UNIT 23

ENVIRONMENTAL CHEMISTRY

Learning Outcomes:

After carefully studying this unit students will be able to:

- Recognize various reactions, occurring in the atmosphere.
- Recognize that the release CO_x, SO_x, NO_x, VOC_x are associated with the combustion of hydrocarbon fuels.
- Outline problems associated with release of pollutants, including acid rain and the formation by free radical reactions of hazardous inorganic and organic compounds e.g PAN.
- Describe causes and impacts of urban smog.
- Explain greenhouse effect and global warming as resulting in climate change.
- Explain the build up to and recognize the adverse effects of ozone in the atmosphere.
- Describe the role of CFC's in destroying ozone in the atmosphere.
- Describe the role of ozone in the stratosphere in reducing the intensity of harmful UV radiation reaching the earth.
- List possible alternatives to the use of CFC's.
- Recognize and describe alternatives to the use CFC'c.
- Recognize and describe various water pollutants.
- Explain the various parameters of water analysis.
- List some major products of the petrochemicals industry, together with their uses.

Introduction:

In this chapter, we will turn our attention to environmental issues, associated with earth's atmosphere. Air and water pollutions are the major problems in most of the world's cities and they often take on regional dimensions. The atmosphere, a part of the environment, acts as repository for emissions from combustion and from many other human activities. The air can be cleansed by natural mechanisms but these can be overwhelmed by the amount of pollutants being produced. Human activities are increasing the atmosphere concentration of carbon dioxide and other greenhouse gases. In addition, the stratospheric ozone shield, which protects us from the ultraviolet rays, is threatened by the emission of ozone destroying chemicals.

Likewise, water quality is as important issue as water quantity. Although most of the water supply is returned to the stream flow after use, its quality is inevitably degraded. The quality of surface and ground water is of concern due to two distinct points of view that is human health and welfare and the health of aquatic ecosystems. Both aspects of water quality are enhanced by minimizing the impacts of human activities, but the specific issues and control measures are different.

Atmosphere is one of the four spheres of our environment. The other three being lithosphere, hydrosphere and biosphere. Atmosphere is the envelop of gases, surrounding the earths surface. It plays a key role to sustain life on earth and save it from the hazardous environment of the outer space. The atmosphere absorbs most of the cosmic rays from the outer space and harmful radiation such as U.V through ozone (O_3) layer.

In addition, the atmosphere maintains the heat balance of the earth through absorption of energy from the sun and re-emitted.

The atmosphere can be divided into:

i. Troposphere ii. Stratosphere

iii. Mesosphere iv. Thermosphere and

v. Exosphere

S. No.	Zone/Sphere	Altitude (in km)	Temperature range (^{0}C)	Important Chemical Species
1.	Troposphere	0-11	15 to -56	N_2,O_2, CO_2,H_2O, Ar
2.	Stratosphere	11-50	-56 to -2	O_3 (ozone), N_2, O_2
3.	Mesosphere	50-85	-2 to -92	NO^+, O_2^+
4.	Thermosphere	85-500	-92 to 1200	O_2^+ , NO^+ , O, O^+

Fig: 23.1 The atmospheric division

23.1 CHEMISTRY OF THE TROPOSPHERE:

Troposphere extends from the surface of the earth upto 11 kilometers. It constitutes about 10% of the atmosphere's height but contains 80% of its mass. The temperature in this sphere ranges from 15^0C to -56^0C. (Table, 23.1). The important chemicals that exist in this sphere are N_2, O_2,CO_2 and H_2O. It is also a region of much turbulence, due to the global energy flow that results from the imbalances of heating and cooling rates between the equator and the poles. The temperature in troposphere falls off uniformly with increase in altitude. That is why the air it contains is mixed rapidly by convection.

23.1.1 Chemical Reactions in The Atmosphere:

As mentioned earlier, atmosphere can be divided into four spheres/zones (Table 23.1). The main chemical species in the

atmosphere are N_2, O_2, $H_2O_{(v)}$, O_3, NO^+ and O_2+ etc. In some areas (particularly the industries zones), the atmosphere (troposphere) may also contain SO_x and NO_x gases which are the gases responsible for the acid rain.

$$4NO_2 + 2H_2O + O_2 \rightarrow 4HNO_3$$

$$SO_2 + H_2O + \frac{1}{2}O_2 \rightarrow H_2SO_4$$

The concentration of the acid thus formed can be quite higher, which ultimately reduce the pH of rain water substantially. This results in producing what is called acid rain (Topic 23.2.7). The CO_2 present in the atmosphere (0.036%) also reacts with the rain water, making it slightly acidic (pH ≅ 5.6).

$$H_2O + CO_2 \rightarrow H_2CO_3$$

Carbonic acid

The lightening in air and also in combustion engine of motor vehicles may also ignite reaction between stable molecules of N_2 and O_2, producing NO.

$$N_2 + O_2 \rightarrow 2NO$$

Incomplete combustion of the carbonaceous compounds (hydrocarbons, coal etc) result in the formation of carbon monoxide. e.g

$$\text{Hydrocarbon} + O_2 \rightarrow CO + H_2O + \text{Energy}$$
(limited)

CO, like other pollutants such as SO_x, NO_x, etc pollute the fresh air. At concentration higher than 750 ppm (0.1% of the air), CO may cause loss of consciousness and death occurs quickly.

Many more chemical reactions, occurring in the atmosphere, are involved in the formation of industrial and photochemical smog (Topic 23.2.4 and 23.2.5) similarly the main reaction occurring in the stratosphere (11-50 km) are due to the production and destruction of ozone.

