

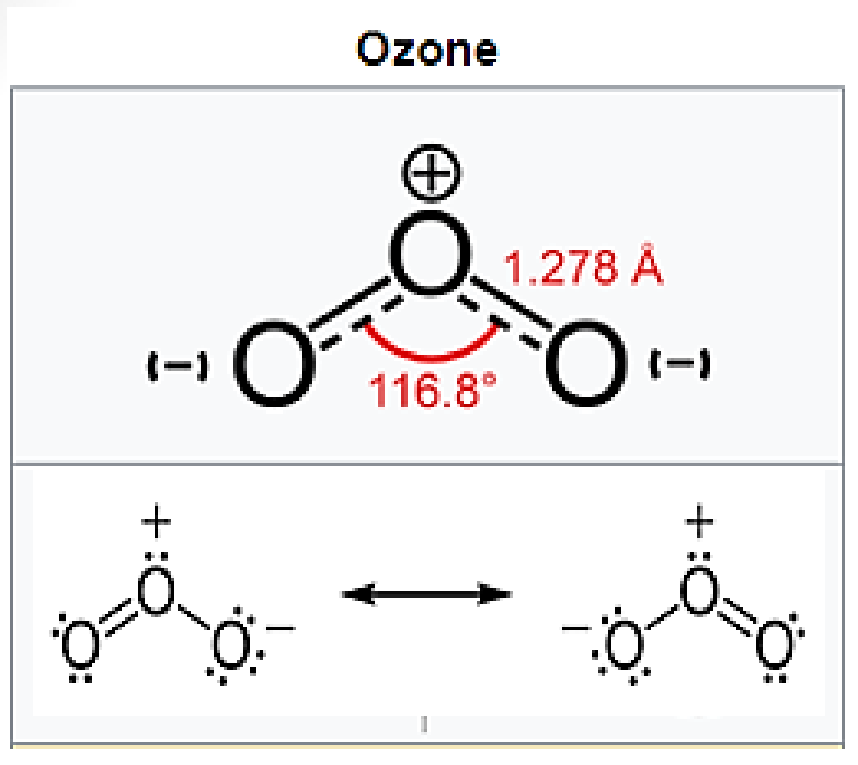
EWCE 105

ENVIRONMENTAL CHEMISTRY
Lecture –10

Lecture Outlines

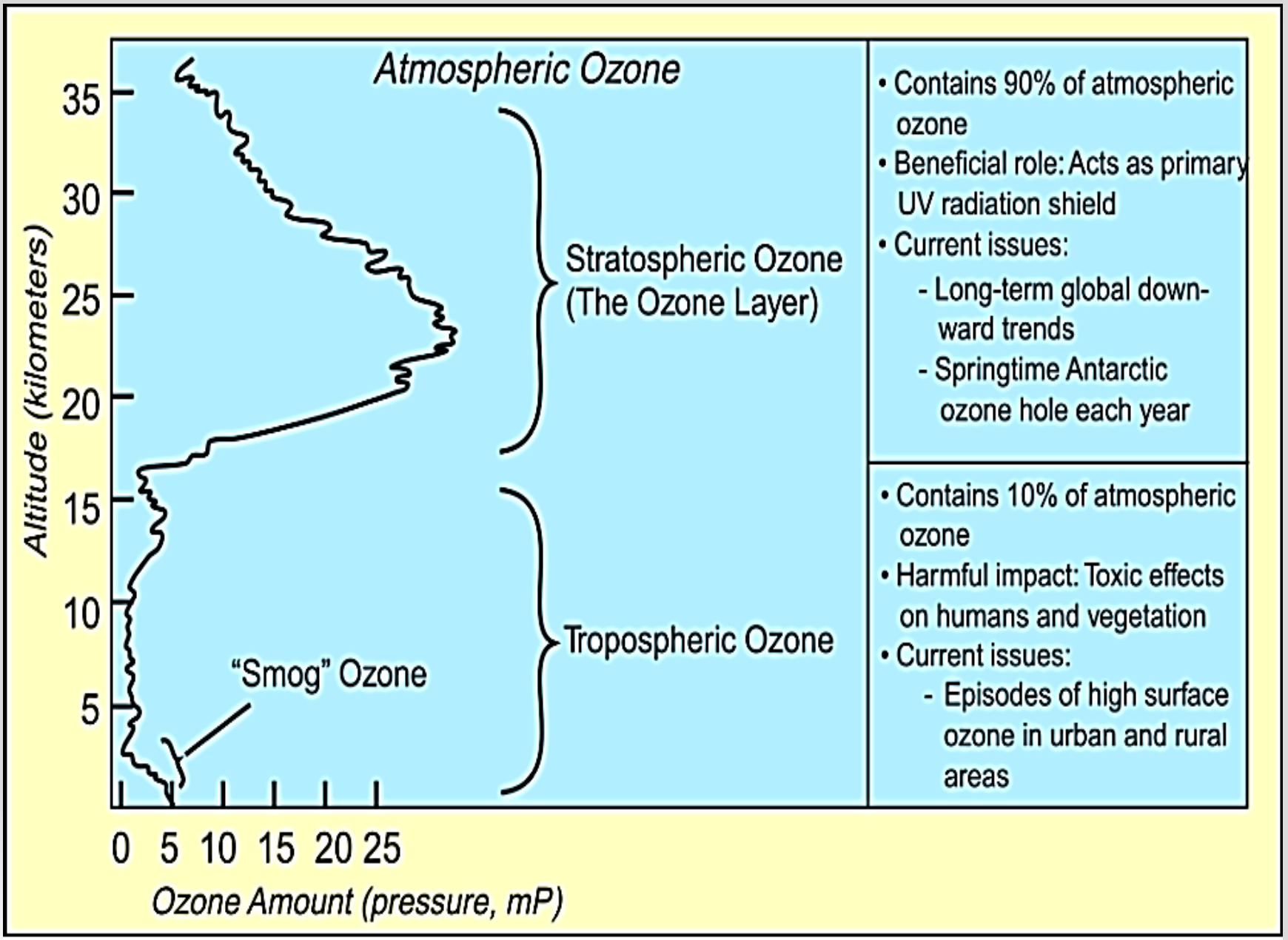
- Structure of the Ozone
- Function of the Ozone Layer
- Formation of the Ozone Layer (Ozone in Stratosphere)
- Catalytic Destruction of the Ozone Layer
- Ozone Hole
- Ozone in Troposphere

