METALLURGY

MINERALS:- "The natural material in which the metal or their compounds occur in the earth is known as mineral". In other words the combined state occurrences of metals are called minerals.

For example: NaCl, NaNO₃, Na₂SO₄, etc. are the minerals of 'Na'. Similarly $Al_2O_3.2H_2O$ (bauxite), $Al_2O_3.2SiO_2$. 2H₂O (kaolin) are the minerals of 'Al'.

ORE:- "Ores are the minerals from which the concerned metals can be extracted conveniently and economically." For example: Both bauxite (Al₂O₃. 2H2O) and Kaolin (Al₂O₃.2SiO₂.2H₂O) 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, hence kaolin is simply a mineral of aluminium. All ores are minerals however all minerals are not ores.

Distinction between Minerals and Ores:

MINERALS	ORES
The combined state occurrence of metals is called	Ores are the minerals from which the concerned
minerals	metals can be extracted conveniently and
	economically
Extraction of metals from minerals is difficult and	Extraction of metals from ores is convenient and
non-profitable.	profitable.
Minerals contain low percentage of metals but	Ores contain high percentage of metals but low
high percentage of impurities	percentage of impurities
.All minerals are not ores	All ores are minerals
Example: Kaoline ($(Al_2O_3.2SiO_2.2H_2O)$ is a mineral	Example: Bauxite (Al ₂ O ₃ .2H ₂ O) is an ore of
of aluminium	aluminium.

METALLURGICAL OPERATION:- The steps employed for extraction of metals from ores conveniently and economically is called metallurgy or metallurgical operations. The following steps are followed during th e process of metallurgical operation.

- Step-I:- Ore Dressing (Crushing and Grinding)
- Step-II:- Concentration or Ore (Removal of Impurities from Ore)
- Step-III:- Oxidation (Conversion of ore to Metal Oxide)
- Step-IV:- Reduction (Extraction of Metal from Metal Oxide)
- Step-V: Refining /Purification (Obtaining Pure Metal from its Impure form)

STEP-I : ORE DRESSING (CRUSHING and GRINDING)

The ores obtained from mines are in the form of huge lumps. These are first crushed into small Pieces with the help of jaw crusher and then grinded in to their powder form with the help of stamp mill or a ball mill. This process is called grinding or pulverization of ore.

STEP-II : CONCENTRATION

The process of removal of maximum impurities (gangue or matrix) from the ore is called concentration or ore dressing. The method of concentration to be followed depends upon the nature of the impurities present.

METHODS OF CONCENTRATION

1. 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 or pulverized ore spread over a specially designed Table called Wilfley Table. The table contains a number of transverse grooves. The table is kept slightly inclined position and is provided with a rocking motion. When water is spread over the ore, lighter impurities are washed away while heavier or e particles get deposited in the grooves, which are finally carried out in to the main canal.

2. FROTH FLOATATION METHOD:-

This method is suitable for the concentration of sulphide ores only.

In this method of concentration two interconnected tanks are used. The pulverized ore is added to one tank containing water, little amount of pine or eucalyptus. The mixture is then agitated violently by the paddle stirrer with air blast. Due to the preferential wetting of the sulphide ores by oil than by water, a layer of oil is covered over the surface of sulphide ores. These sulphide ore become lighter and float over the surface of the mixture in form of froth or foam, which are carried out in to the second container.

3. 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 magnetic ores containing non-magnetic impurities are concentrated by this meth od. In this method a belt is tied over two rollers of which one is made up of magnet. Pulverized ore is added ov er the belt through a hopper. The pulverized ore move towards the magnetic pulley along with the rotating belt . The non-magnetic impurities fall directly below the magnetic pulley while the magnetic ore form a separate h eap due to the influence of the magnetic field.

4. **LEACHING**:- 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 discarded and the mother liquor is treated with another suitable chemical reagent to get the pure ore back.

For example impure bauxite ore is treated with dil. NaOH (45%) solution which dissolves bauxite(Al_2O_3) to form soluble sodium meta aluminate.

The solution is filtered to remove the impurities. The solution obtained is diluted with a plenty of distilled water when a precipitate of $AI(OH)_3$ is formed.

 $NaAlO_2 + H_2O \rightarrow Al(OH)_3 \downarrow + NaOH$ The precipitate is separated by filtration ,dried and ignited (heated) strongly to get pure alumina.

 $2AI(OH)_3 \rightarrow AI_2O_3 + 3H_2O$

Leaching process is also employed for concentration of silver and gold ore.

STEP-III OXIDATION (Conversion of ores into Metal Oxides)

In the third step of metallurgical operation the concentrated ores are converted into the respective metal oxides. This is achieved by the following two methods:

1.CALCINATION:-

The process of heating an ore strongly below its melting point in absence of oxygen or in a limited supply of air is called calcination. Various functions of calcination are:

i) It removes moisture.

 $AI_2O_3.2H_2O \rightarrow AI_2O_3 + 2H_2O$

ii) It removes volatile impurities like S, P, As, Sb, etc.

 $S + O_2 \rightarrow SO_2 \uparrow$

 $2P + 5O_2 \rightarrow 2P_2O_5\uparrow$

iii) It oxidizes oxidizable substances ('ous' to 'ic')

 $4FeO + O_2 \rightarrow 2Fe_2O_3$

iv) It decomposes carbonates of alkali and alkaline earth metals into oxides.

 $CaCO_3 \rightarrow CaO + CO_2 \uparrow$

2. **ROASTING:-** The process of heating an ore strongly below its melting point in a free but controlled supply of air is called roasting. Various functions of roasting are:-

i) It removes moisture.	$AI_2O_3.2H_2O$	\rightarrow	Al ₂ O ₃ + 2H ₂ O↑
ii) It removes volatile impurities like S, P, As, Sb,etc.	S + O ₂	\rightarrow	SO₂↑
iii) It oxidizes oxidizable substances ('ous' to 'ic')	4FeO + O ₂	\rightarrow	Fe ₂ O ₃
iv) It decomposes carbonates into oxides.	CaCO₃	\rightarrow	CaO + CO₂ ↑

v) It makes the ore porous.

The process of roasting is carried out in a reverberatory furnace.

STEP- IV REDUCTION (Conversion of metal oxides into metals)

In this step of metallurgical operation the roasted ores (the metal oxides) are reduced into the respective metals. The various methods of reduction are:-

1. **SMELTING** :- The process of heating a roasted ore strongly above its melting point with a suitable quantity of coke or charcoal is called smelting. During the process of smelting, metal oxides are reduced into their respective metals. For the reduction of the oxides of less electro positive metals such as Zn, Fe, Cu, Cr, W etc. the reducing agents like H₂O, CO, Na, K etc are used.

 $PbO + C \rightarrow Pb + CO$

 $CuO + CO \rightarrow Cu + CO2 \uparrow$

During the process of smelting, an additional substance called flux is added which combines with the impurities to form fusible slag.

Impurity + flux \rightarrow slag

Thus, "Flx can be defined as the substance which is added during the process of smelting to convert the gangue or matrix into easily fusible mass called slag".

And "Slag is the fusible mass obtained during the process of smelting when flux combines with impurities". It is not soluble in molten metal.

The nature of the flux to be added depends upon the nature of the impurity present in the ore.

(a) Acidic Flux :- When ore is associated with basic impurities like Cao, FeO, etc the flux used is some acidic substances like SiO₂, Na₂B₄O₇, etc.

CaO	+	SiO ₂	\rightarrow	CaSiO ₃
(Basic impurity)		(Acidic flux)		(fusible slag)
MnO	+	SiO ₂	\rightarrow	MnSiO₃

(b) Basic Flux:-If the ore is associated with acidic impurities like SiO₂, P₂O₅, etc. then basic fluxes are used to remove the impurities.

SiO ₂	+	CaCO₃	\rightarrow	CaSiO ₃
(Acidic impurity)		Basic Flux		slag
P_2O_5	+	3CaO	\rightarrow	Ca₃(PO₄)

Smelting is carried out in a blast furnace which is a tall cylindrical furnace made up of steel plates lined inside with fire bricks. Since the density of slag is lower it floats over the molten metal. The molten metal is tapped out at the bottom of the furnace.

2. ELECTROLYTIC REDUCTION

This method of reduction is employed for the reduction of chlorides or oxides of highly electro positive metals such as Na, K, Ca, Mg, Al etc., because these can't be reduced with carbon as they would form the respective metal carbides. The molten oxides or chlorides of these metals are taken in an electrolytic cell and electricity is passed through the molten mass with the help of two electrodes. The metal ions get discharged and deposited at the cathode.

STEP-V REFINING:

The metals obtained after reduction still contain some impurities. The process of removal of impurities from cr ude metal is called refining. The method of refining to be followed depends upon the nature of the metal and t he impurity contaminated with it.

1. DISTILLATION METHOD:

This method of refining is suitable for volatile metals like Hg, Zn, Pb etc. contaminated with non-volatile i mpurities. The impure metal is heated in a distillation flask attached with a water condenser. During heating th e volatile metal get evaporated and condensed which is collected in a separate container while the non-volatil e impurities left at the bottom of the distillation flask.

2. LIQUATION METHOD

This method is suitable for refining the easily fusible metals containing non-fusible impurities. Normally metals such as Sn, Pb etc. are refined by this method. In this method of refining the impure metal is taken in a sloping

hearth and is heated from the bottom. The metal liquefies and flows down the sloping hearth leaving the impurities on the hearth.

3. ELECTRO REFINING

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 di ssolves in its aqueous salt solution providing metal ions which get discharge deposited over the cathode.

ALLOYS: The material obtained by melting together metals or metals with non-metals or metals with metalloids is called an alloy. Or in other words, "an alloy is an intimately mixed metallic solid mixture of two or more different elements, at least one of which is a metal."

Features of Alloy:

1. Alloys are homogeneous in molten state but they may be either homogeneous or heterogeneous in solid state.

2. Alloys containing mercury as one of the constituent are called amalgams.

3. An alloy must contain a metal.

4. In alloys, chemical properties of the component elements are retained, but certain physical properties are improved.

CLASSIFICATION OF ALLOYS: Alloys can broadly be classified into two categories, such as: A. Ferro alloys B. Non-Ferro alloys

A. **Ferro alloys:** The alloy containing iron as the main constituent is called a ferro alloy. For example: Stainless steel, Manganese steel etc.

B. **Non-ferro alloys:** The alloy which does not contain iron as the main constituent is called non-ferro alloys. For example: Brass, Bronze, Solder, Gun metal, Bell metal etc.

COMPOSITIONS AND USES OF BRASS, BRONZE, BELL METAL, ALNICO, GERMAN SILVER AND DURALUMIN.

Brass:- It is a non-ferrous alloy obtained by mixing copper and zinc. The average composition of commercial brass is **Cu= 60% - 80%** and **Zn =40% - 20%**.

Brass is generally used for (i) making utensils (ii)making condenser tubes, ((iii) Electrical terminals, plugs and lamp fittings, (iv) Cartridge casings (v) Locomotive axle boxes, (vi)hydraulic equipment fittings, bushes bearings, etc

Bronze:- It is non-ferrous alloy obtained by fusing copper and tin. The average composition of bronze is

Cu = 75% - 90% and Sn = 25% -10%

Bronze is used for making (i) statues, (ii) coins (iii) utensils (iv) ornaments (v) musical instruments (vi) ship propellers, etc

Duralumin :- it is also a non-ferrous alloy obtained by fusing metals like aluminum, copper, manganese and magnesium. The average composition of duralumin is **AI = 95%**, **Cu = 4%**, **Mg = 0.5%** and **Mn = 0.5%**

Since it is strong hard and lightweight, it is used for making (i) air craft fittings, air ships, (ii) surgical instruments, (iii) cables and fluorescent tube caps, (iv) automobile and locomotive parts, etc

Alnico:- It is a ferrous alloy obtained by fusing metals like steel, aluminium, cobalt and nickel. Its average composition is Steel(iron) = 50%, Al = 20%, Ni = 21%, and Co = 9%

Due to its high ferromagnetism property its can be used for making (i) strong permanent magnets , (ii) microphones, (iii) electric guitar pickups, (iv)electric motors, (v)loudspeakers, Hall effect sensors, etc.

WATER TREATMENT

Water is the one of most important compounds of hydrogen and oxygen. It is a colourless liquid and possesses a high dielectric constant (80) and therefore, salts are highly ionised when dissolved in water, but not so in other solvents. It is the most convenient universal solvent. In general, water is a good solvent for ionic compounds but a poor one for co-valent compounds.

Classification of water:

All the source of water can broadly be classified in to two categories.

A. Surface Water:- *rain Water *River Water *Sea Water *Lake Water

B. Underground Water:- *Well Water * Spring Water

A. Surface water:

1. Rain water: i. Rain is formed by the continuous evaporation and condensation of surface water.

ii. Rain water is considered to be purest form of natural water.

iii. It does not contain any dissolved minerals.

iv. However during its downward movement, it comes across a number of industrial gases like CO₂, SO₂, SO₃, NOx etc. which dissolves them to form acid rain.

v. All the water obtained as a result of rain fall is not available for further use, because some of it is lost by evaporation, percolation and transpiration.

2. **River water** : i. The over flown surface water (surface run off), which is seen in the form of various streams join together to form river.

ii. It is also formed due to the melting of glaciers.

iii. It contains a high percentage of dissolved minerals like NaCl, KCl, NaNO3, CaCO3, NaHCO3 etc

iv. More is the contact of the water with the soil more is the amount of mineral deposit in the river.

3. Lake water : i. A lake is formed due to the collection of water in a natural basin or depression in a mountainous area or in planes, whereas natural lake is a large body of water within land with impervious bed.

ii. Lake water contains a less percentage of dissolved minerals but a very high percentage of organic matters.

Presence of high percentage of organic matters is due to the decomposition of vegetable matters and dead bodies of animals during natural calamities like flood, tsunami etc.

