



Loknete Dr. Balasaheb Vikhe Patil (Padma Bhushan Awardee)
Pravara Rural Education Society
Arts, Science & Commerce College Kolhar

Atmosphere and Air Pollution

Class- T.Y.B.Sc.

Mr. A. K. Kharde
Asst. Professor Dept. of Chemistry
A. S. C College, Kolhar

Atmosphere and Air Pollution

Introduction:-

Atmosphere is the protective blanket of gases surrounding earth. Atmospheric parameters like pressure, temperature, chemical composition changes with altitude. In recent time human activities are adversely interfere with the natural phenomena in atmosphere. The role of atmosphere is to moderate earth's temperature, absorb energy and damaging U.V. radiation from the sun.

Composition of Atmosphere:-

Atmosphere is made up of three categories of component according to their abundance viz major, minor and trace.

Major components:

N_2	78.09%
O_2	20.94%
H_2O Vapour	0.1-5%

Minor component: Ar 0.934%
CO₂ 0.0325% i.e. 325 ppm

Trace components: Ne 18.2 ppm
He 5.24 ppm
CH₄ 2 ppm
Kr 1.14 ppm
O₃ 0.6 ppm
H₂ 0.5 ppm
N₂O 0.25 ppm
CO 0.12 ppm
NO₂ 0.1 ppm
Xe 0.087 ppm
NH₃ 0.01 ppm
SO₃ 0.0002 ppm

Structure of Atmosphere:-

The rate of change of temperature with increasing altitude is called lapse rate. When temperature increases with increasing altitude, the lapse rate is said to be positive. If temperature decreases with increasing altitude, the lapse rate is said to be negative. On the basis of sign of lapse rate atmosphere is divided into 4 regions, viz troposphere, stratosphere, mesosphere and thermosphere.

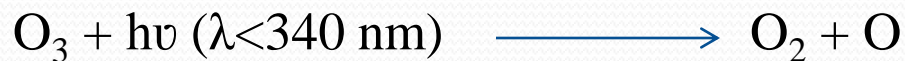
Region	Altitude (km)	Temperature (K)	Sign of lapse rate	Important chemical species
Troposphere	0-11	298-217	(-)	N_2 , O_2 , CO_2 , H_2O
Stratosphere	11-50	217-271	(+)	N_2 , O_2 , O_3 , $(NH_4)_2$, SO_4
Mesosphere	50-85	271-181	(-)	N_2 , O_2 , O_2^+ , NO^+ , N_2^+ , NO
Thermosphere	85-500	181-1473	(+)	N_2 , O_2 , O_2^+ , O^+ , NO^+ , e^- , N_2^+

1. Troposphere:-

Troposphere is the lowest region of atmosphere extending up to the altitude of 11 km. of the total mass of 5×10^{18} kg of atmosphere, troposphere contains 70%. Density decreases exponentially with increasing altitude in tropospheric region. The lapse rate in troposphere is negative. This is because the source of heat for troposphere is the earth's surface radiating I.R. light. The top layer of troposphere is cold with temperature 217 K (-56°C). It is called tropopause. Above tropopause the temperature is higher in the stratosphere. Here the negative lapse rate changes into a positive lapse rate. This is called temperature inversion.

2. Stratosphere:-

Stratosphere is the region of atmosphere ranging from 11 km to 55 km of altitude. Lapse rate in stratosphere is positive i.e. temperature increases with altitude. This is because the source of heat in stratosphere is the process of absorption of solar U.V. radiation from the sun by ozone gas.



O_3 molecule decomposes into dioxygen and atomic oxygen as a result of absorption of U.V. light. This photodecomposition of ozone is regenerated in a 3-body reaction. In this reaction the excess energy released in the formation of O_3 molecule is transferred to the third body M (N_2 or O_2). This increases the kinetic energy of the third body. This energy transfer results in temperature rise in stratosphere.



Net result is that U.V. energy from the sun is transferred into K.E. in stratosphere. Due to U.V. Absorption by O_3 , stratosphere acts as protective shield for life on earth.

3. Mesosphere:-

Mesosphere is the region between stratosphere and thermosphere. Ozone level is very low in this region. Therefore there is no U.V. absorption in this region. As a result the lapse rate is negative in mesosphere. Ionization by absorption of far U.V. occurs to some extent, making mesosphere part of ionosphere.

4. Thermosphere:-

Beyond mesosphere temperature rises with altitude giving a positive lapse rate.

Temperature reaches a value of about 1200°C . Here the atmospheric gases absorb far U.V. radiation from the sun and undergo splitting and ionization.



Chemical and Photochemical Reactions in Atmosphere:-

The present atmosphere is the result of various processes involved in the formation of earth and evolution of atmosphere. Earth is very hot when formed eventually began to cool. The gaseous components began to condense into liquids and solids. At this primitive stage of formation there was no atmosphere on earth. As the earth cooled, the physically trapped and chemically bound gases and liquids escaped through the surface by volcanic activities. Condensation of H₂O led to formation of hydrosphere. The primitive atmosphere contained reduced gases like NH₃, H₂O and CH₄. These got involved in chemical reactions for which the energy was provided by intense U.V. radiation, lightening and radiation from radionuclides.



In the second stage of evolution of atmosphere N_2 become the principal component (0.5 to 2.5 billion years of earth formation). During this period chemical evolution took place, leading to development of first living organisms. These anaerobic organisms derived their energy from fermentation processes in externally synthesized molecules. These anaerobic living forms evolved into photosynthetic organisms which synthesized food within their bodies and produced O_2 as by product.



At this stage of evolution of free O_2 was a biological poison. The O_2 produced was trapped by dissolved Fe(II) to form Fe_2O_3 deposits between 2 and 3 billion years of earth formation. O_2 was then a minor component of atmosphere as the O_2 formed during photosynthesis got utilized also for oxidation of CH_4 , H_2 , NH_3 into CO_2 , H_2O and N_2 respectively.

The 3rd stage of evolution of atmosphere (2.5 to 4 billion years of earth formation) when atmosphere was made of N₂, O₂, Ar, H₂O and CO₂. Towards the end of this stage O₃ formation occurred with absorption of U.V. by O₂.



With formation of O₃ shield, earth become more hospitable for life.

