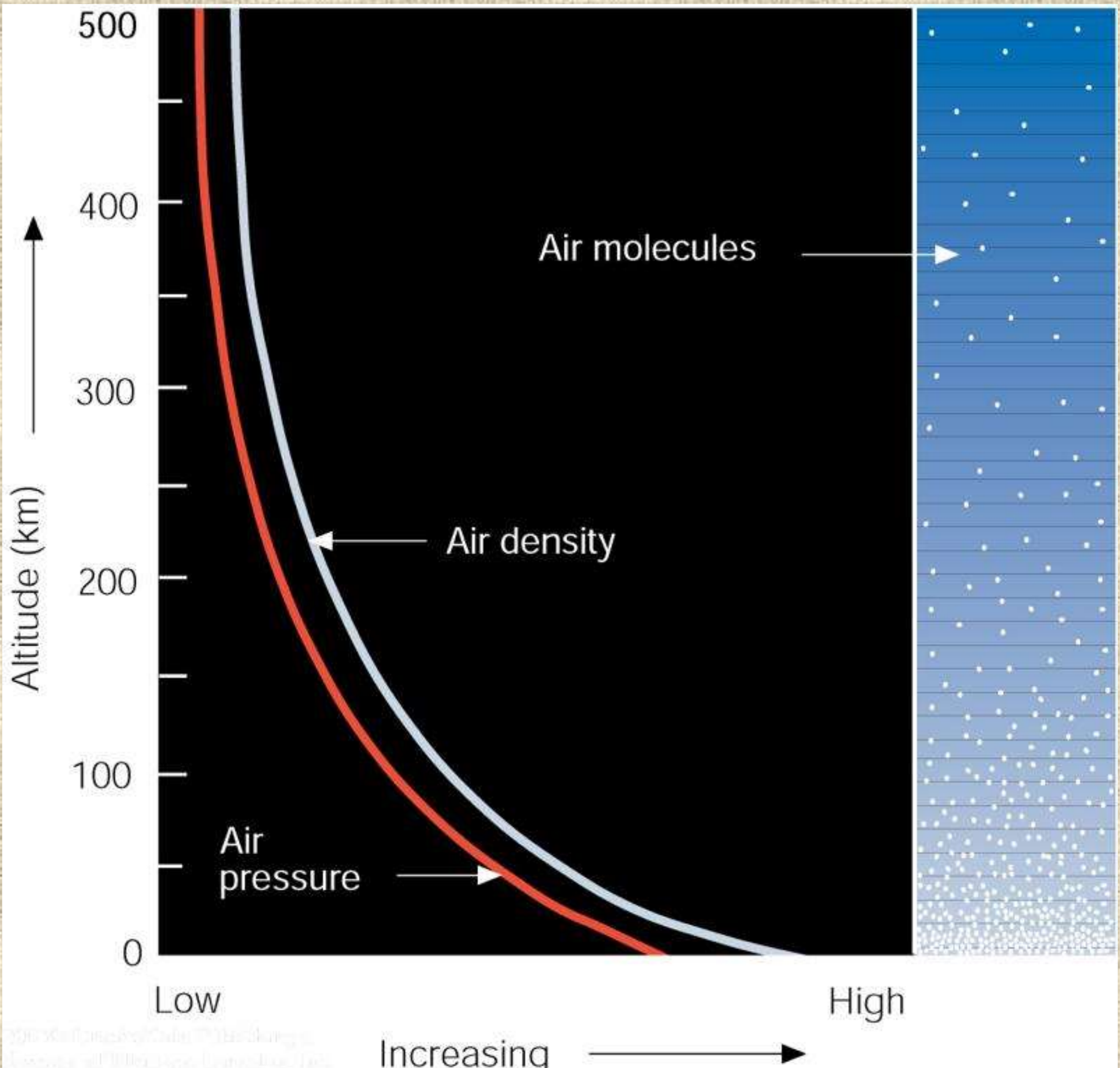
Atmospheric Greenhouse Effect

- ✓ **The warming of the atmosphere by its absorbing and emitting infrared radiation while allowing shortwave radiation to pass through. The gases mainly responsible for the earth's atmospheric greenhouse effect are water vapor and carbon dioxide.**

Aerosols & Pollutants

Human and natural activities displace tiny soil, salt, and ash particles as suspended aerosols, as well as sulfur and nitrogen oxides, and hydrocarbons as pollutants.

Pressure & Density



Gravity pulls gases toward earth's surface, and the whole column of gases weighs 14.7 psi at sea level, a pressure of 1013.25 mb or 29.92 in Hg.

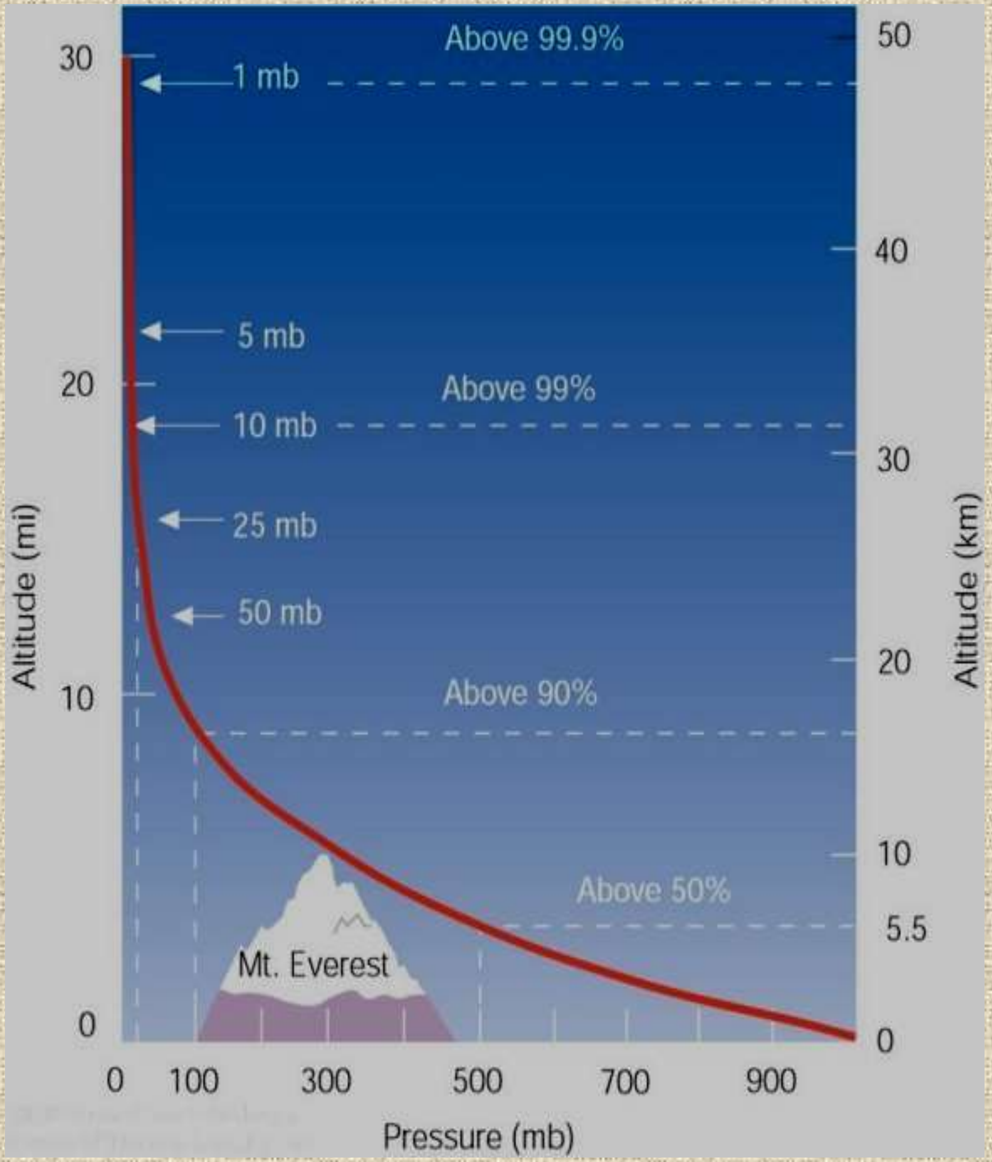
Air pressure : The amount of force exerted Over an area of surface

Air Density: The number of air Molecules in a given Space (volume)

Vertical Pressure Profile

Atmospheric pressure decreases rapidly with height. Climbing to an altitude of only 5.5 km where the pressure is 500 mb, would put you above one-half of the atmosphere's molecules.

