Study Material

On

APPLIED CHEMISTRY & EVS

for

1ST YEAR of all Engineering Branches

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UNIT - 1: AIR AND NOISE POLLUTION

Pollution:

The presence of harmful substances in the air, land, and water, which can have an adverse effect on living beings and on the environment, is called pollution.

Types of pollution:

There are various types of pollution, like

1. Air pollution
2. Water pollution
3. Soil pollution
4. Noise pollution
5. Radioactive pollution, etc.

Pollutant:

Pollutants are materials that cause pollution. Any substance that makes the air, water or any other natural resource toxic is also called a pollutant.

Examples: Various substances such as *heavy metals, pesticides, herbicides, industrial chemicals, and toxins from improperly disposed-of waste*. Also, *Carbon monoxide, Nitrogen oxides, and Sulfur dioxide* are examples of pollutants.

Primary pollutants:

Primary pollutants are pollutants that are emitted directly into the environment or formed during a process. Examples: Carbon monoxide, carbon dioxide, sulphur dioxide, chlorofluorocarbons, lead, Mercury, NO_X, etc.

Secondary pollutants:

Secondary pollutants are pollutants that form in the atmosphere as a result of other pollutants reacting with molecules in the atmosphere. Examples: Peroxyacyl nitrates (PAN), ozone, acid rain, smog, etc.

Air Pollution:

Air pollution may be defined as the "introduction of any foreign material to the atmosphere which causes detrimental effects on the environment, living and non-living systems".

Sources of Air pollution:

1. **Natural sources**: The natural sources of air pollution include:
   - Forest fire
   - Volcanic eruption
   - Sandstorm
   - Tornado
   - Garbage decomposition
2. **Manmade sources**: The manmade sources of air pollution include:
   - Internal combustion engines
   - Boilers
   - Refrigeration units
   - Industrial emission

- Agriculture
- Thermal power plant
- Waste management

Particulate Pollutants: A particulate pollutant is a microscopic or microscopic liquid and solid particles present in the form of suspension in the air. Particulate matter can be released from different types of human activities such as vehicle emissions, smoke particles, dust particles, and ash from industries.

Particulate matter present in the air is mainly of two types- Viable particles and non-viable particles.

- **Viable Particulate Matter:** These particles include lower living organisms such as algae, bacteria, molds, fungi, etc. They are dispersed into the air. Human beings are allergic to these microorganisms and they can also cause different types of diseases in plants and animals.
- **Non-Viable Particulate Matter:** We can classify these particles based on size and their nature. These particulates include smoke, dust, mist, and fumes.

Effects of Particulate Matter

A particulate pollutant is very dangerous to human health, plants, and to the entire climate. Children and elderly people are prone to diseases caused by particulate pollution. However, normal persons can also experience temporary problems.

Effects on Health

Exposure to particulate pollution can cause irritation of eyes, throat, and nose. It can also cause tightness in chest, difficulty in breathing and decrease in lung function.

Lung Cancer

PM vary in shape and size. Fine particulates can enter easily and penetrate deep into the respiratory systems of human and can affect the lungs. It attacks the bronchi and can cause lung cancer.

Asthma

Reports suggest that particulate pollutants can cause asthma with the increase in the fine pollutant globally. Rising rate of diagnoses links asthma to particulate matter pollution.

Cardiovascular Problems

Fine particles can easily enter the body without facing resistance from the body. Therefore fine particles have a drastic impact on the heart and the functions of the heart. Therefore, particulate matter is responsible for many cardiovascular diseases. Frequent exposure to PM can lead to a large amount of inhalation of particles. Therefore, accumulation of PM will cause the buildup of plaque in the arteries and vascular inflammation.

Atherosclerosis

Air pollutant inhalation can cause plaque build-up. This will lead to hardening of arteries and in turn cause heart problems.

Birth Defects and Failed Pregnancy

Particles ability to enter into the body makes it easy to enter any pregnant mothers body and then into the child during long exposure to particulate air pollutants. Thus, the harmful chemical pollutants can cause any type of birth defects. It is also the reason failed pregnancies specifically in town and cities facing extreme levels of pollution.

Death

High levels of aerosols and other pollutants can cause premature death. Air pollution due to coal industries is the cause of many premature deaths every year in India and globally.

Effect on Vegetation and Plants

Particulate pollutants have the ability to block stomatal openings. Therefore, it can retard the photosynthesis process. Hence, air pollutants can damage the plant, reduce crop and vegetation yield, and increase their mortality rate.

Effect on Climate

The rise of particulate pollution is disturbing the environmental balance. Reports suggest particulates matter can negatively impact weather on a regional level. PM decreases the levels of evaporation of water in the Indian Ocean. It is linked to the lack of Indian monsoon or reduction of the Indian monsoon.

Aerosol haze and particulate pollution have the ability to push tropical rainfall and are the reason for a number of droughts human's experiences on a global level. PM causes the decrease in rainfall. It is also responsible for the increase in greenhouse gases and global warming.

Control of Particulate Pollutants:

Particulate pollutants can be controlled by using the following apparatus:

1. Bag Filter
2. Cyclone Separator
3. Electrostatic Precipitator

1. Bag Filter:

Bag filters, commonly known as baghouse or dust collector is a pollution control device used to remove particulate matter from the contaminated gas stream by depositing the particles on bag filters. These bag filters are made up of fabric materials. The filter is usually in the form of cylindrical fabric bags, but it may also be in the form of cartridges that are made up of fabric, sintered metal or porous ceramic. In general, bag filters are capable of collection efficiencies greater than 99 percent. There are following three types of bag filters, and they differ from each other in the method of cleaning the filter material.

1. Shaker bag filters Shaker Bag Filters

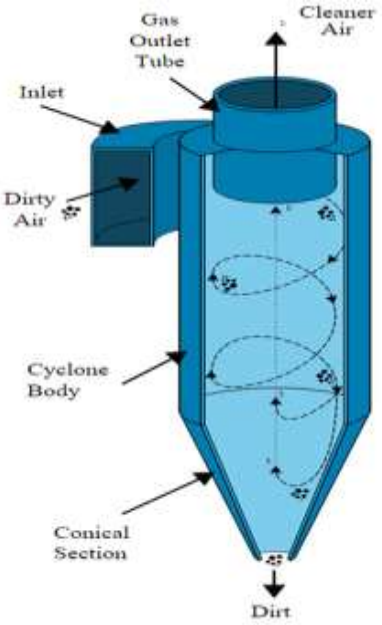
2. Reverse air bag filters

3. Pulse jet type bag filters.

2. Cyclone Separator:

Cyclone separators or simply **cyclones** are separation devices that use the principle of inertia to remove particulate matter from flue gases. A cyclone separator is one of many air pollution control devices which remove larger pieces of particulate matter. In addition, several cyclone separators can operate in parallel, and this system is known as a **multi-cyclone**.

The size of the cyclone depends largely on how much flue gas must be filtered; thus, larger operations tend to need larger cyclones.



In a cyclone separator, dirty flue gas is fed into a chamber. The inside of the chamber creates a spiral vortex, similar to a tornado. The lighter components of this gas have less inertia, so it is easier for them to be influenced by the vortex and travel up it. While larger components of particulate matter have more inertia and are not as easily influenced by the vortex.

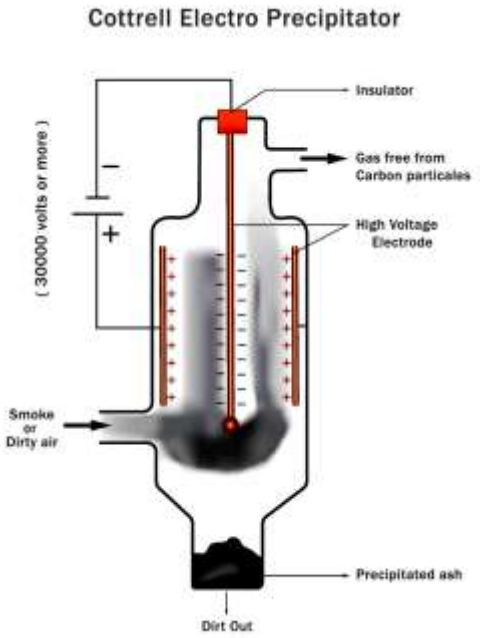
Since these larger particles hit the inside walls of the container and drop down into a collection hopper. These chambers are shaped like an upside-down cone to promote the collection of these particles at the bottom of the container. The cleaned flue gas escapes out the top of the chamber.

Out of all of the particulate-control devices, cyclone separators are among the least expensive. They are often used as a pre-treatment before the flue gas enters more effective pollution control devices.

3. Electrostatic Precipitator (ESP):

An **electrostatic precipitator** is a type of filter that uses static electricity to remove soot and ash from exhaust fumes before they exit the smokestacks. This is a common air pollution control device.

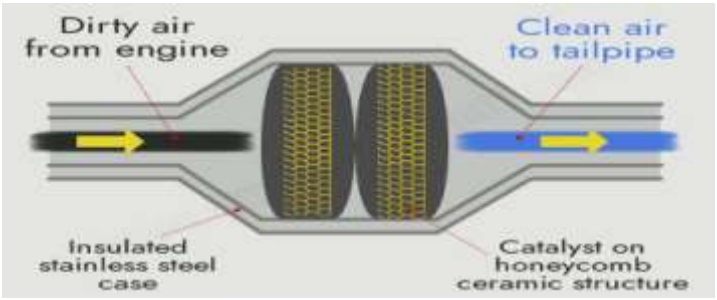
The operation of ESP is very simple. The dirty flue gas escaping through the smokestack is passed through two electrodes. One of the electrodes is charged with a high negative voltage, and this plate causes particulates inside the smoke to obtain a negative charge as they pass by this electrode. On the other hand, the second electrode carries a similarly high positive voltage. The negatively charged soot particles are pulled towards the positive electrode and stick to it. The precipitated soot and ash are then collected at the bottom of the ESP.



Gaseous pollution control:

The following apparatus are used to control gaseous pollution:

1. **Catalytic Converter:** A catalytic converter is an emissions control device. The job of the catalytic converter is to convert harmful pollutants into less harmful emissions before they ever leave the vehicle's exhaust system.



   In the catalytic converter, there are two different types of catalyst chambers: a reduction catalyst and an oxidation catalyst.

   The reduction catalyst is the first stage of the catalytic converter. It uses platinum and rhodium to help reduce the NOx emissions.

   When an NO or NO_2 molecule contacts the catalyst, it converts them into nitrogen and oxygen.

   $$2NO \xrightarrow{Catalyst} N_2 + O_2$$

$$2NO_2 \xrightarrow{Catalyst} N_2 + 2O_2$$

The oxidation catalyst is the second stage of the catalytic converter. It reduces unburned hydrocarbons and carbon monoxide by oxidizing them over a platinum and palladium catalyst. This catalyst aids the reaction of the CO and hydrocarbons with the remaining oxygen in the exhaust gas.

$$2CO + O_2 \xrightarrow{Catalyst} 2CO_2$$

$$C_XH_Y + O_2 \xrightarrow{Catalyst} CO_2 + H_2O$$

Effects of air pollution due to Refrigerants:

The refrigerants used in refrigerators, such as chlorofluorocarbons (CFCs) and hydrofluorocarbons (HFCs), make great contributions towards air pollution. CFCs and HFCs are greenhouse gases that can contribute to ***climate change*** and ***ozone depletion***. When refrigerants are released into the atmosphere, they react with other chemicals to form smog and contribute to ***global warming***. Additionally, the energy used to power refrigerators can contribute to air pollution if it is generated from fossil fuels. Overall, while refrigerators do not directly cause air pollution, the refrigerants and energy used to power them can contribute to air pollution and climate change.

Effects of air pollution due to IC Engines:

Internal combustion engines emit a large numbers of pollutants like particulate matter, NOx, HCs, etc. which contribute towards air pollution. Combustion engines fuelled by petroleum fuels are also a major source of ***GHG emissions***—mainly CO_2 but also other gases such as CH_4 and N_2O which causes global warming.

From a *public health* perspective, emission of particulate matters and nitrogen oxide must be controlled to ensure healthy air, especially in urban areas.

High levels of diesel particulates can be produced by older generation diesel engines, without diesel particulate filters (DPF). More recently, direct injection gasoline engines became another important source of particulate emissions. Diesel particulate matter (DPM) is a mixture composed of solids, organics, and sulphates which has the greatest effect on health.

Diesel emissions contain numerous compounds like poly-nuclear aromatic hydrocarbons (PAH), nitro-PAHs, aldehydes, and other hydrocarbon derivatives. The chemical substances are highly toxic for human health.

Some health studies investigate the effects of “whole diesel exhaust” that includes both gaseous pollutants and the particulate phase.

Effects of air pollution due to Boilers:

Boilers are combustion devices used to heat water or to produce steam. Steam is produced in boilers by heating water until it vaporizes. The steam is then used to produce heat / electricity or to run machinery. I.C. Boilers emit a variety of hazardous air pollutants, particle pollutants and volatile organic compounds. Some of the pollutants emitted are Nitrogen oxide, Sulfur dioxide, Carbon monoxide, Hydrogen chloride, cadmium, mercury etc.

Noise pollution

Noise pollution can be defined as any unwanted or disturbing sound that affects the health and well-being of humans and other organisms.

The sound is typically described in terms of loudness, and it is measured in decibels (dB). Not all sound is considered as noise pollution. According to the World Health Organization (WHO), noise **above 65 dB** can be considered as noise pollution. Noise becomes harmful when it **exceeds 75 dB** and painful above 120 dB.

Sources of noise pollution

The noise pollution is caused mainly due to **industrialization, urbanization and modern civilization.** There are many sources of noise pollution:

- **Industrial sources:** The industries such as textile mills, printing press, metal works etc. contribute heavily towards noise pollution. Many industrial cities in India like Kolkata, Kanpur etc. are more affected as industrial zones are not separated from residential zones specially in case of small-scale industries.
- **Transport vehicles:** In urban areas automobiles are big sources of noise pollution. In the recent past, there has been enormous growth in traffic volume due to increase in number of vehicles such as busses, trains, trucks etc. resulting in increased noise pollution. Airports located near the residential areas create lots of noise pollution during their landing and taking off. Heavy trucks, buses, trains, motor bikes, mopeds etc. also contribute to the noise pollution.
- **Household noise:** The household activity is also a source of many indoor noises such as noise of playing children, infants crying, moving of furniture etc. Domestic gadgets like mixer-grinder, pressure cookers, exhaust fans, washing machines and entertainment equipment such as radio, music system, television sets are all indoor sources of noise pollution.
- **Public address system (PA system):** Many public functions such as political rallies, strikes, elections, religious and other social events etc. use PA system normally in a very loud volume and thus are become the source of noise pollution.
- **Agriculture machines:** Heavy types of machinery and equipment such as tractors, thrashers, powered tillers, harvesters etc. are being used in many agricultural farms. These machineries may create noise pollution of level more than 90 dB to 98 dB.
- **Defense equipment:** A lot of noise pollution is created by artillery, tanks, explosions, shooting practices etc. by defense personnel.
- **Miscellaneous sources:** The construction site, blasting, stone crusher etc. are some of the other sources of noise pollution.

Effects of Noise pollution:

Some of the major effects of noise pollution are:

- **Hearing problems:** Constant exposure to loud levels of noise may result in loss of hearing. It may also reduce our sensitivity to sounds that our ears pick up unconsciously in our day-to-day life.
- **Psychological issues:** Our psychological health may be influenced by noise pollution in working areas such as offices, construction sites or even in homes. It may result in disturbance of sleep, constant stress, fatigue, anxiety, depression etc. These, in turn, may cause more severe and chronic health issues in the later stage of life.
- **Physical problems:** Excessive noise level may cause high blood pressure, headaches, respiratory problems, racing pulse etc.
- **Cognitive issues:** Noise pollution may affect brain responses and ability to focus which may result in low performance levels over time. The study reveals that the school children residing near railway stations or airports have problems in learning.
- **Sleeping disorders:** High level of noise is likely to affect our sleeping pattern and it may lead to very uncomfortable and irritating situations. It may result in early fatigue and affect our performance in the office as well as in home.
- **Cardiovascular issues:** High level of noise may cause high blood pressure, cardiovascular disease and stress-related heart problems.
- **Communication barrier:** Noise pollution may act as a barrier in free communication among the people. This may lead to misunderstanding and also difficulty in understanding each other. It may affect badly the teaching learning process in the classroom, laboratories and workshops.
- **Effect on wildlife:** Noise pollution affects wildlife more than humans as they are more dependent on sound. Animals may suffer from hearing loss and become inefficient in hunting which may lead to disturbing the balance of eco-system.

UNIT - 2: WATER AND SOIL POLLUTION

Water Pollution:

Water pollution may be defined as "the introduction of any foreign material to water bodies which changes its colour, taste or any other physical or chemical composition causing adverse effect on living and non-living things".

Sources of water pollution:

The most significant sources of water pollution are:

- **Sewage (Wastewater):** The sewage water carries pathogens, a typical water pollutant, other harmful bacteria, and chemicals that can cause serious health problems and thereby diseases.
- **Agricultural Pollution:** Excess **c**hemical fertilizers and pesticides are used by farmers are mixed up with runoff water and enter the water bodies to pollute water.
- **Oil Spillage:** Oil spills from pipelines, refineries, ships, etc. enter into the sea. It causes problems for local marine wildlife, including fish, birds, and other aquatic lives.
- **Industrial Waste:** Many toxic chemicals and pollutants are produced from different industries as their waste products which cause water pollution.
- **The burning of fossil fuels:** Fossil fuels like coal and petroleum oil, when burnt, produce a huge amount of ash in the atmosphere. The particles which contain toxic chemicals when mixed with water vapour result in acid rain causing water pollution.
- **River dumping and Marine Dumping:** The garbage produced by households in the form of paper, plastic, food, aluminium, rubber, glass, is collected and dumped into the rivers and seas. They not only cause water pollution but also harm aquatic animals.

Types of water pollutants

Water pollutants can be classified into the following four types:

- Pathogens
- Organic materials
- Inorganic compounds
- Macroscopic pollutants

Pathogens

Pathogen refers to bacteria, viruses, protozoa and more. Excessive number of bacteria can heavily contaminate the water. The two most common pathogenic bacteria include coli-form and E Coli bacteria.

Organic Material

MTBE (methyl tert-butyl ether) is quite a common volatile organic chemical. Earlier MTBE was used as an air-cleaning gas additive. However, it was banned later but the time to erase it completely from water is quite long.

Similarly, the water which contains organic materials can result in deadly diseases like tumours in the testicles, leukaemia, thyroid glands and kidneys, lymphoma, and more.

Inorganic Material

Inorganic materials like heavy metals including copper, arsenic, barium, mercury, zinc, mercury and more can be dangerous water pollutants.

Macroscopic Pollutants

The most common example of macroscopic pollutants is the trash including plastic waste that ends up in the water. Due to their non-biodegradable nature, they end up collecting in oceans and other water bodies. This is a very severe problem causing the 'great pacific garbage patch' which can be compared to the size of France.

Similarly, other types of these pollutants are small plastic pellets, metal, pieces of wood, shipping containers, shipwrecks and more.

Characteristics of water pollutants:

1. **Turbidity:** Turbidity is the measurement of water clarity or transparency. Suspended particles – such as silt, algae, plankton, and sewage make water turbid. These particles scatter and absorb light rays rather than allowing light to be transmitted straight through the water.

   Turbidity of water is measured with a ***Nephelometer***, also known as a turbidity meter. Turbidity meters utilize a light and photo detector to measure light scatter, and read out in units of turbidity, such as *Nephelometric turbidity units (NTU) or Formazin turbidity units (FTU).*

2. **P^H:** P^H is a measurement of acidity or alkalinity of solutions. It may be defined as 'the negative logarithm of H^+ ion concentration in moles per litre. ($P^H = -\text{Log}_{10}[H^+]$). The scale ranges from 0 (very acidic) to 14 (very basic). It is normal for water to have a range of between 6.5 and 8.5 on the scale. P^H in water may fluctuate with differing environmental factors.
3. **Total suspended solids:** Total Suspended Solids (TSS) is a measurement of the total solids in a water or wastewater sample that are retained by filtration. TSS can be measured in real-time with our TSS probe to improve wastewater process control and plant efficiency.
   To measure TSS in real-time, Real Tech's innovative TDS sensors utilize near infrared (NIR) light as measurement in this region minimizes or eliminates interference from other absorbing compounds, improving accuracy and reliability of results.
4. **Total solids:** Total solids are dissolved solids plus suspended and settleable solids in water. In stream water, dissolved solids consist of calcium, chlorides, nitrate, phosphorus, iron, sulphur, and other ions particles that will pass through a filter with pores of around 2 microns (0.002 cm) in size. Suspended solids include silt and clay particles, plankton, algae, fine organic debris, and other particulate matter. These are particles that will not pass through a 2-micron filter.
5. **Biochemical Oxygen Demand (BOD):** Biochemical oxygen demand (also known as BOD or biological oxygen demand) is the amount of dissolved oxygen (DO) consumed by aerobic bacteria growing on

the organic material present in a water sample at a specific temperature over a specific time period. BOD is applied to determine the aerobic destructibility of organic substances.

6. Chemical Oxygen Demand (COD):

Chemical Oxygen Demand is a measure of the amount of oxygen required to break down organic matter in water. It's an important parameter in water quality monitoring, particularly in wastewater treatment.

- COD measures the amount of oxygen consumed by organic matter in water when it's oxidized with a boiling acid potassium dichromate solution.
- COD can indicate the presence of all types of organic matter, including biodegradable and non-biodegradable. High COD levels can be caused by a number of things, including solid waste, food waste, and dying bacteria.
- COD is used to characterize water bodies, sewage, industrial wastes, and treatment plant effluents. It can also be used to monitor compliance, optimize wastewater treatment, and identify pollution sources.
- High levels of organic pollution which may cause waterborne diseases.

COD is typically measured in milligrams per liter (mg/L) or parts per million (ppm). Common COD ranges:

1. Drinking water: <10 mg/L
2. Wastewater: 100-1,000 mg/L
3. Industrial effluent: 1,000-10,000 mg/L

Difference between BOD & COD

BOD	COD
BOD stands for Biological Oxygen Demand.	COD stands for Chemical Oxygen Demand.
It is the amount of oxygen the microbes require to decompose organic matter under aerobic conditions.	It is the total amount of oxygen required to break down both the biodegradable and non-biodegradable organic matter by chemical oxidation.
BOD is a biochemical oxidation process	COD is a chemical oxidation process.
It can be determined by putting a sealed water sample under specific temperature conditions (20^{o}C) for five days.	It can be determined by placing a water sample with a strong oxidizing agent under specific temperature conditions (150^{o}C) for a short period.
It takes several days for the incubation period.	Can be measured relatively quickly, often within a few hours.
Specifically measures biodegradable organic matter.	Measures both biodegradable and non-biodegradable organic substances.
It is always lower than COD.	It is always higher than BOD.
It is used to assess the level of organic pollution, microbial activity, and treatment efficiency.	It is used to quantify the amount of oxidisable pollutants found in water bodies.

Waste Water Treatment:

Primary Methods:

1. Sedimentation:

Sedimentation is a water treatment process that removes suspended particles from water using gravity.

- In sedimentation, water passes through a basin where the velocity is reduced so that gravity can remove particles from the water flow. The particles that settle out are called sludge.
- Sedimentation improves the filtration process by reducing the concentration of particles in the water. It can also reduce the amount of coagulating chemicals needed.
- Sedimentation can be used before coagulation to reduce heavy sediment loads, or after coagulation to reduce the concentration of solids in suspension.
- There are several methods for sedimentation, including horizontal flow, radial flow, inclined plate, ballasted floc, and floc blanket sedimentation.
- Adding coagulants like aluminium sulphate, polyaluminium chloride, or ferric sulphate to the water can speed up the sedimentation process.
- After sedimentation, the water is usually filtered to remove any remaining suspended materials and pathogens.

2. Froth Floatation:

Froth flotation is a wastewater treatment process that uses air bubbles to separate suspended solids, fats, oils, and grease from water:

- Air is dissolved into water under pressure, then released into a flotation tank to create air bubbles. The bubbles trap dispersed particles, which float to the surface and form a froth layer. A skimmer removes the froth, leaving clear water behind.
- Froth flotation is used to remove oil from wastewater in oil refineries, chemical production plants, and other similar industries.
- Froth flotation is also used in mineral processing and paper recycling.

Secondary Methods:

1. Activated sludge treatment

The activated sludge process is a biological wastewater treatment process that uses microorganisms to break down organic matter in wastewater.

The process involves:

- **Mixing and aeration**: Air or oxygen is pumped into a tank to mix and aerate the wastewater and microorganisms.
- **Biological flocs**: The microorganisms grow and clump together to form a mass called activated sludge.
- **Settling**: The sludge settles in a tank, separating it from the treated water.
- **Sludge recycling**: Some of the sludge is recycled back to the aeration tank, while the rest is treated and disposed of.

2. Bioreactor:

A bioreactor is a chamber in a wastewater treatment process that supports a biologically active environment where bacteria and protozoa grow and consume substances in the wastewater. There are many different types of bioreactors, including:

- Membrane bioreactors (MBR)
- Anaerobic membrane bioreactors (AnMBRs)
- Packed bed biofilm reactors
- Moving bed biofilm reactors
- DSFF bioreactors

Bioreactors can be aerobic, anoxic, or anaerobic, depending on the presence of oxygen and nitrates:

- **Aerobic**: Removes organic matter and oxidizes ammonia to nitrate.
- **Anoxic**: Removes nitrogen from nitrates to nitrogen gas.
- **Anaerobic**: Removes organic matter.

Tertiary Methods:

1. Membrane separation technology:

In this method pressurized waste water is passed through a number of semipermeable membranes to separate particles, contaminants, or solutes from water or other fluids. This technology is widely used in water treatment, wastewater reuse, and industrial processes.

Membrane separation applications:

1. Drinking water treatment
2. Wastewater reuse and recycling
3. Industrial process water treatment
4. Desalination
5. Food and beverage processing

Advantages:

1. High removal efficiency for contaminants
2. Compact and space-saving design
3. Low energy consumption
4. Flexibility in operation and control
5. Can be used for a wide range of applications

2. Reverse Osmosis (RO)

Reverse Osmosis

Reverse osmosis (RO) is a water treatment process that uses a semi-permeable membrane to purify wastewater by removing up to 99% of contaminants:

- RO systems force water through a semi-permeable membrane, separating the more concentrated side (more contaminants) from the less concentrated side (fewer contaminants).
- RO is a good choice for wastewater treatment because:
    - It is safer than traditional methods that use chemicals
    - It Requires little maintenance
    - It Saves money by reusing water

RO is used in the wastewater industry for tertiary water treatment. It can also be used to clean industrial wastewater so it can be reused, which helps to relieve pressure on freshwater reserves.

Soil Pollution:

What is Soil Pollution?

Soil pollution refers to the contamination of soil with anomalous concentrations of toxic substances.

Causes, Effects and Preventive measures of Soil Pollution:

1. Excessive use of Fertilizers:

Soil pollution due to excessive fertilizer use has severe environmental and health impacts.

Causes:

1. Over-application of synthetic fertilizers
2. Lack of soil testing and nutrient assessment
3. Poor agricultural practices
4. Inadequate fertilizer storage and handling

Effects:

1. Soil degradation and nutrient imbalance
2. Water pollution through runoff and leaching
3. Air pollution through ammonia emissions
4. Soil microorganism disruption
5. Plant nutrient deficiencies and reduced crop yields
6. Human health risks through food contamination

Preventive Measures:

1. Soil testing and nutrient assessment
2. Balanced and targeted fertilizer application
3. Organic and integrated nutrient management practices
4. Crop rotation and intercropping
5. Minimum tillage or no-till farming
6. Cover cropping and mulching
7. Fertilizer storage and handling best practices
8. Education and training for farmers and agricultural professionals
9. Policy and regulatory frameworks for sustainable fertilizer use

2. Pesticides and insecticides:

Soil pollution due to pesticides and insecticides has severe environmental and health impacts. Here's a comprehensive overview:

Causes:

1. Overuse and misuse of pesticides and insecticides
2. Lack of integrated pest management (IPM) practices
3. Poor application techniques and equipment
4. Inadequate pesticide storage and disposal

Effects:

1. Soil contamination and persistence
2. Groundwater pollution through leaching
3. Surface water pollution through runoff
4. Soil microorganism disruption and decline

5. Beneficial insect and pollinator decline
6. Human health risks through exposure and food contamination
7. Development of pesticide-resistant pests

Preventive Measures:

1. Integrated Pest Management (IPM) practices
2. Crop rotation and biological control
3. Organic and cultural control methods
4. Targeted and minimal pesticide application
5. Proper application techniques and equipment
6. Pesticide storage and disposal best practices
7. Education and training for farmers and agricultural professionals
8. Policy and regulatory frameworks for sustainable pesticide use
9. Monitoring and testing for pesticide residues
10. Development of alternative and sustainable pest control methods

3. Irrigation:

Soil pollution due to irrigation has significant environmental and health impacts. Here's a comprehensive overview:

Causes:

1. Over-irrigation and waterlogging
2. Use of poor-quality water (e.g., saline, wastewater)
3. Inadequate drainage and water management
4. Lack of soil moisture monitoring
5. Irrigation system design and maintenance issues

Effects:

1. Soil salinization and alkalization
2. Waterlogging and reduced soil aeration
3. Nutrient leaching and depletion
4. Soil structure degradation and erosion
5. Increased risk of soil-borne diseases
6. Reduced crop yields and quality
7. Groundwater contamination

Preventive Measures:

1. Efficient irrigation system design and maintenance
2. Soil moisture monitoring and management
3. Use of good-quality water (e.g., rainwater, freshwater)
4. Drip irrigation and precision irrigation techniques
5. Crop selection and rotation for water efficiency
6. Mulching and cover cropping for soil protection
7. Regular soil testing and nutrient management
8. Integrated water management and drainage systems
9. Farmer education and training on sustainable irrigation practices
10. Policy and regulatory frameworks for water conservation and efficient use

4. E-Waste:

Soil pollution due to e-waste has severe environmental and health impacts. Here's a comprehensive overview:

Causes:

1. Improper disposal of electronic waste (e-waste)
2. Lack of recycling and proper treatment facilities
3. Burning of e-waste in open areas
4. Dumping of e-waste in landfills
5. Contamination of soil through e-waste leachate

Effects:

1. Soil contamination with toxic heavy metals (e.g., lead, mercury)
2. Presence of hazardous chemicals (e.g., PCBs, dioxins)
3. Soil acidification and nutrient depletion
4. Groundwater pollution through leaching
5. Bioaccumulation of toxins in plants and animals
6. Human health risks through exposure and food contamination

Preventive Measures:

1. Responsible e-waste disposal and recycling
2. Establishment of proper treatment and recycling facilities
3. Implementation of extended producer responsibility (EPR)

4. Education and awareness campaigns for consumers
5. Encouragement of sustainable consumption and production patterns
6. Development of environmentally friendly products
7. Regular monitoring and testing of soil and groundwater
8. Remediation and restoration of contaminated soil
9. Policy and regulatory frameworks for e-waste management
10. International cooperation and agreements for e-waste control

UNIT - 3: SOLID WASTE MANAGEMENT

SOLID WASTE GENERATION

In our daily life, we generate lots of used solid materials and throw them away. Solid waste is a complex mixture of diverse materials. The composition of waste varies from season to season, region to region. It cannot be transported through water into the streams nor can be readily escape into the atmosphere. Solid wastes are generated from various sources/activities of the society, such as waste from households, public institutions, offices, markets, restaurants, industry, construction sites, agricultural activities etc.

Sources and Characteristics of Municipal Solid Wastes

Municipal solid waste is defined as waste collected and treated by or for municipalities. It comprises both liquid and solid wastes.

Sources of Municipal Solid Wastes

Main sources of municipal solid wastes may be classified into the following categories:

1. *Residential sources:* Wastes from household and residential areas. These are the major sources of municipal solid wastes.
2. *Institutional sources:* Wastes from government and public institutions such as schools, college universities, government offices etc.
3. *Commercial establishments:* Wastes from business centres such as food and drink establishments, shops, banks etc.
4. *Health facilities:* Wastes from hospitals and other health facilities.
5. *Construction and demolition activities:* Wastes from various types of construction and demolition activities such as construction of apartments, demolition of slums etc.
6. *Industrial sources:* Wastes from various types of industrial processes.
7. *Agricultural sources:* Wastes from agricultural activities.
8. *Open areas:* Wastes from roadside dustbins, street sweeping and other public places.
9. *e-wastes*: Waste from electronic devices like computers, phones, radio etc. and household appliances such as cookers, washing machines etc.

Characteristics of Municipal Solid Wastes

Identification of characteristics of municipal solid waste is important for its proper management. The characteristic of solid waste includes physical and chemical parameters.

Physical characteristics

They are important for the selection and operation of equipment and also for the analysis and design of disposal facilities. It may include the following parameters:

Density: Density of waste is its mass per unit volume (Kg/m3). It is required for the design of landfills, storage, and type of collection and transport vehicles.

Moisture content: It is the ratio of the weight of water to the total weight of waste. Cost of collection, transport and economic feasibility of waste treatment by incineration depends upon the moisture content of the waste.

Size of waste constituents: Size of raised constituents are required for the design of mechanical separators, shredder and waste treatment processes.

Calorific value: It is the amount of heat generated from combustion of unit weight of a substance, expressed in kcal/kg.

Permeability: The permeability of compacted wastes is an important physical property because it governs the movement of liquids and gases in a landfill.

Compressibility: It is the degree of physical changes in the solid waste when subjected to pressure.

Chemical characteristics

The chemical characteristics of Municipal solid waste may include PH value, Nitrogen, Phosphorus, and potassium, total carbon etc. and bio-chemical characteristics may include carbohydrates, proteins, natural fibre etc. Heavy metals, pesticides, insecticides etc. may fall under toxicity characteristics.

Biodegradable and Non-biodegradable Solid Wastes

Biodegradable wastes: These are the waste materials which can be easily degraded by natural factors like microorganisms (e.g., bacteria, fungi etc.), abiotic components (e.g., sunlight, water, oxygen etc.). They transform them into simple organic matters which can be used as fertilizers, manure, compost, biogas and more. Therefore, this makes them eco-friendly. Biodegradable wastes, found in municipal solid wastes include green waste, food waste, paper waste, biodegradable plastics etc. Some of the wastes includes human waste, slaughterhouse waste etc.

Non-biodegradable wastes: These are the wastes which cannot be decomposed or degraded by natural agents. Therefore, they remain in the ecosystem for long duration without decompose and harm our environment. They are not at all eco-friendly. Most of the inorganic waste such as plastic cups, bottles, e-wastes etc. come under non-biodegradable category. Some of these wastes which can be recycled and can be used again are known as “Recyclable waste and those which cannot be used again are known as “non-recyclable waste”.

Sources and Characteristics of e-wastes

Sources of e-waste:

Various source of e-waste may be categorized into following categories:

Home Appliances: It may include, Microwaves, Home Entertainment Devices, Electric cookers, Heaters, Fans etc.

Electronic Utilities: Heating Pads, Remote Controls, Television Remotes, Electrical Cords, Lamps, Night Lights, Treadmills, Smart Watches, Heart Monitors, etc. may be included in this category.

Communications and Information Technology Devices: Cell phones, Smartphones, Desktop Computers, Computer Monitors, Laptops, etc. may fall under this category.

Office Equipment: This category may include, Copiers/Printers, IT Server Racks, IT Servers, Cords and Cables, Phone & PBX systems, Audio & Video Equipment, Network Hardware, Power Strips & Power Supplies, Uninterrupted Power Supplies (UPS Systems), Power Distribution Systems (PDU's), etc.

Medical Equipment: This category may include, Dialysis Machines, Imaging Equipment, Video Equipment, Power Supplies, Uninterrupted Power Supplies (UPS Systems), etc.

Home Entertainment Devices: It may include, DVDs, Stereos, Televisions, Video Game Systems, etc.

Characteristics of e-Waste

e-waste contains both hazardous and non-hazardous substances in their components.

Hazardous substances: The hazardous substances that are mostly found are plastic, lead, mercury, cadmium, arsenic, CFCs, PVC etc. These substances have a great potential to harm or pollute the environment and human health (carcinogenic diseases, liver, kidney, brain damages etc.).

Non-Hazardous substances: These are the substances which can be used again without harming the environment. The different metals when they are recycled back, have a great advantage in the manufacturing processes of different industries. For example, the aluminium, copper and gold that is often found in electronic goods is considered to be non-hazardous. Plastic and glass are the material found in computer parts are also not hazardous.

Sources of Bio-medical waste

The sources of biomedical wastes are the place or location, where these wastes are generated. The sources may be classified into two broad categories: Major and Minor sources.

Major sources generate more amount of the wastes compared to the minor sources and on regular basis. These sources include Hospitals, Emergency care facilities, dialysis centres, transfusion centres, blood banks, clinical laboratories, research laboratories, mortuaries, veterinarians and nursing homes.

Minor sources include medical clinics, cosmetic clinics, home care and paramedics.

Characteristics of Bio-medical waste

Biomedical waste is characterized on the basis of its source of generation and level of hazard to the environment. It can be classified into two categories: non-hazardous wastes and hazardous wastes.

Non-hazardous Bio-medical wastes are type of waste which does not pose any direct threat to the people and environment as they are non-toxic by nature. But still, it should not be thrown be in open areas or sewer line because of the risk it may pose threat to the environment. The non-hazardous wastes may include wash water, paper cartoons, packaging materials, food remnants etc. These wastes are generated mainly from various organizations, maintenance of hospital and health care centres.

Hazardous Bio-medical wastes are the waste which pose direct threat to the people and environment because of their toxic and infectious characteristics. The various hazardous wastes may include:

1. Infectious wastes: Infectious waste containing pathogens (bacteria, viruses, parasites, fungi etc.) in large quantity may pose threat to the humans. Infectious wastes include human/animal tissue, feces and urine from the infected patients, blood-soaked bandages, surgical gloves, cultures, swabs used to inoculate cultures, isolation wards waste, equipment that have been in contact with the infected patient etc.
2. Pathological wastes: Human tissues or fluids e.g., body parts, blood and other body fluids, foetuses etc.
3. Pharmaceutical wastes: It contains pharmaceuticals of expiry date, contaminated pharmaceutical bottles, boxes etc.
4. Radioactive wastes: The treatment where radioactive isotopes are used generate radioactive waste like nuclear medicine treatments, cancer therapies and medical equipment. Radioactive waste has the potential to harm the human health.

METALLIC WASTES

Several kinds of heavy metals such as alloy steel, aluminium, copper, zinc, lead etc. are used in industrial process every day in very large quantity. Rapid industrialization has raised the demand for these metals, at the same time, the reserve of high-grade ores is also depleting. Metallic wastes are generated during various industrial processes. Heavy metals like Au, Ag, Ni, Cu, Zn, Cr etc. are found in these metallic wastes. These valuable metals can be recovered from these waste materials by recycling process such as ***calcination, roasting, smelting, refining etc***. and reused. Microorganisms such as Penicillium, Aspergillus acid, thiobacillus trioxane, Leptospiral ferroxidase and Sulphurous acid are also used for recovering the metals. Metals can be recycled repeatedly without degrading their properties. Steel is the most recycled material on the planet. The other highly recycled metals include aluminium, copper, silver, brass and gold. Because of its recycling property, scrape/waste metal has value, which motivates people to collect it for the sale and recycling processes. Recycling of metals also has environmental impact. It helps in preserving natural resources. It also has social impact as it helps in creating jobs in the society. Recycling process includes collection of scrap metals, sorting from the mixed scrap metal stream, processing, melting in a large furnace, purification, solidifying and transportation.

NON-METALLIC WASTES

A large portion of non-metallic wastes consists of wastepaper, wood, lubricants, plastics, glass, rubber textiles, printed circuit boards etc. Due to growing consumer demand, the quantity of generation of these wastes is increasing day by day. Recycling process of these waste materials is complex and expansive resulting in increased volume of dumps and landfills.

a. Lubricant

It is a substance used to reduce the friction between various parts of the machinery. A lubricant can be in liquid, gaseous or even semisolid forms. Used oils such as engine lubrication oil, hydraulic fluids, and gear oils which are used in cars, bikes, or lawn mowers can pollute the environment, if they are not recycled or disposed-off properly. Used oil can be re-refined into lubricants, processed into fuel oils, and can be used as raw materials for the refining and petrochemical industries.

b. *Plastics*

In our day-to-day life we use many plastic objects like carry bags, containers, bottles, etc. which are normally thrown to the environment after they are being used.

Most of the plastics are non-biodegradable. Plastic pollution on land endangers plants and livestock, as well as humans who live off the land. Also, plastic pollution is seen in oceans which has adverse effects on aquatic lives. Animals can be poisoned by plastic pollution that can have a negative impact on human food supplies.

c. *Rubber*

Rubber is a polymer material and is one of the essential materials in many applications due to its unique properties such as high elasticity, very durable and high resistance to the environmental agents. It is widely used in automobile sectors, healthcare, household etc. However, this unique property of rubber making it very difficult to degrade easily.

Increase of rubber waste has become major threat for the environment globally. Land fill dumping and open burning are among the common methods of disposing waste rubber which leads to water, air and soil pollution. Waste and discarded rubber should be utilized in various applications such as erosion control, back water and floatation device, cement concrete, bitumen products etc.

COLLECTION AND DISPOSAL

Municipal Solid Wastes (MSW) consists of everyday items, we use and throw them away. This mainly comes from our home, schools, colleges, offices, business centers, hospitals etc. These wastes can be categorized into two categories: (i) bio-degradable waste of waste such as food and kitchen waste, flowers, leaves, fruits, paper etc. (ii) non-biodegradable wastes such as construction and demolition

wastes, plastic, glasses, e-wastes etc. Due to rapid urbanization, India is facing big challenges in municipal solid waste management. Solid waste management involves three basic functional elements, collection, processing and disposal of the solid wastes.

Collection of Municipal Solid Waste (MSW)

Solid waste collection is the first functional element of solid waste management. It refers to collection of solid wastes from the places such as residential, institutional, commercial, public parks and industrial area as well. Following basic collection system of solid wastes collection may be adopted based on the availability of services:

Door-to-door collection: This is the most commonly used system of solid waste collection. It is carried out on regular basis as per the pre-informed timings and scheduling.

Collection from roadside: In this system, waste generators place their waste containers or bags on the roadside on a pre-decided day/or days for collection.

Block collection system: In this system, waste generators are responsible for bringing their waste to collection vehicle.

Communal system: In this system, the collection points/container is located in a public place and the waste generators need to keep their waste into the designated place/container. Based on the mode of operation, methods of collection of solid waste from collection points, may be of two types; (i) Hauled-container system and (ii) Stationary-container system.

Hauled-container system*:* In this system an empty storage container also called as drop-off box is hauled to the storage site to replace the container full of waste, which is then hauled to the processing point, transfer station or disposal site.