Earth's Radiation Balance:-

Earth maintain steady state having high degree of order and low entropy, with optimum climatic conditions supporting life. This is the result of radiation balance maintained on earth. Earth receives large input of solar energy. Total solar flux incident an upper atmosphere is 1340watt/m².

66% of this is absorbed by earth and is utilized in raising the temperature of land, water and air, and also for bringing about various physical, chemical and biochemical processes. 34% of the solar flux is reflected from the surface and clouds and scattered from the particles in atmosphere. This fraction of solar flux that is reflected and scattered is called albedo. It contributes significantly to the overall energy balance of earth. Solar radiation is mainly visible light ($\lambda = 300-700\text{nm}$) while the radiation given away by earth is mainly in the I.R. region ($\lambda = 10,000\text{nm}$). The process of radiation of energy by earth to outer space can be considered to have three stages, viz i) Reflection from earth surface. ii) Transmission from earth surface to cloud and iii) Radiation by clouds to outer space.

Another phenomenon called greenhouse effect has great significance in governing the heat balance of earth. The outgoing I.R. radiation given away by earth is of wavelength $2-40\ \mu$ (i.e. $2000-40000\ \text{nm}$) Part of this outgoing radiation is absorbed by certain atmospheric gases like CO_2 & H_2O vapour ($12.0-16.3\ \mu$ and $4-8\ \mu$ respectively).

Characteristics of Atmospheric Reactions:-

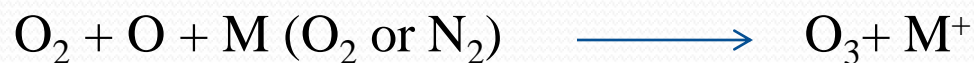
Atmospheric chemical reactions are characterized by low concentration and low partial pressures of the reacting species involved. Detection and analysis of atmospheric reactions is therefore difficult.

Another Characteristic of atmospheric reactions is that they are photochemical reactions. The chemical species involved in atmospheric reactions are exposed to light. Absorption of light by chemical species brings about reactions which otherwise would not have occurred at that temperature or without catalyst. Absorption of high energy light produces three type of reactive species like electronically excited molecules or atoms, free radicals and ionized atoms or molecules. These species initiate further reactions.

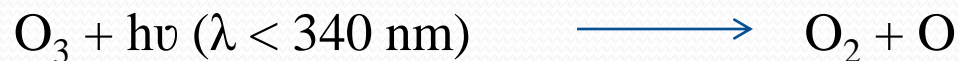
Chemistry of O₃, SO_x, NO_x, and Chlorides in atmosphere

1. Ozone Chemistry in atmosphere:- In troposphere natural abundant of O₃ is very low.

Generation of O_3 is a stage in the reaction sequence leading to formation of photochemical smog due to autoexhaust pollution. In stratosphere O_3 plays very important role of absorbing U.V. radiation and thereby saves the life on earth from this tissue damaging radiations. O_3 is formed in stratosphere in two steps, viz., photodecomposition of O_2 and three body reaction.



In the second step the third body M, either O_2 or N_2 molecule, absorbs the excess energy liberated in the O_3 formation and thereby stabilizes the O_3 molecule. O_3 strongly absorbs U.V. light with wave length less than 340 nm. As a result only a small fraction of U.V. light reaches lower atmosphere and life gets protected from severe radiation damage.



Formation of O_3 and Photodecomposition of O_3 together constitute a chain reaction in stratosphere leading to a stable concentration of O_3 . The O_3 concentration is maximum at 30 km altitude in stratosphere, where the O_3/O_2 ratio is about 10^{-6} . The chain can be interrupted by thermal decomposition.



Depletion of stratospheric ozone is found to have occurred due to human activities. The phenomenon is described as ozone hole. Chlorofluorocarbon chemical mainly responsible for ozone hole.

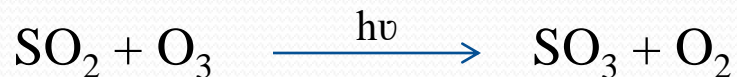
2. SO_x Chemistry in atmosphere:-

Source:- SO_x, oxides of sulphur include SO₂ and SO₃. Naturally SO₂ exists in atmosphere in trace amount (0.2 ppb). Natural source of SO₂ are i) Volcanic activity which directly introduces SO₂ in air. ii) Anaerobic decay of dead organic residues which release H₂S into atmosphere which in turn gets oxidised to SO₂.



Catalysis by aerosol particles is required for oxidation with O_3 in troposphere.

SO_2 may be oxidised by O , O_2 and O_3 to SO_3 as follows.



Reactions:- Oxidation of SO_2 with O_2 catalysed by particulate matter is the most important pathway for gas phase reaction of SO_2 .



Both SO_2 and SO_3 react with water to form sulphurous and sulphuric acid. The sulphurous acid gets oxidised rapidly, particularly in presence of metal salt particles which serve to nucleate raindrops.



Sink:- Once H_2SO_4 is formed it may react with ammonia or metal salts to produce sulphates.



SO_2 itself also forms sulphate rapidly in presence of NH_3 and moist air.



Sulphuric acid and sulphate then precipitate with rain.

Chemistry of Nitrogen oxides in Atmosphere:-

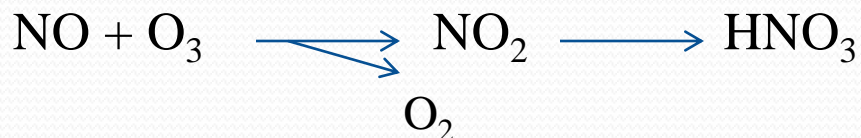
i) Nitrous Oxide (N₂O):-

Sources: Denitrifying bacteria release N₂O into atmosphere. N₂O is uniformly distributed over globe. In unpolluted air N₂O level is 0.25 ppm.

Reactions: Residence time of N₂O in atmosphere is 10 years. In stratosphere it decomposes photochemically into NO.



Sink: The sink for N₂O in stratosphere is conversion into nitrous and nitric acid, which rain down to earth.



ii) Nitric Oxide (NO) & Nitrogen Dioxide (NO₂):-

Source: NO and NO₂ together are referred to as NO_x. Natural bacterial action discharges about 5×10^3 tonnes of NO_x mainly in the form of NO, every year all over the world.

