Chapter

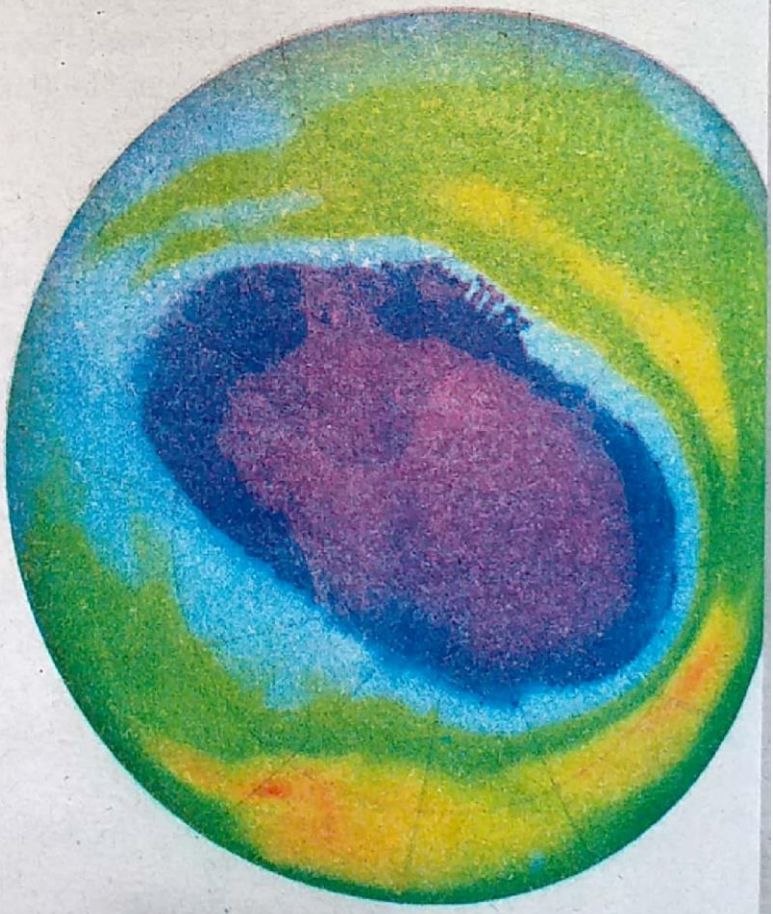
14

Environmental Chemistry I

(The Atmosphere)

In this chapter you will be able to:

- Define atmosphere.
- Explain composition of atmosphere.
- Differentiate between stratosphere and troposphere.
- Summarize the components of stratosphere and troposphere.
- Describe major air pollutants.
- Describe sources and effects of air pollutants.
- Explain ozone formation.
- Describe acid rain and its effects.
- Describe ozone depletion and its effects.
- Describe global warming.



Introduction

Approximately 4.5 billion years ago, the earth at the time of its formation was a hot mass which could not sustain life. With the passage of time it cooled gradually and due to the condensation of steam into water, the formation of atmospheric gases and ozone layer in the atmosphere (stratosphere) made the earth suitable for life.

The branch of chemistry which deals with the study of environment and the changes occurring in it, is termed as environmental chemistry.

The environment is composed of

a = Lithosphere b = Hydrosphere

c = Biosphere d = Atmosphere

Atmosphere

Atmosphere is the protective blanket of the air around the earth surface. It is a mixture of different gases like N_2, O_2, CO_2, Ar etc.

14.1 Composition of atmosphere

The atmosphere is very important segment of the environment because it is responsible for sustaining the life on earth as it absorbs the dangerous cosmic and uv (Ultra-violet) radiations coming from the sun. The major constituents of atmosphere are N_2 and O_2. Its minor constituents are CO_2 and Ar (Argon) and some trace gases.

The mass of atmosphere is approximately 4.5 to 5×10^{15} metric tones. The temperature and pressure of atmosphere changes with the increase in altitude. The temperature ranges from $-92°C$ to $1200°C$. The pressure of atmosphere at the sea level is 1 atm but at high altitude (about 100 km) above the sea level it decreases to 3×10^{-7} atm, the density of atmosphere is 0.0013 g/cm^3, which gradually decreases with altitude.

14.2 Layers of Atmosphere

The total height of atmosphere from the earth surface is about 500 km.