23.1.2 Air Pollutants and Their Effects (COx, NOx, VOC's, SO_x O_3)

The term air pollution generally refers to substances that on local and regional scales directly harm animals, plants and people and their artifacts. Clean and dry air contains 78.09% nitrogen, 20.94% oxygen by volume. The remaining 0.97% is comprised of gaseous mixture of CO_2, He, Ar, Kr, Xe and nitrous oxide (N_2O). A wide range of chemicals can pollute the air. They include carbon monoxide, sulphure dioxide, toxic organics, nitrogen oxides and volatile organic compound (VOC's).

- **Carbon Monoxide**

Carbon monoxide mainly results from the incomplete combustion of carbonaceous compounds. It is termed as asphyxiating pollution because it can displace (O_2) bound to hemoglobin (Hb).

$$HbO_2 + CO \rightarrow COHb + O_2$$

Oxyhaemoglobin complex — Carboxyhaemoglobin complex

The Fe binding sites in hemoglobin bind CO 320 times more tightly than O_2. The main source of CO to the environment are the vehicles, which emit the exhaust gases containing CO. When the concentration of the CO inhaled, reaches 100 ppm particularly in the closed spaces like tunnels, parking garages etc. It may result in headaches and shortness of breath. The severity of the effects depends on the duration of the exposure and level of exertion. At a concentration higher than 750 ppm (0.1% of the air molecules), loss of consciousness and death occurs quickly.

- **Sulphur Dioxide (SO_2):**

The main sources of sulphur dioxide (SO_2) emission to contaminate air, are combustion of coal and the smelting of metals (metallurgy) particularly copper. The sulphur content of the refined petroleum is generally quite low but the sulphur content of coal is quite high. The sulphur in coal is converted to SO_2 at high temperatures of combustion. SO_2 itself is a lung irritant and is harmful to people suffering from respiratory diseases. However, the most damaging health effects in urban atmosphere are not by SO_2 but by the sulphuric acid aerosol formed from its oxidation. Sulphuric acid not only irritates the fine vessels of the pulmonary region, causing them to swell and block the passages, but is also the major contributor to the acid rain (see 23.2.7).

- **Nitrogen oxides NOx and Volatile Organic Compound (VOC's):**

Nitrogen oxide (NO_x) and volatile organic compounds (VOC's) are not the direct air pollutants in that they rarely affect health directly. Rather, they are the main ingredients in the formation of photochemical smog (see

23.2.5) which is a brown blanket, covering many cities world wide. Although most damage from smog results from the action of ozone (O_3) and other oxidants, these oxidants can not build up without the combined action of NO_x and VOC's. Controlling smog formation requires reducing emission of NO_x and VOC's. Almost all NO_x emissions are due to fossil fuel combustion, whereas the major sources of VOC's emissions are the industrial processes, solvent utilization and on-road and non-road vehicles.

- **Ozone (O_3) as Pollutant:**

While anthropogenic emissions or man made activities are destroying ozone in the stratosphere (Fig: 23.1 of table 23.1), they are helping to create ozone in the troposphere through the phenomenon of photochemical smog. While ozone in the stratosphere protects us from the harmful effects of U.V rays, ozone at ground level is quite harmful. Producing cracks in rubber, destroying plants, and causing respiratory distress and eye irritation in humans. These effects set in at quite low concentrations, around 100 ppb.

23.1.3. Automobile, Pollutants and the Catalytic Converter:

The major pollutants, present in the exhaust gases emitted by automobiles, are carbon monoxide (CO), nitric oxide (NO) and the hydrocarbons (HC's). These gases disturb the stoichiometric ratio of the clean air and thus cause air pollution. When present in sufficient amount, they cause damage to human health and plants life.

One way of reducing emissions is to remove the pollutants from the exhaust gases. In automobiles, this is accomplished with a three-way

catalytic converter, so named because it reduces emissions of hydrocarbons (HC's), carbon monoxide (CO) and nitric oxide (NO). In order to deal with both NO and unburned gases, the converter has two chambers in succession (Fig: 23.4).

In the reducing chamber NO is reduced to N_2 by hydrogen. Hydrogen is generated at the surface of a rhodium (Rh) catalyst by the action of water on unburned fuel molecules.

$$HC's + H_2O \rightarrow H_2 + CO$$
$$2NO + 2H_2 \rightarrow N_2 + 2H_2O$$

In the oxidation chamber, air is added and the CO and unburned hydrocarbons are oxidized to CO_2 and H_2O at the surface of pt/pd catalyst.

$$2CO + O_2 \xrightarrow{pt/pd} 2CO2$$
$$HC's + 2O_2 \xrightarrow{pt/pd} CO_2 + 2H_2O$$

The catalytic converter is quite effective in reducing automobile emission of pollutants.

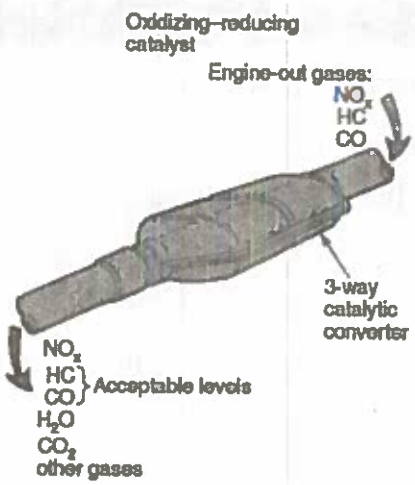


Fig. 23.2

Fig: 23.4: The three-way catalytic remover for HC's, NO and CO, from automobile exhaust.