(One MB= 0.0145038 Pound-force per square inch)



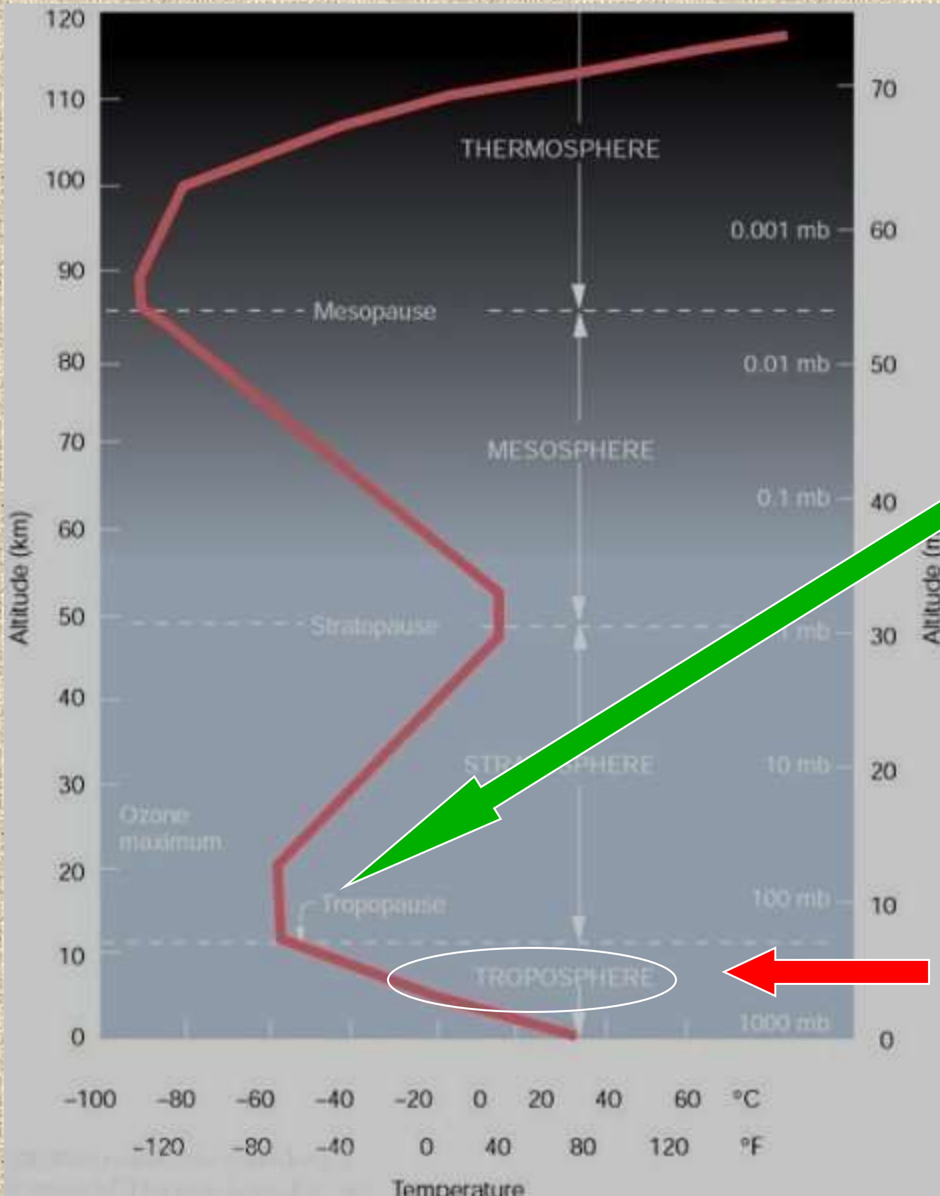
Lapse Rate

- The rate at which air temperature decreases with height.
- The standard (average) lapse rate in the lower atmosphere is about 6.5°C per 1 km or 3.6°F per 1000 ft.

Temperature Inversion

- A reversal of the normal behaviour of temperature in the troposphere.
- An increase in air temperature with height.

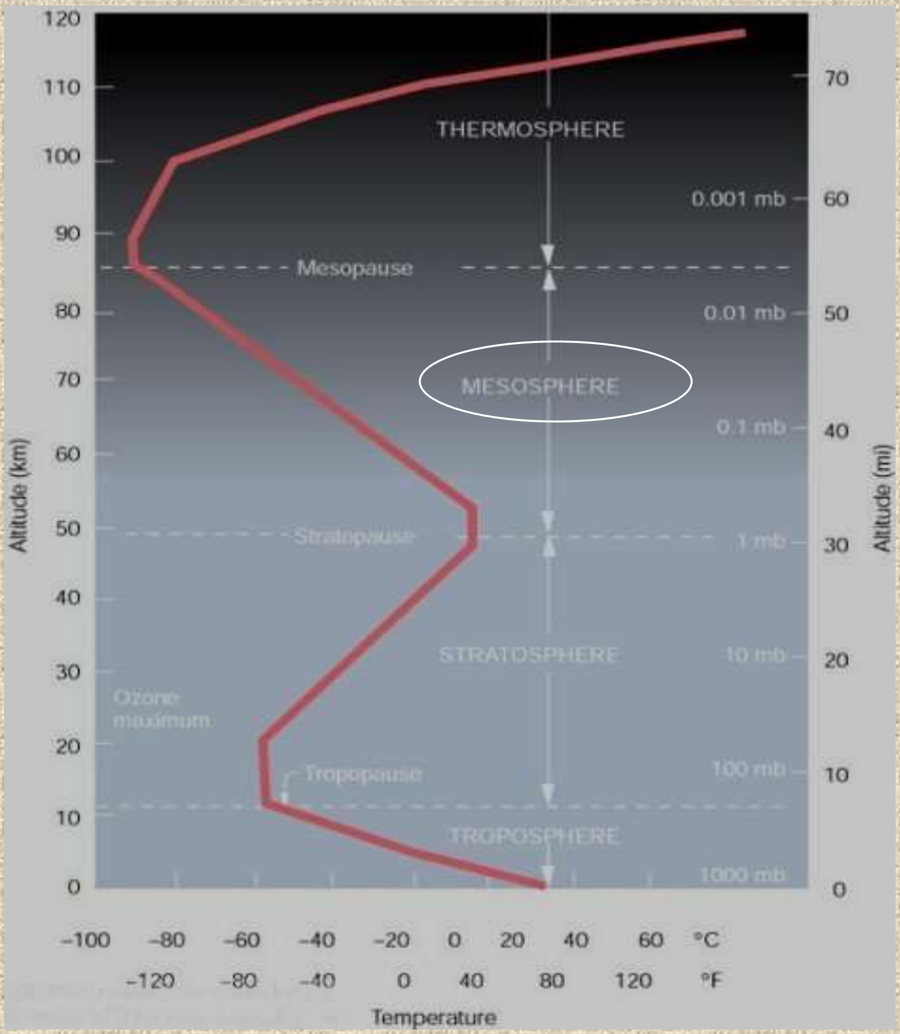
Atmospheric Layers

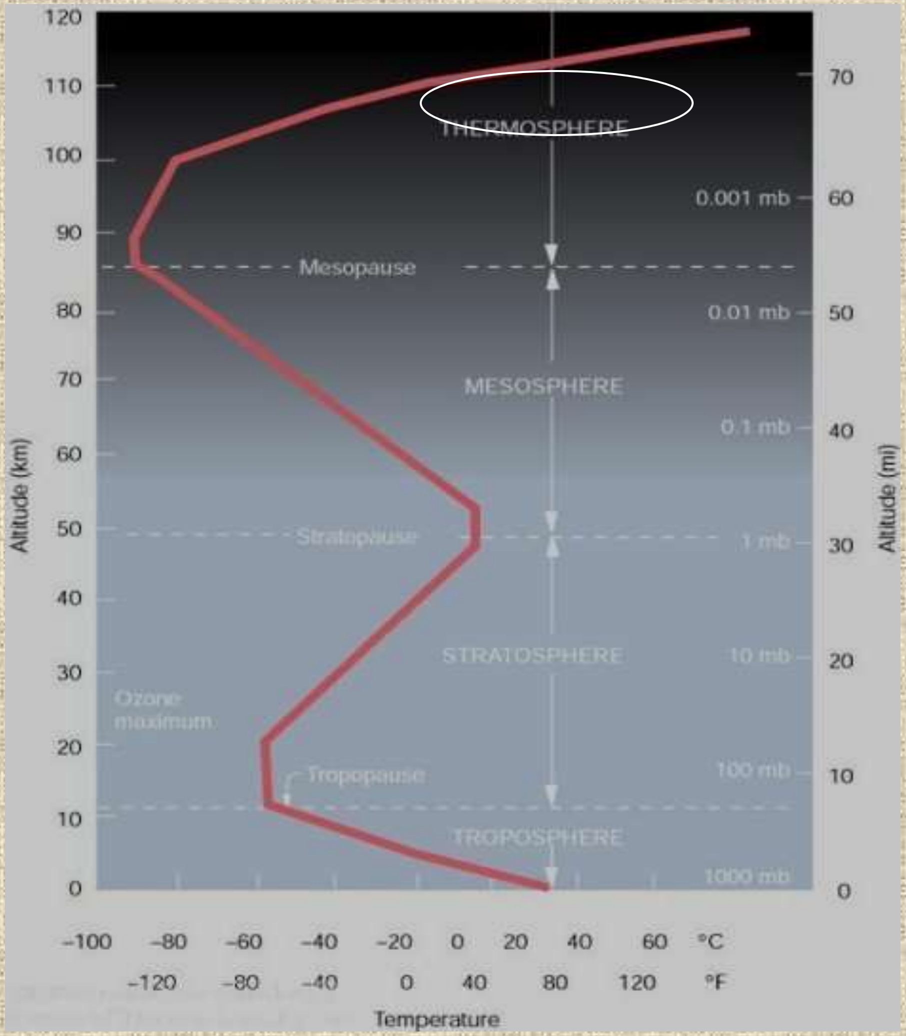


Tropopause separates Troposphere from Stratosphere. Generally higher in summer Lower in winter.