Structure of the Ozone



- **Ozone or tri-oxygen,** is an inorganic molecule with the chemical formula O_3.
- It is a pale blue gas with a distinctively pungent smell.

Where is Ozone Found in the Atmosphere ?



OZONE: Sources

The **photochemical mechanisms** that **give rise** to the **ozone layer** were **discovered** by the British physicist Sydney **Chapman** in 1930.

Ozone in the Earth's stratosphere is created by :

- Ultraviolet light striking ordinary oxygen molecules containing two oxygen atoms (O_2), splitting them into individual oxygen atoms (atomic oxygen).
- The atomic oxygen then combines with unbroken O_2 to create ozone, O_3.

About **90 % of the ozone** in the atmosphere is contained **in the stratosphere**. **Ozone concentrations** are **greatest** between about **20 and 40 km**, where they **range** from about **2 to 8 ppm**.

OZONE: Sources

The ozone molecule is **unstable** (although, **in the stratosphere, long-lived**) and when ultraviolet light hits ozone it splits into a molecule of O_2 and an individual atom of oxygen, a continuing process called the **ozone-oxygen cycle**.

Chemically, this can be described as:

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

- Ozone is produced naturally by photochemical reactions in the stratospheric ozone layer --"good ozone".
- Ozone has increased in troposphere due to photochemical smog reactions -- "bad ozone"

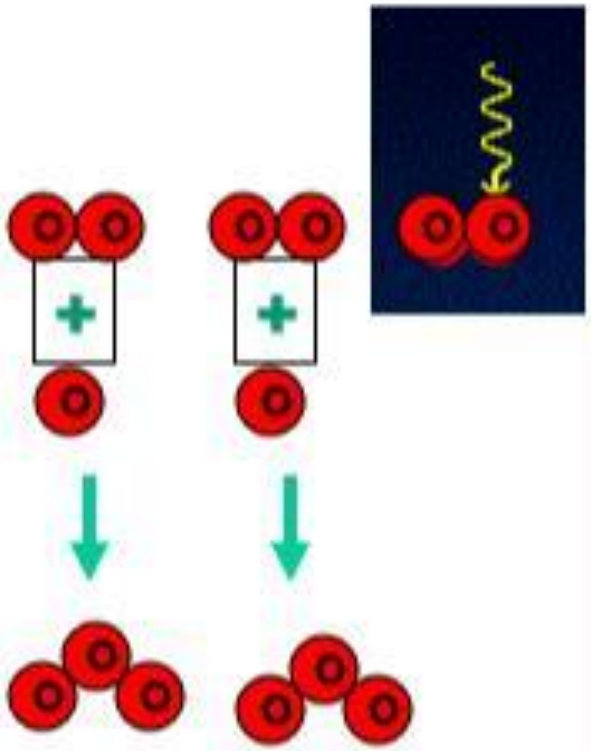
Characteristics of Ozone in Stratosphere

- Most of the UV radiation is absorbed in the upper stratosphere where it generates heat, and only a small fraction reaches the lower altitudes.

- Maximum of relative concentration of O_3, around 10 ppm is found within the range of 25-30 km high in stratosphere.

- Ozone in the stratosphere absorbs damaging ultraviolet radiation strongly of 220 to 330 nm wavelength.

