Subject: Applied Chemistry

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Topic: WATER and ITS TREATEMENT

Unit No:
Lecture No:
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Introduction:

Like air water is one of the few basic materials which is of prime importance for the preservation of life on this earth. All are aware of the uses of water for drinking, cooking, bathing and farming etc., but few know the importance of water as an engineering material. For the existence of all living beings (humans, animals and plants) water is very crucial. Without water we cannot survive and almost all human activities–domestic, agricultural and industrial demand use of water. Although water is nature's most wonderful and abundant compound but only less than 1% of the world's water resources is available for the ready use. As engineering material water is used for producing steam in boilers to generate hydroelectric power, furnishing steam for engines, for refrigeration and air conditioning, for construction of concrete structures for manufacturing purposes and as a solvent in the chemical process.

SOURCES OF WATER:

The various sources of water are:

1. **Surface water** – It is any source of water body above the ground. It includes rivers, ponds, lakes, reservoirs etc.
2. **Underground water** – Ground water sources are beneath the land surface and include springs and wells.
3. **Rain water** – It is the purest form of water and the main source of water in tropical communities.
4. **Sea water** – Sea water contains number of salts like chlorides, carbonates, bicarbonates, sulfates of sodium, potassium, calcium, magnesium etc. It is neither suitable for drinking nor in industrial applications.

Types of Impurities present in water:

The natural water is usually contaminated by different types of impurities.

They are mainly three types.

- Physical impurities
- Chemical impurities
- Biological impurities

1. Physical impurities:

- They are the suspended solids that are not completely soluble in water and are present as particles. They impart visible turbidity to the water. Colour in water is caused by metallic substances like salts. Turbidity is due to the colloidal, extremely fine suspensions such as insoluble substances like clay, slit, and micro-organisms.
- *Taste:* presence of dissolved minerals in water produces taste. Bitter taste can be due to the presence of Fe, Al, Mn, Sulphates and lime. Soap taste can be due to the presence of large amount of sodium bicarbonate.

2. Chemical impurities:

- *Inorganic chemicals:* Cations (Al^{+3}, Ca^{+2}, Mg^{+2}, Fe^{+2}, Zn^{+2}, Cu^{+2}, Na^{+}, K^{+}), Anions (Cl^{-}, SO_4^{-2}, NO_3^{-}, HCO_3^{-}, F^{-}, NO_2^{-})
- *Organic chemicals:* dyes, paints, petroleum products, pesticides, detergents, drugs textile materials, other organic related materials.

3. Biological Impurities:

- Biological impurities are Algae, pathogenic bacteria, fungi, viruses, pathogens, parasite-worms.

4. Colloidal impurities:

- They are the very finely divided dispersion of particles in water. These particles are so small that these cannot be removed by ordinary filters and are not visible to the naked eye.

Hardness

Hardness of water is defined as the property which prevents the lathering of soap. This is due to presence of certain salts of Ca^{2+}, Mg^{2+} and other heavy metals dissolved in it. Soaps are sodium or potassium salts of higher fatty acids like oleic acid or palmitic acid or stearic acids ($C_{17}H_{35}COONa$). Hard water does not give lather with soap while soft water gives lather readily with soap.

Causes of Hardness: Soap with hard water reactions

When soap comes in contact with soft water lather is produced due to stearic acid.

$$\underset{\text{(Sodium stearate)}}{C_{17}H_{35}COONa} + H_2O \rightarrow \underset{\text{(Stearic acid)}}{C_{17}H_{35}COOH} + NaOH$$

When soap comes in contact with hard water, sodium stearate will react with dissolved calcium and magnesium salts and produce calcium stearate or magnesium stearate which is white precipitate. This insoluble white precipitate prevents lathering of soap.

$$\underset{\text{(Sodium stearate)}}{2C_{17}H_{35}COONa} + CaCl_2 \rightarrow \underset{\text{(insoluble scum)}}{(C_{17}H_{35}COO)_2Ca} + 2NaCl$$

$$\underset{\text{(Sodium stearate)}}{2C_{17}H_{35}COONa} + MgSO_4 \rightarrow \underset{\text{(insoluble scum)}}{(C_{17}H_{35}COO)_2Mg} + Na_2SO_4$$

Different types of water have different degrees of hardness. The different types of water are commercially classified on the basis of degree of hardness as follows:

Hardness	Name of water
0-70mg/liter	Soft water
70-150mg/liter	Moderate hard water
150-300mg/liter	Hard water
300mg/liter and above	Very hard water

Effects of Hard Water

(a) In domestic uses. For washing and bathing, hard water creates difficulties, since it does not form lather freely with soap. It also creates sticky precipitates that deposit on bath tub, body, clothes etc. until all the Ca/Mg salts get precipitated. Thus a lot of soap gets wasted also.

For cooking hard water creates similar difficulties by producing scum on the bottom of the vessels. Due to the presence of hardness producing salts in hard water, boiling point gets elevated and during cooking a lot of fuel is wasted. Pulses etc. do not cook in hard water. Taste of tea, coffee becomes unpleasant.

Drinking of hard water is also problematic since it affects the digestive system and at the same time the possibility of deposition of calcium oxalate crystals in the urinary tract is alarming.

(b) In industrial uses. For textile industry and dyeing industry, hard water causes the usual problem of deposition of insoluble salts that interfere with the proper dyeing and printing of the fabrics. The stains of iron salts also are undesirable on fabrics. Hard water also hampers the economy by wastage of soap as it does not form good lather.

- ❒ For sugar industry, the salts responsible for hardness create difficulties in sugar refining and crystallization of sugar and the sugar becomes deliquescent.
- ❒ Calcium and magnesium salts also interfere with the smooth and glossy finish of the papers in the paper industry. Iron salts interfere with the colour of the paper.
- ❒ In laundry, hard water causes wastage of costly soap and also interferes with the coloration due to the staining of iron salts.
- ❒ The hydration of cement and final hardening of cement are affected by use of hard water in concrete making.
- ❒ Hard water is not suitable for preparing drug solutions in pharmaceutical industry.
- ❒ For steam generation in boilers, hard water creates many problems like: (i) scale and sludge formation, (ii) corrosion, (iii) priming and foaming and (iv) caustic embrittlement.

Degree of hardness

The total hardness of water is caused by eight different dissolved salts of calcium and magnesium, [$Ca(HCO_3)_2$, $Mg(HCO_3)_2$, $CaCl_2$, $MgCl_2$, $CaSO_4$, $MgSO_4$, $Ca(NO_3)_2$ and $Mg(NO_3)_2$]. Hence the hardness of water is expressed in terms of calcium carbonate equivalents. The weight of different hardness salts causing hardness are converted to weight equivalent to that of calcium carbonate. $CaCO_3$ is selected for expression of hardness because the molecular weight of $CaCO_3$ is 100, which is easy for calculation and it is the most insoluble salt and all the dissolved salts of calcium are precipitated as $CaCO_3$.

Name of the salt	Molecular weight
$Ca(HCO_3)_2$	162
$Mg(HCO_3)_2$	146
$CaCl_2$	111
$MgCl_2$	95
$CaSO_4$	136
$MgSO_4$	120
$CaCO_3$	100

The method for calculating degree of hardness will be clear from the following formula: Hardness of water in terms of calcium carbonate equivalents = (Amount of hardness causing salts/ Molecular weight of hardness causing salts) × 100

Why $CaCO_3$ as reference for Hardness?

(1). $CaCO_3$ is stable, non-hygroscopic and is obtained in pure form. Therefore a standard hard water solution can be prepared by dissolving accurately weighed $CaCO_3$ in dilute HCl and make up to a known volume.

(2). $CaCO_3$ is insoluble in water. Therefore it can be easily precipitated in water treatments.

(3). Molecular weight of $CaCO_3$ is 100, so mathematical calculations are easy.

Expression of hardness – Units

1Parts Per Million: Parts of $CaCO_3$ equivalent hardness per 10^6 parts of water.

1 ppm = 1 part of $CaCO_3$ equivalent hardness present in 10^6 parts of water.

Milligram per liter: Number of milligrams of calcium carbonate equivalent hardness present in 1 liter of water.

1mg/L = 1 mg of $CaCO_3$ equivalent hardness present in 1 liter of water.

At 4^oC, 1 liter of water is equal to 1kg of water.

1L of water weight = 1Kg of water

1Kg = 1000gms

= 1000 x 1000 mg

1L = 10^6 mg

It becomes number of parts of $CaCO_3$ equivalent hardness causing salts in one million parts of water. Therefore 1mg/L is equal to 1ppm.

Degree Clark: (°Cl): It is the number of grains (1/7000 lb) of $CaCO_3$ equivalent hardness per 70,000 parts of water.

1Clark = 1 grain of $CaCO_3$ equivalent hardness per gallon of water.

= 1 part of $CaCO_3$ of hardness per 70,000 parts of water.

Degree French (°Fr): It is the parts of $CaCO_3$ equivalent hardness per 10^5 parts of water.

1^0French =1 part of $CaCO_3$ per 10^5 parts of hard water

Milliequivalents per litre: No of milliequivalents of hardness present per liter of water.

1m eq./L= 1 m eq. of $CaCO_3$ per / liter of water = 50 mg /L of $CaCO_3$eq. = 50ppm

Relation between various units of hardness:

1 ppm = 1mg/L = 0.1^0Fr = 0.07 ^{0}Cl = 0.02 m eq./L

Total hardness of the sample water= 121ppm = 121mg/L

121x0.07=8.47^oCl and 121x0.1=12.1^oFr

Permanent hardness= 101mg/l, 101ppm, 7.07^oCl, 10.1^oFr

Temporary hardness=20mg/l, 20ppm, 1.4^oCl and 2^0Fr

Types of Hardness

Hardness of water is mainly two types

1. Temporary Hardness
2. Permanent Hardness

1. Temporary Hardness:

It is caused mainly due to the presence of dissolved bicarbonates of calcium, magnesium and other heavy metals. The salts mainly responsible for temporary hardness of water are Calcium bicarbonate $Ca(HCO_3)_2$ and Magnesium bicarbonate $Mg(HCO_3)_2$.

When bicarbonates are decomposed, yielding insoluble carbonates or hydroxides, this gets deposited as a crust at the bottom of vessel. Temporary hardness can be largely removed by mere boiling of water. On boiling bicarbonates converts into corresponding carbonates which are insoluble. They can be removed by filtration.

$$Ca(HCO_3)_2 \rightarrow CaCO_3 + H_2O + CO_2$$

(Calcium bicarbonate)

$$Mg(HCO_3)_2 \rightarrow Mg(OH)_2 + 2CO_2$$

(Magnesium bicarbonate)

2. Permanent Hardness:

It is due to the presence of dissolved chlorides and sulphates of calcium, magnesium, iron and other metals. The salts responsible for permanent hardness are $CaCl_2$, $MgCl_2$, $CaSO_4$, $MgSO_4$, $FeSO_4$, $Al_2(SO_4)_3$. Permanent hardness cannot be removed by boiling but it can be removed by the use of chemical agents.

Total hardness of water =Temporary hardness + Permanent hardness

So, How to Remove the Permanent Hardness of Water?

We use certain chemical methods to remove the permanent hardness of water, which are:

1. Treating the Water with Washing Soda

In this method, we add washing soda, i.e., Na_2CO_3 to the hard water. It combines with chloride salts of calcium and magnesium present in the water to form compounds.

2. Calgon's Method

In this method, when Calgon, i.e Sodium Hexametaphosphate ($Na_6P_6O_{18}$) is added to the water, each of its molecules ionizes to give two Na^+ ions and one complex anion. This complex anion further releases Na^+ ions and captures all the Ca^{2+} or Mg^{2+} ions. These ions become a part of the complex anion. In this manner, water is freed from Ca^{2+} or Mg^{2+} ions. Now, it contains only Na+ ions only. Therefore, it no longer remains hard, i.e., becomes soft.

3. Ion-Exchange Method

In this method, we add a Permutit (a complex inorganic salt) called zeolite (Sodium Aluminum Silicate) or ($AlNa_{12}SiO_5$) to the water, which is insoluble in water. On adding this to water, the ion-exchange process starts between it and the Ca^{2+} or Mg^{2+} ions. In this way, water becomes free from Ca^{2+} or Mg^{2+} ions, and no longer remains hard.

4. Synthetic Resins Method

In this method, we use synthetic ion-exchange resins (RNa^+), which is insoluble in water. When it is added to water, an exchange between RNa^+ and Ca^{2+} or Mg^{2+} ions occurs. This process frees water from Ca^{2+} or Mg^{2+} ions. So, water no longer remains hard, and it becomes soft.

Estimation of temporary & permanent hardness of water

Estimation of Hardness of Water by EDTA method (Complexometric titration)

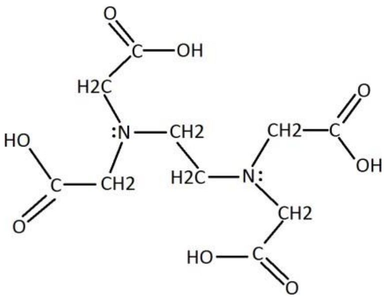
Hardness in water is due to the presence of dissolved salts of calcium and magnesium. It is unfit for drinking, bathing, washing and it also forms scales in boilers. Hence it is necessary to estimate the amount of hardness producing substances present in the water sample.

The estimation of hardness is based on complexometric titration. Hardness of water is determined by titrating with a standard solution of ethylene diamine tetra acetic acid (EDTA) which is a complexing agent. Ethylene Diamine Tetra Acetic acid (EDTA) is a reagent that forms EDTA-metal complexes with many metal ions. In alkaline conditions (pH>9) it forms stable complexes with the alkaline earth metal ions Ca^{2+} and Mg^{2+}. EDTA can combine with metal ion in 1:1 ratio to form a chelate structure.

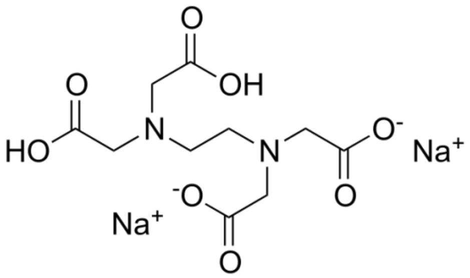
$$Ca^{2+} + H_2Y^{2-} \longrightarrow \underset{\text{colourless}}{CaY^{2-}} + 2H^+$$

$$Mg^{2+} + H_2Y^{2-} \longrightarrow \underset{\text{colourless}}{MgY^{2-}} + 2H^+$$

EDTA is Ethylene Diamine Tetra Acetic acid. The structure of EDTA is as shown below. Since, EDTA is insoluble in water; its disodium salt is used as a complexing agent.



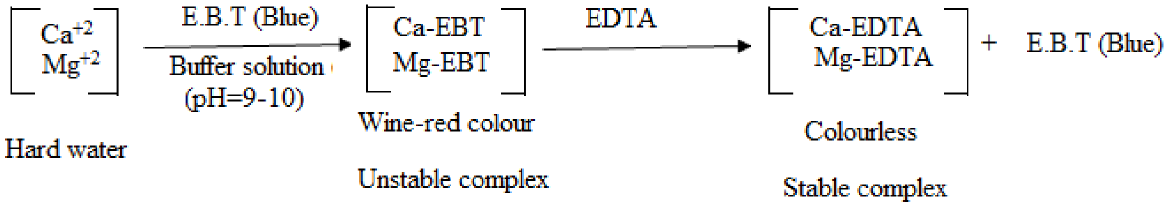
EDTA



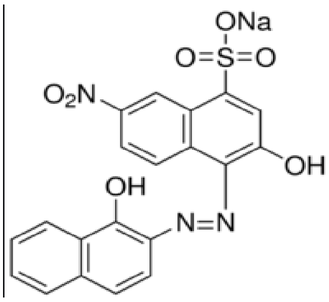
Disodium salt of EDTA

Basic Principle

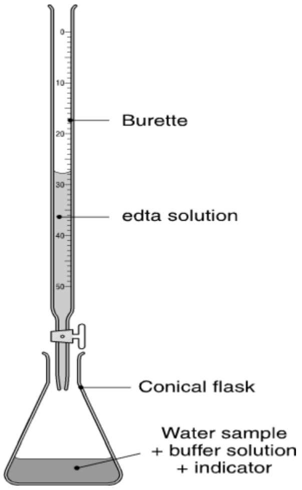
Total hardness is due to the presence of bicarbonates, chlorides and sulphates of calcium and magnesium ions. The total hardness of water is estimated by titrating the water sample against EDTA using Eriochrome Black-T (EBT) indicator. Initially EBT forms a weak EBT- Ca^{2+}/Mg^{2+} wine red coloured complex with Ca^{2+}/Mg^{2+} ions present in the hard water. On addition of EDTA solution, Ca^{2+}/Mg^{2+} ions preferably forms a stable EDTA-Ca^{2+}/Mg^{2+} complex with EDTA leaving the free EBT indicator in solution which is steel blue in color in the presence of ammonia buffer. Thus the end point is the change of color from wine red to blue.



Structure of EBT:



In EDTA methods, the known water sample is titrated against standard EDTA solution using EBT as indicator in the presence of basic buffer solution (NH_4OH-NH_4Cl; pH=10). At the end point the wine red color changes to blue.



#Role of Buffer NH_4Cl + NH_4OH: To maintain pH10. M-EDTA complex is more stable at pH 10. M-EBT complex formation is more favorable at pH10.

Experimental procedure:

1. Preparation of standard hard water: Dissolve 1.0g of $CaCO_3$ in minimum amount of dil. HCl and make up to 1000ml in a standard flask with distilled water.

$$\textbf{Molarity} = \frac{\textbf{wt. of } CaCO_3}{\textbf{Mol. wt. of } CaCO_3} = \frac{1}{100} = 0.01M$$

2. Standardization of EDTA: Add 4g of disodium salt of EDTA to 1L of distilled water. Fill the 50ml burette with the EDTA solution.

Pipette out 20ml of standard hard water into a conical flask. To it add 2ml NH_4Cl-NH_4OH buffer, 4 drops of EBT. Upon adding EBT the water turns into wine red color. The wine red color is due to the formation of the Ca-EBT complex. Upon titration with the EDTA the water color changes from wine red to blue color.

Let the volume of EDTA consumed by standard hard water be ‘a’ ml. Repeat the titration to get concurrent values.

Molarity of Hard water: $M_1V_1 = M_2V_2$

M_1 = Molarity of Std hard water = 0.01M
V_1 = Volume of Std hard water = 20mL
M_2 = Molarity of EDTA solution =?
V_2 = Volume of EDTA solution - Burette reading = a mL

$$M_2 = \frac{M_1V_1}{V_2} = \frac{0.01M \times 20mL}{a\ mL} = M_2$$

3. Estimation of total hardness of water: Pipette out 20 ml of sample water into a conical flask. To it add 2ml of NH_4Cl-NH_4OH buffer solution and 4 drops of EBT. Titrate with EDTA solution till the wine red color of the solution changes to blue.

Let the volume of EDTA consumed by sample water be ‘b’ ml. Repeat the titration for concurrent values.