Troposphere – Temp decrease w/height
Most of our weather occurs in this layer
Varies in height around the globe, but
Averages about 11 km in height.

Continue…

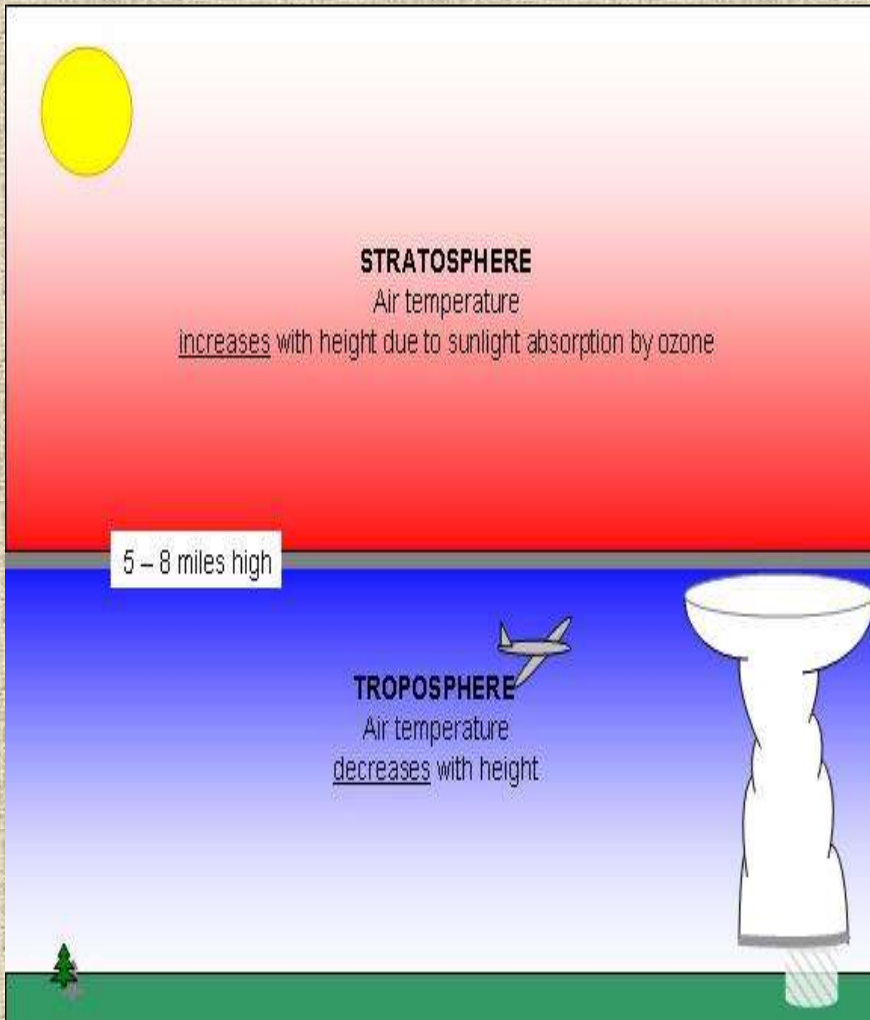


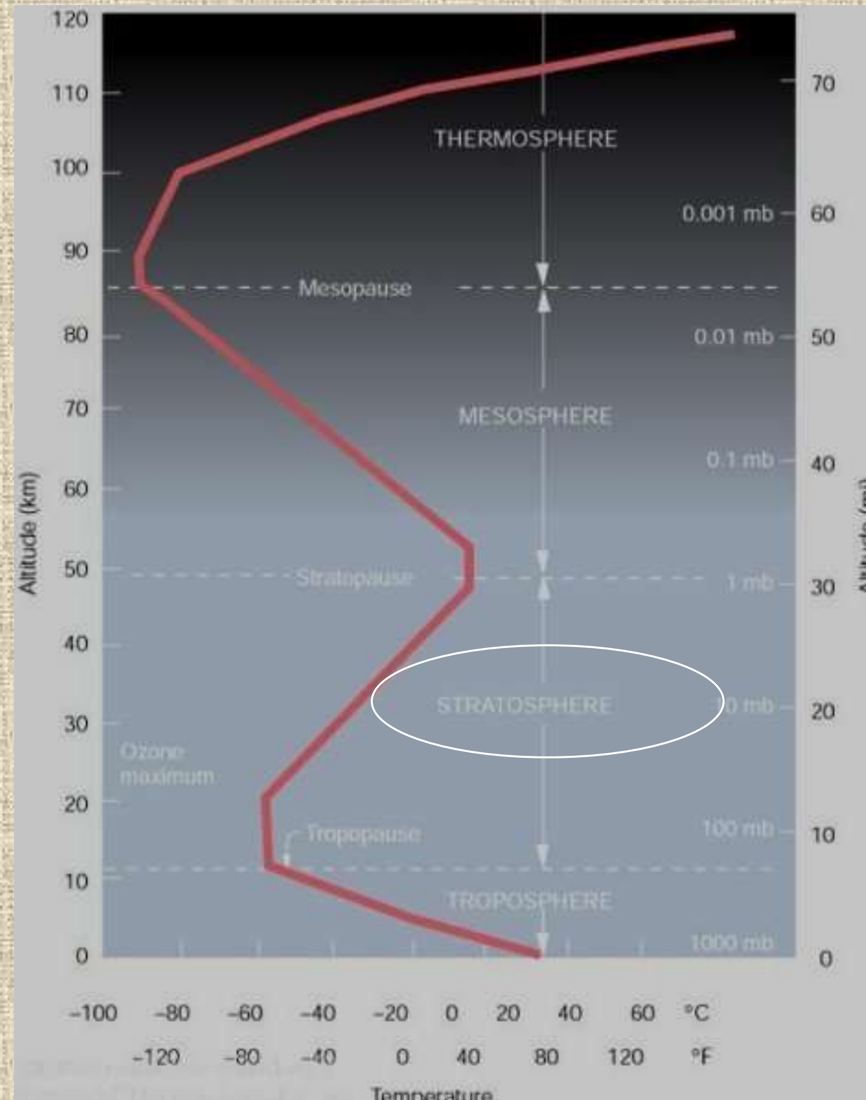


Mesosphere: Middle atmosphere – Air thin, pressure low, Need oxygen to live in this region. Air quite Cold, -90°C (-130°F) near the top of mesosphere

Thermosphere: Hot layer" – oxygen molecules absorb energy from solar Rays warming the air. Very few atoms and molecules in this Region.