Stationary-container system*:* In this system the containers used for the storage of waste, remain at the point of collection. The collection vehicle stops alongside the storage containers, and collection crews load the waste from the storage containers into the collection vehicles and then transport the wastes to the processing point, transfer station or disposal site.

Disposal of Municipal Solid Waste (MSW)

Disposal is the third functional element of solid waste management after collection and processing. In past, dumps and disposal at river and sea were the common practice. Now a days, due to inherent environmental problem, it is not allowed. However, waste dumping in open area and burning continue to one of the most popular methods in India. Most of the cities and town dispose of their wastes in low-lying areas in the outskirts of the city which leads to various environmental and human health issues. The wastes dumped on the roadside, sometimes overflowing from drains or floating on the surface of the river is very common phenomenon in India. At present, sanitary landfill method is used more frequently for the disposal of municipal solid waste.

3R, Principles

The 3R principle refers to reducing waste, reusing and recycling resources and products. All 3Rs help us to reduce the amount of waste we generate. It is one of the principles of solid waste management. Basically, the 3R concept is a sequence of steps on how to manage waste properly. The first of 3Rs, reducing is the best way to go about managing solid waste. It is quite simple, the less we use the less waste we will produce. Some of ways mentioned below may help in reducing the waste generation:

• Buying products with less packaging to minimize the waste generated from product packaging.

• Avoiding disposable goods such as paper plates, cups, napkins, etc.

• Buying durable goods to avoid frequent disposal.

• Use electronic mail for communication wherever possible.

The second of 3Rs, is reuse. It makes economic and environmental sense to reuse products. If you reuse something as opposed to throwing it keeps away the waste from landfills. Sometimes it involves creativity also. Some of the ways are mentioned below:

- Reuse products in different ways. For example, use a coffee can to pack tiffin; use plastic microwave dinner trays as picnic dishes.
- Sell old clothes, appliances, toys and furniture or donate them to charities.
- Use ceramic coffee mug instead of paper cups.
- Use grocery bags or bring your own bags to the store.

The final and probably the best-known R of 3Rs stands for recycling. It involves manufacturing of new products from the old and used materials, using necessary recycling process. Begin recycling at home and at work:

- Buy products from recycled materials.
- Purchase recycled materials for office supply, equipment etc.
- Use recycled paper for letterhead, copier paper, newsletter etc.

Energy Recovery

Energy recovery from waste means conversion of waste into various forms of energy such as heat, electricity, fuel etc. It can be done through variety of processes, such as combustion, gasification, anaerobic digestion etc. Municipal solid waste (MSW) contains both organic as well as inorganic substances. The latent energy present in its organic fraction can be recovered for suitable utilization by adopting suitable waste processing and treatment methodologies.

The option of energy recovery from wastes may be kept open and should be incorporated in the over-all scheme of waste management along with the 3Rs concept. Energy can be recovered from the organic fraction of waste (biodegradable as well as non-biodegradable) basically through two methods as mentioned below:

(i) ***Thermo-chemical conversion***: In this process, organic matters are decomposed using thermal de-composition to produce either heat energy or fuel oil/gas. This process is useful for the wastes

containing high percentage of organic non-biodegradable matter and low moisture content. The main technological options under this category include Incineration and *Pyrolysis/ Gasification*.

(ii) ***Bio-chemical conversion***: In this process, organic matters are decomposed by microbial action to produce methane gas. This process is preferred for wastes having high percentage of organic bio-degradable matter with high level of moisture/ water content, which helps microbial activity. The main technological option under this category is *Anaerobic Digestion.*

Parameters affecting Energy Recovery: The parameters which affect the recovery of Energy from Wastes (including MSW), includes: Quantity of waste, and its Physical and chemical characteristics (quality). The actual production of energy also depends upon the specific treatment process employed, in addition to the above two parameters.

Sanitary landfill

Sanitary landfill is a method of waste disposal used more frequently now a days. It is an engineering burial of wastes. It consists of spreading waste on the ground, compacting it, and covering it with the soil. There are generally two methods of sanitary land filling: Area method and Trench method.

The area method is used, when excavation is not possible, especially when the ground water level is high.

Trench method is used when it is possible to excavate. This method has the benefit of having the cover material right at the site from the earth excavated from the trench. Sanitary landfill sites are kept isolated from the environment until it become safe. It is considered to be safe for the environment when it is completely degraded biologically, chemically and physically. The gas produced from the byproducts of sanitary landfill can be used as fuel for combustion or they can be processed into another fuel.

Hazardous waste

The wastes containing toxic substances are known as Hazardous waste. These are generally generated from industry, hospital and residence. These wastes may be in the form of solids, liquids or gases. These wastes can have very harmful effects on the human health and environment, when left inappropriately treated or managed. Improper hazardous waste storage or disposal frequently contaminates ground water and surface water. It can also be source of dangerous land pollution. Many pesticides, herbicides, paints, industrial solvents, fluorescent light bulbs and mercury-containing batteries are classified as hazardous wastes, so are the medical waste products such as cultures, human tissue, contaminated gloves, sharps, PPE kit etc.

Because of the harmful nature hazardous waste cannot be disposed of by common means. Depending on the physical and chemical state of the waste, treatment and solidification processes might be required. Hazardous waste needs to be treated scientifically. Hazardous waste may contain either of the properties like ignitability, reactivity, corrosivity and toxicity.

Disposal of Hazardous waste

The disposal of hazardous wastes in a proper manner is very much essential for both citizens and business owner as well. In general, these wastes were regularly disposed of into landfills. Our natural water systems used to get contaminated due to continuous seeping of chemicals from the dumped wastes which in turn were very much harmful for humans as well as for animals and aquatic organisms. Hence, it became very much essential that the hazardous wastes are properly disposed so that these harmful effects can be reduced as much as possible. Some of the methods discussed below can be adopted for the safe disposal of hazardous wastes:

Incineration: By burning the waste materials in high temperature can destroy the toxic wastes. Although the method of incineration releases toxic gases which may affect our environment, but now a days more effective incinerators are developed that limit the quantity of emissions released in the atmosphere. Flammable wastes can also be burned and used as energy sources.

Recycling: It is one of the best methods to reduce quantity of hazardous wastes. We must try to reuse the used materials instead of just throwing them away, although it may need some creativity. Most flammable materials can be recycled into industrial fuel. Some materials with hazardous constituents can be recycled, such as lead acid batteries etc.

Sharing or Donating: If we have anything extra and find it unusable, may be shared or donated to someone who need it. By sharing or donating, we will be able to reduce hazardous wastes generation.

Carbon footprint

A carbon footprint is a measure of the amount of greenhouse gases released into the atmosphere by a person, organization, event, or product. It's calculated by adding up all the emissions from every stage of a product or service's life, including production, use, and end-of-life.

- Carbon footprints include emissions from all gases that contribute to global warming, such as carbon dioxide (CO_2), methane (CH_4), nitrous oxide (N_2O), and fluorinated gases.
- Carbon footprints are usually expressed in units of carbon dioxide equivalents, which accounts for the different amounts of heat each gas traps.
- We can reduce our carbon footprint by making small changes to our actions, such as eating less meat, taking fewer connecting flights, and line drying our clothes. We can also use public transportation, bicycles, or electric scooters.

Carbon credit

A carbon credit is a permit that allows the owner to emit a certain amount of carbon dioxide or other greenhouse gases. Carbon credits are generated by projects that reduce, avoid, or remove greenhouse gas emissions.

- Carbon credits are generated by projects that remove carbon from the atmosphere, such as reforestation, or reduce the amount of carbon released into the atmosphere, such as renewable energy projects.
- One carbon credit represents the reduction or removal of one metric ton of carbon dioxide or its equivalent.
- Carbon credits can be bought, sold, transferred, and exchanged in carbon markets.
- Organizations that are regulated under a cap-and-trade system can use carbon credits to meet their cap. If an organization produces fewer tons of carbon emissions than it is allocated, it can sell or hold the remaining carbon credits.
- Projects that generate carbon credits are independently audited to verify the amount of carbon emissions they have avoided or reduced.
- It can also have other positive benefits, such as empowering communities, protecting ecosystems, and restoring forests.

ENVIRONMENTAL MANAGEMENT IN THE FABRICATION INDUSTRY

An environmental management system (EMS) is a structured system designed to help manufacturing industries including fabrication industry to manage their environmental impacts and improve environmental performance caused by their products. Fabrication industry requires to adopt strategies and activities that help in reducing the environmental impact. ISO14001:2015 sets out the criteria for an environmental management system which helps an organization to set up their effective environmental management system.

ISO14001:2015 specifies the requirements for an EMS that an organization or industry can use to improve its environmental performance and manage its environmental responsibilities in a systematic manner that contributes to the environmental sustainability. It also helps an organization/industry to achieve the expected outcomes of its EMS, which provide value for the environment.

UNIT –4: ELECTROCHEMISTRY AND CORROSION

Electrochemistry is the branch of chemistry which deals with the study of inter conversion of electrical energy and chemical energy.

Electronic concept of Oxidation, Reduction and Redox reactions:

Oxidation: Oxidation may be defined as the loss of electron/s by an atom, ion or molecule.

Examples:

$Na - e^- \rightarrow Na^+$

$Ca - 2e^- \rightarrow Ca^{2+}$

$Fe^{2+} - e^- \rightarrow Fe^{3+}$

Reduction: Reduction may be defined as the gain of electron/s by an atom, ion or molecule.

Examples:

$Na^+ + e^- \rightarrow Na$

$Ca^{2+} + 2e^- \rightarrow Ca$

$Fe^{3+} + e^- \rightarrow Fe^{2+}$

Redox Reaction or Net reaction: The chemical reaction in which both oxidation and reduction takes place simultaneously is called a redox reaction. Oxidation and reduction go side by side.

Examples:

$Zn + Cu^{2+} \rightarrow Zn^{2+} + Cu$

$Cl_2 + 2Fe^{2+} \rightarrow 2Cl^- + 2Fe^{3+}$

$H_2 + F_2 \rightarrow 2HF$

Electrolytes: The chemical substances which allow electricity to pass through their molten, fused or solution state are called electrolytes. Examples:

- All acids: HCl, HNO_3, H_2SO_4, H_2CO_3, CH_3COOH, etc.
- All alkalis: NaOH, KOH, $Ca(OH)_2$, NH_4OH, etc.
- All salts: NaCl, KCl, $CaCl_2$, $NaNO_3$, etc.

Electrolytes undergo dissociation/ionization in to ions in aqueous solution.

Non-electrolytes: The chemical substances which do not allow electricity to pass through their molten, fused or solution state are called non-electrolytes. Examples: Uera, Sugar, glucose, fructose, sucrose, etc.

Non-electrolytes do not ionise in aqueous solution.

Classification of Electrolytes: Depending upon the degree of ionisation/dissociation electrolytes may be classified into two types. (a) Strong electrolytes and (b) weak electrolytes.

(a) Strong Electrolytes: The electrolytes which undergo almost complete ionisation in aqueous solution are called strong electrolytes. Examples:

- Acids like: HCl, HNO_3, H_2SO_4, etc.
- Alkalis like: NaOH, KOH, etc.
- All salts: NaCl, KCl, $CaCl_2$, $NaNO_3$, etc.

(b) Weak Electrolytes: The electrolytes which undergo partial ionisation in aqueous solution are called weak electrolytes. Examples:

- Acids like: H_2CO_3, HCOOH, CH_3COOH, etc.
- Alkali like: NH_4OH

Faraday's 1st Law of Electrolysis: The law may be stated as "During electrolysis, the amount of substances deposited/liberated at an electrode is directly proportional to the quantity of electricity passed through the electrolyte".

Mathematically,

$$W \propto Q$$

But, Q = I X T

$$\Rightarrow W \propto I \times T$$

$$\Rightarrow W = Z \times I \times T$$

Where, W = Amount of substance in gram

Q = Quantity of electricity or Charge in coulomb

I = Current in ampere

t = time of flow of current in second.

Z = Electrochemical equivalent (ECE)

When, I = 1 ampere; t = 1 second,

W = Z

Thus, electrochemical equivalent is numerically equal to the amount of substance deposited or liberated at the electrode when 1 ampere of current is passed through an electrolyte for 1 second. Or it

is the amount of substance deposited or liberated at the electrode when 1 coulomb of charge is made to flow through an electrolyte.

A bigger unit of charge is Faraday.

1 Faraday = 96500 coulomb

Experimentally it is observed that when 1 Faraday (96500 C) of charged is passed through an electrolyte 1gram equivalent of the substance is deposited at the electrode.

96500 Coulomb of charge deposits 1 gram equivalent

$\Rightarrow$ 1 coulomb of charge deposits $\frac{1 gram equivalent}{96500 C}$

Hence, Electrochemical Equivalent (Z) = $\frac{1 gram equivalent}{96500 C} = \frac{Atomic mass / Valency}{96500}$

Unit of 'Z' is gram equivalent/coulomb.

Note: 1 mole of electrons carries 1 Faraday or 96500 Coulomb of charge.

Question 1: How many grams of silver will be deposited at the cathode by the passage of 10 ampere of current through an aqueous solution of $AgNO_3$ for 1 hour?

Solution:

Given Data: I = 10 Ampere

t = 1 hr = 3600 Sec.

$$Z = \frac{1 gram equivalent}{96500 C} = \frac{Atomic mass / Valency}{96500} = \frac{108/1}{96500} = \frac{108}{96500} = 0.0011$$

Applying Faraday's 1st Law of electrolysis

W = ZIt = 0.0011 X 10 X 3600 = 39.6 gram.

Question 2: How many coulombs are required for the following changes?

i. One mole Ca^{2+} into Ca.

ii. Two moles of Al^{3+} into Al.

Solution:

i. $\mathbf{Ca^{2+} + 2e^- \rightarrow Ca}$

1 mole of electrons carries 96500 coulombs.

$\Rightarrow$ 2 moles of electrons carry (2 x 96500) coulomb = 193000 Coulombs.

ii. $\mathbf{2Al^{3+} + 6e^- \rightarrow 2Al}$

1 mole of electrons carries 96500 coulombs.

$\Rightarrow$ 6 moles of electrons carry (6 x 96500) coulomb = 579000 Coulombs.

Question 3: How many coulombs of charge are required to get 10 grams of calcium from molten $CaCl_2$?

Solution:

W = 10 gm, Q =?

W = Z Q

$$= \frac{Eq.mass/Valency}{96500} \text{ x Q}$$

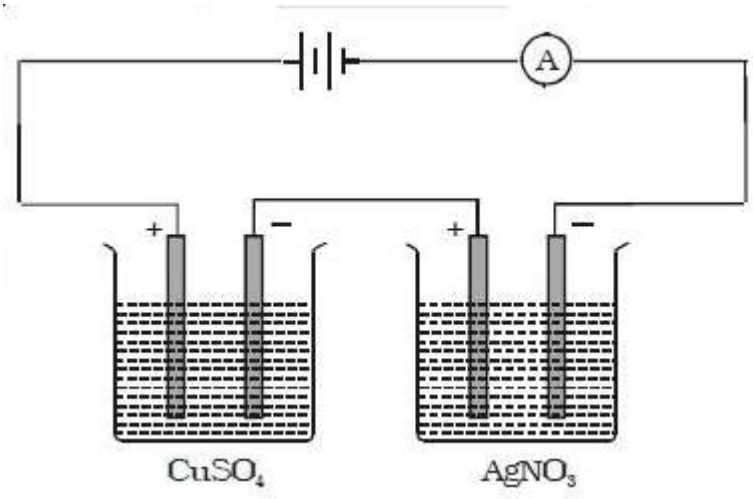
$$\Rightarrow 10 = \frac{40/2}{96500} \text{ x Q} \quad \Rightarrow \quad Q = 10 \times \frac{96500}{20} = 48250 Coulomb$$

<u>Faraday's 2nd Law of Electrolysis</u>:

The law may be stated as "when the same quantity of electricity is passed through different electrolytes connected in series, the amounts (W) of substances deposited at various electrodes are directly proportional to their equivalent masses (E)".

Mathematically,

$$W \propto E$$



Let us consider two electrolytic solutions $AgNO_3$ and $CuSO_4$ taken in two different electrolytic cells. Both the cells are connected in series and the same quantity of electricity is passed through the electrolytes.

Applying Faraday's 2nd law of electrolysis,

$W_{Ag} \propto E_{Ag}$ ----------(1)

$W_{Cu} \propto E_{Cu}$ ---------(2)

From equation (1) and (2), we have

$$\Rightarrow \frac{W_{Ag}}{W_{Cu}} = \frac{E_{Ag}}{E_{Cu}} \quad \Rightarrow \quad \frac{W_{Ag}}{W_{Cu}} = \frac{\frac{E_{Ag}}{96500}}{\frac{E_{Cu}}{96500}} = \frac{Z_{Ag}}{Z_{Cu}}$$

In general, $\boxed{\frac{W_1}{W_2} = \frac{E_1}{E_2} = \frac{Z_1}{Z_2}}$ or $W \propto E \propto Z$

Question: 1. The same quantity of electricity is passed simultaneously through acidulated water and copper sulphate solution. Weights of hydrogen and copper liberated are 0.0132 and 0.4164 gram respectively. Find out the equivalent weight of copper.

Solution: Weight of hydrogen W_{H_2} = 0.0132 gm

Weight of copper W_{Cu} = 0.4164 gm

Equivalent weight of hydrogen E_{H_2} = 1.008

Equivalent weight of copper E_{Cu} = ?

Applying Faraday's 2nd law of electrolysis,

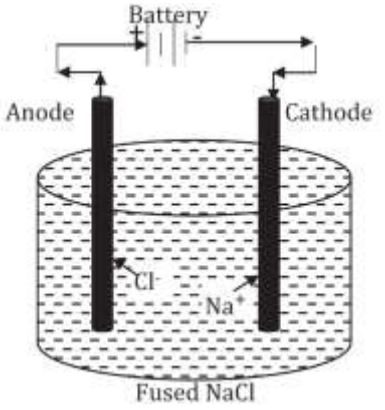
$$\frac{W_{H_2}}{W_{Cu}} = \frac{E_{H_2}}{E_{Cu}} \Rightarrow E_{Cu} = E_{H_2} \times \frac{W_{Cu}}{W_{H_2}} = 1.008 \times \frac{0.4164}{0.0132} = 31.79$$

Industrial Application of Electrolysis:

The significant industrial applications of electrolysis are as follows

1. Electrometallurgy
2. Electroplating
3. Electrolytic Refining

1. **Electrometallurgy:** The process of extraction of metals from their ores by electrolysis is called electrometallurgy. Some active metals like sodium, magnesium, potassium and calcium are extracted by the electrolysis of their corresponding fused metal salts, while other metals are obtained from its aqueous solution. The fused metal salt (acts as electrolyte) is taken in an electrolytic cell with suitable electrodes. When electricity is passed through the electrolyte, metal gets deposited at the cathode.



Example: Extraction of sodium metal from fused NaCl.

The fused NaCl is taken in an electrolytic cell using graphite electrodes. When electricity is passed through the fused NaCl, the following changes take place at different electrodes.

$NaCl \rightarrow Na^+ + Cl^-$

At Anode: $2Cl^- - 2e^- \rightarrow Cl_2$ (liberated)

At Cathode: $2Na + 2e^- \rightarrow 2Na$ (deposited)

Thus, metallic sodium is collected at the cathode.

2. **Electroplating:** The process of applying coating of one metal (superior) over another metal (inferior) by electrolysis is called electroplating. Electroplating is carried out for three main purposes: (a) protection, (b) decoration, and (c) repairing.

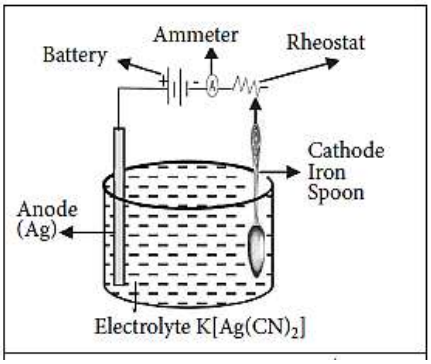
In this process, the article to be electroplated is cleaned thoroughly by the hot solution of alkali or soap to remove the grease or grit or dirt. Then it is treated with dilute acid to remove the oxide layer or other impurities that stickup to the article. The treatment with dilute acids is called *acid pickling*.

Further, it is washed with water and then carefully polished by polishing paper. The cleaned article is then suspended into the electrolytic cell and mount as a cathode. A pure metal plate or rod whose coating is to be applied is used as anode. A suitable aqueous salt solution of the anodic metal is used as electrolyte.

On passing electric current, the metallic ions from the electrolyte get deposited on the article made as a cathode. The equivalent amount of anode gets dissolved in the form of metal ions and passes into the electrolyte.

Smooth and brighter deposits are obtained

i) at low temperature,
ii) high current density,
iii) high metal ion concentration of electrolyte and iv)
iv) at specific pH.



Example: Electroplating of silver on the iron spoon is carried out in a rectangular tank of steel. The iron spoon, which is to be electroplated, is cleaned thoroughly by boiling with caustic soda to remove dirt or grit or grease. Further, it is washed with water until it is free from caustic soda. Then it is placed in an acid tank containing dilute acid to remove the oxide layer present on the spoon. Further, it is washed with water to remove excess acid and polished with polishing paper. Then iron spoon is made as a cathode, and the anode is made up of a pure silver metal plate. The anode and cathode are suspended in the electrolyte in the cell of potassium argentocynide $K[Ag(CN)_2]$. On passing the direct electric current, at applied voltage, the iron spoon gets plated with smooth and brighter deposits of silver. Silver anode gets slowly dissolved in solution by giving Ag^+ ions.

Reaction at Anode:

$$Ag - e^- \rightarrow Ag^+$$

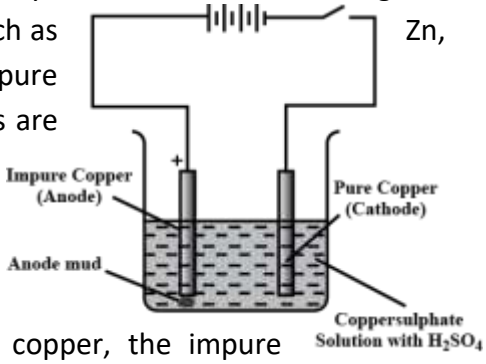
(silver anode)

Reaction at Cathode:

$$Ag^+ + e^- \rightarrow Ag$$

(From Electrolyte)

3. **Electrorefining:** The process of purifying impure metals by electrolysis is called electrorefining. This method is employed to refine the less electro positive metals such as Zn, Pb, Al, Cu etc. The impure metal bar is used as anode while a pure metal (same metal) bar is taken as cathode. Both the electrodes are dipped in a suitable aqueous salt solution of the concerned metal. During the process of electrolysis, the impure metal dissolves in its aqueous salt solution providing metal ions which get discharged and deposited over the cathode.



Example: Electrorefining of copper: In the electrorefining of copper, the impure

copper is used as anode, while a pure copper plate is used as cathode. Both the electrodes are dipped in an acidified $CuSO_4$ solution which acts as an electrolyte. When electricity is passed, the copper ions present in the electrolyte migrate towards the cathode where they get discharged and deposited.

Reaction at Anode:

$$Cu - 2e^- \rightarrow Cu^{2+}$$

(Impure Copper anode)

Reaction at Cathode:

$$Cu^{2+} + 2e^- \rightarrow Cu$$

(From Electrolyte)

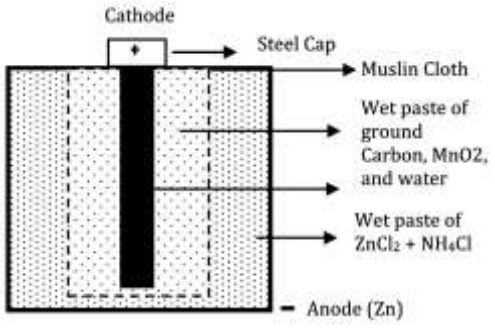
On the other hand, an equivalent quantity of copper dissolves to form copper ions. The impurities present in the impure copper bar settle down at the bottom of the electrolytic tank and is called anode mud. In this way pure copper is obtained at the cathode.

Primary Cell or Dry Cell

Primary cells are the electrochemical cells which are non-rechargeable. The electrochemical reactions in these batteries are non-reversible.

Construction:

The dry cell consists of a graphite rod at the centre surrounded by a paste of manganese dioxide (MnO_2), ground carbon and water. This whole arrangement is placed in muslin cloth, which allows some ions to pass through it. At the top of the graphite rod steel/brass cap is present, which represents the positive terminal. Around the muslin cloth, a paste of zinc chloride and ammonium chloride is covered with a metallic zinc container that acts as an anode representing a negative terminal.



Reaction at Anode (At Zn Electrode)

$Zn \rightarrow Zn^{2+} + 2e^-$ (Oxidation Reaction)

Reaction at Cathode

$2MnO_2 + 2NH_4^+ + 2e^- \rightarrow Mn_2O_3 + 2NH_3 + 2H_2O$ (Reduction Reaction)

As a result of redox reaction in the cell, electrons flow from anode to cathode, which represents the generation of electricity. A primary cell develops 1.5 V of electricity. As chemical are responsible for electricity generation, this cell is known as an electrochemical cell, and hence spontaneous chemical reactions are taking place. The dry cell does not have a long life, as acidic ammonium chloride corrodes the zinc container, even when it is not in use.

Secondary Cell

A secondary cell, also known as a rechargeable battery, is a cell that can be recharged after use. In this type of cells chemical energy is converted into electrical energy when charged, and the chemical reaction can be reversed when discharged. They are used in many consumer electronics and electric vehicles.

The process of storing electrical energy in an accumulator is called charging, while the reverse process of providing electrical energy is known as discharging. Several storage cells are connected in series to make up a storage battery. These storage cells are of different types like alkaline type, lead-acid storage cells, lithium-ion batteries.

(A) Lead- Acid Storage cell or Lead Accumulator

Storage cells are operated in both like voltaic cells and as electric cells. When operating as a voltaic cell, it supplies electrical energy and is finally discharged. When being recharged, the cell operates as an electrolytic cell.

In a lead-acid storage cell, the cathodes are made of spongy lead (Pb), and the anodes are made of lead oxide (PbO_2).

The electrodes are connected in parallel. Lead plates are placed in between the two lead oxide plates. These plates are separated from adjacent ones by insulators such as a strip of glass or rubber, or wood. These are then immersed in 20% dilute H_2SO_4 (with specific gravity 1.15 at 25°C).

During discharging:

During discharging, the lead electrodes enter into the solution with the formation of lead ions. Therefore, oxidation takes place at the lead electrode.

Reactions at Lead (Pb) Electrode

$Pb \longrightarrow Pb^{2+} + 2e^-$ (Oxidation Reaction)

Active electrode Pb enters into the electrolyte in the form of ions by the loss of electrons. The lead ions formed react with sulphate ions to form lead sulphate precipitate.

$Pb^{2+} + SO_4^{2-} \longrightarrow PbSO_4 \downarrow$ (Lead sulphate Precipitate)

Reactions at Lead oxide (PbO_2) Electrode

Lead oxide electrode also enters into the electrolyte in ionic form by accepting electrons from the external circuit. Hence reduction reaction occurs at the lead oxide electrode. Here reduction takes place.

$PbO_2 + 2e^- + 4H^+ \longrightarrow Pb^{2+} + 2H_2O$ (Reduction Reaction)

Lead ions formed react with sulphate ions from the electrolyte to form lead sulphate precipitate.

$Pb^{2+} + SO_4^{2-} \longrightarrow PbSO_4$

Lead Sulphate

So, the overall redox reaction in lead storage cell is:

$Pb + PbO_2 + 4H^+ + 2SO_4^{2-} \longrightarrow 2PbSO_4 + 2H_2O + Energy$

During discharging, lead and lead oxide electrodes slowly dissolve in the electrolyte, releasing Pb^{2+}. The amount of lead sulphate and water increases in the electrolytes during discharging while the percentage of H_2SO_4 decreases during discharging. A pair of Pb and PbO_2 gives 2 Volt of electricity. It gives 2 Volt of electricity during fully charged conditions, gradually decreasing during discharging up to 1.6 to 1.7 Volt.

During charging:

When both electrodes are covered with lead sulphate, the cell stops functioning as a voltaic. The reactions taking place during discharging are reversed by passing external electromotive force (e.m.f.) greater than 2 volts from an external supply.

Reactions at Pb (Lead) Electrode

Pb^{2+} ions are present in the electrolyte as $PbSO_4$.

$Pb^{2+} + 2e^- \longrightarrow Pb$ (Reduction Reaction)

Regeneration of electrode

Reactions at PbO_2 (Lead oxide) Electrode

$Pb^{2+} + 2H_2O \longrightarrow PbO_2 + 2e^- + 4H^+$ (Oxidation Reaction)

Regeneration of PbO_2 electrode

Hence net reaction during charging is

$2PbSO_4 + 2H_2O + Energy \longrightarrow Pb + PbO_2 + 4H^+ + 2SO_4^{2-}$

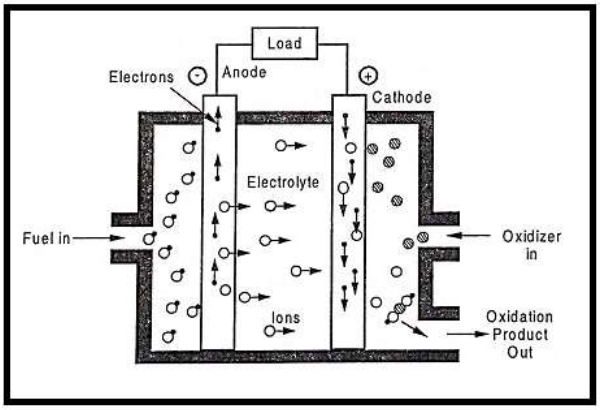
The redox cell reaction during discharging and charging can be shown as

$$PbO_2 + Pb + 2H_2SO_4 \underset{\text{Charging}}{\overset{\text{Discharging}}{\rightleftharpoons}} 2PbSO_4 + 2H_2O$$

Distinction between Electrolytic cell and Electrochemical cell		
1	It converts electrical energy into chemical energy.	It converts chemical energy into electrical energy.
2	Electricity is consumed. Require source of energy.	Produce electricity, it is a source of energy.
3	Redox reactions are non-spontaneous chemical reactions	Redox reactions are spontaneous chemical reactions.
4	Anode (+ve) terminal oxidation take place	Anode (-ve) terminal oxidation take place
5	Cathode (-ve) terminal reduction take place	Cathode (+ve) terminal reduction take place

(B) <u>Fuel Cell</u>

Fuel cells are electrochemical cells which can convert the chemical energy contained in a readily available fuel oxidant system into electrical energy by an electrochemical process, in which fuel is oxidized at the anode. A fuel cell consists of an electrolyte and two electrodes. However, the fuel and the oxidizing agent are continuously and separately supplied to the cell's electrodes at which they undergo reactions. Fuel cells have high efficiency and are pollution free.



The basic arrangement in the fuel cell can be represented as follows:

Fuel | Electrode | Electrolyte | Electrode |oxidant

The essential process in the fuel cell is

Fuel + Oxygen ⟶ Oxidation products +Electricity

One of the simplest and most successful fuel cell is the hydrogen-oxygen fuel cell. It consists of an electrolytic solution such as 25% KOH solution and two inert porous electrodes. Hydrogen and oxygen gases are bubbled through the anode and cathode compartment, respectively, where the following reactions take place

At Anode $2H_2 \longrightarrow 4H^+ + 4e^-$

$4H^+ + 4OH^- \longrightarrow 4H_2O$

At Cathode $O_2 + 2H_2O + 4e^- \longrightarrow 4OH^-$

Redox $2H_2 + O_2 \longrightarrow 2H_2O$

The standard emf of the cell is 1.23 V

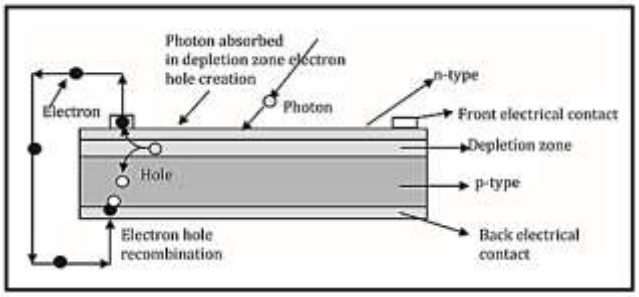
In actual practice, the emf of the cell is 0.8 to 1.0 V. Usually, large numbers of these cells are stacked together in series to make a battery called fuel cell battery or fuel battery.

Hydrogen gas reacts with electrolytes and solid conducting structures to produce $2H^+$ ions. Two protons react with hydroxyl ions of the electrolyte to form water, which dilutes the KOH electrolyte. Two electrons are made available to the external circuit. The hydroxyl ions which are thus used up are replenished from the cathode reaction, in which O_2 reacts with two water to produce $4OH^-$ ions, taking up the four electrons from the outer circuit.

When hydrogen is used as fuel, the electrodes are made of either graphite impregnated with finely divided platinum, or an alloy of palladium and silver, or nickel. Electrolytes used most often are aqueous KOH or H_2SO_4 solution.

(C) Solar cell

Solar energy obtained from the sun is converted into electrical energy directly by using a photovoltaic cell. A photovoltaic cell consists of a p-type semiconductor (such as Si doped with B) in contact with an n-type semiconductor (such as Si doped with P).



The sunlight travels in packets of energy called photons. The electric current is generated inside the depletion zone of the p-n junction diode. When a photon of light is incident and absorbed by one of these atoms in the n-type silicon material, it will dislodge an electron, creating a free electron and a hole. The free electron and hole have sufficient energy to jump out of the depletion zone. The electron is attracted to the positive charge of the p-type material and travels through the external circuit, creating a flow of electric current. The hole created by the dislodged electron is attracted to the negative charge of n-type material and migrates to the back electrical contact. Electrons move from n-type material and enters into p-type material from back electrical contact where it combines with the hole which restores electrical neutrality.

Generally, a solar panel is made up of 32, 36, 48, 60, 72 and 96 photovoltaic cells. The solar array is a system made up of a group of solar panels connected together. A solar panel comprising 32 cells typically can produce 14.72 volts output.

Corrosion:

The process of deterioration or destruction and consequent loss of a solid metallic surface through an unwanted chemical, electrochemical and biochemical attack by its environment is called corrosion.

Examples:

(i) Rusting of Iron

(ii) Tarnishing of silver

(iii) Formation of Green Film on Copper/Bronze.

Types of corrosion

The primary factors which initiate corrosion of metals are atmospheric air and water. Based on the environment, corrosion is classified into

(i) Dry or Chemical Corrosion (ii) Wet or Electrochemical Corrosion

(i) Dry Corrosion or Chemical Corrosion:

It occurs in the absence of moisture or conducting electrolyte medium. Chemical corrosion is defined as the direct chemical attack on metals by atmospheric gases such as oxygen, halogen, hydrogen sulphide, sulphur dioxide, nitrogen, anhydrous inorganic liquid etc. present in the environment. This causes an oxide/sulphide layer to form over the surface of metals and alloys.

Example:

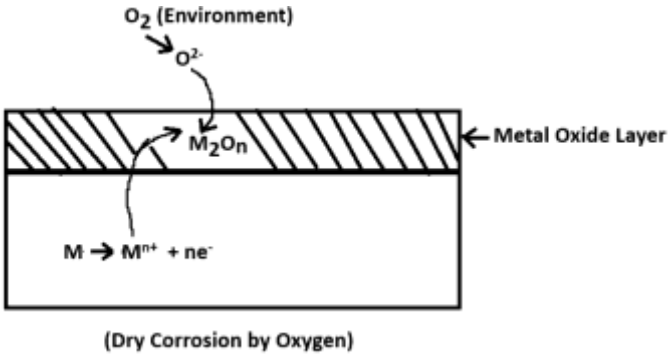
(i) Silver materials undergo chemical corrosion by atmospheric H_2S gas.
(ii) Iron metal undergoes chemical corrosion by HCl gas.

Types of dry or chemical corrosion

- Corrosion by Oxygen or Oxidation corrosion
- Corrosion by Hydrogen or other gases.

Corrosion by Oxygen or Oxidation Corrosion:

This type of corrosion occurs due to the direct attack of oxygen on the metallic surface at low or high temperatures in the absence of moisture. Alkali metals (Li, Na, K, etc.) and alkaline earth metals (Mg, Ca, etc.) are rapidly corroded by oxygen at low temperature. On the other hand, almost all metals (except Ag, Au and Pt) are oxidized.



(Dry Corrosion by Oxygen)

The nature of the oxide formed plays an important role in oxidation corrosion process.

Metal + Oxygen $\rightarrow$ Metal oxide (corrosion product)

When oxidation starts, a thin layer of oxide is formed on the metal surface and the nature of this film decides the further action. Different metals form different types of layers with oxygen.

(i) **Stable layer -** A Stable layer is fine grained in structure and can get adhered tightly to the parent metal surface. Hence, such a layer behaves as protective coating which prevents further attack of oxygen. The oxide films on Al, Sn, Pb, Cu, Pt, etc., are stable and tightly adhering in nature.

(ii) **Unstable Oxide layer:** This is formed on the surface of noble metals such as Ag, Au, Pt. The metallic state is more stable than oxide. Hence, it decomposes back into the metal and oxygen. Hence, oxidation corrosion is not possible with noble metals.

(iii) **Volatile Oxide layer:** The oxide layer volatilizes as soon as it is formed. Hence, always a fresh metal surface is available for further attack. This causes continuous corrosion. MoO_3 is volatile in nature.

(iv) **Porous layer:** In such a case, the atmospheric oxygen has access to the underlying surface of metal, through the pores or cracks of the layer, thereby the corrosion continues unobstructed, till the entire metal is completely converted into its oxide. Magnesium alloys undergo this type of corrosion.

Wet or Electrochemical corrosion

Electrochemical corrosion involves:

i The formation of anodic and cathodic areas or parts in contact with each other
ii Presence of a conducting medium
iii Corrosion of anodic areas only and
iv Formation of corrosion product somewhere between anodic and cathodic areas.

This involves the flow of electron-current between the anodic and cathodic areas.

At anodic area oxidation reaction takes place (liberation of free electron). Hence corrosion always occurs at anodic areas.

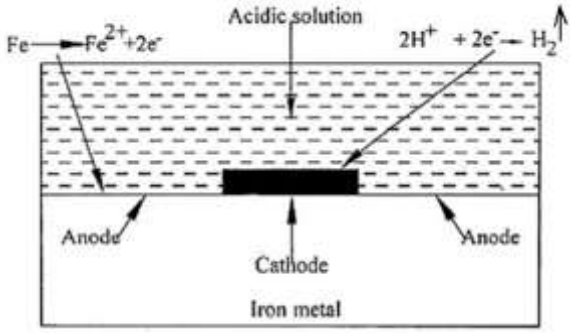
$$M(metal) \rightarrow M^{n+} + ne^{-}$$

The metal ions (M^{n+}) thus formed dissolves in solution and form compounds such as oxide.

At cathodic area, reduction reaction takes place (gain of electrons). At the cathodic part, dissolved constituents in the conducting medium accepts the electrons to form some ions like OH^- and O^{2-}.

Depending on the nature of the corrosive environment, cathodic reaction consumes electrons with either by

(a) Evolution/Liberation of Hydrogen
(b) Absorption of Oxygen



(A) Hydrogen Evolution / Liberation Type:

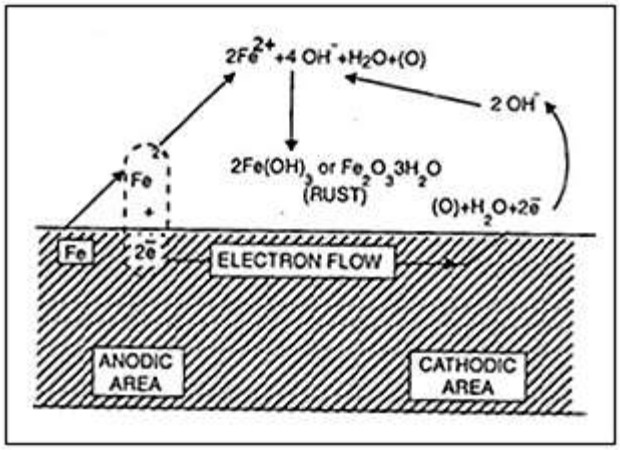
All metals above hydrogen in the electrochemical series have a tendency to get dissolved in acidic solution with simultaneous evolution of hydrogen. It occurs in acidic environment. Consider the example of iron

At Anode: $Fe \longrightarrow Fe^{2+}+2e^{-}$

These electrons flow through the metal from anode to cathode, where H^+ ions of acidic solution are eliminated as H_2 gas.

At Cathode: $2H^+ + 2e^- \longrightarrow H_2$

(B) Oxygen Absorption Type:



Rusting of iron in neutral aqueous solution of electrolytes like NaCl solution in the presence of atmospheric oxygen is a common example of this type of corrosion. The surface of iron is usually coated with a thin film of iron oxide. However, if this iron oxide film develops some cracks, anodic areas are created on the surface; while the well metal parts act as cathodes.

At Anode: At the anodic area the metal get oxidized into metal ion with the liberation of electrons.

$Fe \rightarrow Fe^{2+} + 2e^-$

The free electrons flow towards the cathodic area where they react with moist air (oxygen) to form hydroxide ions.

At Cathode:

$\frac{1}{2} O_2 + H_2O + 2e^- \rightarrow 2OH^-$

The Fe^{2+} ions and OH^- ions diffuse and form, ferrous hydroxide.

$Fe^{2+} + 2OH^- \rightarrow Fe(OH)_2$ (ppt)

If enough oxygen is present, ferrous hydroxide is easily oxidized to ferric hydroxide, which is nothing but rust.

$4Fe(OH)_2 + O_2 + 2H_2O \longrightarrow 4Fe(OH)_3$ (Yellow rust $Fe_2O_3.H_2O$)

Difference between Dry Corrosion and Wet Corrosion

Aspect	Dry Corrosion	Wet Corrosion
Definition	Corrosion occurs in the absence of moisture.	Corrosion occurs in the presence of moisture or water.
Mechanism	Chemical reaction between metal and gases.	Electrochemical reaction involving an electrolyte.
Medium	Gaseous medium (e.g., oxygen, sulfur dioxide).	Aqueous medium (e.g., water, acids, salts).
Temperature Requirement	Usually occurs at high temperatures.	Can occur at room temperature or higher.
Rate of Corrosion	Slower compared to wet corrosion.	Faster due to electrochemical processes.
Surface Layer	Forms an oxide layer, which can be protective or non-protective.	Forms rust or other compounds, usually non-protective.
Examples	Oxidation of iron in a furnace.	Rusting of iron in humid air.

Factors affecting Rate of Corrosion:

The rate of corrosion depends upon the nature of metals and the nature of the corroding environment.