4. Sea water : i. Sea water is considered to be the most impure form of natural water.

ii. Sea water contains about 3.5% dissolved minerals of which about 2.6% is only NaCl.

iii. The percentage of minerals is gradually increasing day by day due to the continuous evaporation of sea water.

iv. Besides NaCl, it also contains other minerals such as Na₂SO₄, KHCO₃, Mg(HCO3)₂, Ca(HCO₃)₂, KBr, MgBr₂ etc. B. **Underground water** : The sources of water which supply water from below the earth's surface are known as underground water. In this type of source, the water that has percolated into the ground is brought on the surface.

Underground water is of two types: a. Spring water b. Well water

- a. **Spring water**: i. Spring is formed due to the melting of glaciers. It is also formed in the mountainous area. During rainy season a part of rain water percolates into the surface of earth. It dissolves many minerals which are in the way of this water. During its downward journey when it meets hard rock, it retards back and emerges out as spring in some weak areas.
 - ii. It is a clearer form of natural water.

iii. It contains high percentage of dissolved minerals and thus its hardness is very high.

- b. Well water: i. It is a clearer from of natural water.
 - ii. It is obtained by digging the surface of earth to a high depth.
 - iii. It contains many dissolved minerals
 - iv. It also contains some organic matters.

CLASSIFICATION OF WATER:

Based upon the action with soap solution water is classified as (a) Soft Water and (b) Hard Water

i. Soft water: Water which produces enough foam or lathers with soap solution easily, is called soft water.

ii. Hard water: Water which does not produce much foam or which does not lathers with soap solution is called hard water.

Hardness of water: The characteristic of water by virtue of which it prevents the formation of foam with soap solution is called hardness of water.

The hardness of water arises due to the presence of certain dissolved minerals like Ca (HCO₃) $_2$, Mg(HCO₃) $_2$, CaCl₂, MgCl₂, FeSO₄, etc in water.

The unit of Hardness: Parts per million (PPM).

Types of Hardness :-Depending upon the types of salts present the hardness in water classified as

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, $[Ca(HCO_3)_2, Mg(HCO_3)_2]$. Temporary hardness is also called carbonate hardness.

B. Permanent of hardness: The permanent hardness of water arises due to the presence of chlorides of Ca, Mg (CaCl₂, MgCl₂) and sulphates of certain heavy metals like Fe (FeSO₄).

REMOVAL OF HARDNESS or SOFTENING OF WATER: The process of /removal of the hardness producing salts from hard water is called water softening/ softening of water. It mainly involves decreasing the concentration of calcium and magnesium salts in Water.

A. Removal of Temporary Hardness: The temporary hardness producing salts if present in water then it can easily be removed just by boiling the water. When hard water is boiled, the soluble $Ca(HCO_3)_2$ and $Mg(HCO_3)_2$ are decomposed in to insoluble carbonates, which are removed by filtration.

Ca(HCO ₃) ₂	\rightarrow	CaCO ₃ +	H ₂ O +	CO₂↑
Hard Water	boil∆	(insoluble)		
Mg(HCO ₃) ₂	\rightarrow	MgCO ₃ +	H ₂ O +	CO₂↑
Hard Water	boil∆	(insoluble)		

*In another method, temporary hardness if present in water can be removed by adding calculated quantity of slaked lime to hard water with stirring. The bicarbonates present in water will change to insoluble carbonates, which will be filtered off to get soft water.

Ca(HCO ₃) ₂	+	Ca(OH)₂	\rightarrow	2CaCO ₃	+	$2H_2O$		
Hard Water				(insoluble)				
Mg(HCO₃)₂	+	Ca(OH) ₂	\rightarrow	MgCO ₃ +	C	CaCO₃	+	$2H_2O$
Hard Water				(insoluble)	(ir	nsoluble		

B. **Removal of Permanent Hardness**: Removal of permanent hardness requires chemical treatment. Various methods used for the removal of permanent hardness are described below.

1. LIME SODA PROCESS (L – S PROCESS) :-

Principle: 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 in to insoluble substances.

CaCl₂	+	Na ₂ CO ₃	\rightarrow	CaCO₃↓ + 2NaCl
(soluble)				(Insoluble)
$MgCl_2$		+ Ca(OH) ₂	\rightarrow	$Mg(OH)_2 \downarrow + CaCl_2$
(soluble	e)			(Insoluble)

The precipitate or sludge formed is then removed by filtration to get soft water.

Functions Of Lime [Ca(OH)₂] :-

(i)	It removes the acid molecules (if present) in water
	2HCl + Ca(OH) ₂ \rightarrow CaCl ₂ + H ₂ O
	$H_2SO_4 + Ca(OH)_2 \rightarrow CaSO_4 + 2H_2O$
(ii)	It removes dissolved CO2 from water
	CO_2 + $Ca(OH)_2 \rightarrow CaCO_3 + H_2O$
(iii)	It removes the temporary hardness producing salts (bicarbonates if Ca, Mg) from water.
	$Mg(HCO_3)_2 + Ca(OH)_2 \rightarrow MgCO_3 + CaCO_3 + 2H_2O$
(iv)	It removes iron , aluminium salts from water.
	$FeSO_4 + Ca(OH)_2 \rightarrow CaSO_4 + Fe(OH)_2$

(v) It removes permanent hardness producing Mg-salts.. $MgSO_4 + Ca(OH)_2 \rightarrow CaSO_4 + Mg(OH)_2$

Functions Of Soda Ash[Na₂CO₃] :-

It removes the permanent hardness producing calcium and magnesium salts as their insoluble carbonates.

Lime-Soda process is of two types.

a. COLD L - S PROCESS: Principle:-

A calculated quantity of lime and soda is treated with hard water at room temperature. Lime and soda react with the hardness causing chemicals present in hard water and the precipitates or sludge formed are removed by filtration.

Construction of Apparatus: The apparatus consists of a conical shaped steel, containing a rotating shaft at the middle. Also it contains a wood fiber filter.

Working Process: Hard water and a calculated quantity of lime, soda along with a little quantity of coagulant are introduced into the apparatus. When the shaft rotates water is properly mixed with lime and soda. The soluble hardness causing chemicals present in hard water react with lime and soda to form insoluble sludge.

CaCl ₂ +	Na ₂ CO ₃	\rightarrow CaCO ₃ \downarrow +	2NaCl
hard water	Soda	ppt	
MgCl ₂ +	Ca (OH) ₂	\rightarrow Mg (OH) ₂ \downarrow +	CaCl ₂
hard water	lime	ppt	

Coagulant aggregates the finely divided sludge particles which settle down in the conical sedimentation tank. The sludge is then removed from time to time through its outlet. Water is now allowed to pass through the wood-fiber filter to get soft water. The residual hardness left in this process is about 50 - 60 ppm.



b. HOT LIME SODA PROCESS:-

Priniciple : This process involves treatment of hard water with a calculated quantity of lime and soda in presence of super-heated steam (at 80°Cto 150° C).

Apparatus: The apparatus consists of three main parts: 1. Reaction tank: Here the reaction of lime and soda with the hard water takes places. 2. Conical sedimentation tank: Here the precipitates (sludge)

are formed and deposited. 3. Filtering unit: It consists of a number of layers of gravels which is used to filter water.

Working Process: Hard water along with a calculated quantity of lime and soda are introduced in to the reaction tank. Also super-heated steam at 80° C – 150° C is passed in to it. The soluble hardness causing chemicals present in the hard water react with lime and soda to form insoluble sludge which settles down in the conical sedimentation tank. The sludge formed is removed periodically through its outlet. Water is then allowed to pass thorough the filtering unit to get soft water. The residual hardness left in this process is only about 15 - 30 ppm.



Continuous hot lime-soda softener.

Comparison Between Cold L-S Process and Hot L-S Process

	COLD L-S PROCESS	HOT L-S PROCESS
1	In this process calculated quantity of dry slaked lime	In this process calculated quantity of dry slaked lime
	[Ca(OH) ₂] and soda ash(Na ₂ CO ₃) are added to hard	[Ca(OH) ₂] and soda ash(Na ₂ CO ₃) are added to hard water
	water at room temperature(25°C) with stirring	at 80°C to 150°C with stirring
2	Since reactions are taking place at low temp. then	Since reactions are taking place at higher temp. then this
	this process is slower	process is faster/ quicker
3	It takes about 24 hours to complete the reactions	It takes about 15 minutes to 1hour to complete the
		reactions
4	Due to low temp the size of ppt. forms is very small	Due to higher temp the size of ppt. forms is bigger.
5	Smaller sized ppt. does not settle easily and filtration	bigger sized ppt. settles easily and the filtration process
	process is difficult	becomes easier.
6	In order to settle the ppt. another chemical called	No coagulant is required to settle the ppt.
	coagulant is added to hard water along with Ca(OH) ₂	
	and Na ₂ CO ₃ .	
7	After filtration, the soft water contains about 50ppm	After filtration, the soft water contains about 15ppm to
	to 60 ppm residual hardness producing salts.	30 ppm residual hardness producing salts.

So, from the above discussion it is clear that , the hot L-S process is preferable to cold L-S process.

2. ION EXCHANGE PROCESS (ORGANIC) : [Deionization process or De-mineralization process]

In this method ion-exchange resins are used. These are insoluble long chained, organic copolymers having micro-porous structure. These resins contain either acidic or basic functional groups capable of exchanging their H⁺ or OH⁻ ion with the ions present in hard water. Ion-exchange resins are of two types.

Cation-exchange resigns (RH⁺): These resins contain acidic functional groups like – COOH, – SO₃H etc. which can exchange their H⁺ ions with the cations of the hardness causing chemicals present in hard water.

Ca²⁺ R_2 -Ca²⁺ 2R-H⁺ \rightarrow $2H^+$ (Cation-Exchange Resin) hard water **Exhausted Resin** 2R-H⁺ Mg²⁺ $R_2 Mg^{2+}$ \rightarrow 2H⁺ + **Exhausted Resin** (Cation-Exchange Resin) hard water

Anion-exchange resigns (ROH⁻): These resins contain basic functional groups like $R-OH^-$, $R-NH_2$ which can exchange their OH^- ions with the anions of hardness causing chemicals.

R—OH [−]	+	CI [–]	\rightarrow	$R-CI^-$	+	OH⁻
Anion-Excahange Resi	in	hard water	E	xhausted Resin		
2 R-OH	+	SO4 ²⁻	\rightarrow	$R_2 - SO_4^{2-}$	+	20H ⁻
Anion-Excahange Resir	۱	hard water	Ex	hausted Resin		
2 R-OH	+	CO ₃ ²⁻	\rightarrow	$R_2 - CO_3^{2-}$	+	20H
Anion-Excahange Resir	۱	hard water	Ex	hausted Resin		



Process: In this process there are two vertical columns/ towers in order to exchange the cations and anions of the hardness producing salts separately.

*Hard water is first passed through the cation-exchange column called Zero-carb which is filled with cation exchange resin(R-H⁺). When hard water passes through the resin, the cations (Ca^{2+} , Mg^{2+} , etc.) present in water get exchanged by the H⁺ ions of the cation exchange resin.

	2R-H⁺	+	Ca ²⁺	\rightarrow	R_2 -Ca ²⁺	+	2H⁺
(Cation-E	xchange Res	in)	hard water	Ex	hausted Resin		
	2R-H⁺	+	Mg ²⁺	\rightarrow	$R_{2}Mg^{2+}$	+	2H⁺
(Cation-E	xchange Res	in)	hard water	Ex	hausted Resin		

So, the water which flows down at the bottom of the cation-exchange column, contains water molecules, anions and the released H^+ ions.

Now this water along with anions and released H⁺ ions enters into the anion- exchange column/ tower called de-acidite, which is filled with anion exchange resin (R-OH⁻). When water passes through the resin, the anions (Cl⁻, $SO_4^{2^-}$, $CO_3^{2^-}$ etc) get exchanged by OH⁻ ions of the resin.

$R-OH^-$	+	CI [–]	\rightarrow	R—CI [−]	+	OH⁻
Anion-Excahange R	esin	hard water	Ext	nausted Resin	1	
2 R-OH	+	SO4 ²⁻	\rightarrow	$R_2 - SO_4^{2-}$	+	20H ⁻
Anion-Excahange Re	sin	hard water	Exha	austed Resin		
2 R-OH	+	CO3 ²⁻	\rightarrow	$R_2 - CO_3^{2-}$	+	20H
Anion-Excahange Re	sin	hard water	Exha	austed Resin		

Now, the water which comes down at the bottom of the anion exchange column do not contain any ion. So this water is the soft water and is called de-ionised water or de-mineralised water.

Regeneration of resins:

*When the capacities of cation and anion exchangers to exchange H^+ and OH^- ions respectively are lost , then they are said to be exhausted. These will be no longer exchange the cations and anions of hard water with the H^+ and OH^- ions of exchangers.

*Since the cost of exchangers are very high, then it is not economical to replace the exchangers frequently. So, it is necessary to regenerate the capacities of expired/ exhausted exchangers for further exchange of ions. *The capacities of exhausted cation exchange resin will be regenerate by passing a solution of dil. HCl or dil. H₂SO₄ through the expired resin. The column is washed with de-ionised water and theb washings are drained to the sink.

R ₂ -Ca ²⁺	+	2HCI	\rightarrow	2R-H⁺	+	$CaCl_2$
(exhausted resin)			(Re	egenerated re	esin)	

The capacities of exhausted anion exchange resin will be regenerate by passing a solution of dil. NaOH through the expired resin. The column is washed with de-ionised water and theb washings are drained to the sink.

R-Cl ⁻	+	NaOH	\rightarrow	R-OH ⁻	+	NaC I
(exhausted resin)			(Rege	nerated resin)		
$R_2 - SO_4^{2-}$	+	2NaOH	\rightarrow	$2R-OH^{-}$	+	2NaCl
(exhausted resin)		(Regenerated resin)				

The residual hardness left in this process in only about 2 ppm. The regenerated ion exchange resins are then used again for exchange of ions.