23.1.4 Industrial Smog:

Smog, in simple words, is the combination of smoke and fog. Smog causes a brownish coloration in the atmosphere, and thus reduces the visibility in the area. This situation ultimately leads to an increased death rates, particularly in large cities such as Los Angeles, Tokyo, Chicago, Lahore, Faisal Abad and Islamabad etc.

Industrial smog is formed, when exhaust pipes throw smoke and other materials into the air, produced by burning of the fossil fuels such as coal, oil and natural gas. The major products are CO_2, H_2O and smoke (carbon) particles.

The fossil fuel, coal, contributes large amounts of combustion products to the atmosphere. Coal is a complex substance made up primarily of carbon containing materials. Its burning produces mostly CO_2.

$$C + O_2 \rightarrow CO_2$$

CO_2 and H_2O in some ways may be considered pollutants. They cause relatively little trouble. Other minor combustion products are the major pollutants. For instance, most of the fossil fuels contain small amounts of sulphur compounds. These, on combustions, form sulphur dioxide, SO_2

$$S + O_2 \rightarrow SO_2$$

The tremendous quantities of coal that are burned for power production and in the blast furnace for making steel release a sizeable SO_2 to the atmosphere which causes to pollute the clean air. SO_2 is an obnoxious pollutant primarily because it gradually reacts further to form sulphur trioxide SO_3. Then in the presence of water or water vapours,

droplets of H_2SO_4 are formed as a result of this reaction.

$$SO_3 + H_2O \rightarrow H_2SO_4$$

H_2SO_4 is corrosive to such diverse materials as building stones and the human respiratory tract.

Another coal-burning power station pollutant is soot, (primarily particles of carbon) which gives smoke its persistent dark colour. The soot also plays its role in the industrial smog. Incomplete combustion of the coal and natural gas may result in the formation of carbon monoxide gas or soot. CO is a lethal gas and at a concentration of 750 ppm in air, it may kill a person, if inhaled. At a level of above 100 ppm, carbon monoxide causes nausea, headache and shortness of breath. If exposed for a bit longer period, it causes loss of consciousness. CO plays vital role in the formation of smog. It is evident, that industrial activities are now so great that they can seriously modify the earths atmosphere, and thus can affect the earths average temperature and our climates.

23.1.5 Photochemical Smog:

Air pollution can be divided into two types. In one type, materials produced from the combustion of coal, oil and gasoline directly create trouble. In the other type, sunlight acts on air pollutants to produce photochemical smog. Photochemical smog can form wherever large quantities of automobile and industrial exhausts are trapped by an inversion layer over a locality that is exposed to sunshine. Photochemical smog is charactorized by an accumulation of brown, hazy fumes, containing ozone (O_3) and other oxidants. Nitrogen oxides (NO_x) and volatile hydrocarbons (HC's), photochemical smog, a condition that affect an increasing number of cities and their surroundings.

Nitrogen dioxide, NO_2 is the only common atmospheric molecule capable of absorbing visible light near the ground level. Its spectrum (Fig: 23.3) has maximum absorption at about 400 nm, in the blue region. It is this absorption that gives smoggy air its brown tint. The unstable photo exited NO_2 dissociates to NO and O atoms.

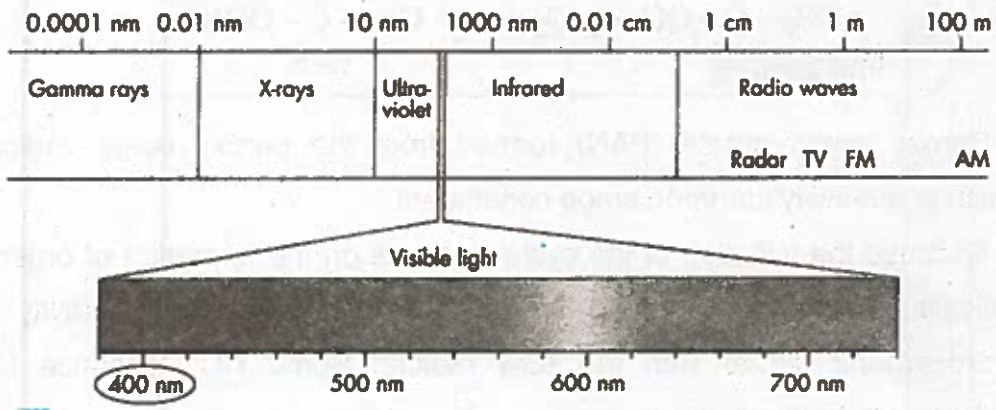


Fig. 23.3

$$NO_2 + h\upsilon \xrightarrow{<400nm} NO_{(g)} + O$$

The oxygen atoms (O) react immediately with the surrounding O_2 molecules to produce ozone (O_3).

$$O_2 + O \rightarrow O_3$$

The O_3 can react with NO to regenerate NO_2. A photochemical cycle is thus, established in these reactions. Hydrocarbons are also needed for smog formation. They produce carboxyl radicals by the reaction of O_3 with hydrocarbon.

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

The organic radical react with O_2 and produce acylperoxy radical which react with NO_2 and produce PAN.