Reactions: The average residence time of NO is 4 days and that of NO₂ is 3 days in atmosphere. NO_x react readily in the atmosphere and reaction initiated by sunlight.



Sink: NO_x in atmosphere finally end up as HNO₃, nitrates or organic nitrogen compounds. Many source and sinks of NO_x in troposphere are yet to be identified.





Man made sources release 5×10^7 tonnes of NO_x annually which is 10^4 times more than natural discharge.

iii) Chlorine Chemistry in Atmosphere:-

Sources: Volcanoes inject Cl_2 and HCl directly into stratosphere. Both of them generate chlorine atoms in that region.



Reactions: Cl atoms catalyse the removal of O_3 in stratosphere as shown below.



Chlorofluorocarbons are the man made chemicals that are found to be another source of Cl in stratosphere.

Air Pollution:- Natural processes like forest fire, volcanic eruptions, microbiological process, ocean sprays contribute towards natural air pollution which is beyond the control of human beings. Burning of fuels, various industrial, chemical, biological processes and space research activities which are man made pollutants.

Definition of Atmospheric Pollution:-

Weber in 1982 has defined atmospheric pollution as, “ The presence of substances in the ambient atmosphere, resulting from the activity of man or from natural process causing adverse effect to man and environment.”

Primary Air Pollutants:- Some Primary air pollutants are.

- i) Carbon monoxide, CO
- ii) Nitrogen oxides, NO_x
- iii) Sulphur oxides, SO_x
- iv) Hydrocarbons, HC
- v) Particulates SPM or TSP

1) Carbon monoxide:- Carbon monoxide is tasteless, colourless, odourless gas which is heavier than air and has low solubility in water.

Source: Natural gas emission, marsh gas oxidation, electrical discharge during storms, volcanic eruptions, seed germination, seedling growth are some geophysical and biological processes which are the natural sources of CO.

Some Sources of CO are.

- i) Transportation:- It contribute 64% through automobiles, air craft and rail roads.
- ii) Industrial Processes:- Petroleum, Paper, iron and steel, chemical industries contribute 10%.

Sink:- There are large natural sink.



Some Chemical Process involved in CO formation.

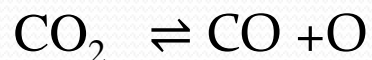
i) Incomplete Combustion:-



ii) Reduction of CO_2 :-



iii) Dissociation of CO_2 :-



Control of CO Pollution:-

CO emission in vehicular exhaust may be lowered by using a “lean” fuel, which is a mixture of fuel and air in which fuel is less and air is more.

Effect of CO Pollution:-

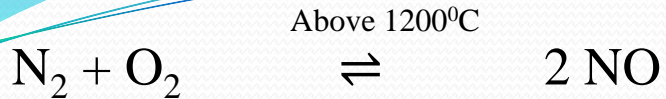
- i) Effect of CO on humans
- ii) Effect of CO on plants

2) Nitrogen Oxides NO_x:-

Sources and Sinks of NO_x:- About 5×10^3 tonnes of NO_x mainly NO is discharged by natural bacterial action in the atmosphere every year. Man-made sources release 5×10^7 tonnes of NO_x per year. The major man-made source is through combustion of coal, oil, natural gas, petrol, gasoline for various purposes in power plants, industry, transportation.

Sink:- Natural bacterial processes, photochemical reactions, act as huge sinks for NO_x. The end products are HNO₃ in acid rain, nitrates and photochemical smog.

Some chemical processes involved in NO_x formation:-



These high temperatures are achieved during combustion process involving air composed of 80% nitrogen and 20% oxygen.

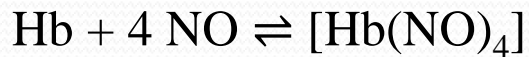
Another process is known as photolytic cycle of NO₂. This reaction is also favoured at high temperatures.

Control of NO_x Pollution:-

NO_x emitted from thermal power plants, industrial process ranges between 50-1000 ppm. Thermodynamic, kinetic and chemical equilibrium consideration can help in controlling NO_x levels. Some factors such as low temperature, use of inert gas and low excess air at combustion or firing or recirculating exhaust can be employed to reduce the emission of NO_x at source.

Effect of NO_x pollution:-

i) Effect on Human:- NO_x is more toxic substance found in atmosphere. NO₂ is four time toxic than NO. NO has tendency to bind with haemoglobin and reduces oxygen transport capacity of blood.



The formation and dissociation of this complex depends upon concentration of NO of blood.

ii) Effect on Plants:- Exposure on plant to 10 ppm of NO causes reversible decrease in the rate of photosynthesis. The plant tissue injury is occur due to NO. Nitrogen dioxide suppresses growth of plants, damage tissues and produces spots on plant leaf.

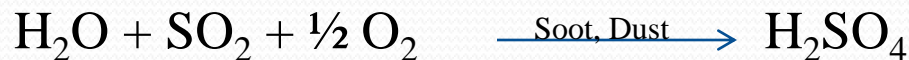
3) Sulphur Oxide SO_x:-

Sources and Sink of SO_x: Major source of SO₂ is volcanic eruption. The biological decay of sulphate and decay of sulphur containing organic matter produces H₂S.

Sink: The residence time of SO₂ is 4 days. Oceans are ready sinks for SO₂. About 4 x 10⁷ tonnes of SO₂ per year is transferred to ocean. While in presence of moisture, catalyst and sunlight SO₂ is converted to H₂SO₄ and finds sink in form of acid rain.

Some chemical process involved in SO_x formation:

Most of SO₃ is formed due to catalytic oxidation of SO₂ in presence of sunlight and third body, M like particulate matter (soot, dust or metal oxide).



Control of SO_x Pollution:

Use of low sulphur containing fuel

Desulphurisation of fuel

Use of substitute fuel

Removal of SO_x from fuel

Effects of SO_x Pollution:-

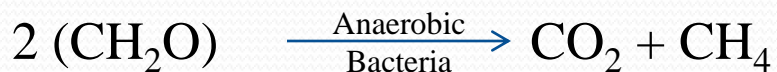
- i) Effect on humans: SO₂ is intensely irritating to eyes and respiratory tracts which produces breathlessness and coughing at 5-20 ppm level for period of 8 hours.
- ii) Effect on Plants: Prolonged exposure of plants to SO₂ produces chronic injury in plants. It make the vein area green.