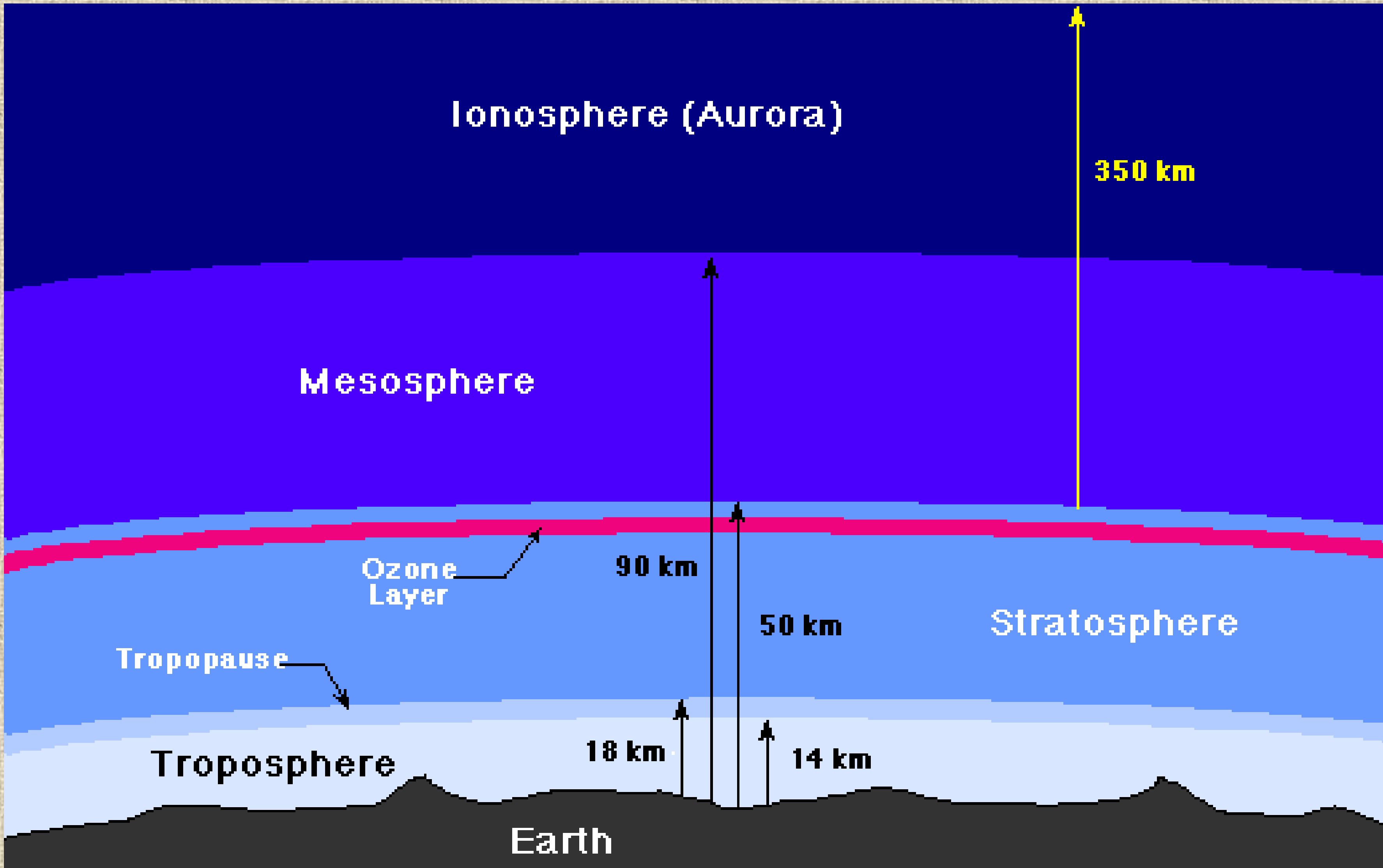
Temperature Profile





Temperature inversion in stratosphere

Ozone plays a major part in heating the air At this altitude



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UV Index (UVI)

- A global index recommended by the both World Health Organization and World Meteorological Organization in 1994.
- The index is a simple measure of the UV radiation level at the Earth's surface and an indicator of the potential for skin damage.
- UV radiation (250 - 400 nm) reaching the Earth's surface.
- It's directly proportional to the intensity of UV radiation that causes sunburn on human skin.
- It's an important to raise public awareness and to alert people about the protective measures of UV radiation.

UVI	1	2	3	4	5	6	7	8	9	10	>10
Category	Low		Moderate			High		Very High			Extreme
Colour	Green		Yellow			Orange		Red			Purple
Pantone Matching System	375		102			151		032			265
RGB (8 bit values)	40r 149g 0b		247r 228g 0b			248r 89g 0b		216r 0g 29b			107r 73g 200b

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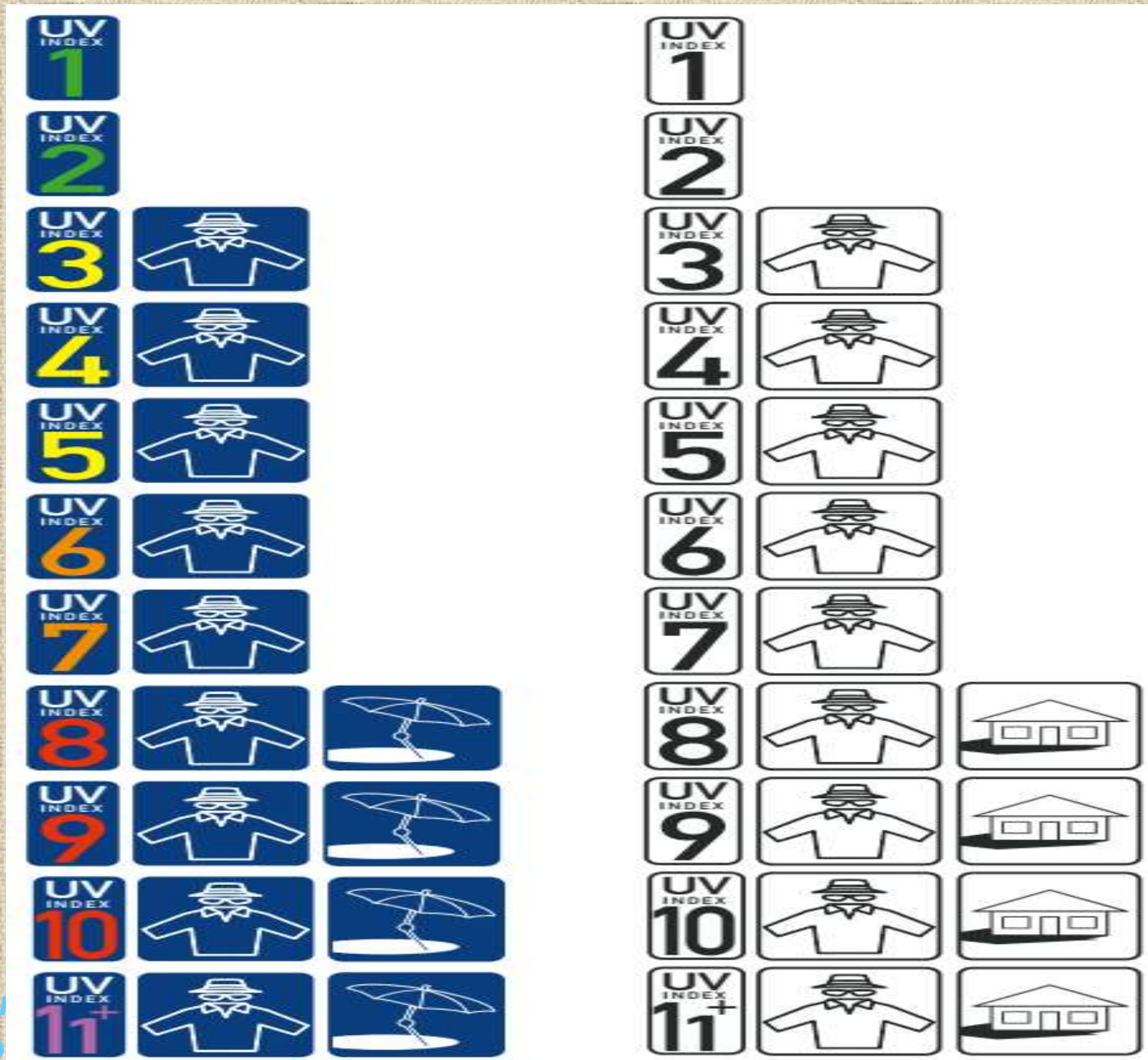
UV INDEX 1
UV INDEX 2
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UV INDEX 9
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UV INDEX 11+
UV INDEX 1
UV INDEX 2
UV INDEX 3
UV INDEX 4
UV INDEX 5
UV INDEX 6
UV INDEX 7
UV INDEX 8
UV INDEX 9
UV INDEX 10
UV INDEX 11+

Filtering of sunlight's UV component by atmosphere

Three Types of UV Radiations:

- ✓ **UV-A (315-400 nm):**
  - ✓ Causes some damage but is not really absorbed well by O_3.
  - ✓ The amount of ground-level UV-A is relatively unaffected by ozone depletion
- ✓ **UV-C (100-280 nm):**
  - ✓ Most damaging region, but most strongly absorbed by O_3.
  - ✓ Not affected by ozone depletion (at typical levels) –
  - ✓ Any depletion merely causes UV-C to penetrate more deeply into the atmosphere
  - ✓ But still not reach ground level.

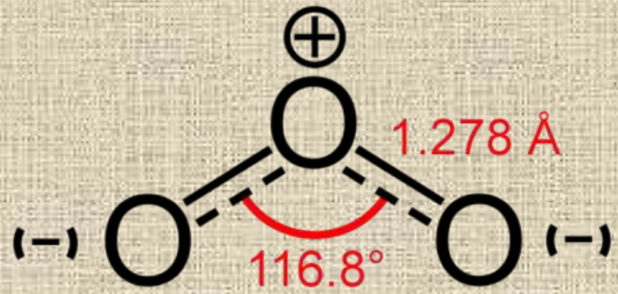
Continue…

- ✓ **UV-B (280-315 nm):**
  - ✓ **T**his is the region with the greatest overlap between ground-level sunlight and action spectrum, and
  - ✓ it lies on the "tail" of the O3 absorption spectrum.
  - ✓ It is this region that is most strongly affected by ozone depletion

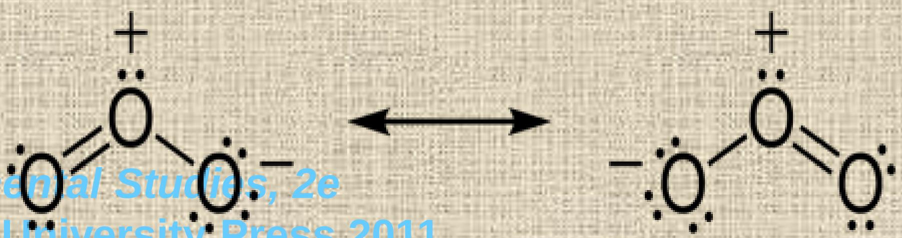
- ❑ All UVC and approximately 90% of UVB radiation is absorbed by ozone, water vapour, oxygen and carbon dioxide.
- ❑ Environmental factors that influence the UV level
  - ❑ Sun Height
  - ❑ Latitude
  - ❑ Altitude
  - ❑ Cloud Cover
  - ❑ Ozone
  - ❑ Ground Reflection

Stratospheric Ozone

What is ozone?