(A) Nature of metals

Many factors related to the nature of metals contribute to the rate of corrosion. Some of them are -

(i) **Position in Electrochemical Series:** The metal higher in electrochemical series is more active and suffers corrosion. The rate and extent of corrosion is directly proportional to electrode potential difference between them.

(ii) **Over Voltage:** The over voltage of a metal in a corrosive environment is inversely proportional to corrosion rate. For example, the over voltage of hydrogen is 0.7 v. When zinc metal is placed in 1 M sulphuric acid, the rate of corrosion is low. When we add small amount of copper sulphate to dilute sulphuric acid, the hydrogen over voltage is reduced to 0.33V. This results in the increased rate of corrosion of zinc metal.

(iii) **Purity of Metal:** Impurity of a metal generally causes heterogeneity and form small electrochemical cells and the anodic part gets corroded. For e.g. Zn metal containing impurity such as Pb or Fe undergoes corrosion. The rate and extent of corrosion increases with the extent of impurities.

(iv) **Nature of the Surface Film:** When metals are exposed to atmosphere, practically all metals get covered with a thin surface film of metal oxide. The ratio of the volume of metal oxide to the metal is known as specific volume ratio. Greater the specific volume ratio, lesser is the oxidation corrosion rate. For e.g. the specific volume ratio of Ni, Cr, W are 1.6, 2.0 and 3.6 respectively. Rate of oxidation corrosion is least for tungsten (W).

(v) **Nature of the Corrosion Product:** Following factors contribute to the nature of corrosion Product.

- **Solubility of Corrosion Products:** If the corrosion product is soluble in the corroding medium, then corrosion proceeds at a faster rate otherwise if it is insoluble, corrosion will be suppressed e.g. $PbSO_4$ formation in case of Pb in H_2SO_4.
- **Volatility of Corrosion Products:** If the corrosion product is volatile, it evaporates as soon as it is formed, thereby leaving the underlying metal surface exposed for further attack. This causes rapid and continuous corrosion. For example, Mo forms MoO_3 volatile oxide.

(vi) Physical State The rate of corrosion is influenced by physical state of the metal (such as grain size, orientation of crystals, stress, etc.). The smaller the grain size of the metal or alloy, the greater its solubility will be and hence greater the corrosion will be. Moreover, areas under stress, even in a pure metal, tend to be anodic and corrosion takes place at these areas.

(B) Nature of the Corroding Environment

(i) Temperature: The rate of corrosion increases with the increase in temperature, because the reaction as well as diffusion rate of ions in the corrosion medium increases.

(ii) Humidity of Air: The rate of corrosion will be more when the relative humidity of the environment is high. The moisture acts as a solvent for oxygen, carbon dioxide, sulphur dioxide etc. in the air to produce the electrolyte which is required for setting up a corrosion cell.

(iii) Effect of pH: Rate of corrosion increases with decrease in pH. If pH>10, the rate of corrosion ceases due to the formation of protective coating of hydrous oxides on the metal.

If pH is between 3-10, the rate of corrosion depends upon the presence of oxygen on the cathodic area for reduction. Higher the concentration of O_2, higher the rate of corrosion. If pH<3 rate of corrosion is high even in the absence of air due to evolution of hydrogen at the cathodic region.

(iv) Presence of Impurities in Atmosphere: Atmosphere in industrial areas contains corrosive gases like CO_2, H_2S, SO_2 and fumes of HCl, H_2SO_4 etc. In the presence of these gases, the acidity of the liquid adjacent to the metal surfaces increases and its electrical conductivity also increases, thereby the rate of corrosion increases.

(v) Presence of Suspended Particles in Atmosphere: In case of atmospheric corrosion:

- If suspended particles are chemically active in nature (like NaCl, Ammonium sulphate), they absorb moisture and act as strong electrolytes, thereby causing enhanced corrosion.
- If the suspended particles are chemically inactive in nature (e.g., charcoal), they absorb sulphur gases and moisture and slowly enhance corrosion rate.

(vi) Conductance of medium: The Conductivity rate of corrosion increases with the increase in conductance of medium. For example, the rate of corrosion of metal will be higher in wet atmosphere than dry atmosphere due to more conductance. Similarly, metal undergoes rapid corrosion in ocean water than in river water.

INTERNAL CORROSION PREVENTION MEASURES:

Some of the methods of internal prevention of corrosion are:

1. **Purification of metals**

   The impurities present in metal decrease their corrosion resistance. Hence, purification of metals may be carried out by appropriate methods of purification. Based on the properties and composition of different metals to be purified, different methods of purification of metals like Distillation, Liquation, Poling, Electrolysis, Zone Refining, Vapour Phase Refining, Chromatographic Methods, etc. are employed.

2. **Alloying**

   The use of corrosion resistant alloys should be used for prevention of corrosion. Several corrosion resistant alloys have been developed for specific purposes and environment.

   For example,

   (a) Stainless steel containing chromium produces an exceptionally coherent oxide film which protects the steel from further attack.
   (b) Cupro -nickel (70% Cu + 30% Ni) alloys are now used for condenser tubes and for bubble trays used in fractionating columns in oil refineries.
   (c) Highly stressed Nimonic alloys (Ni -Cr-Mo alloys) used in gas turbines are very resistant to hot gases.

3. **Heat Treatment**

   Heat treatment is found to affect corrosion rates. Both ferrous as well as non-ferrous metals undergo heat treatment before putting them to use. Heat treatments can be used to homogenize cast metal alloys to improve their hot workability, to soften metals prior to, and during hot and cold processing operations, or to alter their microstructure in such a way as to achieve the desired mechanical properties. Over the course of this process, the metal's properties such as electrical resistance, magnetism, hardness, toughness, ductility, brittleness and corrosion resistance will change.

Thermal treatment of metallic alloys is also used to alter the surface chemistry of a material. This is achieved by diffusing carbon, nitrogen and other gaseous or solid material on to the surface of the component. These processes are used to give defined surface hardness and to improve wear, corrosion and fatigue resistance.

Heat treatment is the process of heating and cooling metals, using different methods to obtain desired properties. The physical properties of steel change on heating and cooling. The following are some heat treatment methods by which steel of different properties are obtained.

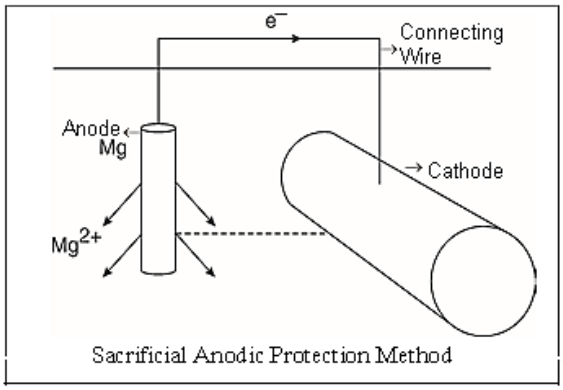
(i) **Annealing:** It is the process of heating steel to a bright red heat and then cooling it slowly. By this, steel becomes soft and pliable.
(ii) **Hardening or Quenching:** It is the process of heating steel to bright redness and then cooling suddenly by putting in oil or water. By doing so, steel becomes very hard and brittle.
(iii) **Tempering:** It is the process of heating the hardest steel to a temperature much below redness and cooling it slowly. The steel thus obtained is neither too hard nor too soft. It is also not so brittle.

The annealed specimen with coarser grain displayed better corrosion resistance. The corrosion rate results for annealed specimens were 35% lower than the other heat-treated specimens. Heat treatment can be defined as a combination of heating and cooling operations applied to a metal or alloy in its solid state to obtain desired properties.

EXTERNAL CORROSION PREVENTION MEASURES:

1. Cathodic Protection

The basic principle of cathodic protection is that the metal structure is made preventing it from corrosion.



Sacrificial Anodic Protection Method

There are two types of cathodic protection.

(A) Sacrificial Anodic Protection method

In this method the metallic structure to be protected is connected by a wire to a more anodic metal, so that all the corrosion is concentrated at this more active metal like Mg, Zn, Al and their alloys. The more active metal itself gets corroded slowly, while the parent structure which is cathodic is protected. The more active metal so employed is called "sacrificial anode". Whenever the corroded sacrificial anode is consumed completely, it is replaced by a fresh one.

Applications

Some of the applications are

(i) Protection of buried pipelines, underground cables from soil corrosion.

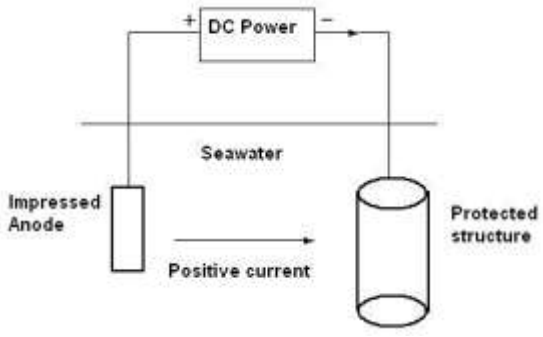
(ii) Protection from marine corrosion of cables, ship hulls, piers etc.

(iii) Insertion of magnesium sheets into the domestic water boilers to prevent the formation of rust.

(iv) Calcium metal is employed to minimize engine corrosion.

(B) Impressed current cathodic Protection

In this method an impressed current is applied in opposite direction to nullify the corrosion current and convert the corroding metal from anode to cathode. Usually, the impressed current is derived from a direct current source (like battery or rectifier on AC line) with an inert anode, like graphite, high silica iron, scrap iron, stainless steel or platinum. Usually, a sufficient DC is applied to an inert anode, buried in the soil (or immersed in the corroding medium) and connected to the metallic structure to be protected. The anode is composed of coke breeze or gypsum which enhances the electrical contact with the surrounding soil.



Impressed current cathodic protection has been applied to open water box coolers, water tanks, buried oil or water pipes, condensers, transmission line towers, laid up ships etc. This protection technique is useful for large structures for long term operations.

2. Anodic Protection:

Galvanization is commonly used for anodic protection. Galvanization is the process of coating a layer of zinc on iron by hot dipping or by electrolysis process.

Hot dip galvanization process involves the following steps

(i) Iron sheet is passed through an organic solvent to remove oil or grease present on it.

(ii) Then it is washed with dil. H_2SO_4 (pickling) to remove any rust (oxide layer) present on the surface.

(iii) Then it is treated with a mixture of aqueous solution of zinc chloride ($ZnCl_2$) and ammonium chloride (NH_4Cl) which acts as flux and then dried.

(iv) The treated sheet is dried and dipped in molten zinc at 430^0 – 470°C.

(v) Excess zinc present on iron sheet is removed by rolling, wiping or passing blast of air.

Applications:

Galvanization is used for roofing sheets, buckets, bolts, nuts, nails, pipes etc. Galvanizing and tinning by hot dipping is more economical than electroplating. Hot dipping is limited to the coating of low melting point metals like Zn, Sn and Al over iron. But galvanized utensils cannot be used for preparing and storing food stuff, especially acidic ones since zinc gets dissolved in all acids forming highly toxic compounds.

3. Organic Inhibitors

Inhibitors are organic or inorganic substances which decrease the rate of corrosion. Usually, the inhibitors are added in small quantities to the corrosive medium. Inhibitors are classified as follows

- Anodic inhibitors (chemical passivators)
- Cathodic inhibitors (adsorption inhibitors)
- Vapour phase inhibitors (volatile corrosion inhibitors)

(A) Anodic Inhibitors

The substances which reduce or slow down the rate of anodic reaction (oxidation) are known as anodic inhibitors. Examples include alkalis, chromates, phosphates, molybdates, and nitrates. These inhibitors have high oxygen content. These inhibitors react with the newly formed metal ions to form insoluble precipitates which are adsorbed on the metal surface which makes a protective layer on the metal for which corrosion inhibited.

(B) Cathodic Inhibitors

The substances which reduce or slow down the rate of cathodic reaction (reduction) are known as cathodic inhibitors. They achieve this by either slowing the reaction itself or forming a barrier on the surface, like a protective film. Examples include organic compounds like amines and imidazoles, as well

as inorganic compounds like Na_2SO_3, zinc, nickel and magnesium salts, which can form insoluble precipitates. Depending on the nature of the cathodic reaction in an electrochemical corrosion, cathodic inhibitors are classified into

a. **In an acidic solution:** The main cathodic reaction is the liberation of hydrogen gas; the corrosion can be controlled by slowing down the diffusion of H^+ ions through the cathode. e.g., Amines, Mercaptans, Thiourea etc.

$$2\,H^+ + 2e^- \longrightarrow H_2$$

b. **In a neutral solution:** In a neutral solution, the cathodic reaction is the adsorption of oxygen or formation of hydroxyl ions. The corrosion is therefore controlled either by eliminating oxygen from the corroding medium or by retarding its diffusion to the cathodic area.

The dissolved oxygen can be eliminated by adding reducing agents like Na_2SO_3.

The diffusion of oxygen can be controlled by adding inhibitors like Mg, Zn or Ni salts.

$$\tfrac{1}{2}\,O_2 + H_2O + 2e^- \longrightarrow 2OH^-$$

(C) Vapour Phase Inhibitors

Vapor Phase Inhibitors (VPIs), also known as Vapor Corrosion Inhibitors (VCIs), are substances that release a corrosion-inhibiting vapor into the air to protect metal surfaces from corrosion. This vapor forms a protective layer on the metal, preventing contact with corrosive elements like moisture.

- VPIs are designed to release a non-toxic, non-hazardous vapor into the surrounding air.
- The released vapor condenses onto the surface of metal components, forming a thin, invisible layer.
- This protective layer acts as a barrier, preventing corrosion-causing elements like water vapor, moisture, and airborne contaminants from reaching the metal surface.
- VPIs can protect various types of metals, including ferrous and non-ferrous metals.

Examples are Dicyclohexyl ammonium nitrate, dicyclohexyl ammonium chromate, benzotriazole, phenylthiourea etc.

UNIT – 5: CHEMISTRY OF FUELS AND LUBRICANTS

Fuel: Fuel is a combustible substance, containing carbon as the main constituent, which on proper burning gives large amount of heat and can be used economically for domestic and industrial purpose. E.g. Wood, coal, petrol, diesel, kerosene, liquefied petroleum gas (LPG), compressed natural gas (CNG), hydrogen gas, ethanol etc. During the process of combustion of fuel, the atoms of carbon, hydrogen etc. combine with oxygen with the simultaneous liberation of heat at rapid rate.

$$Fuel + Oxygen \rightarrow Product/s \ + \ Heat$$

$$C + O_2 \rightarrow CO_2 + 94.1 \ Kcal/mol$$

These new compounds have less energy and, therefore the energy released during the combustion process is the difference in the energy of reactants and that of the product formed.

Combustion of fuel: It is a temperature rising exothermic reaction between a fuel and oxygen.

Classification of fuel:

A. On the basis of their occurrence, fuels may be classified into two categories: -

1. **Natural Fuels:** Such fuels are found in nature. Ex-Wood, coal, petroleum, natural gas etc.
2. **Artificial Fuels:** Such fuels are prepared from natural fuels. Ex-Coke, kerosene, petrol, water gas, producer gas etc.

B. Based on their physical state, fuels may be classified into three categories:

1. **Solid Fuels**: Fuels which are found in their solid state at room temperature are generally referred to as Solid Fuels. *Ex-Wood, coal, charcoal, straw etc.*
2. **Liquid Fuels:** Most liquid fuels are derived from the fossilized remains of dead plants and animals by exposure to heat and pressure in the Earth's crust. *Ex-Petroleum, Kerosene, Petrol, Diesel, alcohol etc.*
3. **Gaseous Fuels:** Most gaseous fuels are composed of hydrocarbons, carbon monoxide, hydrogen, or a mixture of them all. *Ex- Natural gas, Coal gas, Producer Gas, Water Gas, Hydrogen etc.*

Calorific value of fuel:

Calorific value may be defined as "the amount of heat energy produced by the complete combustion of a unit mass or unit volume of fuel in air or oxygen."

Units of Calorific value are: Cal/gm, Kcal/Kg, KJ/Kg, B.Th.U/lb (British Thermal Unit/pound) etc.

(A) Higher Calorific Value (HCV) or Gross Calorific Value

HCV It is the total heat generated when a unit quantity of fuel is completely burnt and the products of combustion are cooled down to 15^0C.

(B) Lower Calorific Value (LCV) or Net Calorific Value

LCV It is the net heat produced when a unit quantity of fuel is completely burnt, and the products of combustion are allowed to escape.

$$LCV = HCV - Latent\ heat\ of\ vapourisation\ of\ water$$

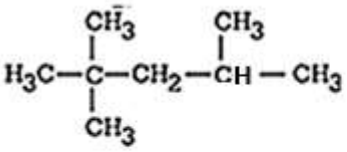
LCV = HCV – Latent heat of condensation of the water vapour produced

= HCV (Mass of H per unit weight of the fuel burnt × 9 × latent heat of vaporisation of water)

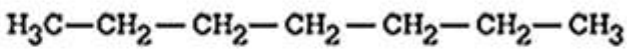
Fuel rating of Petrol and Diesel (Octane number and Cetane number)

Octane number: The octane number of gasoline is percentage of iso-octane in a mixture iso-octane and n-heptane which has the same knocking characteristics as that of the test fuel under similar experimental condition.

It has been found that n-heptane knocks very badly, its anti-knock value has arbitrary been given zero and iso-octane gives very little knocking, so its anti-knock value has been given as 100.



iso-octane
Octane No. =100

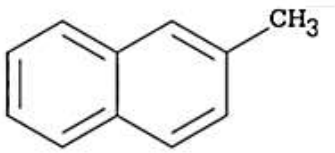


n-heptane
Octane No. = 0

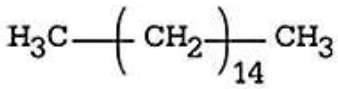
Fuel of octane number 80 and fuel mixture of 80% iso octane and 20% n-heptane produces same amount of knock. The higher the octane number lesser is the knocking. The octane number of gasolines may be increased by the addition of fuels of higher knock value. The anti-knock properties of gasoline are usually enhanced by adding tetra ethyl lead (TEL) [$Pb(C_2H_5)_4$] and the process is called doping. The addition of a small amount of TEL to a gasoline of low anti-knock values usually increases the octane number to a very considerable extent. About 0.5mL of tetra ethyl lead per litre is added for motor spirits and about 1 mL TEL per litre is generally added to aviation petrol.

Cetane Number: The knocking characteristics of diesel oil are expressed in terms of cetane number. Cetane[$C_{16}H_{34}$] is a saturated hydrocarbon with a very short ignition lag than any commercial diesel fuel. Hence its cetane rating is taken as 100. On the other hand, α-methyl naphthalene [$C_{11}H_{10}$], an aromatic

hydrocarbon has very long ignition lag as compared to any commercial diesel oil. Hence, the cetane rating is taken as zero.



α methyl naphthalene
(Cetane No.=0)



Cetane or n-Hexadecane
(Cetane No.=100)

Cetane number of a diesel fuel is the percentage by volume of cetane in a mixture of cetane and liquid alpha-methylnaphthalene, which exactly matches its knocking characteristics with diesel oil under test.

The higher the cetane number, the better is the quality of the fuel. The cetane number of diesel oil can be improved by adding substances called dopes. For example, ethyl nitrile, ethyl nitrate, iso-amyl nitrate and acetone peroxide can be used as dopes. The dopes are added only in small amounts, and they are not effective on low cetane number fuels.

In petrol engines knocking is due to the spontaneous combustion of the last portions of the fuel, whereas knocking in a diesel engine is due to delay in the spontaneous combustion of the first part of the fuel. Thus, oil of high octane number has low cetane number and vice- versa. Furthermore, crude oil which gives petrol of high octane number gives a diesel oil of low cetane number.

Chemical Composition, Calorific Values and Applications of Fuels:

SN	Fuel	Chemical Composition	Calorific Value	Applications
1	Liquefied Petroleum Gas (LPG)	Propane, n-butane, isobutane, propylene, butylene, small quantity of ethane, pentane, ethylene and pentene may also be present.	11,850 Kcal/Kg	Domestic fuel, industrial fuel, heating appliances and vehicles, motor fuel in internal combustion engine (IC-engine)
2	Compressed Natural Gas (CNG)	Methane – 95% Ethane and Nitrogen – 4% Propane and Carbon monoxide – 1%	12,600 Kcal/Kg	Automotive Fuel
3	Water Gas (Blue Gas)	Carbon monoxide and Hydrogen	2670 Kcal/m^3	Synthesis of Ammonia, methyl alcohol, illuminating gas, heating and lighting purpose, welding purpose.
4	Coal Gas	Hydrogen, Methane, Ethylene, Acetylene, Carbon monoxide	4500 Kcal/m^3	Lighting, heating, fuel for cooking, illuminant.

		and Nitrogen		
5	Producer Gas	Carbon monoxide and Nitrogen	1300 Kcal/m^3	Heating open hearth furnace, muffle furnace, reducing agent in metallurgical operation.
6	Biogas	Methane, Carbon dioxide, Hydrogen and Nitrogen	5300 Kcal/m^3	Domestic fuel, lighting, water pumps, cutting machines.

Lubricants:

Lubricants are the substances applied in between the sliding/rolling surfaces with a view to reduce the frictional resistance between them.

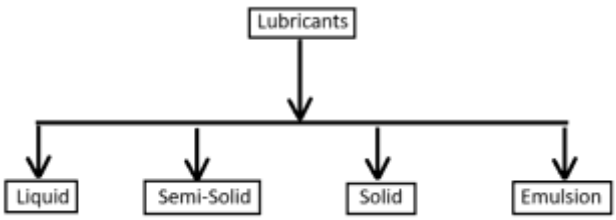
Lubrication is crucial for machinery, reducing friction, wear, and heat, thus extending equipment lifespan and improving efficiency.

Functions of Lubricants:

The main functions of lubricants are as follows:

1. It reduces friction in machines.
2. It reduces wearing and tearing of machinery parts.
3. It reduces loss of energy.
4. It reduces noise pollution.
5. It reduces the expansion of metals.
6. It increases the efficiency of engines.
7. It enhances the durability of machinery parts.
8. It acts as a coolant by removing frictional heat.
9. It prevents foreign material penetration, rust, and corrosion.
10. It reduces maintenance costs.
11. It reduces power loss in IC engines.

Classification of Lubricants



Liquid Lubricants, classification and Properties

Liquid lubricants are classified into three categories i.e.

(1) Natural or animal or Vegetable oil

(2) Mineral or Petroleum oil

(3) Synthetic or Blended oil.

Liquid Lubricants: Classification and Properties		
Type of Liquid Lubricant	Examples	Composition and Properties
Natural/Vegetable/Animal oil	➢ Animal Oils: Tallow Oil. Whale oil, Lard oil. Seal Oil, Fish oil. ➢ Vegetable oils: Olive oil. Cotton seed oil, Castor oil, Palm Oil, Rapeseed Oils, etc.	➢ Animal oils contain saturated fatty acids and monounsaturated fatty acids, ➢ Vegetable oils contain polyunsaturated fatty acids and oleic acids. ➢ Unstable in oxidative and thermal environment. ➢ Costly, undergo easy oxidation to give gummy products and hydrolyze easily on contact with moist air or water. Hence, it is rarely used as blending agents in petroleum-based lubricants to get improved oiliness.
Mineral Oil or Petroleum Oil	➢ Paraffins, Napthenes. aromatic or mixed aromatic and aliphatic hydrocarbons. ➢ Petroleum fractions	➢ Lower molecular weight hydrocarbons with about 12 to 50 carbon atoms. ➢ Contains sulphur oxygen. phosphorous. nitrogen etc. ➢ Generally lower viscosity index (Vl) (≈120 or less). ➢ As they are cheap available in abundance and stable under service conditions, hence are widely used. ➢ Oiliness Of mineral Oils is less. So the addition of higher molecular weight compounds like Oleic acid and stearic acid increases the oiliness of mineral oil. ➢ Pour point is in the range of -6^0C to -60^0C. ➢ Lower flash may provide sludge and vamish deposits.
Synthetic or Blended Oil	Hydrocarbons produced by polymerization. poly (alpha- olefins). Organic esters. polyglycols. silicones.	➢ Desirable Characteristics Of lubricating oil can be improved by adding small quantity of various additives. The Oils thus obtained are known as blended or compound oils. ➢ The addition of higher molecular weight compounds like oleic acid. stearic acid. palmitic acid or vegetables oil like coconut Oil, castor oil. etc. increases the Oiliness Of mineral oil. ➢ No impurities. ➢ High viscosity index. ➢ Pour point in the range of to .50'C.

		➢ Higher flash point to non-flammable. ➢ Generally free of sludge and varnish deposits. They are of two types a) Chemically active additives-e.g. detergents. Anti-wear agent, dispersant, oxidation inhibitors. b) Chemically inert additives-They improve the physical properties e.g. viscosity index improver, foam inhibitors, emulsifier. de-emulsifiers.

Semi-Solid Lubricants: Classification and their Properties:

Semi-solid lubricants are obtained by combining lubricating oil with thickening agents such as grease. Lubricating oils may be petroleum oil or synthetic hydrocarbon. The thickeners may be special soaps of Li, Na, Ca, Ba, Al etc. Non soap thickeners include carbon black, silica gel, polyurea and other synthetic polymers, clays, etc. Grease can support much heavier load at lower speed. Internal resistance of grease is much higher than that of lubricating oils.

Therefore, it is better to use oil instead of grease. Grease cannot effectively dissipate heat from the bearings, so work at relatively lower temperature. The most important semi-solid lubricants are greases and Vaseline.

Types of Semi Solid Lubricants	**Properties**	**Uses**
Soda Based	Sodium soaps are used as a thickening agent in mineral or petroleum oil. They are slightly soluble in water. They can be used up to 175^0C	➢ When a machine works at slow speeds and high pressures. ➢ Where spilling or spurting oil from the bearings is detrimental to the product being manufactured, for example in textile mills, paper and food product manufacture. ➢ Where oil cannot be maintained in position due to bad seal.
Lithium Based	Lithium soaps are emulsifying with petroleum oil. They are water resistant and used up to 15^0C.	

Calcium Based	Calcium soaps are emulsifying with petroleum oil. They are water resistant and used up to 80^0C.	➢ Where the bearing has to be sealed against entry of dirt, water, dust and grit.

Solid Lubricants: Classifications and Properties:

A solid lubricant is a material that separates two moving surfaces under boundary conditions and decreases the amount of wear. Graphite, molybdenum disulphide (MoS_2), boron nitride (BN)x are mostly used as a solid lubricant. They are used under high temperature and high pressure.

- **Graphite:** It is most widely used as a solid lubricant. Graphite has layered structure. Layers are held together with the help of weak Vander Waals' forces which facilitate the easy sliding of one layer over the other layer. It is very soapy to touch, non-inflammable. It is used at high temperature (around 450°C) condition.
- **Molybdenum disulphide (MoS_2):** It is sandwich-like structure in which hexagonal layer of molybdenum (Mo) lies between two hexagonal layers of sulfur (S) atom. Like graphite the layers are held together with weak Vander Waals forces. It is stable up to 400^0C. It is used in high vacuum. It adheres even more strongly to the metal or other surfaces.

Classification of Solid Lubricants:

The various types of solid lubricants are as under:

i. ***Structural Lubricants:*** Structural lubricants are those whose lubricating properties are due to their layer lattice structure. Example graphite, molybdenum disulphide, talc, mica, vermiculite etc. These function by cleaving within themselves and fixing themselves on or into bearing surface.

ii. ***Mechanical Lubricants:*** They form continuous adherent film on the rubbing surfaces and reduce the wear. Example: Metals and plastics are characterized by their sacrificial wear.

iii. ***Soaps:*** Soap function by in situ formation of compounds in the metal surface by the interaction of fatty acids and the metal.

iv. ***Chemically Active Lubricants:*** These include extreme pressure additives and other chemicals which interact with the metal surface to produce a lubricating layer. Examples are phosphates, chlorides and oxidising agents.

v. ***Refractories, Ceramics and Glass:*** These are used in defense programs and rocketry. Combinations of refractory materials work satisfactorily as lubricants for short periods at high temperatures. Glass functions by softening at the operating temperature and assists in hydrodynamic lubrication.

MECHANISM OF LUBRICATION:

Sl.No	Thick film/Fluid film/ Hydrodynamic Lubrication	Thin film/ Boundary Lubrication
1	The lubricating oil forms a uniform film of a thickness of more than 10,000 A^0 in between two moving or sliding surfaces.	The lubricating oil forms a uniform film of a thickness of about 1,000 A^0 in between two moving or sliding surfaces.
2	Hydrocarbon oils of lower molecular weight with about 12 to 50 carbon atoms are considered to be satisfactory lubricants for thick-film lubrication.	Vegetable oil, animal oil and mineral oil are suitable for this type of lubrication. Graphite and molybdenum disulphide are also suitable for thin film lubrication.
3	In this case, the coefficient of friction ranges from 0.001 to 0.03.	In this case, the coefficient of friction ranges from 0.05 to 0.15.
4	The lubrication should have minimum viscosity.	The lubricant should have more oiliness.
5	The lubricant neither gets adsorbed on nor chemically reacts with a metallic surface.	The lubricants may be absorbed on or chemically reacts with metallic surfaces
6	This lubrication is used in machines working under light load and at high speed.	This lubrication is used in machines working under heavy load and slow speed.
7	Useful in delicate and light machines like watches, clocks, guns, scientific equipment.	Useful in Bearing, gears, tractor rollers, lathes, railway track joints, concrete mixture etc.

Physical Properties of Lubricants:

1. **Viscosity:** Viscosity is the important physical property of a lubricant and is a measure of the intermolecular interactions of the oil and hence of the resistance to flow. Viscosity is the property of a fluid that determines its own resistance to flow. Or scientifically a force in dynes required to move 1cm square of the liquid over another surface with a velocity of 1 cm per sec. The unit of viscosity is poise. If the viscosity of the oil is too low, a liquid oil film cannot be maintained between two moving/sliding surfaces. On the other hand, if the viscosity of the oil is too high, excessive friction will result. The lower the viscosity, greater will be the flow ability. If temperature increases, viscosity of the lubricating oil decreases. If the pressure increases, viscosity of lubricating oil increases. Thus, a good lubricating oil is that whose viscosity does not change with temperature.
   Higher viscosity lubricants are thick and don't flow, while lower viscosity lubricants have a closer consistency to water and do flow.
2. **Viscosity Index:** The variation of viscosity of a liquid with temperature is called viscosity index. Viscosity of liquids decreases with increasing temperature and, consequently, the lubricating oil becomes thinner as the operating temperature increases. Hence, viscosity of good lubricating oil should not change much with change in temperature, so that it can be used continuously, under varying conditions of temperature. The rate at which the viscosity of lubricating oil changes with temperature is measured by an arbitrary scale, known as viscosity index (V. I). If the viscosity of lubricating oil falls rapidly as the temperature is raised, it has a low viscosity index. On the other hand, if the viscosity of lubricating oil is only slightly affected on raising the temperature, its viscosity index is high. Hence, a lubricant should have high viscosity index.

Viscosity Index Improvers (VII) or Viscosity Modifiers (VM)

Viscosity Index Improvers, or Viscosity Modifiers influence the viscosity temperature trend. VIIs are polymers with a variable molecular weight belonging to the following main categories:

- Hydrogenated ethylene-propylene copolymers (also called Olefin Co-Polymers, (OCP)).
- Hydrogenated polyisoprenes.
- Poly-metacrylates (PMA).
- Hydrogenated styrene-isoprene copolymers.
- Poly-isobutenes (PIB).

3. Oiliness:

- Oiliness of a lubricant is the measure of its capacity to stick on to the surface of machine parts under condition of pressure or load.
- When a lubricating oil of poor oiliness is applied under high pressure, it gets squeezed out from the surface and lubrication stops.
- If the oil has good oiliness, it can remain in place and can give lubrication even under pressure.
- It is an important property of a lubricant under boundary or thin film lubrication conditions.
- Mineral oils have very poor oiliness whereas animal and vegetable oils have good oiliness.
- The oiliness of mineral oils is generally improved by adding small quantities of high molecular weight fatty acids like oleic acid, stearic acid, chlorinated esters of these acids, etc.
- There is no perfect method for the determination of absolute oiliness of on oil, only relative oiliness is considered while selecting a lubricating oil for a particular job.

4. Flash Point:

- The flash point of a lubricant is the lowest temperature at which vapours of the material gives a flash for a moment when an ignition source brought near to it.
- The lubricating oil should have flash point reasonably higher than its working temperature.

5. Fire Point:

- The fire point of a lubricant is the lowest temperature at which the vapour of the lubricant continues to burn for at least 5 seconds when an ignition source brought near to it.
- In most cases, the fire points are 40°C to 50°C higher than the flash points.
- A good lubricant should have fire point much above the working temperature.

6. Cloud Point:

- When the lubricant oil is cooled slowly, the temperature at which lubricating oil becomes cloudy in appearance is called cloud point.
- Cloud point of a lubricant indicates the suitability of lubricant oil when the machines are working under cold conditions.
- The cloud point of a lubricant should be much lower than the working temperature.

7. Pour Point:

- The lowest temperature at which the lubricant oil becomes semi-solid and ceases to flow is called pour point.
- The pour point indicates the suitability of lubricant oil when machine is working under cold condition.
- The pour point of a lubricant should be much lower than the working temperature.

Chemical Properties of Lubricants:

1. Coke Number or Carbon Residue

Coke number or Carbon residue of lubricant is the tendency to form carbon deposits after heating under high-temperature conditions under specific conditions.

A high coke number suggests a lubricant's tendency to form carbon deposits, which can lead to engine problems, such as reduced efficiency, increased wear, and even engine damage. A low coke number is generally desirable, indicating that the lubricant is less prone to forming deposits. The type of base oil, additives used, and operating conditions of the lubricant can all influence the coke number.

2. Total Acid Number (TAN):

Total Acid Number (TAN) is a measure of acid concentration present in a lubricant. The acid concentration of a lubricant depends on the presence of additives, acidic contamination, and oxidation by-products.
TAN is determined by the amount of potassium hydroxide in milligrams that is needed to neutralise the acids in one gram of oil. TAN is a crucial parameter for assessing the quality and condition of oils and lubricants, as increased acidity can lead to corrosion, degradation, and reduced performance.

Importance of TAN

- It is an important quality measurement of crude oil and used as a guide in the quality control of lubricating oil formulations.
- Testing for TAN is essential to maintain and protect equipment, preventing damage in advance.
- TAN testing is a measure of both the weak organic acids and strong inorganic acids present within oil.

3. Saponification Value (SV) or Saponification Number (SN)

Saponification value of lubricating oil is the number of milligrams of potassium hydroxide (KOH) required to saponify one gram of fatty oil.

The saponification value is a measure of the average molecular weight (or chain length) of the fatty acids present in the lubricant sample, specifically those in the form of triglycerides.

- A high saponification value suggests shorter fatty acid chains (lower molecular weight).
- A low saponification value indicates longer fatty acid chains (higher molecular weight).
- Saponification value can indicate the presence of vegetable and animal oil additives in blended lubricating oils.

Characteristics Properties of good lubricants:

A good lubricant should have the following characteristics properties:

1. It should have appropriate (moderate) viscosity.

2. It should have high viscosity index.
3. It should have high oiliness.
4. It should have high flash point and high fire point.
5. It should have low cloud point and low pour point.
6. It should have low coke number.
7. It should have low TAN value.
8. It should have high thermal and oxidation stability.
9. It should have high corrosion resistant capacity.
10. It should have demulsibility property.

UNIT – 6: ATOMIC STRUCTURE, CHEMICAL BONDING AND SOLUTION

ATOMIC STRUCTURE

Introduction:

According to *Dalton's Atomic theory* "Every matter is composed of very small particles called 'atoms' (Greek, a = cannot be; tom = cut) which cannot be further subdivided". But modern research revealed that an atom is divisible and has a rather complex structure containing a large number of sub-atomic particles such as electrons, protons, neutrons, mesons, leptons, antiprotons, neutrinos, antineutrinos, positrons, quarks etc.

Fundamental Particles:

The sub-atomic particles 'electrons, protons and neutrons' are called fundamental particles of all matters.

Electron: Electron is a fundamental sub-atomic particle having negligible mass of 9.11×10^{-31}kg and carrying a charge of -1.602×10^{-19} Coulomb.

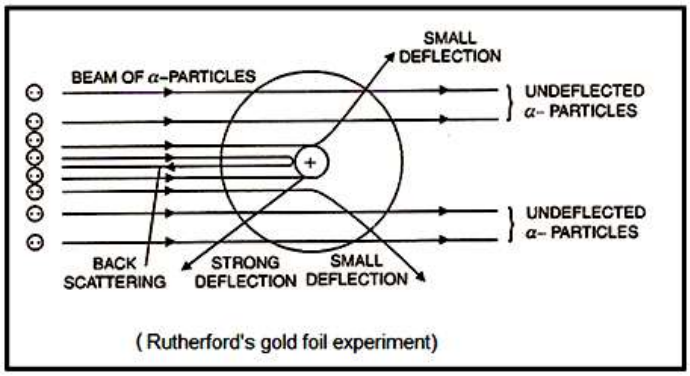
Proton: Proton is a fundamental sub-atomic particle having mass of 1.672×10^{-27}kg and carrying a charge of $+1.602 \times 10^{-19}$ Coulomb.

Neutron: Neutron is a fundamental sub-atomic particle having mass of 1.675×10^{-27} Kg and carrying no charge.

Fundamental Particle	Mass	Charge	Relative Charge
Electron	9.11×10^{-31}Kg	-1.602×10^{-19} Coulomb	– 1
Proton	1.672×10^{-27} Kg	$+1.602 \times 10^{-19}$ Coulomb	+1
Neutron	1.675×10^{-27} Kg	0	0

Rutherford's Gold-foil Experiment/Rutherford's α-scattering Experiment: (Discovery of Nucleus)

In 1911, **E.** ***Rutherford*** gave the first information about the almost-correct-picture of an atom. He bombarded a number of α-particles *(He^{2+} ions)* emitting from a radioactive material like Uranium on a very thin gold foil. A circular zinc sulphide **(ZnS)** screen was provided at the back side of the gold foil in order to register the impressions made by the α-particles.



(Rutherford's gold foil experiment)

Observations and Conclusions:

*From the **α-** scattering experiment, Rutherford observed that:*

1. Most of the α-particles went un-deflected, i.e. they passed straight through the gold foil without any deviation. This clearly indicates that most of the parts of an atom are empty.
2. A few α-particles were found to be deflected strongly from their normal paths. This indicates the presence of a heavy positively charged body inside the atom. This heavy positively charged body is called nucleus.
3. A very few (0.01%) α-particles were found to be retracted their original paths (deflected through almost 180^0). This indicates that the size of nucleus is very small. The size of atomic nuclei is of the order of 10^{-13} cm.

RUTHER FORD'S ATOMIC MODEL:

Based on the conclusions drawn from the α-scattering experiment, Rutherford proposed an atomic model, as follows:

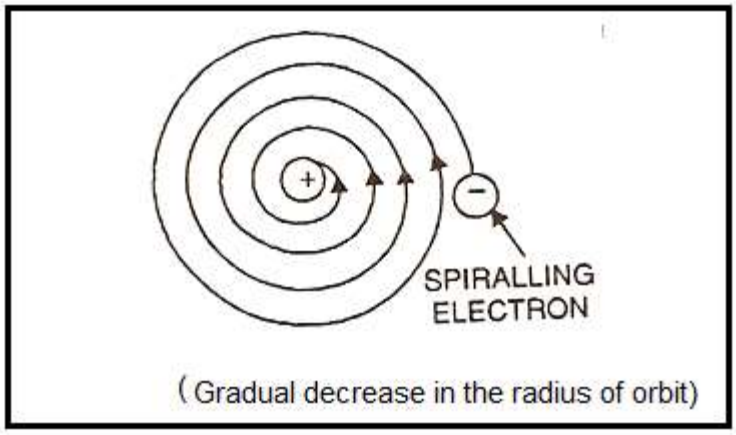
1. An atom consists of two parts; they are (i) Nucleus and (ii) extra nuclear part.
2. Every atom consists of a very small but heavy positively charged body, called nucleus.
3. The whole mass of an atom is concentrated at the nucleus.
3. Electrons revolve around the nucleus with tremendous speed, like planets revolve around the sun. Therefore, the electrons are also called as planetary electrons.
4. The electrostatic force of attraction (acting inward) between the nucleus and electrons is balanced by the centrifugal force (acting outward) arising due to the motion of electrons. That is why electrons do not fall into the nucleus.

DRAWBACKS OR FAILURES OF RUTHERFORD'S ATOMIC MODEL:

1. Stability of Atom:

The theory fails to explain the stability of atoms. According to the law of electrodynamics (by Clark Maxwell), whenever a charged particle revolves around another charged particle, the revolving charged particle emits (loses) energy continuously.

As the energy of the revolving electron decreases, it should be attracted towards the nucleus, and should follow a spiral path and ultimately fall into the nucleus. However, this never happens.



2. The model is silent about the definite energy and velocity possessed by the revolving electrons.

3. The theory fails to explain ***atomic spectra***.

4. It fails to explain the cause of chemical combinations.

BOHR'S ATOMIC MODEL (THEORY)

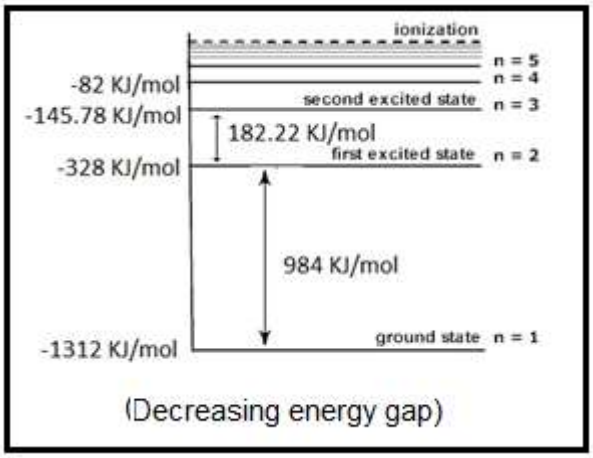
An almost correct picture of atomic model was provided by a **Dutch physicist *Niels Bohr* in 1913**. The Bohr's Atomic model is based on '**Planck's Quantum Theory'** and **'quantization of energy'**.

Postulates of Bohr's atomic model:

1. Every atom consists of a heavy positively charged body at the center called 'nucleus' and electrons revolve around the nucleus in certain permitted definite circular paths called 'shells', 'orbits' or 'stationary states'.

2. The stationary states or shells are designated as **K, L, M, N, O.....etc.** for 1st, 2nd, 3rd, 4th.....shells respectively.

3. Each shell is associated with a certain definite quantity of energy. Hence the shells are also called '**Energy levels'**.



(Decreasing energy gap)

4. The energy content increases on moving from lower to higher shells and become zero for the shell which is present at an infinite distance from the nucleus.