4) Hydrocarbon HC:-

Sources: Anaerobic decomposition of organic matter by bacteria produce considerable amount of methane. Methane is released from sediments in water logged conditions and from flooded rice fields. Most HC emitted to atmosphere through plants are known as terpenes (essential oils).

Sink: The mean residence time of methane is about 4-7 years. Hydrocarbons are removed from atmosphere in variety of chemical and photochemical reactions. Most important reaction is conversion of HC in photochemical smog.

Some Chemical Processes involving HC: Anaerobic bacterial decomposition of organic matter in sediment, soil and water produce methane.



In the presence of some catalytic intermediate CH₄ is oxidized.



Control of HC:

- i) HC can be controlled by modifying combustion of internal engine.
- ii) To achieve complete combustion of fuel into CO₂ and H₂O exhaust system reactors should be developed.
- iii) Some substitute fuels like CNG should be used in place of petrol which will produce less pollutants.
- iv) Modern pollution free power sources like solar battery, H₂ fuel should replace present internal combustion engines.
- v) Use of catalytic converter.

Effect of HC:

Effect on human: Aromatic hydrocarbons are carcinogenic compounds. The secondary pollutant like free radicals and photochemical smog are more hazardous.

Particulate Matter:-

Inorganic Particulate Matter:

i) Metal and Metal oxides: Inorganic metal oxides mostly formed when fuel is burnt.

The coal, containing iron pyrite forms Fe_3O_4 .



The CaCO_3 present in ash is oxidised to CaO .



Fe_2O_3 , Al_2O_3 , MgO , SiO_2 , are some oxides commonly found in atmosphere.

ii) Toxic Metals: Most of the toxic metals are classified as heavy metals. Hg, Pb, Co, As, V, Ni, Cu etc are found in polluted atmosphere.

iii) Aerosol (mist and fog) formation: Mist is formed due to dispersion of liquid water into particles of large size in air. When SO_x , NO_x , and metal ions (Mn, Fe, Ni, Cu), soot are present in atmosphere at the time of formation of fog or mist then the droplets contain H_2SO_4 , $(\text{NH}_4)_2\text{SO}_4$, CaSO_4 etc in dissolved state.



In presence of ammonia or calcium oxide, H_2SO_4 aerosol gives new aerosols.



iv) Fly ash: Due to combustion of high ash fossil fuel atmosphere is polluted by mineral particulate mostly in form of oxides. When fuel like coal or lignite is burnt the smaller ash particles called “Fly ash” are emitted from stack to the atmosphere. Fly ash contains carbon, oxides of Si, Fe, Al, Ca, Ni, Na, K, Mg, P along with some carbonates and sulphates.

v) Asbestos: It is a term which refers to fibrous material composed of any different crystalline silicates. Fibers are built up from many hollow cylindrical “fibrils”. Each fibril is composed of layers of tetrahedral SiO_4 and close packed OH^- ions. Mg^{2+} hold OH^- to the side of $(\text{Si}_4\text{O}_{10})_8$ layer on which unshared oxygen is located.

Organic Particulate Matter:- Significant concentration of organic compounds

like long chain Hydrocarbons, Polycyclic Aromatic Hydrocarbons (PAH), Nitrogen and sulphur containing organics are found as fine particles in atmosphere.

Odd carbon n-alkanes are found in aerosols, fatty (alcohols, acids, esters) compounds with even carbon are predominantly located in atmosphere. Nitrogen containing compound like amines, amides, polynuclear aza heterocyclics are identified in air. Sulphur containing dimethyl sulphate, monomethyl sulphuric acid are detected in atmosphere.

Sampling:-

To determine the quality of air it is extremely important that sampling is correct. Some factors should be considered.

i) Total volume of sample collected

- ii) If concentration is more volume may be less.
- iii) The selection of proper analytical method suitable for the concentration.
- iv) The sampling rate and sampling time. The rate may vary from $0.003 \text{ m}^3/\text{min}$ to $3.0 \text{ m}^3/\text{min}$. The sampling time is generally a 3 hour period.
- v) The hour of day and place of sample collection.

Sampling of vapours and gases.

i) Absorption: Gaseous pollutants are collected by their absorption in suitable solvent. Gaseous pollutants like HF are absorbed by water. Alkaline solutions are suitable for acidic pollutant gases like SO_x , NO_x while acidic solutions are best suited for alkaline gas like NH_3 . Oils are used for collecting hydrocarbons.

Different types of absorbing systems are used a) impinger counter current scrubber b) packed columns c) fritted glass scrubbers.

ii) Cold trapping: Any gaseous pollutant in air can be separated by cold trapping.

In the collectors maintained at low temperatures the gases or vapours are frozen or liquified and are trapped.

iii) Adsorption: Activated charcoal is the best adsorbent for gases and vapours in air. The adsorbent besides charcoal, like Al_2O_3 , silica gel, 'molecular sieves' are also used effectively at low temperature. After adsorption the adsorbent is washed with suitable solvent like ethanol, CS_2 etc.

The collected samples can be analysed by using suitable technique.

Sampling of Particulates: Sampling and control of particulates are connected.

i) Filtration: Oldest, simple and least expensive method is filtration using suitable filter material.

Cellulose filter paper - Metals, anions

Glass fibers - Organic compounds

Silica felts - trace inorganic species

In High-volume air sampler large volume upto 2000 m^3 at rate $1.7 \text{ m}^3/\text{min}$ is pumped. Glass fiber filters are used with 99% efficiency.

ii) Impingers: Filtration cannot easily separate particles by diameter because as pores are clogged by larger particles smaller ones are trapped. A cascade of impingers may be used for this purpose.

A high velocity air stream is directed at a surface (dry or wet). The cascade impactor directs the air stream against collection slides through increasingly smaller size orifices provides stepwise collection of smaller particles.

iii) Electrostatic precipitator, thermal precipitator, gravity settlers are some other control equipments which can be used as samplers.