3. Permutit or Zeolite Method: (Inorganic ion exchange method)

Zeolite is hydrated sodium alumino silicate capable of exchanging reversibly its sodium ions for Ca2+ and Mg2+, having general formula Na₂O.Al₂O₃.xSiO₂.yH₂O. Natural zeolite has formula Na₂O.Al₂O₃.4SiO₂.2H₂O and is non-porous and also known as natrolite. Other zeolites used for water softening are gluconites, green sand, etc.

Synthetic zeolites or permutit are porous and possess gel / glassy structure.

Process : in this process, hard water is percolated at a specified rate at ordinary temperature, through a bed of zeolite kept in a cylinder.

The hardness causing ions ($Ca2^+$ and Mg^{2+}) are retained by zeolite as CaZe and MgZe, while out going water contains sodium salts. Reactions taking place in this process are

Na₂Ze	+	Ca(HCO₃)₂	\rightarrow	2NaHCO ₃	+	CaZe
Na₂Ze	+	Mg(HCO ₃) ₂	\rightarrow	2NaHCO ₃	+	MgZe
Na₂Ze	+	$CaSO_4$	\rightarrow	Na_2SO_4	+	CaZe
Na₂Ze	+	MgSO ₄	\rightarrow	Na_2SO_4	+	MgZe

4. Calgon Process :

Calgon is a trade name for the complex salt $Na_2[Na_4(PO_3)_6]$. When calgon is added to hard water, the Ca^{2+} and Mg^{2+} ions in hard water are rendered ineffective due to the formation of water soluble complex ions. This is also known as sequestration.

The complex calcium and magnesium ions do not form any ppt. with soap. Therefore, they readily form lather with soap solution. Modern detergents contain sodium hexametaphosphate which removes hardness due to Ca²⁺ and Mg²⁺ ions and wastage of soap.

LUBRICANTS

Lubricants are the substances , which are used between two moving or sliding surfaces to reduce the frictional resistance arises between them.

The process of reducing the frictional resistance between two moving or sliding surfaces, by using a lubricant between them, is called **lubrication**.

When a lubricant is used between two moving or sliding surfaces, then it will fill the irregularities of both surfaces and form a thick layer between them. This lubricant layer separates the two surfaces so that there will be no direct contact or interlocking between the two surfaces. Thus the frictional resistance between the surfaces will get reduced.

Functions of Lubricants / Purposes of Lubrication :-

Followings are the major functions of lubricants

- (1) It reduces frictional resistance between moving or sliding surfaces
- (2) Minimizes the wear and tear of machine parts.
- (3) It minimizes loss of energy in form of heat.
- (4) It reduces waste of energy, so that the efficiency of machine is enhanced.
- (5) It reduces expansion of metal by local frictional heat.
- (6) It avoids the chances of seizure of machine parts.
- (7) It reduces the maintenance and running cost of the machine.
- (8) It acts as a sealing agent and minimizes the leakage of gas.
- (9) It acts as a cooling agent by removing the heat of friction.
- (10) It should have high flash point, high fire point, low cloud point, low pour point and high viscosity index.

CLASSIFICATION OF LUBRICANTS :-

On the basis of their physical states, the lubricants are classified as (a) Liquid Lubricants/ Lubricating oils, (b) Semi-solid Lubricants / Greases and (c) Solid Lubricants

(a) Liquid Lubricants / Lubricating Oils :- Liquids which are introduced between two moving or sliding surfaces so as to reduce the frictional resistance between them, are termed as liquid lubricants or lubricating oils. These are further classified as (i) Animal / vegetable oils, (ii) mineral / petroleum oil and (iii) Blended / Syntheticoil.

(i)Animal/ Vegetable Oil :- These are the animal or plant extracts which are used to reduce the frictional resistance between moving or sliding surfaces. (eg) coconut oil, castor oil, til oil, lard oil, whale oil, cord oil, etc.

These oils have very good oiliness and are easily available. But however these oils (i) are costly, (ii) undergo oxidation easily, (iii) easily hydrolyse in moisture, (iv) form gummy or sticky mass on exposure to air, (v) do not exhibit lubricating action properly at high and low temperature.

(ii) **Mineral / petroleum oil** :- these oils are obtained by fractional distillation of petroleum. The shorter chain hydrocarbon oils have lower viscosity than longer chain hydrocarbons oils.

These are most widely used lubricants, because these are (i) cheap, (ii) available in abundance, (iii) quite stable under service conditions. But however, these have poor oiliness as compared to animal / vegetable oils. These can not retain their lubricating action at extreme conditions.

(iii) **Blended / Synthetic Oil** :- The oils obtained by adding specific additives to the mineral iols to improve their properties, are called blended / synthetic oils.

*Oiliness of mineral oils can be improve by adding vegetable oils and fatty acids to it.

* Fatty esters, thio organic materials, chloro organic compounds, etc are added to improve the workability at high pressure.

*Phenol, chlorinated wax with naphthalene are added to decrease pour point.

*Hexanol is added to improve viscosity index. Thickeners like polysterene polyesters, etc are added to increase viscosity.

*Antifoaming agents like glycerol, glycols are added to decrease foam formation.

*Tricresyl phosphate is added as abrasion inhibitors.

(b) Semi-solid Lubricants / Greases :-

Grease are semi-solid substances used between two moving or sliding surfaces to reduce the frictional resistance .

*In greases a soap is dispersed through out a liquid lubricating oil especially petroleum or synthetic oil containing any of the additives.

*Greases are prepared by the saponification of fat (such as tallow or fatty acid) with alkali (like ;ime, caustic soda, etc.), followed by adding hot lubricating oil with agitation. The amount of mineral added determines the consistency of the finished grease. Soap are acting as gelling agent, which give an interconnected structure containing the added oil. Solid thickening agents like clay, bentonite, colloidal silica, carbon black, etc are added to grease to improve the heat resistance property.

*Greases are used

(1) in situations where oil can not remain in place, due to high load, low speed, sudden jerk, etc.

(2) in bearing and gears that work at high temperature.

(3) in situations where bearing need to be sealed against entry of dust , dirt, grit, or moisture.

(4) in situations where spurting or dripping of oil is undesirable, as these may degrade the quality due to dripping.

Types of Greases :- (a) Calcium based grease or cup grease is an emulsion of petroleum oil with calcium soap. These are cheapest, insoluble in water(resistant to water), can be used at low temperature (below 80^oC).

(b)Soda based greases are petroleum oil thickened by sodium soaps. These are not water resistant and can used upto 175°C.

(c) Lithium based greases are petroleum oil, thickened by lithium soaps. These are water resiatant and suitable for use at very low temperature(15°C) only.

(d) Axle greases are very cheap resin greases, prepared by adding lime to resin and fatty oils followed by fillers like talc or mica. These are water resistant, suitable for equipments working under high loads, low speeds, etc.

(c) Solid Lubricants :-

These are the solid substances which are used between moving or sliding surfaces to reduce the frictional resistance. These can be used either powder form or mixed with oil or water. When used with oil it is called oildag when used with water it is called aquadag. (eg) Graphite, Molybdenum Disulphide, Boron Nitride, Talc, Soap Stone, Mica, etc.

Solid Lubricants are used where

- (1) Operating conditions are such that a lubricating film cannot be secured by use of lubricating oils or greases.
- (2) Contamination of lubricating oil or greases by dust, dirt, grit are unacceptable.
- (3) The operating temperatures or load is too high, even for a semi-solid lubricant to remain in position.
- (4) Combustible lubricants must be avoided.

Graphite :- Graphite is the most widely used solid lubricant.

It is soapy to touch (slippery), non-inflammable, not oxidized in air below 375°C. In absence of air it can be used up to very much higher temperature.

It can be used either in powder form or as suspension in water (aquadag) or oil (Oildag)

As lubricant it is used in air compressors, lathes, food stuff industry, railway track joints, open gears, chains, cast iron bearings, IC engines, general machine work shops, etc.

Molybdenum Disulphide (MoS) :- It is another solid lubricant used after graphite.

It possess very low coefficient of friction, and is stable in air upto 400°C. Due to poor inter laminar attraction , low shear strength occurs in a direction parallel to the layers.

As a lubricant, it can be used as dry powder, aquadag or oildag, or as greases. A mixture of 70%MoS, 23% alkali silicates and 7% graphite si used as lubricant in space vehicles. MoS in its powder form is spread over the surfaces sliding at high velocities when it fills low spots in metal surfaces forming its film.

Boron Nitride :- It is slippery, soft refractory solid like graphite. Its structure resembles with that of Graphite.

It works upto 3000°C. Thus, its lubrication film provides good wear resistance and seizure resistance.

As lubricant it is used in xerographic process and laser printers as charge leakage barrier, in cosmetics like foundations, eye shdows, blushers, kohl pencils, lipsticks, etc, as a substrate for semiconductors, microwave transparent windows.

FUELS

A fuel is a combustible substance , containing carbon as main constituent and on proper combustion gives huge amount of heat, which can be used economically for domestic and industrial purposes. (eg) wood, coal, petroleum oil, natural gas, diesel, kerosene, LPG, producer gas, water gas, coal gas, etc. **Classification of Fuels** :-

(A) Based upon their occurrence (preparation), fuels are classified as (a) Primary/ Natural fuels and (b)Secondary/ artificial fuels.

Primary / Natural Fuels :- These are the fuels which are directly obtained from nature as such. (eg) wood, coal, crude petroleum oil , natural gas, marsh gas

Secondary / Artificial Fuels :- These fuels are prepared from primary fuels. (eg) charcoal, petrol, kerosene, diesel, coal gas, producer gas, water gas, LPG, etc.

- (B) Based upon their physical state of aggregation, fuels are classified as
 - (a) Solid Fuels :- Wood, Coal, Charcoal, Coke, Dung cake, etc
 - (b) Liquid Fuels :- petrol, Naptha, kerosene, Diesel oil, Heavy oil, etc.
 - (c) Gaseous Fuel :- LPG, CNG, Coal gas, Wood gas, Water gas, Producer gas, Bio Gas etc.

Characteristics of Good Fuels :- A good fuel

(1) Should possess high calorific value.

Calorific Value (CV) of a fuel can be defined as the amount of heat liberated by burning unit mass or unit volume of fuel completely in oxygen. Calorific value of fuels help to rate / grade the fuels. Higher is the calorific value better is the quality of fuel.

- (2) Should have moderate ignition temperature. Ignition temperature of a fuel is the minimum temperature up to which a fuel must be preheated , so as to burn smoothly.
- (3) Should have moderate velocity of combustion/ moderate rate if combustion.
- (4) Should not contain more percentage of non-combustible substance or ash content.
- (5) Should have low percentage of moisture content.
- (6) Should not produce toxic / poisonous gas during combustion.
- (7) Should be cheap and plentily available.
- (8) Should easy to transport and easy to store without any risk.
- (9) Combustion process of the fuel should be easily controllable.
- (10)Products of combustion of the fuel should not be harmful and should burn without much smoke.

Solid Fuels :- solid fuels are those solids which have carbon as chief constituent and on combustion produces huge quantity of heat. (eg) Wood, charcoal, Coal, Coke, Dung cake, etc

 (a) Wood :- Wood is a primary fuel as it is directly obtained from forest. A freshly cut wood contains about 25% to 50% moisture which is reduced to maximum 15% on air drying. The average composition of air dried moisture free wood is Carbon = 50%, oxygen = 35%, nitrogen= 7%, Hydrogen 6% and ash content = 2%

CV :- Its calorific value varies between 3500 Kcal/Kg to 4500 Kcal/Kg.

In presence of sufficient oxygen it burns with long non- smoky flame leaving behind very little amount of ash. However, with insufficient oxygen it forms smoke.

Uses :- (1) It is mostly used as a domestic fuel. (2) Due low CV, it is not used as industrial fuel.

(b) Coal :- It is a highly carbonaceous fuel obtained from mining. It is formed by coalification of vegetable matters and animals for millions of years under high pressure and temperature. Its main constituents are carbon, hydrogen, and oxygen along with nitrogen and sulphur and traces of non-combustible inorganic matter.

The progressive transformation of vegetable and animal matters to anthracite coal results in

- (i) decrease in moisture content
- (ii) decrease in H,O,N,S content with rise in carbon content.
- (iii) decrease in volatile matter content
- (iv) increase in calorific value
- (vi) increase in hardness.

Various types of coals are (i) Peat, (ii) Lignite (iii) Bituminous and (iv) Anthracite

(i)**Peat** :-It is a brown fibrous jelly like mass and assumed as the early stage of coalification. It is an uneconomical fuel as it contains as much as 80% to 90% water. But, on air drying for 2 to 3 months, it burns freely.

The average composition of air dried peat is C = 60%, H = 5.9%, O = 34.1%

Its Calorific Value is 5400 Kcal/ Kg.

Dried peat is used as a domestic fuel.

(ii) **Lignite** :- This type of coal is also known as brown coal as it is a soft, brown coloured variety of coal. It is considered as lowest ranked coal. It is compact in texture and contains 20% to 60% moisture. On air drying it breaks into small pieces.

Air dried lignite has average composition C = 67%, H = 5.2%, O = 27.8%

Its calorific value varies between 5500 Kcal/ Kg to 7000 Kcal/ Kg.

It burns with long smoky flame.

Lignite coal is dried, powdered and pressed into small briquettes which are used as domestic fuel, in industries for steam raising (boiler fuel), and for preparation of producer gas.

(iii) **Bituminous (common coal)** :- It is pitch black to dark grey coals. It has a laminated structure of alternate very bright and dull layers. It is most widely used coal. It is harder than lignite and contains more percentage of carbon.

The average composition of bituminous coal is C = 90%, H = 5% and O = 5%

Its calorific value is 8000 Kcal/ Kg to 8500 Kcal/ Kg.

Like lignite coal , bituminous coal burns with smoky flame.

It is largely used in industries in making metallurgical coke, coal gas and steam for raising temperature and domestic heating.

(iv) **Anthracite** :- It is hardest, deep black and lusturous coal. It has highest percentage of carbon and lowest amount of volatile matter and moisture content.

Its average composition is C = 94% , H = 3.5 % , O = 2.5 % along with traces of nitrogen, moisture content and ash content.

Its calorific value is 8600 Kcal/ Kg to 8700 Kcal/ Kg.