5. The energy levels are not equally spaced.

6. Through a large number of concentric circles are possible around the nucleus, only those circular paths are allowed for the electrons to revolve for which the **angular momentum** value (mvr) isa whole number multiple of $\frac{h}{2\pi}$, that is

$mvr = n \frac{h}{2\pi}$, where n = 1, 2, 3,.....

Here, *m = mass of the electron,*

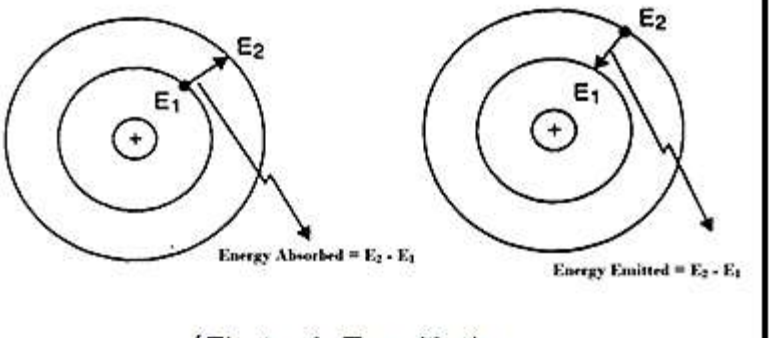
v = tangential velocity of the revolving electron,

r = radius of the orbit.

h = Planck's constant,

7. When the electrons in an atom are in their normal energy state (ground state), they keep on revolving in their respective orbits without losing energy.

8. When external source of energy is supplied to an atom, the electrons jump



(Electronic Transition)

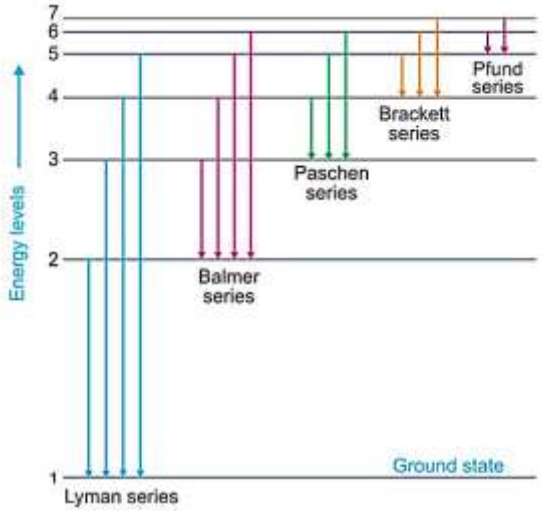
from lower ground states to the higher excited states by absorbing energy. Electrons in the excited states are unstable and jump back to the lower ground states by releasing energy. The energy thus released appears in the form of light which is the origin of spectral lines.

Failures of Bohr's Atomic Model:

1. According to Bohr's atomic model, the path followed by electrons is two-dimensional circular. But modern research (Heisenberg's Uncertainty Principle) revealed that electrons revolve in three-dimensional paths called orbitals.
2. It fails to explain the spectra of multi-electron species.
3. It fails to explain the relative intensities of spectral lines.
4. It fails to explain the splitting up of spectral lines when exposed to electric field (Stark Effect) and magnetic field (Zeeman Effect).
5. It fails to explain the cause of chemical combinations.

Explanation of Hydrogen Spectrum based Bohr's Theory

When electric discharge is passed through a sealed tube containing hydrogen gas and the radiation produced is analyzed with the help of a photo spectrometer or prism then six series of colours are obtained. These are Lyman, Balmer, Paschen, Brackett, P-fund, and Humphry series.



When electricity is passed through hydrogen gas, the hydrogen molecules get dissociated into hydrogen atoms. The hydrogen atoms absorb energy, and the electrons get excited to the higher energy levels. In the excited the electrons are unstable and jump back to the ground state either directly or in a stepwise manner by releasing light energy of different frequencies. When electrons jump from Higher energy levels to the 1^{st}, 2^{nd}, 3^{rd}, 4^{th}, 5^{th}, and 6^{th} levels, the series of lines are called Lyman, Balmer, Paschen, Brackett, P-fund, and Humphry series respectively.

Series	1^{st} line		2^{nd} line		3^{rd} line		Spectral Region
	n_1	n_2	n_1	n_2	n_1	n_2	
Lyman	1	2	1	3	1	4	Ultraviolet
Balmer	2	3	2	4	2	5	Visible
Paschen	3	4	3	5	3	6	Infrared
Brackett	4	5	4	6	4	7	Infrared
P-fund	5	6	5	7	5	8	Infrared
Humphrey	6	7	6	8	6	9	Far infrared

Heisenberg Uncertainty Principle

Heisenberg's uncertainty principle may be stated as "it is impossible to measure both the position and the momentum of a microscopic particle simultaneously with absolute accuracy". This principle is based on the wave-particle duality of matter. Since atoms and subatomic particles have very small masses, any increase in the accuracy of their positions will be accompanied by an increase in the uncertainty associated with their velocities.

Mathematically,

$$\Delta x \times \Delta p \geq \frac{h}{4\pi}$$

Where, Δx = Uncertainty in Position

Δp = Uncertainty in momentum

Accurate measurement of position or momentum automatically indicates larger uncertainty (error) in the measurement of the other quantity.

Heisenberg's principle applies to only dual-natured microscopic particles and not to macroscopic particles whose wave nature is minimal.

Since both position and momentum of an electron (microscopic particle) cannot be determined simultaneously, how we can say that electrons are moving in a specific fixed path. This is a direct clash with Bohr's atomic theory. This leads to the idea of atomic orbital.

Atomic Orbital:

The three-dimensional space or region around the nucleus where the probability of finding an electron is maximum is called an orbital. Generally, there are four types of orbitals, which are *s, p, d and f*.

Quantum Numbers:

The set of numbers used to describe the position and energy of the electron in an atom are called quantum numbers. There are four quantum numbers, namely, principal, azimuthal, magnetic and spin quantum numbers.

Principal Quantum Numbers (*n*)

1. It is denoted by the letter 'n'.
2. It represents the major energy level of the shell in which the electron is present.
3. Its values may be: 1, 2, 3, 4, ……∞.
4. For n = 1, 2, 3, 4, …., the shells are designated as K, L, M, N, …….respectively.
5. The maximum no. of electrons a shell can hold is given by $2n^2$.

Shell	n	Maximum no. of electrons ($2n^2$)
K	1	$2 \times 1^2 = 2$
L	2	$2 \times 2^2 = 8$

M	3	2 x 3^2 = 18
N	4	2 x 4^2 = 32 and so on…

6. With the value of 'n' we can calculate the energy content of a shell.
7. With the help of 'n' we can calculate the distance between the nucleus and the electron in a shell.
8. Larger the value of 'n' larger is the size of the electron cloud.

Azimuthal or angular momentum or subsidiary or secondary quantum number (l):

1. It is denoted by the letter 'l'.
2. It represents the number of sub-shells present in a given shell.
3. The values of 'l' may be l = 0, 1, 2, 3, ……., (n – 1).
4. For l = 0, 1, 2, 3, ….the corresponding sub-shells are called s, p, d, f, …….sub-shells respectively.

Shell	n	l	Sub-shells
K	1	0	1s
L	2	0, 1	2s, 2p
M	3	0, 1, 2	3s, 3p, 3d
N	4	0, 1, 2, 3	4s, 4p, 4d, 4f

5. A sub-shell can hold a maximum no. of (4l + 2) electrons.

Sub-shell	l	No. of electrons (4l + 2)
K	0	(4x0 + 2) = 2
L	1	(4x1 + 2) = 6
M	2	(4x2 + 2) = 10
N	3	(4x3 + 2) = 14

6. The angular momentum of an electron in an orbital is given by $\sqrt{l(l+1)}\frac{h}{2\pi}$

Magnetic Quantum Numbers (m or m_l)

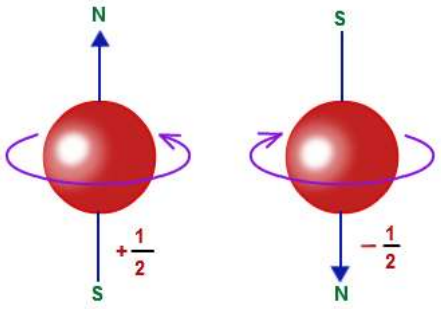
1. It is represented by m or m_l.
2. It represents the presence of sub-subshells or orbitals present in a sub-shell.
3. Its value may be, $m = -l$ ……..0…….+ l.

Subshell	l	m	Orbitals
s	0	0	s
p	1	-1, 0, +1	p_x, p_y, p_z
d	2	-2, -1, 0, +1, +2	$d_{xy}, d_{yz}, d_{xz}, d_{x^2-y^2}, d_{z^2}$
f	3	-3, -2, -1, 0, +1, +2, +3	----------

Note: Orbitals having same or nearly same energy content are called degenerate orbitals.

Spin Quantum Numbers: (s or m_s)

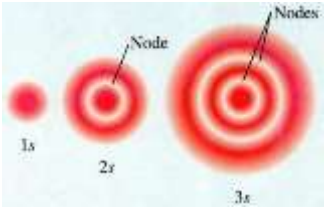
1. It represents the direction of spin of electrons around the nucleus along its own axis.
2. It has two values, s = + ½ and s = – ½ .



Shapes of Orbitals:

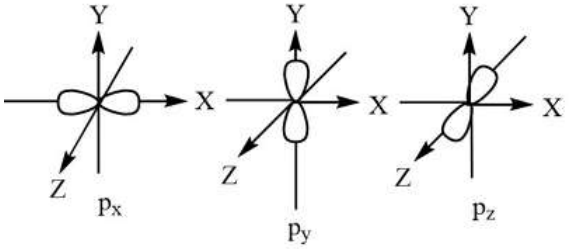
a. Shapes of s- orbitals.

- S – orbitals are spherically symmetrical in nature.
- The size and energy increase with the increase in the principal quantum numbers. Thus, the order of size and energy is 1s < 2s < 3s < ……..
- The region or the space in between two orbitals where the probability of finding an electron is zero is called 'nodal surface' or 'node'.



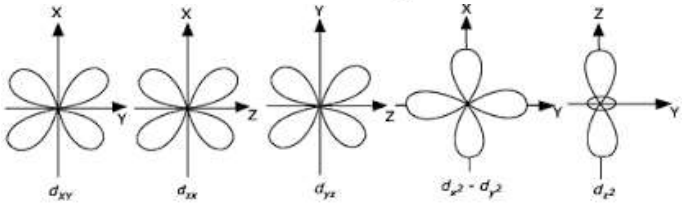
b. Shapes of p – orbitals:

- p-orbitals are dumbbell in shapes.
- A p-subshell has 3 related orbitals. They are p_x, p_y and p_z.
- The plane passing through the nucleus on which the probability of finding an electron is zero is called nodal plane.



c. Shapes of d – orbitals:

- The d – orbitals are double dumbbell in shape.
- A d – subshell has 5 related orbitals namely,
  $d_{xy}, d_{yz}, d_{xz}, d_{x^2-y^2}$ *and* d_{z^2}.



Aufbau Principle:

The word *"Aufbau"* means **"building up".** This principle describes how the subs-hells are filled with electrons.

Aufbau principle may be stated as **"electrons are filled in different sub-shells in order of their increasing energy content"**.

The sub-shell with lowest energy is filled with electrons first and those with higher energies are filled with electrons later. The energy content of the various sub-shells can be compared by

(n+*l*') rule.

The (n + *l*') Rule:

i. The sub-shell having lower (n+ *l*') value possesses lower energy and is filled first.

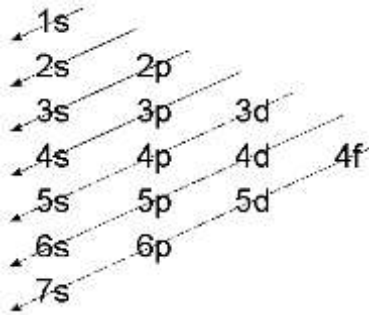
ii. If the (n + *l*') value for two given sub-shells are equal, then the one with lower value of 'n' possesses lower energy and is filled first.

Following the (n+ *l*') rule, let us compare the energy possessed by various sub-shells.

Sub-shell→	**1s**	**2s**	**2p**	**3s**	**3p**	**3d**	**4s**	**4p**	**4d**	**4f**	**5s**	**5p**
(n+ *l*')	1+0 =1	2+0 =2	2+1 =3	3+0 =3	3+1 =4	3+2 =5	4+0 =4	4+1 =5	4+2 =6	4+3 =7	5+0 =5	5+1 =6

Hence the increasing order of energy content of sub-shells is

1s < 2s < 2p < 3s < 3p <4s <3d < 4p < ...



ELECTRONIC CONFIGURATIONS: -

Electronic configuration is the arrangement of electrons of an atom in different sub-shells/orbitals in the increasing order of their energy content. The electronic configurations of some elements are given below:

Elements	**Electronic configurations**	**Elements**	**Electronic configurations**
$_{1}$H	$1s^1$	$_{16}$S	$1s^2\ 2s^2 2p^6\ 3s^2 3p^4$
$_{2}$He	$1s^2$	$_{17}$Cl	$1s^2\ 2s^2 2p^6\ 3s^2 3p^5$
$_{3}$Li	$1s^2\ 2s^1$	$_{18}$Ar	$1s^2\ 2s^2 2p^6\ 3s^2 3p^6$
$_{4}$Be	$1s^2\ 2s^2$	$_{19}$K	$1s^2\ 2s^2 2p^6\ 3s^2 3p^6 4s^1$
$_{5}$B	$1s^2\ 2s^2 2p^1$	$_{20}$Ca	$1s^2\ 2s^2 2p^6\ 3s^2 3p^6 4s^2$
$_{6}$C	$1s^2\ 2s^2 2p^2$	$_{21}$Sc	$1s^2\ 2s^2 2p^6\ 3s^2 3p^6 4s^2 3d^1$
$_{7}$N	$1s^2\ 2s^2 2p^3$	$_{22}$Ti	$1s^2\ 2s^2 2p^6\ 3s^2 3p^6 4s^2 3d^2$
$_{8}$O	$1s^2\ 2s^2 2p^4$	$_{23}$V	$1s^2\ 2s^2 2p^6\ 3s^2 3p^6 4s^2 3d^3$
$_{9}$F	$1s^2\ 2s^2 2p^5$	**$_{24}$Cr**	$\mathbf{1s^2\ 2s^2 2p^6\ 3s^2 3p^6 4s^1 3d^5}$

$_{10}$Ne	$1s^2\ 2s^2 2p^6$	$_{25}$Mn	$1s^2\ 2s^2 2p^6\ 3s^2 3p^6 4s^2 3d^5$
$_{11}$Na	$1s^2\ 2s^2 2p^6\ 3s^1$	$_{26}$Fe	$1s^2\ 2s^2 2p^6\ 3s^2 3p^6 4s^2 3d^6$
$_{12}$Mg	$1s^2\ 2s^2 2p^6\ 3s^2$	$_{27}$Co	$1s^2\ 2s^2 2p^6\ 3s^2 3p^6 4s^2 3d^7$
$_{13}$Al	$1s^2\ 2s^2 2p^6\ 3s^2 3p^1$	$_{28}$Ni	$1s^2\ 2s^2 2p^6\ 3s^2 3p^6 4s^2 3d^8$
$_{14}$Si	$1s^2\ 2s^2 2p^6\ 3s^2 3p^2$	**$_{29}$Cu**	$\mathbf{1s^2\ 2s^2 2p^6\ 3s^2 3p^6 4s^1 3d^{10}}$
$_{15}$P	$1s^2\ 2s^2 2p^6\ 3s^2 3p^3$	$_{30}$Zn	$1s^2\ 2s^2 2p^6\ 3s^2 3p^6 4s^2 3d^{10}$

Exceptional Electronic Configuration: Some elements like 'Cr' and 'Cu' show exceptional electronic configurations.

The electronic configurations of 'Cr' & 'Cu' should be:

$_{24}$Cr = [Ar]$4s^2 3d^4$ &$_{29}$Cu = [Ar]$4s^2 3d^9$ respectively.

But the actual electronic configurations are

$_{24}$Cr = [Ar]$4s^1 3d^5$ &$_{29}$Cu = [Ar]$4s^1 3d^{10}$

The exceptional electronic configuration is due to the fact that half-filled and ful-filled orbitals are more stable due to the orbital symmetry and exchange energy.
In case of Cr, one of the electrons of 4s sub-shell is transferred to the 3d sub-shell to become half-filled and stable. On the other hand, in the case of Cu, one of the electrons of 4s sub-shell is transferred to the 3d sub-shell to become full-filled and stable.

Assignment:

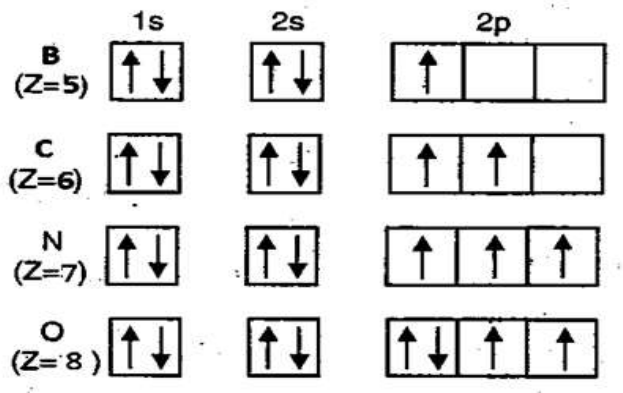
Q 1. Write down the electronic configurations of the following: O^{2-}, Ca^{2+}, P^{3-}, Ti^{2+}, Cr^{3+}, Cu^{2+}.
Q 2. Arrange the following sub-shells in the increasing order of their energy content: 3d, 5p, 4s, 4p, 6s, 4d.
Q 3. What is (n+l) rule? Which out of 4s and 3d sub-shells has lower energy?
Q 4. What do you mean by $3d^2$?

Hund's Rule: -

Hund's rule may be stated as **"Pairing of electrons do not take place in the degenerate orbitals of *p, d,* and *f*-sub shells until each degenerate orbital in the given sub-shell contains one electron."**

The above is due to the reason that electrons being identical in charge repel each other when present in the same orbital. This repulsion can, however, be minimized if two electrons move as far apart as possible by occupying different degenerate orbitals.

Let us consider the electronic configurations of the following elements.



Incase of boron the 5th electron is occupied by the $2p_x$orbital. In carbon the 6th electron will not be paired with the electron of the $2p_x$ orbital, rather it will be occupied by the $2p_y$ orbital. Similarly, in case of nitrogen all the 2*p* – electrons will remain unpaired. The rule is also called 'maximum multiplicity rule' because the total spin value of all the electrons of degenerate orbitals of a given sub-shell becomes maximum if they are arranged as per Hund's rule.

Assignment

Q 1. How many vacant orbitals are there in C, O, P and Ti?

Q 2. How many unpaired electrons are there in N, F, Fe and Na^+?

Q 3. What do you mean by $3d^5$?

Pauli's Exclusion Principle:

The principle may be stated as "No two electrons in an atom can have all the four quantum numbers alike".

Any two electrons in an atom can have the same three quantum numbers, but the fourth one must be different.

Let us consider two electrons e_1 and e_2 belong to the 1st shell or K – shell of an atom. The probable quantum numbers for the two electrons can be:

Electron	n	*l*'	m	s
e_1	1	0	0	+ ½
e_2	1	0	0	- ½

From the above tabulation we can see that three out of four quantum numbers are same, while the 4th quantum number, i.e. the spin quantum numbers, are different. The principle is called 'exclusion principle' as it excludes the possibility of more than two electrons in an orbital.

CHEMICAL BONDING

Chemical Bonding: Chemical bonding may be defined as "the force of attraction which holds together the constituent atoms in a molecule or ion".

Cause of chemical bonding:

1. **Attainment of stability:** Every atom tries to attain stability.
2. **Noble gas configuration:** Every atom tries to attain the electronic configuration of the nearest noble gas.
3. **Electrostatic force:** Oppositely charged ions attract each other to form chemical bonds.
4. **Tendency to minimize energy:** When atoms approach each other the energy of the system decreases and the atoms attain stability.

Types of Chemical Bonding:

Depending upon the mode of bond formation (transfer or sharing of electrons), chemical bonding may be classified into the following types:

1. Ionic Bonding or Electrovalent bonding
2. Covalent bonding
3. Co-ordinate bonding or Dative Bonding
4. Hydrogen bonding
5. Metallic bonding

IONIC OR ELECTROVALENT BONDING:

"The chemical bond which is formed by the complete transfer of one or more valance electrons from one atom to another is called ionic or electrovalent bond and the compound formed is called ionic compound or electrovalent compound".

Features of Ionic bond: The formation of ionic bond involves:

- ☞ Formation of a positive ion by loss of electron/s from one kind of atom.
- ☞ Formation of a negative ion by gain of electron/s from another kind of atom.
- ☞ Electrostatic force of attraction between the oppositely charged ions.

Conditions for the formation of Ionic bond:

1. ***Nature of element:*** Atoms of different elements form ionic bonds. Atoms of the same element never form *ionic bond*.
2. ***Low Ionization potential:*** Ionization potential of an element is the quantity of energy required to remove one valence electron from an isolated, neutral, gaseous atom. One of the combining atoms should have low IP. The elements of **Gr 1 and Gr 2** of the modern periodic table have low ionization potential; and hence they can form *ionic bonds*.

3. ***High Electron Affinity:*** It is the amount of energy released when an extra electron is added to an isolated, neutral, gaseous atom. Another participating atom should have high electron affinity. The elements of **Gr 16** and **Gr 17** of the modern periodic table have high electron affinities; and hence they can form *ionic bonds*.
4. ***High Lattice Energy:*** The quantity of energy involved during the formation of or breaking of one mole of an ionic bond is called lattice energy. The higher the lattice energy greater is the stability of the ionic compound. Thus, the lattice energy of ionic compounds should be high.

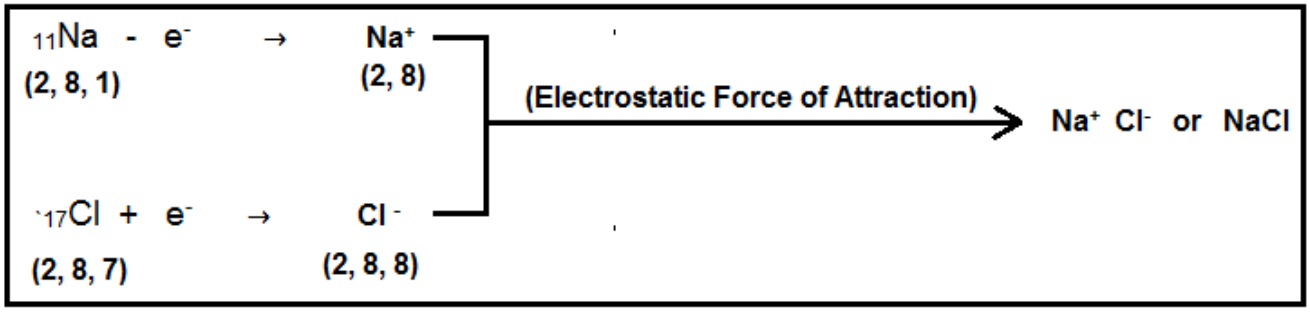
Example: I: Formation of NaCl.

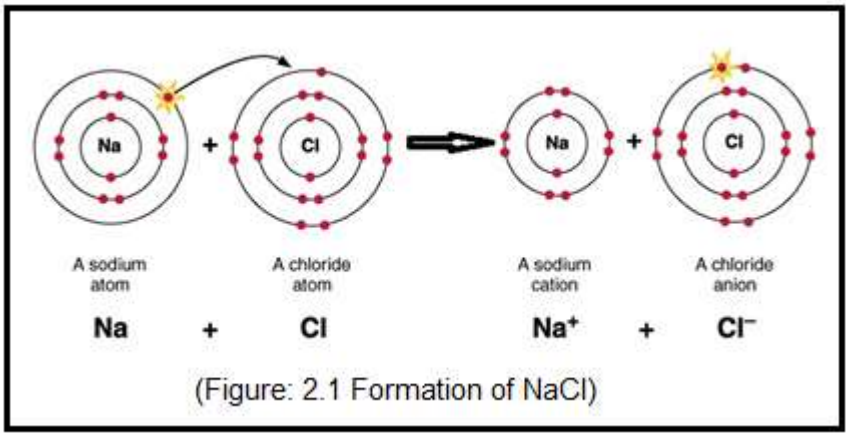
The electronic configurations of Na and Cl are given below:

$_{11}Na - 1s^2 2s^2 2p^6 3s^1$

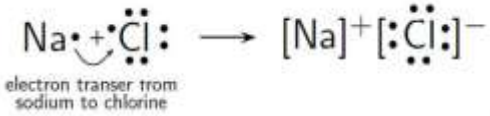
$_{17}Cl - 1s^2 2s^2 2p^6 3s^2 3p^5$

The electronic configurations indicate the presence of one and seven valence electrons in sodium and chlorine respectively. During the formation of NaCl, the sodium atom donates its valence electron completely to the chlorine atom (Fig. 2.1). Na becomes Na^+ with 8 electrons in valence shell and attains the nearest noble gas configuration of Ne; while Cl atom becomes Cl^- ion with '8' electrons in valence shell and attains the nearest noble gas configuration of Ar.





(Figure: 2.1 Formation of NaCl)



Now the electrostatic force of attraction between the oppositely charged ions Na^+ and Cl^- results in the formation of **NaCl**.

Other examples of ionic compounds: *KCl, KBr, KI, CaF_2, $CaBr_2$, CaI_2, Na_2O, K_2O, CaO, MgO, Na_2S, K_2S etc.*

COVALENT BOND:

The chemical bond formed by the mutual (equal) sharing of valence electrons between two atoms is called covalent bond and the compound formed is called covalent compound.

The number of electrons shared by an atom during covalent bond formation is called **covalency**. A covalent may be formed between the atoms of similar or dissimilar elements. When two, four and six electrons are shared between two atoms, then a single, double and a triple bond are formed respectively.

Example: I: Formation of H_2 molecule.

The electronic configuration of 'H' is

$$_1H - 1s^1$$

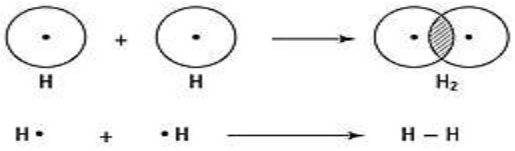


Figure: 2.3

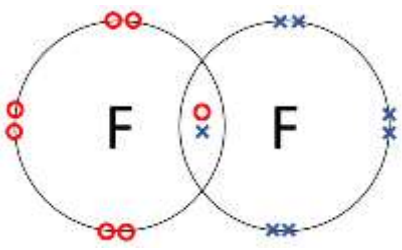
The electronic configuration indicates the presence of 1 valence electron in 'H' and requires one more electron to become duplet. Thus, each hydrogen atom shares its electron with each other to form a covalent bond (Fig. 2.3).

Example : 2 :Formation of F_2 molecule.

The electronic configuration of 'F' is

$$_9F - 1s^2 2s^2 2p^5$$

The electronic configuration indicates the presence of 7 valence electrons in 'F' and requires one more electron to become an octet. Thus, each fluorine atom shares one of its valence electrons with each other to form a covalent bond.



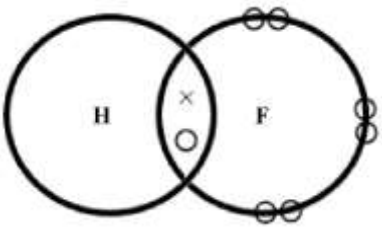
Example :3: Formation of HF molecule.

The electronic configuration of 'H' and 'F' are:

$_1$H - $1s^1$

$_9$F - $1s^2 2s^2 2p^5$

The electronic configurations indicate the presence of 1 and 7 valence electrons in 'H' and 'F' respectively. The hydrogen atom requires 1 more electron to become duplet, while the fluorine atom requires 1 more electron to become octet. Thus, the hydrogen and fluorine atoms share one of their valence electron each to form a covalent bond.



Other examples of covalent compounds: , Br_2, I_2, BF_3, $AlCl_3$, HCl, SiO_2,etc.

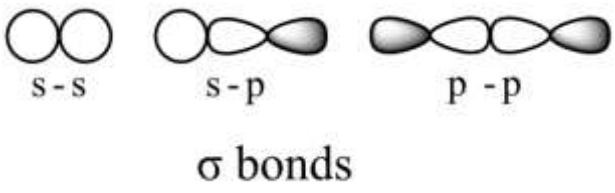
Concept of Orbital Overlapping:

Orbital overlap is the concentration of orbitals on adjacent atoms in the same region of space, allowing electrons to be shared and form a covalent bond. The greater the extent of this spatial overlap, the stronger and more stable the resulting bond.

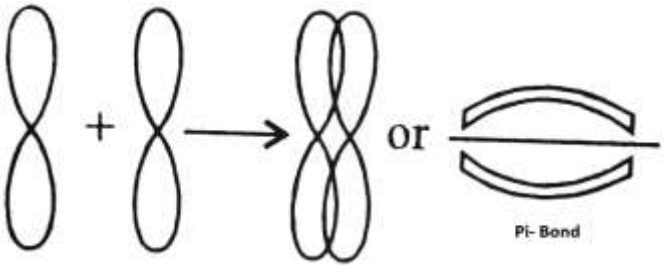
Types of Orbital Overlap

Depending on how the atomic orbitals approach and merge, they form different types of chemical bonds:

- **Sigma** (σ) **Bonds:** A sigma bond is formed by the head-on (axial) overlapping between s-s, s-p or p-p atomic orbitals. The electron density is concentrated symmetrically along the inter-nuclear axis. A sigma bond can exists alone. A sigma bond is stronger than a pi bond due to greater extent of overlapping in case of sigma bond.



- **Pi** (π) **Bonds:** A pi bond is formed by the side-wise overlapping between p-p atomic orbitals. The electron density is distributed above and below the inter-nuclear axis. A pi bond cannot exists alone. A pi bond is weaker than a sigma bond.



Hybridization:

The process of intermixing atomic orbitals having the same or nearly same energy content of an atom to give altogether different orbitals called hybrid orbitals having equivalent shape, size and energy is called ***hybridization***.

Steps involved in hybridization:

1. Promotion or Excitation: For some atoms excitation of electrons to the higher atomic orbitals is required.
2. Reorientation: The atomic orbitals then get intermixed with each other to form a new set of orbitals called hybrid orbitals.

Characteristics of Hybridization

Some of the following characteristics of Hybridization is give below-:

1. The orbitals of one and the same atom participate in hybridization.
2. The atomic orbitals having same or nearly same energy content can participate in hybridisation.
3. The number of hybrid orbitals equals the number of hybridising orbitals.
4. The hybrid orbitals formed are similar in shape, size and energy.
5. Only the atomic orbitals and not the electrons get hybridised.
6. The hybrid orbitals are so directed in space to have a stable arrangement and provide the molecule a proper shape.

Types of Hybridization: Depending on the number and the types of atomic orbitals get intermix, hybridization may be of the following types: sp, sp^2, sp^3, dsp^2, sp^3d^2, d^2sp^3, etc.

Hybridization in $BeCl_2$(Beryllium chloride):

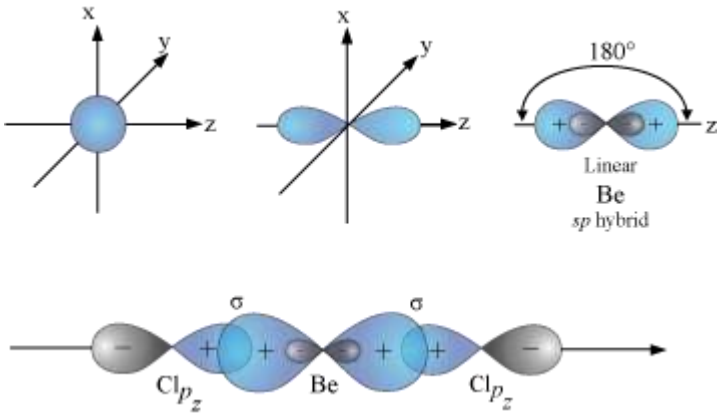
In $BeCl_2$, the central atom Beryllium uses sp hybridization. The electronic configuration of 'Be' in the ground state is:

$_4Be : 1s^2 2s^2$

One of its 2s electrons is promoted to empty $2p_x$ orbital. Thus, in the excited state, the electronic configuration of 'Be' is

$_4Be^* : 1s^2 2s^1 2p_x^1 2p_y^0 2p_z^0$

The 2s and $2p_x$atomic orbitals of 'Be' get intermixed with each other to form two sp hybrid orbitals with equivalent shape size and energy.



These two half-filled orbitals form two σ bonds with chlorine. Therefore, $BeCl_2$ is linear and the bond angle between the two hybrid orbitals is 180°.

Hybridization in BF_3 (Boron fluoride):

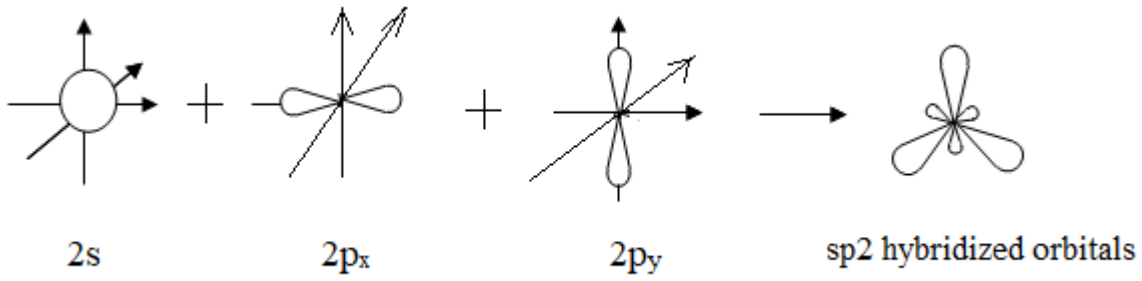
In BF_3, the central atom Boron uses sp^2 hybridization. The electronic configuration of 'B' in the ground state is:

$_5B : 1s^2 2s^2 2p_x^1 2p_y^0 2p_z^0$

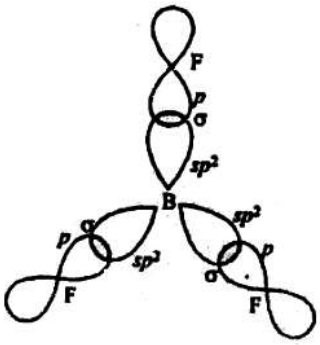
One of its 2s electrons is promoted to empty $2p_y$ orbital. Thus, in the excited state, the electronic configuration of 'B' is

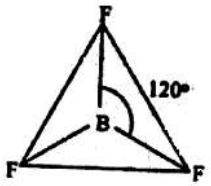
$_5B^* : 1s^2 2s^1 2p_x^1 2p_y^1 2p_z^0$

The 2s, $2p_x$ and $2p_y$ atomic orbitals of 'B' get intermixed with each other to form three sp^2 hybrid orbitals with equivalent shape size and energy.



Each sp^2 hybrid orbitals of boron overlap with the $2p_z$ orbital of fluorine to form three sigma bonds. The shape of BF_3 is trigonal planar with bond angle 120^0.





Hybridization in CH_4 (Methane):

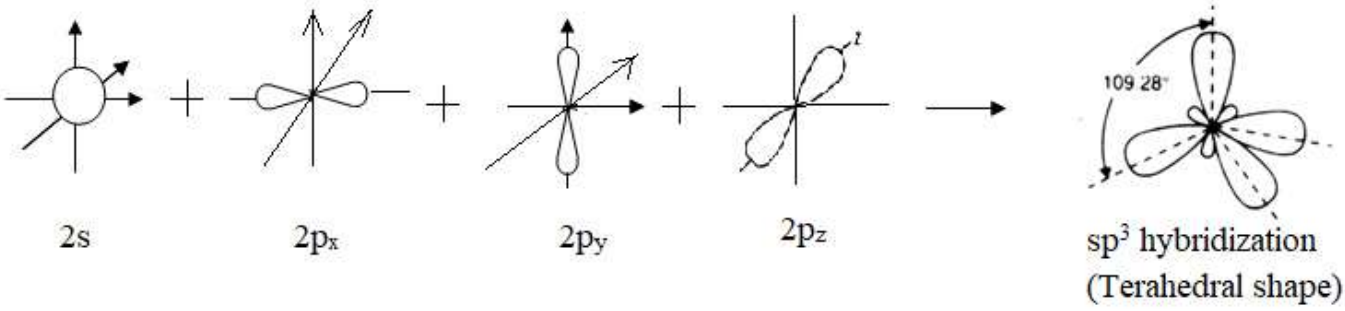
In CH_4 the central atom carbon uses sp^3 hybridization. The electronic configuration of 'C' in the ground state is:

$_6C - 1s^2 2s^2 2p_x^1 2p_y^1 2p_z^0$

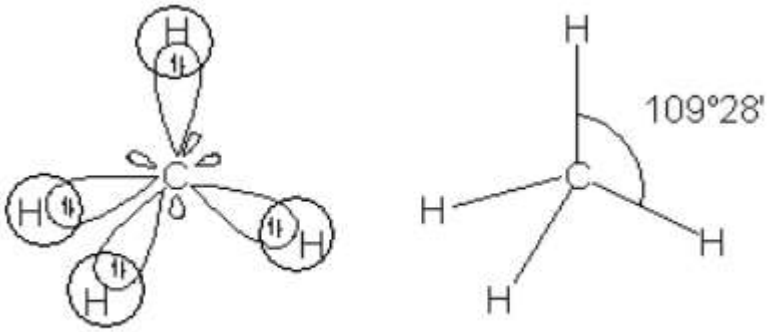
One of the electrons of 2s orbital gets excited to the $2p_z$ orbital. The electronic configuration of carbon in the excited state is:

$_6C^* - 1s^2 2s^1 2p_x^1 2p_y^1 2p_z^1$

The 2s, $2p_x$, $2p_y$ and $2p_z$ orbitals of carbon atom get intermix with each other to form four sp^3 hybrid orbitals, all with equivalent shape size and energy.



Each sp^3 hybrid orbital of carbon overlaps with the 1s orbitals of hydrogen atoms to form four sigma bonds. The shape of CH_4 is tetrahedral with bond angle $109^0 28'$.



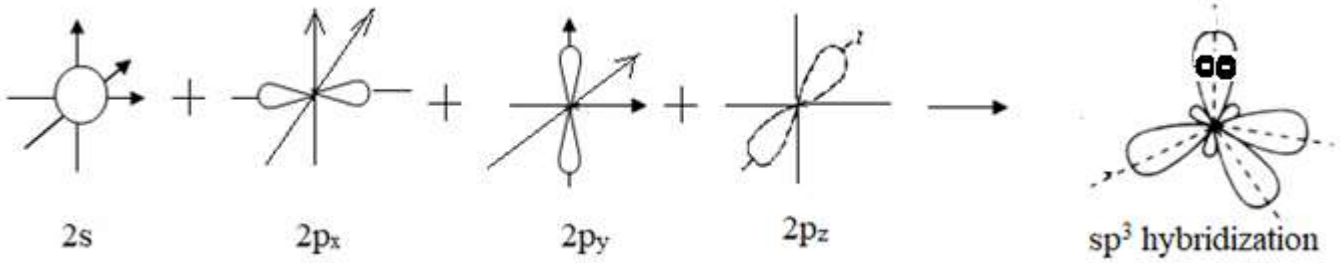
Tetrahedral structure of methane

Hybridization in NH_3 (Ammonia):

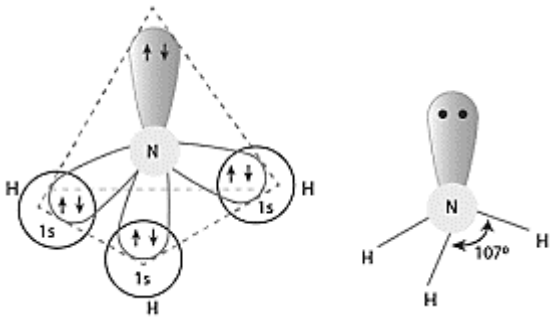
In NH_3 the central atom nitrogen uses sp^3 hybridization. The electronic configuration of 'N' in the ground state is:

$_6N - 1s^2 2s^2 2p_x^1 2p_y^1 2p_z^1$

The 2s, $2p_x$, $2p_y$ and $2p_z$ orbitals of nitrogen atom get intermix with each other to form four sp^3 hybrid orbitals.



Out of the four hybrid orbitals, one is occupied by a lone pair of electrons. The remaining three sp^3 hybrid orbitals of 'N' overlap with the 1s orbitals of 'H' to form three sigma bonds. Due to the presence of a lone pair of electrons over nitrogen atom, the shape of NH_3 molecule is pyramidal with a reduced bond angle of 107^0.

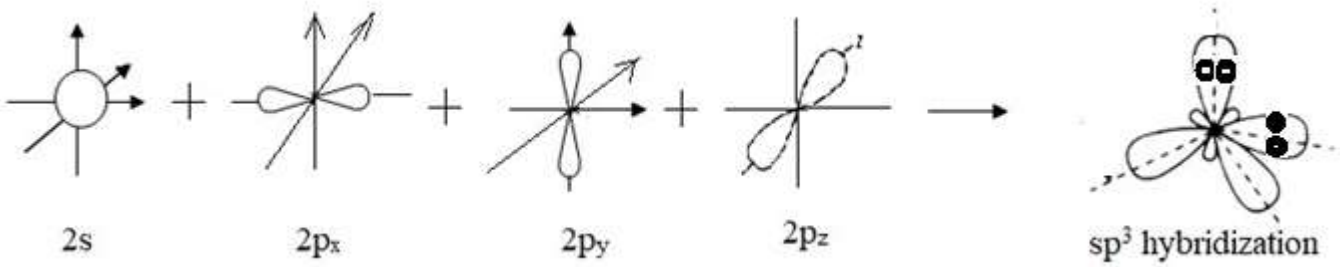


Hybridization in H_2O(Water):

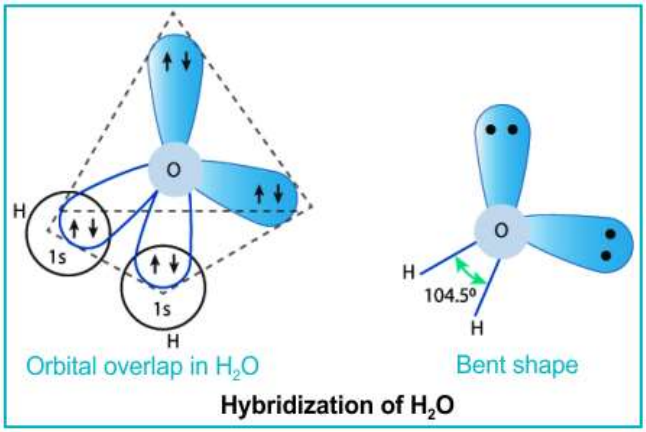
In H_2O, the central atom 'O' uses sp^3 hybridization. The electronic configuration of 'O' in the ground state is:

$_8O - 1s^2 2s^2 2p_x^2 2p_y^1 2p_z^1$

The 2s, $2p_x$, $2p_y$ and $2p_z$ orbitals of oxygen atom get intermix with each other to form four sp^3 hybrid orbitals.