Atmosphere can be divided on several basis but the most important division is on the basis of temperature and density. The atmosphere can be divided into the

following four layers or zones.

1. Troposphere.
2. Stratosphere.
3. Mesosphere.
4. Thermosphere.

14.2.1 Troposphere:

It is the lowest layer of atmosphere which is close to the earth surface. The average height of this layer from the earth surface is about 11 km. Its height depends upon the latitudes, seasons and pressure.

At equator its height from the earth surface is 16 km and at $45°$ Latitude is 9.65 km while its average height from the earth surface is 10 to 11 km. The change in temperature of atmosphere with increase with height is called "Lapse rate". If the temperature decrease with height, it is called "negative lapse rate" while temperature increase with height is called "positive lapse rate".

The change from positive lapse rate to negative lapse rate" at the troposphere is called "temperature inversion".

Most of the weather phenomena takes place in troposphere. The cloud formation also takes place at the top of troposphere.

The temperature range is from 60 to $-56°C$.

Major components of troposphere are N_2, O_2, CO_2 and H_2O vapours. It constitutes about 70% of the atmosphere.

14.2.2 Stratosphere:

It is the second layer of atmosphere which is above the troposphere. The stratosphere extends from 11 km to 50 km $(39\,km)$. The major component of stratosphere is ozone "O_3". Therefore, it is also called "ozonosphere"

The concentration of ozone increases with the increase of height and is maximum at 30 km. The stratosphere shows positive lapse rate because the temperature increases from $-56°C$ to $-2°C$ with height. The increase in temperature is due to the presence of ozone which absorbs the uv –radiations of the sun.

The stratosphere absorbs uv radiations, thus protecting living organisms on earth surface from harmful effects of the uv radiations.

14.2.3 Mesosphere:

The third layer of atmosphere above stratosphere is called mesosphere. Its height is from 50 km to 85 km. The major components of this region are O_3^+ and NO^+.

The decrease in temperature from $-2°C$ to $-92°C$ with increasing height is due to low level of U.V absorbing species like O_3.

14.2.4 Thermosphere:

The fourth zone of atmosphere just above mesosphere is thermosphere. This layer ranges from 85 to 500 km. The temperature increases from $-92°C$ to $1200°C$ with increase in height and shows positive lapse rate. The increase in temperature is due to the absorption of uv –radiations by different gases. After absorption of radiations, they undergo ionization process.

$$O_2 \xrightarrow{h\upsilon} O_2^+ + e^-$$

The important components of thermosphere are O_2^+, NO^+, O^+ etc.

Due to the presence of ions, the thermosphere is also called ionosphere.