It burns with no smoke and high local heat. So, it is used for steam raising, house hold purpose, in metallurgical operations, etc.

Advantages of Solid Fuel :- (1) These are easy to transport,

(2) These are convenient to store without any risk.

- (3) Their cost of production is very low.
- (4) These possess moderate ignition temperature

Disadvantages of Solid Fuel :- (1) their ash content is very high.

- (2) Their large portion of heat is wasted during combustion.
- (3) They burn with clinker formation.
- (4) Their combustion process can not be controlled easily.
- (5) Their cost of handling is high.
- (6) Their calorific value is lower than liquid or gaseous fuels.
- (7) These require large excess of oxygen for complete combustion.
- (8) These can not be use in internal combustion engines.

Liquid Fuels :-

Crude Petroleum oil is the primary liquid fuel. It is dark greenish brown, viscous oil found deep in earth's crust. It is composed mainly of various hydrocarbons like paraffins, olefins, aromatics, cyclo-paraffins, napthalenes, together with small amount of organic compounds containing oxygen, nitrogen and sulphur.

Its average composition is C = 79.5% to 87.1%, H = 11,5% to 14.8%, S = 0.1% to 3.5%, N + O = 0.1% to 0.5%. It is a mixture of a number of useful secondary fuels such as petroleum ether, gasoline or petrol, kerosene, diesel oil, heavy oil / lubricating oil, etc, which can be obtained by fractional distillation of crude petroleum oil in oil refineries.

Among the above useful fractions petrol, kerosene and diesel oil are the most important fractions which are largely used as fuels.

(a) Gasoline / Petrol / Motor Spirit :-

* It is obtained between temperature range of 40° C – 120° C during fractional distillation of crude petroleum oil.

*It is a mixture of hydrocarbons such as C_5H_{12} (pentane) to C_8H_{18} (Octane). Gasoline Having high octane number / octane rating is assumed as better fuel than other gasolines.

*octane number of a gasoline is the percentage of iso-octane in a mixture of iso-octane and n-heptane, which matches the fuel under test in knocking characteristics.

*The average composition of gasoline is C = 84%, H = 15%, N + O + S = 1%.

- * Its density is 0.72 to 0.75.
- *Its calorific value is 11,250 KCal / Kg.

*It is highly inflammable and volatile.

* It is used as a fuel in internal combustion engines , automobiles, aeroplanes, water pumps, etc.

(b) Kerosene oil :-

- *This fraction of liquid fuel is obtained between 180°C 250°C during the fractional distillation of crude petroleum oil.
- *It is mixture of hydrocarbons such as $C_{10}H_{22}$ (decane) to $C_{16}H_{34}$ (hexadecane).
- *The average composition of kerosene oil is C = 84%, H = 16%, and S \leq 1%.
- * Its density is 0.75 to 0.85.
- * Its calorific value is 11,100 Kcal / Kg.
- * it is mostly used as a domestic fuel in stoves, fuel in jet engines, Water pumps, motors and for making oil gas.

(c) Diesel Oil :-

- *This fraction of liquid fuel is obtained between 250°C 320°C during the fractional distillation of crude petroleum oil.
- * It is mixture of hydrocarbons such as $C_{15}H_{32}$ (pentadecane) to $C_{18}H_{38}$ (octadecane).
- * The average composition of kerosene oil is C = 85%, H = 12%, and N + O + S = 3%.
- * Its density is 0.86 to 0.95.
- * Its calorific value is 11,000 Kcal / Kg.
- *It is used as a fuel in diesel engines such as light and heavy vehicles, generators, pumps motors, etc.

Advantages of Liquid Fuels :-

- (1) These have higher CV than solid fuels.
- (2) These burn without forming dust, ash, clinker, etc.
- (3) Combustion process can be easily controlled.
- (4) These can be easily transport through pipes.
- (5) Loss of local heat is very low due to greater cleanliness.
- (6) These require less excess air for complete combustion.
- (7) These require less furnace space for combustion.
- (8) These can be used in internal combustion engines.

Disadvantages :-

- (1) Cost of liquid fuel is relatively much higher as compared to solid fuels.
- (2) Costly storage tanks are required for storing liquid fuels.
- (3) Due to high volatility and inflammable nature, the storing of liquid fuels is highly risky.
- (4) These give bad odour.
- (5) Specially designed furnaces, burners and spraying apparatus are required for efficient burning.
- (6) Chocking of sprayers is a drawback of oil firing.

Types of Diesel Oils :-

 Low Sulphur Heavy Stock (LSHS) :- Low Sulphur Heavy Stock is residual fuel processed from indigenous crude. This fuel is in lieu of furnace oil in the same applications where furnace oil is suitable. However, LSHS has higher pour point, higher calorific value and lower sulphur content than furnace oil. These are used for steam raising in boilers of power plants, heating of furnaces, aboard ships, and in industrial plants.

- (2) Furnace Oil / Fuel Oil :- Fuel oil also known as furnace oil is a fraction obtained from petroleum distillation, either as distillate or a residue. It is also known as heavy oil or marine fuel.
 Fuel oil is made of long hydrocarbon chains, particularly alkanes, cycloalkanes, and aromatics.
 Calorific values of these oils are of the order of 10,000 Kcal / Kg.
 These are used for steam raising in boilers of power plants, heating of furnaces, aboard ships, in industrial plants, as a domestic fuel.
- (3) Light Diesel Oil (LDO) :- Light Diesel Oil (LDO) is a blend of components from the distillation process of crude oil. Its boiling point range is 150°C 400°C and the hydrocarbon range is C₁₂ to C₁₈. It is also known as distillate fuel or marked oil since it is marked with a coloring substance. It is used in engines with an rpm less than 750 such as stationary marine engines installed in ships, diesel engines used for electricity generation.
- (4) **High Speed Diesel (HSD)** :- Like Light Diesel Oil, High Speed diesel (HSD) is a blend of components from the distillation process of crude oil. Its boiling point range is 150° C 400° C and the hydrocarbon range is C_{12} to C_{18} .

It is a brown coloured oily liquid with pungent smell.

It is normally used as a fuel in medium and high speed compression ignition engines which have rpm more than 750. (eg) commercial vehicles(like trucks, buses, lorries, cars, jeeps), stationary diesel engines, locomotives, pumps, etc.

High speed diesel is better than normal diesel oil, because the cetane number of HSD varies between 56 - 60 while the cetane number of normal diesel varies between 45 - 55.

Gaseous Fuels :-

(a) Producer Gas :-

Producer Gas is essentially a mixture of combustible gases like carbon monoxide (CO), hydrogen(H_2) and non-combustible gases like carbon dioxide(CO₂), nitrogen (N_2).

*It is prepared by passing air mixed with a little steam over a red hot bed of Coke or Coal, maintained at about 1100°C in a special reactor called "gas producer".

*Its average composition is CO = 22% to 30%, H_2 = 8% to 12%, CO₂ = 3%, N_2 = 52% to 56%.

*Its Calorific Value is about 1300 Kcal / m³.

* It is used (i) for heating open hearth furnaces, muffle furnaces, retorts, etc and (ii) as a reducing agent in metallurgical operations.

Its calorific value can be increase up to 4015 Kcal / Kg if oxygen gas (not air) and super heated steam at 30 atmospheric pressure are passed over red hot coke or coal. Here, at high pressure CH4 gas forms along with CO, H₂, CO₂, and N₂ gas.

(b) Water Gas :-

Water gas is essentially a mixture of combustible gases like carbon monoxide (CO) and hydrogen (H_2) , with a little non-combustible gases like carbon dioxide (CO_2) and nitrogen (N_2) .

*It is prepared by passing alternatively steam and little air through a bed of red hot Coke or Coal maintained at about 900°C to 1000°C in a reactor.

* Its average composition is CO = 41%, H_2 = 51%, CO_2 = 4%, N_2 = 4%.

*Its Calorific Value is about 2800 Kcal / m³.

*It is used as (i) a source of hydrogen, (ii) an illuminating gas, (iii) a fuel gas, (iv) a gas for welding purposes(because its flame is short and very hot).

* If it is carbureted by adding gaseous hydrocarbons then its calorific value will increase up to 4500Kcal/M³. This gas is then called carbureted water gas having composition $H_2 = 35\%$, CO =25%, hydrocarbons =35%, and CO₂ + N₂ =5%.

(c) Coal Gas :-

Coal Gas is mixture of number of a number of lower hydrocarbons along with CO, H_2 , CO_2 , and N_2 .

*It can be prepared on large scale by the carbonization of coal or heating coal in absence of air (destructive distillation), at 1300°C either in coke ovens or gas making retorts. Thus this gas is also called coke oven gas.

* It is a colourless gas having characteristic odour. It is lighter than air and burns with a long smoky/ sooty flame.

* Its average composition is H2 = 40%, CH4 = 32%, CO = 7%, C2H2 = 2%, C2H4 = 3%, N2 = 4%,

CO2 = 1% and rest = 4%.

*Its calorific value is 4900Kcal /m3.

*It is used as (i) illuminant in cities and towns, (ii) a fuel gas, (iii) a reducing agent in metallurgical operations.

(d) Natural Gas :-

It is a primary gaseous fuel and is generally associated with petroleum deposits.

*It is obtained from wells dug in the oil bearing regions.

* When it occurs along with petroleum in oil wells. It is called wet gas. The wet gas is treated to $removeC_3H_8$, C_3H_6 , C_4H_{10} , C_4H_8 which are used as LPG. On the other hand, when gas is associated with crude oil, it is called dry gas.

*Before use ,the natural gas is purified to remove objectionable ingredients such as water, dust, grit, H_2S , CO_2 , N_2 and heavier liquefiable hydrocarbons (C_3H_8 , C_3H_6 , C_4H_{10} , C_4H_8).

*Its average composition is $CH_4 = 70\% - 90\%$, $C_2H_6 = 5\% - 10\%$, $H_2 = 3\%$, $CO + CO_2 = rest$.

* Its Calorific Value varies from 12000 KCal/m³ to 14000 KCal/m³.

*It is used (i) as an excellent domestic fuel and can be transported over very large distances in pipe lines. (ii) for the manufacture of a number of chemicals by synthetic processes.

(iii) as a raw material for the manufacture of carbon black and hydrogen.

(iv) as a fuel for automobiles in compressed form in place of petrol and diesel.

(v) for preparation of synthetic proteins by microbiological fermentation of methane.

(e) Liquified Petroleum Gas (LPG) :- LPG can be obtained as a by-product during cracking of heavy oils or from Natural Gas. It is dehydrated, desulphurised and traces of odorous organic sulphides especially ethyl mercaptans are added to give warning of gas leak.

*It is colourless, odourless, highly volatile, highly inflammable and burns with blue flame . the odour smell during LPG gas leakage is due to the presence of ethyl marcaptans which has a typical odour.

* Its average composition is n – butane = 27%, iso- butane = 25%, Butene = 43%, Propene = 2.5%, Propane = 2.5% with or without no ethane.

* Its Calorific Value is about 27,800 Kcal /m³.

* It is mostly used as (i) a domestic fuel and industrial fuel, (ii) a motor fuel.

(e) Compressed Natural Gas (CNG) :-

It is a primary gaseous fuel and is generally associated with petroleum deposits.

*It is obtained from the upper portion of wells dug in the oil bearing regions.

* It is colourless and odourless gaseous mixture. It is very cheap and burns with pale blue flame releasing huge amount of heat.

* Its average composition is CH_4 (methane) = 70% - 90%, C_2H_6 (ethane) = 4% - 9%, with traces of propane and butane.

* Its Calorific Value is 12500 Kcal / m³.

* It is used (i) as a fuel for vehicles,

- (ii) as a domestic and industrial fuel,
- (iii) as a source of carbon used in tyre industry.
- (iv) for production of hydrogen gas needed for fertilizer industry.
- (v) Specially CNG is used in low emissive vehicles like ULEV, Ford CNG Pickups, CNG HONDA Civic Gx.

Advantages of Gaseous Fuels. :-(1)These can transported easily through gas pipe lines to the actual place of need.

(2) they can be lighted at moment's notice.

- (3) these have high heat content and high calorific values than liquid and solid fuels.
- (4) their combustion process can be easily controlled.
- (5) these burn without any soot, smoke and donot leave any ash.
- (6) these are clean in use.
- (7) they burn without heat loss , due to convection currents.
- (8) these burn in slight excess of air supply.
- (9) these are also used in internal combustion engines.
- (10) these do not require any special burners for combustion

Disadvantages of Gaseous Fuels :- (1) Very large storage tanks are required to store these.

- (2) since these are highly inflammable then there is more chance of fire hazards during their use.
- (3) these are more costly than solid and liquid fuels.

POLYMERS

Polymers are the macromolecules or giant molecules, built-up by linking together a large number of small / simple molecules through covalent bonds in a regular fashion. (eg) polyethene, polypropene, polyster, PVC, Teflon, Bakelite, nylon -6,6 etc.

Monomers are the small / simple molecules which will combine with each other as repeating units to form the polymer molecules. (eg) ethene is the monomer of polyethene, phenol and formaldehyde are monomers of Bakelite, vinyl chloride is monomer of PVC.

$n[CH_2 = CH_2]$	\longrightarrow	[$-CH_2$ $-CH_2$ $-CH_2$ $-CH_2$ $-CH_2$ $-CH_2$ $-]_n$
Ethene		polyethene
(monomer)		(polymer)

A **homo-polymer** is that polymer which is formed by the combination of identical monomers or repeating units through covalent bonds in a regular fashion. It is a whole number multiple of a monomer.

A **co-polymer** is that polymer which is formed by the combinations of two or more different monomers through covalent bonds.

Polymerisation is the process of obtaining a polymer by the combination of a number of monomers. **Degree of Polymerisation** can be defined as the number of repeating units of monomers, present in a polymeric chain. In another way ,the whole number ratio between the molecular mass of polymer and the molecular mass of monomer is termed as the degree of polymerization.

It is denoted as 'n'.