Molarity of Hard water: $M_2V_2 = M_3V_3$

M_2 = Molarity of EDTA solution (from step 2)
V_2 = Volume of EDTA solution - Burette reading = b mL
M_3 = Molarity of Std hard water = ?
V_3 = Volume of Std hard water = 20mL

$$M_3 = \frac{M_2V_2}{V_3} = \frac{M_2 \times b\ mL}{20\ mL} = x\ moles$$

Total hardness of Water = ‘x’moles x 10^5 (to convert into ppm)
= ‘x’moles x 100 x 1000 = x ppm

4. Estimation of permanent hardness of water: Boil 100 ml of water in a beaker till it reduces to 20 ml. (Boiling remove temporary hardness). Cool & filter into a 100 ml standard flask .Wash the precipitate with distilled water. Pipette out 20 ml of the water sample into a comical flask and add 2ml of buffer solution, 4 drops of EBT. Titrate with EDTA until wine red solution changes to blue color.

Let the volume of EDTA consumed with boiled water be ‘c’ ml. Repeat the titration for concurrent values.

Permanent Hardness: $M_2V_2=M_4V_4$

M_2 = Molarity of EDTA solution (from step 2)
V_2 = Volume of EDTA solution - Burette reading = c mL
M_4 = Molarity of Std hard water = ?
V_4 = Volume of Std hard water = 20mL

$$M_4 = \frac{M_2V_2}{V_4} = \frac{M_2 \times c\ mL}{20\ mL} = y\ moles$$

Permanent hardness of Water = ‘y’ moles x 10^5 (to convert into ppm)

= ‘y’ moles x 100 x 1000 = y ppm

Temporary hardness = Total hardness – Permanent hardness

= (M_3 X 100 X 1000) – (M_4 X 100 X 1000) ppm

Numerical Problems:

Problem-1: *A sample of water is found to contains following dissolving salts in milligrams per liter* $Mg(HCO_3)_2 = 73$, $CaCl_2 = 111$, $Ca(HCO_3)_2 = 81$, $MgSO_4 = 40$ *and* $MgCl_2 = 95$. *Calculate temporary and permanent hardness and total hardness.*

Solution:

Name of the hardness causing salts	Amount of the hardness causing salts(mg/Lit)	Molecular weight of hardness causing salts	Amounts equivalent to $CaCO_3$ (mg/Lit)
$Mg(HCO_3)_2$	73	146	73×100/146 = 50
$CaCl_2$	111	111	111×100/111 = 100
$Ca(HCO_3)_2$	81	162	81×100/162 = 50
$MgSO_4$	40	120	40×100/120 = 33.3
$MgCl_2$	95	95	95×100/95 = 100

Temporary hardness = $Mg(HCO_3)_2 + Ca(HCO_3)_2$ = 50 + 50 = 100 mgs/Lit.

Permanent hardness = $CaCl_2 + MgSO_4 + MgCl_2$ = 100 + 33.3 + 100 = 233.3 mgs/Lit.

Total hardness = Temporary hardness + Permanent hardness = 100 + 233.3 = 333.3 mgs/Lit.

Problem-2: *A sample of water is found to contains following dissolving salts in milligrams per litre* $Mg(HCO_3)_2 = 16.8$, $MgCl_2 = 12.0$, $MgSO_4 = 29.6$ *and* $NaCl = 5.0$. *Calculate temporary and permanent hardness of water.*

Solution:

Name of the hardness causing salts	Amount of the hardness causing salts(mg/Lit)	Molecular weight of hardness causing salts	Amounts equivalent to CaCO3 (mg/Lit)
$Mg(HCO_3)_2$	16.8	146	16.8×100/146 = 11.50
$MgCl_2$	12.0	95	12.0×100/95 = 12.63
$MgSO_4$	29.6	120	29.6×100/120 = 24.66
NaCl	5.0	NaCl does not contribute any hardness to water hence it is ignored.	

Temporary hardness = $Mg(HCO_3)_2$ = 11.50mgs/Lit.

Permanent hardness = $MgCl_2 + MgSO_4$ = 12.63 + 24.66 = 37.29mgs/Lit.

Problem-3: *A sample of water is found to contains following analytical data in milligrams per litre* $Mg(HCO_3)_2 = 14.6$, $MgCl_2 = 9.5$, $MgSO_4 = 6.0$ *and* $Ca(HCO_3)_2 = 16.2$. *Calculate temporary and permanent hardness of water in parts per million, Degree Clarke's and Degree French.*

Solution:

Name of the hardness causing salts	Amount of the hardness causing salts(mg/Lit)	Molecular weight of hardness causing salts	Amounts equivalent to $CaCO_3$ (mg/Lit)
$Mg(HCO_3)_2$	14.6	146	14.6×100/146 = 10
$MgCl_2$	9.5	95	9.5×100/95 = 10
$MgSO_4$	6.0	120	6.0×100/120 = 5
$Ca(HCO_3)_2$	16.2	162	16.2×100/162 =10

Temporary hardness [Mg $(HCO_3)_2$ + Ca $(HCO_3)_2$] = 10 + 10 = 20mg/Lit = 20ppm

= 20×0.07°Cl = 1.4°Cl

= 20×0.1°Fr = 2°Fr

Permanent hardness [$MgCl_2$ + $MgSO_4$] = 10 + 5 = 15mg/Lit = 15 ppm

= 15×0.07°Cl = 1.05°Cl

= 15×0.1°Fr = 1.5°Fr

Problem-4: *Calculate the amount of temporary and permanent hardness of a water sample in Degree Clarke's, Degree French and Milligrams per Litre which contains following impurities.* $Ca(HCO_3)_2$ *= 121.5 ppm,* $Mg(HCO_3)_2$*= 116.8 ppm,* $MgCl_2$ *= 79.6 ppm and* $CaSO_4$ *= 102 ppm.*

Solution:

Name of the hardness causing salts	Amount of the hardness causing salts(ppm)	Molecular weight of hardness causing salts	Amounts equivalent to $CaCO_3$ (ppm)
$Ca(HCO_3)_2$	121.5	162	121.5×100/162 = 75
$Mg(HCO_3)_2$	116.8	146	116.8×100/146 = 80
$MgCl_2$	79.6	95	79.6×100/95 = 3.37
$CaSO_4$	102	136	102×100/136 = 75

Temporary hardness [$Mg(HCO_3)_2$ + $Ca(HCO_3)_2$] = 75 + 80 = 155 ppm

= 155×0.07°Cl = 10.85°Cl

= 155×0.1°Fr = 15.5°Fr

= 155×1mg/Lit = 155 mg/Lit

Permanent hardness [$MgCl_2$ + $CaSO_4$] = 10 + 5 = 15mg/Lit = 15ppm

= 15×0.07°Cl = 1.05°Cl

= 15×0.1°Fr = 1.5°Fr

Problem-5: *In a hardness estimation by EDTA method 50 ml of a sample water required 30 ml of std EDTA solution. Calculate hardness of sample water? Given that 1ml of EDTA solution is equivalent to 1.8 mg of* $CaCO_3$ *(Here you are provided with a standardized EDTA).*

Solution: 1 ml of EDTA solution is equivalent to 1.8 mg of $CaCO_3$

Hardness estimation

50 ml sample water consumed 30 ml of EDTA

I.e. 50 ml sample water = 30 x 1.8 mg of $CaCO_3$.

Then, 1 ml of sample water = $\frac{30 \text{ x } 1.8}{50}$ mg of $CaCO_3$.

Therefore 1000 ml sample water = $\frac{30 \text{ x } 1.8}{50} \times 1000$ mg = 1080 mg of $CaCO_3$

Then hardness = 1080 ppm.

Problem-6: *50 ml of standard hard water containing 1mg of* $CaCO_3$*/L consumed 20 ml of EDTA. 50 ml of sample water consumed 25 ml of EDTA. Calculate the total hardness. (Here you are provided with standard hard water solution, you have to standardize EDTA then find out the total hardness).*

Solution: Standard Hard water 1mg of $CaCO_3$ per litre

That means 1000 ml Std. Hard water contains 1mg of $CaCO_3$

Then 1 ml Std. Hard water contains 1/1000 mg = 0.001 mg of $CaCO_3$

<u>Standardization of EDTA</u>

20 ml of EDTA for 50 ml standard hard water

I.e. 20 ml of EDTA = 50 ml X 0.001 mg/ml of $CaCO_3$

Then, 1 ml EDTA $= \frac{50 \times 0.001}{20} = 0.0025$ mg of $CaCO_3$.

<u>Estimation of total hardness</u>

50 ml sample water consumed 25 ml of EDTA

I.e. 50 ml sample water = 25 x 0.0025 mg of $CaCO_3$.

Then, 1 ml of sample water $= \frac{25 \times 0.0025}{50}$ mg of $CaCO_3$.

Therefore 1000 ml sample water $= \frac{25 \times 0.0025}{50} \times 1000 = 1.25$ mg of $CaCO_3$

Then hardness = 1.25 ppm.

<u>Problem-7:</u> 50 ml of standard hard water containing 1mg of CaCO3/ml consumed 20 ml of EDTA. 50ml of sample water consumed 25 ml of EDTA. Calculate the total hardness. *Here you are provided with standard hard water solution, you have to standardize EDTA then find out the total hardness.*

<u>Solution:</u> Standard Hard water: 1mg of $CaCO_3$ per ml

That means 1ml Std Hard water contains 1mg of CaCO3

<u>Standardization of EDTA</u>

20 ml of EDTA for 50 ml standard hard water

I.e. 20 ml of EDTA = 50 ml X 1 mg/ml of $CaCO_3$

Then, 1 ml EDTA $= \frac{50 \times 1}{20} = 2.5$ mg of $CaCO_3$.

<u>Estimation of total hardness</u>

50 ml sample water consumed 25 ml of EDTA

I.e. 50 ml sample water = 25 x 2.5 mg of $CaCO_3$.

Then, 1 ml of sample water $= \frac{25 \times 2.5}{50}$ mg of $CaCO_3$.

Therefore 1000 ml sample water $= \frac{25 \times 2.5}{50} \times 1000 = 1250$ mg of $CaCO_3$

Then hardness = 1250 ppm.

<u>Problem-8:</u> *Calculate the hardness of 0.01 M $AlCl_3$ solution.*

<u>Solution:</u> Hardness (in ppm) = Molarity x Valency of Hardness causing salt x 50000 ppm

= Normality x 50000 ppm (Al^{3+})

Hardness (in ppm) = 0.01 M x 3 x 50000 = 1500 ppm

<u>Problem-9:</u> *Calculate the hardness of 0.01 N $AlCl_3$ solutions.*

<u>Solution:</u> Hardness (in ppm) = Normality x 50000 ppm (Al^{3+})

Hardness (in ppm) = 0.01 N x 50000 = 500 ppm

Problem-10: Calculate the hardness of 0.01 M $CaCO_3$ solution.

Solution: Hardness (in ppm) = Molarity x Valency of Hardness causing salt x 50000 ppm

Hardness (in ppm) = 0.01 M x 2 x 50000 = 1000 ppm

Problem-11: The hardness of a solution is 1000 ppm. Calculate the molarity solution.

Solution: Hardness (in ppm) = Molarity x Valency of Hardness causing salt x 50000 ppm

= Normality x 50000 ppm (Take standard $Ca^{2+}CO_3^{2-}$ valence)

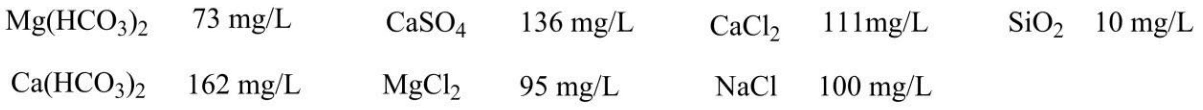
Molarity $= \frac{\text{Hardness in ppm}}{Valancy*50000} = \frac{1000}{2*50000}$ = 0.01 M

Problem-12: Calculate the hardness of 0.01 M $Al_2(SO_4)_3$ solution.

Solution: Hardness (in ppm) = Molarity x Valency of Hardness causing salt (Al^{3+}) x 50000 ppm

Hardness (in ppm) = 0.01 M x 3 x 50000 = 1500 ppm

Problem-13: Calculate the temporary and permanent hardness of water sample having the following analysis.



$Mg(HCO_3)_2$	73 mg/L	$CaSO_4$	136 mg/L	$CaCl_2$	111mg/L	SiO_2	10 mg/L
$Ca(HCO_3)_2$	162 mg/L	$MgCl_2$	95 mg/L	NaCl	100 mg/L		

Solution: Temporary hardness = $Mg(HCO_3)_2 + Ca(HCO_3)_2$

Permanent hardness = $CaSO_4 + MgCl_2 + CaCl_2$

Hardness (in $CaCO_3$ equivalents)

= $\sum$ mass of hardness producing substance × $\frac{MW\ \ of\ \ CaCO3/valancy}{MW\ of\ Hardness\ producing\ subatance/valancy}$

Total hardness (due to $Mg(HCO_3)_2$ = 73 mg/L, $Ca(HCO_3)_2$ = 162 mg/L, $CaSO_4$ = 136 mg/L, $MgCl_2$ = 95 mg/L, $CaCl_2$ = 111 mg/L)

Total Hardness (in CaCO3 equivalents)

$= 73\times\frac{100/2}{146/2} + 162\times\frac{100/2}{162/2} + 136\times\frac{100/2}{136/2} + 95\times\frac{100/2}{95/2} + 111\times\frac{100/2}{111/2}$

= 50 + 100 + 100 + 100 + 100 = 450 ppm

Temporary hardness (due to $Mg(HCO_3)_2$ = 73 mg/L, $Ca(HCO_3)_2$ = 162 mg/L)

$= 73\times\frac{100/2}{146/2} + 162\times\frac{100/2}{162/2}$ = 50 + 100 = 150 ppm

Permanent hardness = Total – temporary hardness = 450–150 = 300 ppm.

Problem-14: Calculate the hardness of given sample of water, if 50 ml of sample water gives endpoint with 20 ml of EDTA solution. 20 ml of standard hard water of concentration 0.02 M gives end point with 25 ml of EDTA solution.

Molarity of Standard hard water solution M_1 = 0.02 M

Solution:

Standardization (Finding the concentration of EDTA solution using standard hard water)

V_1 = 20 ml V_2 = 25 ml

Standard Hard water (pH 10) Vs EDTA (EBT indicator wine red to blue)

(M_1 = 0.02 M) (M_2)

$M_1V_1 = M_2V_2$

Then molarity of EDTA: $M_2 = (M_1V_1)/V_2$ = (0.02 x 20)/(25) = 0.016 M

Estimation of hardness

V3= 50 ml   V4 = 20 ml

Sample water (pH 10) vs EDTA (EBT indicator wine red to blue)

(M_3) $(M_4= M_2)$

Molarity of sample water M3? Now, $M_3V_3 = M_4V_4$

Then, $M_3 = (M_4V_4)/V_3$ = (0.016 x 20)/(50) = 0.0064 M

Hardness in ppm is Molarity x 100000 ppm = 0.0064 x 100000 = 640 ppm

Problem-15: 100 ml sample water required 13.5 ml of 0.02 N EDTA solutions for hardness estimation. 100 ml sample water was boiled and removed the precipitate by filtration. This filtrate required 6 ml of EDTA. Calculate temporary hardness

Solution:

Estimation of hardness

V3 = 100 ml; V4 = 13.5 ml

Sample water (pH 10) vs. EDTA (EBT indicator wine red to blue)

(N_3) $(N_4= 0.02$ N)

Normality of sample water N_3? $N_3V_3 = N_4V_4$

Then, $N_3 = (N_4V_4)/V_3$ = (0.02 x 13.5)/(100) = 0.0027 N

Hardness in ppm = Normality x 50000 ppm = 0.0027 x 50000 = 135 ppm

Estimation of permanent hardness

V_5 = 100 ml V_6 = 13.5 ml

Sample water (pH 10) vs EDTA (EBT indicator wine red to blue)

(N_5) $(N_6= 0.02$ N)

Normality of sample water after boiling N_5? $N_5V_5 = N_6V_6$

Then, $N_5 = (N_6V_6)/V_5$ = (0.02 x 6)/(100) = 0.0012 N

Permanent Hardness in ppm is Normality x 50000 ppm = 0.0012 x 50000 = 60 ppm

Temp. Hardness = total – perm = 135-60 = 75 ppm.

Softening of water by Ion exchange resin process or deionization process or demineralization process

- The process of complete removal of all ions present in water is known as demineralization process
- The process is done by using ion exchange resin process.
- These resins are highly insoluble cross linked organic polymers with porous structure.
- They contain functional groups attached to the polymeric chains are responsible for ion exchange property.
- The functional groups used are either acidic or basic in nature.
- Depending on functional groups Ion exchange resins are classified into two types.

1. Cation Exchange Resins

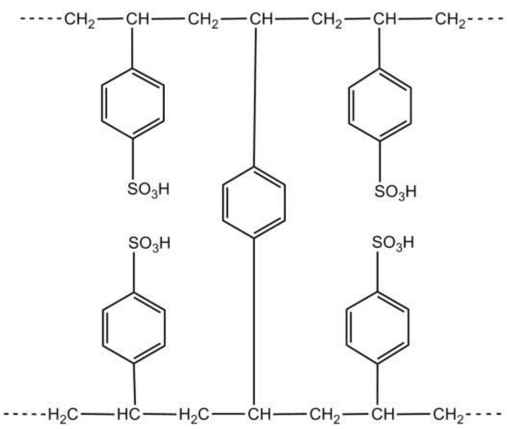
2. Anion Exchange Resins

1. Cation Exchange Resins:

- These are mainly poly-styrene polymers which contain acidic functional groups (like –COOH or –SO_3H).
- The acidic functional group is capable of exchanging its H^+ ions with cations present in water.