The Chapman Mechanism



The Chapman Mechanism

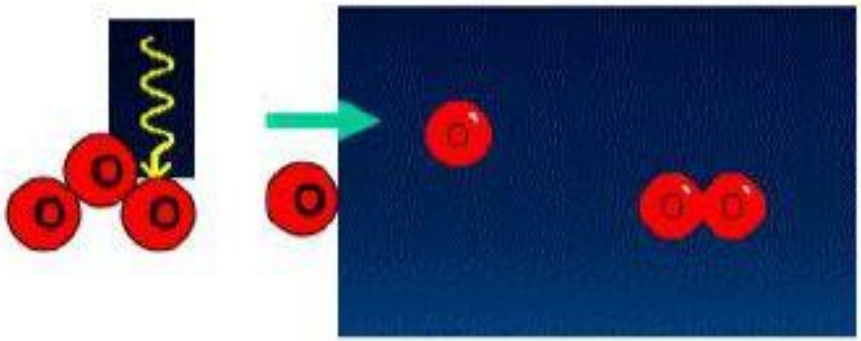
Ozone exists in the upper atmosphere as a consequence of photochemical reactions between molecular oxygen and sunlight:

$$O_2 + O_2 + O_2 + \text{sunlight}$$

$$\rightarrow O_2 + O + O + O_2$$

$$\rightarrow O_3 + O_3$$

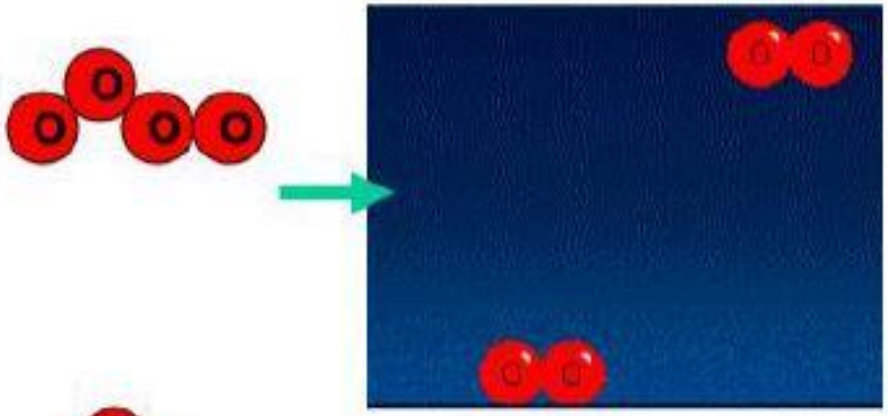
The Chapman Mechanism



Ozone is destroyed naturally by reaction with ultraviolet radiation:

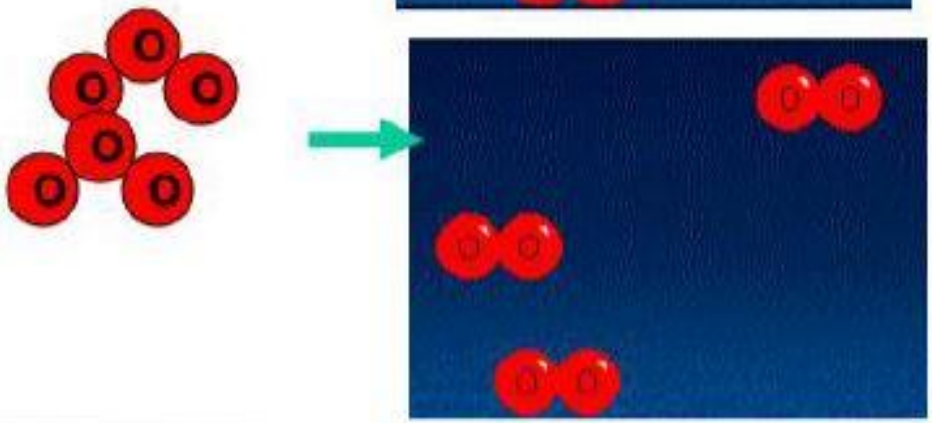
$$O_3 + UV \rightarrow O_2 + O$$

This is part of how the ozone layer protects the earth's surface from ultraviolet radiation.



Ozone is also destroyed naturally by reactions promoted by collisions with atomic oxygen:

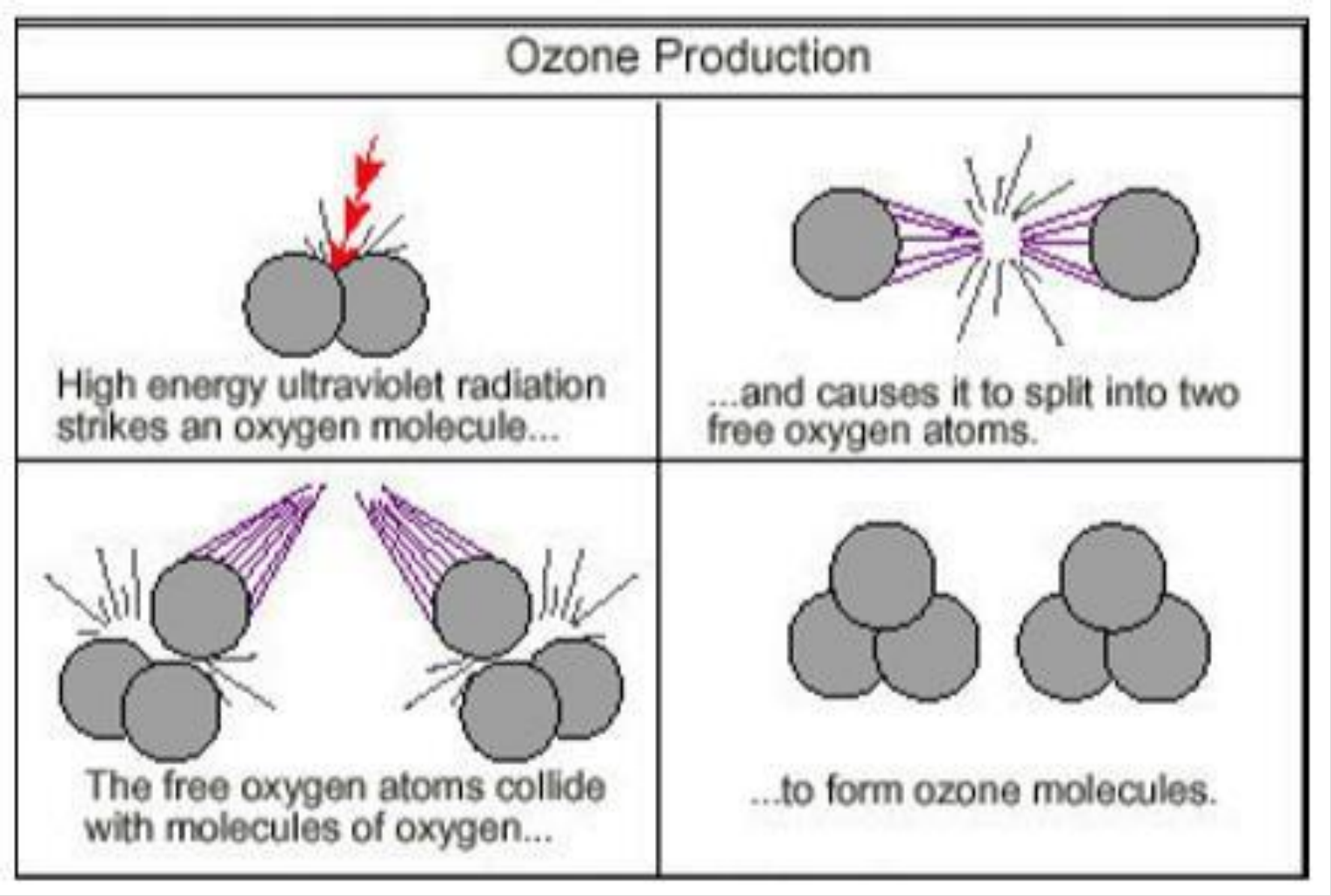
$$O_3 + O \rightarrow 2\,O_2$$



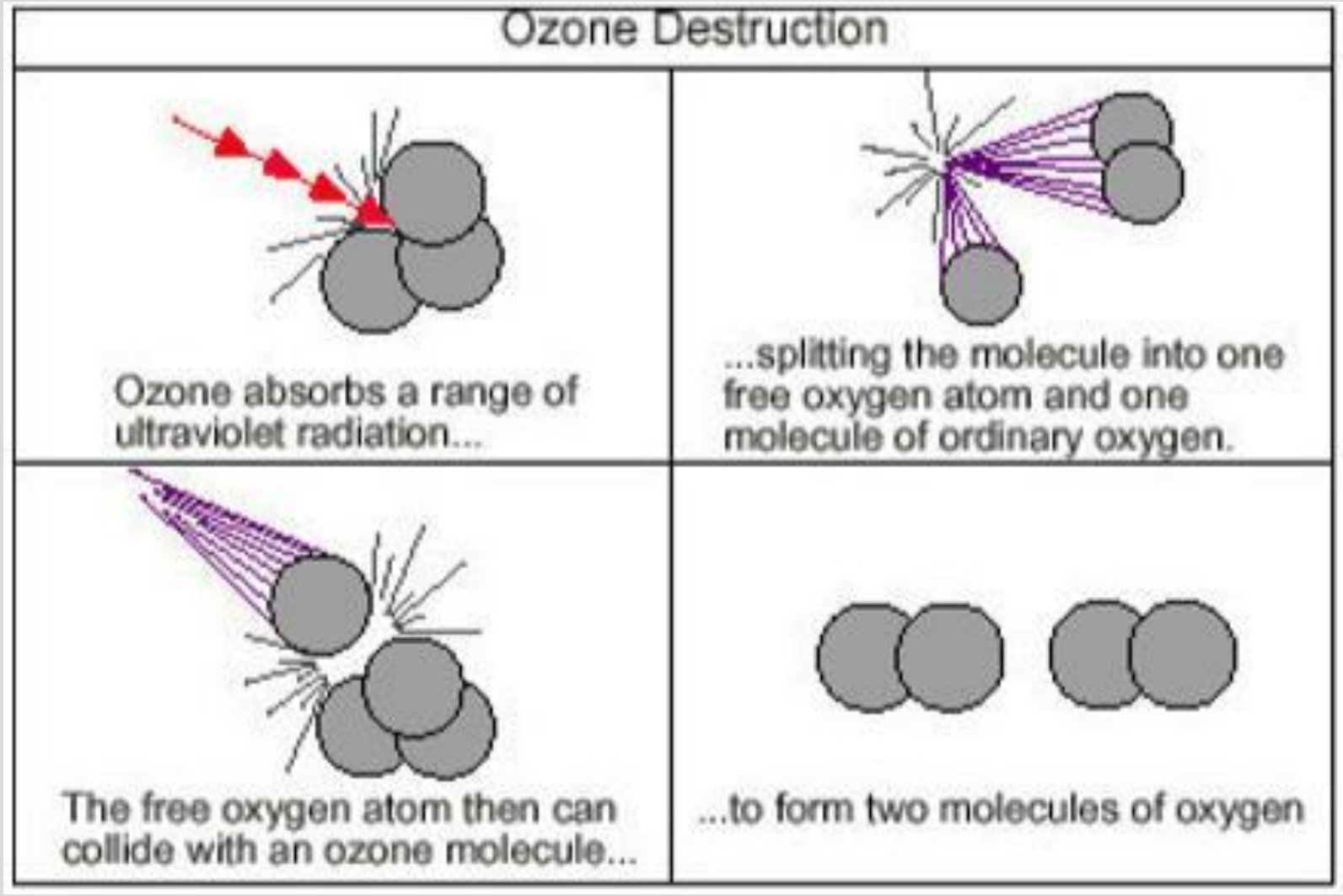
As well as being destroyed by collisions with itself:

$$O_3 + O_3 \rightarrow 3\,O_2$$

Ozone Cycle


Ozone Production
High energy ultraviolet radiation strikes an oxygen molecule...
...and causes it to split into two free oxygen atoms.
The free oxygen atoms collide with molecules of oxygen...
...to form ozone molecules.

Ozone Cycle


Ozone Destruction
Ozone absorbs a range of ultraviolet radiation...
...splitting the molecule into one free oxygen atom and one molecule of ordinary oxygen.
The free oxygen atom then can collide with an ozone molecule...
...to form two molecules of oxygen

Ozone Layer Depletion

- Sources of Ozone Depleting Molecules in the Stratosphere
  - Naturally occurring species - (H_2O)
  - Artificial, "man-made" species

    CFC's, CCl_4, CH_3Br
    - NO from supersonic aircrafts

- The artificial compounds have the most severe effect

Catalytic Destruction of Ozone

- Four main "families" of chemicals responsible for catalyzing ozone destruction:

1. Nitrogen oxides: NO_x
2. Hydrogen oxides: HO_x
3. Chlorine: ClO_x
4. Bromine: BrO_x

A common type of catalytic destruction cycle (there are others)

$$Y + O_3 \rightarrow YO + O_2$$

$$YO + O \rightarrow Y + O_2$$

where Y = NO, OH, Cl or Br

Catalytic Destruction of Ozone

- Simplified stratospheric chlorine chemistry

There are no tropospheric sinks for CFCs; that is, the processes that remove most chemicals in the lower atmosphere – destruction by sunlight, rain-out, and oxidation – do not break down CFCs. The reasons are that CFCs are transparent to sunlight, are essentially insoluble, and are nonreactive in the oxygen-rich lower atm.

However, when they wander to the upper part of the stratosphere, reactions do occur. The highly energetic UV radiation splits up the CFC, releasing chlorine.
When this happens, the following two reactions can take place:

$$Cl + O3 = ClO + O2; \qquad ClO + O = Cl + O2$$

In the first reaction, chlorine combines with ozone to produce chlorine monoxide (ClO), which in the second reaction combines with monatomic oxygen (O) to produce chlorine again.
Following this, the chlorine can enter into another reaction with ozone and cause additional ozone depletion. This series of reactions is known as a catalytic chain reaction.

It has been estimated that each chlorine atom may destroy approximately 100,000 molecules of ozone over a period of 1 or 2 years before the chlorine is finally removed from the stratosphere.