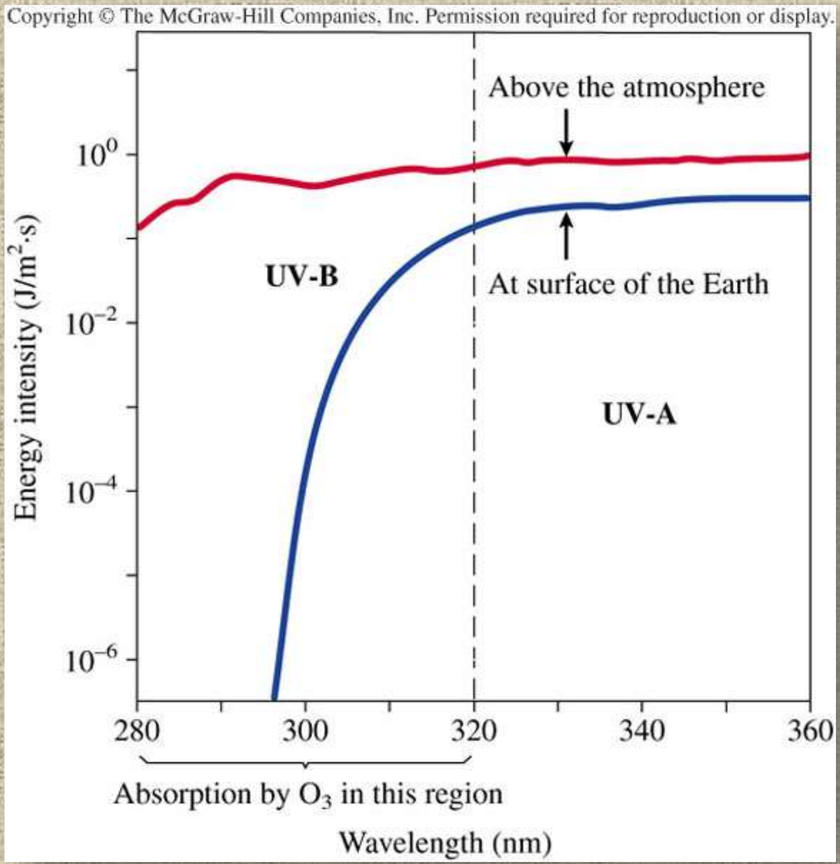
- The Greek word ‘ozein’, meaning to smell
- Ozone has a pungent/sharp odour.
- Smell something like burning electrical wiring
- Ozone is an irritating, corrosive, colorless gas
- Ozone is made of three oxygen atoms
- The central atom is sp^2 **hybridized** with one lone pair.
- **Ozone** is a polar molecule with a dipole moment of 0.53 D.
- O3 is less stable than O2 , because it wants to return to the diatomic state by giving up an oxygen atom



Why care about ozone?

- How important is the ozone in our atmosphere
- why are scientists so concerned about its increase near the surface of the earth
- Its disappearance higher up in the atmosphere?
- What does the ozone layer do for us?

- Ozone is the only major atmospheric constituent that absorbs significantly between 210 and 290 nm.
- Without it life would have remained underwater
- The ozone layer is a consequence of oxygen-only chemistry.



The Ozone layer: A natural sunscreen of the earth

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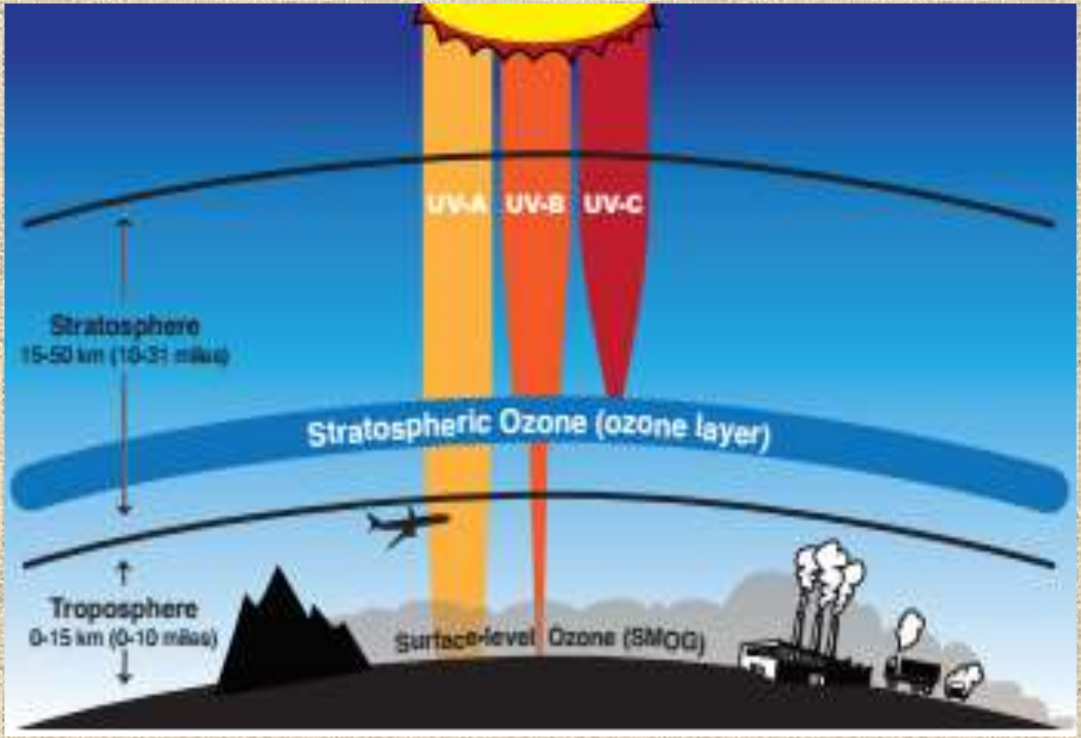
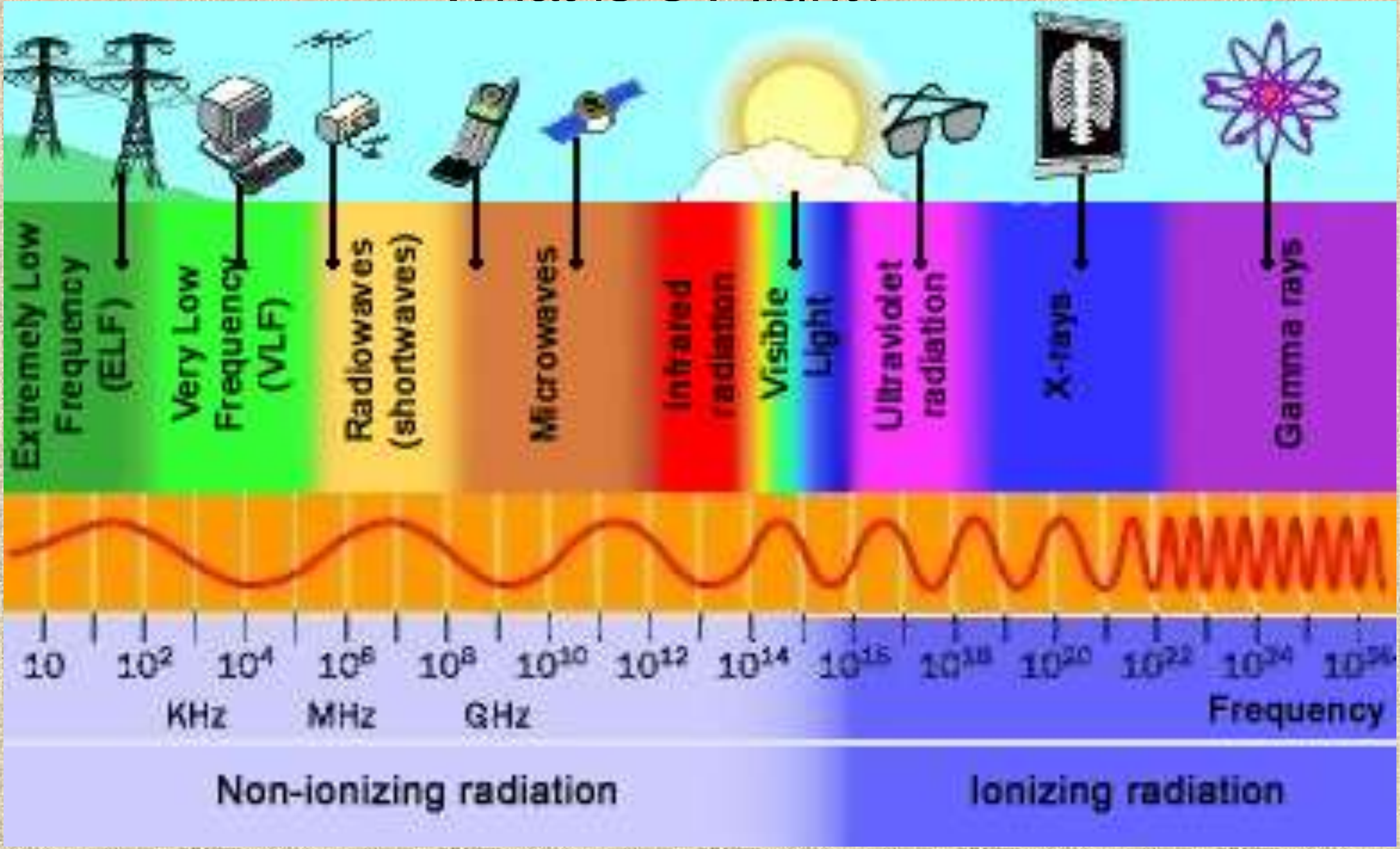


