CHAPTER - 16

OZONE HOLE

Ozone is a natural gas; it is an allotrope of oxygen consisting of three atoms of oxygen bound together in a non-linear fashion. The chemical symbol of ozone is O3.

It is found in two different layers of the atmosphere. Ozone in the troposphere is "bad" because it dirties the air and helps to form smog, which is not good to breathe. Ozone in the stratosphere is "good" because it protects life on Earth by absorbing some of the sun's harmful Ultra Violet (UV) rays.

The ozone layer is very important because the configuration of the ozone molecule and its chemical properties are such that ozone efficiently absorbs ultraviolet light, thus acting like a sun-screen.

> The UV rays cause direct damage to the genetic material or DNA of animal and plant cells. Exposure of mammals to UV light has been shown to act on the immune system, thereby making the body more susceptible to diseases.

In doing so, ozone protects oxygen at lower altitudes from being broken up by the action of ultraviolet light and also keeps most of the ultraviolet radiation from reaching the earth's surface.

It helps in reducing the risks of mutation and harm to plant and animal life. Too much UV rays can cause skin cancer and will also harm all plants and animals. Life on Earth could not exist without the protective shield of the ozone layer.

Do you know?

- Hoolock Gibbon is the only ape found in India. Rest of the monkeys are all macaques and langurs. In India is distributed in the northeast India.
- Palms are typically unbranched trees with only one trunk (columnar stem), called the "caudex," which ends in a crown of large leaves.

16.1. OZONE HOLE

16.1.1. Change in equilibrium

- The equilibrium between the formation and destruction of ozone, has been upset by the influx of several substances into the atmosphere which react with ozone and destroy it.
- The rate at which ozone is being destroyed is much faster than the rate at which it is being formed.
- It implies that there is a significant decrease in the concentration of ozone in a particular region of the atmosphere, hence the name 'ozone hole'.
- The best example of such an ozone hole is the atmosphere over the Antarctic which has only about 50 percent of the ozone that originally occurred there. The actual realization of ozone-depletion came only in 1985.

16.1.2. Sources

chlorofluorocarbons (CFCs):

CFCs molecules are made up of chlorine, fluorine and carbon.

Where it is used?

They are used as refrigerants, propellents in aerosol sprays, foaming agents in plastic manufacturing, fire extinguishing agents, solvents for cleaning electronic and metallic components, for freezing foods etc .

Two-thirds of CFC is used as refrigerants while one-third is used as blowing agents in foam insulation products.

Why CFCs are used?

CFCs has a wide and varied application due to its properties like non-corrosiveness, non-inflammability, low toxicity and chemical stability, etc.

Lifetime & removal of CFCs

Unlike other chemicals, CFCs cannot be eliminated from the atmosphere by the usual scavenging processes like photodissociation, rain-out and oxidation.

In fact, the residence time of CFCs in the atmosphere estimated to be between 40 and 150 years. During this period, the CFCs move upwards by random diffusion, from the troposphere to the stratosphere.

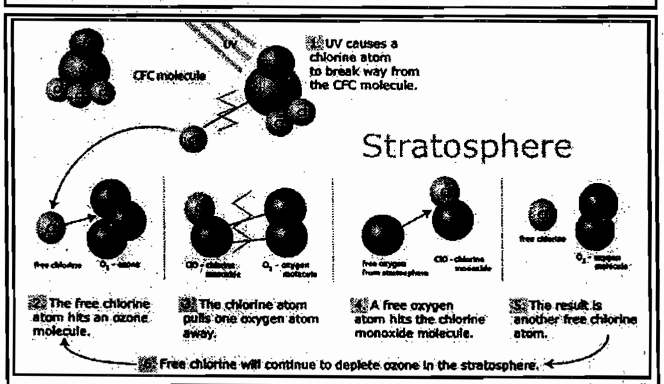
The escape of CFCs

The CFCs enter into the atmosphere by gradual evaporation from their source. CFCs can escape into the atmosphere from a discarded refrigerator. Since the CFCs are thermally stable they can survive in the troposphere. But in the stratosphere, they are exposed to UV radiation.

The chemical reaction

The molecules of CFCs when exposed to UV radiation break up, thus freeing chlorine atoms. A free chlorine atom reacts with an ozone molecule to form chlorine monoxide (ClO). The molecules of chlorine monoxide further combine with an atom of oxygen. This reaction results in the formation of an oxygen molecule (O_2) and reformation of the free chlorine atom (Cl).