Out of the four hybrid orbitals, two are occupied by lone pair of electrons. The remaining two sp^3 hybrid orbitals of 'O' overlap with the 1s orbitals of 'H' to form two sigma bonds. Due to the presence of two lone pair of electrons over oxygen atom, the shape of H_2O molecule is 'bent' shape or 'V' shape with a reduced bond angle of 104.5^0.



CO-ORDINATE BOND:

The chemical bond formed by the partial donation and partial sharing of a lone pair of electrons between two atoms (or ions) is called a co-ordinate or dative bond.

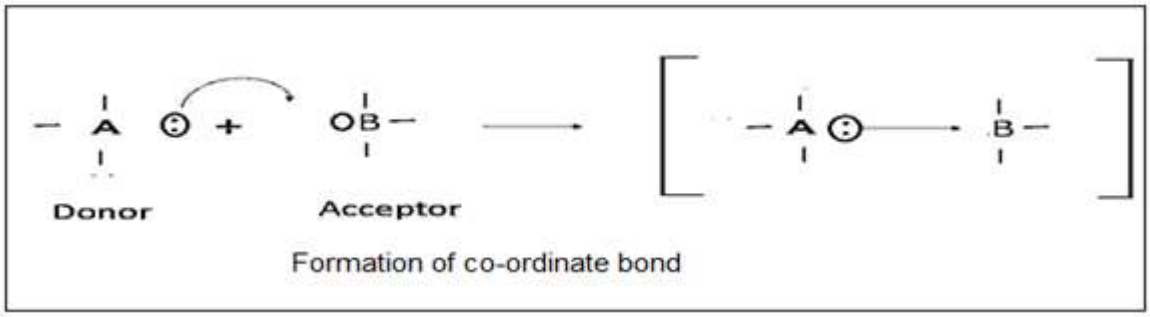
Conditions for the formation of co-ordinate or Dative bond:

i. *One of the participating atoms should have at least one lone or unshared pair of electrons.*

ii. *The other atom should be short of a pair of electrons than the nearest inert gas element.*

The lone pair of electrons present over one atom is partially shared by both the combining atoms. A co-ordinate bond is represented by an arrow (→) sign**,** the head of which points towards the acceptor atom, while the tail points towards the donor atom.

Since co-ordinate bonds have some polar character, it is also known as dative or semi-polar bond or co-ionic bond.



Formation of co-ordinate bond

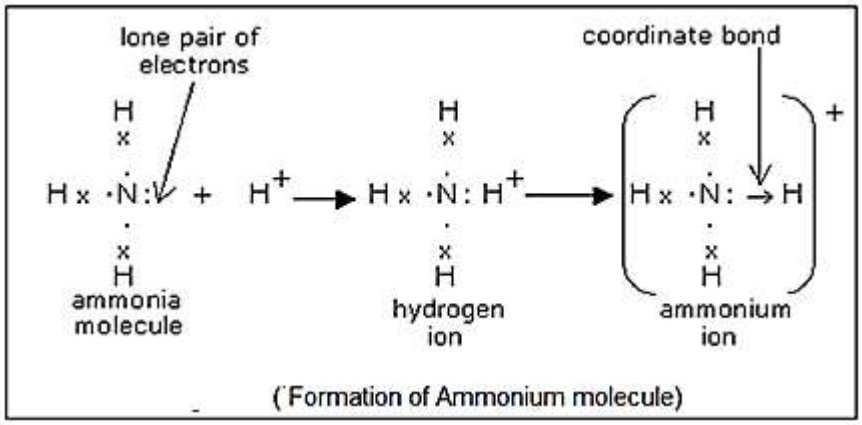
Example: 1: Formation of ammonium ion (NH_4^+).

Ammonium ion (NH_4^{+}) is formed by the combination of NH_3 and H^+ ion.

$NH_3 + H^+ \rightarrow NH_4^+$

Ammonia (NH_3) contains a lone pair of electrons over 'N' while 'H^+' ion contains no electron and requires two electrons to become duplet.

Thus, the unshared pair of electrons over nitrogen in NH_3 is partially shared with H^+ ion and a Co-ordinate bond is formed.



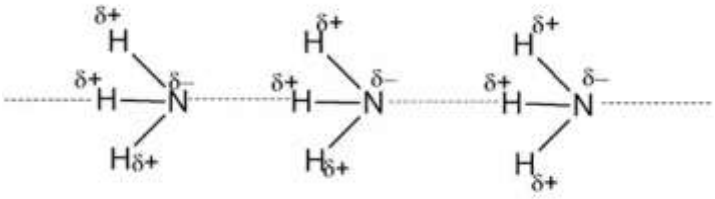
(Formation of Ammonium molecule)

<u>Hydrogen Bonding:</u>

The week force of intermolecular attraction between the hydrogen atom of a molecule and a most electronegative atom like F, O or N of the same or different molecules is called hydrogen bond.

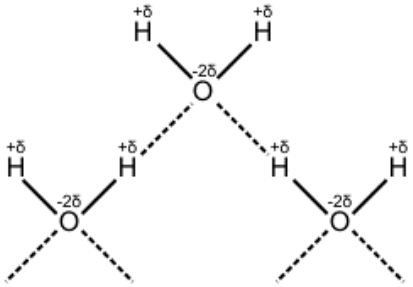
Hydrogen bonding in NH_3:

In NH_3, nitrogen is more electronegative than hydrogen. Thus, the nitrogen atom drags the shared pair of electrons towards it in H – N bond and develops a partial negative charge over it. On the other hand, H' develops a partial positive charge on it. Now the weak force of attraction between the partially positively charged $H^{\delta+}$ and the partially negatively charged $N^{\delta-}$ forms hydrogen bonds.



Anomalous Properties of NH_3 due to hydrogen bonding:

1. Because of strong intermolecular hydrogen bonding, NH_3 exists as an associated molecule.
2. Due to intermolecular hydrogen bonding NH_3 is highly soluble in water.
3. Ammonia has a higher boiling point than PH_3.



Hydrogen bonding in H_2O:

In H_2O, oxygen is more electronegative than hydrogen. Thus, the oxygen atom drags the shared pair of electrons towards it in H – O bond and develops a partial negative charge over it. On the other hand, 'H' develops a partial positive charge on it. Now the weak force of attraction between the partially positively charged $H^{\delta+}$and the partially negatively charged $O^{\delta-}$forms hydrogen bonds.

Anomalous Properties of H_2O due to hydrogen bonding:

The following are the anomalous properties of water due to hydrogen bonding:

1. It exists as associated molecules.
2. It exists in liquid state while other hydrides of the group exist in gaseous state.
3. It has high surface tension.
4. It has high heat of vaporization.
5. It has decreased viscosity under pressure.
6. It has the properties of cohesion, adhesion and higher density than similar compounds which do not show hydrogen bonding.

<u>Metallic Bonding:</u>

The chemical bond which is formed between metal atoms is called a metallic bond.

It is a form of chemical bonding that arises from the electrostatic attractive force between conduction electrons and positively charged metal ions. It happens between similar atoms of metal in a free state. Valence electrons move freely among all metal atoms. Metallic bonding accounts for many physical properties of metals, such as lustre, malleability, resistivity, thermal conductivity and electrical conductivity, strengths and ductility. Such bonds are characterized by the following features.
Examples of substances having metallic bonding: Na, K, Fe, Cu, Al, etc.

SOLUTIONS

Solute: Solutes are the substances that dissolve in solvents to form a solution. Solutes can be solids, liquids or gases. Solutes are present in lesser amount than solvents.

Solvent: Solvents are the substances that dissolve solutes. Liquids are the most common solvents, but gases and solids can also be used. Solvents are present in higher amount compared to solutes.

Solution: Solutions are mixtures of two or more substances. A solution can be in solid, liquid and gaseous state.

$$\boldsymbol{Solute + Solvent \rightarrow Solution}$$

Atomic weight/mass:

The atomic mass of an element may be defined as "the average relative mass of one atom of the element as compared to the mass of an atom of carbon (^{12}C) taken as 12".

Unit: amu (atomic mass unit) or simply '*u*'.

For example:

Element	***Atomic mass in amu***
H	*1.008 ≈ 1*
N	*14*
O	*16*

Atomic masses of some elements are given below:

Element	**Symbol**	**Atomic Weight in a.m.u**
Hydrogen	*H*	*1*
Helium	*He*	*4*
Lithium	*Li*	*7*
Berylium	*Be*	*9*
Boron	*B*	*11*
Carbon	*C*	*12*
Nitrogen	*N*	*14*
Oxygen	*O*	*16*
Fluorine	*F*	*19*
Neon	*Ne*	*20*
Sodium	*Na*	*23*
Magnesium	*Mg*	*24*
Aluminium	*Al*	*27*

Silicon	*Si*	*28*
Phosphorous	*P*	*31*
Sulphur	*S*	*32*
Chlorine	*Cl*	*35.5*
Argon	*Ar*	*40*
Potassium	*K*	*39*
Calcium	*Ca*	*40*
Chromium	*Cr*	*52*
Iron	*Fe*	*56*
Copper	*Cu*	*63.5*
Bromine	*Br*	*80*
Silver	*Ag*	*108*
Lead	*Pb*	*207*

Modes of Expression of Concentration of solutions:

The following are the modes of expression of concentrations of solutions:

Molarity, Normality, Molality, Mass percentage, Volume percentage, mole fraction, ppm, ppb, etc.

1. Molarity (M):

Molarity of a solution may be defined as "the number of gram mole of the solute present per liter of solution".

Unit = gram mole/liter or M.

Mathematically,

$M = \frac{w \times 1000}{M_s \times V_{ml}}$; Where w = weight of the solute in gram

Ms = Molecular weight of the solute.

V_{ml} = Volume of solution in ml.

Molar solution:

The solution containing 1 gm mole of the solute per liter of solution is called a 'molar' solution.

For example: The solution containing 36.5 gm of HCl, 40 gm of NaOH, 58.5 gm of NaCl or 98 grams of H_2SO_4 per liter of solution is called molar solution.

NOTE: 1. Deci molar solution means (1/10) M solution, Semi-molar solution means (½) M solution, centi-molar solution means (1/100) M solution.

2. The solution whose strength is known is called *a standard solution.*

PROBLEMS FOR DISCUSSION:

QUESTION: 1. *0.4 gm of caustic soda (NaOH) is present in 200 ml of its solution. Find out the molarity of the solution.*

Solution **: Given Data**

weight of solute (w) = 0.4 gm

Volume of solution (V_{ml}) = 200 ml.

Mol.wt. of solute (NaOH), M_S = 23.+16+1 = 40 amu.

Thus, Molarity (M) $= \frac{w \times 1000}{M_S \times V_{ml}} = \frac{0.4 \times 100}{40 \times 200}$= 0.05 M

Hence, the molarity of the solution is 0.05M.

QUESTION:2. *How many grams of caustic potash (KOH) are required to prepare 1.5 lit. of a decimolar solution?*

Solution **: Given Data**

Weight of solute(w) = ?

Volume of the solution (V_{ml}) = 1.5 lit = 1500 ml.

Molecular weight of solute, Ms for KOH =39+16+1 =56 amu

Molarity of the solution = 1/10 M = 0.1M

Thus, $M = \frac{w \times 1000}{M_S \times V_{ml}} \Rightarrow\ w = \frac{M \times M_S \times V_{ml}}{1000} = \frac{0.1 \times 56 \times 1500}{1000}$= = 8.4 gram.

Thus, 8.4 gm *of caustic potash is required to prepare 1.5 lit. of deci-molar solution.*

2. Mole Fraction (X)

The mole fraction of a component is the number of moles of that component in the solution divided by the total number of moles in the given solution.

$$\textbf{Mole fraction of Solute} = \frac{\boldsymbol{No.of\ moles\ of\ Solute}}{\boldsymbol{No.of\ moles\ of\ Solute + No.of\ moles\ of\ Solvent}}$$

$$\textbf{Mole fraction of Solvent} = \frac{\boldsymbol{No.of\ moles\ of\ Solvent}}{\boldsymbol{No.of\ moles\ of\ Solute + No.of\ moles\ of\ Solvent}}$$

Note: Mole fraction of solute + mole fraction of solvent = 1

Q. 1. A mixture of gases contains 4 moles of H_2, 8 moles of N_2 and 2 moles of O_2. Find the mole fractions of each component.

Solution:

$$\text{Mole fraction of } H_2 = \frac{n_{H_2}}{n_{H_2} + n_{N_2} + n_{O_2}} = \frac{4}{4+8+2} = \frac{4}{14} = 0.28$$

$$\text{Mole fraction of } N_2 = \frac{n_{N_2}}{n_{H_2} + n_{N_2} + n_{O_2}} = \frac{8}{4+8+2} = \frac{8}{14} = 0.57$$

$$\text{Mole fraction of } O_2 = \frac{n_{O_2}}{n_{H_2} + n_{N_2} + n_{O_2}} = \frac{2}{4+8+2} = \frac{2}{14} = 0.14$$

Q. 2. A mixture of gases contains 4 gm of H_2, 14 gm of N_2 and 8 gm of O_2. Find the mole fractions of each component.

Solution:

$$\text{No. of moles of } H_2 = \frac{Mass\ of\ H_2}{Molecular\ mass\ of\ H_2} = \frac{4}{2} = 2$$

$$\text{No. of moles of } N_2 = \frac{Mass\ of\ N_2}{Molecular\ mass\ of\ N_2} = \frac{14}{28} = 0.5$$

$$\text{No. of moles of } O_2 = \frac{Mass\ of\ O_2}{Molecular\ mass\ of\ O_2} = \frac{8}{32} = 0.25$$

$$\text{Mole fraction of } H_2 = \frac{n_{H_2}}{n_{H_2} + n_{N_2} + n_{O_2}} = \frac{2}{2+0.5+0.25} = \frac{2}{2.75} = 0.72$$

$$\text{Mole fraction of } N_2 = \frac{n_{N_2}}{n_{H_2} + n_{N_2} + n_{O_2}} = \frac{0.5}{2+0.5+0.25} = \frac{0.5}{2.75} = 0.18$$

$$\text{Mole fraction of } O_2 = \frac{n_{O_2}}{n_{H_2} + n_{N_2} + n_{O_2}} = \frac{0.025}{2+0.5+0.25} = \frac{0.025}{2.75} = 0.009$$

3. Parts per million (PPM)

Parts per million may be defined as "the ratio between the no. of parts of solute dissolved to a million parts of the total volume.

$$\boldsymbol{ppm = \frac{No.\ of\ parts\ of\ the\ component}{Total\ no.\ of\ parts\ of\ all\ components} \times 10^6}$$

$$\boldsymbol{ppm = \frac{weight\ of\ solute}{Volume\ of\ solution} \times 10^6}$$

Q 1. What is the concentration, in ppm, if 0.025 g of KCl is dissolved in 100 grams of water?

Solution:

Given Data:

Weight of solute = 0.025 gm

Weight of solution = 0.025 + 100 = 100.025 gm.

$$\boldsymbol{ppm = \frac{weight\ of\ solute}{weight\ of\ solution} \times 10^6 = \frac{0.025}{100.025} \times 10^6 = 249.94\ ppm.}$$

Q 2. 500 cc of an aqueous solution contains 10 gm of NaOH. Calculate its concentration in ppm.

Solution:

Given Data:

Weight of solute = 10 gm

Weight of solution = 500 cc.

$$\boldsymbol{ppm = \frac{weight\ of\ solute}{Volume\ of\ solution} \times 10^6 = \frac{10}{500} \times 10^6 = 20,000\ ppm.}$$

4. **Mass Percentage (w/w):**The mass percentage of a solute may be defined as " the mass of solute in grams present in 100 gm of the solution".

$$\boldsymbol{Mass\ \%\ of\ solute = \frac{mass\ of\ solute}{Total\ mass\ of\ solution} \times 100}$$

Q 1. What is the concentration in terms of mass percent of a solution in which 40 g of salt is dissolved in 200 mL of water?

Solution:

1 ml of water has a mass of 1 g.

So, mass of 200 ml of water = 200g

Mass of the solution = mass of the solute + mass of the solvent = 200 + 40 = 240 g

$$Mass\ \%\ of\ solute = \frac{mass\ of\ solute}{Total\ mass\ of\ solution} \times 100 = \frac{40}{240} \times 100 = 16.66\%$$

5. **Volume Percentage (v/v):** The volume percentage of a solute may be defined as "the volume (in cc) of solute i present per 100 cc of the solution".

$$\boldsymbol{Volume\ \%\ of\ solute = \frac{Volume\ of\ solute}{Total\ volume\ of\ solution} \times 100}$$

Q 1. 10 cc of HCl is present in 200 cc of its solution. Calculate the volume percentage of HCl in the solution.

Volume of solute (HCl) = 10 cc.

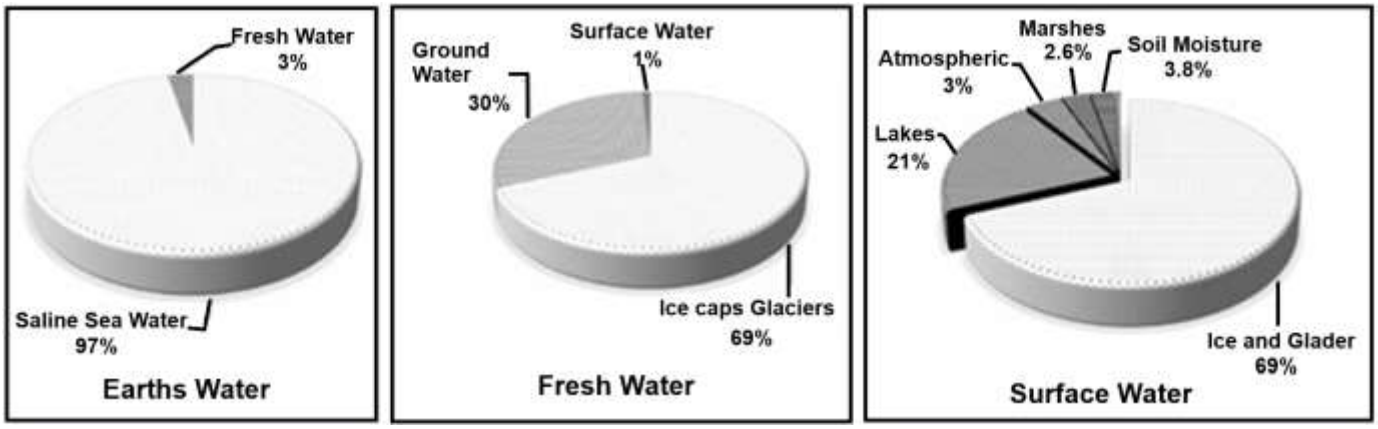
Volume of solution = 200 cc.

$$Volume\ \%\ of\ solute = \frac{Volume\ of\ solute}{Total\ volume\ of\ solution} \times 100 = \frac{10}{200} \times 100 = 5\%$$

UNIT – 7: WATER AND WATER TREATMENT

Graphical representation of water distribution on Earth:

Graphical Representation of Water Distribution on the Earth Different pie charts are helpful to understand the existence and distribution of available water on the earth. Out of total existing water, only 3% of water is freshwater, while the remaining 97% of water is saline or seawater. Almost 99% of it is locked up in ice and the ground; only a slight 1% of all is surface water. Fig. 2.3 shows the breakdown of surface freshwater. 69% of this water is locked up in ice, and another 21% is found in lakes. Soil moisture contains 3.8% water, the atmosphere contains 3% water and swamp and marshes have 2.6% water. Rivers account for a small percentage of fresh water i.e. 0.49%, large portion of which is available for living organisms.



Classification of water based on soap test:

1. Soft water: - Water which lathers or produces enough foam with soap solution is called soft water.

Ex: - Rainwater, de-mineralized water, distilled water etc.

1. **Hard water: -** Water which does not lather or does not produce enough foam with soap solution is called hard water. Instead, it forms a curdy white precipitate.

Ex: - Sea water, river water, Pond water etc.

Hardness of water:

It is the characteristic of water which prevents the lathering of soap due to the presence of bicarbonate, sulphate and chloride of calcium and magnesium in it.

Distinction between soft water and hard water

SN	Soft Water	Hard Water
1	It has low mineral content.	It has high mineral content.
2	It does not contain Ca and Mg ions.	It contains Ca and Mg ions.
3	Soap is not wasted.	A large quantity of soap is wasted.
4	React with soap to form lather.	React with soap to form precipitates.
5	It does not have ill effects on domestic and industrial use.	It has ill effects on domestic and industrial use.
6	It is suitable for drinking.	It is not suitable for drinking.

Types of hardness:

Hardness of water is of two types:

A. Temporary or Carbonate hardness

B. Permanent or Non-carbonate hardness

A. **Temporary hardness:** The temporary hardness of water arises due to the presence of bicarbonates of **Ca and Mg, [$Ca(HCO_3)_2$, $Mg(HCO_3)_2$]**.

It is named temporary hardness because the soluble bicarbonates decompose into insoluble carbonates simply on heating. Thus, water becomes soft. It is also called carbonate hardness.

B. **Permanent hardness: The** permanent hardness of water arises due to the presence of chlorides of Ca, Mg ($CaCl_2$, $MgCl_2$).It is named permanent hardness because such a hardness cannot be removed by simply boiling the water.

Unit of hardness

(1) PPM – Parts per million.

(2) mg/L – Milligrams per Litre.

Causes of poor lathering of soap in hard water:

Hard water contains calcium and magnesium ions. When soap comes in contact with hard water, these ions form calcium and magnesium salts of fatty acids which are insoluble in water. These calcium or magnesium salts precipitate out in the form of scum.

Soap reacts with hard water as

$$\underset{\text{(Sodium stearate)}}{2C_{17}H_{35}COONa} + \underset{\text{(Impurity in hard water)}}{MgSO_4} \rightarrow \underset{\text{(Magnesium stearate)}}{(C_{17}H_{35}COO)_2Mg} + Na_2SO_4$$

Problems caused by the Use of Hard Water in the Boiler

Water is helpful to a great extent in several industries. However, when hard water used for different processes, it gives other ill effects. Water containing dissolved salts of sulphates, carbonates, chlorides of calcium, magnesium and iron salts have an adhesive impact on steam boilers. The manufacturing

industries need water for a different purpose, out of which steam generation is of the utmost importance. Hence, water for raising steam in boilers must be soft and must not contain dissolved matter to avoid sludge, scale, priming and foaming problems in the boiler.

(A) Sludge

Due to the continuous boiling of water, the concentration of dissolved salt inside the boiler is increased. When the salt concentration reaches the saturation point, salts are thrown out of the water, precipitating on the inner wall of the boiler.

The loose and slimy precipitate deposited on the inner wall of boiler is known as sludge.

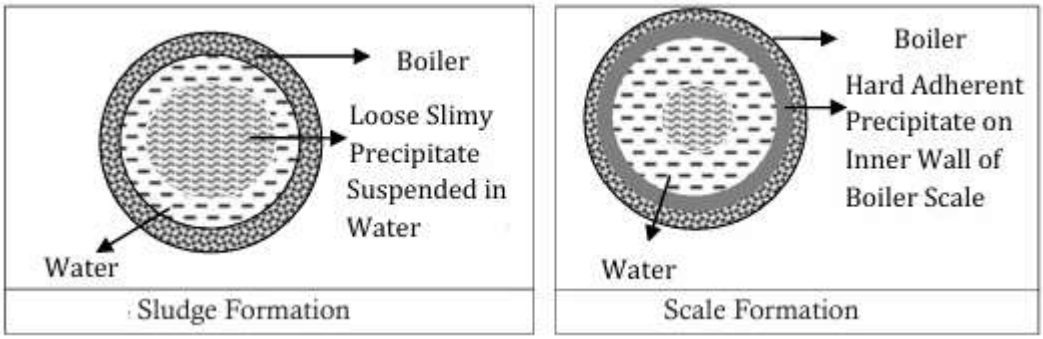
Excessive sludge formation disturbs the working of the boiler. It settles in the regions of poor water circulation such as pipe connection, plug opening, thereby causing even choking of the pipes.

Properties of Sludge

- Sludges are soft and less permeable precipitate.
- Sludges are poor conductors of heat.
- These are formed at comparatively cooler portions of the boiler.
- Sludges are formed by substances that have greater solubility in hot water. e.g. $MgCO_3$, $MgCl_2$, $CaCl_2$, $MgSO_4$ etc.

Prevention of Sludge Formation

- We can decrease sludge formation by using well soften water.
- Frequently blowdown operation by drawing off a portion of the concentrated water.
- Mechanical means by scrapping off the sludge with a wire brush.
- Giving thermal shocks.



(B) Scale

While continuously boiling the water inside the boiler, the salt concentration reaches the saturation point, the salts are thrown out of the water in the form of precipitates on the inner wall of the boiler. They are formed due to the presence of sulphate and silicates of calcium and magnesium.

The hard adhering coating deposited on the inner wall of boiler is known as scale.

Properties of Scale

- The scale is very hard and firmly adhered to the boiler.
- It is difficult to remove them, even with the hammer or chisel.
- It is a bad conductor of heat.

<u>Prevention of the Scale Formation</u>

- The formed precipitate can be removed by thermal shocks with chisel hammer treatment.
- Internal conditioning with different chemicals as phosphate, carbonate, calgon, tannin, agar gel, sodium aluminate, EDTA.

Difference between Sludge and Scale

Sludge	Scale
Soft, loose and slimy precipitate	Hard deposits
Non-adherent deposits and can be easily removed	Stick very firmly to the inner surface of the boiler and are very difficult to remove
Softer and less permeable	Harder and more permeable
Poor conductor of heat	Bad conductor of heat
Formed generally at the colder portion of the boiler	Formed generally at the hotter part of the boiler
Decreases efficiency of the boiler but are less dangerous.	Decreases efficiency of the boiler and more dangerous.
There will be fewer chances of explosion due to sludges formation.	There will be more chances of explosion due to scale formation.
They are generally formed due to salts like $CaCl_2$, $MgCl_2$, $MgSO_4$, $MgCO_3$ in the water.	They are generally formed due to salts like $CaSO_4$, $Mg(OH)_2$, $CaCO_3$, $CaSiO_3$, $Ca_3(PO_4)_2$, CaO.
The precipitate can be removed by blowdown operation, scrapers and brushing	The precipitate can be removed by different methods like thermal shocks, chiselling, hammer treatment along with some chemical like HCl, phosphate, carbonate, calgon, tannin, agar gel, sodium aluminate, EDTA.

(C) Priming:

When the boiler is being steamed rapidly, some liquid water particles are mixed with the steam. Priming is the conveyer of variable amounts of droplets of water in the steam.

(D) Foaming

Foaming is the production of persistent foam and bubbles in boilers. Formed bubbles do not break easily. Foaming is generally due to the presence of substances like oils.

<u>Causes of Priming and Foaming</u>

The causes of priming and foaming are as follows:

- Presence of a large amount of dissolved solids.
- High steam velocities.
- Sudden boiling.
- Improper boiler designs.
- The sudden increase in steam production rate.

Priming and Foaming can be Avoided by:

- Fitting mechanical steam purifiers.
- Avoiding rapid change in steaming rate.
- Maintaining low water level in boilers.

- Efficient softening and filtration of the boiler feed water. Adding antifoaming chemicals like castor oil.
- Removing oil from boiler water by adding compounds like sodium aluminate.

Problems due to priming and Foaming:

Due to priming and foaming following problems are generated in the boiler:

- Causes caustic embrittlement.
- Chocking of outlets.
- Do not allow steam to flow quickly due to the presence of foam.

Effect of Priming and Foaming

In boiler, water priming and foaming usually occur together because:

- The actual height of the water column cannot be adequately judged, thereby making the maintenance of the boiler pressure becomes difficult.
- Dissolved salts in water are carried by wet steam to different machinery parts, where salt gets deposited as water evaporates.
- Life of machinery decreases.

(E) **Corrosion**

Boiler corrosion is the decay or destruction of boiler material by a chemical or electrochemical environment. Corrosion of boiler takes place due to following reasons:

- Dissolved oxygen
- Dissolved carbon dioxide
- Dissolved salts

Causes of Boiler corrosion:

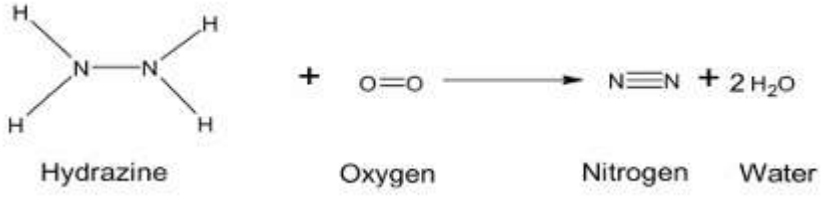
(i) Dissolved Oxygen

Dissolved oxygen present in water interacts with boiler material at steaming temperature to form ferrous hydroxide. Formed ferrous hydroxide further reacts with oxygen to form ferric oxide.

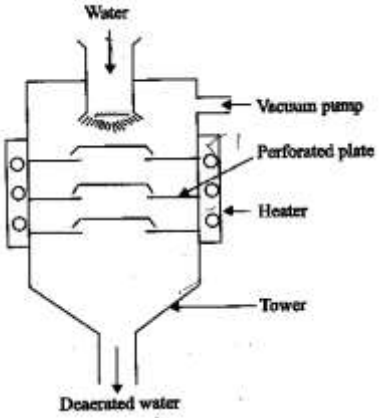
$$2Fe + 2H_2O + O_2 \rightarrow 2Fe(OH)_2 \downarrow$$
$$2Fe(OH)_2 + O_2 \rightarrow 2[Fe_2O_3.2H_2O] \downarrow$$

(a) Removal of Oxygen by using Chemicals

There are different chemicals like hydrazine, sodium sulphite, tannin, which are used to remove dissolved oxygen. In the case of hydrazine reacts with dissolved oxygen to form nitrogen and water. Suppose we use a dissolved oxygen sensor and find that amount of dissolved oxygen in boiler water is increased; in that case, these chemicals react with dissolved oxygen and easily remove dissolved oxygen from boiler water.



Dissolved nitrogen is harmless, and there is no change in the percentage of dissolved solids after the addition of nitrogen.



(b) Removal of Dissolved Oxygen by Heating

Water is passed through the tower, which contains perforated plates, heating arrangement from the side and vacuum pump arrangement. High-temperature low pressure, and large exposed surface reduce the dissolved oxygen in water.

(ii) Dissolved CO2

Water associated with dissolved CO_2 forms carbonic acid, which has a slow corrosive effect on boiler material. Water containing bicarbonates is also the source of CO_2.

$$CO_2 + H_2O \rightarrow H_2CO_3 \text{(Carbonic acid)}$$

$$Mg(HCO_3)_2 \rightarrow MgCO_3 + H_2O + CO_2^{\uparrow}$$

Removal of CO_2 by using ammonia

Carbon dioxide can be removed by adding calculated amount of ammonia.

$$H_2O + NH_3 \rightarrow NH_4OH$$

$$NH_4OH + CO_2 \rightarrow (NH_4)_2CO_3 + H_2O$$

Removal of Carbon dioxide by Heating

The solubility of gases in water reduces with the rise in temperature. Thus, water is heated to a high temperature to remove dissolved carbon dioxide. If it is not removed, they are responsible for corrosion of the boiler material.

(iii) Dissolved Salts

The presence of some salts like magnesium chloride in water can corrode boilers. When $MgCl_2$ combines with water, it forms magnesium hydroxide along with hydrochloric acid as a byproduct.

$$MgCl_2 + 2H_2O \rightarrow 2Mg(OH)_{2\downarrow} + 2HCl$$

The liberated acid reacts with the iron metal of the boiler in chain-like reactions producing HCl again and again. Hence the presence of a small amount of $MgCl_2$ will cause corrosion of iron to a large extent.

$$Fe + HCl \rightarrow FeCl_2 + H_2$$
$$FeCl_2 + 2H_2O \rightarrow Fe(OH)_2 + 2HCl$$

During the water softening process, a small quantity of sodium carbonate is added. In high pressure boilers, sodium carbonate decomposes to give sodium hydroxide and carbon dioxide.

$$Na_2CO_3 + H_2O \rightarrow 2NaOH + CO_2$$

Due to the formation of sodium hydroxide, water becomes alkaline. The numbers of minute cracks are observed on the inner wall of boiler. This alkaline water flows into such minute cracks by capillary action. Here due to water evaporation, dissolved caustic soda is left behind. The amount of caustic soda goes on increasing due to progressive evaporation. The alkaline action of caustic soda attacks the surrounding areas of cracks, thereby dissolving the iron material of the boiler.

Precautions to avoid Corrosion due to Salts

- Supply water which is free from salts like $MgCl_2$.

- By using sodium phosphate instead of sodium carbonate for water softening.
- By adding tannin or lignin as additives to the boiler water since these blocks the minute cracks.
- By adjusting the alkalinity of water to an optimum level (pH 7-8)

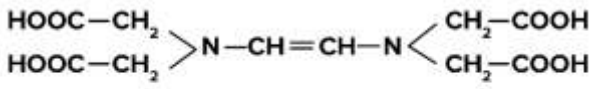
Quantitative measurement of water hardness by EDTA method:

The estimation of hardness of water is of great importance for the chemical industry in general. There are various methods available for estimating the hardness of water.
Some of them are:

1. Soap titration method
2. Alkali titration method
3. EDTA method

Estimation of hardness of water by **EDTA method:**

EDTA is Ethylene Di-amine Tetra Acetic acid. The structure of EDTA is



(EDTA)

In this method the water sample is titrated against EDTA solution using Eriochrome-Black-T indicator (EBT) at a pH of 8-10. Ammonia buffer solution (NH_4Cl & NH_4OH mixture) is used to maintain the required P^H.
When the EBT indicator is added to the water sample, it forms wine red coloured weak complex with Ca^{2+} and Mg^{2+} ions.

$$[Ca^{2+}Mg^{2+}] \; + \; EBT \xrightarrow{P^H=8-10} [Ca\,Mg - EBT]Complex$$

When this solution is titrated against EDTA, it replaces the indicator from the weak complex form stable EDTA complex. When all the hardness causing ions are complexed by EDTA, the indicator is set free. The color of the free indicator is steel blue. Thus, the end point is the change of color from wine red to steel blue.

$$[Ca\,Mg - EBT]Complex + EDTA \xrightarrow{P^H=8-10} [Ca\,Mg - EDTA] + EBT$$

Wine red coloured weak complex Stable complex Steel blue

Preparation of solutions
EDTA Solution
It is prepared by dissolving 4 gms of EDTA in 1000 ml of distilled water.
Standard hard water

1 gm of pure $CaCO_3$ is dissolved in minimum quantity of HCl and then made up to 1000 ml using distilled water.

∴ 1 ml of standard hard water ≡ 1 mg of $CaCO_3$ equivalent hardness.

EBT indicator

0.5 gms of EBT is dissolved in 100 ml of alcohol.

Buffer solution

67.5 gms of NH4Cl and 570 ml of NH_3 are dissolved and the solution is made up to 1000 ml using distilled water.

Standardization of EDTA

50 ml of standard hard water is taken in a clean conical flask. 10 ml of buffer solution and 4-5 drops of EBT indicator are added in to the conical flask and titrate it against EDTA solution taken in the burette. The end point is the change of colour from wine red to steel blue.

Let the volume of EDTA consumed be V_1 ml

Estimation of total hardness of water sample

50 ml of the given hard water sample is taken in clean conical flask and is titrated against EDTA as before.

Let the volume of EDTA consumed be V_2 ml

Estimation of permanent hardness of water sample

100 ml of the same hard water sample is taken in a 250 ml beaker. It is boiled for 15 minutes. During boiling temporary hardness gets removed. It is then cooled and filtered, and the volume is made up to 100 ml in a standard flask by adding distilled water.

50 ml of the made-up solution is pipetted out into a clean conical flask and is titrated against EDTA as before.

Let the volume of EDTA consumed be V_3 ml.

Calculations

Standardization of EDTA

1 ml of Std. hard water = 1 mg of $CaCO_3$

50 ml of Std. hard water = 50 mgs of $CaCO_3$

50 ml of Std. hard water consumes = V_1 ml of EDTA

∴ V_1 ml of EDTA ≡ 50 mgs of $CaCO_3$ equivalent hardness.

Or,1 ml of EDTA ≡ 50 V1 mgs of $CaCO_3$ equivalent hardness.

Estimation of total hardness of water sample

50 ml of the given hard water sample consumes = V_2 ml of EDTA

= $V_2 \times 50/V_1$ mgs of $CaCO_3$ equivalent hardness

[∴ 1 ml of EDTA = 50 V_1 mgs of $CaCO_3$]

∴ 1000 ml of the given hard water sample = $V_2 \times 50 / V_1 \times 1000 / 50$

= $1000 \times V_2 / V_1$mgs of $CaCO_3$ equivalent hardness

∴ Total hardness = $1000 \times V_2/V_1$ ppm

Estimation of permanent hardness of water sample

50 ml of the same hard water sample after boiling, filtering, etc., consumes = V_3 ml of EDTA

= $V_3 \times 50/V_1$ mgs of $CaCO_3$ equivalent hardness

∴ 1000 ml of the given hard water sample = $V_3 \times 50/V_1 \times 1000/50$

= $1000 \times V_3/V_1$ mgs of $CaCO_3$ equivalent hardness

∴ Permanent hardness = $1000 \times V_3/V_1$ ppm

Temporary hardness

Temporary hardness = Total hardness − Permanent hardness

= $[1000 \times V_2 /V_1] - [1000 \times V_3/V_1]$

∴ Temporary hardness = $1000/V_1(V_2 – V_3)$ ppm.

Q 1. 100 ml of a water sample requires 20 ml of EDTA solution for titration. 1 ml of EDTA solution is equivalent to 1.1 mgs of $CaCO_3$. Calculate hardness in ppm.

Solution

Given 1 ml of EDTA solution = 1.1 mgs of $CaCO_3$

∴ 20 ml of EDTA solution = 20×1.1 mgs of $CaCO_3$

= 22 mgs of $CaCO_3$

100 ml of water sample requires = 20 ml of EDTA Solution

= 22 mgs of $CaCO_3$

∴ 1000 ml of water sample = $\frac{22}{100} \times 1000 = 220$ mgs/lit or ppm

Q 2.100 ml of a sample of water requires 18 ml of an EDTA solution for titration. 22 ml of the same EDTA solution was required for the titration of 100 ml of standard hard water containing 1 gm $CaCO_3$ per litre. Calculate hardness of water sample in ppm.

Solution

Given 1 litre of std. hard water contains 1 gm of $CaCO_3$

i.e. 1000 ml of std. hard water contains 1000 mgs of $CaCO_3$

∴ 1 ml of std. hard water = 1 mg of $CaCO_3$

22 ml of EDTA = 100 ml of std. hard water

= 100×1 mg of $CaCO_3$

∴ 1 ml of EDTA = 100/22mgs of $CaCO_3$

100 ml of sample of water = 18 ml of EDTA

$= \frac{100}{22} \times 18 = 81.818$ mg of $CaCO_3$

∴for 1000 ml of sample water = 81.818 X 10 mg of $CaCO_3$

Hardness = 818.18 mgs/lit or ppm.

Q 3. 0.28 gm of $CaCO_3$ was dissolved in HCl and the solution was made up to one litre with distilled water. 100 ml of the above solution required 28 ml of EDTA solution on titration. 100 ml of hard water sample required 33 ml of same EDTA solution on titration. 100 ml of this water, after boiling cooling and filtering required 10 ml of EDTA solution on titration. Calculate the temporary and permanent harness of water.

Solution

Given 1000 ml of std. hard water contains = 0.28 gm of $CaCO_3$

i.e., 1000 ml of std. hard water contains = 0.28 × 1000 mgs of $CaCO_3$

= 280 mgs of $CaCO_3$

∴ 1 ml of std. hard water = 0.28 mg of $CaCO_3$

28 ml of EDTA = 100 ml of the std. hard water

= 100 × 0.28 mgs of $CaCO_3$

= 100 × 0.28 = 28 mg of $CaCO_3$

∴1 ml of EDTA = 1 mg of $CaCO_3$.

Total hardness

100 ml of hard water = 33 ml of EDTA

= 33 × 1 mgs of $CaCO_3$

= 33 mgs of $CaCO_3$

∴ 1000 ml of hard water = $\frac{33}{100} \times 1000 = 330$ mgs/lit or ppm.

<u>Total Dissolved Solids (TDS)</u>

Total dissolved solids (TDS) is the total amount of dissolved salts like calcium, magnesium, potassium, sodium, bicarbonates, chlorides, and sulphates and some small amounts of organic matter that are dissolved in water.

Sources of dissolved solids in water:

TDS in drinking-water comes from natural sources, sewage, urban run-off, industrial wastewater, and chemicals used in the water treatment process, and the nature of the piping or hardware used to convey the water, i.e., the plumbing.

The total dissolved solids test provides a qualitative measure of the amount of dissolved ions but does not tell us the nature or ion relationships. In addition, the test does not provide us insight into the specific water quality issues such as hardness, salty taste, staining, odour, corrosiveness, or the presence of trace metals and microbiological contaminants. Therefore, the total dissolved solids test is used as an indicator test to determine the general quality of the water. The following table can be used as a generalization of the relationship of TDS to water quality problems:

Cations combined with:	Negative impact
Carbonate	Scale formation, bitter taste
Chlorides/Sulphates	Salty, brackish taste, corrosion, odours

How Does Total Dissolved Solids become a problem?

- ☞ If the total dissolved solids are too low, it is possible that the water may be corrosive to metal piping and fixtures and therefore have a bitter or off-taste because of corrosion byproducts. This may also mean the water could have elevated levels of trace metals either leached from the piping in the home or from the aquifer.
- ☞ If the total dissolved solids are extremely high, the water would have a salty taste, greatly corrode the metal piping, and cause the premature failure of appliances.

An elevated TDS indicates the following:

- The concentration of the dissolved ions may cause the water to be corrosive with a salty taste as well as result in scale formation, decreasing the efficiency of hot water heaters.
- It would also suggest that there are many ions that are above the Primary or Secondary Drinking Water Standards, such as an elevated level of nitrate, arsenic, aluminium, copper, lead, etc.