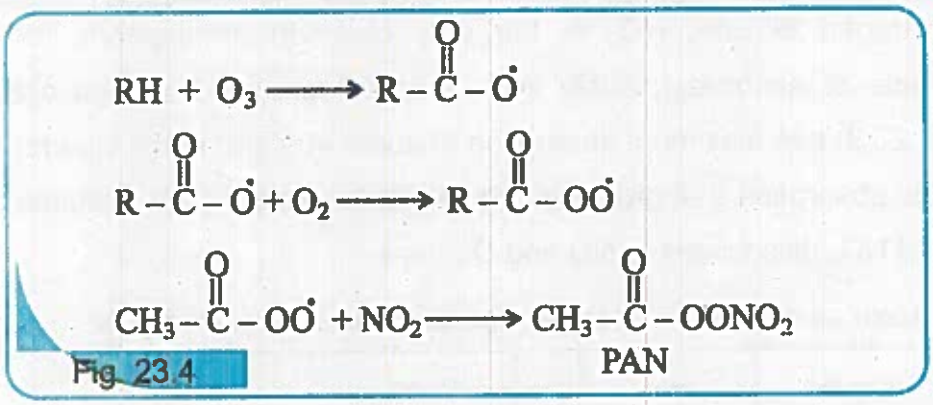


Fig. 23.4

Peroxy acetyl nitrate (PAN) formed from the peroxy acetyl radical, which is relatively common smog constituent.

Because the initiation of the cycle depends on the formation of organic radicals, the extent of smog formation depends on the reactivity of hydrocarbons (HC's) with the (O_3) radical. Some HC's produce few radicals, others many more.

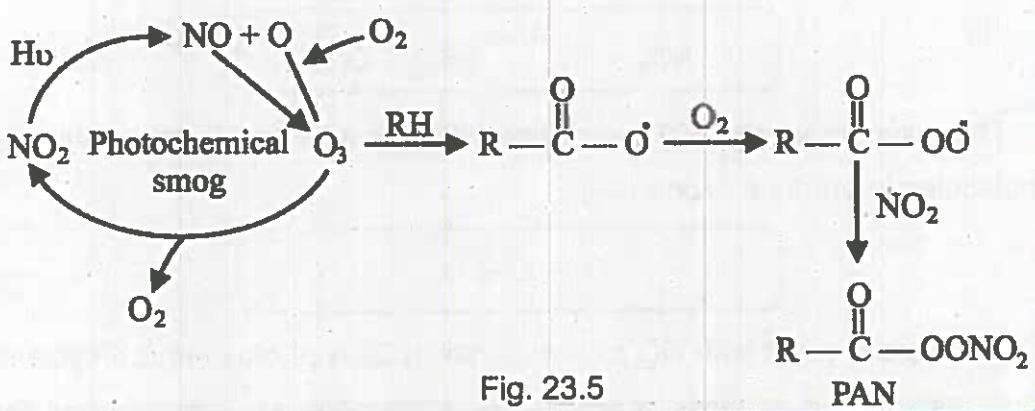


Fig. 23.5

23.1.6: Global Warming and Climate Change:

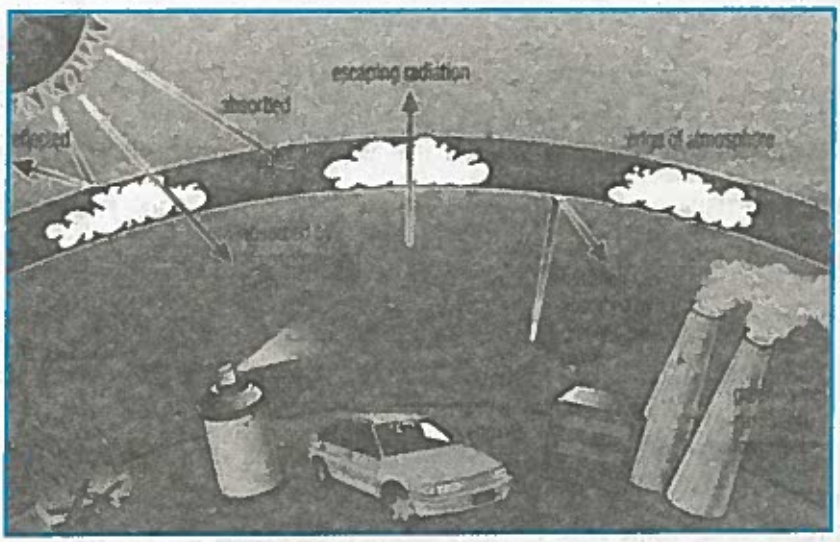
Several climatic changes are attributed to the large emissions of pollutants into the atmosphere. Generally, the global climate changes are studies from two aspects.

i. Global warming or the greenhouse effect.

ii. Destruction of the ozone layer in the stratosphere. The later will be discussed at length in "the chemistry of stratosphere" (topic 23.3).

The Green House Effect:

Scientists believe that the earth maintains its long-term average temperature as a result of a balance between the heat received from the sun and the heat emitted to space by the earth. The sun like a high-temperature electric light bulb, emits ultraviolet (U.V) and visible radiation. The earth like a cool radiant heater, emits mostly infrared (IR) radiation.



(Fig. 23.6).

Carbon dioxide gas is colourless and, like all the other colourless matter, it does not absorb visible radiation. Consequently it doesn't absorb much of the sunlight, which is mostly in the visible region, that penetrates the outer atmosphere. However, atmosphere richer in CO_2 would capture a larger proportion of the radiation being emitted by the earth's surface. As a result

the temperature of the atmosphere and of the earth's surface would gradually increase. Like the glass, in a green house, CO_2 lets sunlight enter, but prevents the I.R radiation from escaping.

The increase in the temperature of the earth's surface that is expected to result from an increase in CO_2 in the atmosphere is said to be a "green house effect". The major gas contributing 50% to green house effect is CO_2. Other gases (CH_4, CFC's, SO_2, and NOx) together contribute the rest of 50%.