Examples of CFC's : Freons (CF_2Cl_2)

- Ozone Depletion

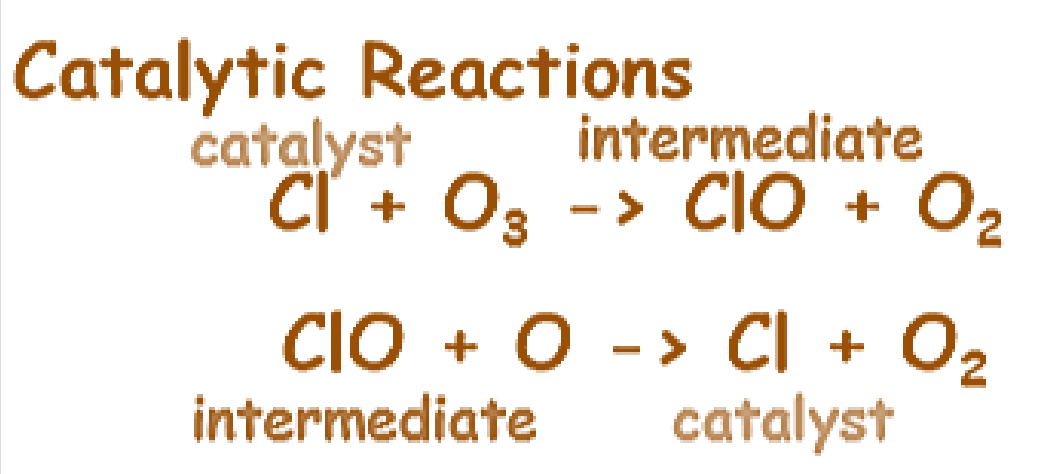


Chlorofluorocarbons (CFCs) are anthropogenic compounds that have been released into the atmosphere since the 1930s in various applications such as in **air-conditioning**, **refrigeration**, blowing agents in foams, **insulations and packing materials**, propellants in aerosol cans, and as solvents.

Examples of CFC's : Freons (CF_2Cl_2)

- Ozone Depletion

Consequences of Competing Reactions



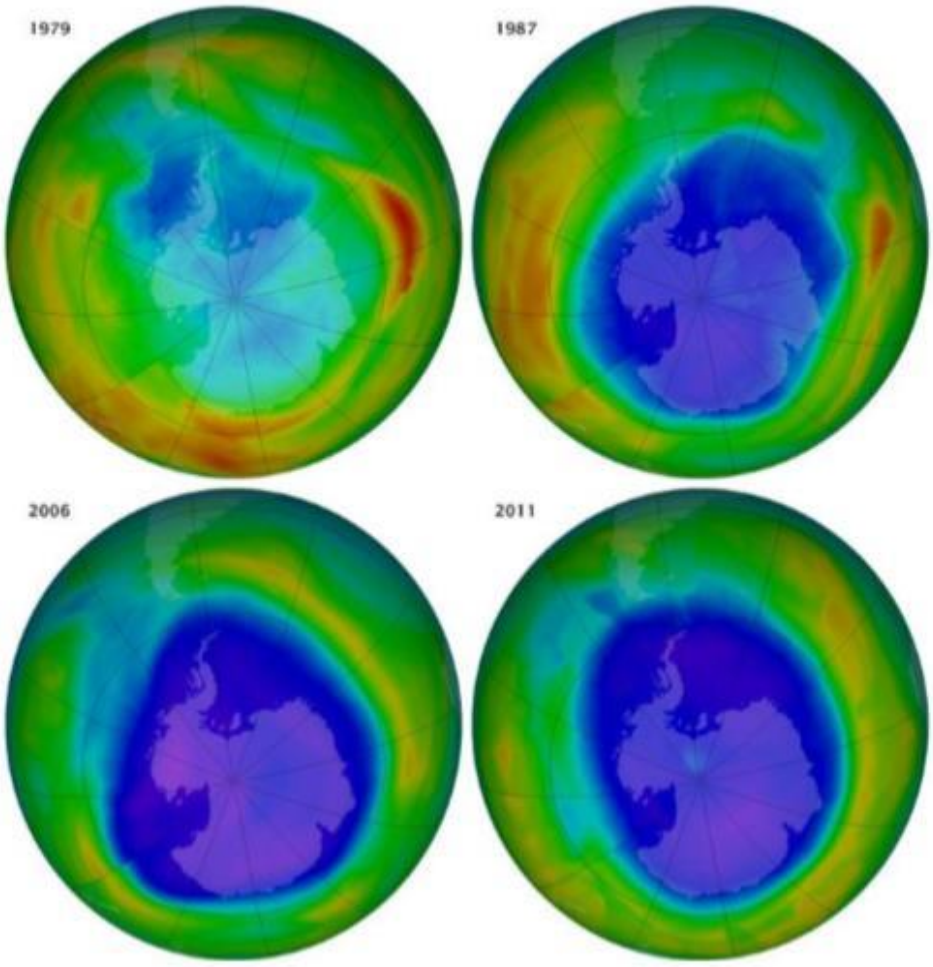
Ozone Hole

- A **region of marked thinning of the ozone layer in high latitudes**, chiefly in **winter**, attributed to the chemical action of CFCs and other atmospheric pollutants.
- The **resulting increase in ultraviolet light** at **ground level** gives **rise to an increased risk of skin cancer**.

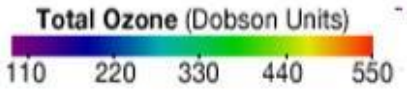
Dobson unit (DU)

A **unit of measurement for the total amount of ozone** in the atmosphere above a point on the earth's surface, **one Dobson unit being equivalent to a layer of pure ozone 0.01 mm thick at standard temperature and pressure**.