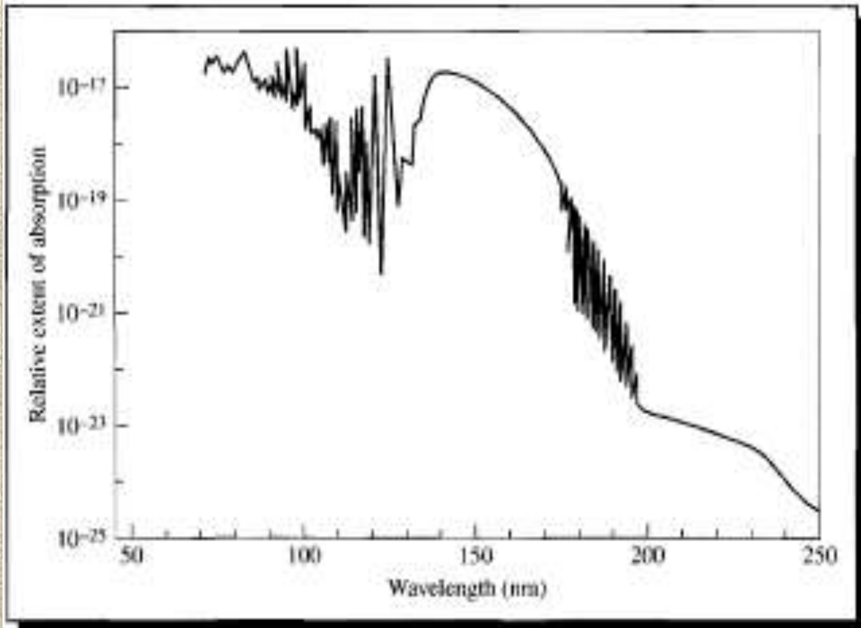
- The "ozone layer" refers to the ozone within stratosphere,
- 90% of the earth's ozone resides
- Ozone selectively absorbs UV radiation

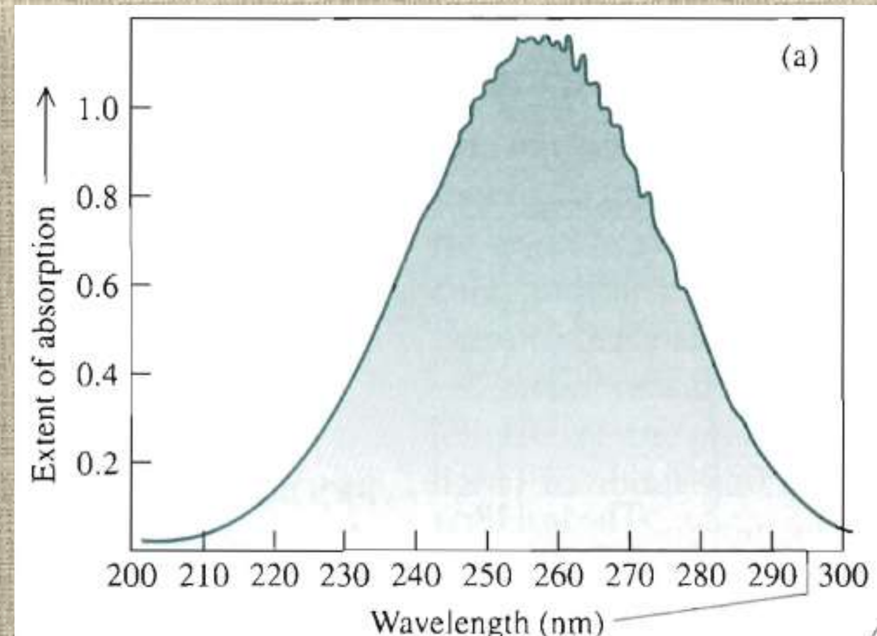
What is UV light?



Stratospheric ozone is a naturally-occurring gas that filters the sun's ultraviolet (UV) radiation.

Absorption spectrum of O_2 and O_3





- ✓ All the atoms and molecules absorbs selectively
- ✓ Spectrum depends upon the structure and the energy level of their electron.
- ✓ O_3 filters in the whole range of 220-320 nm

Chemistry of Ozone/Ozone Formation

Stratospheric ozone (O3) is produced by the combination of an oxygen atom (O) with an oxygen molecule (O2).

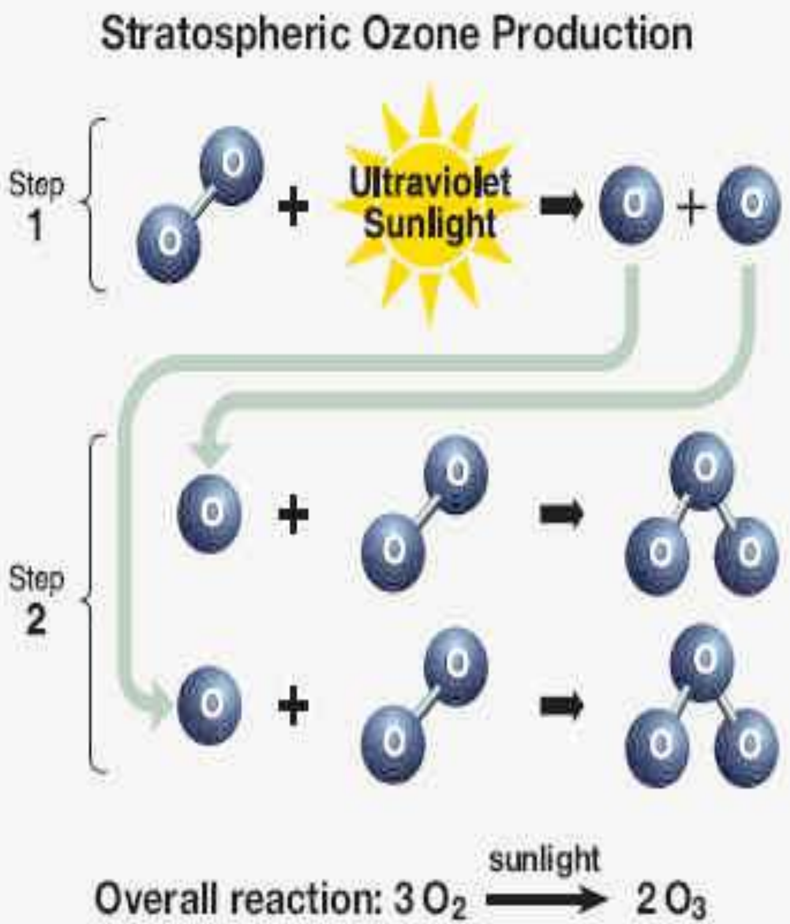


Figure Q2-1. Stratospheric ozone production. Ozone is naturally produced in the stratosphere by a two-step reactive process. In the first step, solar ultraviolet radiation (sunlight) breaks apart an oxygen molecule to form two separate oxygen atoms. In the second step, each atom then undergoes a binding collision with another oxygen molecule to form an ozone molecule. In the overall process, three oxygen molecules plus sunlight react to form two ozone molecules.

The Chapman Cycle:

- 1930
  - Sydney Chapman proposed a series of reactions to account for the ozone layer: t*he Chapman Cycle*
  - The *Chapman Cycle* explains how the ozone layer is formed and maintained. Describe this process in some detail.
  - Four chemical reactions
    - *Initiation*

$$O_2 + \text{light} \rightarrow 2O \ (120 – 210 \text{ nm})$$

    - *Propagation* (cycling)

$$O + O_2 + M \rightarrow O_3 + M^* \text{ (generates heat)}$$

$$O_3 + \text{light} \rightarrow O_2 + O \ (220 – 320 \text{ nm})$$

    - *Termination* $O_3 + O \rightarrow 2O_2$

Countinue…

Typical rates for the four reactions are:

1.10^6 molecules of O_2 photodissociate per second

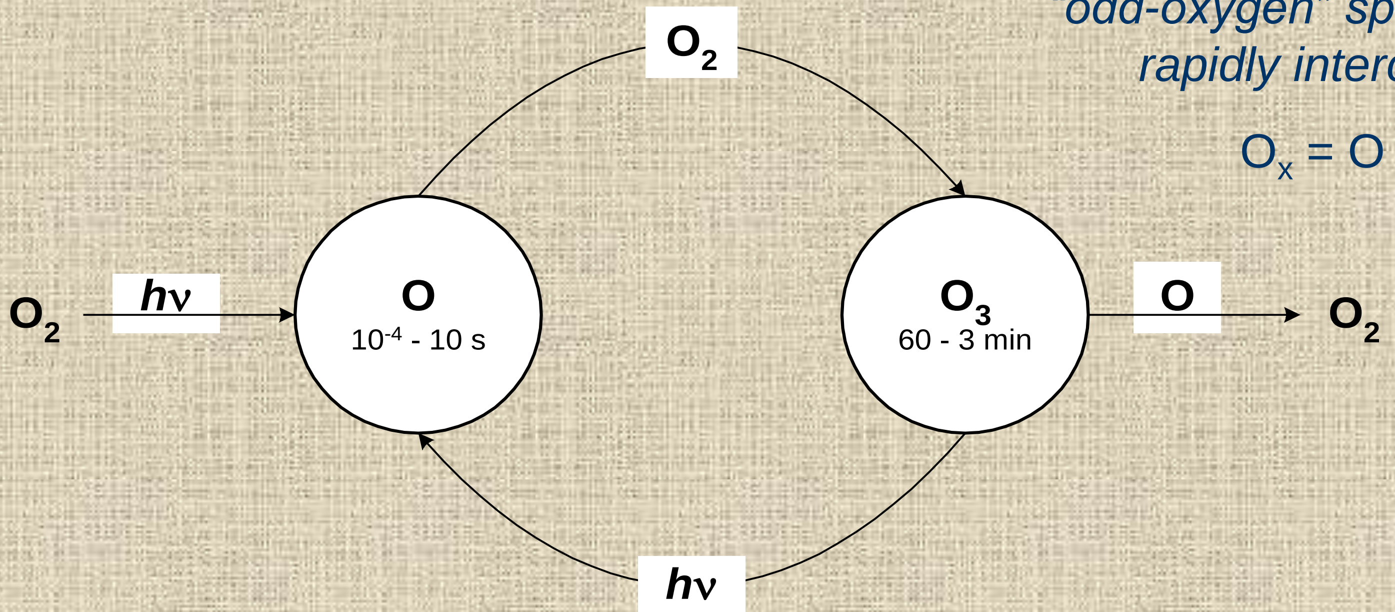
2.10^5 molecules of O_3 react with O per second

3.10^8-10^9 "cycles" of O_x conversions occur per second

Thus, the typical "chain length" of the cycles is about 1000.

In other words, the rate of interconversion among O_x species is (***very roughly***) one thousand times faster than the rate of O_x production or loss.

The Chapman Cycle: ***Oxygen-only Chemistry***



"odd-oxygen" species (O_x) are rapidly interconverted

$O_x = O + O_3$

- The production of Ox (and hence O3) is by photodissociation of O2.
- The rate of this photodissociation is proportional to the uv light intensity that causes the photodissociation times the absolute concentration of dioxygen.
- Above the stratosphere there is plenty of uv light but fewer O2 molecules (air is thinner) while below the stratosphere there is plenty of O2 molecules but not much uv light.
- Thus it makes sense (qualitatively) that ozone is created in the stratosphere only

Ozone Layer Depletion

- The decrease in the concentration of ozone (O_3) in stratosphere
- It has been discovered that stratospheric ozone is depleting as a result of anthropogenic/man-made substances
- There are a number of chemical reactions that can deplete stratospheric ozone; however, some of the most significant of these involves the catalytic destruction of ozone by halogen radicals such as chlorine and bromine (CFC).
- Chief Cause: Widespread use of chlorofluorocarbons (CFCs)
- This depletion makes humans more vulnerable to the UV-B rays which are known to cause skin cancer and other genetic deformities.

CFCs

- ❑ CFCs are powerful O_3 destroyers. They are used in the following ways:
- ✓ As coolants in the compressors of refrigerators and air conditioners.
- ✓ To clean electronic circuit boards used in computers, telephones, etc.
- ✓ In the manufacture of foams for mattresses and cushions, disposable Styrofoam cups, packaging material, cold storage, etc.

Ozone Hole

The thinning of ozone layer or reduction in concentration of ozone especially over the area of Antarctic continent is known as ozone hole, which covers approximately seven million square kilometer.

Continue…

- What are CFCs? What are they used for?
- CFCs are ***chlorofluorocarbons***; they are small molecules that contain chlorine, fluorine and carbon atoms.
- Usually there are only 1-2 carbon atoms.
- CFCs are sometimes called ***Freons***
- CFCs are referred to by a number.
- The most common CFCs are:
  - **CFC-11, CFC-12, CFC-113**

CFC-11: $CFCl_3$

CFC-12: CF_2Cl_2

CFC-113: CF_3CCl_3

HCFC-22: CHF_2Cl

- HCFCs are CFCs that contain hydrogen. This makes them more reactive to the OH radical, decreasing their tropospheric lifetime. That means that, on a pound-per-pound basis, HCFCs (“soft CFCs”) destroy less stratospheric ozone than CFCs (“hard CFCs”) because a smaller fraction of HCFCs “survive” to reach the stratosphere

Destruction of Ozone Layer by CFCs

Prof. Sherwood Rowland and Mario Molina discovered that chlorofluorocarbons could be photolyzed by high energy photons in the stratosphere

"Hard" CFCs are unreactive to OH and other reactive radicals in the troposphere.

They are also pretty insoluble in water. That means their tropospheric lifetimes are easily long enough that the majority of tropospheric CFCs pass through the tropopause into the stratosphere.

Once there, they are subject to light of shorter wavelengths (ie, more energetic photons). In particular, many CFCs absorb in the "uv window" (centered at 205 nm) between strong O_2 and O_3 absorption. That means most can photodissociate in the bottom half of the stratosphere.

Photodissociation releases chlorine atoms:

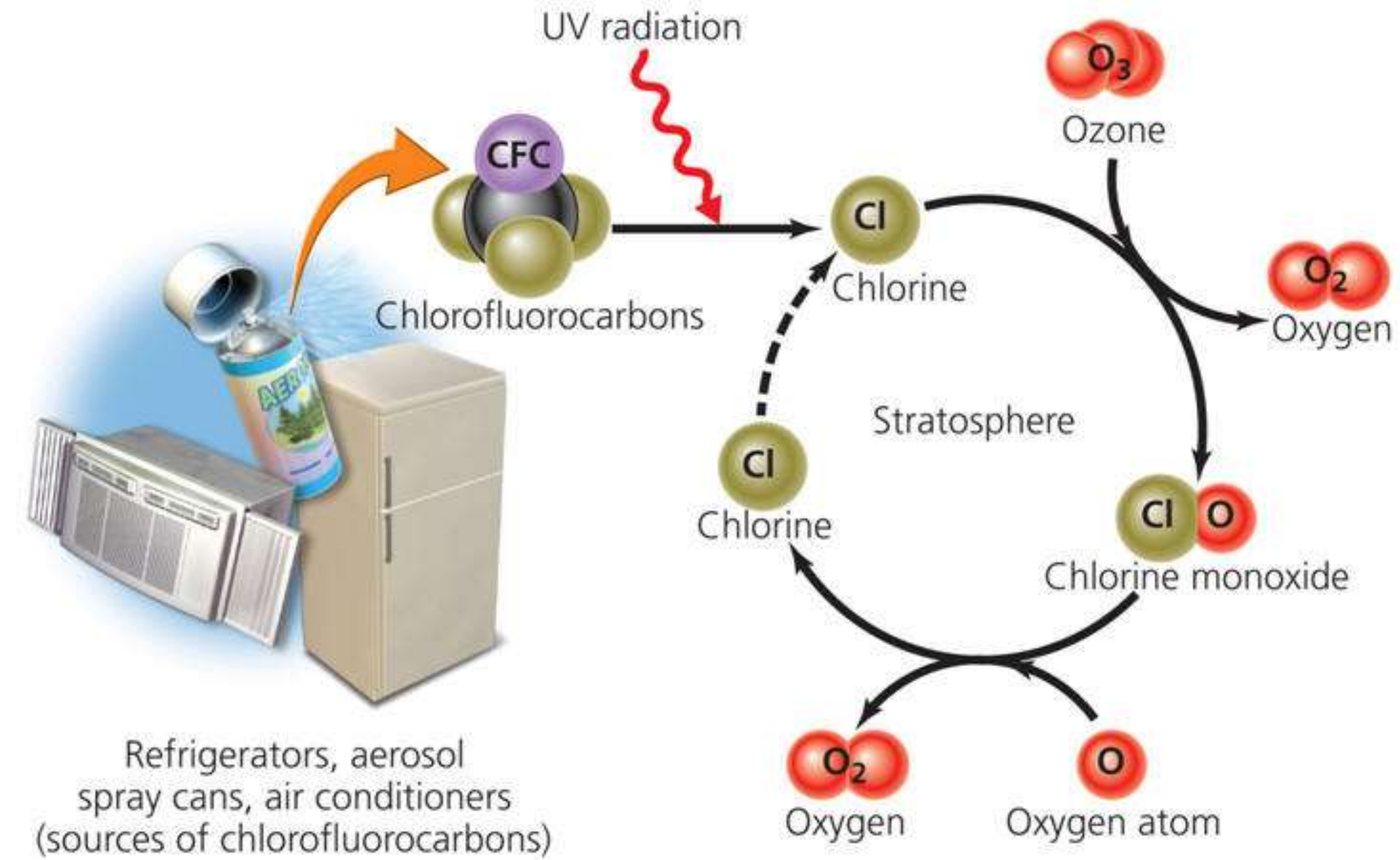
For example: $CFCl_3$ + light → $CFCl_2$ + Cl (l < 225 nm)