Human activities are increasing the atmospheric concentration of CO_2 and other green house gases, thereby altering the way the sun's heat is distributed on the earth's surface and in the atmosphere. In addition, the stratospheric ozone shield, which protects us from the sun's U.V radiation, is threatened by the emission of ozone destroying chemicals. The earth's average temperature is being increased (global warming) which ultimately changes our climates. Human health will also be affected due to spread of infectious diseases, such as yellow fever, dengue and malaria. The most serious outcome would be rise in sea level, floods and pattern of rain fall.

23.1.7 Acid Rain:

The concept of acid rain is also associated with polluted air. The term acid rain is referred to all precipitation (rain, dew and snow) which is more acidic then natural water with pH = 7.0. Rain water is generally, slightly acidic (pH = 5.6). it is due to the varying amounts of the dissolved CO_2 which is a common constituent (0.036%) of the earth's atmosphere.

$$H_2O + CO_2 \rightarrow H_2CO_3$$

Carbonic acid

Therefore, any precipitation having a pH of less than 5.6, would be classified as acid rain. To the acidifying effect of CO_2, must be added the contribution other than acidic constituents of the atmosphere, particularly HNO_3 and H_2SO_4. These acids can both be formed naturally. HNO_3 derives from NO produced in lightening and forest fires, while H_2SO_4 derives from volcanoes and from biogenic sulphur compounds. The oxides of nitrogen and sulphur emitted within the atmosphere react with the moisture in the air or rain water to form nitric acid and sulphuric acid.

$$4NO_2 + 2H_2O + O_2 \rightarrow 4HNO_3$$

$$SO_2 + H_2O + \frac{1}{2}O_2 \rightarrow H_2SO_4$$

In polluted areas, the concentrations of these acids can be much higher and can reduce the pH of rain water substantially over extended regions, producing what is known as "acid rain". Acid rain can fall quite far from the sources of pollution, due to long-range atmospheric transport. In particular, acid rain is a serious problem for areas down-wind of coal-fired power plants.

Acid rain, on one hand, is a serious threat to the human life as it contaminates the drinking water and on the other hand is a pressing problem for plants, animals aquatic life and building material. Heavy metals e.g. Cu, Hg and Pb are also dissolved by acid rain producing various toxic effect.

Acidic streams and lakes or rivers affects the aquatic life. High acidity may result in killing of fish, reduces their growth and causes their reproductive failure. Hatching of fish eggs is prevented due to change in pH of water. Moreover, green algae and many forms of beneficial bacteria, which are essential to aquatic life, are also killed as a result of acidity in water. Plant growth is seriously inhibited due to acid rain. In addition, the acid rain also corrodes buildings monuments, statues and metals.

$$CaCO_{3(s)} + H_2SO_{4(aq)} \rightarrow CaSO_{4(ppt)} + CO_2 + H_2O$$

23.2: CHEMISTRY OF THE STRATOSPHERE:

As mentioned earlier in this chapter (Table 23.1) stratosphere is the part of atmosphere which extends from 11-50 km. The temperature of the stratosphere ranges from -56^0C to -2^0C. The important chemical species that exists in this sphere is ozone (O_3), which acts as a protective shield (layer) for the survival of life on the earth from the harmful effects of sun's U.V radiation. The temperature of this sphere increases with increasing altitude.

Production and Distruction of Ozone:

The formation of ozone requires both oxygen atoms and oxygen molecules. Ozone is formed in the stratosphere when O_2 molecules absorb solar energy (radiation). The U.V photons of the sun have enough energy to split O_2 molecules into oxygen atoms high in the atmosphere.

$$\lambda < 242nm$$

$$O_2 + h\upsilon \rightarrow 2O$$

(The symbol "hυ" is used for photon and $\lambda < 242nm$ indicates the wave length range in which photons can induce the reaction).

The oxygen atoms produced in the reaction, then combine with oxygen molecules to form ozone.

$$O + O_2 \rightarrow O_3$$

In the atmosphere ozone layer occurs as a band at intermediate altitudes, between 25 and 30 km. At low altitudes, there are ample oxygen molecules but few unattached oxygen atoms. At high altitudes free oxygen atoms are more prevalent but there are few oxygen molecules. Conditions most suitable for ozone formation are found at intermediate altitudes, where both oxygen molecules and free oxygen atoms are present.

Ozone is also destroyed by solar radiation. When O_3 absorbs a solar U.V photons it dissociates into O_2 and O.

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

Also when O_3 encounters a free oxygen atom (O), the two can combine to form two O_2 molecules.

$$O_3 + O \rightarrow 2O_2$$

The concentration of O_3 depends on the relative rates of the formation and destruction reactions.

Depletion of Ozone layer

Certain man-made organic compounds such as chlorofluro carbons, CFC's (Freon) and the bromine-containing halons are used for many purposes. CFC's have been widely used as refrigerants, blowing agents for plastic foams, propellants for aerosol sprays and solvents for cleansing

micro electronic components. The halons have used as fire extinguishers. The heavy bromine-containing molecules provide a blanket of the gas that effectively smothers flames. The CFC's and halons have been enormously useful in these applications because they are nontoxic and nonflammable. Moreover they are not subject to oxidation, either in flame or biochemical. CFC's and halons are, therefore, not destroyed in the troposphere when released. They are only destroyed in the stratosphere by the action of U.V photons. The result of absorbing U.V photons is to break the weakest bond in the molecules either C – Cl or C-Br.

$$RX + h\upsilon \rightarrow R + X$$

Once released, chlorine and bromine destroy ozone via the following reactions.