So, Degree of Polymerisation (n) = $\frac{\text{Molecular mass of Polymer}}{\text{molecular mass of monomer}}$

Types of Polymerisation :-

(A) Addition or Chain Polymerisation :- In this type of polymerization a number of identical monomers are added one after another through covalent bonds, without elimination of any simple compound.
 *The polymer forms here is called addition polymer and is an exact multiple of the original monomeric molecule.

*The monomers must contain one or more double bonds, which by intermolecular rearrangement, may make the molecule bifunctional.

*Some addition polymers are polythene, PVC, Teflon, Nylon, Polypropylene, Polystyrene, Polyacrylonitrile, poly methacrylate, etc.

 $n[CH_2 = CH_2] \longrightarrow n[--CH_2 - CH_2 -$

(B) **Condensation or Step Polymerisation** :- It is that type of polymerization in which reactions occur between monomers containing polar groups which form polymer along with elimination of simpler molecules like H₂O, NH₃, HCL, etc.

*Thus condensation polymerization is an intermolecular combination, and it takes place through the different functional groups (in the monomer) having affinity for each other. When monomer contains three functional groups, it may give rise to a cross linked polymer.

* Nylon-6:6, Nylon6:10, etc are some condensation polymers.

$NH_2(CH_2)_6NH_2$	+	HOOC(CH ₂) ₄ COOH	>	
(hexamethylene diamine)		(Adipic Acid)		(Nylon-6,6)

(C) **Copolymerisation** :- When two or more monomer species undergo joint polymerization then the process is Called Copolymerisation.

*The polymers formed here are high molecular weight compounds and are called copolymers.

* example Bakelite, styrene- butadiene rubber(SBR), nitrile butadiene rubber (GRS), etc.

$n[CH_2 = CH - CH = CH_2]$	+ $n[C_6H_5-CH = CH_2]$	 	СН₂−СҢ − Ӈп
butadiene	styrene	SBR	Ċ ₆ H₅

Comparison Between Thermoplastic Polymers and Thermosetting Polymers

	Thermoplastic Polymers	Thermosetting Polymers
1	These are formed by addition polymerization	These are formed by condensation polymerization
2	These have usually long chain linear structures	These have three dimensional cross linked structure
3	These will soften and melt on heating and	These do not soften on heating but rather become
	harden again on cooling	hard. On prolonged heating, these start burning.
4	These can be remoulded, recast and reshaped	These can not be remoulded or reshaped as these
	by heating to a suitable temperature.	retained their shape and structure.
5	These are usually soft, weak and less brittle.	Thes are usually hard, strong and more brittle
6	These can be reclaimed from wastes	Thes can not be reclaimed from wastes.
7	These are usually soluble some organic	Due to strong bond and cross- linking, these are
	solvents	insoluble in almost all organic solvents.
8	(eg) Polythene, PVC, Teflon, Polystyrene,	(eg) Bakelite, urea formaldehyde resin, terylene,
	Nylon, polypropylene, Polyacrylo nitrile, etc	melamine-formaldehyde resin, etc.

Poly-Vinyl Chloride (PVC) :-

Poly vinyl chloride (PVC) is obtained by heating water emulsions of vinyl chloride in presence of small amount of benzoyl peroxide or H_2O_2 in an autoclave under pressure.



On compounding with plasticizers like tricresyl phosphate, dibutyl phthalate etc, plasticized PVC can be obtained.

Properties :- (1) It is a colourless, odourless, horny material, (2) It is non-inflammable and chemically inert substance, (3) It is resistant to light, acids and alkalis, (4) It is soluble in hot chlorinated hydrocarbons such as ethyl chloride, (5) pure PVC has a high softening point (148°C) and a greater stiffness and rigidity as compared to polythene, but is brittle, (6) It can be moulded easily.

Uses :- (A) Rigid or unplasticized PVC has superior chemical resistance and high rigidity, but brittle. So it is used for making (1) sheets for tank lining, (2) electrical insulators, light fitting (3) safety helmets, gramophone records, plastic dolls (4) refrigerator components, rain coats, hand bags (5) cycle and motor cycle mud guards .

(B) Plasticized PVC is used for making (1) rain coats, table clothes, curtains
(2) electrical insulators like coverings of electrical cables,
(3) injection syringes, floor tiles, tool handles, toys,
(4) conveyor belts, thermal insulating foam used in cinema halls, buildings and in air crafts.
(5) radio and television components.

Polyethylene :-

Polyethylene or polyethene (PE) is obtained by the polymerization of ethylene/ethene in presence of traces of oxygen at 150°C to 250°C and 1500 atomsphere pressure.

 $n[CH_2 = CH_2] \xrightarrow{} -CH_2 - CH_2 - CH_2 - CH_2 - H_2 - H_2$

By using free radical initiator, low density polyethene (LDPE) is obtained, while by using ionic catalyst high density polyethene (HDPE) is obtained.

Properties :- (1) It is a rigid, waxy, transparent, non-polar solid.

(2) It exhibits considerable chemical resistance to acids, alkalis and salt solutions.

(3) It is a bad conductor of electricity.

(4) It swollen and permeable to most oils and organic solvents.

(5) Due to high symmetrical chain structure , it crystallizes easily.

High Density Polyethene (HDPE) :- The high density polyethene (HDP) is completely linear, has better chemical resistance, particularly to organic solvents, has a higher softening point and greater rigidity than low density polyethene.

Uses :- Polyethene is used for

(1) making high frequency insulator parts,

- (2) making bottle caps, flexible bottles, toys,
- (3) Kitchen and domestic appliances, buckets
- (4) making sheets for the packing materials, bags for packing,
- (5) making coated wires and cables, tubes , pipes
- (6) chemical plants, etc.

Bakelite :- Like other phenolic resins or phenoplasts, Bakelite is a condensation polymer.

It is prepared by condensing phenol with formaldehyde in presence acidic or alkaline catalyst. So,

Bakelite is a phenol- formaldehyde resin.

The initial reaction results in the formation of *o*- and *p*- hydroxyl methyl phenol, which results to form a linear polymer called novolac.

During moulding hexamethylene tetramine $[(CH_2)_6N_4]$ are added. The addition of hexamethylene tetramine provides formaldehyde, which converts the soluble and fusible novolac into a hard infusible, and insoluble cross linked solid called Bakelite..

Low degree of polymerization leads to formation of **soft bakelites**, high degree of polymerization leads to the formation of **hard bakelites**.

Properties :- (1) Bakelite is a hard, rigid, scratch resistant solid.

- (2) It is infusible, water resistant and insoluble
- (3) these are resistant to non-oxidizing acids, salts, and many organic solvents, but are reactive towards alkalis.
- (4) It possess excellent electrical insulating character.
- Uses :- It is used for
 - (1) making electrical insulator parts like switches, plugs, switch boards, heater handles, etc.
 - (2) making moulded articles like telephone parts, cabinets for radio and television,
 - (3) impregnating fabrics, wood and paper
 - (4) making adhesives for grinding wheels
 - (5) making paints and varnishes
 - (6) as hydrogen exchanger in water softening.
 - (7) Making bearings, used in propeller shafts for paper industry, and rolling mills.

RUBBERS / ELASTOMERS

Rubbers (also Known as Elastomers) are high polymers having elastic properties in excess of 300 percent. Thus a rubber-band can be stretched to 4 to 10 times its original length and as soon as the stretching force is released, it returns to its original length and as soon as the stretching force is released, it returns to its original length and as soon as the stretching force is released, it returns to its original length.

The unstretched rubber is amorphous. As the stretching is done, the macro-molecules(polymers) get partial aligned with respect to another, there by causing crystallization and consequent stiffening of rubber. On

releasing the stress, the rubber chain get reverted back to their original coiled state and it becomes amorphous again.

Natural Rubber :- Natural rubber consists of basic material latex, which is a dispersion of isoprene. So, natural rubber is a polymer of **isoprene (2 – methyl buta – 1,3 – diene**). During polymerization isoprene molecules polymerize to long coiled chains of **cis-polyisoprene**.

Natural rubber is made from the saps of plants like havea brasillians and guayule mostly found in tropical and semi-tropical countries. The rubber latex is obtained by making incisions in the bark of the rubber trees and allowing the sap to flow out into small vessels.

Drawbacks of Raw / Natural Rubber :-

- (1) It is plastic in nature (i.e) it becomes soft at high temperature and too brittle at low temperature.
- (2) It is weak (I,e) Its tensile strength is 200 kg / cm².
- (3) It has large water absorption capacity.
- (4) It is non-resistant to non-polar solvents like vegetable and mineral oils, gasoline, benzene and CCl₄.
- (5) It is easily attacked by oxidizing agents.
- (6) It perishes, due to oxidation in air.
- (7) It swells considerably in organic solvents and gradually disintegrates.
- (8) It possesses marked tackiness .
- (9) It has little durability.
- (10) When stretched to a great extent, it suffers permanent deformation.

Vulcanisation :-

To improve the properties of raw rubber, it is compounded with some chemicals like sulphur, hydrogen sulphide, benzoyl chloride, etc. In most cases sulphur is compounded for vulcanization.

The process involves in heating the raw rubber with sulphur to 100°C to 140°C. The added sulphur combines chemically at the double bonds of different rubber springs. Vulcanization thus serves to stiffen the material by a sort of anchoring and consequently preventing intermolecular movements of rubber springs. The extent of stiffness depends upon the amount of sulphur added.

Advantages of Vulcanization :-

- It has good tensile strength and extensibility.when a tensile force is applied, it bear a load of 2000 Kg / cm² before it breaks.
- (2) It has good resilience.
- (3) It has low absorption tendency.
- (4) It has higher resistance to oxidation and to absorption.
- (5) It has much higher resistance to wear and tear as compared to raw rubber.
- (6) It is a better electrical insulator.
- (7) It is resistance to organic solvents.
- (8) It has useful temperature range of -40° C to 100° C.
- (9) It has slight tackiness.

(10) It has low elasticity is low, depending on the extent of vulcanization.

Synthetic Rubbers or Elastomers :-

An elastomer or synthetic rubber is any vulcanisable man-made rubber like polymer, which can be stretched to at least twice its length, but it returns to its original shape and dimensions as soon as stretching force is released.

- (1) **Styrene Rubber (GR S or BuNa S)** :- It is that type of synthetic rubber which is formed by the co-polymerization of butadiene (about75%) and styrene (about 25%) by weight.
- $n[CH_{2} = CH CH = CH_{2}] + n[CH_{2} = CH(C_{6}H_{5})] \xrightarrow{-(-(CH_{2} CH = CH CH_{2}) CH CH(C_{6}H_{5}))}{(butadiene 75\%)} (styrene 25\%) copolymerization (styrene butadiene rubber(SBR))$
- Properties :- (1) it possesses high abrasion resistance, (2) it has high load bearing capacity and resilience, (3) it get readily oxidize in presence of ozone, (4) it swells in oils and solvents, (5) it can be Vulcanise in the same way as natural rubber,
- **Uses** :- It can be used for manufacturing (1) motor tyres, (2) Floor tiles, (3) foot wear components, Shoe soles, (4) gaskets, (5) wires and cable insulations, (6) tank lining, (7) adhesives, (8) carpet backing, etc.
 - (2) Nitrile Rubber (GR A or BuNa N) :- It is that type of synthetic rubber which is formed by the co-polymerization of butadiene and acrylo nitrile.
 - $n[CH_2 = CH CH = CH_2] + n[CH2 = CH(CN)] ------ \rightarrow (-[CH_2 CH = CH CH_2] CH CH(CN))_{n---} (butadiene)$ (nitrile- butadiene rubber)

Properties :- (1) It possesses excellent resistance to heat, sunlight, oils, acids and salts, but less resistance to alkalis to natural rubber.92) vulcanized rubber is more resistant to heat and aging than natural rubberand may be exposed to high temperature.

Uses :- It is used for (1) making conveyor belts, (2) high altitude air craft components, (3) tank-lining, (4) hoses, gaskets, (5) printing rollers, (6) adhesives, (7) oil-resistant foams and auto-mobile parts, etc.

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BIOFERTILIZERS

Biofertilizers are living organisms that enrich the nutrient quality of the soil. It refers to the use of microbes instead of chemicals to enhance the nutrition of the soil. As a result, it is also less harmful and does not cause pollution.

*This is what makes them so important to organic farming because they are completely environment-friendly. *Biofertilizers are the products containing one or more species of microorganisms which have the ability to mobilize nutritionally important elements from non usable to usable form through biological processes such as nitrogen fixation, phosphate solubilisation, excretion of plant growth *promoting substances or cellulose and biodegradation in soil, compost and other environments.

*The need for the use of biofertilizer arises mainly for two reasons. First, because increase in the use of biofertilizers leads to increased crop productivity, second, because increased usage of chemical fertilizer leads to damage in soil texture and raises other environmental problems.

*The role of biofertilizers in agriculture assumes special significance, particularly in the present context of increased cost of chemical fertilizer and their hazardous effects on soil health.

Types of Biofertilizers:

- 1. Bacteria
- 2. Fungi
- 3. Cyanobacteria

Bacteria :- The nitrifying bacterias present on the nodules of roots of legumes is a great example of biofertilizers. The nodules are formed by the association of the bacterium 'Rhizobium' with the roots of these plants. This association is beneficial and is, therefore, called 'symbiotic'.

The nodules help in fixing atmospheric nitrogen into organic forms which can then be used as nutrition by the plants. Adding Rhizobium cultures to fields has become a common practice to ensure an adequate amount of nitrogen in the soil.

Other examples of bacteria that act as biofertilizers include Azospirillum and Azotobacter. These bacteria are freeliving in the soil. Azotobacter is usually used with crops like cotton, wheat, mustard, maize etc.

Fungi :- Symbiotic associations exist between plants and fungi too. These associations are called 'Mycorrhizae'. The fungus in this association absorbs phosphorus from the soil and provides it to the plant. Plants that grow with these associations also show other advantageous characteristics such as:

- 1. Tolerance to drought conditions and salinity.
- 2. Resistance to root-borne pathogens.
- 3. An overall increase in plant growth and development.