Chlorine atoms deplete odd oxygen (O_x) largely by the following cycle

$Cl + O_3 \rightarrow ClO + O_2$

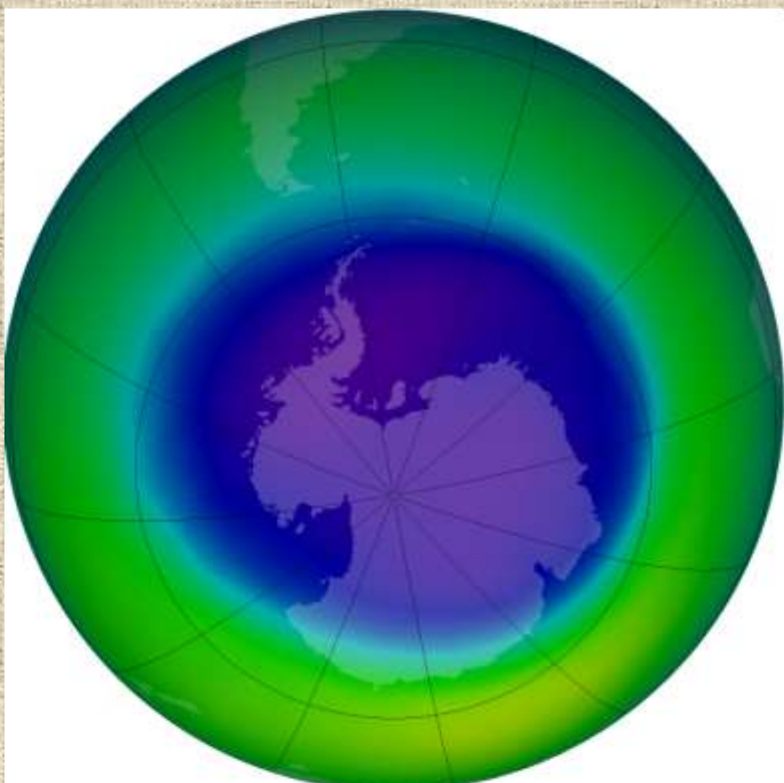
$ClO + O \rightarrow Cl + O_2$ (Rowland-Molina theory of O_3 depletion)

(Overall reaction) $O_3 + O^o \rightarrow 2O_2$


UV radiation
CFC
Chlorofluorocarbons
Cl
Chlorine
O_3
Ozone
O_2
Oxygen
Stratosphere
Cl
Chlorine
Cl O
Chlorine monoxide
O_2
Oxygen
O
Oxygen atom
Refrigerators, aerosol
spray cans, air conditioners
(sources of chlorofluorocarbons)

The “Ozone Hole”

What is the “ozone hole?” When did it first appear? How does it form?



The ozone hole is the region over Antarctica with total ozone 220 Dobson Units or lower. (The avg total column ozone in the atmosphere is about 300 DU.)

Ozone hole in Sept 2005. Source: NASA

Why care about diminished ozone?

1. A diminished ozone layer allows more radiation to reach the Earth's surface. For people, overexposure to UV rays can lead to skin cancer, cataracts, and weakened immune systems.
2. Increased UV can also lead to reduced crop yield and disruptions in the marine food chain. UV also has other harmful effects.

Environmental Effects of O_3 Layer Depletion

- Damage to land plants
- Decrease in population of aquatic community
- Increase in the rate of skin diseases and cancers in human beings
- Disturbance in climate patterns
- Corrosion of materials

Harmful effects of UV rays on people

- Skin cancer
- Premature aging (photo aging) of the skin (different from normal chronological aging)
- Cataracts and eye disorders (corneal sunburn and blindness)
- Immune system damage
- Most biological effects of sunlight arise because UV-B can be absorbed by DNA molecules
- A 1% decrease in overhead ozone is predicted to result in a 2% increase in UV-B intensity at ground level.

Continue…

Effects of UV rays on aquatic Ecosystems

1. Decreasing the abundance of phytoplankton - affects the food stock for fishes and the absorption of CO_2
2. Decreasing the diversity of aquatic organisms - reduces food stock and also destroys several fish and amphibians.
3. Damage to plant cell DNA molecules - makes plants more susceptible to pathogens and pests
4. Reductions in photosynthetic capacity in the plant - results in slower growth and smaller leaves
5. Causes mutations in mammalian cells and destroys membranes

What is being done about the depletion of the ozone layer?

- The United States, along with over 180 other countries, recognized the threats posed by ozone depletion and in 1987 adopted a treaty called the Montreal Protocol to phase out the production and use of ozone-depleting substances.
- Roughly 3% global stratospheric ozone has been depleted.
- The Montreal Protocol was signed in 1987 by 46 countries, including the US. It entered into force in 1989.
- By 1996, developed countries phased out use of CFCs, halons and CCl4; developing countries have until 2010.
- Developed countries are scheduled to phase out production of HCFCs by 2030; developing countries have until 2040.

Summary of Policy responses to Ozone depletion

- **Coordinating committee on Ozone Layer** (CCOL) established by UNEP in the 1970's
- **Mario Molina** and **Sherwood Rowland** showed in 1974 that CFC gases destroy ozone
- **Vienna Convention** for the protection of the ozone layer held in 1985
- **Montreal Protocol** to ban substances that deplete the ozone layer held in 1987.
- **Amendments to the Montreal Protocol**: London - 1990, Copenhagen - 1992 and Montreal - 1997.

Variation in Light Energy with wavelength

$$E = h\nu$$

$$\lambda = \frac{c}{f} = \frac{hc}{E}$$

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

h= 6.63 x 10^{-34} Js and c= 3 x 10^{8} m/s

For convenience, the product *hc in the equation above can be evaluated* on a molar basis to yield a simple formula relating the energy absorbed by 1 mole of matter when each molecule in it absorbs one photon of a particular wavelength of light. If the wavelength is expressed in nanometers, the value *of hc is 119,627 kJ mol^{-1} nm, so the equation becomes:*

$$E = 119{,}627/\lambda$$

Fate of O_2 and O_3 in the presence of UV light

$$O_2 \longrightarrow 2\,O \qquad \Delta H^\circ = 498.4 \text{ kJ mol}^{-1}$$

$$\Delta H^\circ = \Sigma\Delta H_f^\circ \text{ (products)} - \Sigma\Delta H_f^\circ \text{ (reactants)}$$

In the case of the reaction above,

$$\Delta H^\circ = 2\,\Delta H_f^\circ\,(O, g) - \Delta H_f^\circ\,(O_2, g)$$

From data tables, we find that ΔH_f° (O, g) = +249.2 kJ/mol, and we know that ΔH_f° (O_2, g) = 0 since O_2 gas is the stablest form of the element. By substitution,

$$\Delta H^\circ = 2 \times 249.2 - 0 = 498.4$$

Wavelength (longest) of the light required for dissociation of oxygen molecule

$$E = hc/\lambda \qquad E = 119{,}627/\lambda$$

$$\lambda = 119{,}627 \text{ kJ mol}^{-1} \text{ nm}/498.4 \text{ kJ mol}^{-1} = 240 \text{ nm}$$

Thus any O_2 molecule that absorbs a photon from light of wavelength 240 nm or shorter has sufficient excess energy to dissociate.

$$O_2 + \text{UV photon } (\lambda < 240 \text{ nm}) \longrightarrow 2\,O$$

$$O_2 + \text{photon } (\lambda > 240 \text{ nm}) \longrightarrow O_2^* \longrightarrow O_2 + \text{heat}$$

$$O_2 + \text{photon } (\lambda < 240 \text{ nm}) \longrightarrow O_2^* \longrightarrow 2\,O \quad \text{or} \quad O_2 + \text{heat}$$

- Reaction which occurs in the presence of light are called?

Photochemical

What is the energy, in kilojoules per mole, associated with photons having the following wavelengths? What is the significance of each of these wavelengths? [redacted]

(a) 280 nm (b) 400 nm (c) 750 nm (d) 4000 nm

Numericals

1.) A laser emits light of frequency 4.74 x 10^{14} sec^{-1}. What is the wavelength of the light in nm?

2.) A certain electromagnetic wave has a wavelength of 625 nm.
a.) What is the frequency of the wave?
b.) What region of the electromagnetic spectrum is it found?
c.) What is the energy of the wave?

3.) The blue color of the sky results from the scattering of sunlight by air molecules. The blue light has a frequency of about 7.5 x 10^{14} Hz.

a.) Calculate the wavelength, in nm, associated with this radiation.

1 Hz = 1 s^{-1}

b.) Calculate the energy, in joules, of a single photon associated with this frequency.

h= 6.63 x 10^{-34} Js and c= 3 x 10^{8} m/s

Answer

- Q1 6.32×10^2 nm
- Q2 a $\nu = 4.80 \times 10^{14}\ s^{-1}$
- Q2b Visible Region (~400 – 750 nm)
- Q2c 3.18×10^{-19} J
- Q3 a 4.0×10^2 nm
- Q3b 5.0×10^{-19} J

- Revision