Some Effects of Atmospheric Pollution:-

Effects in Biosphere:-The primary pollutants are generally converted to acid H_2CO_3 , H_2SO_4 , HNO_3 and are deposited in rain, snow, fog causing “acidic precipitation”.

While in atmosphere the plant leaves and stems are affected. Leaf spotting breakdown of plant tissues, cellular respiration abnormality, are generally observed. The acid rain affects soil and water polluting the other segment of environment and consequently affecting plants and organism present there. The SPM affects photosynthesis in plants.

Acid rain due to air pollution:

Acid rain is defined as rain water having pH less than 5.6. This is due to the fact that normal rain has slightly acidic pH as the atmospheric carbondioxide with 325 ppm dissolves in rainwater forming carbonic acid. The equilibrium is established as.



The acidity of normal rain water is due to H^+ ions. Therefore pH of normal rain water is not '7' but 5.6.

Most of SO_x and NO_x entering into troposphere is converted into H_2SO_4 and HNO_3 by chemical and photochemical reactions and result into acidic precipitation, which is known as acid rain.

Corrosion of Metals due to Air Pollution:-

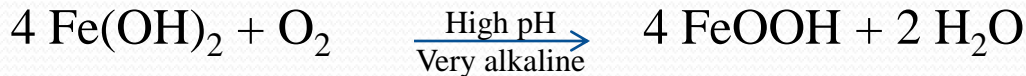
The presence of pollutant gases in air accelerates the process of corrosion. The damage due to corrosion is observed in Fe, Zn, Cu, Al and several alloys and building materials.

The end product of pollutant gases SO_x , NO_x is highly reactive viz., H_2SO_4 and HNO_3 . The corrosion rate of all metals increase in presence of SO_x , NO_x , SPM, humidity and high temperature.

Corrosion of Iron: Corrosion of iron is observed maximum in industrial sectors. The SO₂ present in the atmosphere initiate the corrosion. The corrosion reactions are electrochemical in nature that occurs on surface of metal in presence of moisture.



Further the reactions proceed according to the pH of the medium.



In neutral or slightly acidic medium Fe(OH)₂ is replaced by Fe(II) hydroxo complexes involving Cl⁻ or SO₄²⁻

The net result is that Fe atom is transferred from iron metal and is deposited as FeOOH. The presence of rust, surface particles and humidity helps absorption of SO₂. If the metal has several cracks and defects then corrosion is enhanced.



Corrosion of Zinc:

Iron and steel structure is generally galvanised by using zinc coating in form of $ZnCO_3$. The concentration of SO_2 in atmosphere determines the corrosion rate of Zn. The formation of soluble $ZnSO_4$ in presence of SO_2 probably increases the corrosion rate.

Corrosion of Copper:

The protective oxide film or aluminium interacts with acid formed by SO_2 in atmosphere and end product is $Al_2(SO_4)_3 \cdot 18H_2O$.

Formation of Smog due to air pollution:-

Smog is term coined from combined words smoke and fog. It is a man made pollutant in urban areas.

There are mainly two types of smog

Reducing Smog	Oxidising Smog
It was first noted in London.	It was first noted in Los Angeles.
Sooty particulate, SO ₂ are the primary pollutants.	HC and NO _x are the primary pollutants.
Industrial and other fuels contains sulphur (FeS ₂) are the major sources.	Automobile emissions are the major source.
Reducing in nature.	Oxidising in nature.
Occurs at relatively low temperature and humid atmosphere.	Occurs at relatively high temperature and low humidity.
Occurs mostly in winter during early morning.	Occurs mostly in summer during mid day.
Aerosol, H ₂ SO ₄ sulphates, sulphonic acids are secondary pollutants.	O ₃ , free radicals, PAN HNO ₃ , aldehydes, particulate nitrite, sulphates are the secondary pollutants.
Irritation in throat and lungs is the first effect on human.	Eye irritation is the first effect on human.

Reducing Smog:-

The large surface area of fog droplets allows the catalysis of oxidation of SO₂.



The metal ions Mn(II) or Fe(II) present in smoke and fly ash pass into solution from nucleating particles and catalyze oxidation of aqueous SO₂.



Therefore rapid production of sulphuric acid aerosol is possible when the three components are present. Synergism in London fog due to synergistic DPM produce large amount of reducing smog.

The effect of reducing smog is throat irritation, cough, shortness of breath and chest constriction and may cause death. The smog kills leaf cells and produces spots on leaves.

Oxidising Smog (Photochemical Smog):-

Now a day during sunny day when temperature is high and automobile traffic is heavy this type of smog occurs in many metropolitan cities. It is characterised by brown hazy fumes and eye irritation.

The analysis of smog shows that it contains high levels of oxidants mainly ozone. It also includes NO_2 and PAN (Peroxyacetyl nitrate). Following reactions occur.

- i) NO is converted to NO_2
- ii) When all NO disappears, O_3 begins to appear.
- iii) The HC are oxidised.
- iv) Variety of free radicals are formed.
- v) The reaction like chain initiation, chain propagation chain branching takes place.
- vi) The net formation of oxidants depends upon Non Methane Hydro Carbon (NMHC) and NO_x ratio and sunlight.
- vii) The product are aldehyde, PAN, PBzN, (Peroxy Benzoyl Nitrate).

The important reaction is formation of O₃. A very small amount of NO₂ present is sufficient to start the complex series of reactions. NO from hot autoexhaust is converted to NO₂.



The photolysis of NO₂ by solar light in 300-400 nm produces atomic oxygen.



M is the third body which absorbs excess energy to stabilize O₃. The high concentration of ozone is anthropogenic (man made). The NO emitted react with ozone to regenerate NO₂.



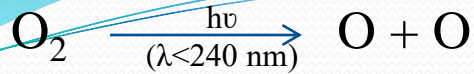
Ozone Layer:-

About 90% of ozone occur in stratosphere. The maximum concentration of ozone is at the altitude of about 25 km in the stratosphere. The region between the altitude range 15 to 30 km, where ozone is present in relatively high concentration, is the ozone layer which is also called ozonosphere.