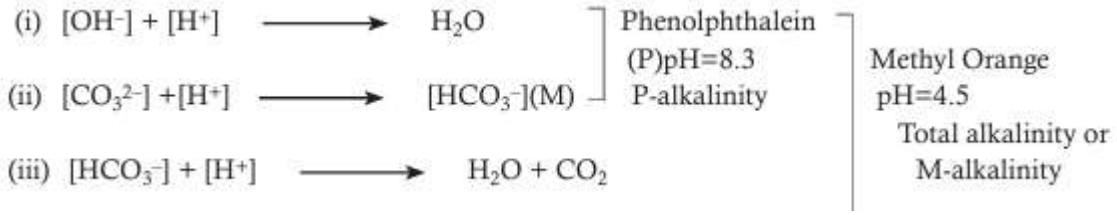
Classification Total Dissolved Solids	
Freshwater	0 to 1000 mg/L
Slightly Saline	1000 to 3000 mg/L
Moderately Saline	3000 to 10,000 mg/L
Very Saline	10,000 to 35,000 mg/L
Briny	> 35,000 mg/L

Quantitative Determination of Water Hardness by Alkalinity Estimation

Alkalinity is defined as the measure of the acid neutralizing capacity of water. The alkalinity of water is attributed to the presence of the

- Caustic alkalinity (due to OH^- and CO_3^{2-} ions)
- Temporary hardness (due to HCO_3^- ions)

These can be estimated separately by titration against standard sulphuric acid, using phenolphthalein and methyl orange as indicators. The determination is based on the following reactions:



The sample water is first titrated against a standard H_2SO_4 solution using phenolphthalein indicator. The end-point indicates the completion of the reaction (i) and (ii) only. Then the sample water is titrated against the same acid using methyl orange indicator. The end-point indicates the completion of reactions i, ii and iii.

$$P = OH^- + \frac{1}{2} CO_3^{2-}$$

$$M = OH^- + CO_3^{2-} + HCO_3^-$$

The possible combinations of ions causing alkalinity in water are: (i) OH^- only or (ii) CO_3^{2-} only or (iii) HCO_3^- only or iv) OH^- and CO_3^{2-} together or CO_3^{2-} and HCO_3^- together.

The possibility of OH^- and HCO_3^- ions together is ruled out, because they combine instantaneously to form CO_3^{2-} ions.

$$OH + HCO_3^- \longrightarrow CO_3^{2-} + H_2O$$

Thus OH^- and HCO_3^- ions can not exist together in water. On the basis of same reasoning, all the three (OH^-, CO_3^{2-} and HCO_3^-) can not exist together.

$$Alkalinity = \frac{(Volume\ of\ Acid) \times (Strength\ of\ Acid) \times 50 \times 1000}{Volume\ of\ water\ sample} ppm\ or\ mg/L$$

Calculation of Alkalinity of Water

Alkalinity Condition	Alkalinity due to the Presence of		
	OH^- (ppm)	CO_3^{2-} (ppm)	HCO_3^- (ppm)
P= 0	0	0	M
P = M	P = M	0	0
P = $\frac{1}{2}$M	0	2P	0
P < $\frac{1}{2}$ M	0	2P	(M-2P)
P > $\frac{1}{2}$ M	(2P-M)	2(M-P)	0

Interpretation of table is as follows

(1) When P=0, both OH^- and CO_3^{2-} are absent and alkalinity, in that case, is due to HCO_3^- only.

(2) When P=M, only OH^- ions are present because neither CO_3^{2-} nor HCO_3^- ions are present. Thus, alkalinity due to OH^- =P=M

(3) When P= $\frac{1}{2}$M, only carbonate ions are present since, half of the carbonate neutralisation reaction $CO_3^{2-} + H \longrightarrow HCO_3^-$ takes place with phenolphthalein while complete carbonate neutralisation reaction $CO_3^{2-} + H^+ \longrightarrow HCO_3^-$;

$HCO_3^- + H^+ \longrightarrow H_2O + CO_2$ occurs when the methyl orange indicator is used.

Thus alkalinity due to CO_3^{2-} =2P

(4) When P<$\frac{1}{2}$M In this case, besides CO_3^{2-}, HCO_3^- ions are also present. Now alkalinity due to

CO_3^{2-} = 2P Therefore, alkalinity due to HCO_3^- = (M–2P)

(5) When P>$\frac{1}{2}$M In this case, besides CO_3^{2-}, OH^- ions are also present. Half of CO_3^{2-} (i.e.

$HCO_3^- + H^+ \longrightarrow CO_2 + H_2O$ equal to (M–P)

So alkalinity due to complete CO_3^{2-} = 2(M–P)

Therefore, alkalinity due to OH^- = M-2(M–P) = (2P–M)

Units of Alkalinity: $CaCO_3$ equivalent, ppm, mg/L

<u>Water Softening Techniques:</u>

A. Lime Soda Process: In this process hard water is treated with a calculated quantity of lime and soda. Lime and soda convert the soluble hardness causing chemicals present in hard water into insoluble substances called sludges. The precipitate or sludge formed is then removed by filtration to get soft water.

$$\underset{\text{(soluble)}}{CaCl_2} + \underset{\text{soda}}{Na_2CO_3} \rightarrow \underset{\text{(insoluble)}}{CaCO_3\downarrow} + 2NaCl$$

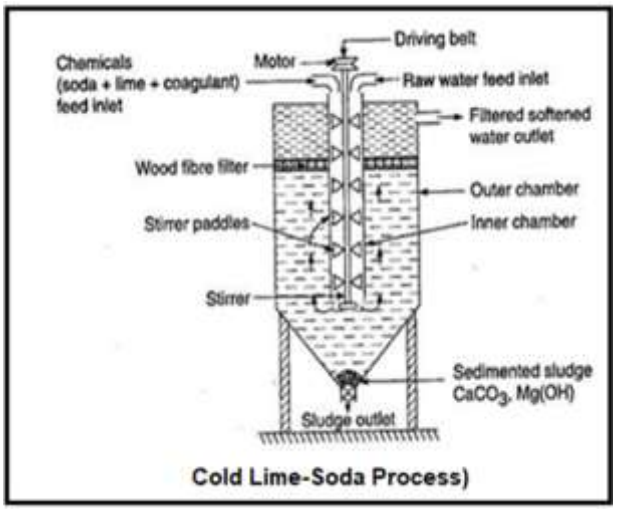
$$\underset{\text{(soluble)}}{MgCl_2} + \underset{\text{soda}}{Ca(OH)_2} \rightarrow \underset{\text{(Insoluble)}}{Mg(OH)_2\downarrow} + CaCl_2$$

Lime-Soda process is of two types.

(a) Cold Lime soda process (b) Hot lime soda process

(a) Cold Lime Soda Process:

Principle: When hard water is treated with calculated amount of lime [$Ca(OH)_2$] and soda (Na_2CO_3) at room temperature 25ºC, the soluble Ca and Mg salt present in hard water are chemically converted into ppt. of calcium carbonate ($CaCO_3$) and magnesium hydroxide [$Mg(OH)_2$]. These ppts are removed by filtration. Thus, soft water is obtained.



Cold Lime-Soda Process)

$CaCl_2$ + Na_2CO_3 → $CaCO_3\downarrow$ + 2NaC

hard water soda ppt

$MgCl_2$ + $Ca(OH)_2$ → $Mg(OH)_2\downarrow$ + CaCl

hard water lime ppt

Process:

The apparatus consists of a conical shaped steel tank. Raw water, lime, soda and coagulants are added from the top inner vertical circular chamber which is fitted with rotating shaft carrying many paddles. The dissolved salts of Ca and Mg combine with lime soda and coagulants and form an insoluble precipitate as sludge. Softened water rises upwards, and the heavy sludge settles down. Then the softened water passes through wood fibre filter and the filtered soft water is collected through the outlet. The sludge setting down at the bottom is removed. The residual hardness left in this process is about 50 - 60 ppm.

Dis-advantages:

- It is a slow process because reactions during water softening take place in very dilute solutions and room temp.
- It requires coagulant for setting particles of ppt. formed during reaction of water softening.
- Softening capacity of this process is less.
- Soft water obtained by this process consists of dissolved gases.

(b) Hot Lime Soda process:

Principle: This process involves treatment of hard water with lime and soda at a temp. of 80-150^{0}C.

Process: In the hot lime soda process, the reactions take place at higher temperature near the boiling point of water. The chemical mixing process is the same as the cold lime soda process, but steam is applied in mixture tank. As a result, precipitation becomes almost complete very quickly.

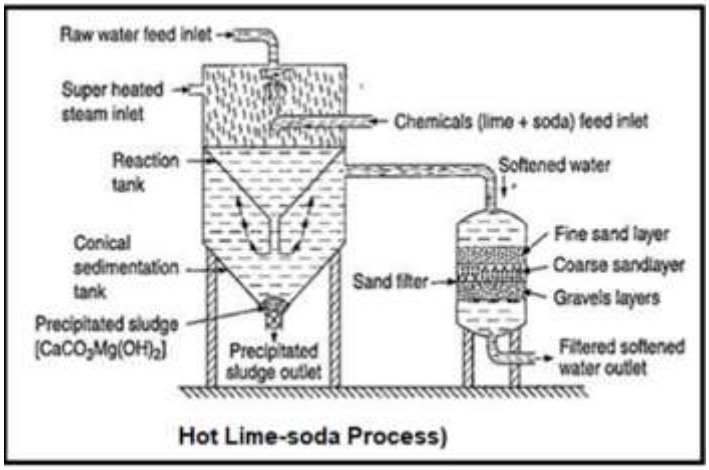
Apparatus:

The apparatus consists of 3 main parts.

(a) Reaction tank – in which hard water, lime & soda are mixed thoroughly.

(b)Conical sedimentation vessel – in which sludges settle down.

(c)Sand filter – where sludge is completely removed.



Hot Lime-soda Process)

Advantages:

1. It is much more economical.
2. The reaction is completed within a short period.
3. The reaction proceeds faster. Hence the softening capacity is increased.
4. No coagulant is required, as the sludge settles down easily.
5. Dissolved gases like CO_2, air etc. are removed.
6. Under hot conditions, the viscosity of water is lowered. Thus, filtration becomes easier.
7. Pathogenic bacteria are destroyed.
8. The residual hardness left in this process is much lower (15-30 ppm) as compared to that in the cold L-S process (50-60 ppm).

Disadvantages:

For efficient and economical softening careful operation and skilled supervision is required.

Disposal of large amounts of sludge creates problems.

This can remove hardness only up to 15 ppm, which is not suitable for high pressure boilers.

Difference between cold lime soda process & hot lime soda process

Cold Lime soda process	Hot lime soda process
1. This process is conducted at room temp. (25^0C)	This process is conducted at 80^0 to 150^0 C.
2. It is costlier.	It is much more economical.
3. The process takes longer time to complete.	It takes comparatively less time for completion.
4. The reaction is slower.	The reaction proceeds faster. Hence the softening capacity is increased.
5. Coagulant like alum is required.	No coagulant is required, as the sludge settles down easily.
6. Dissolved gases do not escape.	Dissolved gasses like CO_2, air etc. are removed.

7. Filtration is comparatively slower.	Under hot condition the viscosity of water is lowered. Thus, filtration becomes easier.
8. Pathogenic bacteria are not destroyed.	Pathogenic bacteria, if any, are destroyed.
9. The residual hardness left is more, i.e., 50 – 60 ppm.	The residual hardness left in this process is much lower (15-30 ppm) as compared to that in the cold L-S process (50-60 ppm).

Zeolite Process:

Zeolite Softening Process is the process of removing permanent as well as temporary hardness of the water. Zeolite Softening occurs when magnesium (Mg) and calcium (Ca) zeolites (insoluble) in water get precipitated. In this zeolite softening process, zeolite works as a catalyst which helps in exchanging ions from Ca^{2+} or Mg^{2+} with sodium ions.

Certain complex inorganic salts possess the property of exchanging calcium and magnesium ions present in hard water for Na^+ ions. An important salt of this type is sodium aluminium orthosilicate or sodium zeolite ($Na_2Al_2Si_2O_8.xH_2O$), commonly known as permutit (artificially synthesized zeolite).

Zeolite Softening Process of Water

When hard water containing magnesium and calcium ions passes through a zeolite bed of sodium, then sodium (Na^+) ions get displaced or replaced by the ions of Mg^{2+} and Ca^{2+} and when the replacement is complete i.e. all the sodium ions get replaced by Mg^{2+} and Ca^{2+} ions then the zeolite get inactivated. This zeolite then gets regenerated by passing brine solution through the inactive zeolite bed. This process of softening water is mainly used in laundry.

Reactions involved:

$Ca^{2+} + Na_2Al_2Si_2O_8.xH_2O \rightarrow CaAl_2Si_2O_8.xH_2O + 2Na^+$

$Mg^{2+} + Na_2Al_2Si_2O_8.xH_2O \rightarrow MgAl_2Si_2O_8.xH_2O + 2Na^+$

Advantages

- Clean and easy process.
- The equipment occupies less space as well as it is compact.
- Time effective i.e. it does not require much time for water softening.
- Easy to maintain.
- No precipitation of impurities occurs.

Limitations

- Turbidity in water may cause clogging in the zeolite bed.
- The presence of large quantities of Mn^{2+} or Fe^{2+} coloured ions must be removed from water as they may produce their own zeolites.

- Mineral acids present in water must be neutralised with soda as they may destroy the bed of zeolites.

Ion – Exchange Process [Deionization or De-mineralization process]:

In this method, the ions responsible for hardness are exchanged with other ions which don't make water hard. In this method ion exchange resin are used.

Organic ion-exchangers (Ion-exchange resins): -

These are organic polymers having:

(i) high molecular weight.

(ii) Open and permeable molecular structure.

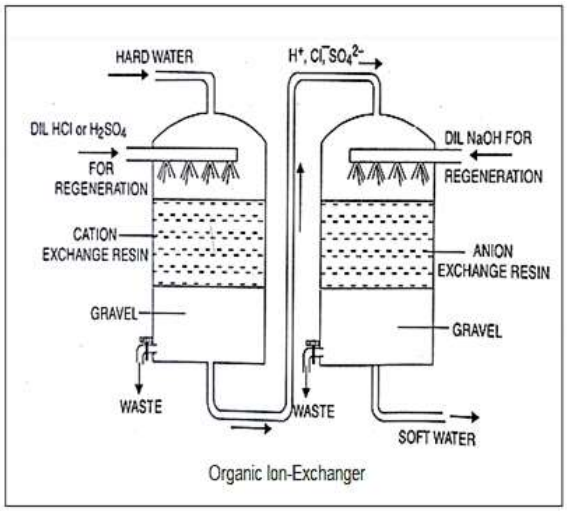
(iii) acidic (-COOH, $-SO_3H$) or basic groups ($-OH^-$, $-NH_2$) attached with them.

Ion-exchange resins are of two types:

(a) Cation-exchange resin($R-H^+$): If the active ion in ion-exchanger is a cation, generally acidic functional groups, the resin is called cation-exchange resin, Ex – ($Resin-H^+$)

(b) Anion-exchange resin ($R-H^-$): If the active ion in ion-exchanger is an anion, generally basic functional groups, the resin is called anion-exchange resin Ex – ($Resin-OH^-$)

Process: The hard water is passed through a column of cation exchange resin called zero-carb. All the cations present in hard water get exchanged with H^+ ions of the resin.



Organic Ion-Exchanger

$$2RH + Ca^{2+} \rightarrow R_2Ca + 2H^+$$

(Cation-Exchange Resin) hard water — Exhausted Resin

$$2RH + Mg^{2+} \rightarrow R_2Mg + 2H^+$$

(Cation-Exchange Resin) hard water — Exhausted Resin

Then the hard water is passed through the column of anion exchange resin. All the anions present in water get exchanged with OH- ions of the resin.

$$ROH + Cl^- \rightarrow RCl + OH^-$$

(Anion-Exchange Resin) hard water — Exhausted Resin

H^+ and OH^- ions released from the cation and anion exchange columns respectively get combined to produce water molecules.

$H^+ + OH^- \rightarrow H_2O$

Thus, the water coming out from the exchanger is free from cations as well as anion. Such water is known as deionized or demineralized water.

Regeneration of resins:

When all the H^+ and OH^- ions of the resins are exchanged by the cations and anions present in hard water, then the resins are said to be exhausted, and regeneration can be done.

The cation-exchange resin can be regenerated by the treatment with diluted acids like dil. HCl or dil.H_2SO_4.

$$\underset{\text{(Exhausted resin)}}{R_2Ca} + 2HCl \rightarrow \underset{\text{(Regenerated resin)}}{2RH} + CaCl_2$$

Similarly, the anion-exchange resin can be regenerated by the treatment with dilute alkali like, dil NaOH solution.

$$\underset{\text{(Exhausted resin)}}{RCl} + NaOH \rightarrow \underset{\text{(Regenerated resin)}}{ROH} + NaCl$$

The regenerated resins may be used again.

Advantages of Ion – Exchange Process –

ii. This process can be used to soften highly acidic or alkaline water.

iii. It produces water of very low hardness (up to 2 ppm). So, it is good for treating water for use in high pressure boilers.

Dis-advantages of Ion – Exchange Process:

- ☞ The equipment is costly and more expensive chemicals are needed.
- ☞ If water contains turbidity, then output of the process is reduced.

<u>Municipal Water Treatment:</u>

Depending upon the type of impurities, different methods are employed for purification of water for potable use. The following sequential steps are taken for municipal water treatment.

1. *Screening:* Removes the floating materials like leaves.
2. *Coagulation:* Removes finely divided suspended particles.
3. *Sedimentation:* Removes suspended impurities likes and clay etc.
4. *Filtration:* Removes colloidal impurities and large organisms.
5. *Disinfection:* Kills the bacteria.

1. Screening:

The raw water is allowed to pass through screens of appropriate size. Floating impurities like rags, paper, leaves, etc., are screened by the sieve and water is passed through the holes.

2. Coagulation:

Coagulation is the process by which the fine, suspended, and colloidal impurities are removed from the water by the addition of suitable chemicals as coagulants. The commonly used coagulants are Al_2SO_4, Alum [$K_2SO_4(Al_2SO_4)_3 24H_2O$], Ferrous Sulphate ($FeSO_4.7H_2O$), Sodium Aluminate ($NaAlO_2$). These coagulants react with water to form gelatinous precipitates in the form of hydroxides known as floc that absorbs the finely suspended and colloidal particles, which settle down rapidly. It is the most effective and economical means to remove impurities:

$$Al_2(SO_4)_3 + 6H_2O \rightarrow 2Al(OH)_3 + 3H_2SO_4$$

$$NaAlO_2 + 2H_2O \rightarrow Al(OH)_3 + NaOH$$

The efficiency of the coagulation process can be increased by using coagulant aids such as lime, fullers earth, bentonite clay and polyelectrolyte. Coagulants are generally added in the solution form to the water with the help of mechanical flocculators provided with stationary or rotating baffles.

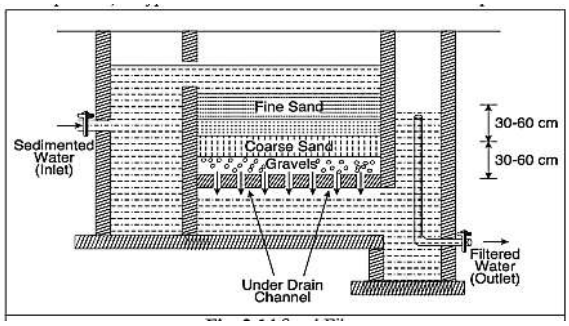
3. Sedimentation:

Sedimentation is a process of removing suspended impurities. Suspended particles settle down due to the force of gravity. This process takes two to eight hours and removes 70%–75% of suspended impurities. It is done in large settlement tanks or reservoirs.

4. Filtration:

In this method, suspended impurities, all types of insoluble colloidal and bacterial impurities are removed by passing water through a bed of proper-sized material through filtration process. Two types of filters are commonly used for filtration. Types of filtrations:

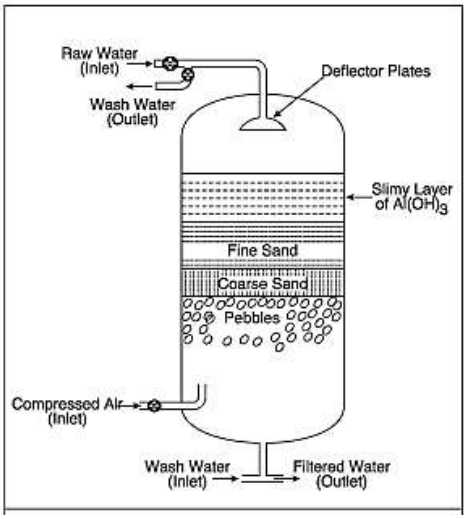
(A) Gravity Sand filter:



It consists of a large, rectangular tank made of concrete and a process medium, known as filter medium, which retains solid particles but allows the passage of water. It consists of three layers. The upper layer consists of fine sand. The middle layer consists of coarse sand and the bottom layer consists of gravel. It is provided with an inlet for sedimented water and an under-drain channel at the bottom for the exit of filtered water. Sedimented water enters the sand filter from the top and is uniformly distributed over the fine sand layer. As the water percolates through the sand bed, finely suspended particles and most of the germs and bacteria are retained by the top layer. Clear and filtered water is collected and is drawn out. The rate of filtration becomes slow after some time due to clogging

of pores of the top sand layer by the impurities. Therefore, the portion of the top fine sand layer is scrapped or replaced by a new sand layer.

(B) Pressure filter



It consists of a cylindrical vertical steel tank. The tank consists of three layers of filtering media, one above the other. The bottom layer consists of Pebbles, the middle layer consists of coarse sand and the top layer consists of fine sand. The impure, sedimented water is mixed with a small amount of alum solution, and then water is forced through filter bed under pressure. Alum forms the slimy layer on the filter bed, and this helps in the removal of colloidal and bacteriological impurities. The function of the deflector plate, which is provided at the top, is to distribute the slimy layer of alum uniformly over the top of the filter bed. Filtered water comes out from the bottom of the cylinder. These filters are widely used for industrial purposes.

5. <u>Sterilization or Disinfection:</u>

Sterilization, also known as disinfection, is the process of killing or inactivating microorganisms, such as bacteria, viruses, and protozoa, to prevent waterborne diseases.

Some common methods used in water sterilization are:

1. **Boiling**
2. **Chlorination**
3. **Ozonolysis**
4. **UV-Rays Treatment**
5. **Membrane Technology**

a) Boiling: Water for domestic purposes may be sterilized by simple boiling method by boiling the water for about 20–30 min. This method kills harmful disease-causing bacteria and germs. This process is very expensive for municipal supply of water, and in addition, a large quantity of fuel is required to boil water on a large scale. It does not provide any protection for further contamination of water.

b) Chlorination: It is the most important method for sterilization of water. Chlorination is done by using the following methods:

- Chlorine Gas or Concentrated Aqueous Solution.
- Bleaching Powder
- Chloramine.

(i) Chlorine gas or Concentrated Aqueous Solution:

Chlorine is used directly as a gas/tablet or as chlorine water. It is a powerful germicide and most commonly used disinfectant. It reacts with water to form hypochlorous acid and nascent oxygen, both of which are powerful germicides.

$Cl_2 + H_2O \rightarrow HOCl + HCl$
$HOCl \rightarrow [O] + HCl$

Advantages:

- It is cheap, easily available disinfectant and effective at low concentration.
- It can be used at high and low temperatures.
- It is stable and does not deteriorate on keeping.
- Chlorine residue can be maintained in treated water, which provides additional safety for preventing regrowth of bacteria.

Disadvantages: Excess of chlorine produces an unpleasant taste and odour in water.

(ii) *Bleaching Powder ($CaOCl_2$)*:
Bleaching powder is a strong oxidizing agent. When water is treated with bleaching powder, hypochlorous acid is formed. It releases nascent oxygen which deactivates the enzymes of micro-organisms and thus the metabolic activities will stop, and the microorganisms will be killed.

$CaOCl_2 + H_2O \rightarrow Ca(OH)_2 + Cl_2$

Disadvantages:

- Excess of bleaching powder creates bad taste and odour to water.
- It introduces calcium hardness in water due to the formation of $Ca(OH)_2$.
- It is unstable, hence its storage is difficult.

(iii) Chloramine (NH_2Cl)
By mixing chlorine and ammonia in 2:1 ratio, chloramine is formed. Whenever water is treated with chloramines, hypochlorous acid is formed which protects it from recontamination.
Advantages: Excess dose of NH_2Cl does not create bad odour and taste in water.
Disadvantages: Excess of chlorine produces an unpleasant taste and odour in water

c) Ozonolysis Method:
Ozone is a highly unstable and excellent disinfectant. It breaks down and gives nascent oxygen which is a very powerful oxidizing agent and kills all the bacteria and germs present in water.

Advantages:

- ☞ It removes colour and odour from water.
- ☞ It improves the taste of water.

- ☞ The excess dose of ozone is not harmful, because it releases oxygen on decomposition.

d) UV-Rays Method:

When water is exposed to UV-rays from electric mercury lamps that is immersed in water, most of the pathogenic bacteria are destroyed. This method is widely used for the disinfection of swimming pool water.

Advantages:

- ➢ It does not require any chemicals.
- ➢ It does not produce any odour in water.

Disadvantages: It is very expensive, so it is not widely used on a large scale.

e) Membrane Technology Method:

Membrane filtration is a technique for purifying water samples. In this procedure, water is drawn through a special porous membrane designed to trap microorganisms larger than 0.45 μm. Water is forced through membranes made of synthetic materials, cellulose acetate, cellulose nitrate (collodion), polyamide (nylon), polycarbonate, polypropylene, and polytetrafluoroethylene (Teflon by the application of high pressure. Membrane processes are widely used for removal of bacteria, microorganisms, particulates, and natural organic material, which can impart colour, tastes, and odour to water and react with disinfectants to form disinfections by products. The four types of membrane filtration are known as reverse osmosis, nanofiltration, ultrafiltration and microfiltration, in order of increasing pore size.

UNIT –8: ENGINEERING MATERIALS

Metallurgy

Natural Occurrence of Metals:

Mostly, the metals occur in nature in a combined state but sometimes they can also occur in the free state.

Native metals: The metals which occur in nature in their pure form or uncombined form are called native metals. Such metals have very low reactivity. Examples of native metals are gold (Au), silver (Ag), and platinum (Pt).

Mineral: - The natural material in which the metal or their compounds occur in the earth's crust is known as mineral.
Example: Bauxite ($Al_2O_3.2H_2O$) and Kaolin ($Al_2O_3.2SiO_2.2H_2O$) are the minerals of Aluminium.
Ores: - Ores are the minerals from which the metals concerned can be extracted conveniently and profitably.
Example: Both Bauxite and Kaolin are the minerals of 'Al'. However, 'Al' can be extracted easily and profitably from Bauxite. Thus, Bauxite is an ore of 'Al'. On the other hand, it is difficult and non-profitable to extract 'Al' from Kaolin, thus Kaolin is only a mineral of 'Al'.
All ores are minerals, but all minerals are not ores.

Minerals and Ores of Iron, Aluminium and Copper

Metals	Minerals	Formula
Fe	Haematite	Fe_2O_3
	Magnetite	Fe_3O_4
	Limonite	$Fe_2O_3.3H_2O$
Al	Bauxite	$Al_2O_3.2H_2O$
	Cryolite	Na_3AlF_6
Cu	Copper pyrite	$CuFeS_2$
	Copper glance	Cu_2S
	Cuprite	Cu_2O

Gangue: The earthly impurities such as sand, mud, clay, etc. contaminated with ores are called gangue or, matrix.

Brief account of General principle of metallurgy:

The process of extraction of metals from ores conveniently and profitably is called metallurgy or metallurgical operation. The following steps are followed during the process of metallurgical operation.

1. ***Crushing and grinding.***
2. ***Concentration or Ore dressing.***
3. ***Oxidation.***

4. ***Reduction.***
5. ***Refining.***

1. **CRUSHING AND GRINDING**:- The ores obtained from mines are in the form of solid rocks. These are first crushed into small pieces with the help of jaw crusher and then grinded into their powder form with the help of stamp mill or ball mill. The powdered form of ore is called pulverized ore.
2. **CONCENTRATION OR ORE DRESSING**: - The process of removal of maximum impurities (gangue or matrix) from the powdered ore is called ore concentration. The method of concentration to be followed depends upon the nature of the impurities present. The following are the different methods of concentration:

(i) Gravity Separation Method: - This method of concentration is adopted only when there is a gravity difference between the ore and impurities. Normally, Carbonate and oxide ores are heavier than the impurities associated with them and hence they are concentrated by this method. In this method the powdered ores are kept in some containers over a specially designed table called Wilfley table.

The table contains a number of horizontal grooves. The table is kept slightly in an inclined position and is provided with a rocking motion. When water is spread over the ore, lighter impurities are washed away while heavier ore particles get deposited in the grooves, which are finally carried out into the main canal.

(ii) Froth Floatation Method: -

This method is generally used for the concentration of sulphide ores. In this method, two interconnected tanks are used. In one of the tanks, a mixture of oil (pine oil), water and a little quantity of mineral acid is agitated strongly by blowing air through it. Due to the preferential wetting of the sulphide ores by oil than by water, a layer of oil gets covered over the surface of sulphide ores. These sulphide ores become lighter and float over the surface of the mixture, which are carried out into the second container along with the foam formed due to agitation.

(iii) Magnetic Separation method: -

This method of concentration is suitable only when there is a difference in magnetic behavior between the ores and the impurities. Normally, the magnetic ores containing non-magnetic impurities are concentrated by this method. In this method, a belt is tied over two rollers of which one is made of a magnet. Powdered ore is added over the belt through a hopper. The magnetic part of the ore is attracted by the magnetic roller and forms a heap near it. Whereas the non-magnetic part of the ore forms a separate heap a little away from magnetic part.

(iv) <u>Leaching</u>: -

This is a chemical method in which the impure ore is treated with a suitable solvent which dissolves the ore leaving behind the impurities. The solution is filtered, impurities are removed, and the mother liquor is treated with another suitable chemical reagent to get the pure ore.

For example: Impure bauxite ore is treated with dil NaOH solution which dissolves Bauxite to form soluble sodium meta-aluminate.

$$Al_2O_3.2H_2O + 2NaOH \rightarrow 2NaAlO_2 + 3H_2O$$

The solution is filtered to remove the impurities. The solution obtained is diluted with plenty of distilled water when a precipitate of $Al(OH)_3$ is formed.

$$NaAlO_2 + 2H_2O \rightarrow Al(OH)_3 + NaOH$$

The precipitate obtained is dried and heated strongly to get pure alumina from which aluminium is extracted.

$$2Al(OH)_3 \xrightarrow{\Delta} Al_2O_3 + 3H_2O$$

3. OXIDATION: - In this step of metallurgical operation, the concentrated ores are converted into their respective metal oxides. This is achieved by the following two methods:

(i) Calcination:

It is the process of heating the concentrated ore in the absence of air. It is used for hydrated and carbonate ores.

The calcinations process is carried out to

- convert carbonate ores into metal oxide.
- remove water from the hydrated ores.
- remove volatile impurities from the ore.

For example,

$$ZnCO_3 \xrightarrow{Calcination} ZnO_{(s)} + CO_{2(g)}$$

$$FeCO_3 \xrightarrow{Calcination} FeO_{(s)} + CO_{2(g)}$$

$$Fe_2O_3.3H_2O \xrightarrow{Calcination} Fe_2O_{3_{(s)}} + 3H_2O$$

$$CuCO_3.Cu(OH)_2 \xrightarrow{Calcination} 2CuO_{(s)} + CO_{2(g)} + H_2O$$

(ii) Roasting:

It is the process of heating the concentrated ore strongly in the presence of excess air, below melting point of ore. This method is used for extraction of sulphide ores. This process is used for converting sulphide ores to metal oxide. In this process, the following changes takes place:

- the sulphide ores undergo oxidation to their oxides.
- the sulphide ores undergo oxidation to their sulphate.
- moisture is removed.
- volatile impurities are removed.

For example,

$$2ZnS_{(s)} + 3O_{2(g)} \xrightarrow{Roasting} 2ZnO_{(s)} + 2SO_{2(g)}$$

$$4FeS_{2(s)} + 11O_{2(g)} \xrightarrow{Roasting} 2Fe_2O_{3(s)} + 8SO_{2(g)}$$

4. **REDUCTION**: - In this step of metallurgical operation, the roasted ores are reduced to convert the metal oxides into the respective metals. The method used for reduction of metal oxide depends upon the nature and chemical reactivity of metal. The metals can be grouped into the following three categories on the basis of their reactivity:
   - ☞ Metals of low reactivity.
   - ☞ Metals of medium reactivity.
   - ☞ Metals of high reactivity.

   These different categories of metals are extracted by different techniques. The different steps involved in separation are as follows:

   (a) Reduction by Heating

   Metals placed low in the reactivity series are very less reactive. They can be obtained from their oxides by simply heating in air.

   $$2HgS_{(s)} + 3O_{2(g)} \xrightarrow{Heat} 2HgO_{(s)} + 2SO_{2(g)}$$

   $$2HgO_{(s)} \xrightarrow{Heat} 2Hg_{(l)} + O_{2(g)}$$

   (b) Chemical Reduction

   The metals in the middle of the reactivity series, such as iron, zinc, lead, copper etc. are moderately reactive. These are usually present as sulphides or carbonates. Therefore, before reduction, the metal sulphides and carbonates must be converted to oxides. This is done by roasting and calcinations. The oxides of these metals cannot be reduced by heating alone. Therefore, these metal oxides are reduced to the free metal by using reducing agents like carbon, aluminium, sodium or calcium.

   Reduction with Carbon

   The oxides of moderately reactive metals (occurring in the middle of reactivity series) like zinc, copper, nickel, tin, lead etc. can be reduced by using carbon as reducing agent. Coke is very commonly used as a reducing agent because it is cheap.

   $$ZnO_{(s)} + C_{(s)} \xrightarrow{Heat} Zn_{(s)} + CO_{(g)}$$

   $$PbO_{(s)} + C_{(s)} \xrightarrow{Heat} Pb_{(s)} + CO_{(g)}$$

   $$Fe_2O_{3(s)} + 3C_{(s)} \xrightarrow{Heat} 2Fe_{(s)} + 3CO_{(g)}$$

   Disadvantage of using carbon as reducing agent is that small traces of carbon are added to metal as impurity, which contaminates the metals.

Note:

Flux and Slag:

The metal ores sometimes contain non-fusible impurities. Flux is a substance that chemically combines with gangue (earthy impurities), which may still be present in the roasted or calcined ore to form an easily fusible material called slag.

Solid impurities + Flux → Fusible Slag

Flux is of two types, acidic flux and basic flux.

(a) Acidic Flux

If non-fusible impurities are basic, then the acidic flux is used.

Example

In the extraction of copper, iron impurities are removed by SiO_2.

$$\underset{Acidic\ Flux}{SiO_2} + \underset{Basic\ impurity}{FeO} \rightarrow \underset{Fusible\ Slag}{FeSiO_3}$$

(b) Basic Flux

If non-fusible impurities are acidic, then basic flux is used.

Example:

$$\underset{Basic\ Flux}{MgCO_3} + \underset{Acidic\ impurity}{SiO_2} \rightarrow \underset{Fusible\ Slag}{MgSiO_3} + CO_2$$

$$\underset{Basic\ Flux}{CaO} + \underset{Acidic\ impurity}{SiO_2} \rightarrow \underset{Fusible\ Slag}{CaSiO_3}$$

Reduction with Carbon Monoxide

Certain metals can be obtained from oxides by reduction with carbon monoxide in the furnace.

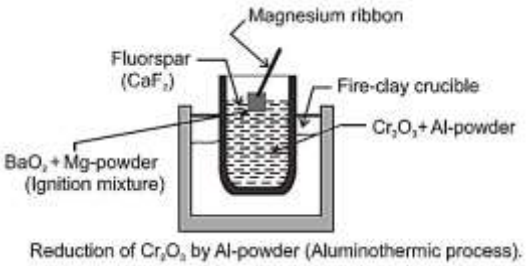
$$Fe_2O_{3(s)} + 3CO_{(g)} \xrightarrow{Heat} 2Fe_{(s)} + 3CO_{2(g)}$$

$$CuO_{(s)} + CO \xrightarrow{Heat} Cu + CO_{2(g)}$$

$$PbO_{(s)} + CO \xrightarrow{Heat} Pb + CO_{2(g)}$$

Reduction with Aluminium

Alumino-Thermic Process: This method is used to reduce such metallic oxides (eg. Cr_2O_3, MnO_2) which cannot be reduced by carbon. Here metal oxide is mixed with aluminium powder taken in a crucible and ignited is ignited by means of magnesium ribbon, inserted into aluminium and barium peroxide mixture



Reduction of Cr_2O_3 by Al-powder (Aluminothermic process).

inside the crucible. The reaction is exothermic and produce a very high temperature of about 3000 ^{0}C. The oxide is reduced into metal and Al_2O_3 is formed.

$$CrO_3 + 2Al \rightarrow Al_2O_3 + 2Cr + Heat$$

$$3MnO_2 + 4Al \rightarrow 2Al_2O_3 + 3Mn + Heat$$

The impurities are removed as slag by heating the metal with suitable flux.

(c) Reduction by Electrolysis or Electrolytic Reduction

The oxides of active metals (which are high up in the activity series) are very stable and cannot be reduced by carbon or aluminium. These metals are commonly extracted by the electrolysis of their fused salts using suitable electrodes. This is also called electrolytic reduction i.e. reduction by electrolysis. The process of extraction of metals by electrolysis process is called electrometallurgy.

Example

Aluminium oxide is very stable and aluminium cannot be prepared by reduction with carbon.

It is prepared by the electrolysis of molten alumina (Al_2O_3).

$$\underset{\text{(From molten Alumina)}}{Al^{3+}} + \underset{\text{(From Cathode)}}{3e^-} \xrightarrow{Heat} \underset{\text{(At cathode)}}{Al}$$

Thus, aluminium metal is collected at the cathode.

5. **REFINING:** The metals obtained after reduction still contain some impurities. The process of removal of impurities from crude metal is called refining. The method of refining to be followed depends upon the nature of the metal and the impurity contaminated with it. The following are the methods of refining:
   - **(i) Distillation Method**: - This method of refining is suitable for volatile metals like Hg, Zn, Cd contaminated with non-volatile impurities. The impure metal is heated in a distillation flask attached with a water condenser. During heating the volatile metal gets evaporated and condensed which is collected in a separate container while the non-volatile impurities are left at the bottom of the distillation flask.
   - **(ii) Electro refining**: - This method is employed to refine the less electropositive metals such as Zn, Pb, Cu, Al, Ag, Au, etc. The impure metal bar is used as anode while a pure metal (same metal) bar is taken as cathode. Both the electrodes are dipped in a suitable aqueous salt solution of the concerned metal. During the process of electrolysis, the impure metal dissolves in its aqueous salt solution providing metal ions which get discharged and deposited at the cathode.
   - **(iii) Liquation**: This method is applicable for metals with low melting points such as tin, lead, bismuth, etc. In this method the impure metal is heated and then it flows on a sloped

surface. The pure metal will collect at the bottom of the slope while the impurities will remain behind.

(iv) **Poling:** Poling is a method used for metals that have oxidized impurities to purify them. Poling is mainly used to purify metals that are in the impure form like copper or tin of copper oxide or tin oxide. In the poling method a log of wood is taken that is still green and then used to stir the liquid metal. The hydrocarbons of the green wood reduce the metal, and the oxygen leaves as CO_2 gas.

(v) **Vapour-Phase Refining:** In vapour-phase refining, for releasing a metal from impurities, it is first converted into a suitable volatile compound by heating it. And the heating requirements are:

- The metal used for this process should form a volatile compound with a suitable reagent.
- The volatile compound that is to be used should be easily decomposable so that the recovery is easy. $Ni + 4CO \rightarrow Ni(CO)_4 \xrightarrow{Heat} Ni + 4CO$.

(vi) **Zone refining:** It is a special method used to purify metals. In this method, metals are purified to a very high degree. Impure metal rod is placed in a container filled with inert gas. Then a circular heater is placed around the rod at the top for heating the impure metal. And when the heater shifts to the next zone, the pure metal cools and crystallizes. The impurities that are melted will move along with the movement of the heater and shift to the next zone. All these impurities are then collected to the last zone and then it can be separated.

(vii) **Cupellation:** This method is used to purify silver containing lead as impurity. In this method the impure silver is heated in a current of air. The impurity, i.e. lead present in the metal gets oxidized into volatile lead oxide, which leaves the heating apparatus called cupel leaving behind pure silver.

Alloys: An alloy is a homogeneous material obtained by mixing metals or metals with non-metals or metals with metalloids.

Types of alloys:

1. **Ferro Alloys:** The alloy containing iron is called a ferro alloy.
   Example: Stainless Steel, Manganese Steel etc.
2. **Non-Ferro Alloy:** The alloy which does not contain iron is called a non-ferro alloy.
   Example: Brass, Bronze, Gun metal etc.
3. **Amalgam:** Alloys containing mercury as one of the constituents is called amalgam.
   Example: Silver Amalgam, Sodium amalgam, Copper amalgam is used for filling dental cavities; Tin amalgam is used for silvering cheap mirrors.

Purpose of alloying:

Alloys are made to:

- **Enhance the hardness of a metal:** An alloy is harder than its components. Pure metals are generally soft. The hardness of a metal can be enhanced by alloying it with another metal or nonmetal.
- **Lower the melting point:** Pure metals have a high melting point. The melting point lowers when pure metals are alloyed with other metals or nonmetals. This makes the metals easily fusible. This property is utilized to make useful alloys called solders.
- **Enhance tensile strength:** Alloy formation increases the tensile strength of the parent metal.
- **Enhance corrosion resistance:** Alloys are more resistant to corrosion than pure metals. Metals in pure form are chemically reactive and can be easily corroded by the surrounding atmospheric gases and moisture. Alloying a metal increases the inertness of the metal, which, in turn, increases corrosion resistance.
- **Modify colour:** The color of pure metal can be modified by alloying it with other metals or nonmetals containing suitable color pigments.
- **Provide better cast ability:** One of the most essential requirements of getting good castings is the expansion of the metal on solidification. Pure molten metals undergo contraction on solidification. Metals need to be alloyed to obtain good castings because alloys expand.

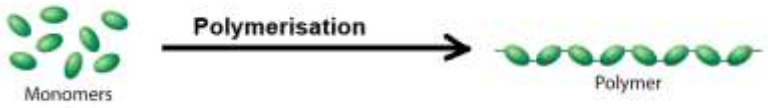
Some important Alloys with their compositions and uses:

Sl. No.	Alloy	Composition	Properties and Uses
1	Brass	Cu (60% - 80%) Zn (20% - 40%)	Brass is highly malleable, corrosion and tarnish resistance. It has good thermal and electrical conductivity. It is used in making: Decorative items, scientific instruments like telescope, microscope, barometers, etc., sanitary fittings, musical instruments, electrical components, etc..
2	Bronze	Cu (75% - 90%) Sn (10% - 25%)	Bronze has high tensile strength, superior resistance to wear and saltwater corrosion, and low-friction properties. It is used for making: Utensils, statues, coins, medals, marine hardware, musical instruments, etc.
3	Stainless Steel	Fe (74 Cr (18%) Ni (8%)	It is corrosion and rust resistant. It has also high tensile strength, heat resistance, excellent ductility, and is fully recyclable It is used in making: Utensils, surgical instruments, ornamental pieces, cycle and automobile parts, etc.
4	Alnico	Fe (50%)	It has exceptional temperature stability, resistance to

		Al (20%) Ni (20%) Co (10%)	corrosion, and high magnetic flux density. It is used in making permanent magnets.
5	Duralumin	Al (95%) Cu (4%) Mn (0.5%) Mg (0.5%)	It is hard, lightweight, corrosion resistant and highly ductile. It is used in making Aero plane parts, spacecraft, ships and pressure cooker.