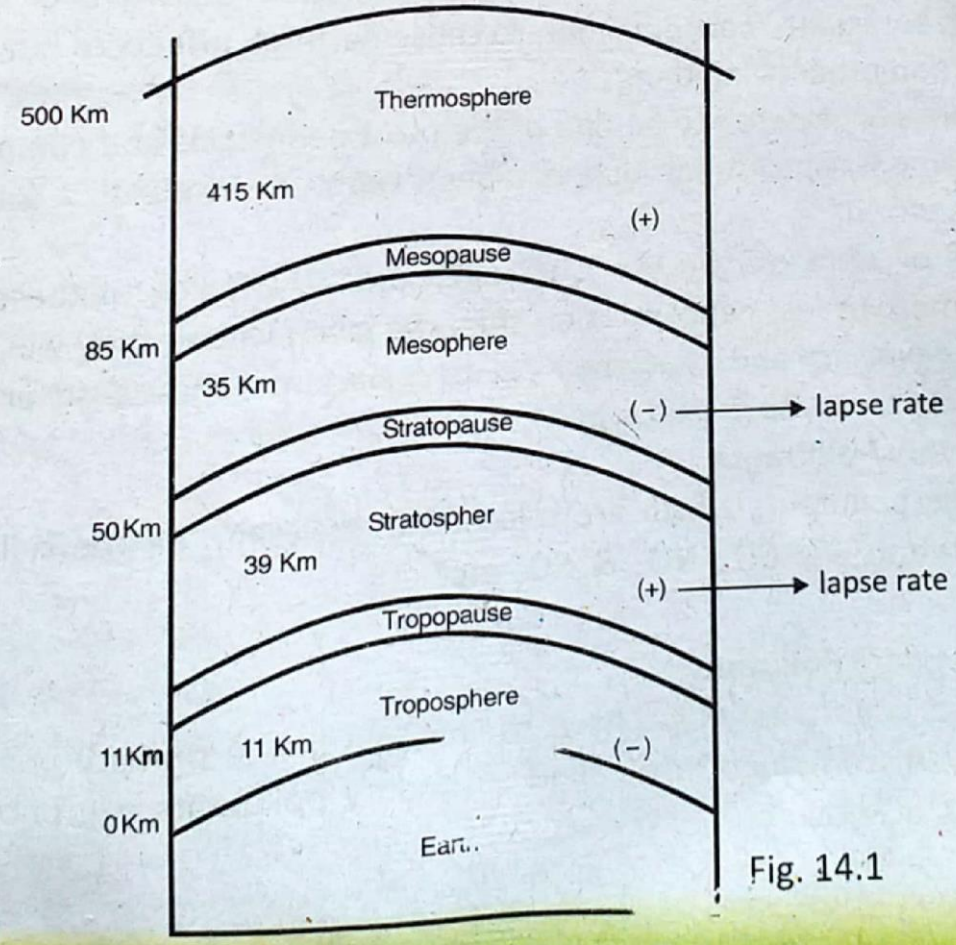


Fig. 14.1

Importance of Atmosphere

Atmosphere plays an important role for living organisms as.

1: It protects earth by absorbing dangerous cosmic rays of the sun.
2: It plays a role in maintaining the heat balance of earth by absorbing the heat radiations reemitted by earth surface.
3: Atmosphere allows visible radiations coming from the sun as a result we can see. If atmosphere did not allow the visible radiations then we would not be able to see any thing.
4: It is the main source of different gases which are important for life i.e. oxygen which is essential for life on earth. Carbon dioxide is essential for plants photosynthesis and nitrogen is also useful macro nutrient for plants.
5: Atmosphere is a vital carrier of the water from oceans to land which is very important for hydrological cycle.

14.3 Air Pollution

According to world Health organization (WHO), air pollution may be defined as.

"The substances released to air either by human activities or by natural activities, in sufficient concentration to cause harmfull effects to human beings, vegetation and other living things."

Air pollution is considered to be one of the most dangerous and common kind of the environmental pollutions that has been reported in most of the industrial parts of the world.

Air consists of 21 % oxygen, 78 % nitrogen and 0.03% CO_2. If these gases are present in more or less concentration than the given values, they will be harmful for living organisms and thus they act as pollutants and cause air pollution.

Major air pollutants are of two types.

i. **Primary Pollutants:**
Those pollutants which are released directly into air are called primary pollutants e.g. CO_2, NO_2 & SO_2 etc.

ii. **Secondary Pollutants:**
Those pollutants which have their origin in the primary pollutants and derived from them are called secondary pollutants e.g. photochemical smog ,acid rain etc.

The pollutants may be classified on the basis of state of matter.

1. Particulates: These are the small particles of liquids and solids.
2. Gaseous pollutants: The different gases present in air act as pollutants are CFC, CO, NO, NO_2, SO_2 etc.

14.3.1 Sources of Air pollution

A: Sources of Particulate Pollutants

There are two major sources for the emission of the particulate matter which are.

1. **Natural Sources:**
   The natural sources for particulate pollutants emission are volcanic eruption, soil erosion by wind, dust storms, natural forest fires and salt spray from oceans.
   The contribution of the natural sources towards the particulate emission is greater than man made sources. It has been estimated that natural sources release 800 – 2000 million tonnes of particulate matter per year in air.

2. **Anthropogenic Sources:**
   The anthropogenic or man made sources are the combustion of fuels, wood, construction, mountain blasting, mining and other industrial processes.
   It has been estimated that man made sources release 200 – 400 million tonnes of particulate matter per year.
   The most common anthropogenic source is fly ash from power plants, smelters and smoke from incomplete combustion processes.

B: Sources of Gaseous Air Pollutants:

1: Carbon monoxide

a. **Natural Sources:**
   The contribution of natural sources towards carbon monoxide (CO) emission is not much greater. The natural sources are volcanic eruptions, natural gas emission, electrical discharges during storms, seed germination and marsh gas production etc.

b. Anthropogenic Sources:

Most of the CO production results from the human activities.