Ozonosphere is responsible for absorption of ultra violet radiation ($\lambda=220$ to 330nm) from the sun. This radiation is harmful to life as it damages the biological molecule. Due to its absorption in ozonosphere, this harmful uv radiation from the sun does not reach the earth's surface and thereby the life on earth gets protected. Ozone layer is called earth's protective shield or earth's protective umbrella.

By absorption of uv radiation ozone itself undergoes decomposed. Formation and decomposition of ozone in the stratosphere occur by chain reaction.

Formation of ozone:-



Decomposition of ozone:-



Mechanism of Ozone Depletion:-

Ozone is depleted by catalytic chain reaction.



i) Hydroxyl Radical Catalysis:-

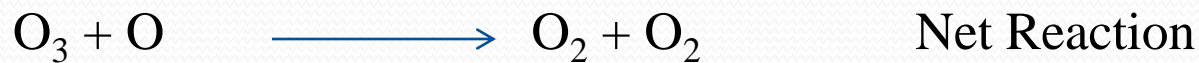
The hydroxyl radical accounts for about half of the total ozone destruction in the lower stratosphere (16 to 20 km). Hydroxyl radical is produced in the stratosphere by reaction of excited O atoms with a hydrogen source H₂O or CH₄, both being components of natural atmosphere.



Hydroxyl radicals are also produced in the stratosphere by photolysis of water.

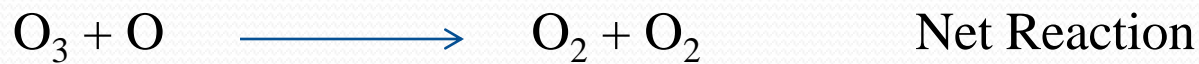


The hydroxyl radicals catalyse the destruction of O_3 in the following manner.



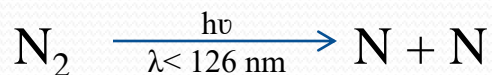
ii) Chlorine atom catalysis:-

Chlorine atoms are highly efficient catalysts.



iii) Nitric Oxide Catalysis:-

Nitric oxide is produced in stratosphere by reactions involving atomic nitrogen and oxygen species and also nitrous oxide, as shown below.

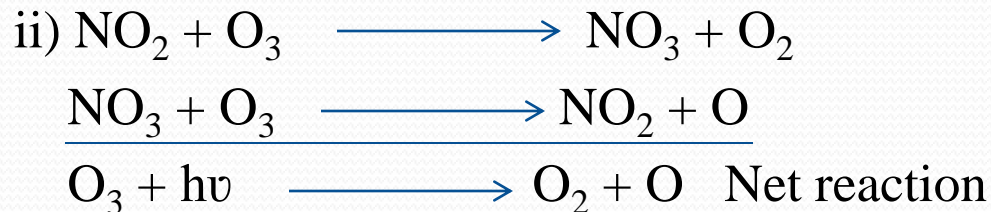
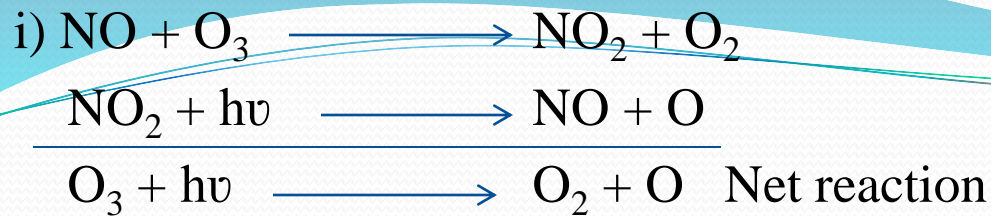


NO can catalyse the depletion of O_3 as shown below.



iv) Null and holding cycles:-

The catalytic effect of various species in ozone depletion is nullified or temporarily limited by some reactions which are described as null and holding cycles. Two important null cycles involving nitrogen oxides are shown below.



Net result of both these null cycles is photolysis of ozone. They are important only in day time.

Effect of Ozone Depletion:-

Ozone depletion has direct effect on penetration of UV in troposphere. Sunlight has maximum intensity in the visible region. (400 to 800 nm). The flux of UV radiation is low. Absorption of UV in upper atmosphere obstructs its penetration into troposphere and this is of great relevance to the life on earth. UV radiation from sun is divided into three categories on the basis of effects on the organisms. Radiation in the range 315 nm – 400 nm is UV-A which are not harmful to living species. UV-B with wavelengths 280-315 nm can be harmful to plants and animal on prolonged exposure.

UV-C is the shorter wavelength (< 280 nm) radiation having high energy and rapidly damages all types of biota. The most hazardous UV-C radiation does not reach troposphere because it is efficiently and totally absorbed by O₂, O₃ and other species in upper atmosphere, in the process of their decomposition. UV-B radiation is only partially absorbed.

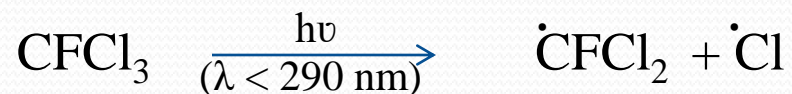
Climatic effects of Ozone Depletion:- Green house warming effect in the troposphere is also expected to have cooling effect in the stratosphere. There are many speculations regarding climatic effects of stratospheric cooling. One speculation is that there would be cooling effect in Arctic stratosphere which would increase PSCs and corresponding further depletion in O₃ level similar to ozone hole in Antarctica. Another speculation is that increase in temperature difference between warmer troposphere and cooler stratosphere would increase wind, which would affect the global flow of energy.

Chlorofluorocarbons (CFCs):-

Chlorofluorocarbons (CFCs) are the manmade chemicals which are found to be responsible in increasing the load of Cl atoms in stratosphere and thereby causing rapid ozone depletion. The properties of CFC's like low viscosity, low surface tension, low boiling point make them suitable for use as refrigerant and aerosol propellant. Due to their non-toxic, non inflammable and non-reactive nature CFC's were hailed as miracle chemicals. It is also used as cleaning solvents, in dry cleaning, propellants for making plastic foams and sterilizing surgical instruments. Due to their stability and very long residence time in the troposphere had diffused into the stratosphere and causing ozone depletion.