Chlorine +	→	Chlorine monoxide + oxygen
Chlorine monoxide + monoxide (o)	→	Chlorine + Oxygen
Net reaction :		
ozone + monoxide (o)	→	oxygen + oxygen



CFC Ozone Depletion

The depletion of O3 is catalystic. The element that destroys O3 (i.e chlorine) is being reformed at the end of cycle. A single chlorine atom destroys thousands of ozone molecules before encountering reactive nitrogen or hydrogen compounds that eventually return chlorine to its reservoirs.

Do you know?

Barking deer/common muntjac is the mammal with the lowest recorded chromosome number. It gives calls similar to barking, usually on sensing a predator. Status – least threatened.

CFC substitutes – characteristics

- The substitute for CFCs should be safe, low cost, increased energy efficiency of CFC replacement technology, effective refrigerants with low ozone layer depletion potential (ODP) and low global warming potential (GWP).
- CFC-12 (R-12) is a widely used refrigerant. HFC 134a (R-134a) is the most promising alternative (R-143a) and (R-152a) can also be used.

16.1.4. Nitrogen Oxides :

Source

The sources of nitrogen oxides are mainly explosions of thermonuclear weapons, industrial emissions and agricultural fertilizers.

The chemical reaction

Nitric oxide (NO) catalytically destroys ozone.

Nitric oxide + ozone	→	Nitrogen dioxide + Oxygen
Nitrogen dioxide + monoxide	→	Nitric oxide + Oxygen

The escape of N_2O

Nitrous oxide (N_2O) is released from solid through denitrification of nitrates under anaerobic conditions and nitrification of ammonia under aerobic conditions. This N_2O can gradually reach the middle of the stratosphere, where it is photolytically destroyed to yield nitric oxide which in turn destroys ozone.

Other substances:

Bromine containing compounds called halons and HBFCs, i.e. hydrobromo fluorocarbons [both used in fire extinguishers and methyl bromide (a widely used pesticide)]. Each bromine atom destroys hundred times of more ozone molecules than what a chlorine atom does.

Bromine + ozone	→	Bromine monoxide + Oxygen
Bromine monoxide + chlorine monoxide	→	Oxygen + Bromine + chlorine

Bromine (Br) combines with ozone forming bromine monoxide (BrO) and Oxygen (O2). The BrO further reacts with chlorine monoxide (ClO) to give oxygen (O2) and free atoms of bromine (Br) and chlorine (Cl). This free atoms can further react with ozone.

Sulphuric acid particles: These particles free chlorine from molecular reservoirs, and convert reactive nitrogen into inert forms thus preventing the formation of chlorine reservoirs.

Carbon tetrachloride (a cheap, highly toxic solvent) and methyl chloroform (used as a cleaning solvent for clothes and metals, and a propellant in a wide range of consumer products, such as correction fluid, dry cleaning sprays, spray adhesives) and other aerosols.

Monitoring the Ozone Layer

- Some organizations that help in monitoring the atmosphere and form a network of informations communication about the atmosphere, including ozone layer monitoring are:
- World Meteorological Organization (WMO)
- World Weather Watch (WWW)
- Integrated Global Ocean Services Systems (IGOSS)
- Global Climate Observing System (GCOS)

16.1.5. Role of polar stratospheric clouds in ozone depletion.

There are three types of stratospheric clouds. They are :

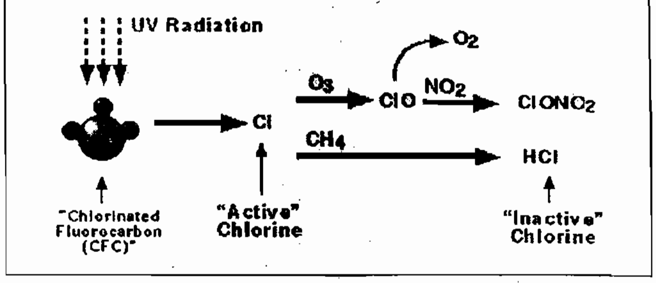
1. Nacreous clouds extend from 10 to 100km in length and several kilometers in thickness. They are also called 'mother-of-pearl' clouds due to their glow with a sea-shell like iridescence.
2. The second type of clouds contain nitric acid instead of pure water.
3. The third type of clouds have the same chemical composition as nacreous clouds, but form at a slower rate, which results in a larger cloud with no iridescence.