It has been estimated that about 75% of CO emission results from automobiles due to internal combustion engine. Another major contributor of CO emission is the forest fires (16.9%) and agricultural burning (7.2%).

The third contributor is the iron and steel industries (9.6%). Cigarette smoke also contains fairly highly concentration of CO. Therefore, smoking is also a contributor of CO emission.

2: Oxides of Nitrogen:

Besides the free nitrogen (N_2) different oxides of nitrogen e.g. Nitrous oxide (N_2O), Nitrogen dioxide (NO_2) and nitric oxide (NO) are also present in the atmosphere.

The concentration of nitrous oxide (N_2O) is higher than the other two oxides of nitrogen.

Sources:

Both the natural and anthropogenic sources are responsible for the emission of oxides of nitrogen.

a: Natural Sources:

The natural sources for emission of oxides of nitrogen are soil, bacteria and other microorganisms. e.g. pseudomonas bacteria convert atmospheric N_2 gas into oxides of nitrogen.

It is important that the contribution of natural sources towards NO_x emission is greater than anthropogenic sources. It has been estimated that natural sources release about 5×10^8 tonnes of NO_x per year.

b: Anthropogenic Sources:

The man made sources responsible for the emission of oxides of nitrogen are automobiles, industries, furnaces, thermal power plants and the most important are the emission from jet engine aeroplanes.

3. Sulphur Oxides SO_x :

Another cause of air pollution is the presence of two colourless gaseous compound i.e. Sulphur dioxide (SO_2) and Sulphur trioxide (SO_3).

a. Natural Sources of SO_x :

The natural sources contribute more pollution of SO_x than man made sources. Out of total SO_x emission 67% is the result of natural sources.

The natural sources are volcanic eruptions, rocks weathering, sulphate spray from oceans and other biological activities. These sources emit either SO_2 or H_2S which then oxidizes to SO_2 as.

$$2H_2S + 3O_2 \longrightarrow 2SO_2 + 2H_2O$$

b. Anthropogenic Sources:

About 33% of total SO_x pollution is caused by man made sources.

The combustion of fossil fuels i.e. coal and oil is the major cause for SO_x emission because these are contaminated with sulphur. Out of 33% about 75% is contributed by these combustion processes. Other man made sources are transportation (2%,) industries (22%) and combustion of other sulphur containing compounds (1%.)

14.4 Acid Rain

Normal rain water which is slightly acidic because of dissolved CO_2 has a pH of 5.6.

During thunder storms, the PH of rain water can be much lower due to nitric acid (HNO_3) and sulphuric acid (H_2SO_4) formed by lightning.

The rain having pH less than 5.6 is called acid rain. Rain with low pH as 2.1 has been reported. This value is lower than the PH of vinegar and lemon juice.