Cyanobacteria :-These are blue-green bacteria found in water and on land. They also help fix atmospheric nitrogen. Examples are Oscillatoria, Nostoc, Anabaena etc. The symbiotic association between the aquatic fern Azolla and Anabaena is very important for rice fields. In this association, Anabaena receives carbon and nitrogen from the plant in exchange for fixed nitrogen. This adds organic matter to the soil enhancing the fertility of rice fields.

Nowadays, many biofertilizers are commercially available in the market for farmers to buy and use. These not only help replenish the soil nutrients but also reduce the dependency on chemical fertilizers. This helps in maintaining the mineral content of the soil and reduces <u>pollution</u> to a great extent.

Advantages of Using Biofertilizers

Some of the advantages associated with biofertilizers include:

- They are eco- friendly as well as cost effective
- Their use leads to soil enrichment and the quality of the soil improves with time.
- Though they do not show immediate results, but the results shown over time are spectacular.
- These fertilizers harness atmospheric nitrogen and make it directly available to the plants.

• They increase the phosphorous content of the soil by solubilising and releasing unavailable phosphorous.

- Biofertilizers improve root proliferation due to the release of growth promoting hormones.
- Microorganism converts complex nutrients into simple nutrients for the availability of the plants.
- Biofertilizer contains microorganisms which promote the adequate supply of nutrients to the host plants

and ensure their proper development of growth and regulation in their physiology.

- They help in increasing the crop yield by 10-25%.
- Biofertilizers can also protect plants from soil born diseases to a certain degree.

PESTICIDES

Pesticides are chemical substances that are meant to kill pests. In general, a pesticide is a chemical or a biological agent such as a virus, bacterium, antimicrobial, or disinfectant that deters, incapacitates, kills, pests.

The Food and Agriculture Organization (FAO) has defined pesticide as:

Any substance or mixture of substances intended for preventing, destroying, or controlling any pest, including vectors of human or animal disease, unwanted species of plants or animals, causing harm during or otherwise interfering with the production, processing, storage, transport, or marketing of food, agricultural commodities, wood and wood products or animal feedstuffs, or substances that may be administered to animals for the control of insects, arachnids, or other pests in or on their bodies.

Types Of Pesticides :-Pesticides are often referred to according to the type of pest they control. Pesticides can also be considered as either **biodegradable pesticides**, which will be broken down by microbes and other living beings into harmless compounds, or **persistent pesticides**, which may take months or years before they are broken down.

There are many different types of pesticides, each is meant to be effective against specific pests. The term "-cide" comes from the Latin word "to kill."

Algaecides are used for killing and/or slowing the growth of algae.

Antimicrobials control germs and microbes such as bacteria and viruses.

Biopesticides are made of living things, come from living things, or they are found in nature.

Disinfectants control germs and microbes such as bacteria and viruses.

Fungicides are used to control fungal problems like molds, mildew, and rust.

Herbicides kill or inhibit the growth of unwanted plants, aka weeds.

Insecticides are used to control insects.

Insect Growth Regulators disrupt the growth and reproduction of insects.

Miticides control mites that feed on plants and animals. Mites are not insects, exactly.

Molluscicides are designed to control slugs, snails and other molluscs.

Mothballs are insecticides used to kill fabric pests by fumigation in sealed containers.

Natural and Biological Pesticides control pests using things found in nature, or man-made versions of things found in nature.

Ovicides are used to control eggs of insects and mites.

Pheromones are biologically active chemicals used to attract insects or disrupt their mating behavior. The ratio of chemicals in the mixture is often species-specific.

Rodenticides are used to kills rodents like mice, rats, and gophers.

Wood Preservatives are used to make wood resistant to insects, fungus and other pests.

Herbicides are used to destroy weeds

Benefits of pesticides

(1)Improving productivity :- Food grain production, which stood at a mere 50 million tons in 1948–49, had increased almost fourfold to 198 million tons by the end of 1996–97 from an estimated 169 million hectares of

permanently cropped land. Pesticides have been an integral part of the process by reducing losses from the weeds, diseases and insect pests

(2) Protection of crop losses/yield reduction :- Weeds reduce yield of dry land crops . Severe infestation of weeds, particularly in the early stage of crop establishment, ultimately accounts for a yield reduction. Herbicides provided both an economic and labour benefit.

(3) Vector disease control :- Vector-borne diseases are most effectively tackled by killing the vectors. Insecticides are often the only practical way to control the insects that spread deadly diseases such as malaria, typhoid, cholera, etc. Disease control strategies are crucially important also for livestock.

(4) Quality of food :- In countries of the first world, it has been observed that a diet containing fresh fruit and vegetables far outweigh potential risks from eating very low residues of pesticides in crops. Increasing evidence shows that eating fruit and vegetables regularly reduces the risk of many cancers, high blood pressure, heart disease, diabetes, stroke, and other chronic diseases.

(5) Other areas – transport, sport complex, building :- The transport sector makes extensive use of pesticides, particularly herbicides. Herbicides and insecticides are used to maintain the turf on sports pitches, cricket grounds and golf courses. Insecticides protect buildings and other wooden structures from damage by termites and wood boring insects.

Hazards of Pesticides :-

- (1) Direct impact on humans :-
- (2) Impact through food commodities
- (3) Impact on environment
- (4) Surface water contamination
- (5) Ground water contamination
- (6) Soil contamination
- (7) Effect on soil fertility (beneficial soil microorganisms)
- (8) Contamination of air
- (9) Non-target organisms

ATOMIC STRUCTURE

FUNDAMENTAL PARTICLES OF ATOM

There are three fundamental particles present the atom. They are, electrons, protons, and neutrons. **Electron** :-

An Electron is that sub-atomic particle which has a unit negative charge and a mass equal to1/1835th of the mass of hydrogen atom.

It is discovered by J. J. Thomson

It is denoted as 'e' or $_{-1}e^0$

Mass of Electron = 9.11 X 10^{-28} gm or 9.11 X 10^{-31} kg

Charge of Electron = 1.602×10^{-19} C or 4.803×10^{-10} esu.

Charge on 1 mole electron is 96500 coulombs.

Proton :-

A proton is that sub-atomic particle which has a unit positive charge and mass equal to mass of hydrogen atom. Magnitude of its charge is same as that of electron but opposite in sign.

It was discovered by Goldsein

It is denoted as ' \mathbf{p} ' or ' \mathbf{H} ' or $_{1}\mathbf{H}^{1}$

Mass of proton = 1.67×10^{-24} gm or 1.67×10^{-27} kg

Charge of proton = 1.602×10^{-19} C

Charge on 1 mole proton is 96500 coulombs

Neutron :-

*A neutron is a neutral sub-atomic particle having mass same as mass of hydrogen atom.

It was discovered by James Chadwick.

It is denoted as '**n**' or $_0$ **n**¹ Mass of neutron = 1.675 X 10⁻²⁴ gm or 1.67 X 10⁻²⁷ kg and charge = 0

Atomic Number (Z) :-

The number of unit positive charges (no. Of protons) present in the nucleus of an atom is called its atomic number. It is also the no of electrons present in neutral atoms. It is represented as Z.

Mass Number (A) :-

The sum of the no. of protons and no. of neutrons present in the nucleus of atom , is called the mass number of atom. It is represented as A .

Mass Number = No. of Protons + No. of Neutrons

(i.e)	A = p+n	(Where A = mass number, p = number of protons and n = no of
or	A = Z+n	neutrons)
or	A= e+n	

Isotopes :-

Isotopes are the atoms, having same atomic Numbers but different mass numbers.

 $_{92}$ U 234 , $_{92}$ U 235 , $_{92}$ U 238 , etc

These occupy same position in periodic table,

 $_{1}\text{H}^{1}$, $_{1}\text{H}^{2}$, $_{1}\text{H}^{3}$

These have same numbers of protons but different no of neutrons.

These may have same similar chemical properties, but have different physical properties.

Isobars :-

Isobars are those atoms which have different atomic numbers but same mass numbers.

₆C¹⁴, ₇N¹⁴ ₁₈Ar⁴⁰, ₂₀Ca⁴⁰

These occupy different position in periodic table.

These have different chemical properties and physical properties.

These have different no of protons and neutrons.

Isotones :-

Isotones are the atoms or species which have same numbers of neutrons.

 ${}_{6}C^{14}$, ${}_{8}O^{16}$ ${}_{19}K^{39}$, ${}_{20}Ca^{40}$

These have different positions in periodic table

These have different no of protons but same no of neutrons

These have different physical as well as different chemical properties.

Discovery of Nucleus :-

Rutherford bombarded $alpha(\alpha)$ particles to a very thin sheet of gold foil and placed a circular screen coated with zinc sulphide at the other side of gold foil.

*His observations :-

(a) most of α -particles passed through gold foil without any deviation from their normal path.

(b) few particles deviated through certain angles from their normal path.

(c) very few particles(about 1 or 2 out of 20000) retraced to their normal path.

* His conclusions:-

(a) Since most particles passed through gold foil without any deviation, then most of space of an atom is empty or vacant.

(b) Since some particles deviated through certain angles, then there must be a positively charged, heavy particle is present at the centre of the atom.

(c) As very few particles retraced back, then the size of the positively charged particle is very small.

* He named this extremely small, positively charged, heavy particle as nucleus.

Rutherford's Atomic Model :-

After the discovery of nucleus Rutherford proposed a model of an atom, which was named after him as Rutherford's Atomic Model. According to him an atom has two parts named as **nucleus** and **extra nuclear part**. **Nucleus** :-

The extremely small, positively charged, heavy particle present at the centre of the atom, is the nucleus.

*The nucleus is so small that its radius is about 10⁻¹³cm.

* the nucleus is positively charged as it contains the protons only.

*The nucleus is heavy as almost of all of the weight of atom is concentrate in the nucleus.

Extra Nuclear Part :-

Excluding the nucleus the rest part of the atom is called extra nuclear part.

*The negatively charged electrons are revolving around the nucleus in extra nuclear region (space around the nucleus) in high speeds in circular paths like planets revolving around the sun.

*during revolution, the force of attraction arises between negatively charged electrons and positively charged nucleus is balanced by centrifugal force.

Failure of Rutherford Model / Draw Back of Rutherford's Atomic Model :-

According to Clark Maxwell, when a charged body moves under the influence of attractive force, will continuously loose energy.

As per Rutherford atomic model, negatively charged electrons revolve under centrifugal force. So, during its revolution the electron will continuously loose its energy.

When the electron looses its energy then it will come nearer and nearer towards the nucleus in a spiral path and finally fall on to the nucleus for which the nucleus may collapse.

But, we know that the revolving electrons are never fall on to nucleus and nucleus does not collapse. So, Rutherford could not explain the stability of the atom. Later this defect was rectified by Neils Bohr.

Bohr's Atomic Model :-

Neils Bohr made a correlation between Rutherford atomic model and Planck's quantum theory. He then proposed his model of atom. This model successfully explains the line spectrum of hydrogen atom and the rectification of defect of Rutherford atomic model.

Main postulates of his atomic model are

(1) An atom consists of a massive positively charged body and negatively charged electrons. The positively charged body is called nucleus and the electrons are revolving around this nucleus in few circular non-radiating fixed paths called stationary states or orbits.

(2) Each orbit is associated with definite amount of energy, for which these are also called stationary energy levels or stationary energy states or Shells. He designated these Shells as K,L,M,N,...... so on starting from the nucleus.

(3) The amount of energy associated with each shell is given as

 $E_n = -1312/n^2$ Kj/mole where n is the no of shell

So, the energies of shells increase with increase in distance from nucleus. i.e energy of K-shell < L-shell < M-shell < N-shell <so on. Thus, K-shell possess lowest possible amount of energy.

Again, shells are not equally spaced and energy difference between two successive shells are not same. It goes on decreasing with increase in value of n.

(4) An electron not only revolves in one shell but also in others. However, the permissible orbits are those in which the angular momentum of electron is quantised (i.e) angular momentum of electron must be an integral multiple of $h/2\pi$ and is given as

 $mvr = nh/2\pi$

(5) So long as electron revolves in an orbit, it neither emit energy nor absorb energy.

(6) When an electron looses energy, then it will jump from higher orbit to lower orbit and the amount of energy looses by electron is given as

$$\Delta E = E_2 - E_1$$

(7) When an electron absorbs energy, then it will jump from lower orbit to higher orbit and the amount of energy absorbs by electron is given as

$$\Delta E = E_2 - E_1$$

The higher energy state here is termed as excited state.

Rectification of Defect of Rutherford Atomic Model:-

As per Planck's theory a body can emit or absorb energy discontinuously in form of discrete units.

According to Bohr, when electron looses energy it jumps from higher orbit to lower orbit. On further loss of energy it will jump to next lower orbit, and ultimately it jumps to K-shell.

Since K-shell is nearest to nucleus (there is no shell below K-shell) and it possess lowest possible amount of energy, then there is no question that electron will jump on to nucleus on loosing energy. So, Bohr rectified the defect of the Rutherford's atomic model and explained the stability of atom.

Limitations of Bohr's Atomic Model :-

Though Bohr's atomic model successfully explains the stability of atoms, but it has the following limitations.

- (1) It explains the line spectra of hydrogen or other monoelectronic species. But, fails to explain the spectra of poly electronic species.
- (2) Bohr's atomic model tells electrons are revolving in circular orbits which are two dimension. But, modern researches showed that the electrons are revolving in elliptical orbits in three dimensions.
- (3) It couldn't explain the shapes and bond angles of atoms and molecules.
- (4) It fails to explain Zeeman Effect and Stark Effect.
- (5) It fails to explain Heisenberg Uncertainty Principle.
- (6) It fails to explain the dual nature of matter.

Bohr- Bury Scheme :-

Bohr and Bury collectively put forwarded few principles regarding filling up of electrons in various shells/orbits. These principles are

 An orbit/ shell can not contain more than 2n² numbers of electrons, where n is the value of the orbit. Thus

Shell	Value of n	No. of Electrons(2n ²⁾
K-shell	1	2
L-shell	2	8
M-shell	3	18
N-shell	4	32

- (2) Outermost orbit can not contain more than 8 electrons.
- (3) Pneultimate {(n-1)th} orbit can not contain more than 18 electrons.
- (4) Antepneultimate {(n-2)th} orbit can not contain more than 32 electrons.
- (5) It is not necessary to fill up an orbit completely before the filling up of another starts.