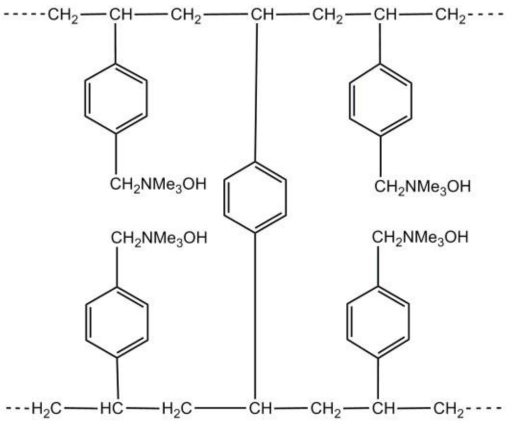
$2RH + Ca^{2+}$ ------------> $R_2Ca + 2H^+$
Acidic resin

$2RH + Mg^{2+}$ ----------> $R_2Mg + 2H^+$
Acidic resin



Anion Exchange Resins:

- These are mainly poly-styrene polymers which contain basic functional groups (like –CH2-NMe_3OH).
- The basic functional group is capable of exchanging its OH^- ions with anions present in water.



$$R'OH + Cl^- \text{----------}> R'Cl + OH^-$$

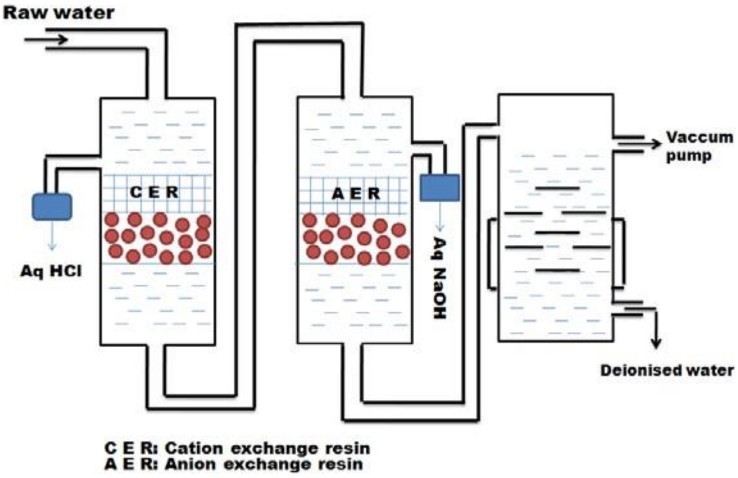
$$2R'OH + SO_4^{2-} \text{----------}> R'_2SO_4 + 2\ OH^-$$

Basic resin

Process:

Step1: The hard water is passed through a cylindrical tank packed with cation exchange resin bed. The cation exchange removes cations like Ca^{2+} and Mg^{2+} etc from water and equivalent amount of H^+ ions are released from resin to water.

Step2: The hard water is then passed through another column packed with anion exchange resin. It removes all hardness causing anions like $SO4^{2-}$, Cl^- and HCO_3^- from water and equivalent amount of OH^- ions are released from resin to water.



Regeneration

When cation exchanger losses capacity of producing H^+ ions and anion exchanger losses capacity of producing OH^- ions, they are said to be exhausted. The exhausted cation exchanger is regenerated by passing it through dilute sulphuric acid.

$$R_2Ca^{+2} + 2H^+ \rightarrow 2RH^+ + Ca^{+2}$$

The exhausted anion exchanger is regenerated by passing a dilute solution of NaOH.

$$R_2SO_4^{-2} + 2OH^- \rightarrow 2ROH^- + SO_4^{-2}$$

Merits of Ion-exchange process

1. This process can be used to soften highly acidic or alkaline water.

2. It produces water of very low hardness (2ppm). So it is very good for treating water for use in high-pressure boilers.

3. The operational expenses are less because the resins can be regenerated.

Demerits of Ion-exchange process

1. The equipment is costly and more expensive chemicals are needed.

2. If water contains turbidity, the output of the process is reduced. The turbidity must be below 10 ppm; else it has to be removed by coagulation and filtration.

POTABLE WATER

The water which is used for drinking is called potable water.

Specification of potable water/drinking water

1. It should be sparkling clear and odorless.

2. It should be pleasant in taste.

3. It should be perfectly cool.

4. Its turbidity should not exceed 10ppm.

5. It should be free from objectionable dissolved gases like hydrogen sulphide.

6. It should be free from minerals such as lead, arsenic, chromium and manganese salts.

7. Its alkalinity should not be high.

8. Its pH should be about 8.0.

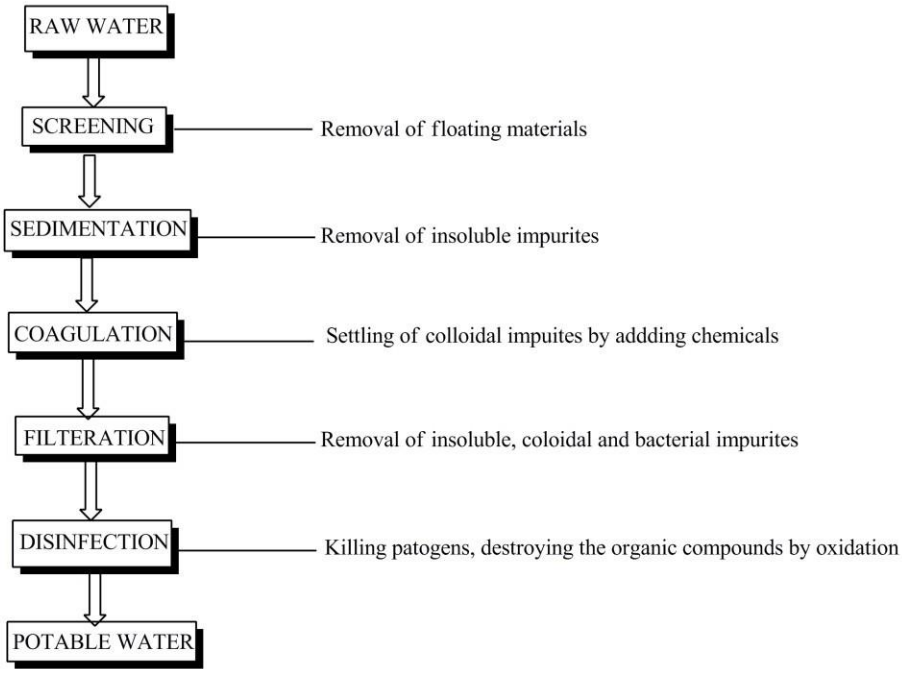
9. It should be reasonably soft.

10. Its total dissolved solids should be less than 500 ppm.

11. It should be free from disease-producing micro-organisms.

12. Chloride, fluoride and sulphide contents should be less than 250ppm, 1.5ppm and 250ppm, respectively.

Steps involved in treatment of potable water



1. Screening

To protect the main units of a treatment plant and to aid in their efficient operation, it is necessary to use screens to remove any large floating and suspended solids that are present in the inflow. These materials include leaves, twigs, paper, rags and other debris that could obstruct flow through the plant or damage equipment. There are coarse and fine screens.

Coarse screens are steel bars spaced 5–15 cm apart, which are employed to exclude large materials (such as logs and fish) from entering the treatment plant, as these can damage the mechanical equipment. The screens are made of corrosion-resistant bars and positioned at an angle of 60º to facilitate removal of the collected material by mechanical raking.

Fine screens, which come after the coarse screens, keep out material that can block pipework at the plant. They consist of steel bars which are spaced 5–20 mm apart. A variation of the fine screen is the microstrainer which consists of a rotating drum of stainless steel mesh with a very small mesh size (ranging from 15 μm to 64 μm, i.e. 15–64 millionths of a metre). Suspended matter as small as algae and plankton (microscopic organisms that float with the current in water) can be trapped. The trapped solids are dislodged from the fabric by high-pressure water jets using clean water, and carried away for disposal.

2. Aeration

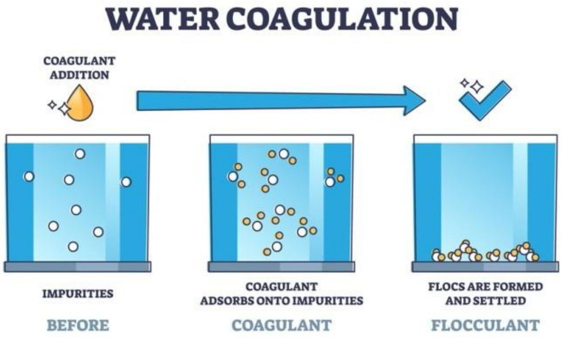
After screening, the water is aerated (supplied with air) by passing it over a series of steps so that it takes in oxygen from the air. This helps expel soluble gases such as carbon dioxide and hydrogen sulphide (both of which are acidic, so this process makes the water less corrosive) and also expels any gaseous organic compounds that might give an undesirable taste to the water. Aeration also removes iron or manganese by oxidation of these substances to their insoluble form. Iron and manganese can cause peculiar tastes and can stain clothing. Once in their insoluble forms, these substances can be removed by filtration.

In certain instances excess algae in the raw water can result in algal growth blocking the sand filter further down the treatment process. In such situations, chlorination is used in place of, or in addition to, aeration to kill the algae, and this is termed pre-chlorination. This comes before the main stages inthe treatment of the water. (There is a chlorination step at the end of the treatment process, which is normal in most water treatment plants). The pre-chlorination also oxidises taste- and odour-causing compounds.

3. Coagulation and flocculation

After aeration, coagulation takes place, to remove the fine particles (less than 1 μm in size) that are suspended in the water. In this process, a chemical called a coagulant (with a positive electrical charge) is added to the water, and this neutralises the negative electrical charge of the fine particles. The addition of the coagulant takes place in a rapid mix tank where the coagulant is rapidly dispersed by a high-speed impeller.

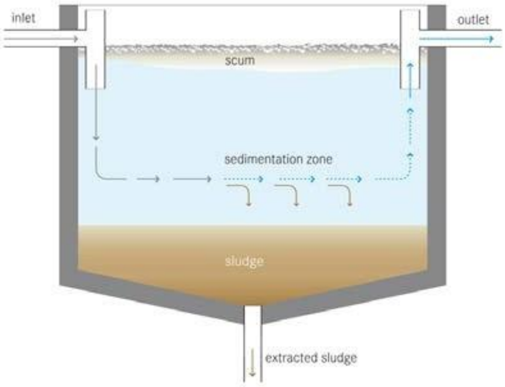
Since their charges are now neutralised, the fine particles come together, forming soft, fluffy particles called ‘flocs’. (Before the coagulation stage, the particles all have a similar electrical charge and repel each other, rather like the north or south poles of two magnets.) Two coagulants commonly used in the treatment of water are aluminium sulphate and ferric chloride.



The next step is flocculation. Here the water is gently stirred by paddles in a flocculation basin and the flocs come into contact with each other to form larger flocs. The flocculation basin often has a number of compartments with decreasing mixing speeds as the water advances through the basin. This compartmentalized chamber allows increasingly large flocs to form without being broken apart by the mixing blades. Chemicals called flocculants can be added to enhance the process. Organic polymers called polyelectrolytes can be used as flocculants.

4. Sedimentation

Once large flocs are formed, they need to be settled out, and this takes place in a process called sedimentation (when the particles fall to the floor of a settling tank). The water (after coagulation and flocculation) is kept in the tank for several hours for sedimentation to take place. The material accumulated at the bottom of the tank is called sludge; this is removed for disposal.



5. Filtration

Filtration is the process where solids are separated from a liquid. In water treatment, the solids that are not separated out in the sedimentation tank are removed by passing the water through beds ofsand and gravel. Rapid gravity filters, with a flow rate of 4–8 cubic metres per square metre of filter surface per hour (this is written as 4–8 m–3 m–2 h–1) are often used.

When the filters are full of trapped solids, they are backwashed. In this process, clean water and air are pumped backwards up the filter to dislodge the trapped impurities, and the water carrying the dirt (referred to as backwash) is pumped into the sewerage system, if there is one. Alternatively, it may be discharged back into the source river after a settlement stage in a sedimentation tank to remove solids.

6. Sterilization of surface water/Removal of micro-organisms in water (Disinfection):

The process of destroying/killing the disease producing Bacteria, microorganisms, etc. from the water and making it safe for use, is called disinfection.

Disinfectants:

The chemicals or substances which are added to water for killing the bacteria are called disinfectants. The chemicals used in this process are called Disinfectants.

It is done by following methods:

1. Boiling: By boiling water for 10-15 minutes, all the disease producing bacteria is killed and the water becomes safe for use.

2. By adding Bleaching powder: 1 kg of bleaching powder is added to 1000 kiloliters of water and left undisturbed for several hours that produces hypochlorous acid (powerful germicide).

$CaOCl_2 + H_2O \rightarrow Ca(OH)_2 + Cl_2$

$Cl_2 + H_2O \rightarrow HCl + HOCl$ (Hypochlorous acid)

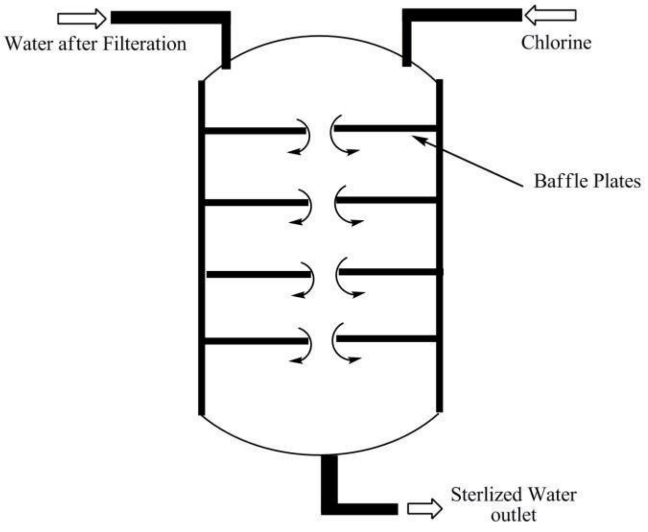
Germs+ $HOCl \rightarrow$ Germs are killed

3. By using Chlorine:

Chlorination is the process of purifying the drinking water by producing a powerful germicide like hypochlorous acid. When this chlorine is mixed with water it produces hypochlorous acid which kills the germs present in water.

$$H_2O + Cl_2 \rightarrow HOCl + HCl$$

Chlorine is basic (means pH value is more than 7) disinfectant and is much effective over the germs. Hence chlorine is widely used all over the world as a powerful disinfectant. Chlorinator is an apparatus, which is used to purify the water by chlorination process.



Chlorinator Apparatus

Advantages

(1). Effective and economic

(2). It leaves no salt impurities

(3). Chlorine is available in pure form

(4). It requires little space for storage.

Disadvantages:

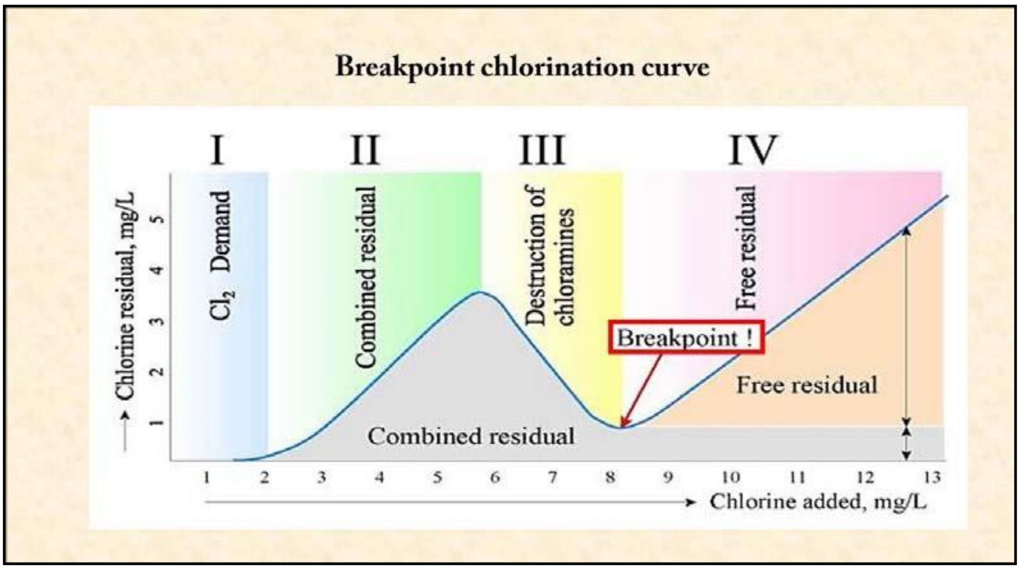
(1). Bad taste and unpleasant odour.

(2). Irritation on mucous membrane if used in excess.

(3). Ineffective at high pH value.

Break-Point of Chlorination:

- By chlorination, organic matter and disease producing bacteria are completely eliminated which are responsible for bad taste and bad odour in water.
- Calculated amount of chlorine must be added to water because chlorine after reacting with bacteria and organic impurities or ammonia, remains in water as residual chlorine which gives bad taste, odour and toxic to human beings.
- When certain amount of chlorine is added to the water, it leads to the formation of chloro-organic compounds and chloramines.
- The point at which free residual chlorine begins to appear is known as "Break-Point"
- The amount of chlorine required to kill bacteria and to remove organic matter is called break point chlorination.
- Break point determines whether chlorine is further added or not.



- From the graph, it is clear that :
- In phase I, 'a' gm of chlorine added oxidizes reducing impurities of water.
- In phase II, 'b' gm of chlorine added forms chloramines with nitrogen compounds present in the water.

$$H_2O + Cl_2 \longrightarrow HOCl \text{ (Hypochlorous acid)}$$

$$HOCl + NH_3 \longrightarrow NH_2Cl + H_2O \text{ (Monochloramine)}$$

$$HOCl + NH_2Cl \longrightarrow NHCl_2 + H_2O \text{ (Dichloroamine)}$$

$$HOCl + NHCl_2 \longrightarrow NCl_3 + H_2O \text{ (Trichloroamine)}$$

- The chlorine at this phase is present as the combined chlorine.
- In phase III, 'c' gm of chlorine added causes destruction of chloramines. The trichloroamine on addition of chlorine is eliminated as Nitrogen gas.
- The concentration of the chlorine at this point dips. The addition of chlorine to water at the dip or

break is called break point chlorination.

- The remaining ‘d’ gm of chlorine added is seen as residual Chlorine. At this point, the chlorine acts as a disinfectant and kills the micro organisms.

Advantages:

- Complete destruction of pathogens.
- Complete oxidation of organic compounds, ammonia and other reducing impurities.
- Prevents weed growth.
- Prevents growth of microbes.

4. By Chloramines: When chlorine and ammonia are mixed in the ratio of 2:1 by volume, chloramine is formed.

$$Cl_2 + NH_3 \rightarrow ClNH_2 + HCl$$

$$ClNH_2 + H_2O \rightarrow HOCl + NH_3$$

Hypochlorous acid, which is formed by the dissolution of chloramines in water, reacts with micro-organisms and inactivates the enzymes present in it so that the micro-organisms are destroyed.

Dechlorination:

If excess of chlorine is added then it can be dechlorinated by passing it through activated carbon or by adding SO_2 / Na_2SO_3.

$$SO_2 + Cl_2 + H_2O \rightarrow H_2SO_4 + 2HCl$$

$$Na_2SO_3 + Cl_2 + H_2O \rightarrow Na_2SO_4 + 2HCl$$

Factors affecting efficiency of chlorine:

- Efficiency increases with rise of temperature.
- Initially, micro-organisms death rate is maximum with time and then keeps on decreasing.
- Kills micro organisms.

UV Light

- 254nm UV light damages the RNA & DNA in bacteria.
- Also destroys chemical contaminants present in water.
- The water should be free from turbidity if you choose UV light

Desalination of Brackish water

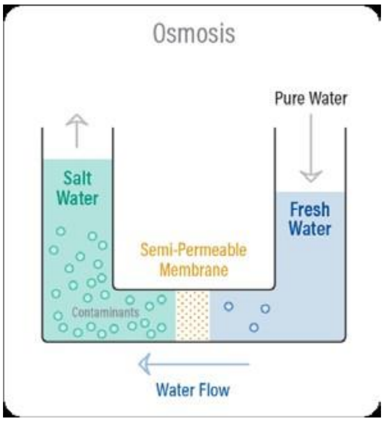
The process of removing common salt from the water, is known as desalination. Water containing high concentration of dissolved solids with peculiar salty or brackish taste is called brackish water. Sea water is an example for brackish water as it contains about 3.5% of dissolved salts.