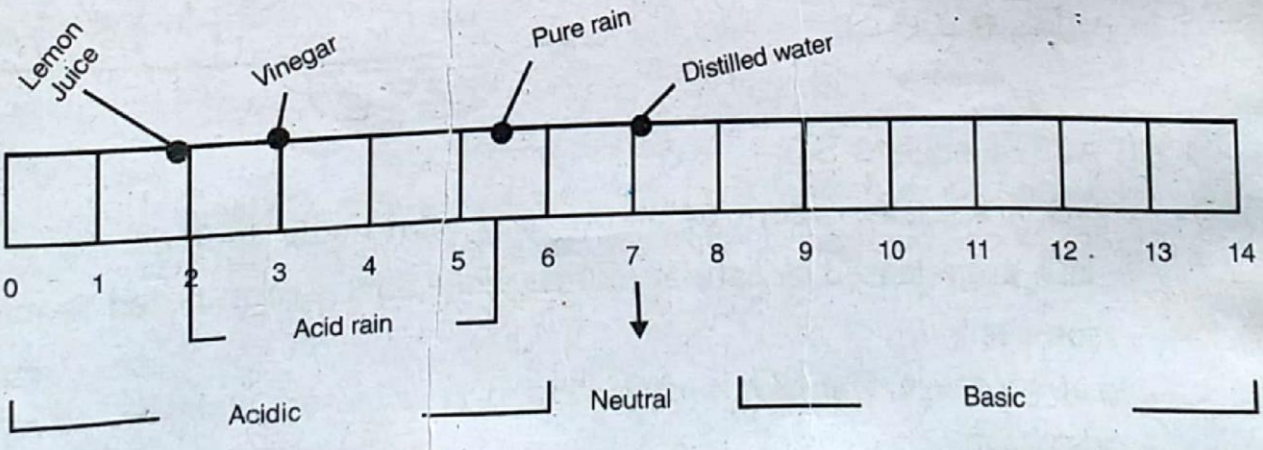


Figure: *pH of acid rain*

In common language the acid rain means the excessive acid in rain water, it is one of the adverse effects of the air pollution.

The energy sources release different pollutants in air which are then converted to different acidic compounds causing increase in acidity of the rain water.

14.4.1 Mechanism:

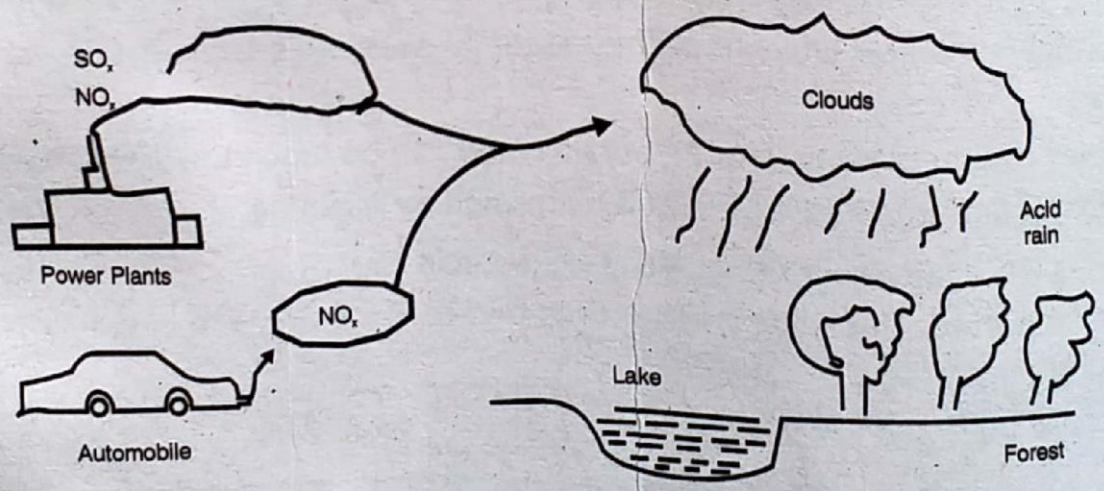
The atmosphere is always loaded with different types of the pollutants like oxides of sulphur "SO_x"oxides of Nitrogen " NO_x" and other organic compounds.

Every energy source that we use like coal, wood and oil contain sulphur (S) nitrogen (N) and other hydrocarbons. When these fuels are burnt in the air then these are converted into their respective oxides as sulphur to SO_x and nitrogen to NO_x.

These oxides are highly soluble in rain water and thus react with rain water producing different acids as

SO_x are converted to H_2SO_4 and NO_x to HNO_3

The organic compounds are oxidized to CH_3COOH.



1. Acid rain due to SO_x.

   SO_x are released both by natural and man made sources. About 67% of SO_x are released by natural sources while 33% is contributed by man made sources

   In atmosphere. The SO_2 is oxidized to SO_3.

   $$2SO_2 + O_2 \longrightarrow 2SO_3$$

The SO_3 is highly reactive and soluble in rain water producing H_2SO_4.

$$SO_3 + H_2O \longrightarrow H_2SO_4$$

2. Acid Rain Due to NO_x

The other major source of acid rain is NO_x.

About 5×10^8 tones of NO_x are released by natural sources and about 5×10^7 tones of NO_x are released by man made sources every year.

The NO_x are converted to HNO_3 as

$$NO + O_3 \xrightarrow{h\nu} NO_2 + O_2$$

$$NO_2 + O_3 \longrightarrow NO_3 + O_2$$

$$NO_2 + NO_3 \longrightarrow N_2O_5$$

$$N_2O_5 + H_2O \longrightarrow 2HNO_3$$

3. **Acid rain due to CO_2**

$$CO_2 + H_2O \longrightarrow H_2CO_3$$ carbonic acid.