Polymers

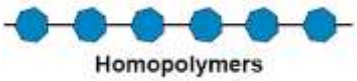
Polymerisation: The chemical process in which a large no of smaller molecular units is joined together to get a bigger unit of high molecular weight is called polymerisation.



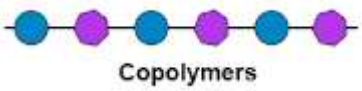
Monomers: The single units that undergo repeated addition forming a polymer are called monomers.
Examples: Ethene is the monomer of polythene, vinyl chloride is the monomer of PVC.

Polymer: The bigger unit of high molecular weight obtained due to the polymerisation of monomer units is called a polymer.
Examples: Polythene, PVC, Teflon, Polystyrene, Terylene, Nylon, Bakelite, etc.

Homopolymer: The polymer containing monomer units of the same chemical composition is called a homopolymer.
Examples: Polythene, PVC, Teflon, Polystyrene, etc.



Copolymer: The polymer containing monomer units of different chemical compositions is called a Copolymer.
Examples: Bakelite, Terylene, Nylon, Buna-S, Buna-N, etc.



Degree of polymerisation: The total no of monomer units present in a polymer is called degree of polymerisation or it is the ratio of the average molecular weight of polymer to the weight of monomer.

$$Degree\ of\ Polymerisation\ (DP) = \frac{Average\ molecular\ weight\ of\ polymer}{molecular\ weight\ of\ monomer}$$

Classification of Polymers:

Polymers may be classified as thermoplastic and thermosetting plastics.

Thermoplastics: These are the polymers obtained by addition polymerisation. In this type of polymerisation, the monomer units are simply get added with each other without elimination of any simple molecules. Examples: Polythene, Polystyrene, Teflon, etc.

Thermosetting plastics: These are the polymers obtained by condensation polymerisation. In this type of polymerisation, the monomer units are added with each other with the elimination of simple molecules such as HCl, H_2O, NH_3, etc. Examples: Terylene, Nylon, Bakelite, etc.

Addition Polymerisation: In this type of polymerisation the monomer units are simply get added to each other without elimination of simple molecules.

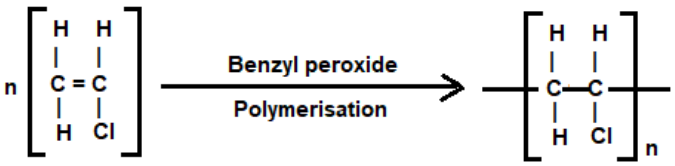
Condensation Polymerisation: In this type of polymerisation simple molecules such as HCl, H_2O, NH_3, etc. are eliminated.

Distinction between Thermoplastics & Thermosetting.

	Thermoplastics	Thermosetting
1	These are formed by addition polymerization.	These are formed by condensation polymerization.
2	These are generally linear polymers.	These are three dimensional cross-linked polymers.
3	These are soft.	These are hard and rigid.
4	These are soluble in some solvents.	These are insoluble in any solvent.
5	These become soft on heating and become hard on cooling.	These burn to char on prolong heating.
6	These can be remoulded, reshaped and recycled.	These cannot be remoulded, reshaped and cannot be recycled.
7	Examples: Polythene, PVC, Nylon, etc.	Examples: Bakelite, Urea-formaldehyde resin, Terylene, etc.

Preparation and uses of Thermoplastics:

1. **Polyvinyl chloride (PVC):** PVC is obtained by the polymerization of Vinyl chloride in presence of benzyl peroxide under pressure.



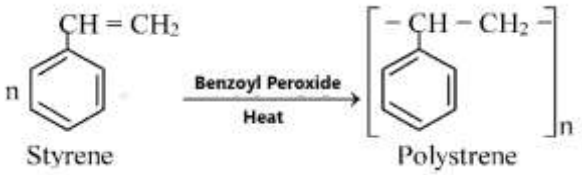
Vinyl chloride (Monomer)

Polyvinyl chloride (Polymer)

Uses: It is used for making:

- Sheets for tank lining
- Safely helmets.
- Credit cards
- Refrigerator components
- Tyres, cycle and motorcycle mudguards
- Raincoat
- Tablecloths
- Electrical insulators
- Chemical containers, etc.

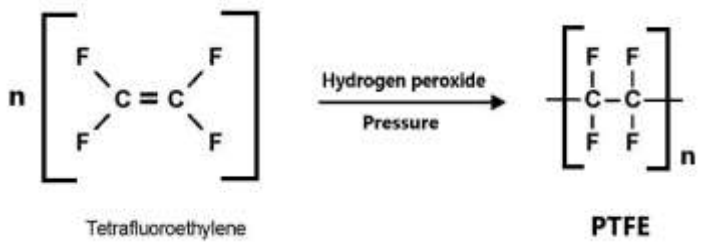
2. Polystyrene (PS): Polystyrene is obtained by the polymerization of styrene in the presence of benzoyl peroxide.



Uses: It is used for making:

- Food packaging, household appliances,
- consumer electronics products,
- building and construction,
- insulation foam, panels,
- bath and shower units,
- lighting, and plumbing fixtures.
- Medical items include tissue culture trays, test tubes, petri dishes, diagnostic components, etc.

3. Teflon (Polytetrafluoroethylene or PTFE): Teflon is obtained by the polymerization of styrene in presence of hydrogen peroxide under high pressure.



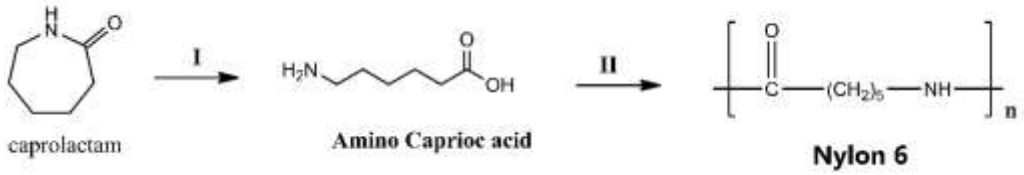
Uses: It is used for making:

- Non-stick cookware,

- Chemical containers and pipes
- High frequency electrical insulators like switch, plug, etc.
- dental industry for filling, etc.

Preparation and uses of Thermosetting plastics:

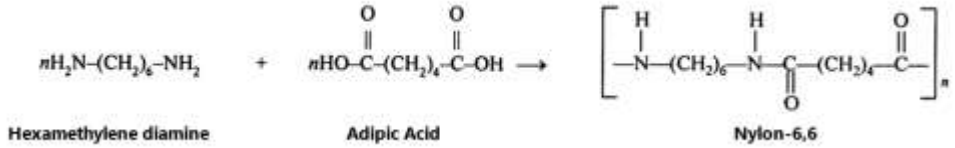
1. **Nylon-6:** Nylon 6 is synthesized by ring-opening polymerization of caprolactam. When caprolactam is heated at about 533 K in an inert atmosphere of nitrogen for about 4–5 hours, the ring breaks and undergoes polymerization.



Uses: It is used for making:

- Bristles of toothbrushes,
- Surgical sutures,
- threads, rope,
- nets,
- knitted garments, etc.

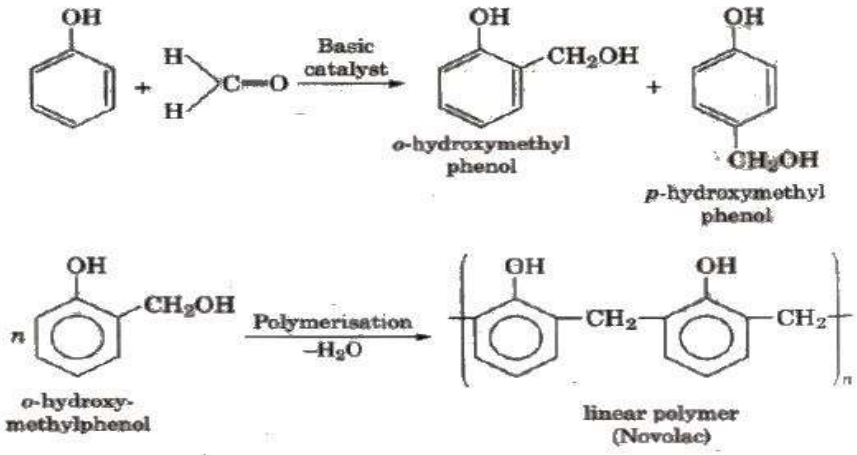
2. **Nylon - 6,6:** Nylon-6,6 is prepared by condensation polymerization of hexamethylene diamine with adipic acid at high temperature and pressure.



Uses: It is used for making:

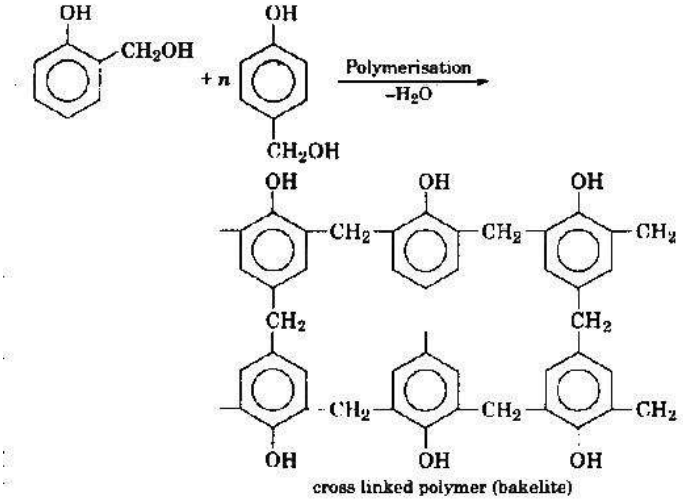
- Airbags,
- tyres,
- ropes,
- conveyor belts,
- parachutes,
- swimwear, etc.

3. **<u>Bakelite (Phenol-Formaldehyde Resin)</u>:** It is obtained by the polymerization of *phenol and formaldehyde*. When phenol and formaldehyde are reacted together two isomeric compounds *O-hydroxy methylphenol and P-hydroxy methylphenol are obtained.*



The orthohydroxymethylphenol thus formed undergoes polymerization with phenol to form a linear polymer compound called **"NOVOLAC"**.

During the process of polymerization, a little quantity of hexamethylene tetraamine *[$(CH_2)_6N_4$]* is added which converts 'novolac' into a hard resinous mass ***called Bakelite.***



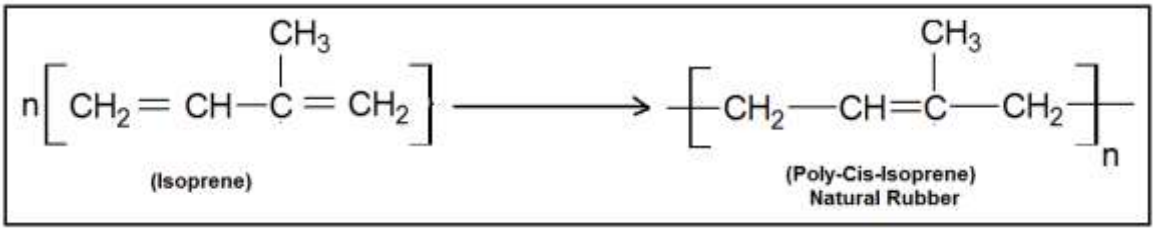
Uses: *It is used in the manufacture of:*

i. Electrical insulators like plug, switch etc.
ii. Cabinets for Radio and TV
iii. Telephone parts
iv. Paints, varnishes
v. Hydrogen exchange resin for softening of hard water.

Rubber:

Rubber is a substance which can be stretched in length after applying the force and regain its original shape and dimensions after removal of the force. This property of rubber is called elasticity. A rubber molecule is having a spring or coil-like nature.

Natural rubber consists of "***isoprene***" as the monomer units, which is in the form of the polymer poly cis-isoprene. Thus, natural rubber is nothing but the polymer ***poly cis isoprene*.**



Draw backs of natural rubber:

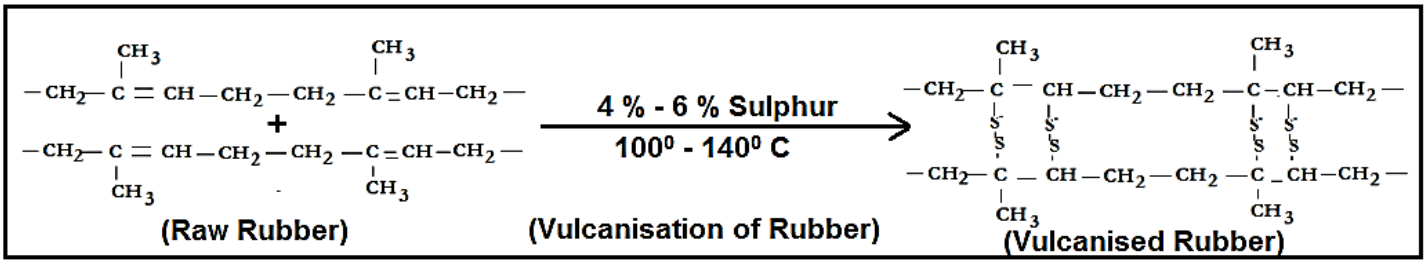
Natural rubber or raw rubber has the following drawbacks:

i. It has very low thermal stability
ii. It has very low tensile strength
iii. It has high water absorption capacity.
iv. It is attacked by atmospheric oxygen and ozone.
v. It is attacked by acids and alkalis.
vi. *It has the property of tackiness.*

Vulcanization of rubber:

Natural rubber is a thermoplastic. There are no cross links between the polymer chains. It becomes soft and sticky when heated. It is not hard and tough. The properties of natural rubber can be modified and improved by the process of vulcanization. To improve the properties of natural rubber, it is heated with sulphur or sulphur containing compounds at a temperature of *100^0 -140^0C.*

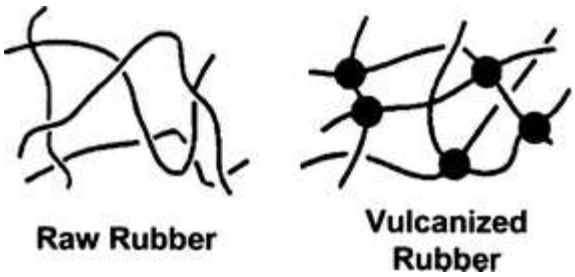
The chemical process in which natural rubber is heated with 4% to 6% sulphur or sulphur containing compounds at 100^0 – 140^0C with a view to overcome the drawbacks of natural rubber is called



vulcanization.

During vulcanizationsulphur cross-links are formed in between the layers of polyisoprene at the carbon atoms containing double bond.

The formation of cross links makes *rubber hard, tough with greater tensile strength*. Although natural rubber is thermoplastic substance, yet on vulcanization, it is set into a given shape which is retained.



Advantages of Vulcanization:

After vulcanization, almost all the drawbacks of raw rubber are eliminated. Vulcanized rubber:

i. has higher thermal stability
ii. has comparatively lower tensile strength
iii. has low water absorption capacity.
iv. is not attacked by atmospheric oxygen and ozone.
v. is resistant to acids and alkalis.

UNIT-9: ECOSYSTEM

Environment: Environment can be defined as a sum total of all the living and non-living elements and their effects that influence human life.

Environmental Science: Environmental science is an interdisciplinary academic field that draws on ecology on ecology, geology, meteorology, biology, chemistry, engineering, and physics to study environmental problems and human impacts on the environment.

Ecosystem: An ecosystem is a community of living organisms (plants, animals and microbes) in a particular area. Thus, an ecosystem is a structural and functional unit of biosphere. It is made up of living and non-living beings and their physical environment.

Structure of Ecosystem:

1. Biotic (Living Components)

Biotic components in ecosystems include organisms such as plants, animals, and microorganisms. The biotic components of ecosystem comprise of the following trophic levels:

1. **Producers (First Trophic Level)** − Producers otherwise called autotrophs prepare their food by themselves. They form the first level of every food chain. Plants and one-celled organisms, some types of bacteria, algae, etc. come under the category of Autotrophs. Virtually, almost all autotrophs use a process called photosynthesis to prepare food.
2. **Consumers** − At the second trophic level, there are consumers who depend upon others for food.
   - **Primary Consumers (Second Trophic Level)** − Primary consumers eat the producers. They are called herbivores. Deer, turtle, and many types of birds are herbivores.
   - **Secondary Consumers (Third Trophic Level)** − Secondary consumers based at the third trophic level eat plants and herbivores. They are both carnivores (meat-eaters) and omnivores (animals that eat both animals and plants). In a desert ecosystem, a secondary consumer may be a snake that eats a mouse. Secondary consumers may eat animals bigger than they are. Some lions, for example, kill and eat buffalo. The buffalo weighs twice as much as the lions do.
   - **Tertiary Consumers (Fourth Trophic Level)** − Tertiary consumers are animals eating other carnivores. The secretary bird in Africa and the King Cobra specialize in killing and eating snakes but all snakes are carnivores. The leopard seal eats mostly other carnivores - mainly other seals, squids, and penguins, all of which are carnivores.
3. **Decomposers** − Decomposers which don't always appear in the pictorial presentation of the food chain, play an important part in completing the food chain. These organisms break down dead organic material and wastes. Fungi and bacteria are the key decomposers in many ecosystems; they use the chemical energy in dead matter and wastes to fuel their metabolic processes. Other decomposers are detritivores—detritus eaters or debris eaters.

Understanding the food chain helps us know the feeding interrelationship and interaction between an organism and the ecosystem. It also enables us to know the mechanism of energy flow in an ecosystem.

2. Abiotic (Non-living Components)

Abiotic components consist of climate or factors of climate such as temperature, light, humidity, precipitation, gases, wind, water, soil, salinity, mineral, topography, and habitat. The flow of energy and the cycling of water and nutrients are critical to each ecosystem on the earth. Non-living components set the stage for ecosystem operation.

Food chain and food web

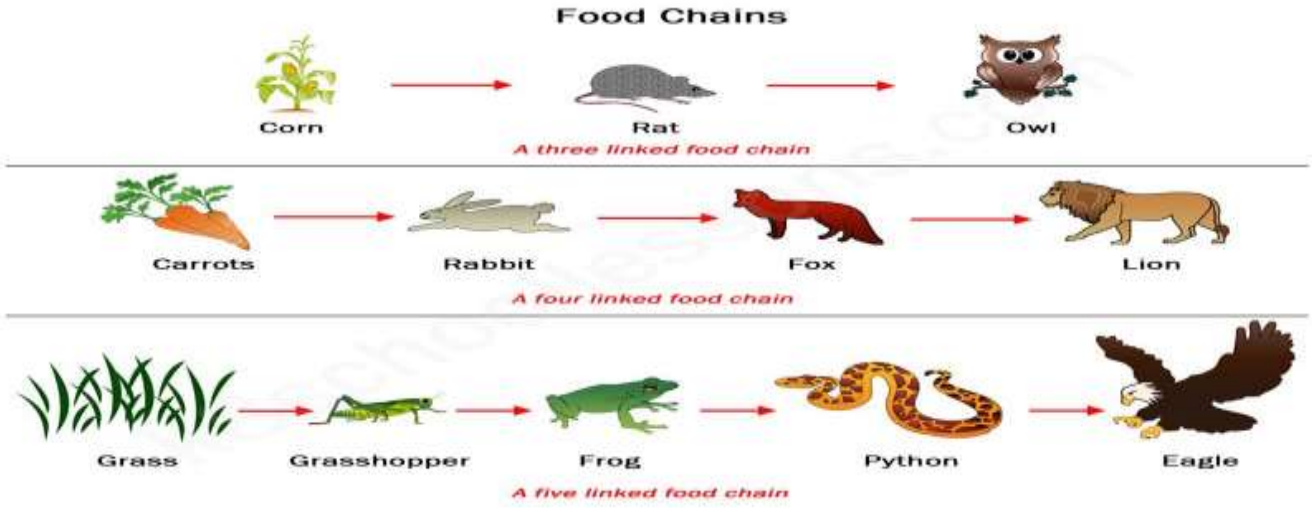
Food Chain

In scientific terms, a food chain is a chronological pathway or an order that shows the flow of energy from one organism to the other. In a community which has producers, consumers, and decomposers, the energy flows in a specific pathway. Energy is not created or destroyed. But it flows from one level to the other, through different organisms.

A food chain shows a single pathway from the producers to the consumers and how the energy flows in this pathway. In the animal kingdom, food travels around different levels. To understand a food chain better, let us take a look at the terrestrial ecosystem.

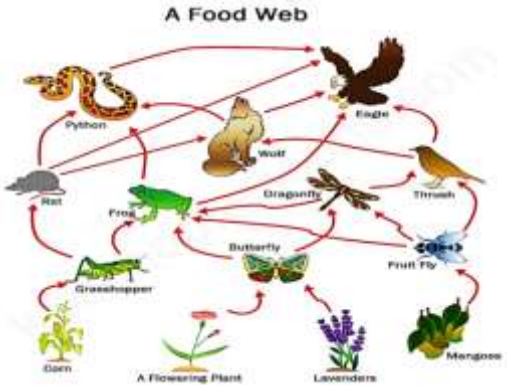
Example of food chain

Grass (Producer)→Goat (Primary Consumer) → Man (Secondary consumer)



Food Web:

The word 'web' means network. Food web can be defined as 'a network of interconnected food chains so as to form a number of feeding relationships amongst different organism of a biotic community.



A food chain cannot stand isolated in an ecosystem. The same food resource may be a part of more than one chain. This is possible when the resource is at the lower tropic level.

A food web comprises all the food chains in a single ecosystem. It is essential to know that each living thing in an ecosystem is a part of multiple food chains.

A single food chain is the single possible path that energy and nutrients may make while passing through the ecosystem. All the interconnected and overlapping food chains in an ecosystem make up a food web.

Food webs are significant tools in understanding that plants are the foundation of all ecosystem and food chains, sustaining life by providing nourishment and oxygen needed for survival and reproduction. The food web provides stability to the ecosystem.

The tertiary consumers are eaten by quaternary consumers. For example, a hawk eats owls. Each food chain ends with a top predator and animal with no natural enemies (such as an alligator, hawk, or polar bear).

Aquatic Ecosystem

An aquatic ecosystem includes a group of interacting organisms which are dependent on one another and their water environment for nutrients and shelter. Examples of aquatic ecosystem include oceans, lakes and rivers.

An aquatic ecosystem includes freshwater habitats like lakes, ponds, rivers, oceans and streams, wetlands, swamp, etc. and marine habitats include oceans, intertidal zone, reefs, seabed and so on. The aquatic ecosystem is the habitat for water-dependent living species including animals, plants, and microbes.

1. Pond Ecosystem or Freshwater Aquatic Ecosystem:

They cover only a small portion of earth nearly 0.8 per cent. Freshwater involves lakes, ponds, rivers and streams, wetlands, swamp, bog and temporary pools. Freshwater habitats are classified into lotic and lentic habitats. Water bodies such as lakes, ponds, pools, bogs, and other reservoirs are standing water and known as lentic habitats. Whereas lotic habitats represent flowing water bodies such as rivers, streams.

- **Lotic Ecosystems**

They mainly refer to the rapidly flowing waters that move in a unidirectional way including the rivers and streams. These environments harbor numerous species of insects such as beetles, mayflies, stoneflies and several species of fishes including trout, eel, minnow, etc. Apart from these aquatic species, these ecosystems also include various mammals such as beavers, river dolphins and otters.

- **Lentic Ecosystems**

They include all standing water habitats. Lakes and ponds are the main examples of Lentic Ecosystem. The word lentic mainly refers to stationary or relatively still water. These ecosystems are home to algae, crabs, shrimps, amphibians such as frogs, for both rooted and floating-leaved plants and reptiles including alligators and other water snakes are also found here.

- **Wetlands**

Wetlands are marshy areas and are sometimes covered in water which has a wide diversity of plants and animals. Swamps, marshes, bogs, black spruce and water lilies are some examples in the plant species found in the wetlands. The animal life of this ecosystem consists of dragonflies and damselflies, birds such as Green Heron and fishes such as Northern Pike.

Terrestrial ecosystem

A terrestrial ecosystem is a land-based community of organisms and the interactions of biotic and abiotic components in a given area. Terrestrial ecosystems cover approximately 140 to 150 million km^2, which is about 25 to 30 percent of the total earth surface area.

Types of Terrestrial Ecosystems

There are different types of terrestrial ecosystems, which are widely distributed around the geological zones. They include:

a) **Forest Ecosystem:**

These types of ecosystems include temperate deciduous forest, plantation forests and tropical rain forests. They serve as a natural habitat for a vast range of living species and also comprise the highest species diversity. Forests cover nearly 30 to 35 million square kilometres of the earth's surface and more than 300 million species of plants and animals live in forests.

b) **Grasslands Ecosystem:**

Grasslands are the most dominant type of vegetation and these types of environments occur naturally in several parts of the world. These types of terrestrial ecosystems serve as a home for a wide diversity of animal species, such as elephants, giraffes, hyenas, jackrabbits, lions, rhinos, warthogs and zebras. Other types of grasslands include:

2. Tropical Grasslands
3. Temperate Grasslands

c) **Tundra Ecosystem:**

Tundra denotes Polar Regions, which are characterized by harsh environmental conditions similar to deserts and is usually windswept, snow-covered and treeless. This type of ecosystem is completely filled with frozen soil throughout the year and in summer, the snow melts and shallow ponds are produced. This gives rise to lichens and a few plants with small and colourful flowers. Animals found in the Arctic tundra include herbivorous mammals (lemmings, voles, caribou, arctic hares, and squirrels), carnivorous mammals (arctic foxes, wolves, and polar bears), fish (cod, flatfish, salmon, and trout), insects

(mosquitoes, flies, moths, grasshoppers, and blackflies), and birds (ravens, snow buntings, falcons, loons, sandpipers, terns, and gulls).

d) **Desert Ecosystem:**

The Desert is a barren region of the landscape, which has extremely high or low temperatures and has scarce vegetation. Depending on the climate and temperature, deserts can be classified into hot deserts and cold deserts. There are many lives that are well-adapted to life in the desert. Animals include – Camels, foxes, hyenas, jackals, scorpions, a few varieties of snakes and lizards. The common plants are acacia, cactus and date palms.

Sahara is an example of a hot desert, which is categorized by high temperatures associated with little rainfall and complicated life for both plants and animals.

Ladakh is an example of a cold desert, which is found on the eastern side of Jammu and Kashmir near the Great Himalayas.

Carbon Cycle:

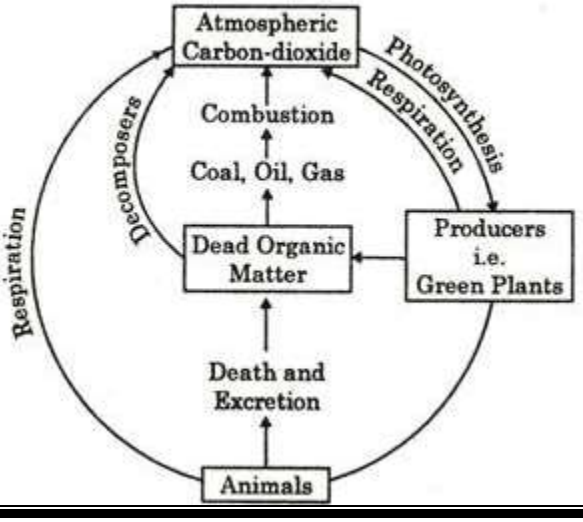
Carbon cycle is the process where carbon compounds are interchanged among the biosphere, geosphere (includes rocks and minerals on earth's surface), pedosphere (soil mantle of the earth), hydrosphere, and atmosphere of the earth.

Carbon cycle shows the movement of carbon in elemental and combined states on earth. Diamond and graphite are the elemental forms of carbon and in a combined state, it is found as carbonates in minerals and as carbon dioxide gas in the atmosphere.

Carbon Cycle Steps

Following are the major steps involved in the process of the carbon cycle:

1. Carbon present in the atmosphere is absorbed by plants for photosynthesis.
2. These plants are then consumed by animals and carbon gets bio-accumulated into their bodies.
3. These animals and plants eventually die, and upon decomposing, carbon is released back into the atmosphere.
4. Some of the carbon that is not released back into the atmosphere eventually becomes fossil fuels.



5. These fossil fuels are then used for man-made activities, which pump more carbon back into the atmosphere.

Carbon Cycle on Land

Carbon in the atmosphere is present in the form of carbon dioxide. Carbon enters the atmosphere through natural processes such as respiration and industrial applications such as burning fossil fuels. The process of photosynthesis involves the absorption of CO_2 by plants to produce carbohydrates. The equation is as follows:

$CO_2 + H_2O + \text{energy} \rightarrow (CH_2O)_n + O_2$

Carbon compounds are passed along the food chain from the producers to consumers. The majority of the carbon exists in the body in the form of carbon dioxide through respiration. The role of decomposers is to eat the dead organism and return the carbon from their body back into the atmosphere. The equation for this process is:

$(CH_2O)_n + O_2 \rightarrow CO_2 + H_2O$

Oceanic Carbon Cycle

This is essentially a carbon cycle but in the sea. Ecologically, oceans take in more carbon than it gives out. Hence, it is called a “carbon sink.” Marine animals convert carbon to calcium carbonate and these forms the raw building materials require creating hard shells, similar to the ones found in clams and oysters.

When organisms with calcium carbonate shells die, their body decomposes, leaving behind their hard shells. These accumulate on the seafloor and are eventually broken down by the waves and compacted under enormous pressure, forming limestone.

When these limestone rocks are exposed to air, they get weathered and the carbon is released back into the atmosphere as carbon dioxide.

Importance of Carbon Cycle

Even though carbon dioxide is found in small traces in the atmosphere, it plays a vital role in balancing the energy and traps the long-wave radiations from the sun. Therefore, it acts like a blanket over the planet. If the carbon cycle is disturbed it will result in serious consequences such as climatic changes and global warming.

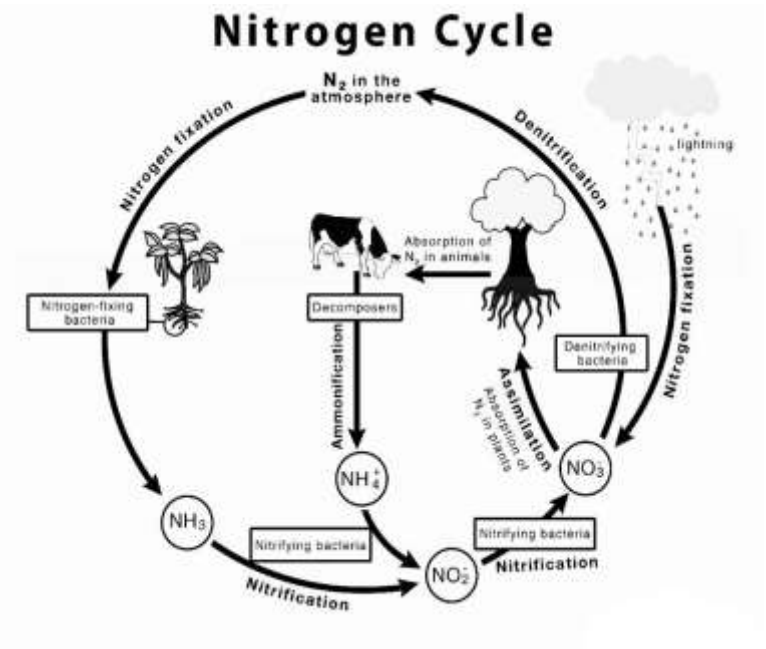
Carbon is an integral component of every life form on earth, from proteins and lipids to even our DNA. Furthermore, all known life on earth is based on carbon. Hence, the carbon cycle plays a vital role in the existence of life on earth.

Nitrogen Cycle:

"Nitrogen Cycle is a biogeochemical process which transforms the inert nitrogen present in the atmosphere to a more usable form for living organisms."

Furthermore, nitrogen is a key nutrient element for plants. However, the abundant nitrogen in the atmosphere cannot be used directly by plants or animals.

It involves several processes such as nitrogen fixation, nitrification, de-nitrification, decay and putrefaction.



Nitrogen gas exists in both organic and inorganic forms. Organic nitrogen exists in living organisms, and they get passed through the food chain by the consumption of other living organisms.

Inorganic forms of nitrogen are found in abundance in the atmosphere. This nitrogen is made available to plants by *symbiotic bacteria* which can convert the inert nitrogen into a usable form – such as nitrites and nitrates.

Nitrogen undergoes various types of transformation to maintain a balance in the ecosystem. Furthermore, this process extends to various biomes, with the marine nitrogen cycle being one of the most complicated biogeochemical cycles.

Nitrogen Cycle Explained – Stages of Nitrogen Cycle

Process of the Nitrogen Cycle consists of the following steps – Nitrogen fixation, Nitrification, Assimilation, Ammonification and De-nitrification. These processes take place in several stages and are explained below:

Nitrogen Fixation Process

It is the initial step of the nitrogen cycle. Here, Atmospheric nitrogen (N_2) which is primarily available in an inert form is converted into the usable form -ammonia (NH_3).

During the process of Nitrogen fixation, the inert form of nitrogen gas is deposited into soils from the atmosphere and surface waters, mainly through precipitation.

The entire process of Nitrogen fixation is completed by symbiotic bacteria, which are known as Diazotrophs. *Azotobacter* and *Rhizobium* also have a major role in this process. These bacteria consist of a nitrogenase enzyme, which has the capability to combine gaseous nitrogen with hydrogen to form ammonia.

Nitrogen fixation can occur either by atmospheric fixation- which involves lightening, or industrial fixation by manufacturing ammonia under high temperature and pressure conditions. This can also be fixed through man-made processes, primarily industrial processes that create ammonia and nitrogen-rich fertilisers.

Nitrification

In this process, the ammonia is converted into nitrate by the presence of bacteria in the soil. Nitrites are formed by the oxidation of ammonia with the help of *Nitrosomonas* bacteria species. Later, the produced nitrites are converted into nitrates by *Nitrobacter*. This conversion is very important as ammonia gas is toxic for plants.

The reaction involved in the process of Nitrification is as follows:

$$\mathbf{2NH_3 + 3O_2 \rightarrow 2NO_2^- + 2H^+ + 2H_2O}$$

$$\mathbf{2NO_2^- + O_2 \rightarrow 2NO_3^-}$$

Assimilation

Primary producers – plants take in the nitrogen compounds from the soil with the help of their roots, which are available in the form of ammonia, nitrite ions, nitrate ions or ammonium ions and are used in the formation of the plant and animal proteins. This way, it enters the food web when the primary consumers eat the plants.

Ammonification

When plants or animals die, the nitrogen present in the organic matter is released back into the soil. The decomposers, namely bacteria or fungi present in the soil, convert the organic matter back into

ammonium. This process of decomposition produces ammonia, which is further used for other biological processes.

De-nitrification

De-nitrification is the process in which the nitrogen compounds make their way back into the atmosphere by converting nitrate (NO_3^-) into gaseous nitrogen (N_2). This process of the nitrogen cycle is the final stage and occurs in the absence of oxygen. De-nitrification is carried out by the denitrifying bacterial species- *Clostridium* and *Pseudomonas*, which will process nitrate to gain oxygen and gives out free nitrogen gas as a by-product.

Importance of Nitrogen Cycle

The importance of the nitrogen cycle is as follows:

1. Helps plants to synthesize chlorophyll from the nitrogen compounds.
2. Helps in converting inert nitrogen gas into a usable form for the plants through the biochemical process.
3. In the process of ammonification, the bacteria help in decomposing the animal and plant matter, which indirectly helps to clean up the environment.
4. Nitrates and nitrites are released into the soil, which helps in enriching the soil with the necessary nutrients required for cultivation.
5. Nitrogen is an integral component of the cell and it forms many crucial compounds and important bio-molecules.

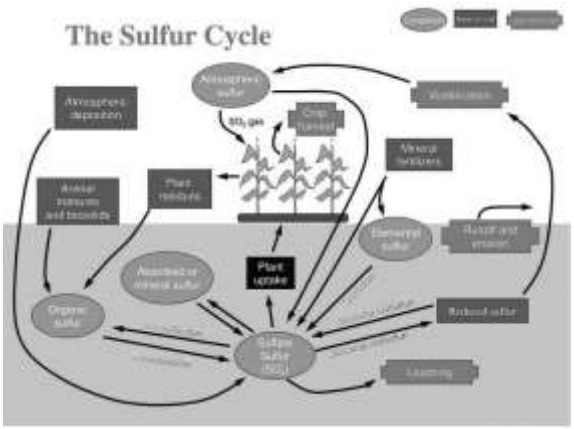
Sulphur Cycle

The sulphur cycle describes the movement of sulphur through the atmosphere, mineral forms and through living things.

Sulphur is one of the most abundant elements on the earth. It is a yellow, brittle, tasteless, odourless non-metal. Sulphur is present in proteins. Plants directly absorb sulphur-containing amino acids such as methionine, cystine, and cysteine.

Sulphur is released into the atmosphere by the burning of fossil fuel, volcanic activities, and decomposition of organic molecules.

On land, sulphur is stored in underground rocks and minerals. It is released by precipitation, weathering of rocks and geothermal vents.



The process of Sulphur Cycle

The process of sulphur cycle is explained below:

- The sulphur is released by the weathering of rocks.
- Sulphur comes in contact with air and is converted into sulphates.
- Sulphates are taken up by plants and microbes and are converted into organic forms.
- The organic form of sulphur is then consumed by the animals through their food and thus sulphur moves in the food chain.
- When the animals die, some of the sulphur is released by decomposition while some enter the tissues of microbes.
- There are several natural sources such as volcanic eruptions, evaporation of water, and breakdown of organic matter in swamps, that release sulphur directly into the atmosphere. This sulphur falls on earth with rainfall.

Steps of Sulphur Cycle

Decomposition of Organic Compounds

Protein degradation releases amino acids that contain sulphur. Sulphates are reduced to H_2S by the action of *De-sulfotomaculum bacteria*.

Oxidation of Hydrogen Sulphide to Elemental Sulphur

Hydrogen sulphide oxidises to produce elemental sulphur. Certain photosynthetic bacteria from the families Chlorobiaceae and Chromatiaceae initiate the oxidation process.

Oxidation of Elemental Sulphur

Elemental sulphur present in the soil cannot be utilized directly by the plants. Therefore, it is converted into sulphates by chemo lithotrophic bacteria.

Reduction of Sulphates

Sulphates are reduced to hydrogen sulphide by *Desulphovibriodesulfuricans.* This occurs in two steps:

- Firstly, the sulphates are converted to sulphites utilizing ATP.
- Secondly, the reduction of sulphite to hydrogen sulphide.

Phosphorous Cycle

"Phosphorus cycle is a biogeochemical process that involves the movement of phosphorus through the lithosphere, hydrosphere and biosphere."

Phosphorus is an important element for all living organisms. It forms a significant part of the structural framework of DNA and RNA. They are also an important component of ATP. Humans contain 80% of phosphorus in teeth and bones.

Phosphorus cycle is a very slow process. Various weather processes help to wash the phosphorus present in the rocks into the soil. Phosphorus is absorbed by the organic matter in the soil which is used for various biological processes.

Since phosphorus and phosphorus-containing compounds are present only on land, atmosphere plays no significant role in the phosphorus cycle.

Steps of Phosphorus Cycle

Following are the important steps of phosphorus cycle:

1. Weathering
2. Absorption by Plants
3. Absorption by Animals
4. Return to the Environment through Decomposition

Weathering

Phosphorus is found in the rocks in abundance. That is why the phosphorus cycle starts in the earth's crust. The phosphate salts are broken down from the rocks. These salts are washed away into the ground where they mix in the soil.

Absorption by Plants

The phosphate salts dissolved in water are absorbed by the plants. However, the amount of phosphorus present in the soil is very less. That is why the farmers apply phosphate fertilizers on agricultural land.

The aquatic plants absorb inorganic phosphorus from lower layers of water bodies. Since phosphate salts do not dissolve in water properly, they affect plant growth in aquatic ecosystem.

Absorption by Animals

The animals absorb phosphorus from the plants or by consuming plant-eating animals. The rate of the phosphorus cycle is faster in plants and animals when compared to rocks.

Return of Phosphorus Back to the Ecosystem

When the plants and animals die they are decomposed by microorganisms. During this process, the organic form of phosphorus is converted into the inorganic form, which is recycled to soil and water.

Soil and water will end up in sediments and rocks, which will again release phosphorus by weathering. Thus, the phosphorus cycle starts over.

Human Impact on Phosphorus Cycle

A number of human activities, use of fertilizers, artificial eutrophication, etc. have a great impact on the phosphorus cycle.

The phosphorus fertilizers increase the level of phosphorus in the soil. Overuse of these fertilizers reduces the fertility of the soil and is also harmful to the microorganisms present in the soil. When these are washed away into the nearby water bodies, they are hazardous to aquatic life.

During the shipping of food from farms to cities, the amount of phosphorus that is washed away in water causes eutrophication. This leads to the growth of algae. These form algal blooms or die, which is toxic to the aquatic ecosystem.

GREEN HOUSE EFFECT:

The greenhouse effect is the process through which heat is trapped near Earth's surface by substances known as 'greenhouse gases.' The phenomenon is like that of green house in which the glass enclosed atmosphere gets heated up due to its insulation from the rest of the environment. The gases such as CO_2, CH_4, CFCs, and water vapours called Greenhouse gases absorb a considerable portion of solar radiation which keeps the earth in a warmth condition, so that the life process is sustained. But, due to the rapid growth of industrialization and population, the concentrations of these gaseous substances are rapidly increasing. Thus, a large fraction of IR radiations and heat waves are absorbed by these gases which help in rising the temperature of the surface of earth.

GLOBAL WARMING:

"Global warming is a gradual increase in the earth's temperature generally due to the greenhouse effect caused by increased levels of carbon dioxide, CFCs, and other pollutants. "

Causes of Global Warming

Following are the major causes of global warming:

1. Deforestation

Plants are the main source of oxygen. They take in carbon dioxide and release oxygen thereby maintaining environmental balance. Forests are being depleted for many domestic and commercial purposes. This has led to an environmental imbalance, thereby giving rise to global warming.

2. Use of Vehicles

The use of vehicles, even for a very short distance results in various gaseous emissions. Vehicles burn fossil fuels which emit a large amount of carbon dioxide and other toxins into the atmosphere resulting in a temperature increase.