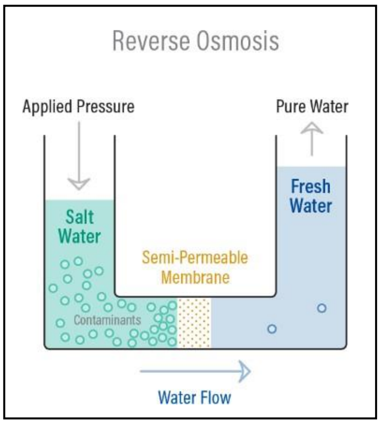
Depending upon the quantity of dissolved salt, water is graded as:

1. Fresh water: less than 1000 ppm of dissolved solids.
2. Brackish water: more than 1000 ppm and less than 3500 ppm of dissolved solids.
3. Sea water: more than 3500 ppm of dissolved solids.

Commonly used methods for the desalination of brackish water is:

1. Reverse Osmosis (Pressure) 2. Electrodialysis (Electrical) 3. Thermal Distillation (Thermal)





Osmosis:

When two solutions of different concentrations are separated by a semi-permeable membrane, which does not permit the flow of dissolved salts, then the solvent flows from lower concentration to higher concentration.

Reverse Osmosis

When two solutions of unequal concentrations are separated by a semi permeable membrane, flow of solvent takes place from dilute to concentrated sides, due to osmosis. If, however, a hydrostatic pressure in excess of osmotic pressure is applied on the concentrated side, the solvent flow is reversed, i.e. solvent is forced to move from concentrated side to dilute side across the membrane. This is the principle of reverse osmosis. This membrane filtration is also called 'super-filtration' or 'hyper–filtration. The membrane consists of very thin films of cellulose acetate, affixed to either side of a perforated tube. However, more recently superior membranes made of polymethacrylate and polyamide polymers have come into use.

Method of purification: The reverse osmosis cell consists of a chamber fitted with a semi permeable membrane, above which sea water/impure water is taken and a pressure of 15 to 40 kg/cm^2 is applied on the sea water/impure water. The pure water is forced through the semi- permeable membrane which is made of very thin films of cellulose acetate.

Advantages:

1. Reverse osmosis possesses a distinct advantage of removing ionic as well as non-ionic, colloidal and high molecular weight organic matter.

2. It removes colloidal silica, which is not removed by demineralization.

3. The maintenance cost is almost entirely on the replacement of the semi permeable membrane.

4. The life time of membrane is quite high, about 2 years.

5. The membrane can be replaced within a few minutes, thereby providing nearly uninterrupted water supply.

6. Due to low capital cost, simplicity, low operating cost and high reliability, the reverse osmosis is gaining ground at present for converting sea water into drinking water and for obtaining water for very high pressure boilers.

Battery chemistry and Corrosion

❖ Storage batteries:

A device that stores chemical energy and releases it as electrical energy is called as battery or storage battery.

Cell is a device in which chemical energy is converted into electrical energy. Many cells connected in series are called battery.

Batteries are classified as follows;

i) Primary battery.
ii) Secondary battery.
iii) reserve battery

Not all batteries are equal; often they are classified under the following categories:

● **Primary battery:** In primary batteries, chemical energy stored in the battery is converted to electrical energy spontaneously as long as active materials are present. In other words, the batteries in which irreversible chemical reaction takes place are called as *primary batteries*. This battery cannot be recharged, because cell reaction is irreversible.

Example: Dry cell, Laclanche cell, Li-MnO_2 battery.

● **Secondary battery:** Secondary cells are the batteries in which reversible chemical reaction takes place. This battery can be recharged by passing electric current. Redox reaction is reversed during recharging. Electrical energy is stored in the form of chemical energy in these batteries and used when needed.

Example: Lead acid battery, Ni-MH battery, Li-ion battery.

Primary cells act only as galvanic cell, whereas, a secondary cell can act both as galvanic cell and electrolytic cell. During discharging it acts as galvanic cell converting chemical energy to electrical energy and during charging process it acts as electrolytic cell converting electrical energy to chemical energy

● **Reserve battery:** In this battery, one of the key component is stored separately, and is incorporated into battery when required. When long storage is required, reserve batteries are often used, since the active component of the cell is separated until needed, thus reducing self-discharge.

Reserve batteries effectively eliminate the possibility of self-discharge and minimize chemical deterioration. Most reserve batteries are used only once and then discarded.

These batteries are used primarily to deliver high power for relatively short periods of time after activation in such applications as radiosondes, fuzes, missiles, torpedoes, and other weapon systems.

The reserve batteries can be classified by the type of activating medium or mechanism that is involved in the activation:

a) Water-activated batteries: Activation by fresh- or seawater.

Example: Mg-AgCl battery. They are activated by adding sea water. These batteries have high reliability and long shelf life, hence they find applications in missiles and submarines.

b) Gas-activated batteries: Activation by introducing a gas into the cell. The gas can be either the active cathode material or part of the electrolyte.

Example is zinc-air batteries where the cell is sealed until use, the seal is removed to admit air and activate the cell when needed.

c) Electrolyte-activated batteries: Activation by the complete electrolyte or with the electrolyte solvent. The electrolyte solute is contained in or formed in the cell.

d) Heat-activated batteries: A solid salt electrolyte is heated to the molten condition and becomes ionically conductive, thus activating the cell. These are known as thermal batteries. Another

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Basic requirements for commercial batteries

- A battery should be reasonably light, compact
- It should have a low self-discharge rate. (Self discharge rate is a measure of how quickly a cell will lose its energy due to unwanted chemical reaction that occur within the cell).
- The internal parts of the battery shouldn't corrode or convert to its inactive forms. (Corrosion affects the functioning of the battery).
- Fast charging increases the changes in the components, shortening the life span of the battery. Therefore should have a slow charge or discharge rate.
- Battery should have a long life even when not in use.
- The voltage of the battery should not vary appreciably during its use.
- Battery size: Primary batteries ranges from tiny button cells (watches) to No. 6 cell used for signal circuit or other long duration applications. Secondary batteries are made in large size(submarines).

❖ Explain the construction and working of Zinc air battery (or) Modern battery?

Zinc air cell : (Modern battery)	
Anode :	Zinc (Zn)
Cathode :	Oxygen
Electrolyte :	Potassium hydroxide (KOH)

Metal –air batteries have attracted much attention because of their extremely high energy densities.

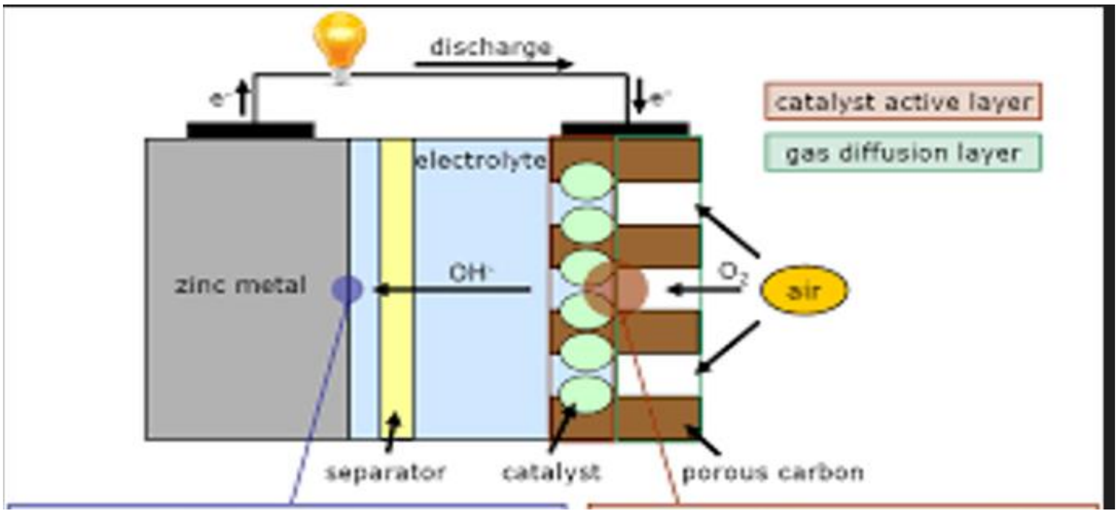
The notable characteristic feature of these batteries is their open-cell structure. Since these batteries use oxygen-gas from air as their cathode.

Among the metal –air batteries, zinc-air batteries have powerful potential for use as alternative storage device, low cost, abundance low, potential environmental benignity, flat discharge voltage and long shelf life.

Working :

1. Zinc air battery is a primary battery, it consists of anode containing granules of zinc mixed with 20% KOH electrolyte.
2. Carbon is catalytically activated to absorb O_2 gas. The solubility of Oxygen was very low at atm. pressure, so, it is necessary to use O_2 in the gas phase.

3. Cathode contains a porous carbon plate which provides site for the reduction reaction O_2 to OH^- by usig the e^- s generated by zinc metal.
4. The OH^- ion migrate from air cathode to zinc anode to complete the cell reaction.
5. The anode and cathode compartments are separated by a separator and both are encased in plastic or ebonite insulator.
The reactions are as follows.



Cell reactions:
At anode: $Zn + 2OH^- \rightarrow Zn(OH)_2 + 2e^-$
At cathode: $\frac{1}{2} O_2 + H_2O + 2e^- \rightarrow 2OH^-$
Over all reaction: $Zn + \frac{1}{2} O_2 + H_2O \rightarrow Zn(OH)_2$

Advantages: **1)** High energy density. **2)** Low cost and compact **3)** Does not produce harmful products.
Applications: Used in Military radio receivers, transmitters, hearing aids.

❖ Write about Lithium ion battery:

- These batteries are rechargeable battery best suited for mobile devices that requires small size, light weight and high performance.
- In this type of batteries lithium compounds are used.
- These batteries are considered as best than pure Lithium based batteries.
- It works on the principle Intercalation Mechanism.
- Lithium-ion battery is a secondary battery. As in lithium cell, it does not contain metallic lithium as anode.
- As the name suggests, the movement of lithium ions are responsible for charging '& discharging. Lithium-ion cell has the following three components.

Lithium ion battery	
Anode :	Lithium doped graphite
Cathode :	Lithium Cobalt (III) Oxide
Electrolyte :	Complex Lithium compounds dissolved in organic solvents.

Discharging Reaction:

During discharging, the Li^+ ions flow anode to the cathode through the non-aqueous electrolyte. Electrons flow from the anode to the cathode through external circuit. The Li^+ ions and electrons combine at the positive electrode and deposit there as Li.

Cell reactions:

At anode: $Li_xC_6 \leftrightarrow xLi^+ + xe^- + 6C$

At cathode: $Li_{1-x}CoO_2 + xLi^+ + xe^- \leftrightarrow LiCoO_2$

Over all reaction: $Li_xC_6 + Li_{1-x}CoO_2 \leftrightarrow 6C + LiCoO_2$

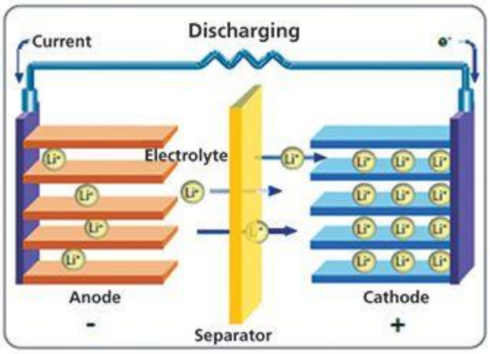
Charging Reaction:

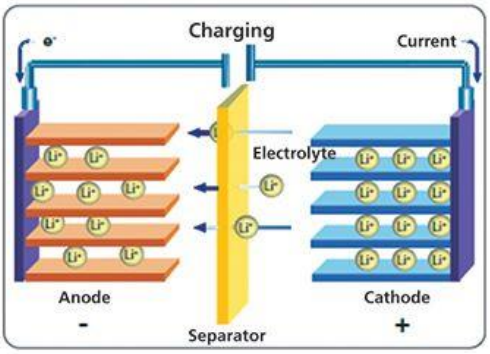
During charging, an external power source, the current ato pass I the reverse direction. The positive terminal of the charging circuit is connected to the cathode of the battery, and negative terminal is connected to the anode.

The cathodic half reaction: $LiCoO_2 \leftrightarrow Li_{1-x}CoO_2 + xLi^+ + xe^-$

The anodic half reaction: $xLi^+ + xe^- + 6C \leftrightarrow Li_xC_6$

In lithium ion battery the Li^+ ions are transported to and from cathode or anode, by the transition metal Cobalt [Co] where cobalt was oxidized from Co^{+3} to Co^{+4} during charging, and reduced from Co^{+4} toCo^{+3} during discharging.





Advantages:

i. They have high energy density than other rechargeable batteries.
ii. They are light weight.
iii. They produce high voltage out of 4 V.
iv. They have improved safety, i.e., more resistance to overcharge.
v. No liquid electrolyte means they are immune from leaking.
vi. Fast charge and discharge rate.

Disadvantages:

1)They are expensive. 2) They are not available in standard cell types.

❖ Applications of lithium ion in electronics and electrical vehicles

- The Li-ion batteries are used in portable devices: these include mobile phones, laptops and tablets, digital cameras and camcorders, electronic cigarettes, handheld game consoles and torches (flashlights).
- Li-ion batteries are used in tools such as cordless drills, sanders, saws and a variety of garden equipment including whipper-snippers and hedge trimmers.
- Because of their light weight, Li-ion batteries are used for energy storage for many electric vehicles from electric cars to pedelec (pedelec is a bicycle where the rider's pedalling is assisted by a small electric motor), from hybrid vehicles to advanced electric wheelchairs, from radio-controlled models and model aircraft to the Mars Curiosity rover.
- They are used in cardiac pacemakers and other implantable devices.
- They are used in telecommunication equipment, instruments, portable radios and TVs, pagers.

❖ Define fuel cell. How fuel cells are represented. Mention its advantages and disadvantages?

Definition: Fuel cells are the galvanic cells which converts chemical energy of fuels into electrical energy by the combustion of fuels.

Fuel + Oxygen → Oxidation products + Electricity

Fuel cell Representation: A fuel cell essentially consists of the following arrangement:

Fuel / electrode / electrolyte / electrode / oxidant.

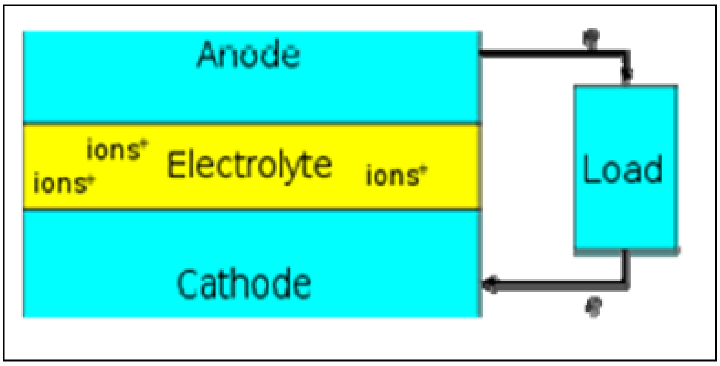
At the anode, fuel under goes oxidation: Fuel → Oxidation product + ne^-

At the cathode, the oxidant gets reduced: Oxidant + ne^- → Reduction products.

The electrons liberated from the oxidation process at the anode can perform useful work when they pass through the external circuit to the cathode.

Advantages of the Fuel cells:-

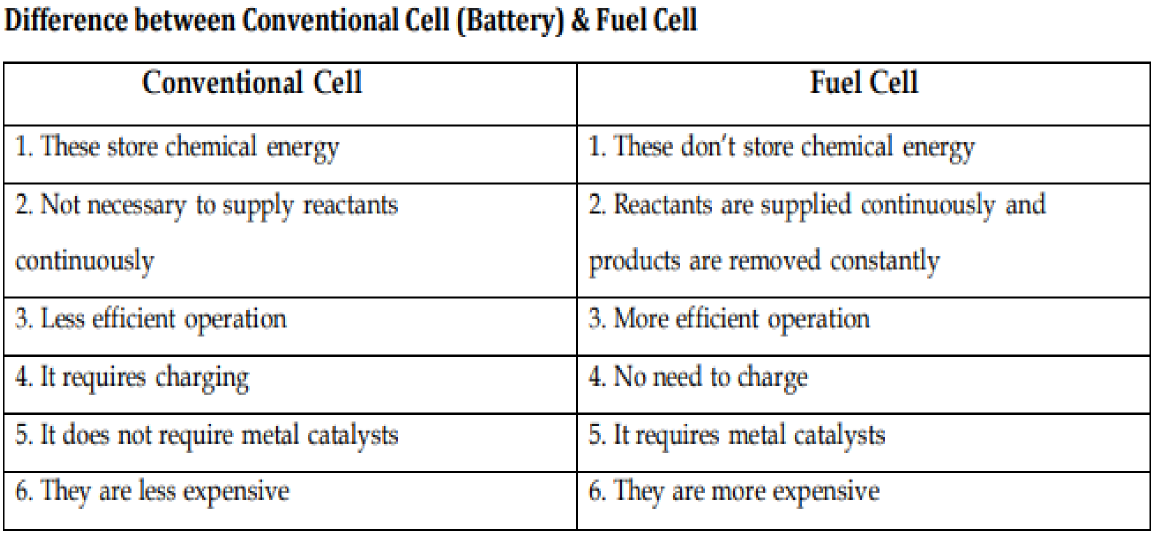
1) Their power efficiency is high.
2) The cells have high energy density.
3) They are ecofrindly.
4) Space required for fuel cell is less.
5) Produce harmless biproducts.
6) Produces direct current for a long time.
7) No moving parts and so elimination of wear and tear.
8) They operate very silently.
9) Absence of harmful waste products.
10) No need of charging.



Limitations of Fuel cells:-

1) Fuel cells produce energy only as long as fuels and oxidants are supplied.
2) Electrodes are very costly.
3) Power output is very costly.
4) Fuels in the form of gases and oxygen need to be stored in tanks under high pressure.
5) Reactions are constantly supplied and the products are constantly removed from the cell.

❖



Difference between Conventional Cell (Battery) & Fuel Cell

Conventional Cell	Fuel Cell
1. These store chemical energy	1. These don't store chemical energy
2. Not necessary to supply reactants continuously	2. Reactants are supplied continuously and products are removed constantly
3. Less efficient operation	3. More efficient operation
4. It requires charging	4. No need to charge
5. It does not require metal catalysts	5. It requires metal catalysts
6. They are less expensive	6. They are more expensive

❖ Describe the construction and working of Methanol-Oxygen Fuel cell?