Ozone Hole



The "Ozone Hole"



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 :Source: NASA

Ozone Hole

Why does the **Ozone Hole form over the Antarctic** and **why in spring**?

- The Antarctic Vortex
- Polar Stratospheric Clouds
- Concentrations of Active Chlorine

The Antarctic Ozone hole

Since the Antarctic ozone hole was first reported in 1985 it has captured the imagination of many people around the world. Every year since then, Antarctic ozone depletion has occurred during the spring (October) in what is now known as the Antarctic ozone hole.

The amount of depletion has varied from about 15% to 80%. In 1988 ozone depletion was 15%. The lesser amount of depletion is thought to be related to the fact that during 1988 there were fewer polar stratospheric clouds over the Antarctic. By contrast, for years when the ozone depletion was greater, the regions with the most ozone depletion were in the lower stratosphere at an altitude between 14 and 24 km, where the polar stratospheric clouds are present. The ozone hole was largest in 1995 (80%), and it lasted longe than in any previous year.

Polar Stratospheric Clouds

Polar stratospheric clouds have been observed for at least the past 100 years at altitudes of approximately
20 km above the polar regions. Polar stratospheric clouds form during the polar winter. During the polar winter the Antarctic air mass isolated from the rest of the atmosphere and circulates about the pole in what is known as the Antarctic polar vortex. The vortex, which rotates counterclockwise because of the rotation of the earth in the Southern Hemisphere, forms as the isolated air mass cools, condenses, and descends. The cooling occurs because the isolated air mass continues to lose heat through radiation, and heat is not supplied because of the lack of sunlight.

Polar Stratospheric Clouds

During the formation of polar stratospheric clouds, nearly all nitrogen oxides (for example, NO2) in the air mass are tied up in the clouds
as nitric acid. The nitric acid particles grow large enough to fall out by gravitational settling from the stratosphere. As NO2 is a sink of chlorine (by the way, chlorine reacts with ozone and responsible for ozone depletion), the loss of NO2 from the polar stratospheric clouds in part facilitates the ozone depleting reactions.

UV light breaks down CFCs to release chlorine, which combines with ozone to form chlorine monoxide (ClO). The chlorine monoxide may then react with nitrogen dioxide (NO2) to form chlorine

nitrate ($ClONO_2$). So chlorine monoxide cannot participate in the catalytic chain reaction to produce chlorine. So chlorine nitrate works as a sink of chlorine and reduces ozone depletion.

Also chlorine released from CFCs may combine with methane (CH_4) to form hydrochloric acid (HCl). Thus NO_2 and CH_4 are two important sinks of stratospheric chlorine.

Ordinarily, most of the chlorine in the stratosphere resides in stable "reservoir" compounds, primarily hydrochloric acid (HCl) and chlorine nitrate ($ClONO_2$). During the Antarctic winter (March to September) and spring (September to December), however, reactions on the surface of the polar stratospheric cloud particles convert these "reservoir" compounds into dimolecular chlorine and nitric acid ($HCl + ClONO_2 = Cl_2 + HNO_3$).

Nitrogen oxides are absent from the Antarctic stratosphere in the winter and early spring; thus chlorine cannot be sequestered to form chlorine nitrate, one of its major sinks. Therefore chlorine is free to destroy ozone.

The role of sunlight in ozone depletion is the reason why the Antarctic ozone depletion is greatest during spring. During winter, even though polar stratospheric clouds are at their most abundant, there is no light over the pole to drive the chemical reactions (i.e. to destroy ozone).

During the early spring (usually around October), however, the sun comes out, providing energy to drive photochemical reactions
($Cl + O3 = ClO + O2$; $ClO + O = Cl + O2$) and cause rapid ozone depletion.

Ozone depletion in the Antarctic vortex ceases later in spring (mid December) as the environment warms up and the polar stratospheric clouds disappear, releasing nitrogen gases back into the atmosphere where it can combine with chlorine, thus removing it (i.e. chlorine) from ozone depleting reactions.

Stratospheric ozone concentrations then increase as ozone-rich air masses again migrate to the polar region.

Ozone Hole

Environmental effects of ozone depletion

Effects on primary productivity in world's oceans-

There has been speculation for some time that ozone depletion might lead to a reduction of primary productivity in the world's oceans. More and more UVB radiations reaching the ocean surface (specifically in the Antarctic ozone hole) can lead to a loss of productivity of the phytoplankton (microscopic marine algae and photosynthetic bacteria that float near the surface of the ocean) and would have a negative impact on a variety of other marine organisms, because they are at the base of the food chain.

The disruption of food chain may eventually affect people who consume marine resources, because fewer resources would be available for harvest.

Effects on global warming-

The planktons are sinks for atmospheric carbon dioxide and their disruption might increase the concentration of CO2 in the atmosphere, thereby increasing global warming.

Substitutes for CFCs

Two substitutes for CFCs are hydrofluorocarbons (HFCs) and hydrochlorofluorocarbons (HCFCs).