14.4.2 Effects of Acid Rain

1. **On Human:**
In human, the acid rain mainly causes damage to lungs, skin and hair. The heavy metals released by acid rain may also cause potential threat to human health. Acid rain also increases the acidity of water which gives rise to "water borne diseases".

2. **On Plants:**
Plants are also damaged by acid rain. It destroys the leaves of the plants. The young plants specially the newly growing buds and tips are seriously damaged by acid rain. Thus growth of plants is affected by acid rain.

3. **On Soil:**
The acid rain leads to increase the acidity of soil and thus affects the availability of plant nutrients.

4. **On Aquatic Life:**

The aquatic life for example fishes, plants and other microorganisms are very sensitive to acidity. They are greatly damaged by acid rain e.g. H_2SO_4 and particles of Cd and Pb are deposited on the snow and when it melts, the pollutants enter the rivers and lakes. This occur at a time when fish spawing and hatching take place, thereby destroying the fish eggs.

5. **Effects on Materials:**

Acid rain causes extensive damage to buildings and sculptures as well as other things made of limestone and marbles as.

$$CaCO_3 + H_2SO_4 \longrightarrow CaSO_4 + CO_2 + H_2O$$

The $CaSO_4$ is soluble in water and washed away with rain water. The deformation of historical statues in Greece and Italy was reported to be due to acid rain. The Taj Mahal in India faces the same fate at present.

14.5 Ozone

Ozone is an allotropic form of oxygen containing three chemically bonded oxygen atoms and its molecular formula is O_3.

The word "ozone" is derived from Greek word meaning smell and the name ozone was given due to its irritating odour. Two forms of oxygen are found in the stratosphere. Molecular oxygen (O_2), which is made up of two atoms of oxygen (O), and ozone (O_3) which is made up of three oxygen atoms. Ozone is formed when intensive ultraviolet radiation from the Sun breaks down O_2 into two oxygen atoms. These highly reactive oxygen atoms can then react with more O_2 to form O_3.

$$3O_2 \xrightarrow{uv} 2O_3$$

14.5.1 Characteristics of ozone.

i. It is bluish in colour.
ii. It has a characteristic smell.
iii. It is respiratory irritant if present excess in air.
iv. Ozone is soluble in water, turpentine oil, glacial acetic acid, and carbon tetrachloride.
v. It can be liquefied at $-112 \cdot 4°C$ which has pale blue colour.
vi. Ozone causes rubber to harden and crack.

14.5.2 Occurrence of Ozone:

Ozone is an important specie present in stratosphere. In stratosphere its concentration increases with increase in height and at about 30 km it reaches to its maximum value of 10 ppm (parts per million)

Due to the presence of Ozone the stratosphere is also called ozonosphere. If all the ozone around the earth surface is condensed, it will form a layer of 2.5mm thickness on earth surface. Ozone is also found over densely populated cities but here it works as pollutant and causes respiratory irritation.

14.5.3 Ozone Depletion

The decrease in the concentration of ozone in stratosphere below its normal or natural level is termed as "ozone depletion" or The formation of hole in ozonosphere (ozone layer) is also called ozone depletion.

Ozon depletion results from the human activities as well as natural phenomena which release many pollutants and other chemical species in the atmosphere. These species react with the ozone layer in the stratosphere and decrease its concentration. The ozone layer is also destroyed by chlorine released due to volcanic activity. Chloro fluoro carbon (CFC) is the main lethal compounds which have been implicated in accelerated depletion of ozone layer. CFC originates from industrial, commercial and house hold appliances.

1. Ozone depletion due to NO_x

Three types of oxides of nitrogen are found in atmosphere e.g. NO (nitric oxide), N_2O (nitrous oxide) and NO_2 (nitrogen dioxide).