Nomenclature of CFC's:- CFC's are given three digit code numbers like CFC-113, (F-113), CFC-214 F-214,

Ozone Depletion Potential of CFC's:- CFC's have a potential for depletion of stratospheric ozone. This is because the CFC's reach stratosphere where they undergo photodecomposition to produce chlorine radical which is able to take part in catalytic cycle.



Stability and Reactions of CFCs:- CFCs have very long residence time/life in the troposphere. They cannot absorb the low energy UV radiation ($\lambda = 290 \text{ nm}$) available in troposphere and thereby do not undergo bond dissociation in the troposphere. CFCs do not react at significant rates with tropospheric O_3 and HO . Thus, CFCs do not have any chemical sink in troposphere. CFCs do not react with or dissolve in water, hence are not removed by rainouts. Tropospheric lifetime of CFCs is more than 60 years. CFCs gets chance to diffuse into stratosphere which requires about 30-40 years.

In stratosphere CFCs are exposed to high energy UV-B and UV-C radiation.

Absorption maximum of CFCs is 170-220 nm. UV absorption by O₂ and O₃ in stratosphere has a window from 195 to 210 nm which is not absorbed by them.

CFCs absorb light and undergo bond dissociation. Amongst the various bonds in CFCs, C-F bonds are stronger and shorter than C-Cl bonds. Hence upon light absorption it is the C-Cl bond which undergoes homolysis and $\dot{\text{C}}\text{l}$ radical is formed.



$\dot{\text{C}}\text{l}$ catalyses decomposition of ozone by the reaction



Thus $\dot{\text{Cl}}$ generated in the chain reaction, thereby decomposes large number of O_3 molecule. It is estimated that one molecule of CFC is able to destroy 100000 O_3 molecule before Cl and ClO get destroyed to terminate the chain. The sink for $\dot{\text{Cl}}$ and $\dot{\text{ClO}}$ are reactions with CH_4 and NO_2 to form HCl and ClONO_2 (Chlorine nitrate).



HCl may regenerate Cl on reaction with $\text{HO}\cdot$



Some of HCl and ClONO_2 may diffuse down through tropopause dissolved by rain acting as a permanent sink for $\dot{\text{Cl}}$. Thus CH_4 may result in decreasing O_3 depletion by reacting with $\dot{\text{Cl}}$.

Harmful effects of CFCs:- CFCs exert adverse effect on environment is by accelerating stratospheric ozone depletion. The creation of seasonal ozone hole over Antarctica since mid 1980s is attributed to increased levels of Cl[•] by photodecomposition of CFCs in stratosphere. The subsequent effects of UV penetration on humans, plants and microorganisms are ultimately the harmful effects of CFCs. CFCs are found to be 10⁴ times more efficient in absorbing infrared radiation than CO₂. Thus, CFCs are important greenhouse gases, causing global warming.

CFCs substitutes:-

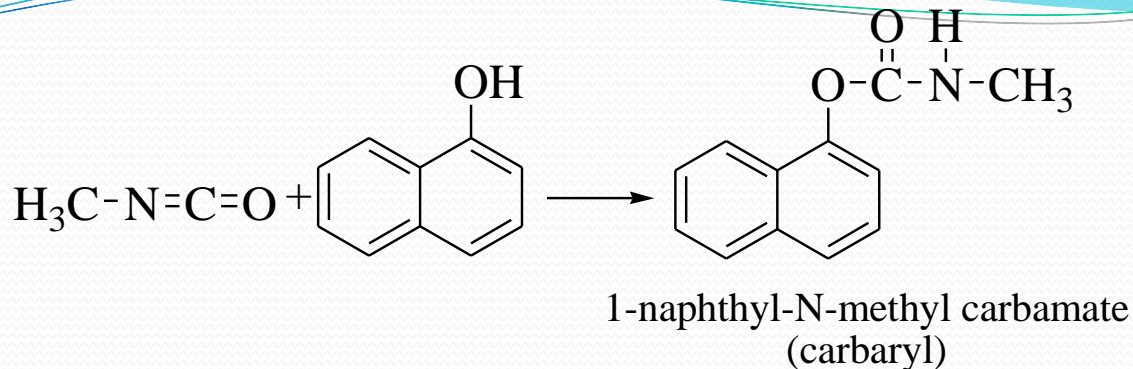
Thus, hydrofluorochloro carbon (HCFCs), hydrofluoro carbon (HFCs) are being introduced as CFCs substitutes. The compound containing no. Cl there is no release of any Cl[•] and thereby no potential to cause any O₃ depletion.

Chemistry of some Air Pollution Incidents:-

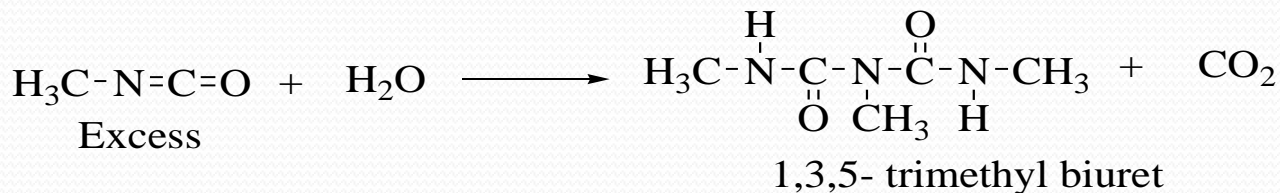
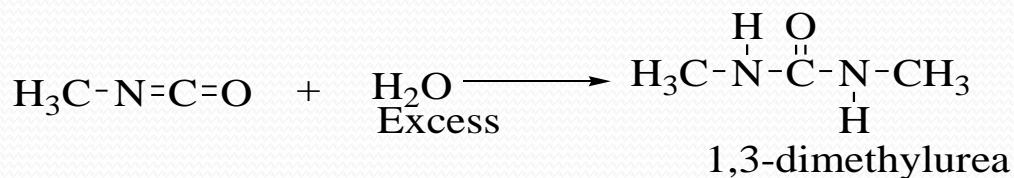
The Bhopal disaster:- Union Carbide factory manufactured a carbamate pesticide known as Carbaryl. On December 3, 1984 due to non functioning of the safety measures in the plant over 50000 lbs of MIC in vapour and liquid form along with phosgene and HCN were expelled to the atmosphere. The incident was disastrous which killed hundreds of people and thousands suffered from acute and chronic injuries. Methyl Iso Cyanate (MIC) is one of the starting compounds in production of carbaryl.