Aufbau Principle :-

Aufbau Principle tells that " Electrons are filled in various sub-shells of an atom as per their increasing order of energies." (i.e) sub-shell which has lower energy must fills first and the sub-shell which has highest energy will fill atlast.

Rules:-

- (1) Sub-shell which has lower (n+l) value has lower energy, where n is the value of principal quantum number and l is the value of azimuthal quantum number.
- (2) In case there are two or more sub-shells have same (n+l) values, then sub-shell having lower n value must fills first.
- (3) The increasing order of energies of sub-shells is 1s <2s < 2p < 3s < 3p < 4s < 3d <4p<.....so on

Hund's Rule :-

The rule states that "No electron pairing takes place in various orbitals of a sub-shell unless and until each degenerate orbital contains atleast one electron."

Atomic Weight:-

It can be defined as the relative average weight of one atom of the element which is comparable to weight of a carbon atom (C^{12}) taken as 12.

*In other words atomic weight of an element means as to how many times it is heavier than 1/12th the mass of an atom of carbon-12.

So, Atomic Weight of an Element = $\frac{\text{Weight of one atom of Element}}{\frac{1}{12}\text{th of the weight of a C-12 atom}}$

*weight equal to 1/12th the weight of C-12 atom is one unit and is written as **amu**.

* When atomic weight of an element is expressed in grams then it is termed as its gram atomic weight.

*Gram Atomic Weight of element = 1 gram atom of the element.

Equivalent Weight :-

It can be defined as the number which shows how many parts by weight of element can combine with or displaces from directly or indirectly by 1.008 parts by weight of hydrogen or 8 parts by weight of oxygen or 35.5 parts by weight of chlorine.

*When equivalent weight of an element is expressed in grams then it is termed as its gram equivalent weight.

*The different equivalent weights possessed by an element when it combines with another element in different proportions , are called variable equivalent weights.

* The equivalent weights of iron (Fe) in FeO and Fe_2O_3 are 28 and 18.67 respectively.

*Gram Equivalent Weight of a substance = 1 Gram Equivalent of the substance

* Atomic Weight of Element = Equivalent Weight X Valency of element.

*Equivalent Weight of element = Atomic Weight / valency

Determination of Equivalent Weight of Elements

(1) If Weight of hydrogen and weight of element are given, then

Equivalent Weight of element = $\frac{\text{weight of Element}}{\text{weight of hydrogen}} X$ 1.008

(2) If Weight of oxygen and weight of element are given, then

Equivalent Weight of element = $\frac{\text{weight of Element}}{\text{weight of oxygen}} \times 8$

(3) If Weight of Chlorine and weight of element are given, then

Equivalent Weight of element = $\frac{\text{weight of Element}}{\text{weight of chlorine}} X 35.5$

(4) If weights of two elements and Eq. Weight of one element is given, then

Equivalent Weight of element A = $\frac{\text{weight of Element A}}{\text{weight of Element B}}$ X Equivalent Weight of Element B

Molecular Weight :-

*It can be defined as the relative average weight of one molecule of the substance which is comparable to weight of a carbon $atom(C^{12})$ taken as 12.

molecular Weight of a substance = $\frac{\text{Weight of one molecule of substance}}{\frac{1}{12}\text{th of the weight of a C-12 atom}}$

* Molecular weight expressed in grams is termed as gram molecular weight.

*Gram Molecular Weight = 1 gram molecule = 1 gm mole

Equivalent Weight of acids :-

*Equivalent Weight of an acid is the number of parts by mass of it which can supply one part by weight of replaceable hydrogen.

* In other way it is the ratio between the molecular weight of acid and the basicity of acid.

Equivalent Weight of acid = Molecular Weight of acid / basicity So.

Basicity of acid is the no of replaceable hydrogen atoms present in one molecule of acid.

Acid	Molecular Weight	Basicity	Equivalent Weight
HCI	1 +35.5 =36.5	1	36.5/1 =36.5
HNO ₃	1+14 +48 =63	1	63/1 =63
H ₂ SO ₄	2+32+64 =98	2	98/2 =49
H ₃ PO ₄	3 + 31 +64 =98	3	98/3 =32.67
CH₃COOH	12+3+12+16+16+1 =60	1	60/1 =60

Equivalent Weight of a Base :-

*Equivalent Weight of a base is the weight of the base which can neutralise gram eq. weight of the acid. *In other way, it is the ratio between the molecular weight of the base and its acidity.

Equivalent Weight of base = Molecular Weight of base / acidity

Acidity of a base is the number of replaceable hydroxyl groups (OH) present in one molecule of a base.

Bsae	Molecular Weight	Acidity	Equivalent Weight
NaOH	23 +16 + 1 =40	1	40/1 =40
КОН	39 + 16 + 1 = 56	1	56/1 =56
Ca(OH) ₂	40 + 32 + 2 = 74	2	74 / 2 =37
AI(OH)₃	27 + 48 + 3 = 78	3	78/3 =26

Equivalent Weight of Salts :-

*Equivalent weight of salt is the ratio between the molecular weight salt and the total valency of metal atom. Equivalent Weight of salt = Molecular Weight of salt / total valency of metal atom Equivalent Weight of salt = Molecular Weight of salt /(no. of metal atom X its valency)

*In other way, Eq. weight of a salt is that weight which combines with one gram eq. of another salt. *Equivalent weight of a compound is the sum of the eq. weight of its constituents atoms or radicals.

Salt	Molecular Weight	Valency	Equivalent Weight
NaCl	23 + 35.5 =58.5	1x1 =1	58.5/1 =58.5
CaCO₃	40 + 12 + 48 =100	1x2 =2	100/2 =50
KNO₃	39 + 14 + 48 =101	1x1 =1	101/1 =101
Al ₂ (SO ₄) ₃	54 + 96 + 192 = 342	2x3 =6	342/6 =57
MgCl ₂	24 + 71 = 95	1x2 =2	95/2 =47.5
Na ₂ CO ₃	26 + 12 + 48 = 106	2x1 =2	106/2 = 53

Solutions :-

*A solution is a homogeneous mixture of two different substances termed as solute and solvent. The solute get dissolve in solvent.

Types of Solutions :-

* A solution is said to be **unsaturated** if it requires more solute to dissolve. Similarly the **saturated solution** is that one which refuses to dissolve more solute.

When a saturated solution is heated it dissolves more solute. After cooling this solution is termed as **super saturated solution**.

*A **standard solution** is that one whose strength is known or given.

Strength / Concentration of Solution :-

* Strength or concentration of a solution is the amount of solute present in known amount of solvent. The strength of solution can be expressed in terms of

(a) Gms. / Litre (b) Normality (c) Molarity (d) Molality (e) Mole Fraction (f) Percent Solution (g) formality

(a) Gms. / Litre :-

*Grams/ Litre: - It is the amount of solute in grams present in 1 litre of solution.

*If w grams of solute present in V ml of solution, then Grams/Litre = $\frac{W}{V}$ x1000

(b) Normality :-

It can be defined as the number of gram equivalents of solute present in 1 litre of solution.

It is denoted by letter N.

Normality of solution
$$= \frac{\text{no.of gm.equivalents of solute}}{1 \text{ Litre of solution}}$$
Normality of solution
$$= \frac{\text{Grams/litre}}{\text{Equivalent Weight of solute}}$$

Normality of solution =
$$\frac{W}{E} \times \frac{1000}{V}$$

Where W:- weight of solute, E:- Eq. weight of solute and V = Volume of solution in ml

*If 1 gram eq. of solute is present in 1 Litre of solution then the solution is termed as a **normal** solution and it has **normality 1N**.

* If 1/2 gram eq. of solute is present in 1 Litre of solution then the solution is termed as **semi normal** solution and it has **normality N/2 or 0.5 N**.

If 1/10th gram eq. of solute is present in 1 Litre of solution then the solution is termed as **decinormal** solution and it has **normality 0.1N or N/10**.

If 1/100th gram eq. of solute is present in 1 Litre of solution then the solution is termed as centi normal solution and it has **normality 0.01N or N/100**.

(c)Molarity (M) :-

It can be define as the number of gram moles of solute present in 1 Litre of its solution.

It is denoted by letter M.

Molarity of solution = no.of gm.moles solute 1 Litre of solution

Molarity of solution = Grams/litre Molecular Weight of solute

Molarity of solution =
$$\frac{W}{M} \times \frac{1000}{V}$$

Where W:- weight of solute, M :- Molecular weight of solute and V = Volume of solution in ml

*If 1 gram mole of solute present in 1 litre of solution then the solution is called a **molar** solution which has **molarity 1M.**

*If 1/2 gram mole of solute present in 1 litre of solution then the solution is called a **semimolar** solution which has **molarity 0.5M or M/2**.

*If 1/10 gram mole of solute present in 1 litre of solution then the solution is called a **decimolar** solution which has **molarity 0.1M or M/10**.

If 1/100th gram mole of solute is present in 1 Litre of solution then the solution is termed as centi molar solution and it has **molarity 0.01M or M/100**.

(d) Molality :-

It can be define as the number of gram moles of solute dissolve in 1 kg (1000gm) of solvent.

It is denoted by letter m.

Molality of solution =
$$\frac{\text{no.of gm.moles solute}}{1 \text{kg of solvent}}$$

Molarity of solution =
$$\frac{W}{M} \times \frac{1000}{W}$$

Where w:- weight of solute, M :- Molecular weight of solute and W = weight of solvent in grams.

*If 1gram mole of solute is dissolve in 1kg of solvent then the solution is called a **molal** solution and has **molality 1m**. If 1/2 gram mole of solute dissolve in 1kg of solvent then the solution is called a **semimolal** solution which has **molality 0.5m or m/2**.

*If 1/10 gram mole of solute dissolve in 1kg of solvent then the solution is called a **decimolal** solution which has **molality 0.1m or m/10**.

If 1/100th gram mole of solute is dissolve in 1kg of solvent then the solution is termed as **centi molal** solution and it has **molality 0.01m or m/100**.

pH :- (Power of Hydrogen Ion Concentration) :-

*pH of a solution can be defined as the negative logarithm of hydrogen ion concentration of solution in moles per litre.

*Mathematically it can be written as $pH = -log_{10}[H^+]$ **pH Values of Different Solutions** :-

Case (a) :- For Neutral Solutions :-

Pure water is a neutral solution

*We know the $[H^+]$ ion concentration of neutral solutions / pure water is 1.0 X10⁻⁷ moles/litre. So, its pH is,

$$pH = -log_{10}[H^+]$$

or
$$pH = -log_{10}(10^{-7})$$

Or, $pH = -(-7)log_{10}10$
Or, $pH = 7$

So, for any neutral solution, pH value is 7 .

Case (b) :- For Acid Solutions :-

*The $[H^+]$ ion concentration of acidic solutions is > 1.0 X10⁻⁷ moles/litre.

Let, the $[H^+]$ ion concentration of acidic solutions is 10^{-6} moles / litre.

So, its pH is

	$pH = -log_{10}[H^+]$
or	$pH = -\log_{10}(10^{-6})$
Or,	$pH = -(-6)\log_{10}10$
Or,	рН = 6

So, **the pH values of any acidic solution is always less than 7**. The values must remain between '0' to '7'. * Lower will be pH value stronger will be the acid. Acids having pH values '0' to 2 are strong acids. Similarly acids having pH values '5' to less than 7 are weak acids.

Case (c) :- For Basic / Alkaline Solutions :-

*The [H⁺] ion concentration of a base/ alkaline solution is < 1.0 X 10^{-7} moles/litre. Let, the [H⁺] ion concentration of a base/ alkaline solution is 10^{-8} moles / litre So, its pH is

 $pH = -log_{10}[H^+]$ or $pH = -log_{10}(10^{-8})$ Or, $pH = -(-8)log_{10}10$ Or, pH = 8

So, **the pH values of any alkali / basic solution is always more than 7**. The values must remain between '7' to '14'. So, the pH values of any basic solution is greater than 7, but less than 14,

* Higher is the pH value stronger will be the base. Bases having pH values between 7 to 9 are considered as weak bases, while those having pH values between 9 to 14 are considered as strong bases. In no case the pH value a base will exceed 14 as the value of ionic product of water for pure water is 10^{-14} .

* Like pH of solution, the pOH value of solution is given as $pOH = -log_{10}[OH^{-}]$ *For any solution pH + pOH =14



Importances of pH in Industries :-

(1) **Sugar Industry** :-The pH of the sugarcane juice is carefully controlled to 7 before processing. Because if, it is acidic (pH < 7), then sucrose ($C_{12}H_{22}O_{11}$) present in juice hydrolyse to glucose ($C_{6}H_{12}O_{6}$) and fructose ($C_{6}H_{12}O_{6}$). Similarly if, the juice is alkaline(pH > 7), then sugar can not be crystallize and coloured substances are formed.

(2) Paper Industry :- pH plays an important role in paper industry. pH affects production yield, paper quality and reagent consumption, for pulp to bind properly and form paper sheet, the pH value is adjusted around 4.5.
(3) Textile Industry :- In all textile processes in which aqueous solutions are used, balancing the pH of the solution is primary. The effectiveness of oxidising and reducing agents is pH dependent. The pH values in garments can be greatly affected by scouring, bleaching, after treatment and final washing.

Before scouring and bleaching pH will be 5.5 to 5.8. After scouring and bleaching pH will be 8.5 to 9.0. During hot wash pH lies between 8.5 to 8.7. After adding softener pH must lie between 6.5 to 6.8.

(4) **Chemical Industry** :-Before discharging the effluents of chemical plants in to the water sources the pH is maintained around 7.Because the acidic and alkaline wastes will cause water pollution, corrosion of bridges, structures, etc.

(5) **Sewage Treatment** :- In sewage treatment plants the pH of sludge is maintained about 7.3 to 7.56 for the growth organisms.