The advantage of HFCs is that they do not contain chlorine. They do contain fluorine and when fluorine atoms are released into the stratosphere, they participate in reactions similar to those of chlorine and can cause ozone depletion. However, fluorine is approximately 1000 times less efficient in those reactions; thus ozone depletion is not thought to be a significant problem in case of HFCs.

The HCFCs contain an atom of hydrogen in place of a chlorine and may be broken down in the lower atmosphere and thus not inject chlorine into the stratosphere. They can cause ozone depletion if they do reach the stratosphere before being broken down but their atmospheric lifetime is considerably shorter than that of the CFCs.

Ozone in the Troposphere

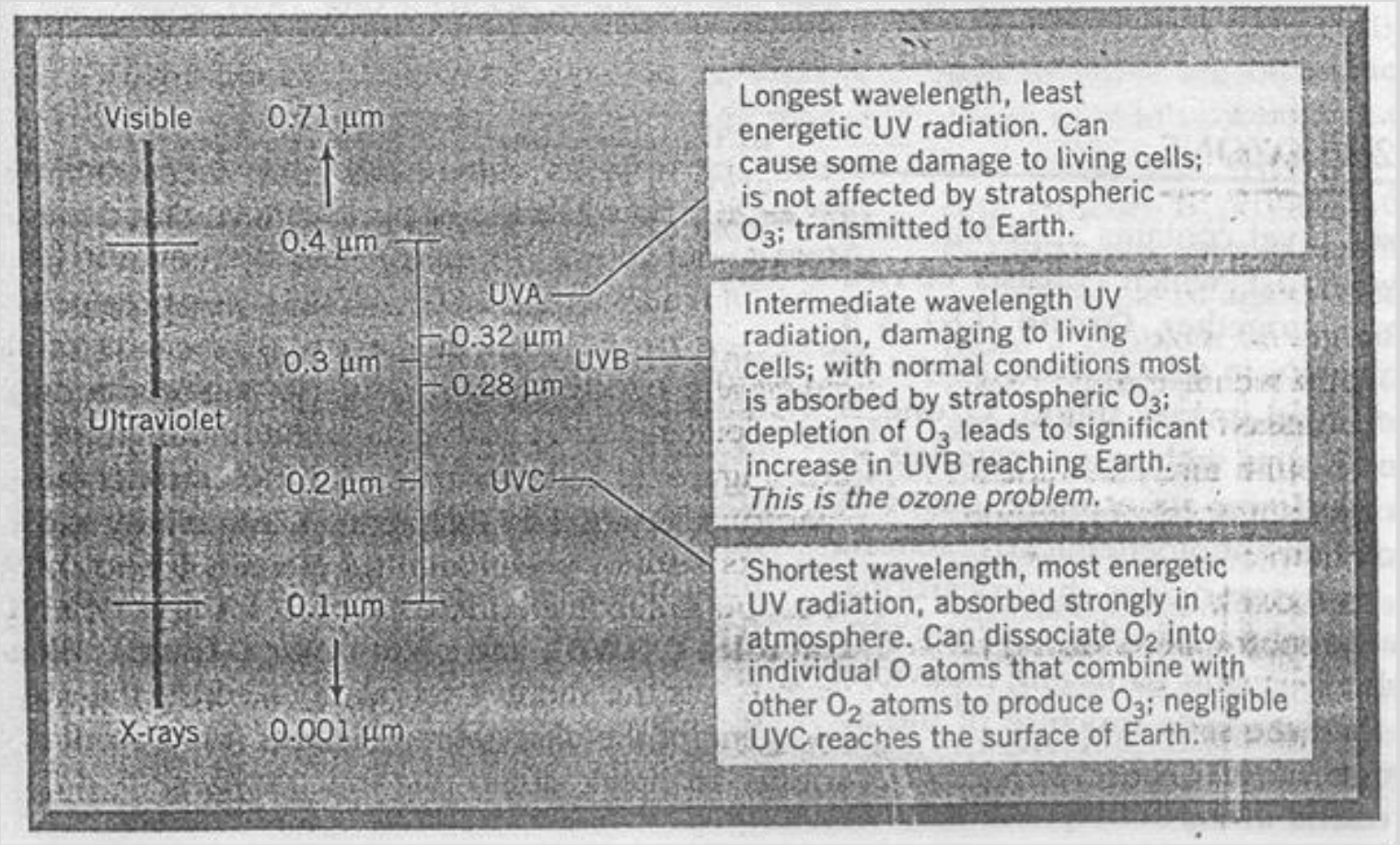
Health and Environmental Effects of Ground Level Ozone

- Ozone is the prime ingredient of smog in most big cities and developed countries.

When inhaled, even at very low levels, ozone can :

- Can cause acute respiratory problems.
- Intensify asthma.
- Can cause significant temporary decreases in lung capacity.
- Cause inflammation of lung tissue.
- Damages the body's immune system defenses.

Parts of electromagnetic spectrum showing UV radiation



Lecture Summary

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- Function of the Ozone Layer
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The End