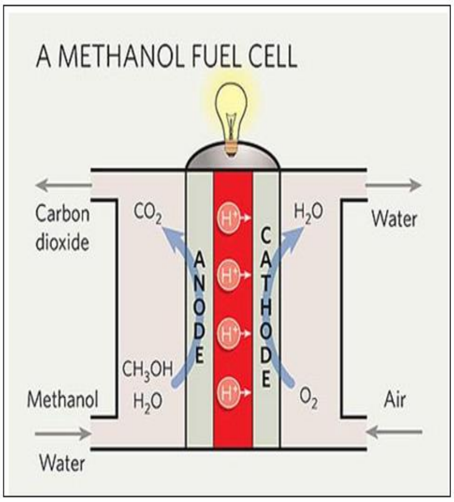
Methanol-Oxygen Fuel cell:- (DMFC)

- ★ Methanol is preferred as a fuel in fuel cells because of the following reasons.
- ★ It has low carbon content.
- ★ It possesses a readily oxidisable alcoholic group.
- ★ It has high solubility in aqueous electrolytes.

Construction:-

It consists of anodic and cathodic compartments and both the compartments contain platinum electrode.

Methanol containing $H_2 SO_4$ is passed through anodic compartments. Oxygen is passed through cathodic compartments. Electrolyte consists of sulphuric acid. A membrane is provided which prevents the diffusion of methanol into the cathode.



Working: - At anode, CH_3OH undergoes oxidation to CO_2 liberates electrons, the liberated electrons taken by oxygen gets reduced into water with liberation of energy at cathode..

Anode reaction: $CH_3OH + H_2O \rightarrow CO_2 + 6H^+ + 6e^-$

Cathode reaction: $3(½O_2) + 6H^+ + 6e^- \rightarrow 3H_2O$

Overall reaction: $CH_3OH + 3(½O_2) \rightarrow CO_2 + 2H_2O$

Fuel (methanol) and air or oxygen are fed to the electrodes. The cell potential is 1.21 V at 25 °C. The acid electrolyte offers the advantage of easy removal of CO 2 , a product of the cell reaction.

Uses:

- In all kinds of portable, automotive and mobile applications like,Powering laptop, computers, cellular phones, digital cameras.
- In Fuel cell vehicles (FCVs).
- It is used in Spacecraft applications.
- It is used in any consumables which require long lasting power compared to Li-ion batteries.
- It is also used in Military applications.

Solid oxide fuel cells

Fuel	H_2, CO
Oxidant	O_2
Electrodes	Ceramic material
Electrolyte	Solid mixture of yitrium oxide and Zircoium oxide
Catalyst	Perovskite
Operatig temperature	700 to 1000°C
Power density	0.1 to 1.5 KW/m^3
Efficiency	55 to 65%

Working: Solid oxide fuel cell utilizes the movement of e^-s ad generate electricity in few basic steps:

Reduction of O_2 into O^{-2} occurs at the cathode these ions can diffuse through the solid oxide electrolyte to the anode, where they can electrochemically oxidize the fuel.

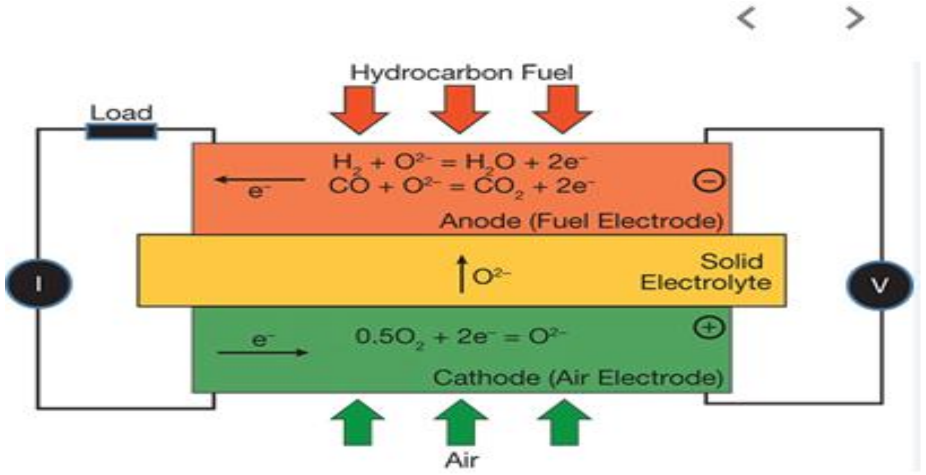
Water was the byproduct is given off as well as two e^-s. These e^-s then flow through an external circuit. Where they can do work. The cycle repeats as that e^-s enter the cathode material again.

Anodic reaction: $H_2 + O^{2-} \rightarrow H_2O + 2e^-$

$CO + O^{2-} \rightarrow CO_2 + 2e^-$

Cathodic reaction : $O_2 + 2e^- \rightarrow 2O^{2-}$

Overall reaction: $H_2 + CO \rightarrow H_2O + CO_2$



Advantages:

1) SOFC has a solid oxide or ceramic electrolyte. Ceramic are used not to become electrically and ionically active until they reach very high temperature.s

2) AOFC include high combined heat and power effieciency, long term stability, fuel flexibility, low emission and relatively low cost.

Disadvantages : Due to high operating temperature which are results is longer startup times and mechanical and chemical compatibility issues.

Applications :

It is used for generating electiricity I motor vehicles.

It is used as power transmission system

Here are three main application of SOFC such as combined cycle power plant, cogeneration and trigeneration and residential application.

Corrosion

- **Definition:** Corrosion is defined as the deterioration of a metal by chemical or electro chemical reactions with its environment.

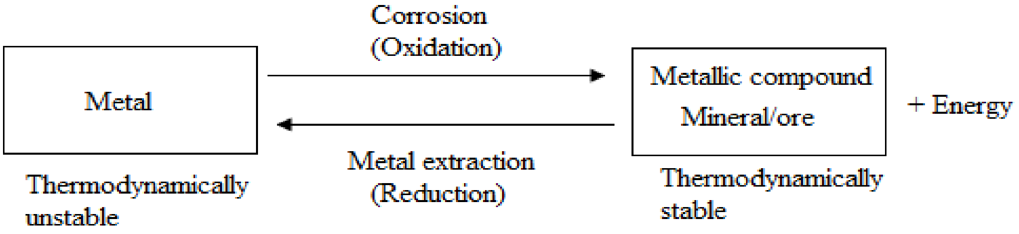
Due to corrosion the useful properties of a metal like malleability, ductility, electrical conductivity and also the surface appearance are lost. The most familiar example of corrosion is rusting of iron when exposed to atmospheric conditions.

Examples:

- Rusting of iron: A layer of reddish brown scale ($Fe_2O_3 . xH_2O$) is formed on the surface of the iron.
- Formation of green layer of basic copper carbonate [$CuCO_3 + Cu(OH)_2$] on the surface of copper.
- Tarnishing of silver: Blackening of surface of silver due to the formation of black layer of silver sulphide on it.

Cause of corrosion:

- The metals exist in nature in the form of their minerals or ores, in the stable combined forms as oxides, chlorides, silicates, carbonates, sulphides etc.
- During the extraction of metals, these ores are reduced to metallic state by supplying considerable amounts of energy.
- Hence the isolated pure metals are regarded as excited states than their corresponding ores.
- So metals have natural tendency to go back to their combined state (minerals/ores).
- When metal is exposed to atmospheric gases, moisture, liquids etc., the metal surface reacts and forms more thermodynamically stabled compounds.



Consequences of corrosion:

- Enormous waste of machineries and different types of metallic materials
- It leads to sudden failure of machines.
- It leads to the decrease in efficiency of machine and frequent replacement of corroded equipment which is an expensive.
- It may leakage of inflammable gas from the corroded pipe lines resulting into fire accidents etc.
- It causes contamination of potable water.
- It has been estimated that 25% of annual world production of iron is wasted due to corrosion.

Theories of corrosion

There are two different types of theories of corrosion 1)Chemical theory 2) Electro chemical theory of corrosion

Dry corrosion (or) Chemical corrosion (or) Direct chemical attack theory (or) Mechanism of dry corrosion:

This type of Corrosion occurs mainly through the direct chemical action of atmospheric gasses like O_2, halogens, H_2S, SO_2, N_2 or anhydrous inorganic liquid with the metal surface.

There are three types of chemical Corrosion:

(1.) Oxidation corrosion (2.) Corrosion due to other gases(3.) Liquid metal corrosion.

(1.) <u>Oxidation corrosion</u>:

- This is carried out by the direct action of oxygen at low or high temperatures on metals in absence of moisture.
- This theory explains dry corrosion.
- Corrosion is initiated in a metal, when it is contacted directly with oxygen.
- Then the metal gets oxidized to metal ions and the electrons so released reduce oxygen to form oxide ion.
- The metal ion and oxide ion combine to form metal oxide on the metal surface.

$$2M \rightarrow 2M^{+n} + 2\,ne^- \quad \text{(Oxidation)}$$

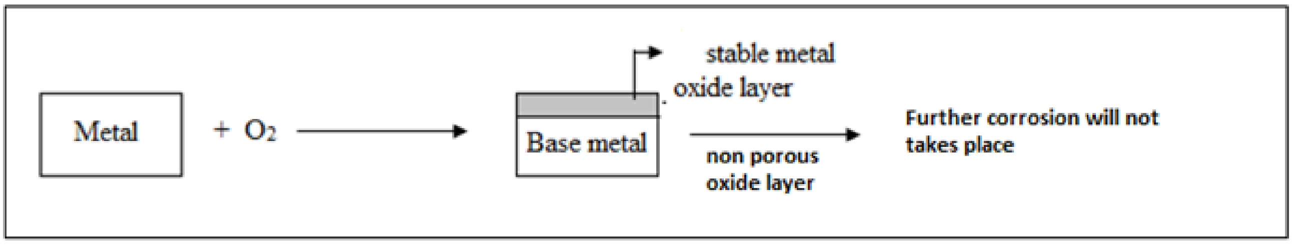
$$\frac{n}{2}O_2 + 2ne^- \rightarrow n\,O^{-2} \quad \text{(Reduction)}$$

$$2M + \frac{n}{2}O_2 \rightarrow M_2O_n \quad \text{(Metal oxide)}$$

- The extent of corrosion depends upon the nature of metal oxide.
- The nature of metal oxide layer formed plays an important role in determining further corrosion.

a) <u>Stable oxide layer</u> (or) <u>Protective and non porous oxide film</u> :

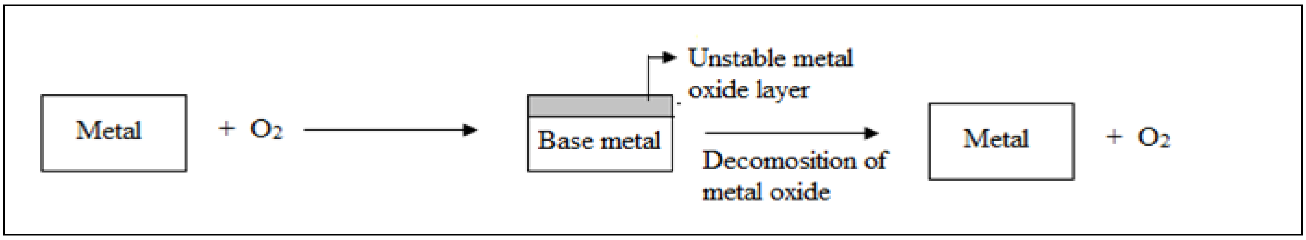
If the metal oxide is stable, it behaves has a protective layer which prevents further corrosion. E.g., The oxide films of Al, Sn, Pb, Cu, Cr, W etc. are stable and therefore further corrosion is prohibited.



(b) <u>Unstable oxide layer</u>:

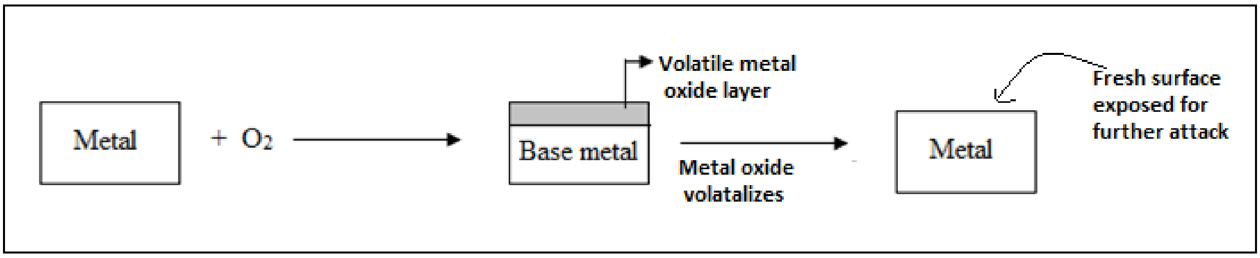
If the metal oxide layer is unstable, the oxide layer formed decomposes back into metal and oxygen. So, oxidation corrosion is not possible.

E.g., Ag, Au and Pt do not undergo oxidation corrosion.



(c) <u>Volatile oxide layer</u>:

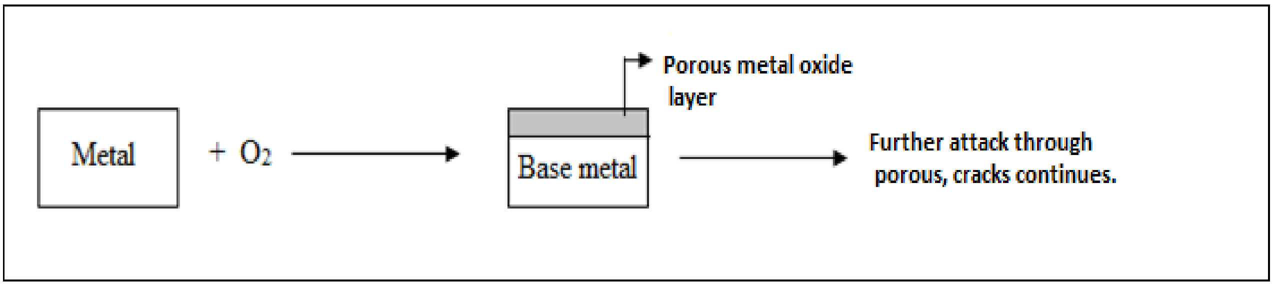
If the metal oxide layer is volatile, then the oxide layer volatilizes after formation and leaves the underlying metal surface exposed for further attack. This causes continuous corrosion which is excessive in molybdenum oxide (MoO3)



(d) Porous and non protective oxide layer:

If the metal oxide layer is porous, the oxide layer formed has pores or cracks. In this case the atmospheric oxygen penetrates through the pores or cracks and corrode the underlying metal surface. This cause continuous corrosion till conversion of metal into its oxide is completed.

Ex: Alkali and alkaline earth metals (Li, Na, K, Mg etc.)



Pilling-Bedworth Rule:

This rule states the extent of protection given by the corrosion layer. An oxide is protective or non – porous if the volume of the oxide is at least as great as the volume of the metal from which it is formed.

It is the ratio of the volume of metal oxide to volume of metal.

$$\text{specific ratio} = \frac{volume of metal Oxide}{Volume of Metal}$$

The smaller the specific ratio, greater the oxide corrosion since the formed oxide film will be porous through which the oxygen can diffuse and increases the corrosion further.

1) If the volume of the metal oxide layer is at least as great as the volume of the metal, no corrosion occurs as the oxidation of metal reaches to zero. i.e; specific ratio ≥ 1

   For example, the specific volume ratios of W, Cr and Ni are 3.6, 2.0 and 1.6 respectively. Consequently the rate of corrosion is least in Tungsten (W).
2) If the volume of metal oxide is less than the volume of the metal, the oxide film will develop cracks and pores. The atmospheric oxygen reaches the metal and increases the corrosion. In this case corrosion is continuous and rapidly increases. i.e; specific ratio < 1

   For example, Li, Na and K.

(2)Corrosion due to other gases:

- This type of corrosion is due to gases like SO_2, CO_2, Cl_2, H_2S, F_2 etc.
- In this corrosion, the extent of corrosive effect depends mainly on the chemical affinity between the metal and the gas involved.
- The degree of attack depends on the formation of protective or non protective films on the metal surface which is explained on the basis of Pilling Bedworth rule.

(i) If the volume of the corrosion film formed is more than the underlying metal, it is strongly adherent, non-porous does not allow the penetration of corrosive gases. For example when Cl reacts with Ag forms AgCl film which prevents further reaction of Cl with Ag.

$$Ag + Cl_2 \rightarrow 2\ AgCl \quad \text{(protective film)}$$

(ii) If the volume of the corrosion film formed is less than the underlying metal, it forms pores/cracks and allow
the penetration of corrosive gases leading to corrosion of the underlying metal.

Ex. In petroleum industry, H_2S gas at high temperature reacts with steel forming a FeS scale.

$$Fe\ (steel) + H_2S \rightarrow FeS \quad \text{(porous)}$$

(3.) Liquid metal corrosion:

- ★ This corrosion is due to chemical action of flowing liquid metal at high temperatures on solid metal or alloy.
- ★ The corrosion reaction involves either dissolution of a solid metal by a liquid metal or internal penetration of the liquid metal into the solid metal.

  Eg. Coolant (sodium metal) leads to corrosion of cadmium in nuclear reactors.

Wet Corrosion (or) Electrochemical corrosion:

- ★ This type of Corrosion occurs where a conducting liquid is in contact with the metal.
- ★ This corrosion occurs due to the existence of separate anodic and cathodic parts, between which current flows through the conducting solution.
- ★ At anodic area, oxidation reaction occurs thereby destroying the anodic metal either by dissolution or formation of compounds. Hence corrosion always occurs at anodic parts.

__Mechanism:__ Electrochemical corrosion involves flow of electrons between anode and cathode.

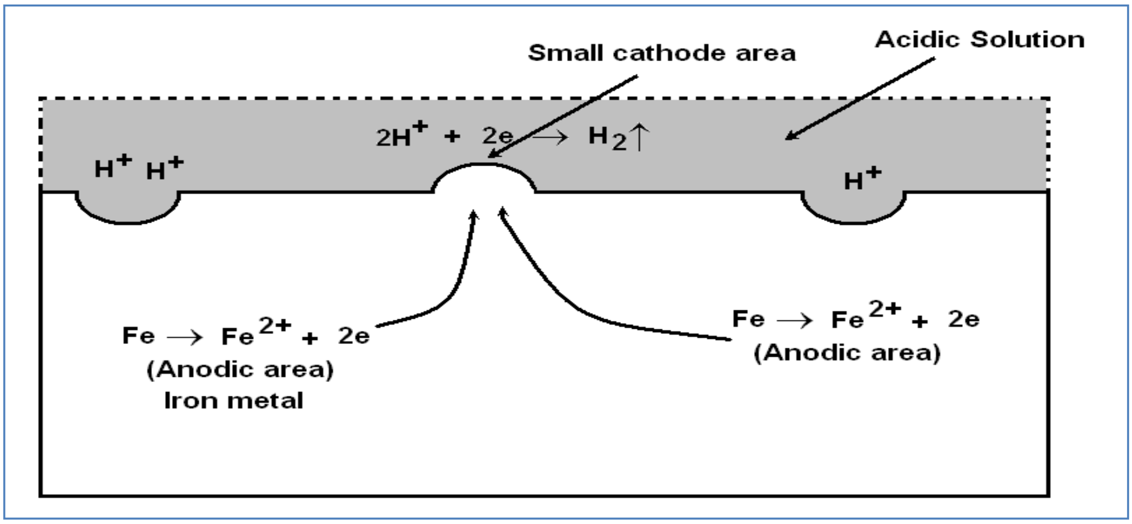
The anodic reaction involves dissolution of metal liberating free electrons.

$$M \rightarrow M^{+n} + ne^-$$

The cathodic reaction consumes electrons with either evolution of hydrogen or absorption of
oxygen which depends on the nature of corrosive environment.