$$X + O_3 \rightarrow XO + O_2$$
$$XO + O \rightarrow X + O_2$$
$$or\ O_3 + O \rightarrow 2O_2$$

Scientists have noted a big hole in the ozone layer due to ozone depletion over Antarctica, for which they believe the CFC's are mostly responsible. Others have put a great deal of effort to find substitutes for CFC's. The main strategy has been to explore the suitability of hydro chlorofluro carbons (HCFC's) and hydrofluoric carbons (HFC's). These molecules have hydrogen as well as chlorine and fluorine substitutions on the carbon. The presence of C-H bonds allows the HCFC's and HFC's to be attacked by the OH radicals and thereby destroyed in the troposphere. At the same time the Cl and/or F substituent's lend these chemicals some of the desirable properties of CFC's, such as low reactivity and fire suppression, good insulating and solvent characteristics and boiling points suitable for use in refrigerator.

Society, Technology and Science

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.

CFCs play a major role in ozone depletion. However, the atmospheric impacts of CFCs are not limited to its role as an active ozone reducer. This anthropogenic compound is also a greenhouse gas, with a much higher potential to enhance the greenhouse effect than CO_2.

Smog is a kind of air pollution. Classic smog results from large amounts of coal burning in an area caused by a mixture of smoke and sulfur dioxide. Modern smog does not usually come from coal but from vehicular and industrial emissions that are acted on in the atmosphere by ultraviolet light from the sun to form secondary pollutants that also combine with the primary emissions to form photochemical smog.

The effect of radiation pollution can include increase risk of developing cancer. Such as lung cancer, skin cancer and thyroid cancer etc and skin burns, genetic changes mutation, change in physical characteristics in animals and human.

The water is purified naturally by distillations, sand filtration, charcoal filtration, reverse osmosis and also by ultraviolet light.

23.3: Water Pollution and Water Treatment:

The quality of surface and ground water is of great concern from two but distinct points of view:

1)Human health and welfare

2)Aquatic ecosystem.

Although most of the water is returned to the stream flow, yet its quality is inevitably degraded. Industrial and mining activities contaminate water with a variety of toxic materials. Agriculture can foul surface and ground waters with excess nutrients and can lead to salinization of soil when irrigation water evaporates, leaving salts behind. The cooling of power plants by circulating water raises the temperature (thermal pollution), with adverse effects on the biota of the receiving waters. Discharge of sewage from homes and commercial establishments, reduces the dissolved oxygen contents, again upsetting the biological balance of surface waters.

All such activities and many more, make water unfit for drinking and public use. Such water is said to be polluted water which needs treatment before it is made fit for public use.

23.3.1 Types of Water Pollutants:

Water that we either use or discard generally contains the following categories of undesirable substances (pollutants).

23.3.1.1 Suspended Solids and Sediments:

Two sub-categories of the undissolved solid material present in water can be recognized. One consists of particles large enough to be

removed by running the water through a filter paper or any other filtering apparatus. The second, consists of particles so small that they can not be removed by such treatments. Those in the second category are called colloids, which are too small to be seen, even with a microscope. They can, however, be detected, because they give water a turbid or cloudy appearance. They are most easily detected by passing a beam of light through the water and observing the scattering of light they produce like a beam of light passing through smoky or foggy air.

23.3.1.2 Dissolved Solids:

The dissolved solid material, present in water, may either be organic or inorganic. The dissolved organic compounds, acting as impurities, enter into water as a result of the growth and the death of aquatic plants, such as algae. Others are contributed by sewage from domestic sewage systems and by industrial wastes. The total amount of organic substances can be estimated from the amount of oxygen or any other chemical (oxidizing agent) needed to oxidize these substances to CO_2 and H_2O.

The dissolved inorganic materials present in water are mostly salts. These on one hand, are essential for human body, but on the other hand, if their concentrations are greater than about 500 ppm, they make water unfit for drinking, and such water is considered to be polluted. The most common salts present in water are carbonates, bicarbonates, sulphates and sulphides of calcium and magnesium. Hardness of water depends primarily on the Ca^{+2} and Mg^{+2} ion contents.

Source of Water Pollution:

Industrial effluents, domestic consumption and agricultural wastes contaminate the surface and ground waters making it unfit for drinking.

Industrial Effluents:

Industries like paper industry, metal industry and petrochemical industries discharge pollutants such as non-degradable organic substances, metals, mineral oils, benzene, toluene, xylene and phenols etc, which contaminate water. Textile industries, tanneries and slaughter houses also contribute towards water pollution. Metals that are released by various industries to pollute water, mainly include arsenic, mercury, lead and cadmium.

a) Smelting of gold, lead, copper, iron and nickel ores can be a source of arsenic pollution. Arsenic in drinking water is a slow poison. It decolorizes the skin (keratoses) which leads to cancer.

b) Mercury's toxicity is associated with almost entirely with eating fish. Sulphate reducing bacteria in sediments generate methyl mercury and release it into the water above, where it is absorbed by fish from the waters passing across their gills or from their food supply. The poisoning of mercury causes numbness of limbs, blurring and even loss of vision and loss of hearing and muscle coordination.

c) Leaded paints, leaded gasoline and lead solder (to seal food and drinks in cans) are the main sources of lead pollution. Lead poisons many thousands of people yearly. Once absorbed in the body, lead enters the blood stream and moves from there to soft tissues.

Higher exposures produce anemia. It also inhibits the enzymes involved in the biosynthesis of haemoglobin.

d) Cadmium inputs to soils and ultimately to surface waters, are mainly from airborne deposition (wet plus dry) and from commercial phosphate fertilizers which contain cadmium as a natural constituent of phosphate ore. Chronic exposure to cadmium causes heart and lung diseases (including lung cancer at high levels), immune system suppression and liver and kidney diseases.