The chlorine released by the breakdown of CFCs exists initially as pure chlorine or as chlorine monoxide (active chlorine / instable) but these two forms react further to form compounds Chlorine nitrate and HCL that are stable (inactive chlorine).

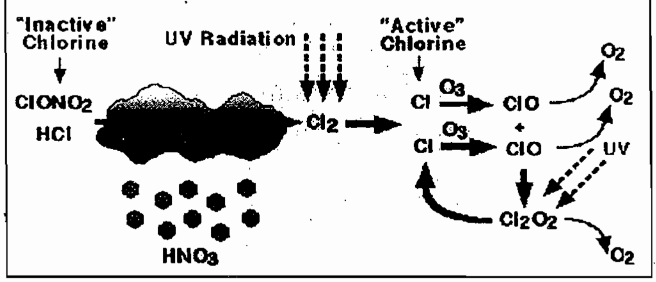
Chlorine + methane	→	HCl + methyliumcation (CH3)
Chlorine monoxide + Nitrogen dioxide	→	Chlorine nitrate

The stable compounds HCL and $CLONO_2$ are reservoirs of chlorine, and therefore for chlorine to take part in reactions of any sort, it has to be freed.

Conversionof Chlorine from "Active" to "Inactive" States



Effect of Polar Stratospheric Clouds



There is a correlation exist between the cycle of ozone depletion and the presence of polar stratospheric clouds (PSCs) i.e. the ice particles of the cloud provided substrates for chemical reactions which freed chlorine from its reservoirs. Usually the reaction between HCl and $ClONO_2$ is very slow, but this reaction occurs at a faster rate in the presence of a suitable substrate which is provided by the stratospheric clouds at the poles.

HCl + Chlorine nitrate	→	molecular chlorine

It results in the formation of molecular chlorine and nitric acid. The molecular chlorine formed in the above reaction can be broken down to atomic chlorine and the ozone depletion reaction would continue. The PSCs not only activate chlorine, but they also absorb reactive nitrogen. If nitrogen oxides were present they would combine with chlorine monoxide to form a reservoir of chlorine nitrate ($ClONO_2$).

Dimer of chlorine monoxide : Stratospheric chlorine monoxide reacts with itself forming a dimer Cl2O2. This dimer is easily dissociated by sunlight, giving rise to free chlorine atoms which can further react to destroy ozone.

Every spring, a hole as big as the USA develops in the ozone layer over Antarctica, in the South Pole. A smaller hole develops each year over the Arctic, at the North Pole. And there are signs that the ozone layer is getting thinner all over the planet.

16.1.6. Why is the ozone hole predominant at the Antarctic?

- The Antarctic stratosphere is much colder. The low temperature enables the formation of Polar stratospheric Clouds (PSCs), below 20 km.
- Ozone absorbs sunlight, causing the characteristic increase in temperature with increase in altitude in the stratosphere. If ozone is being depleted, the air becomes cooler, further adding to the favourable conditions for the formation of PSCs and stabilization of the vortex. The vortex is a ring of rapidly circulating air that confines the ozone depletion in the Antarctic region.
- The longetivity of the Antarctic vortex is another factor, enhancing favourable conditions for the depletion of ozone. The vortex remains, in fact, throughout the polar winter, well into midspring whereas the vortex in the Arctic disintegrates by the time the polar spring (March-April) arrives.
- Typical happenings in the winter months leading to the ozone hole over the Antarctic.
- In June Antarctic winter begins, the vortex develops and the temperature falls enough for the clouds to form.
- During July and August PSCs denitrify and dehydrate the stratosphere through precipitation, hydrochloric acid and chlorine nitrate react on cloud surfaces to free chlorine and winter temperatures drops to their lowest point.
- In September sunlight returns to the centre of the vortex as the austral spring begins and PSCs disappear because of increasing temperature. ClO-ClO and ClO-BrO catalystic cycles destroy ozone.
- During October lowest levels of ozone are reached.
- In November, Polar vortex breaks down, ozone-rich are from the mid-latitudes replenishes the Antarctic stratosphere and ozone-poor air spreads over the southern hemisphere.

16.1.7. Arctic Ozone Hole

- The ozone hole has been increasingly evident over the Arctic as well.
- The Arctic ozone hole which swept across Britain in March 96 was the greatest depletion of ozone ever seen in the northern hemisphere.
- Scientists claim that it had been caused, in past, by a dramatic cooling of the upper atmosphere in the northern latitudes over.
- The ozone depletion over the northern hemisphere has been increasing steadily since the winter of 1992.
- Apart from the build-up of ozone depleting chemicals, the main cause is the increasing cold temperature in the arctic stratosphere which encourages the formulation of PSCs.