__Evolution of hydrogen :__ [Formation of Rust with evolution of H_2 in Wet corrosion]:

★



This type of corrosion occurs in acidic medium.

E.g. Considering the metal Fe, anodic reaction is dissolution of iron as ferrous ions with liberation of electrons.

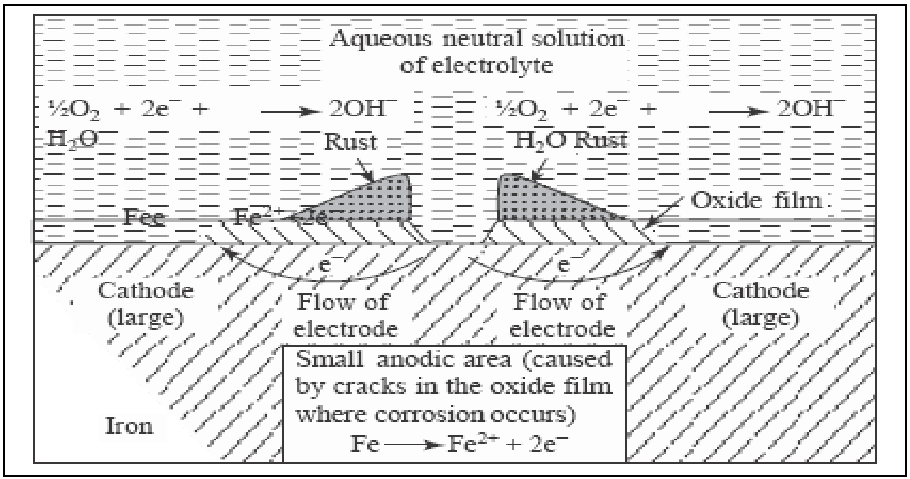
Anode: Fe → Fe^{+2} + 2e- (Oxidation)

- The electrons released flow through the metal from anode to cathode, whereas H+ ions of acidic solution are eliminated as hydrogen gas.

Cathode: $2H^{+}$ + $2e^{-}$ → H2 (Reduction)

- **The overall reaction** is: Fe + $2H^{+}$ → Fe^{+2} + H_2
- This type of corrosion causes displacement of hydrogen ions from the solution by metal ions.
- All metals above hydrogen in electrochemical series have a tendency to get dissolved in acidic solution with simultaneous evolution of H2 gas. The anodes are large areas, where as cathodes are small areas.

<u>Absorption of oxygen</u>*:* [Formation of Rust with evolution of O2 in wet reaction] :



(b)

For example, rusting of iron in neutral aqueous solution of electrolytes in presence of atmospheric oxygen. Usually the surface of iron is coated with a thin film of iron oxide. If the film develops cracks, anodic areas are created on the surface. While the metal parts act as cathodes. It shows that anodes are small areas, while the rest metallic part forms large cathodes. The released electrons flow from anode to cathode through iron metal.

At anode: Fe → Fe^{+2} + 2e- (Oxidation)

At cathode: ½ O_2 + H_2O + 2e- → 2 OH- (Reduction)

- Fe^{2+} ions and OH- ions combine to form Fe $(OH)_2$ precipitate.
- If enough oxygen is present, ferrous hydroxide is easily oxidized to ferric hydroxide.

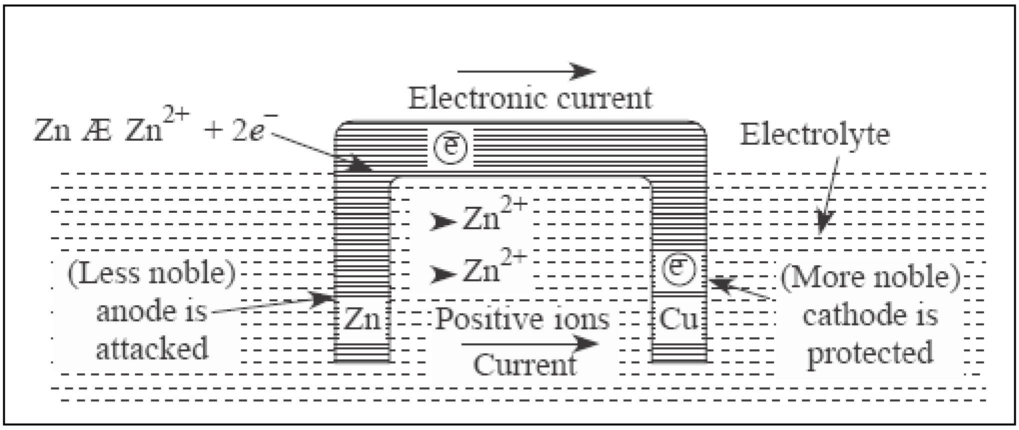
$$4Fe(OH)_2 + O_2 + 2H_2O \rightarrow 4Fe(OH)_3$$

- This product called yellow rust actually corresponds to Fe_2O_3 H_2O.
- If the supply of oxygen is limited, the corrosion product may be black magnetite Fe_3O_4.

<u>Types of Corrosion</u>

What is galvanic corrosion? How is it prevented? Give examples?

Galvanic corrosion: This type of electrochemical corrosion is also called bimetallic corrosion. When two dissimilar metals are connected and exposed to an electrolyte, they will form a galvanic cell. The anodic metal will be oxidised and it will undergo corrosion. Zinc and copper metals connected with each other in an electrolyte medium form a galvanic cell. Zinc acts as anode and undergoes corrosion while cathode will be unaffected.



Eg: When Zn an Cu are connected and exposed to corroding environment, Zinc (higher in electrochemical series) forms the anode; undergoes oxidation and gets corroded. Cu (lower in electrochemical series) acts as cathode; undergoes reduction and protected as the electrons released by Zn flow towards Cu.

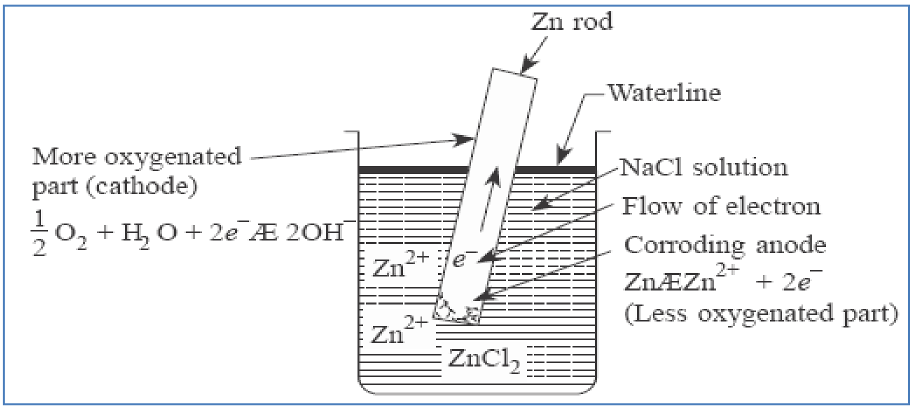
Prevention:

1) Galvanic corrosion can be avoided by coupling metals close to the elec- trochemical series.
2) Fixing insulating material between two metals.
3) By using larger anodic metal and smaller cathodic metal.

Example of galvanic corrosion:

1) Steel screws in brass marine hardware,
2) steel pipe connected to copper plumbing,
3) steel propeller shaft in bronze bearing,
4) zinc coating on mild steel,
5) lead–tin solder around copper wires.

❖ Differential aeration corrosion: or Concentration cell corrosion:

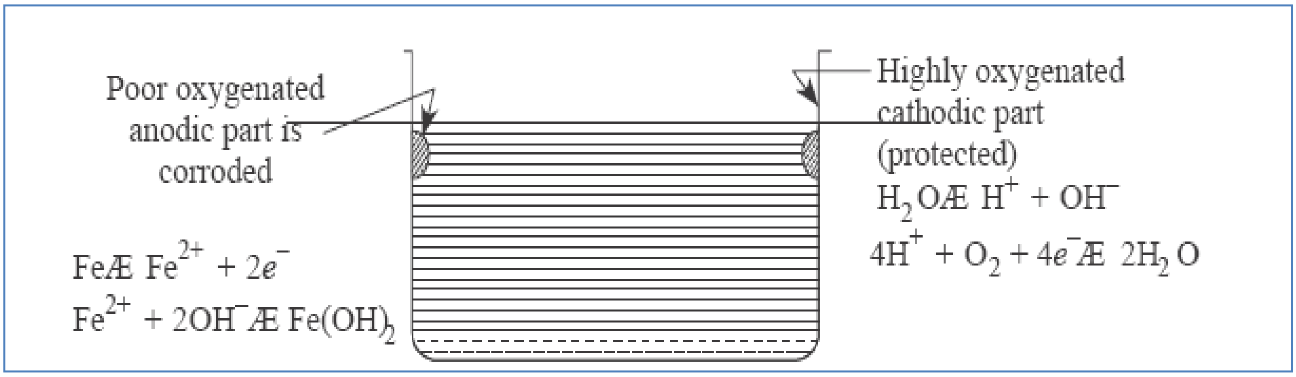


If a metal rod is dipped in an electrolyte, the portion dipped in water is poor in oxygen concentration and works as anode which gets corroded and the portion above water acts as cath- ode which is protected. The system will act as a concentration cell and the chemical reactions for zinc dipped in water are given as:

$Zn(OH)_2$ appears as corrosion products .Examples: Water line corrosion, Drop corrosion.

Waterline corrosion:

It has been observed in the case of an iron tank containing water, that the portion of iron tank just below the water level undergoes corrosion. It is due to the difference in oxygen concentration. Corroding portion is poor in oxygen and acts as anode.



❖ What is Galvanic series? Explain.

Electrochemical reactions are predicted by electrochemical series. A metal having higher position can replace (reduce) other metals that have lower position in the series. For example,

that is,

$Zn + CuSO_4 \rightarrow ZnSO_4 + Cu$

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

Or in other words, zinc will corrode faster than copper.

Some exceptions have been observed in this generalisation. For example, Ti is less reactive than Ag.

Galvanic series is the series of metals that is made keeping in view the process of corrosion of a metal in a particular atmosphere, i.e. sea water. In galvanic series, oxidation potential of metals is arranged in the decreasing order of activity of a series of metals. The series is towards the increasing noble nature.

More anodic: Mg, Mg alloys, Zn, Al, Cd, Fe, Pb, Sn, Ni–Mo–Fe alloys) Brasses, Cu, Ni, Cr–steel alloy, Ag, Ti, Au, Pt towards noble nature.

❖ Explain about the Factors Influencing rate of Corrosion:

The rate and extent of corrosion depends upon various factors.

1. Nature of metal
2. Nature of corroding atmosphere

Nature of the metal:

1. **Position in the galvanic series:**
   Metals which possess low reduction potentials and occupy higher end of galvanic series undergo corrosion easily. Metals which possess high reduction potentials and occupy lower end of galvanic series do not undergo corrosion and they get protected.
2. **Purity of metal:**
   Heterogenity is produced if impurities are present in a metal, which form tiny electrochemical cells at the exposed parts. The anodic parts get corroded. As the extent of exposure and impurities increase, the extent of corrosion increases.
   For example in case of zinc metal;

% Purity	99.999	99.99	99.95	99
Corrosion rate	1	2650	5000	7200

3. **Relative areas of the anodic and cathodic parts:**

   When two dissimilar metals or alloys are in contact, the corrosion of the anodic part is directly proportional to the areas of the cathodic and anodic parts. i.e, the corrosion is more rapid, severe and highly localised if the anodic area is small.

   For example, a small pipe made of steel fitted in a large copper tank.

$$In\ general\ \ Rate\ of\ \ corrosion\ of\ \ anodic\ region \propto \frac{CathodicArea}{AnodicArea}$$

4. **Nature of surface film**:

   In aerated atmosphere, practically all metals produce a thin surface film of metal oxide.

   The ratio of the volumes of the metal oxide formed to the metal is called "specific volume ratio".

$$\boxed{specific\ \ ratio\ \ = \frac{volumeofmetalOxide}{VolumeofMetal}}$$

   If the specific volume ratio is more, the rate of corrosion is less, because the surface of the metal is completely covered by the film, offering protection to the metal surface.

   For example, the specific volume ratios of Ni, Cr, and W are 1.6, 2.0 and 3.6 respectively. The rate of corrosion for tungsten (W) is least even at elevated temperatures.

5. **Physical state of metal**:

   The grain size, orientation of crystals, stress etc. of the metals influence the rate of corrosion. The smaller the grain size of the metal or alloy greater will be the rate of corrosion, because of its high solubility. The areas under stress become anodic and corrosion takes place in these areas.

6. **Volatility of corrosion products:**

   If the corrosion produced volatilizes as soon as it is formed, the metal surface is exposed for further attack. This creates rapid and excessive corrosion.

   For example the corrosion product of molybdenum as molybdenum oxide (MoO3) is volatile.

7. **Passive character of metal**:

   Metals like Ti, Al, Cr, Mg, Ni and Co are passive and they exhibit much higher corrosion resistance than expected from their position in the electrochemical series. This is because the metal forms very thin, highly protective corrosion film, by reacting with atmospheric oxygen. If the film is broken, it compensates the film by re exposure to oxidising conditions. Thus they produce "self healing film". This property is called passive character of metal.

   For example the corrosion resistance of "stainless steel" is due to passive character of chromium present in it.

Nature of corroding environment:

1. **Temperature*:***
   The rate of corrosion reaction and diffusion rate increases with increase in temperature, causing the increase in rate of corrosion.
2. **Humidity of air*:***
   The humidity of air is a deciding factor for rate of corrosion. The relative humidity above which, the rate of corrosion increases sharply is called "critical humidity". The value of critical humidity depends on the physical characteristics of the metal and the nature of corroding atmosphere.
   The reasons for increase of corrosion with humidity are,
   1. The moisture or vapours present in atmosphere furnish water to the electrolyte, essential for setting up an electrochemical cell.
3. **Presence of impurities in atmosphere:** Atmosphere is contaminated with gases like CO2, SO2, H2S; fumes of H2SO4, HCl etc. and other suspended particles in the vicinity of industrial areas. They are responsible for electrical conductivity, thereby increasing corrosion
4. **Nature of ions present in the medium :**
   The presence of ions like silicates in the medium leads to the formation of "insoluble reaction products" like silica gel, on the metal surface which "inhibit" further corrosion. On the other hand chloride ions, if present in the medium destroys the protective film on the surface of the metal.
5. **Amount of oxygen in atmosphere:**
   As the percentage of oxygen in atmosphere increases, the rate of corrosion also increases due to the formation of oxygen concentration cell. The decay of metal occurs at the anodic part and the cathodic part of the metal is protected.

   anodic reaction for iron : Fe ----> $Fe^{+2} + 2e^{-}$

   cathodic reaction : $2\ H_2O + O_2 + 4e^{-}$ -----> $4OH^{-}$

   corrosion product : $2\ Fe^{2+} + 4\ OH^{-}$ ----------> Fe (OH)2

   Fe (OH)2 + $H_2O + O_2$ ----------> Fe(OH)3 -----> $Fe_2\ O_3.3\ H_2O$
   rust
6. **Velocity of ions which flow in the medium:**
   As the velocity of the diffusion of ions in the medium increases, the rate of corrosion increases.
7. ***pH value of the medium*:**
   pH value of the medium has greater effect on corrosion. When pH value is lowered, the corrosion is increases.

❖ Corrosion Control Methods:

As we have discussed the disadvantages and different mechanisms of corrosion so far, it is essential to know the different corrosion control methods. The following are the important control methods of corrosion.

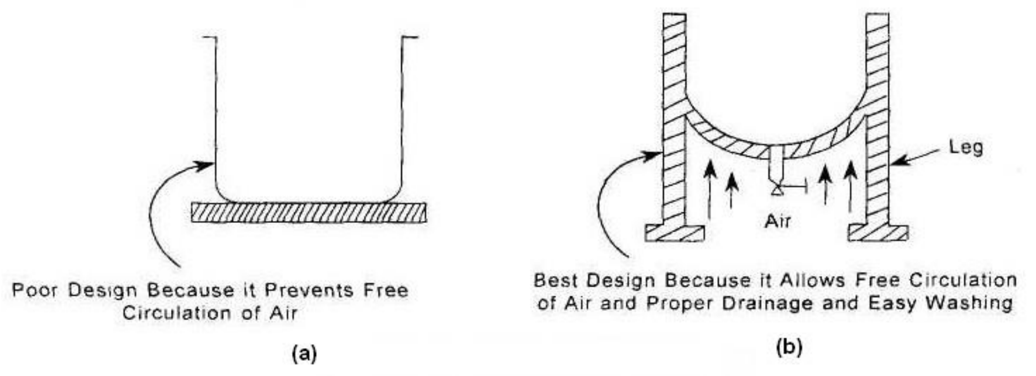
1) Proper designing
2) Using pure metal

3) Using metal alloys
4) Modifying the environment
5) Use of inhibitors
6) Cathodic protection
7) Application of protection coatings.

Proper designing & Selection of material:

The design of the metal under corroding atmosphere must be such that it is uniform and does not produce intense and localised corrosion, important principles of proper designing are:

The design of the equipment should allow free circulation of air proper drainage and easy washing as shown below.