- **Domestic Activities:**

Domestic water contains mainly soaps and detergents. Phosphates, used in the detergent formulation, affects the water quality. Likewise the use of synthetic washing powder has a drastic effect on fresh water, when domestic sewers are discharged into river. In general the domestic pollutants, make water turbid, increase the growth of pathogen causing diseases, impart bad and foul smell to fresh water (eutrophication) and may affect the aquatic life by screening off the sun's light due to the presence of suspended matter.

- **Agricultural Wastes:**

Agricultural areas can have water problems associated with the wide spread application of fertilizers, herbicides and pesticides. Drainage from poultry farms creates an extremely high potential for water pollution. Some herbicides and pesticides can accumulate in the ground water, occasionally threatening farm wells. Fertilizers, used by farmers to increase their yield, can increase the level of nitrate ions in the ground water. The main nitrate hazard is "blue baby syndrome", a condition of respiratory failure in babies having excessive nitrate in their diet.

23.3.1.3 Thermal Pollution

The heavy machinery and power plants get heated when frequently and continuously used for making various industrial products. Some parts of the plants are heated due to friction when they are in contact with each other while manufacturing the industrial products. For high efficiency and to elongate their life time, these parts (components) must be cooled. This is done with cold water. The cooling of power plants and other machinery by circulating water, raises the temperature of the water. This is called "thermal pollution".

Thermal pollution has adverse effects on the biota of the receiving waters. The high-temperature water, when mixed with cold water, increases the solubility of many pollutants (organic and inorganic), salts, ions, causing the water to be more easily polluted, thus affecting the quality of water and make it unfit for drinking and public use.

- **Parameters of Water Analysis:**

Drinking water should qualify the following qualities or parameters. That is it should be.

1. Odorless tasteless and colourless.
2. Free from turbidity causing agents such as suspended solids, dissolved solids, excess of chlorides, sulphates, phosphates etc.
3. Turbidity, not more than 10 ppm.
4. Free from bacteria causing diseases.
5. Slightly alkaline (pH = 7.0 – 8.5).

Water quality is consistently monitored. Many water quality parameters are used to decide weather or not, the given sample of water is fit for drinking. These include the biological oxygen demand (BOD) and

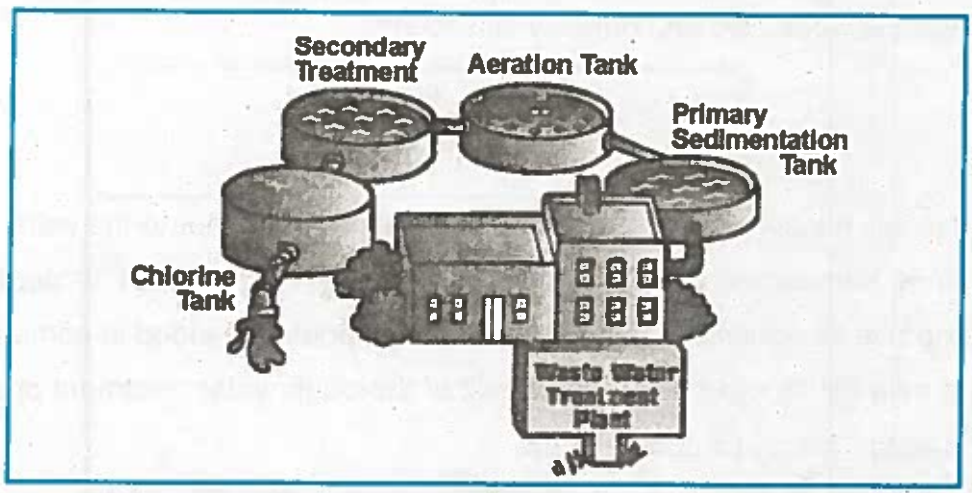
chemical oxygen demand (COD). In BOD, the amount of dissolved oxygen is determined by adding bacteria to the water while in COD it is done by adding chemical oxidizing agents, to the water.

Other parameters, used to check the quality of water, include the determination of total organic carbon (TOC), total dissolved solids (TDS), total suspended solids (TSS), pH and alkalinity, colour and odour etc.

23.3.2 Waste Water Treatment:

Water from a lake or river, that must meet the qualities of drinking water, undergoes a purifying treatment, involving several steps.

1. First, the undissolved (floating and visible) solid materials, if present in water, are removed. Coarse objects are removed by running the water through screens/filters.



2. The finer, colloidal particles that make water turbid, can not be removed by simple filtration. So a flocculating agent that is a substance that forms large gelatinous particles, is added. The

common flocculating agent is aluminium sulphate, $Al_2(SO_4)_3$, often referred to as alum, some lime, $Ca(OH)_2$, is generally also added so that precipitate of aluminium hydroxide, $Al(OH)_3$ which has the desired gelatinous form, is produced.

$$Al_2(SO_4)_3 + 3Ca(OH)_2 \rightarrow 2Al(OH)_{3\,ppt} + 2CaSO_4$$

This precipitate traps both inorganic solid particles and bacteria in the large curd like particles. These particles are then easily removed by filtration through a sand-bed or charcoal.