How ozone is measured?

- The ozone measurement instruments and techniques are varied. Some of them are the Dobson spectrophotometer and the filter ozonometer called M83, and total ozone mapping spectrometer (TOMS) in the Nimbus-7 satellite.

The Umheher technique

- The most common measure of total ozone abundance is the Dobson unit (named after the pioneering atmospheric physical Gordon Dobson) which is the thickness of the ozone column (compressed at Standard Temperature and Pressure (STP)) in milli-centimeters. At STP one Dobson unit is equal to 2.69x1020 molecules per square meter.

16.1.8. Environmental Effects Of Ozone Depletion

Decrease in the quantity of total-column ozone; tend to cause increased penetration of solar UV-B radiation (290-315nm) to the earth's surface. UV-B radiation is the most energetic component of sunlight reaching the earth's surface. It has profound effects on human health, animals, plants, micro-organisms, materials and on air quality.

Effects of human and animal health

- Potential risks include an increase in the incidence of and morbidity from eye diseases, skin cancer and infectious diseases.
- UV radiation has been shown in experimental systems to damage the cornea and lens of the eye. Experiments in animals show that UV exposure decreases the immune response to skin cancers, infectious agents and other antigens and can lead to unresponsiveness upon repeated challenges.
- In susceptible (light-skin coloured) populations, UV-B radiations is the key risk factor for development of non-melanoma skin cancer (NMSC).

Do you know?

All the chameleons have the ability to change color whenever they are subject to changes in stimuli, like a change in light, temperature or emotion. For example, when angered, they are likely to become darker in color.

Effects on terrestrial plants

- Psychological and developmental processes of plants are affected by UV-B radiation.
- Response to UV-B also varies considerably among species and also cultivars of the same species. In agriculture, this will necessitate using more UV-B tolerant cultivars and breeding new ones.
- In forests and grasslands, this is likely to result in changes in the composition of species; therefore there are implications for the biodiversity in different eco-systems.
- Indirect changes caused by UV-B such as changes in plant form, biomass allocation to parts of the plant, timing of developmental phases and second metabolism may be equally or sometimes more important that the damaging effects of UV-B.

Effects on aquatic ecosystems

- Exposure to solar UV-B radiation has been shown to affect both orientation mechanisms and motility in phytoplankton, resulting in reduced survival rates for these organisms.
- Solar UV-B radiation has been found to cause damage in the early developmental stages of fish, shrimp, crab, amphibians and other animals. The most severe effects are decreased reproductive capacity and impaired larval development.

Effects on bio-geochemical cycles

- Increases in solar UV radiation could affect terrestrial and aquatic bio-geochemical cycles, thus, altering both sources and sinks of greenhouse and chemically important trace gases.
- These potential changes would contribute to bio-sphere atmosphere feedbacks that reinforce the atmospheric build-up of these gases.

Effects on air quality

- Reduction in stratospheric ozone and the concomitant increase in UV-B radiation penetrating to the lower atmosphere result in higher photo dissociation rates of key trace gases that control the chemical reactivity of the troposphere.
- This can increase both production and destruction of ozone (O_3) and related oxidants such as hydrogen peroxide (H_2O_2), which are known to have adverse effects on human health, terrestrial plants, and outdoor materials.
- Changes in the atmospheric concentrations of the hydroxyl radical (OH) may change the atmospheric lifetimes of climatically important gases such as methane (CH_4) and the CFC substitutes.)
- Increased tropospheric reactivity could also lead to increased production of particulates such as cloud condensation nuclei, from the oxidation and subsequent nucleation of sulphur, of both antropogenic and natural origin (e.g. carbonyl sulphide and dimethylsulphide.

Effects on materials

- Synthetic polymers, naturally occurring bio-polymers, as well as some other materials of commercial interest are adversely affected by solar UV radiation.
- The application of these materials, particularly, plastics, in situations which demand routine exposure to sunlight is only possible through the use of light-stabilizers and / or surface treatment to protect them from sunlight.
- Any increase in solar UV-B content due to partial ozone depletion will therefore accelerate the photogradation rates of these materials, limiting their life outdoors.

Do you know?

The gray slender loris (primate) It is found in India and Sri Lanka. Its natural habitats are subtropical or tropical dry forests and subtropical or tropical moist lowland forests. It is threatened by habitat loss