These oxides may react with ozone photochemically and cause its depletion.

$$NO \xrightarrow{h\nu} \dot{N}O$$

$$\dot{N}O + O_3 \longrightarrow NO_2 + O_2$$

2. Ozone depletion due to atomic (nascent) oxygen

The atomic oxygen as produced by the following reaction.

$$O_2 \xrightarrow{h\nu} O + O$$

This atomic oxygen is very important and consumes about 18% of the O_3 found in atmosphere.

$$O_3 + O \longrightarrow 2O_2$$

3. Ozone Depletion due to oxides of sulphur

Two types of oxides of sulphur are present in atmosphere SO_2, SO_3 out of both the oxides of sulphur, SO_2 may undergo photochemical reaction with O_3 and causes it dissociation as.

$$SO_2 \xrightarrow{h\nu} \dot{S}O_2$$

$$\dot{S}O_2 + O_3 \longrightarrow SO_3 + O_2$$

14.5.4 Adverse Effects of ozone Depletion

Both living organisms (plants and animals) as well as materials are greatly affected by ozone depletion. Some of the effects are given below.

1. Effect on Human and Animals:

Due to ozone depletion cosmic rays and uv radiations come on earth surface and cause serious problems for both human and animals.

In minor cases, these radiations cause sun burn disease but in major cases damage the skin tissues and causes skin cancer which kills about 12000 people each year in U.S.A.

It has been estimated that 1% decrease in ozone causes 5% increase of skin cancer. Similarly these radiations also cause an eye disease known as "CATARACTS". It has been estimated that 12 million people have become blind due to this disease and about 18 million have lost a part of their eye sight. It also causes pulmonary edema and even death.

Similarly, pink eye and eye cancer cases are also found in cattles when they are exposed to uv radiations by ozone depletion.

Society, Technology and Science

Many people would like to believe that waste disappears when it is burnt. In fact the burnt waste is transformed into ashes and gas. (A large incinerator produces the equivalent of 300 wheelie bins of exhaust gases from its chimneys every second). As this happens, chemical reactions lead to the formation of hundreds of new compounds, some of which are extremely toxic. The number of substances released from a waste incinerator may run into thousands. So far, scientists have identified a few hundred substances as hazardous. Incinerator plants are the source of serious toxic pollutants e.g. dioxins, furans, acid gases, particulates, heavy metals and they all need to be treated very seriously.

2. **Effect on Marine Life:**
   The cosmic and uv radiations are highly energetic. They penetrate water (about 20 m) and kill the micro organisms present there in water which are more sensitive to these radiations.

3. **Effect on Crops:**
   Ozone depletion causes an adverse effect on the production of crops. UV radiations when passes through ozone layer decrease crop production e.g. It has been estimated that 25% increase in UV radition decrease 25% soya been crop product. UV radiation also affect young tobacco and tomato crops.

4. **Effect on Materials:**
   With decrease in ozone layer, the uv radiations reaching the earth surface increase and thus reduce the life time of different commonly used synthetic materials like plastics, cotton nylon and Styrofoam etc.
   It causes rubber to harden and crack. Thus shortening the life of automobiles tyres and other rubber items.
   Due to ozone depletion, the temperature of the earth surface increases and causes "Global warming".

14.6 Global warming

The gradual increase in the average temperature of earth surface due to emission of green house gases.

Global warming is caused by increasing concentration of green house gases produced by human activities such as deforestration and burning fossil fuel. Green house gases include CO_2, CH_4, NO_2 and O_3.

These gases act like a a green house around the earth. They let the visible and ultraviolet rays from the sun into atmosphere. But does not allow the heat to escape back into space. So this entrapped heat causes global warming.

Global warming adversely affects the climate, sea level, ozone layer, crop yield, precipitation (rain and snow fall) and health.