3. Chlorofluorocarbon

With the excessive use of air conditioners and refrigerators, humans have been adding CFCs into the environment which affects the atmospheric ozone layer. The ozone layer protects the earth surface from the harmful ultraviolet rays emitted by the sun. The CFCs have led to ozone layer depletion making way for the ultraviolet rays, thereby increasing the temperature of the earth.

4. Industrial Development

With the advent of industrialization, the temperature of the earth has been increasing rapidly. The harmful emissions from the factories add to the increasing temperature of the earth.

In 2013, the Intergovernmental Panel for Climate Change reported that the increase in the global temperature between 1880 and 2012 has been 0.9 degrees Celsius. The increase is 1.1 degrees Celsius when compared to the pre-industrial mean temperature.

5. Agriculture

Various farming activities produce carbon dioxide and methane gas. These add to the greenhouse gases in the atmosphere and increase the temperature of the earth.

6. Overpopulation

An increase in population means more people breathing. This leads to an increase in the level of carbon dioxide, the primary gas causing global warming, in the atmosphere.

Natural Causes of Global Warming

7. Volcanoes

Volcanoes are one of the largest natural contributors to global warming. The ash and smoke emitted during volcanic eruptions goes out into the atmosphere and affects the climate.

8. Water Vapour

Water vapour is a kind of greenhouse gas. Due to the increase in the earth's temperature, more water gets evaporated from the water bodies and stays in the atmosphere adding to global warming.

9. Melting Permafrost

Permafrost is frozen soil that has environmental gases trapped in it for several years and is present below Earth's surface. It is present in glaciers. As the permafrost melts, it releases the gases back into the atmosphere, increasing Earth's temperature.

10. Forest Blazes

Forest blazes or forest fires emit a large amount of carbon-containing smoke. These gases are released into the atmosphere and increase the earth's temperature resulting in global warming.

Consequences of Global warming:

Rise in Temperature

Global warming has led to an incredible increase in earth's temperature. Since 1880, the earth's temperature has increased by nearly 1 degree. This has resulted in an increase in the melting of glaciers, which have led to an increase in the sea level. This could have devastating effects on coastal regions.

Threats to the Ecosystem

Global warming has affected the coral reefs that can lead to the loss of plant and animal lives. Increase in global temperatures has made the fragility of coral reefs even worse.

Climate Change

Global warming has led to a change in climatic conditions. There are droughts at some places and floods at some. This climatic imbalance is the result of global warming.

Spread of Diseases

Global warming leads to a change in the patterns of heat and humidity. This has led to the movement of mosquitoes that carry and spread diseases.

High Mortality Rates

Due to an increase in floods, tsunamis and other natural calamities, the average death toll usually increases. Also, such events can bring about the spread of diseases that can hamper human life.

Loss of Natural Habitat

A global shift in the climate leads to the loss of habitats of several plants and animals. In this case, the animals need to migrate from their natural habitat and many of them even become extinct. This is yet another major impact of global warming on biodiversity.

OZONE LAYER DEPLETION:

"Ozone layer depletion is the gradual thinning of the earth's ozone layer in the upper atmosphere caused due to the release of chemical compounds containing gaseous bromine or chlorine from industries or other human activities."

This happens when the chlorine and bromine atoms in the atmosphere come in contact with ozone and destroy the ozone molecules. One chlorine can destroy 100,000 molecules of ozone. It is destroyed more quickly than it is created.

Some compounds release chlorine and bromine on exposure to high ultraviolet light, which then contributes to ozone layer depletion. Such compounds are known as Ozone Depleting Substances (ODS).

The ozone-depleting substances that contain chlorine include chlorofluorocarbon, carbon tetrachloride, hydrochlorofluorocarbons, and methyl chloroform. Whereas the ozone-depleting substances that contain bromine are halons, methyl bromide, and hydro Bromo fluorocarbons.

Chlorofluorocarbons are the most abundant ozone-depleting substance. Montreal Protocol was proposed in 1987 to stop the use, production and import of ozone-depleting substances and minimise their concentration in the atmosphere to protect the ozone layer of the earth.

Causes of Ozone Layer Depletion

Ozone layer depletion is a major concern and is associated with a number of factors. The main causes responsible for the depletion of the ozone layer are listed below:

Chlorofluorocarbons

Chlorofluorocarbons or CFCs are the main cause of ozone layer depletion. These are released by solvents, spray aerosols, refrigerators, air-conditioners, etc.

The molecules of chlorofluorocarbons in the stratosphere are broken down by ultraviolet radiations and release chlorine atoms. These atoms react with ozone and destroy it.

Unregulated Rocket Launches

Researches say that the unregulated launching of rockets results in much more depletion of the ozone layer than the CFCs do. If not controlled, this might result in a huge loss of the ozone layer by the year 2050.

Nitrogenous Compounds

The nitrogenous compounds such as NO_2, NO, N_2O are highly responsible for the depletion of the ozone layer.

Natural Causes

The ozone layer has been found to be depleted by certain natural processes such as Sun-spots and stratospheric winds. But it does not cause more than 1-2% of the ozone layer depletion.

The volcanic eruptions are also responsible for the depletion of the ozone layer.

Ozone Depleting Substances (ODS)

"Ozone-depleting substances are the substances such as chlorofluorocarbons, halons, carbon tetrachloride, hydrofluorocarbons, etc. that are responsible for the depletion of the ozone layer."

Following is the list of some main ozone-depleting substances and the sources from where they are released: Refrigerators, air-conditioners, solvents, dry-cleaning agents, fire-extinguishers, adhesives, aerosols, etc.

Effects of Ozone Layer Depletion

The depletion of the ozone layer has harmful effects on the environment. Let us see the major effects of ozone layer depletion on man and environment.

Effects on Human Health

Humans will be directly exposed to the harmful ultraviolet radiation of the sun due to the depletion of the ozone layer. This might result in serious health issues among humans, such as skin diseases, cancer, sunburns, cataract, quick ageing and weak immune system.

Effects on Animals

Direct exposure to ultraviolet radiations leads to skin and eye cancer in animals.

Effects on the Environment

Strong ultraviolet rays may lead to minimal growth, flowering and photosynthesis in plants. The forests also have to bear the harmful effects of the ultraviolet rays.

Effects on Marine Life

Planktons are greatly affected by the exposure to harmful ultraviolet rays. These are higher in the aquatic food chain. If the planktons are destroyed, the organisms present in the food chain are also affected.

Solutions to Ozone Layer Depletion

The depletion of the ozone layer is a serious issue and various programmes have been launched by the government of various countries to prevent it. However, steps should be taken at the individual level as well to prevent the depletion of the ozone layer.

Following are some points that would help in preventing this problem at a global level:

Avoid Using ODS

Reduce the use of ozone depleting substances. E.g. avoid the use of CFCs in refrigerators and air conditioners, replacing the halon based fire extinguishers, etc.

Minimize the Use of Vehicles

The vehicles emit a large amount of greenhouse gases that lead to global warming as well as ozone depletion. Therefore, the use of vehicles should be minimised as much as possible.

Use Eco-friendly Cleaning Products

Most of the cleaning products have chlorine and bromine releasing chemicals that find a way into the atmosphere and affect the ozone layer. These should be substituted with natural products to protect the environment.

Use of Nitrous Oxide should be prohibited

The government should take actions and prohibit the use of harmful nitrous oxide that is adversely affecting the ozone layer. People should be made aware of the harmful effects of nitrous oxide and the products emitting the gas so that its use is minimised at the individual level as well.

UNIT - 10: RENEWABLE SOURCES OF ENERGY

Non-Renewable Energy Resources: The energy resources which cannot be renewed or reproduced are called non-renewable energy resources. Examples: Fossil fuels like petrol, diesel, kerosene, etc. uranium.

Renewable Energy Resources: The energy resources which can be renewed or reproduced are called renewable energy resources. Examples: solar energy, tidal energy, wind energy, etc.

Solar Energy:

Solar energy is the radiant heat and light from the sun that can be captured and used to generate electricity, heat, and cool buildings. It is generally used to generate electricity, to cook food and to desalinate water.

Flat Plate Collector (liquid and air)

- A **Flat Plate Collector** is a heat exchanger that converts the radiant solar energy from the sun into heat energy.
- It collects, or captures, solar energy and uses that energy to heat water in the home for bathing, washing and heating, and can even be used to heat outdoor swimming pools and hot tubs.

Advantages of flat plate collector includes

- easy to manufacture
- low manufacturing Cost
- little maintenance

COMPONENTS OF FLAT PLATE COLLECTOR:

- **Black plate surface** – to absorb incident solar radiation
- **Glass cover** – to transmit radiation to the absorber at the same time prevent heat loss from the surface
- **Tubes** -containing the fluid/air to transfer the heat from the collector
- **Support structure-** to provide protection and hold the collector components

- **Insulation**- in sides and bottom of the collector to prevent heat losses

WORKING PRINCIPLE

- The solar radiation is absorbed by the plate having black surface and then absorbed heat get transferred to the fluid/air filled in the tubes.
- For transfer of heat, either a medium, liquid or air can be used in the flat plate collectors.
- When a metal sheet is placed to solar radiation, the temperature of the sheet will start rising till the rate at which energy (solar radiation) is received is equal to the rate at which energy is getting transferred or lost from the metal sheet.
- The temperature of the metal sheet after which no further increment is noted is termed as the "equilibrium" temperature.
- Now, if the back of the plate is protected with heat insulating material, and the exposed surface of the plate is painted in black colour and it is covered with glass sheets, then the equilibrium temperature will be much higher than that for the simple exposed sheet.
- This metal sheet can be converted into a heat collector by adding a water/air circulating system.
- The absorbed heat from the heat collector gets transferred to the water/air in the tube and finally transferred to a storage tank.

TYPES OF FLAT PLATE COLLECTOR

1. **Water based flat plate collector:**
   - In this type, water is used as a medium of heat transfer.
   - Water is most commonly used as liquid fluid because of its high volumetric heat capacity and high mass density, which allows using small tubes and pipes for the heat transfer.
2. **Air based flat plate collector:**
   - In this type of collector, air is used as the medium of heat transfer instead of liquid/water.
   - This type of plate collector is used for space heating or crop drying.
   - A fan is usually required to facilitate air low in the pipe.

THEORY OF FLAT PLATE COLLECTOR

Theory of flat plate collectors is very simple. When a metal sheet is exposed to solar radiation, the temperature of the sheet will start rising till the rate at which energy (solar radiation) is received is equal to the rate at which energy is transferred or lost from the metal sheet. The temperature of the metal sheet after which no further increment is noted is termed as the "equilibrium" temperature. Now, if the back of the plate is protected with heat insulating material, and the exposed surface of the plate is painted in black colour and it is covered with glass sheets, then the equilibrium temperature will be much higher than that for the simple exposed sheet. This metal sheet can be converted into a heat collector by adding a water/air circulating system. The absorbed heat from the heat collector gets transferred to the water/air in the tube and finally transferred to a storage tank.

IMPORTANCE OF COATING

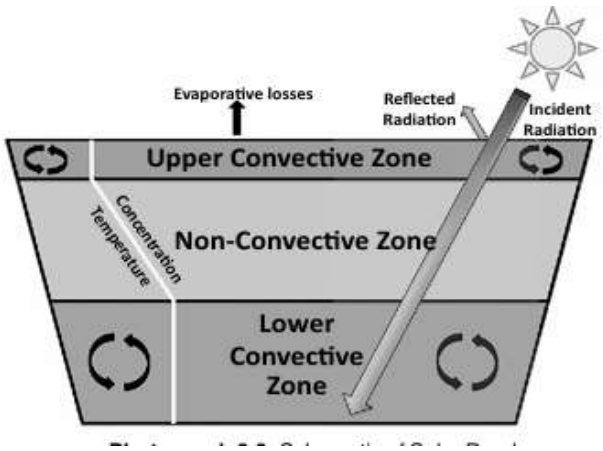
- The solar absorber surface is the fundamental part of a solar thermal collector, as it is responsible for the solar radiation absorption and for reduction of radiation heat losses.
- These plates are usually made of metal having good heat conductor property, usually copper or aluminium. Sometimes these absorber plates are painted with special coatings designed to absorb and retain heat better than the normal black paint.
- Special coatings help to enhance the plate absorber properties such as
  - ✓ High temperature tolerance
  - ✓ Resistance to uv radiation.
  - ✓ Moisture degradation
  - ✓ Durability
  - ✓ Optical characteristics

ADVANCED PLATE COLLECTORS

- In conventional plate collector system, water can be heated up to 80°C, which limits their applications largely for providing hot water and space heating.
- For power generation, the fluid temperatures in the range of 120°C - 130°C is required.
- To achieve this range of temperature, in place of normal plate absorber, evacuated (vacuum) glass tubes coated with selective coating black absorber are used. Plate collector with these arrangements is called as advanced plate collector.
- Using advanced plate collector, temperature can be enhanced to 150°C thereby enhancing application range of the collector to power generation, solar air conditioning system etc.

SOLAR POND

- It is a solar energy collector which is large in size and looks like a pond.
- in an ordinary pond, the sun rays fall on the water and the heated water from within the pond rises and reaches the top but loses the heat into the atmosphere through evaporation. The net result is that the pond water remains at the atmospheric temperature.
- In solar pond, loss of heat from the water is prevented by dissolving salt, concentration of which increases with the depth of water in the pond and making it too heavy to rise.



ZONES OF SOLAR POND:

A solar pond mainly has three zones.

1. Upper convective zone

2. Gradient zone or non-convective zone

3. Storage zone or lower convective zone

1. Upper Convective Zone:

- The top zone is the surface zone called Upper Convective Zone, which is normally at atmospheric temperature and has very little salt content.

2. Lower Convective Zone :

- The bottom zone is the most salty zone. In this zone, the solar energy is stored in the form of heat, and therefore, it is called as the storage zone or Lower Convective Zone.

3.Non-Convective Zone:

- In this zone, the salt content increases with increase in the water depth and thereby creates a density gradient.
- If we consider a particular layer in this zone, water of that layer cannot rise, as the layer of water above this zone has less salt content and is, therefore, lighter.
- Similarly, the water from this layer cannot fall as the water layer below this zone has a higher salt content and is, therefore, heavier.
- Thus, this gradient zone acts as a transparent insulator permitting sunlight to reach the bottom zone but also entrapping it there.

Working principle:

- When sunlight is incident on solar pond, most of the incoming sunlight reaches the bottom and thus the “storage zone” heats up.

- As the loss of heat is prevented from this zone due to the insulator zone just above it, the bottom of the pond is warmed to extremely high temperature and sometimes it may reach more than 80^0C.
- Finally, heated water from the bottom level is transferred to pipes, circulating through the pond to extract thermal energy**.**

Applications of solar pond:

- The solar pond may be used for the production of chemicals, food, textiles and other industrial products.
- It can also be used to warm greenhouse, swimming pools, and other buildings and offices. The heat can also be converted to electricity.
- It is especially useful in remote locations. The solar pond can also purify water for municipal water systems through desalination.

Advantages:

- It can be used all year, day and night, regardless of condition of weather.
- It can be used as an alternative to fossil fuel technologies in rural areas, in less-developed countries, where large ponds can be built.
- It is more cost-effective than energy from the flat-plate solar water-heating systems that are commonly used in the buildings.
- It does not contribute to air pollution.

Disadvantages:

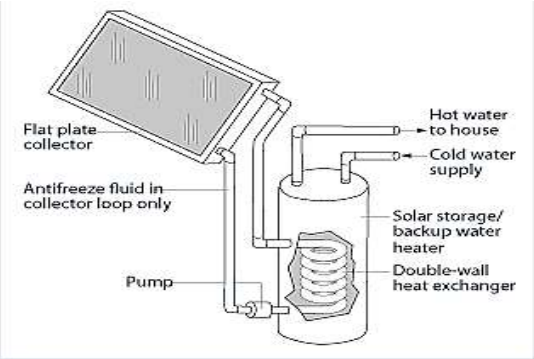
- It requires a large area of land and therefore, may be unsuitable for densely populated areas.
- The pond also requires a continuous and large supply of salt water and also high level of solar energy inputs.
- Regular maintenance is very much needed to keep it in a working condition.
- Though solar ponds can be constructed anywhere, it is economical to construct them at places where low-cost salt, good supply of sea water or water for filling and flushing, high solar radiation, and land at low cost are available.

SOLAR WATER HEATER:

The solar water heater is the simplest application of solar thermal energy. Solar water heaters are classified as active and passive solar water heaters. In active solar water heaters, the water is circulated from the solar collector to the water storage by using a water pump. In passive solar water heaters, heat

is transferred from the collector to the water tank located at the top of the collector by the process of natural circulation.

Components of solar water heater:



The main components of solar water heater include:

1. A collector
2. Insulated tank
3. Supporting arrangements
4. Connecting pipes

Working principle:

- First of all, the Sun rays fall on the Solar Collector, which is consisted of a black absorbing surface (absorber) that absorbs solar radiation and transfers the heat energy to water flowing through it.
- After this, heated water is collected in a tank, insulated to prevent heat loss. Then the circulation of water from the tank through the collector and back to the tank continues automatically. Most solar water heating systems use a pump to circulate the water from the tank to the collector and back. This process continues automatically as long as there is sunlight available, maximizing the efficiency of the system.

Advantages:

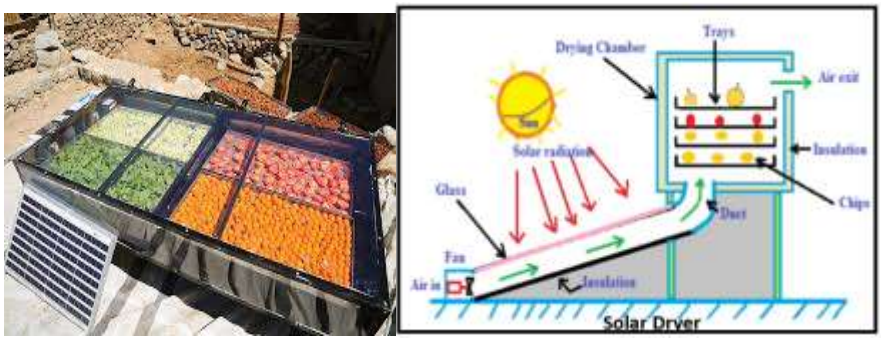
- Solar energy is free and abundant.
- Solar thermal panel occupies less space.
- Solar thermal panels are more efficient.
- We can save money by paying less electricity bill.
- It is an Eco-friendly way to heat water for the domestic need.

Disadvantages:

- Capital investment and installation cost in high.
- Annual maintenance is required to check the working of pump, anti-freezing etc.
- It depends on the availability of direct sun light.
- It is not useful during rainy or foggy days.

SOLAR DRYER:

Solar dryer is a device which is used to remove the moisture from crops, vegetables, chips and fruits with the help of solar radiation or energy. The Solar dryer provide more heat than the atmospheric temperature.



Components of solar dryer:

A solar dryer consists of the following components:

- Transparent glass
- Drying chamber
- Fan & duct
- Insulation
- Drying substance

Working Process:

- The principle of solar drying technique is to collect solar energy by heating up the air volume in solar collectors and transmit the hot air from the collector to an attached drying food chamber where food to be dried are kept.
- This is more hygienic technique of food drying as there is no secondary contamination of food products through rain, dust, insects, birds etc.
- The products are drying by hot air only and there is no direct impact of solar radiation (sunshine) on the products. Solar dryers are suitable for drying large quantity of food products and for small scale farmers and food producers.

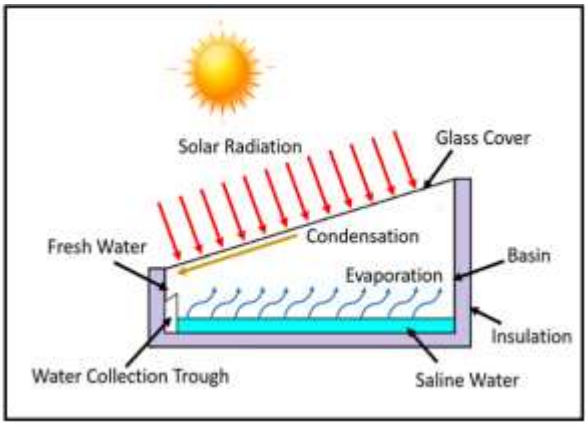
SOLAR STILLS:

- Solar still is a device which is used to convert saline (salt) water or contaminated water into distilled water by vaporization by the heat of sun and condensation. It is originally designed for army and navy.
- Solar still installation may provide about 15 to 50 litres of drinking water per day.

Components of solar stills:

Solar stills consist of

1. Water inlet pipe
2. Container
3. Transparent cover.



4. Blackened surface
5. Insulation
6. Pure water collector

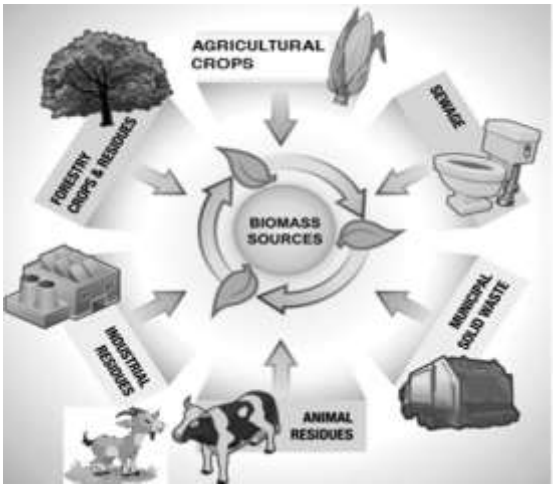
Working process:

- It works on the principle of evaporation and condensation process.
- The solar still absorbs the solar radiation. As the energy is absorbed, it starts to heat the water.
- As the temperature rises, water is converted into steam and evaporates towards the glass ceiling, leaving impurities in the basin below.
- The water slowly condenses on the glass, forming pure water droplets.
- The water droplets roll down into clean water basin which is collected and used for drinking or cooking purpose.

Advantages of solar stills:

- Low maintenance cost.
- Low energy consumption.
- Simple technique required.
- Less skilled labour required.

Biomass:



Biomass is the mass of renewable organic materials that comes from living organism, including plants, animals and microorganisms or from a biochemical perspective, cellulose, lignin, sugars, fats and proteins. It is a source of renewable energy. It has always been a major source of energy for mankind and estimated to contribute *10% to 14%* of the world's total energy supply.

The most common biomass sources used for energy are *plants, wood and organic wastes*. However, major biomass sources may include:

1. Wood and wood processing wastes.

2. Agricultural crops and waste materials.

3. Municipal solid wastes.

4. Animal manure and sewage waters.

Thermal Characteristics of Biomass as Fuel:

Biomass can be a source of liquid fuel or gaseous fuel or solid fuel. Out of these fuels, solid fuel is most commonly used. The important thermal characteristics of solid biomass fuel may include:

- Heat value
- Moisture content
- Composition
- Fuel size and density

Heat Value: Heat value of a fuel may be defined as the amount of heat available in the fuel. It is one of the most important characteristics of a fuel. The heat value of a fuel depends on its chemical composition.

The heat value of a fuel can be expressed as: *the higher heating value or the lower heating value*. The higher heating value (HHV) is the total amount of heat energy available in the fuel, which includes the energy contained in the exhaust gases, whereas lower heating value (LHV) does not include the energy contained in the exhaust gases. The heat content of a fuel usually does not have the fixed value. Hence, the heat value of a biomass fuel should be expressed as a range rather than a fixed value.

Moisture Content: Moisture content effects the burning property of a biomass fuel. Biomass fuel with high moisture content burn less readily than a low moisture content biomass fuel, hence provide less useful heat per unit mass. Therefore, low moisture level fuels are preferred than the high moisture level fuels. Much of the energy in wet fuel is used to heat and vaporize the water. However, extremely dry fuel can cause problems such as dust that spoils equipment or can even contribute to an explosion hazard.

Composition: The composition of various biofuels affects its performance. The main compositional properties include ash content, susceptibility to slagging and fouling, and percent volatiles.

“Ash contents” are the mass fraction of incombustible materials in a biofuel. It is an important parameter, which can reduce the combustion efficiency or clog the ash handling mechanisms.

“Slagging and fouling” problems occurs when the generated ash begins to melt and start depositing inside the combustion equipment. Under certain circumstances, the ash can partially melt, forming deposits on the combustor surfaces (fouling) or hard chunks of material in the base of the combustion chamber (slagging/clinkering). High mineral content as well as dirt in the fuel generally cause fouling and slagging problem. Therefore, fuel should be kept free of soil and other contaminants. Slagging and fouling can be minimized by keeping the combustion temperature low enough to avoid the ash formation.

The “percent volatiles” in a fuel is a property that refers to the fraction of the fuel which gets volatilize and turn to gas when heated to a high temperature. Fuels with “high volatiles” will tend to vaporize before combustion. It is called as flaming combustion. This property may affect the performance of the combustion chamber and should be taken into account while designing a biomass fuel combustor.

Fuel size and density: The size and density of the biomass fuel particles are also important factors that affects its thermal characteristics. They affect the rate of heating and drying during the combustion process and thus burning characteristics of the fuel gets affected. The type of handling equipment depends mainly on the size of the fuel particles. The wrong size fuel may have an impact on the

efficiency of the combustion process, and it may result in jamming or damage of the handling equipment. Smaller-sized fuel is mostly preferred for commercial systems as it is easier to use it in an automatic feed system. Normally, fuel size and density are over-looked and should be given careful consideration while selecting a fuel type.

Anaerobic Digestion:

- Anaerobic digestion is a chemical process through which organic matters such as animal manure, food wastes, wastewater biosolids etc. are broken down by microorganisms (bacteria) in the absence of oxygen.
- During anaerobic digestion process biogas and bio-fertiliser are produced.
- Biogas is mostly comprised of carbon dioxide (CO_2) and methane (CH_4) with very little amount of water vapour and other gases.
- The methane gas thus produced may be used as a fuel for cooking or heating or to generate electricity.
- Anaerobic digestion process is also used in the municipal wastewater treatment. The quantity of solids produced from wastewater treatment can be reduced through anaerobic digestion process thereby reducing its disposal cost.
- Environmental pollution due to animal manure can be avoided using anaerobic digestion process which reduces the volume of waste, produces useful methane and also provides a by-product that can be used as fertilizer.
- Plant waste from agriculture can also be processed by anaerobic digestion process to produce biogas. The residual material left after anaerobic digestion process is called “digestate.” Digestate is rich in nutrients and can be used as fertilizer for crops.

Biogas Production Mechanism:

Biogas is produced by biomass using anaerobic digestion process which involves multistep biological and chemical process. It is beneficial in not only waste management but also energy creation. Biogas can be produced from a variety of raw materials, which may include:

• From industry and enterprises

• Food wastes from shops

• Biowaste generated by consumers

• Sludge from wastewater treatment plants

• Manure and biomass generated from agriculture wastes

The mechanism of biogas production from biomass involves following steps:

1. Collection of Biowastes from various sources.

2. Crushing of biowastes to make its consistency as even as possible and removal of any unwanted nonbiodegradable waste from the mixture.

3. Making of Slurry of the biomass by adding water.

4. Adding slurry to the biogas plant and pumping into the pre-digester tank where enzymes secreted by bacteria break down the biomass into an even finer consistency.

5. Sanitization of the biomass by heating the mixture at 70 ^{0}C and above for minimum one hour. During this process any harmful bacteria present in the biomass is removed.

6. Pumping the sanitized biomass into the main biomass reactor in which biogas production takes place.

7. Fermentation of biomass. In this process, microbes feed on the organic matter, such as proteins, carbohydrates and lipids, and their digestion transforms these matters into methane and carbon dioxide.

8. Breaking of the organic matter into biogas which is mainly a mixture of methane and carbon dioxide, water vapour and other gases, approximately in three weeks duration.

9. Collection of biogas in a spherical gas holder placed at the top of the biogas reactors.

After this, the biogas is ready for use by industries, enterprises and consumers. The residual solids and liquids created in biogas production are referred to as digestate. This digestate goes into a post-digester reactor and from there further into storage tanks. Digestates are well suited for uses such as fertilization or for other gardening purpose.

Utilization of Biogas:

Biogas is produced throughout the anaerobic digestion process. Biogas is a renewable energy source that can be used in a variety of ways. Biogas can be used to:

- Produce mechanical power, heat and/or electricity
- Fuel boilers and furnaces, hot water systems, air heaters.
- To run fuel vehicles; and
- Supply in homes and other business centres for their use

With appropriate cleaning or upgrade, biogas can be used in all applications that were developed for natural gas. The three basic end uses for biogas may categorised as:

Production of heat: The most straightforward use of biogas is as thermal (heat) energy. In areas where fuels are scarce, small biogas systems can provide the heat energy for basic cooking and water heating. It may also be used in gas lighting systems for illumination.

Electricity generation: In most cases, biogas is used as fuel for combustion engines, which convert it to mechanical energy which in turn provide power to an electric generator to produce electricity.

Vehicle fuel: Biogas can be used as a fuel in gasoline vehicles provided the biogas is upgraded to natural gas quality.

Digestate is the material that is left over following the anaerobic digestion process. Digestate can be made into products like, Flowerpots, Soil treatment and Fertilizers.

Storage of Biogas:

Appropriate biogas storage system is essential for the efficiency and safety of a biogas plant. There are two main reasons for storing biogas:

(i) Storage at plant location for on-site usage, as and when it is required and

(ii) Storage at distribution points or systems.

There are two broad categories of biogas storage system:

(i) Internal biogas storage tanks that are integrated with the anaerobic digester and
(ii) External Biogas storage tanks which are separated from the anaerobic digester.

Further, based on its application, it can be classified as; Low-pressure biogas storage, Medium-pressure biogas storage, and High-pressure biogas storage.

Low-pressure biogas storage: It is the simplest and least expensive storage system used for onsite applications and intermediate storage of biogas. This system operates at low pressures below 2 psi. The floating biogas storage tank on the digester form falls under this category. It can be made of steel, fiberglass or a flexible fabric material. Flexible fabric materials commonly used for these gas holders include high-density polyethylene (HDPE), low-density polyethylene (LDPE), and linear low-density polyethylene (LLDPE). Sometimes, a separate tank is also installed along with floating gas holder for the storage of digestate and raw biogas as well.

Medium-pressure biogas storage: Biogas can also be stored at medium pressure (between 2 and 200 psi) biogas storage. However, the additional requirements of safety, scrubbing and high maintenance associated with these tanks make them more costly. To prevent corrosion of the tank components and to ensure safe operation, the biogas must first be cleaned by removing H_2S. Biogas that has been upgraded to bio-methane by removing H_2S, moisture, and CO_2 are stored in these tanks. However, the cleaned biogas must be slightly compressed prior to the storage.

High-pressure biogas storage: Bio-methane is stored in this type of storage. Bio-methane is less corrosive than biogas, in addition being more valuable as a fuel. Usually, production of such fuel exceeds immediate on-site demand; hence the bio-methane must be stored for future use. It is normally stored either as compressed bio-methane (CBM) or liquefied bio-methane (LBM). It is stored in high pressure ranges between 2000 psi to 5000 psi.

Wind Energy:

Wind power technology is one of the fastest growing renewable energy technologies. Wind energy is the kinetic energy associated with the movement of atmospheric air. Wind first hits a turbine's blade, causing them to rotate and turn the turbine connected to them. The turbine shaft is connected to a generator, which produces electricity through electromagnetism principle. The amount of power that can be generated from wind depends upon the size of the turbine and its blade length.

Current status and future prospects of wind energy

Due to the various environmental issues associated with the usage of traditional source of energy, most of the users are on high pressure to start looking for alternatives and sustainable energy to minimize the carbon foot prints and its emission.

Globally the wind generation capacity is increasing very fast.

- It has increased many folds from 7.5 gigawatts (GW) in 1997 to 598 GW by 2018.
- It has been increased by 7% in 2019 to reach the value of 645 GW.
- Between 2009 to 2013 the production of electricity using wind energy has doubled.
- In 2016, wind energy accounted for 16% of the electricity generated by all other renewable energy source.
- Worldwide renewable jobs have increased considerably and reached more than 11 million people in 2018. For creating jobs, China was the highest in the list followed by EU, Brazil, Us and India.

In the recent years, the wind power installations have increased many folds. The developments and advancements in wind power generation systems are rapidly updated and thereby attracting worldwide interest. Global Wind Energy Council suggest that wind energy systems could provide 20% of the global demand for electricity by 2030. Due to the growing demand for electric vehicles as well as public transport, future demand for electricity may increase many folds.

Potential of wind energy to provide 20% of global electricity production by 2050 has been established through various research work. In this respect, the Global Wind Energy Council (GWEC) envisions 5.8 TW of wind energy by 2050. GWEC anticipated that the China would remain the world's largest market with 1789 GW of wind power by 2050. India is predicted to generate (452 GW) of wind power by 2050. Currently India has the fourth highest wind installed capacity in the world with total installed capacity of 39.25 GW (as on 31st March 2021).

Wind energy in India

India's wind energy sector is progressing consistently. It's project operation capabilities and manufacturing base has been increased to about 10,000 MW per annum.

As on March 2021, India currently has the fourth highest wind installed capacity in the world with total installed capacity of 39.25 GW. It has also generated around 60.149 billion Units during 2020-21.

The compound annual growth rate for wind generation has been 11.39% between 2010 and 2020, and for installed capacity, it has been 8.78%. India government is helping private sectors by providing various fiscal and financial incentives such as Accelerated Depreciation benefit, concessional custom duty exemption on certain components of wind electric generators.

In addition to this, Generation Based Incentive (GBI) Scheme was available for the wind projects commissioned before 31 March 2017. In addition to the facilities stated above, following steps have also been taken to promote the installation of wind power generating facilities:

1. Providing technical support including identification of potential sites and wind resource assessment with help of National Institute of Wind Energy, Chennai.

2. The inter-state transmission charges and losses have been waived out, in order to facilitate inter-state sale of wind power. However, to avail this facility, wind power project needs to be commissioned by March, 2022.

3. With an objective to provide a framework for procurement of wind power through transparent process of bidding, guidelines have been issued for Tariff Based Competitive Bidding Process for procurement of power from grid connected wind power projects.

4. Bidding process have been standardised and roles and responsibilities of various stakeholders are also clearly defined.

5. These guidelines are provided with the aim to facilitate the distribution licenses to procure wind power at competitive rates and in a cost-effective manner.

Environmental benefits of wind energy

The main Environmental benefits of wind energy include:

- Wind is an unlimited, freely available renewable resource. Therefore, it is a sustainable technology.
- As the wind is a natural occurrence resource, harvesting the kinetic energy of wind doesn't affect currents of wind cycles in any way.
- It is a clean, non-polluting way to generate electricity.
- It does not emit air pollutants or greenhouse gases.
- It is eco-friendly for generating electricity.
- The maintenance cost of turbines and generation of wind power is minimal.
- Wind power turbines can be placed wherever necessary as it needs very little space.

Environmental problem of wind energy

The major problem of wind energy is the initial cost involved for constructing turbines and wind facilities which is extremely expensive. Other problems may include the following:

- The giant size of wind power turbines distracts viewers from the beautiful surroundings.
- Wind turbines may be dangerous to flying birds.
- Usually, the wind turbines are located in the remote areas. Hence, the cost of travel and maintenance on the turbines increases and is time consuming.
- Offshore wind turbines require boats and can be dangerous to manage.
- Some wind turbines tend to generate a lot of noise which can be unpleasant.
- In the darkness/at night it may be difficult for incoming boats to see wind turbines thus may lead to collisions.

NEED OF NEW ENERGY SOURCES

- The energy produced from any source other than fossil fuels may be termed as new energy or alternative energy.
- At present, we are mostly dependent on the fossil fuels for the power generation, causing depletion of these finite materials. Hence, if we are not careful now, our precious, non-renewable resources may get exhausted soon.
- Also, burning fossil fuel in power plants has much adverse impact on our environment. Entire ecosystem gets destructed due to the various types of pollution created by burning of fossil fuel. Hence, there is a need of new energy sources to overcome all the above stated issues.

Different types of new energy sources

New energy sources may be renewable or non-renewable type. Renewable energy sources are derived from naturally available energy sources such as sun, wind and water. These sources are referred as renewable or sustainable. There are new energy sources which falls under non-renewable category, e.g., nuclear energy source.

There are 8 most used new energy sources:

1. ***Wind energy:*** Wind farms capture the wind flow by using turbine and converting it into electricity.
2. ***Solar energy:*** Solar energy is harnessed directly from radiant energy emitted through sunlight and converting it into heat, electricity or hot water.
3. ***Hydroelectric energy:*** This energy is generated mostly in the dams. Water flows through the turbines located in the dam site to produce electricity.
4. ***Geothermal energy:*** Geothermal power is generated by tapping underground reservoir of hot water and steam. Geothermal electricity can be directly used for the purpose of heating and cooling of buildings.
5. ***Bioenergy:*** Bioenergy is generated from organic materials known as biomass or biofuel. Biogas

generated from anaerobic digestion process and used to generate electricity.

6. ***Nuclear energy:*** Nuclear energy is created in the form of heat through the fission process of atoms.
7. ***Hydrogen energy:*** Hydrogen is used as clean burning fuel as it generates fewer pollutants leading to cleaner environment.
8. ***Ocean Energy:*** Ocean energy refers to all forms of energy derived from sea. The movement of the ocean's waves, tides, and currents carries energy that can be harnessed and converted into electricity to power homes, buildings and cities. Ocean energy is environmentally friendly and renewable source of energy.

Applications of Hydrogen energy

Hydrogen has many applications, including:

- ***Transportation:*** Hydrogen fuel cells can power vehicles, including cars, buses, delivery vans, and semi-trucks. Hydrogen can also be used as a lightweight fuel for air and shipping transportation.
- ***Electricity generation:*** Hydrogen fuel cells can generate electricity by combining hydrogen and oxygen atoms. Hydrogen can also be burned for electricity generation.
- ***Industrial processes:*** Hydrogen is used in industrial processes such as:
    - Petroleum refining
    - Fertilizer production
    - Treating metals
    - Processing foods
    - Metal alloying
- ***Heating:*** Hydrogen can be used to heat homes and businesses.
- ***Backup energy:*** Green hydrogen can be used as a backup energy source for renewable energy plants.
- ***Microgrids:*** Green hydrogen can be used in microgrids to provide electricity to remote areas.
- ***Energy storage:*** Hydrogen storage is an important technology for enabling hydrogen use.

Application Ocean energy resources

Oceans cover more than 70% of earth's surface, making them the world's largest solar collectors. Just a small portion of heat trapped in the ocean can power the entire world. From the ocean mainly two types of energy can be harvested: Thermal energy and Mechanical energy.

Thermal energy: It is harvested from the temperature difference of the warm surface waters and the cool deeper water. The technological concept to harvest the thermal energy in the ocean is universally called "Ocean Thermal Energy Conversion (OTEC)" and is currently under development stage. OTEC converts the temperature difference of warm surface water and cold deeper waters into energy. Depth of cold-water zone is about 1000 m below the surface. The required water temperature difference is minimum 200C to operate the OTEC power cycle on a satisfactory way. Thermal energy resource is concentrated on certain zones. On this zone, approximately 66 developing nations including USA and Australia are located. Ocean thermal energy is used to generate electricity.

Mechanical energy: This energy consisting of both potential and kinetic energy is harvested from the tides, waves and currents of the ocean. Ocean mechanical energy is very different from the ocean thermal energy. Tides, waves and currents are intermittent source of energy whereas; ocean thermal energy is quite constant. The electricity conversion from all the three energy sources usually involves mechanical devices.

Tidal energy conversions: Tides are caused by the interaction of sun-moon-earth system. Tides rise and fall is the product of the gravitational and centrifugal forces, of primarily the moon with the earth. The difference of level between low and high tide is used to produce electricity. The use of tidal energy requires a barrage (dam) across a shallow area, where the difference in the level of low and high tide should be at least 5 meters. The tide basin is filled and gets emptied everyday with the flood tides when the water level rises and with the ebb tides when the water level falls. Low-head turbines are installed in the barrage along with the sluice gates that allows water to flow from one side of the barrage to inside the tidal basin. The difference in elevation creates a hydrostatic head that generates electricity through electrical turbines.

Concept, origin and power plants of geothermal energy

The word geothermal comes from the Greek word Geo means earth and therme means heat. Geothermal energy is basically heat stored within the earth. People all over the world use geothermal energy primarily to heat buildings and to produce electricity.

Concept and Origin of geothermal energy

People in ancient time, including Romans, Chinese and Native Americans has used hot mineral water from natural pools and springs for bathing, cooking and heating purpose. Initially, such uses of geothermal energy were limited to the places where hot water and steam were accessible. The hottest part our planet called the core is situated about 2900 kilometres below earth's surface. Temperature of the core is more than 5000^0C. Radiating heat from core is warming rocks, water, gas and other geological materials. If underground rock formations are heated to temperature about 700^0C-1300^0C they get partly melted and become magma. Magma heats nearby rocks and underground aquifers. From this heated aquifers, hot water can be released through hot springs, steam vents and mud pots. These are the sources of geothermal energy. Their heat can be captured and used directly to heat structures such as buildings, vehicle parking space etc.

Power plants of geothermal energy

Geothermal power plants are used to generate electricity using geothermal energy. Their working principle is similar to the coal or nuclear power plant except the source of power. In geothermal powerplant, earth's heat replaces the boiler of a coal plant or reactor of a nuclear plant. Hot water or steam is extracted from the earth through a series of wells and used in the geothermal power plant.

There are mainly three types of geothermal power plants and the choice of plant depends on the state (steam and water) and temperature of the available geothermal energy.

1. Dry steam power plant

2. Flash steam power plant and

3. Binary cycle power plant

Dry steam power plant: These plants use dry steam from geothermal reservoir. The steam from the production well travels directly to a turbine, which drives a generator to produce electricity. After transferring its energy to the turbine, steam gets condensed and injected back into the earth. These are the oldest type of geothermal power plants. These plants require highest temperature and can only be used where underground temperature is quite high.

Flash steam power plant: Flash steam power plants are the most commonly used geothermal power generation plant today. This is mainly due to the lack of naturally occurring high-quality steam. For this plant, water temperature must be over 180^0C. The underground hot water is pumped through the well into a tank kept at the surface level. The surface water tank is kept under much lower pressure, causing some of the fluid to rapidly vaporise, or flash. The vapour then drives the turbine which in turn drives generator and thus electricity is generated. The unused water, which could not become steam, is cycled back into the well or it can be flashed again in a second tank to extract some more energy.

Binary cycle power plant: Binary cycle power plant differs from other two types of geothermal plant. In this, the water or steam from geothermal reservoir never comes in contact with the turbine or generator unit. Here, a secondary loop (hence the name binary) containing a fluid with a low boiling point, such as pentane or butane is used. The water from the well flows through a heat exchanger, which transfers its heat to the fluid having low boiling point. Water vaporizes from these fluids due to its low boiling point. It is then passed through a turbine, drives it and subsequently, the generator to produce electricity. It is expected that these plants will be most commonly used in future simply because it can make use of water with low temperature than other two types of power plants.

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