(6) **Water Treatment Plant** :- The pH of municipality water supplied remain between 7.2 and 8.0.Lower value may be corrosiveness while high values indicate certain psychological effect.

(7) **In Boilers** :- pH of high pressure boilers are maintained between 9.5 to 10.0 to avoid formation hard scale and caustic embrittlement.

ELECTROLYSIS

Electrolytes and Non-Electrolytes :-

An electrolyte is a substance which will conduct electricity in its aqueous solution or its fused state. So, electrolytes are the liquid conductors. (eg) NaCl solution, HCl, H₂SO₄, CuSO₄,AgNO₃,KCl, etc *Substances which do not allow electric current to flow through its aqueous solution, is called a non-electrolyte. (eg),sugar solution, urea, benzene, alcohol, etc.

Types of Electrolytes :-

Strong electrolytes :- Electrolytes which will undergo almost complete ionisation or dissociation in aqueous solution or which have high degree of ionisation, are called strong electrolytes. (eg) NaCl, NaOH, HCl, H₂SO₄, CuSO₄, KOH, etc.

Weak Electrolytes :-Electrolytes which will undergo slightly ionisation or dissociation in aqueous solution or which have very low degree of ionisation, are called weak electrolytes. (eg)CH₃COOH, H_2CO_3 , NH_4OH , Ca((OH)₂, etc.

Electrolysis :-

*The process of decomposition of an electrolyte in to its constituent ions by the passage of electric current through its aqueous solution or through its fused state, is called electrolysis.



(Electrolysis Process)

* The container or vessel in which electrolysis is carried out, is called a voltameter or electrolytic cell or electrolytic tank.

* During electrolysis the anions move towards anode, loose electron at there and become neutral and get deposit over anode or may undergo some secondary change at there. So, anodic reaction is the oxidation reaction.

*During electrolysis the cations move towards cathode, loose electron at there and become neutral and get deposit over cathode or may undergo some secondary change at there. So, cathodic reaction is the reduction reaction.

Electrolysis of Molten NaCl :-

During Electrolysis of molten NaCl , the electrolyte NaCl splits as Na^+ ion and Cl^- ion .

Now the Cl^- move towards the anode, loose electron at there and become neutral. These neutral atoms are unstable and combine with each other to form Cl_2 gas and liberated as such at the anode.

The Na⁺ ions move towards the cathode , gain electron at there and become neutral. These neutral Na atoms get deposited over the cathode as metallic sodium.

Thus, during the electrolysis of molten NaCl, metallic sodium deposited at cathode and chlorine gas liberated at anode.

Electrolysis of Aqueous NaCl / Brine solution :-



At Anode :- Both Cl⁻ and OH⁻ ions move towards anode. Since the discharge potential of Cl⁻ is less than OH⁻, then Cl⁻ ions are discharged at anode and liberate as Cl₂ gas at there.

 $CI^- - e^- \quad ---- \rightarrow \quad CI \quad (Primary change)$

Cl + Cl ------ $Cl_{2(g)} \uparrow$ (secondary change)

At Cathode :- Both H^+ and Na^+ ions move towards cathode. Since the discharge potential of H^+ ion is less than Na^+ ion, then H^+ ions will discharge easily at cathode and liberate as H_2 gas at there.

H^+	+	e ⁻	\longrightarrow	Н	(Primary change)
н	+	Н	>	$H_{2(g)} \uparrow$	(secondary change)

The remaining OH^- and Na^+ ions combine to form NaOH and remain in solution.

Thus, during electrolysis of aqueous NaCl or brine solution, chlorine gas liberated at anode and hydrogen gas liberated at cathode.

Applications of Electrolysis :-

The principle of electrolysis can be applied for (1) Electroplating, (2) electro typing (3) Electro-refining and (4)Electrolytic Reduction.

Electroplating :-

*Electroplating is process of coating one metal over another metal by using the principle of electrolysis. *Principle of electroplating can be applied for decoration, repairing and protection purposes. Superior metals like chromium, zinc, gold, silver, etc are deposited over baser metals to enhance their beauty. The electro-deposition of metals between broken parts help in repairing the broken machinery. Electroplating is made to avoid rusting as well as eating away of metals due to corrosion.

Process :-The article to be electroplated is used as the cathode. Metal to be deposited on the article is used as anode. The electrolyte is any soluble salt of the metal which is to form the outer surface of the baser metal. Electroplating is carried in a tank called electrolytic tank/cell which is made of cement or glass or fibre or wood.



* The electrolyte should be highly soluble, good conductor, cheap ,and should not undergo oxidation, reduction, hydrolysis, etc.

* When electric current passes through the electrolyte solution, the metal cations from electrolyte move towards cathode(article), gain electron at there and become neutral. These neutral atoms get deposited the article uniformly.

*Low current density, Low temperature and high metal concentration in electrolyte results best deposit. **Electro Refining** :-

* Electro refining is the process of obtaining the pure metal from its impure form by using the principle of electrolysis.



Here the impure metal (copper) is used as anode and a thin rod of this metal (pure form) is used as cathode. An electrolyte solution of this metal is taken in electrolytic cell.

When, current flows through the electrolyte, then metal cations from electrolyte move towards cathode (thin rod), gain electron at there and become neutral. These neutral atoms get deposit over cathode. The anions move towards anode react with metal atoms and form the electrolyte again.

When the process continues, then the weight of cathode gradually increase and the weight of anode will decrease. After some time the anode will disappear and some impurities will present below the anode which is called anode mud.

Electro Typing :-

*Electro- typing is the process used for reproduction of the works of art like wood carvings., printing plates, etc. by using the principle of electroplating. A large number of printing plates are obtained from the original type.

Chrome Plating :-

Chromium coatings are generally very thin and contain a number of pores which increases with increase in thickness of coating , the coating has a tendency to crack.

To avoid cracks owing to pores on chromium coatings, chrome plating is carried out. This is mostly carried out to protect metals from corrosion.

The electrolyte consists of chromic acid and chromic sulphate. The anode consists of lead and 8% antimony. The temperature of the electrolyte solution must be maintained at 40° C.

It produces a hard , corrosion resistant film with attractive appearance and brightness. It is used in auto mobile industry, sanitary fittings, etc.

Zinc Plating :-

Zinc plating is carried on surface of iron to protect the iron from corrosion (rusting). Here a coating of zinc metal is made over surface of iron. Zinc acts as a sacrificing metal. This process is also termed as galvanization.

For zinc plating, acid and alkaline solutions are used for deposition. The electrolyte consists of a solution of zinc sulphate(300gm), sodium chloride(15gm), aluminium sulphate(30gm), boric acid(20gm), and dextrin(15gm)in 1000ml of water.

The alkali solution consists of zinc oxide(40gm), sodium cyanide(100gm), sodium carbonate(10gm) in 1000 ml water.

The temperature is maintained at 30° C to 40° C.

Electro metallurgy :-.

* Electro-metallurgy is the process of obtaining more electropositive metal like Na, K, Ca, Mg, etc. from their ores by using the principle of electrolysis. This process is also called electrolytic reduction.

Faraday's Laws of Electrolysis :-

1st **Law** :- This law gives the relationship between the amount of substance deposited at electrodes and the quantity of current flowing through electrolyte solution.

Statement :- The law states that "the mass of substance deposited at the electrodes during electrolysis, is directly proportional to the quantity of electric current flowing through the electrolyte solution" Explanation :-

let, 'W' be the amount of substance deposited at electrode by passage of 'Q' quantity of current. As per statement, $W \alpha Q$

But, Q = Ct, Where C = the current strength in ampere and t = time of flow in seconds. Thus, $W \alpha Ct$

Or, **W** = **ZCt**, Where Z is the proportionality constant called Electro Chemical Equivalent.

When, C = 1 ampere and t = 1 second

Then, **W** = **Z**

Thus, electro chemical equivalent (**ECE**) of a substance can be define as the amount of substance deposited at electrode by the passage of 1 ampere current for 1 second through the electrolyte solution or by passage of 1 coulomb of electricity.

1 Coulomb = 1 ampere X 1 second

1 Faraday = 96500 coulombs

*1 Faraday is the quantity of charge carried by 1 mole (6.023 X 10 23) of electrons or it is the quantity of current which deposit 1 gm. Equivalent of substance at the electrode.

So, ECE = 1gm. Equivalent / 96500

2nd **Law** :- This law gives relationship between amount substance deposited and its equivalent mass. Statement :- When same quantity of current flows for same time through different electrolyte solutions connected in series, then the amount of substances deposited at electrodes are directly proportional to their chemical equivalents (equivalent masses).

Explanation :-

Consider electrolytes AgNO₃, CuSO₄ and H₂SO₄ connected in series.

Let, W_1 , W_2 , W_3 be the mass silver, mass Copper and mass of hydrogen deposited respectively If, E_1 , E_2 , and E_3 be the equivalent weight of silver, copper and hydrogen respectively, then As per statement $W_{Ag} \ \alpha \ E_{Ag}$, $W_{Cu} \ \alpha \ E_{Cu}$ and $W_H \ \alpha \ E_H$

Or,	weight of silver deposited	Equivalent weight of silver	(i.e)		$= E_1 / E_2$
	weight of copper deposited	equivalent weight of copper		$VV_1/VV_2 =$	
weight of hydrogen deposited		Equivalent hydrogen		\\/ / \\/ - E	- E /E
	weight of copper deposited	equivalent weight of copper	(1.0)	VV3/ VV2 ·	- E3/E2

But, W= ZCt, so, $W_1 = Z_1Ct$, $W_2 = Z_2Ct$, and $W_3 = Z_3Ct$

Thus, $E_1 / E_2 = Z_1 / Z_2$ and $E_3 / E_2 = Z_3 / Z_2$

CORROSION

*Corrosion may be defined as the process involving the conversion of a metal into an undesirable compound(usually oxide) on exposure to atmospheric conditions. It is also called weeping of metals.

*So, corrosion is the irreversible damage or destruction of metals due to a chemical or electrochemical reaction with the environment.

Types of Corrosion :-

Corrosion is generally of two types. (a) direct chemical corrosion / dry corrosion and (b) Electro chemical corrosion / wet corrosion.

***Dry or chemical corrosion** takes place when metal is surrounded by gases like, oxygen, Sulphur dioxide, halogens, hydrogen sulphide, nitrogen, etc. In the surrounding environment.

* **Wet corrosion** takes place when a conducting liquid is in contact with a metal or when two different metals or alloys are dipped in a solution.

The corrosion occurs due to the existence of separate anodic and cathodic parts.

At anodic area oxidation reaction takes place and hence metal near is destroyed by corrosion. No, corrosion occurs near cathodic area as reduction reaction occurs at here.

Atmospheric Corrosion / Rusting of Iron :-

*Decaying or deterioration of metal by chemical or electro chemical reaction with environmental agents is termed as atmospheric corrosion. (eg) rusting of iron, tarnishing of silver, development of green coating on copper, development of green coating on bronze, etc.

* In case of iron corrosion is termed rusting. The rust on iron is hydrated ferric oxide (Fe₂O₃.nH₂O). It is non sticking in nature and peels off exposing more of iron surface.

Commercial form of iron behaves like small electric cells in presence of water containing dissolved oxygen, CO_2 or SO_2 .

At Anode, metallic iron oxidises to Fe²⁺ ion.

 $2Fe \rightarrow 2Fe^{2+} + 4e^{-}$

At Cathode, these electrons combine with water to form hydroxyl ions. $H_2O + O + 2e^- \rightarrow 2OH^-$

The Fe²⁺ ions then diffuse under dissolved oxygen to form Fe³⁺ ions. $2Fe^{2+} + H_2O + O \rightarrow 2Fe^{3+} + 2OH^{-}$

Fe3+ and OH- combine to form hydrated ferric oxide(rust) $2Fe^{3+} + 6OH^- \rightarrow Fe_2O_3$. $3H_2O(rust)$

*Rusting of iron becomes more

(1) If water contains dissolved CO₂ gas.

(2) in saline water then ordinary water

- (3) water contains dissolved impurities.
- (4) water is acidic or pH of water is less than 7.
- (5) water contains metals like Cu and Zn

* Rusting of iron becomes slower

- (1) if iron is pure
- (2) water is alkaline
- (3) water contains metals like chromium and nickel.

Waterline Corrosion :-

It is that type of corrosion which is found along a line just below the level of water meniscus of water stored in a steel tank.

It is due to the difference in oxygen concentration above and below the level of water.



The area above the water level is termed as cathodic part as the concentration of oxygen is more at here. Similarly the area below the water level is termed as anodic part as the concentration of oxygen is less at here. The reactions involved during the corrosion are given as

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

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

$$2Fe(OH)_2 + \frac{1}{2}O_2 \rightarrow Fe_2O_3.2H_2O \text{ (rust)}$$

This type of corrosion mainly occurs in ships, water tanks, etc. It can be prevented to great extent by using specific paints at the surface of ships, water tanks, etc.

Methods to Protect Metal from Corrosion :-

(1) Alloying :-

*Alloying is a method to protect metal from corrosion. The loss of iron due to corrosion / rusting can be minimised by alloying it with chromium or nickel. An uniform / homogeneous alloy can attain maximum corrosion resistance. In many cases the oxide film of another metal formed on the surface of a metal increases the corrosion resistance. (eg) Durrion is a silica –iron alloy. The silicon oxide film on it is highly resistance to acids.

(2) Galvanisation /sacrificial Anode protection :-

*Galvanisation is the process of covering/ coating a layer of zinc over iron to protect iron from rusting. Zinc being more electropositive than iron and has less reduction potential than iron, then it looses electron easily than iron. So, zinc is consumed in the course of time than iron. Hence iron get protected from rusting. This process is also called sacrificial anode protection.

Tin can be used to protect copper but not iron. Because the oxidation potential of tin is more than copper but less than iron. Higher the value of oxidation potential(lower reduction potential) more is the tendency to loose electron. **(3)Anodising** :-

Sometimes metals are coated with thin layers of aluminium oxide to prevent them from corrosion, this process is called anodising.