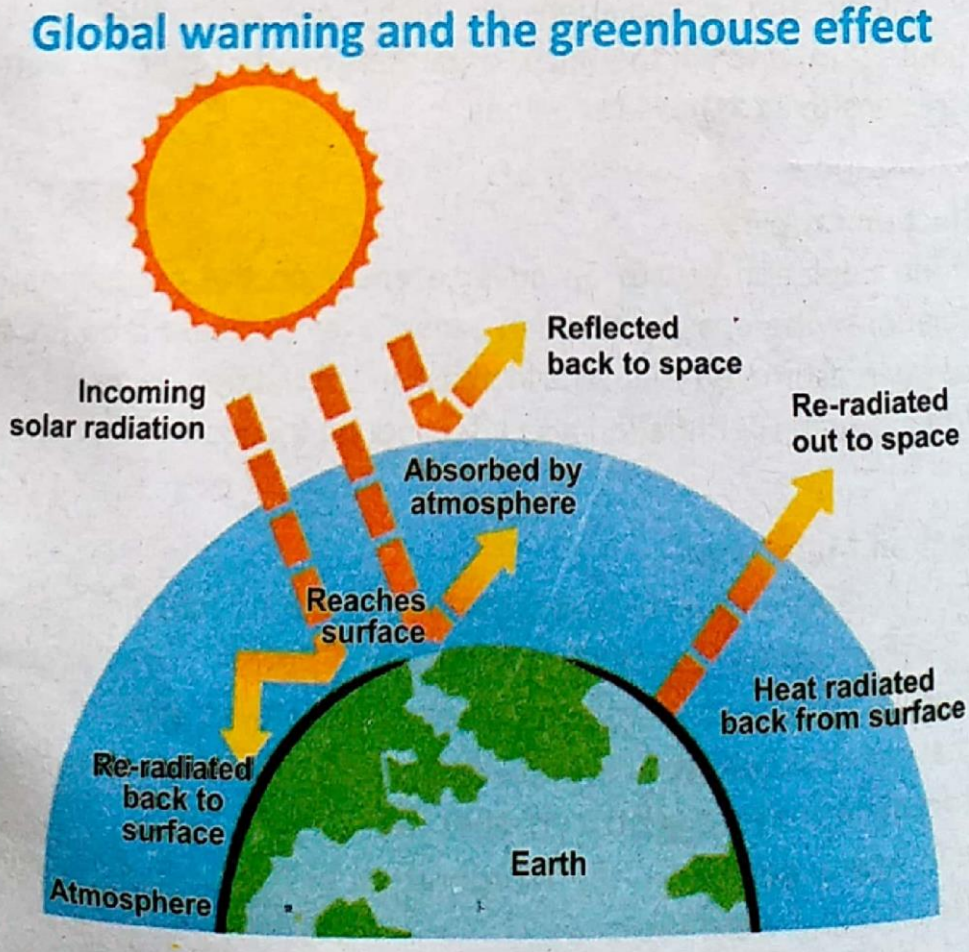


Fig. 14.3

KEY POINTS

- Approximately 4.5 billion years ago the earth was a hot mass which could not sustain life.
- The environment is composed of lithosphere, hydrosphere, biosphere and atmosphere.
- Atmosphere is the protective blanket of the air around the earth surface.
- N_2 and O_2 are major components while CO_2 and Argon are minor components of atmosphere.
- The temperature and pressure of atmosphere changes with increase in height.
- Atmosphere can be divided in four layers or zones i.e. Troposphere, Stratosphere, Mesosphere and Thermosphere.
- The substances released to air by human activities or natural activities which causes harmful affect to human or vegetable are called air pollutants.
- Pollutants are of two types. Primary pollutants and Secondary pollutants.
- Acid rain has a P^H less than 5.6.
- Ozone is an allotropic form of oxygen having molecular formula O_3.
- The formation of hole in ozone layer is called ozone depletion.

EXERCISE

Q.1 Select the suitable option.

i. The major component of troposphere is
   a. Argon b. Nitrogen
   c. Hydrogen d. Carbon

ii. The coldest region in atmosphere is
   a. Troposphere b. Stratophere
   c. Mesosphere d. Thermosphere

iii. Ozone depletion causes
   a. Blood cancer b. Skin cancer
   c. Maleria d. T.B

iv. The PH of acid rain is less than
   a. 14 b. 10
   c. 7 d. 5.6

v. Ozone is _____ gas.
   a. Greenish b. Yellowish
   c. Bluish d. Redish

Q.2 Write Short answers:

i. What is environmental chemistry.
ii. Write short note on stratosphere.
iii. Effect of acid rain on building materials.
iv. What is the importance of atmosphere.
v. List the physical properties of ozone.
iv. What are primary and secondary Air pollutants.

Q.3 Write Long answers:

i. Explain the composition and layers of atmosphere?
ii. What is air pollution explain the major sources of air pollution.
iii. What is ozone depletion? Write its mechanism.
iv. Discuss Acid rain. How does it affect environment.
v. How does ozone depletion adversely affect our life?