Poor Design Because it Prevents Free Circulation of Air
(a)

Best Design Because it Allows Free Circulation of Air and Proper Drainage and Easy Washing
(b)

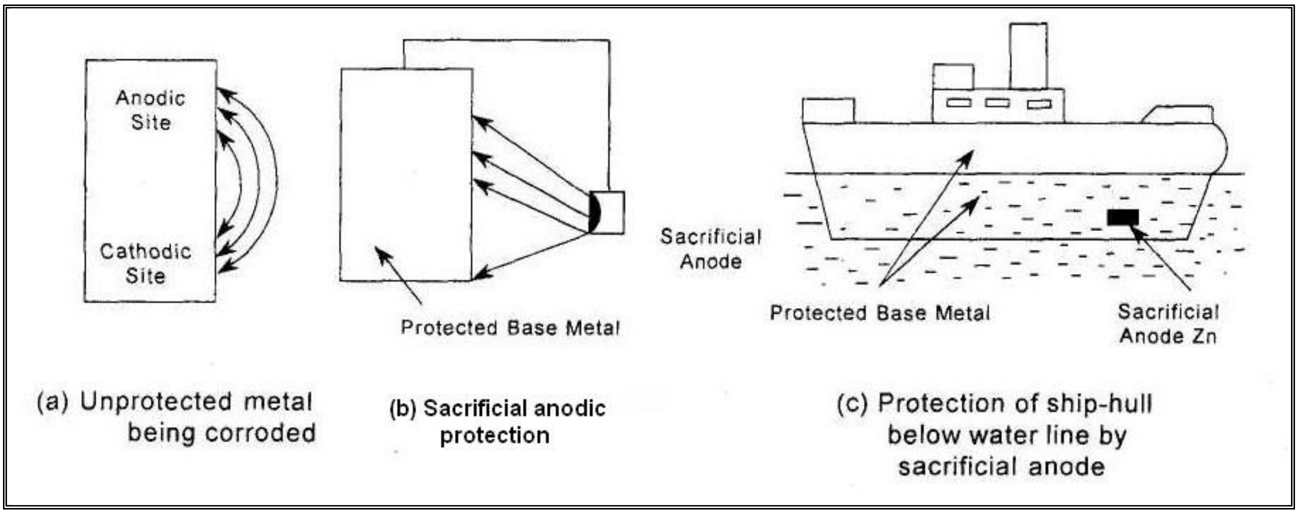
1) Cathodic protection :

- The basic principle of cathodic protection is to force the metal to behave like a cathode.
- The method of protecting the base metal by making it to behave like a cathode is called as cathodic protection.
- There are two types of cathodic protection;
  (a) Sacrificial anodic protection method.
  (b) Impressed current cathodic protection method.

a) <u>Sacrificial anodic protection method</u> :

- In this protection method, the metallic structure to be protected is called a base metal.
- The base metal is connected by a wire to a more anodic metal so that all the corrosion is concentrated at this more anodic metal.
- The more anodic metal itself gets corroded slowly, while the parent structure (cathodic) is protected.
- The more active metal so employed is called sacrificial anode.
- The corroded sacrificial anode is replaced by a fresh one, when consumed completely.
- Metals commonly employed as sacrificial anode are Mg, Zn, Al and their alloys which possess low reduction potential and occupies higher end in electrochemical series.

Eg 1. A ship-hull which is made up of steel is connected to sacrificial anode (Zn-blocks) which undergoes corrosion leaving the base metal protected.



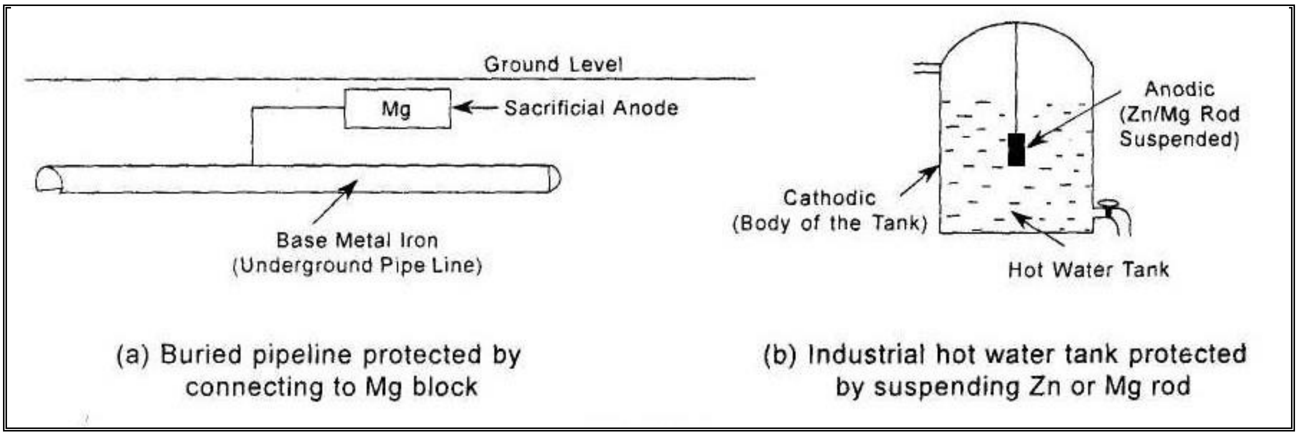
(a) Unprotected metal being corroded

(b) Sacrificial anodic protection

(c) Protection of ship-hull below water line by sacrificial anode

Example 2:

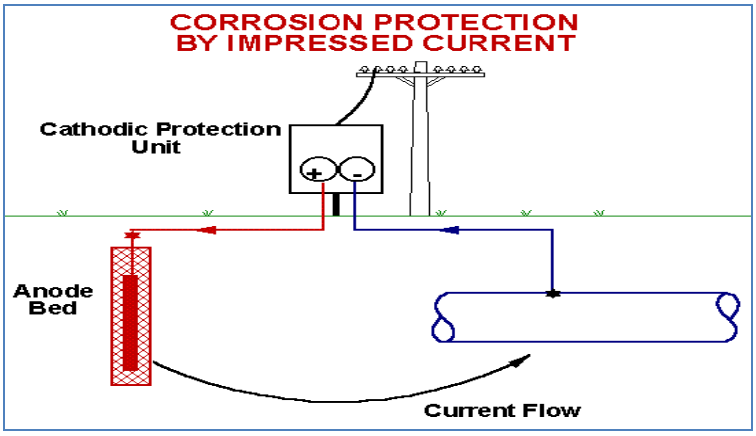
The underground water pipelines and water tanks are also protected by sacrificial anode method. By referring to the electrochemical series, the metal with low reduction potential is connected to the base metal which acts as anode.



(a) Buried pipeline protected by connecting to Mg block

(b) Industrial hot water tank protected by suspending Zn or Mg rod

(b) Impressed current cathodic protection:



- ★ In this method an impressed current little more than corrosion current is applied in the opposite direction to nullify the corrosion current producing a reverse cell reaction.
- ★ Thus the anodic corroding metal becomes cathodic and protected from corrosion.

- The impressed current is taken from a battery or rectified on A.C. line.
- The anode is usually insoluble anode like graphite, high silica iron, scrap iron, stainless steel, or platinum.
- Usually a sufficient D.C. current is passed on to the insoluble anode kept in a 'back fill' composed of coke or gypsum, so as to increase the electrical contact with the surrounding soil.

- This type of impressed current cathodic protection is given to
  (1) open water box coolers (2) water tanks (3) buried water pipe lines or oil pipelines
  (4) condensers (5) transmission line towers (6) marine pipes
- This type of protection is more useful for large structures for long term operations.

Disadvantages of cathodic protection:

1. The cathodic protection may be efficient in protecting a pipeline, yet may increase the corrosion of the adjacent pipelines or metal structure because of stray currents.
2. Capital investment and maintenance costs are more.
3. Special care must be taken that the metal is not over protected, i.e., the use of much higher potential than the open circuit voltage for the metal/metal ion couple in case of impressed current method and the higher anodic metal in the series must be avoided. Otherwise problems related to cathodic reactions like evolution of H2 or formation and accumulation of OH^- will take place.

Inspite of these disadvantages, cathodic protection has been widely used with success, when suitable precautions are taken.

POLYMERIC MATERIALS

INTRODUCTION

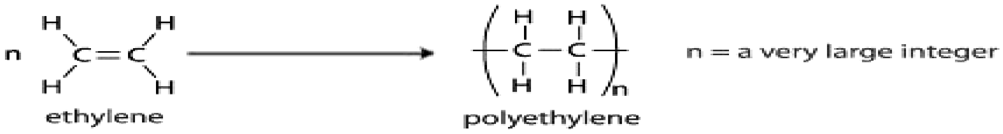
Polymers are the giant molecules produced by the combination of smaller units or molecules. Polymers posses the desirable properties like high strength, light weight, good flexibility, special electrical properties, resistance to chemicals, amenability for quick and mass production and fabrication into complex shapes in a wide variety of colours.

BASIC CONCEPTS

The word polymer is derived from the Greek words polu- meaning "many"; and meros meaning "part". The term was coined in 1833 by Joens Jakob Berzelius.

Many of small molecules (monomers) combine (with covelent bond chains) to form gaint molecule(s). This process is called polymerization. During the polymerization process, some chemical groups may be lost from each monomer.

For example ethylene under polymerization gives polyethylene.



- **Write a note on degree of polymerization.**

Degree of polymerization:

- **It is defined as the number of monomers units in a homo polymer.**
- **Most of the polymers are in the molecular mass range of 5,000 – 2, 00,000.**
- **But incase of hetero polymer, degree of polymerization (D.P) is defined as the ratio of total molecular weight of a polymer to molecular weight of each repeating unit.**
- **In the above equation, ‘n’ is the degree of polymerization.**

$$Dp = \frac{\text{Total Molecular Weight of the Polymer}}{\text{Molecular Weight of Monomeric Unit}} = \frac{Mn}{Mo}$$

$$Mn = Mo\ .\ Dp$$

Mn = Total molecular weight of the polymer

Mo = Molecular weight of monomeric unit

Dp = Degree of Polmerisation

Depending on the degree (No. of Monomer units) of polymerisation, there are two types of polymers.

1. Oligopolymers: Those polymers whose degree of polymerisation is less than 600 are called oligopolymers. These polymers do not possess the engineering properties.

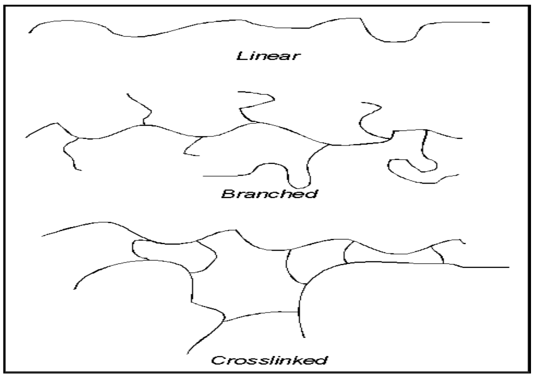
2. Highpolymers: When the degree of polymerisation of a polymer is more than 600, it is called *high polymer.* High polymers possess the desired engineering properties and widely used.

- **Write a note on Functionality of polymers.**

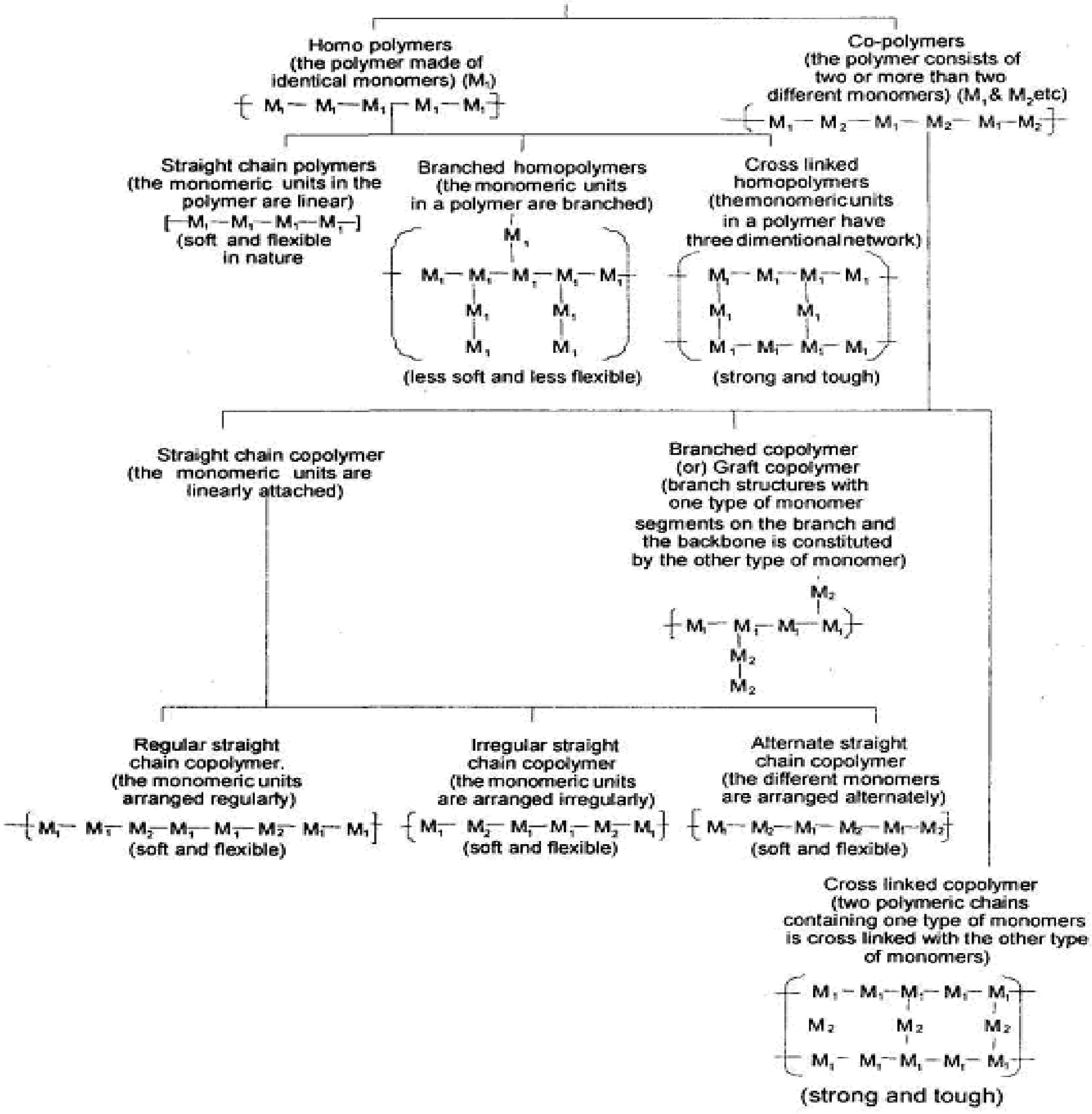
Functionality:

- **The number of active bonding sites of a monomer is referred to as its functionality.**
- **So, the monomer should have two reactive sites (or) bonding sites to form a polymer.**
- **Different types of polymer structure can be obtained based on the functionality of monomeric units.**
- **Case-I:**
  - **Linear or straight chain molecules are formed by the combination of bifunctional monomers which contain two reactive sites.**
  - **Linear polymers are obtained by strong covalent bonds. But different chains are held together by secondary weak vanderwaal’s forces.**
- **Case-II:**
  - **Branched chain polymers are obtained by the combination of trifunctional monomer and bifunctional monomers.**
- **Case-III:**

- **Three dimensional network polymers are obtained by the combination of polyfunctional monomers.**
- **In such polymeric molecules, the movement of monomer units is prevented by strong cross links.**

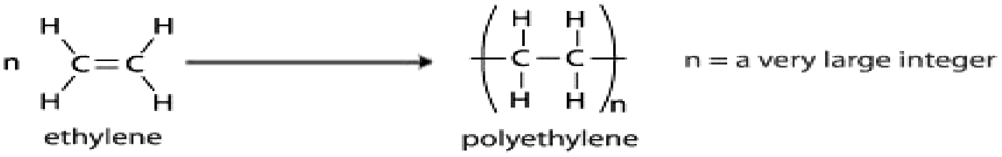


Types of polymers based on nature of polymerisation

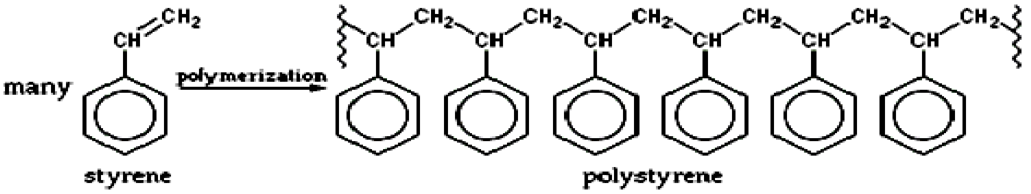


•Write a note on Methods of polymerization (or) •Note on addition and condensation polymerization with examples (or) • Classification of polymers based on methods of polymerization.

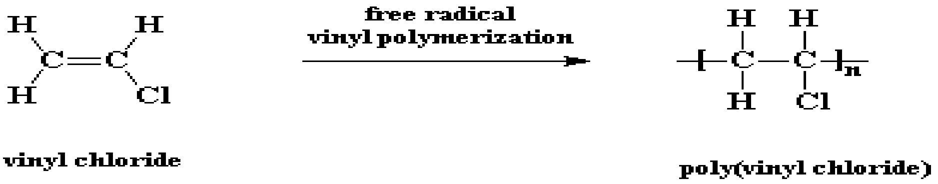
- **Based on their methods of synthesis:**
  - **1.Addition polymerization:**
    - **In this polymerization process, the monomers add together by repeating addition without formation of byproducts to form polymer.**
    - **It can takes place through formation of either radicals or ionic species such as carboanions and carbocations.**
    - **Ex:PE, PS, PVC etc.**
    - **Ex.1 Polyethylene(PE)**



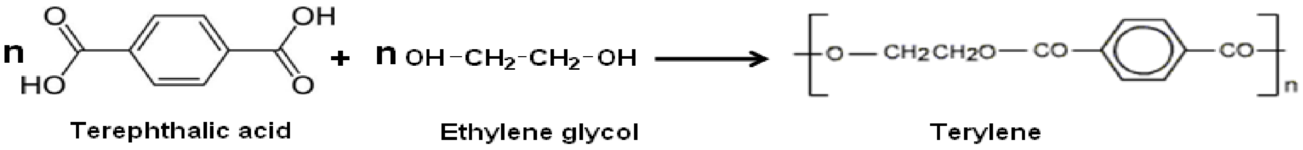
Ex.2 Polystyrene



Ex.3 Polyvinyl chloride



- **2.Condensation polymerization:**
  - **When the molecules of same monomers or different monomers simply linked together by the formation of low molecular weight byproducts, this process is called as condensation polymerization.**
  - **Ex: Nylon-6, Terylene etc.**
  - **Ex: 1.Nylon-6,**
  - **Ex: 1.Terylene.**



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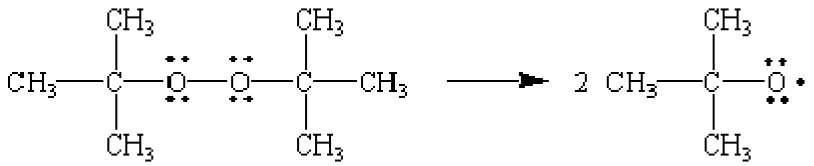
•Differences between Addition & Condensation Polymerisation

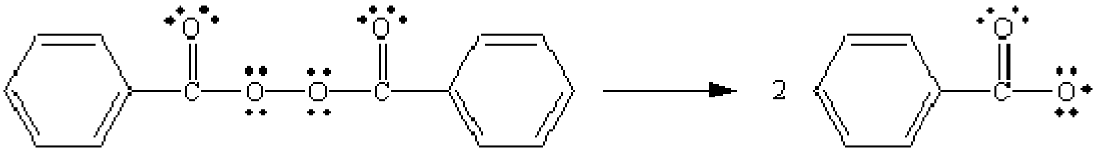
Addition Polymerisation	Condensation Polymerisation
1. Polymer is formed by addition of monomers with out elimination of small molecules.	1. Polymer is formed by two or more monomers by the elimination of small molecules.
2. No by-products are formed.	2. By products are formed.
3. Homo chain polymers, generally thermo plastic is obtained.	3. Hetero chain polymer either thermo plastic or thermo setting can be obtained.
4. The growth of chain is at one active centre.	4. The growth of chain occurs at minimum of two active centres.