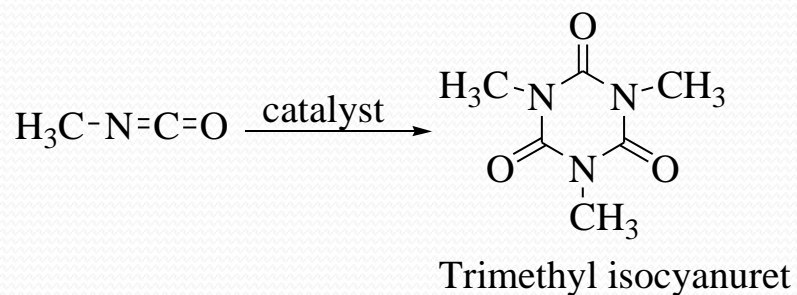
Methyl amine and phosgene are pumped into a reactor. Thereafter HCl gas is separated and MIC is transferred to carbamate production chamber or storage unit and chilled. The MIC produced is always associated with 2% COCl_2



Properties and reactions of MIC:- MIC is gaseous and stored at very low temperature below 0°C using a cover of dry nitrogen as the B.P. is 39.1°C. It is flammable and extremely reactive. It can react with many active hydrogen compounds. All these reactions are vigorous and highly exothermic.

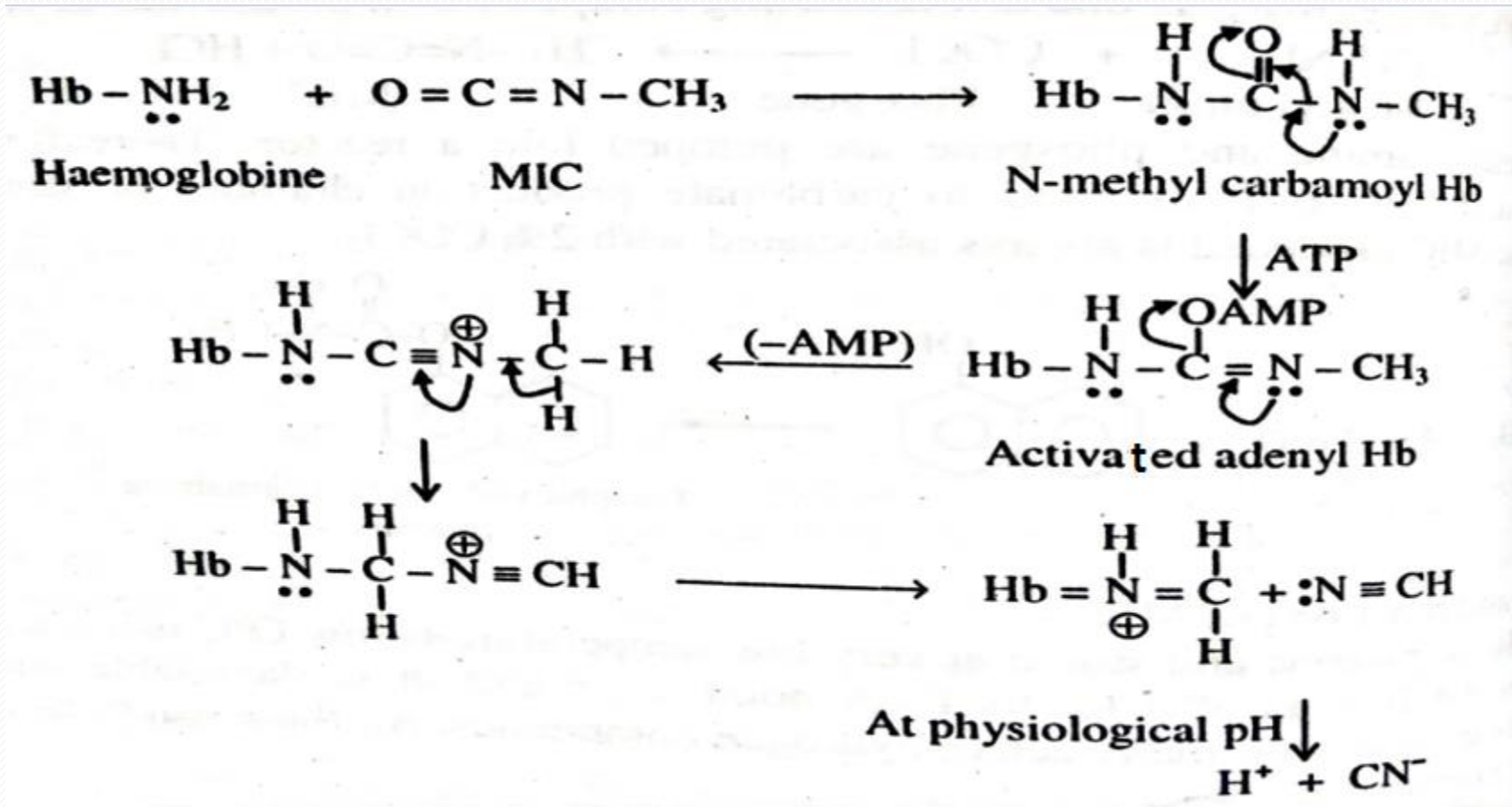


Both reactions at room temperature proceed slowly initially. The rate increases rapidly and being exothermic large heat is given out and MIC starts boiling causing explosion. In presence of catalyst like Fe, Cu, Mn etc. MIC undergoes trimerization. Trace of dust, NaOH or NaCl also acts as catalyst, causing liberation of heat.



At the time of accident the safety valves, the refrigeration system failed. The violent explosive and exothermic reactions must have occurred in presence of water, catalyst and phosgene causing release of tonnes of poisonous gas to the atmosphere.

Biochemical effect of MIC:- T.L.V. for MIC is 0.02 ppm and phosgene is 0.1 ppm. The toxicity of MIC increases in presence of phosgene. Exposure of MIC causes eyeache, chest tightness, breathing troubles. It generates cynide in the body that leads to death.



Thank you!