3. After filtration through the sand-bed, the water is usually treated with chlorine to kill remaining bacteria and other microbes. Chlorination is the widely used method to disinfect water for longer duration of time. The reactions involved are;

$$H_2O + Cl_2 \rightarrow H^+ + Cl^- + HOCl$$

HOCl is weak acid and partially dissociates.

$$HOCl \rightarrow H^+ + OCl^-$$
$$HOCl \rightarrow [O] + HCl$$

It is this nascent oxygen, [O], that gives taste and odour to the water. Thus air is sometimes blown through the water, i.e. the water is aerated to improve its odour and taste. A fluoride compound is added in some plants, to help fight tooth decay. The result of thorough water treatment operation is water, that is as good as new.

23.4 Green Chemistry:

The concept of green chemistry was coined by Paul Anestas of America. He enunciated twelve principles of Green chemistry in 1994

towards ideal synthetic methods to save natural resources. Green Chemistry is the use of chemistry for pollution prevention by environmentally conscious design of chemical products and processes that reduce or eliminate the use or generation of hazardous substances. Green chemistry, also called sustainable chemistry, is a philosophy of chemical research and engineering that minimizes the use and generation of hazardous substances.

Goals of Green Chemistry:

The goal of "Green Chemistry" perspective include the following:

1. To reduce adverse environmental impacts by appropriate and innovative choice of materials and their chemical transformations.
2. Develop processes based on renewable (plant-based) rather than non-renewable (fossil carbon-derived) raw materials.
3. To develop processes that are less prone to obnoxious chemical releases, fires and explosions.
4. To minimize byproducts in chemical transformations through redesign of reactions and reaction sequences. In other words, to achieve better "Atom economy".

$$\% \text{ Atom economy} = \frac{\text{Formula weight of the product}}{\text{sum of the formula weights of all the reactants}} \times 100$$

(Good atom economy means most of the atoms of the reactants are incorporated in the desired products and only small amounts of unwanted byproducts are formed and hence lesser problems of waste disposal or waste treatment).

5. To develop products that are less toxic or which require less toxic raw materials/feed stocks.
6. To develop products that degrade more readily in environment than the current products.
7. To reduce the requirements for hazardous or environmentally persistent solvents and extractants in chemical processes.
8. To improve energy efficiency by developing low temperature and low pressure processes by using new/improved catalysts.
9. To develop efficient and reliable methods to monitor processes (e.g. monitoring reactions and releases) for improved control.

Key Points:

- Environmental chemistry is the branch of chemistry which deals with chemical and biochemical occurrence in nature.
- Pollutant is any substance which contaminate our environment.
- Atmosphere is a big tank of gases, surrounding the earth's surface.
- The term acid rain is referred to all precipitation (rain, snow or dew) which is more acidic than natural water (pH = 7.0).
- Smog is the combination of smoke and fog.
- Water is an important natural resource on this planet.
- An important aspect of water quality is the amount of dissolved oxygen in it.
- The term green chemistry is defined as the invention, design and application of chemical product and process to reduce or to eliminate the use and generation of hazardous substances.
- The smog consisting of high concentration of photochemical oxidants is known as photochemical or oxidizing smog.
- Increased concentration of CO_2 increase the earth's temperature, by greenhouse effect. This in turn result in climate changes and global warming.

Exercise

1. Which one of the following is not a secondary pollutant?

a) Ozone b) H_2CO_3

c) H_2SO_4 d) CO_2

2. Pollutants have adverse effect over

a) Biosphere b) ecosystem

c) Hydrosphere d) All

3. Ozone layer in upper atmosphere is being destroyed by.

a) Chlorofluoro Carbons b) SO_2

c) Smog d) Photochemical Oxidant.

4. Drained sewage has B.O.D.

a) More than that of water b) Less than that of water

c) Equal to that of water d) Non of above

5. Photochemical smog is primarily caused by

a) CO b) CO_2

c) O_3 d) NO_2

6. Result of ozone hole is

a) Acid rain b) Global warming

c) Increased amount of CO_2 d) Greater exposure of earth to U.V

7. Which one of following substances is not present in acid rain?

a) H_2SO_4 b) HNO_3

c) H_2SO_3 d) CH_3COOH

8. Photochemical oxidant PAN is formed by

a) The action of oxide of nitrogen on hydrocarbons in presence if sunlight.

b) Action of carbon dioxide on hydrocarbon in presence of sunlight

c) Action of hydrogen sulphide on hydro carbon in presence of sunlight

d) Action of SO_2 and hydro carbons.

9. Which compound is base for corrosion resistance paints

a) White lead b) Red lead

c) Lead chromate d) All of these

10. The temperature (C°) range of troposphere is

a) 15 to -56 b) 56 to -2

c) -2 to -92 d) -92 to 1200

Short Questions:

1. Why is acid rain considered as a threat to historical monuments?

2. Define the following

a) Contaminants b) Pollutant

c) Eutrophication d) Acid rain

f) B.O.D g) Smog

3. What is importance of dissolved oxygen in water?

4. What methods are employed for control of SO_2 pollution?

5. What are applications of Green Chemistry?

6. Name four major greenhouse gases.

7. Out of CFC's and CO_2 which one has higher potential to cause global warming and why?
8. Why does the rain water normally have pH of about 5.6? When does it become acid rain?

Long Questions:

1. 'Green Chemistry is a new route to the protection of environment'. Comment on it.
2. What is greenhouse effect? How is it causing global warming?
3. What is meant by atmosphere? Explain the various layers of atmosphere.
4. Define air pollutant and discuss its effect.
5. A) What is role of ozone layer in upper atmosphere?
   B) What will happen if ozone is no more present in upper atmosphere?
6. What is water pollution? What are the main sources of water pollution?
7. Write note on the following.

a) Acid rain b) Smog
c) Water treatment d) Chemistry of stratosphere