❖ Free radical chain polymerisation:

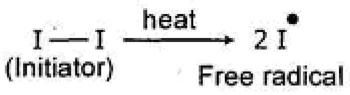
The free radical chain polymerisation can be of homolytic fission process or heteterolytic fission process.

The *initiator* undergoes homolytic fission to produce *free radicals,* which initiates and propagates (rapid chain growth) the polymerisation reaction as given below. Ex. Bynzoyl peroxide(di-tert-butyl peroxide)

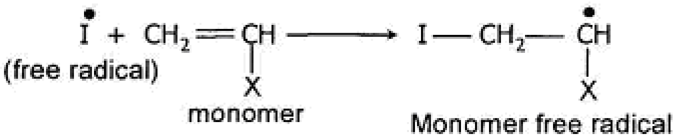




i. Initiation: **Initiators are unstable compounds and undergo *homolytic fission* to produce *free radicals* which react with *n* electrons of the monomer to produce *monomer free radical.***
Theory:

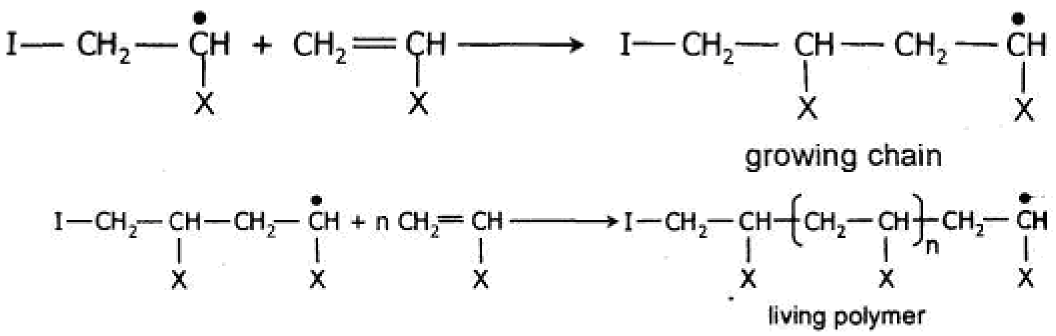


$$\underset{\text{(Initiator)}}{I—I} \xrightarrow{\text{heat}} \underset{\text{Free radical}}{2\overset{\bullet}{I}}$$



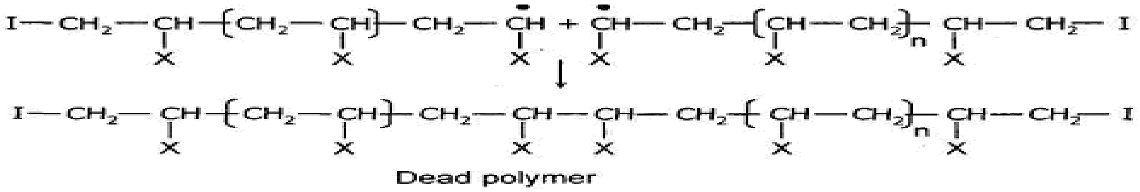
$$\underset{\text{(free radical)}}{\overset{\bullet}{I}} + \underset{\text{monomer}}{CH_2{=}\underset{X}{\underset{|}{CH}}} \longrightarrow \underset{\text{Monomer free radical}}{I—CH_2—\underset{X}{\underset{|}{\overset{\bullet}{CH}}}}$$

ii. Propagation: **The monomer free radical reacts with a number of monomers rapidly resulting the chain growth with free radical site at the end of the chain producing a *living polymer.* By adding fresh monomers to the living polymer with free radical site, again chain growth starts. Hence it is known as *living polymer.***
Theory:

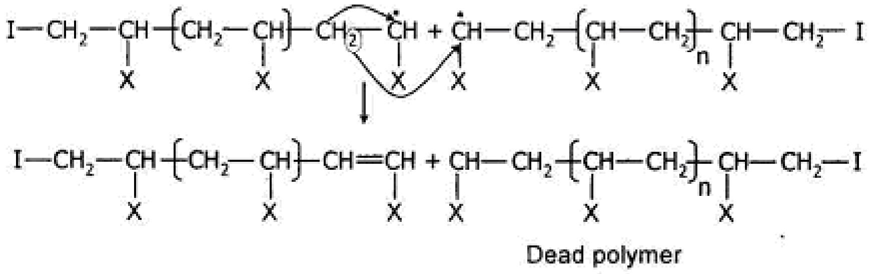


<u>iii. Termination:</u> Termination (to stop chain growth) of the growing polymer chain is carried by *'coupling'* and *'disproportionatiori*, resulting the dead polymer. In *coupling,* the collision of two growing chains causes the union of the two chains at their free radical site producing *a dead polymer.*

Theory:

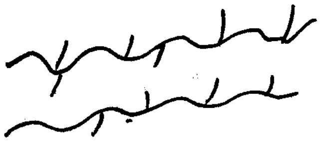
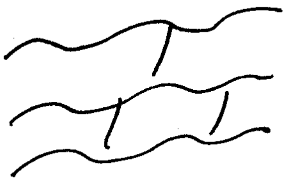


In termination by disproportionate, H from the growing chain is abstracted by the other growing chain, utilising the lone electron for getting stabilised, while the chain which has donated the H gets stabilised by the formation of a double bond.



Classification of polymers

(i) Based on structure / shape

Polymer	structure	Example
a) Linear		HDPE (High Density polythene)
b) Branched		L.D.PE (Low density polyethene
c) cross linked		XLPE (cross-linked polycthene Rubbes Theemosets)

(ii) Based on Origin

a) Natural polymer : Carbohydeates, proteins etc

(b) synthetic polymer : plasties rubbers fibers etc

(iii) Based on Conductance

(a) insulators : Mostly all Polymers are insulators

(b) conducting polymer: Polyaniline, Poly Pyrrole

(iv) Based on Number of monomers

(a) Homo polymer :- Ex polyethene, PVC

(b) Co. polymer :- BuNa-S, BuNa-N

(v) Based on type of monomers

(a) polar : (PET, Nylon)

(b) non polar : (PE, PP)

(vi) Based on Response for heat.

(a) Thermoplastics [soft on heating & hard on cooling] PE, PVC

(b) Thermosets [No change on heating] Bakelite,

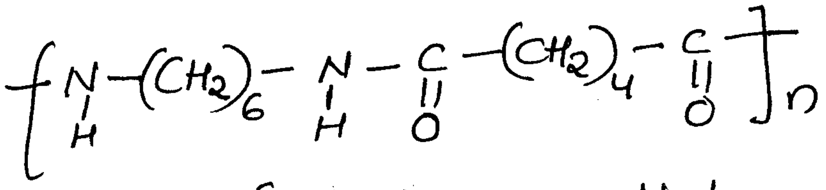
(vii) Based on Environment friendly nature

Biodegradable :

Durable :

Nylon-6:6: It is made by the condensation polymerization of hexamethylene diamine and adipic acid 1:1 molar ratio without an external strong acid.

$$H_2N-(CH_2)_6-NH_2 + nHOOC-(CH_2)_4COOH \xrightarrow[-2nH_2O]{\text{Polymerization}}$$



$$\left[\underset{H}{\underset{|}{N}}-(CH_2)_6-\underset{H}{\underset{|}{N}}-\underset{O}{\underset{||}{C}}-(CH_2)_4-\underset{O}{\underset{||}{C}} \right]_n$$

Nylon 6:6 [(or) Poly hexamethylene adipamide]

Properties: 1) The structure of nylons are linear

(2) The molecular chains are held together by Hydrogen bonds. Thus, nylon have high crystallinity,

which imparts high strength, high melting point, elasticity, toughness, abrasion resistance and retention of good mechanical properties upto 125°C

(3) They are also sterilisable

(4) Nylons are polar polymers, they have good hydrocarbon resistance

Applications

(1) Nylon-6:6 is used as fibers, which find use in making socks, ~~under~~. carpets etc

(2) Nylon-6:6 is used in mechanical engineering for applications like Gears, Bearings, Bushes, Cams etc

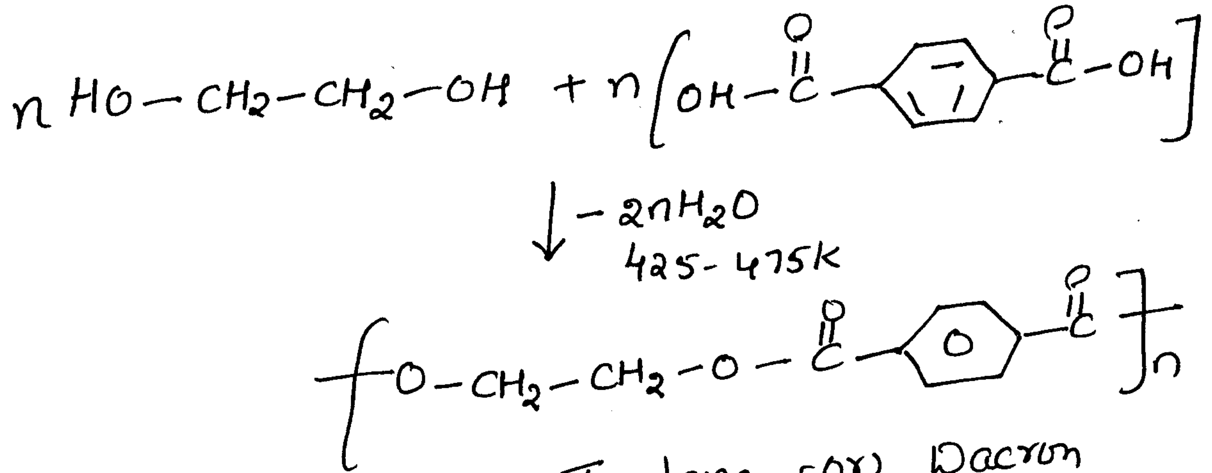
(3) Nylon-6:6 is also used for jacketing electrical ware to provide a tough, abrasion resistant outer cover to protect the primary electrical insulation.

(4) ~~Nat~~ Nylon 6 is mainly used for making tyre cords. filament for ropes bristles for tooth brushes.

Terylene [Poly Ethylene Terephthalate

Polyethylene terphthalate is a copolymer and its monomer units are terephthalic acid [Benzene-1,4-dicarboxylic acid] and Ethylene glycol [Ethane-1,2 diol]

(2) it It is commercially known as Terylene



Terylene (or) Dacron

Properties

1. It has high mechanical strength and dimension stability
2. It is a very strong fibre will suffer little loss in strength when wet
3. It is stable in the temperature range of 40 - 100°C
4. It is elastic in nature
5. It shows creep and abrasion resistance and good insulating properties.
6. It shows low water absorption and at room temp, it is resistant to water, dilute acids, salts, aliphatic and aromatic hydrocarbons and alcohols.

Applications of Terylene

1. It is used for making video and audio tapes.
2. It is used in textile industry for making hard wear clothes and other dress materials
3. It is used for making clear bottles for food and beverages
4. The fibre may be blended with cotton and wool to form another fabrics, like terycot and terywool.

PLASTICS:

The word plastic itself comes from the Greek word plasticos, which means to be able to be shaped or moulded by heat.

Advantages of plastics over other traditional materials (like wood, metals, glass etc):

1) Plastics are available in attractive colours.
2) They do not undergo corrosion.
3) They are not affected by insects.
4) They are light in weight
5) They are cheap.
6) They can be moulded into any shape easily.
7) They are chemically inert.
8) They have good abrasion resistance.
9) They are good insulators of heat and electricity.

Disadvantages:

1. Recycling of plastic is a costly process.
2. Plastic undergo biodegradation after long time.
3. Incineration of plastic causes pollution.
4. Plastics are derived from petrochemicals and their production causes environmental pollution.
5. Plastics are low heat resistance and brittle. They undergo deformation at low temperatures.

Differences between Thermo Plastics &Thermo Setting plastics :

S.no	THERMOPLASTIC RESINS	THERMOSET RESINS
1.	These resins become soft on heating and rigid on cooling.	During fabrication process these resins are moulded. Once moulded or shapened, they can not be softened.
2.	Thermoplastic resins are formed by chain polymerisation.	Thermoset resins are formed by step polymerisation.
3.	They can be reshaped.	They cannot be reshaped
4.	These plastics can be reclaimed from waste.	They cannot be reclaimed from waste.
5.	Thermoplastic resins are soft, weak and less brittle.	Thermoset resins are hard, strong and more brittle.
6.	These resins are usually soluble in organic solvents. Eg: Polyethylene, polyvinyl chloride etc.	Due to strong bonds and cross links, they are insoluble in almost all organic solvents. Eg: Bakelite, Nylon etc.

Write preparation, properties and applications of i) PVC.

i)PVC (Poly vinyl chloride):

Preparation: Poly vinyl chloride is produced by heating vinyl chloride in presence of benzyl peroxide or H2O2.

Properties: PVC is colourless, odourless, non-inflammable and chemically inert powder. Pure resin possesses greater stiffness and rigidity compared to poly ethylene. It is brittle in nature.

Applications: or Uses:

1. P.V.C is mainly used as an insulating material.
2. It is used for making table clothes, rain coats, toys, tool handles, radio components, etc.
3. It is used for making pipes, hoses, etc.
4. It is used for making helmets, refrigerator components, etc.
5. It is used in making cycle and automobile parts.

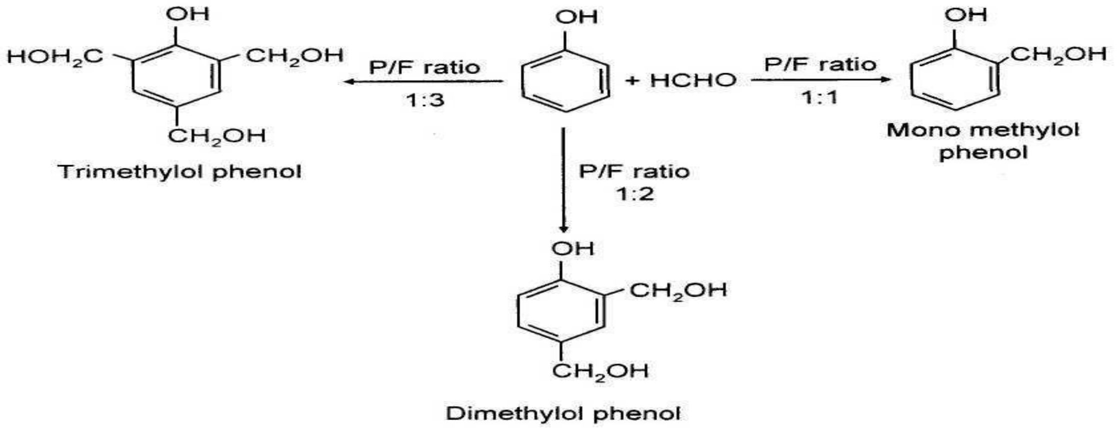
Phenol formaldehyde resins or Bakelite :

Bakelite is a condensation polymer of phenol and formaldehyde

Preparation :

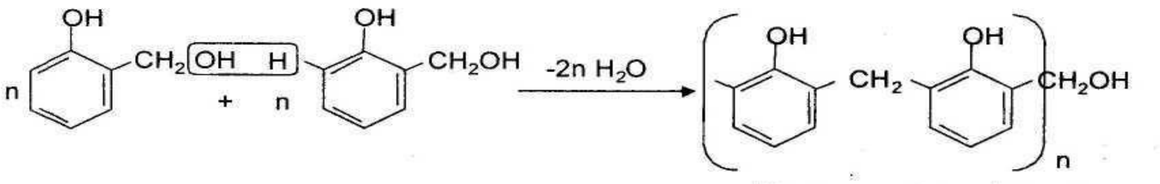
I) stage:

Phenol is made to react with formaldehyde in presence of acid / alkali to produce non - polymeric mono, di, and tri methylol phenols depending on the phenol formaldehyde ratio (P/F ratio)

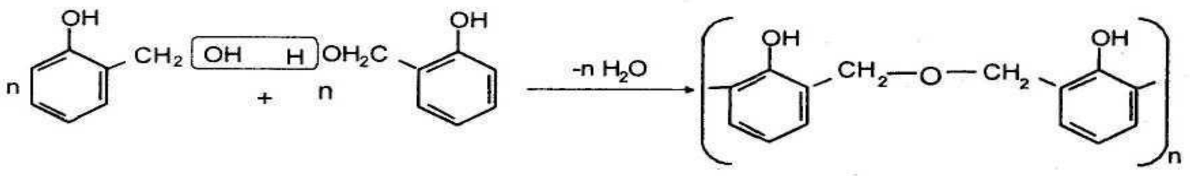


II) Stage:

The mono, di, and tri methylol phenols are heated to produce two types of straight chain resins by condensation of the methylol group with hydrogen atom of benzene ring or another methylol group.

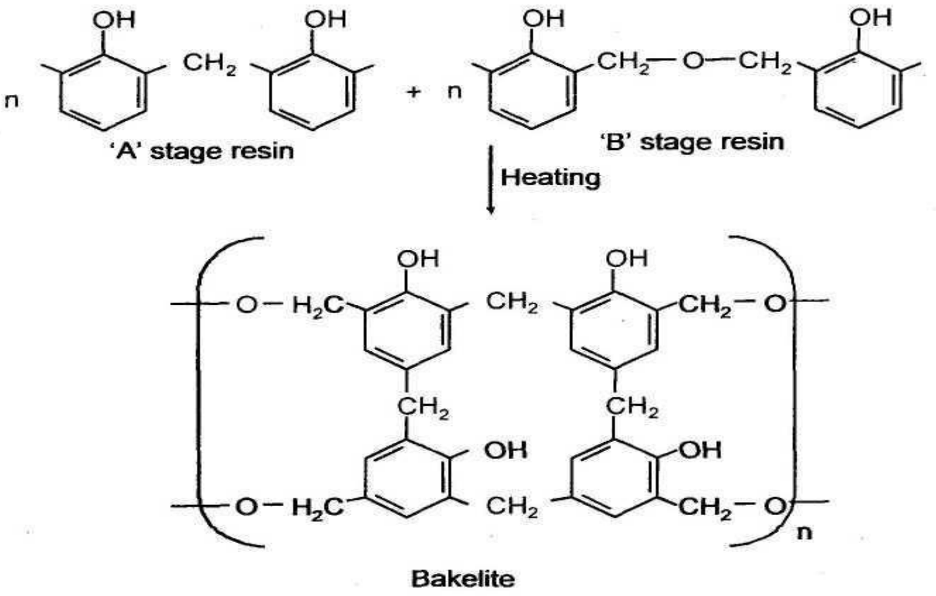


'A' stage resin/resol/Novolac



'B' stage resin/resol/Novolac

III) Stage: This stage of preparation includes heating of 'A' stage resin and 'B' stage resin together, which develops cross linking and bakelite plastic resin is produced.



Properties:

1. Bakelite plastic resin is hard, rigid, and strong.
2. It is a scratch resistant and water resistant polymer.
3. Bakelite has got good chemical resistance, resistant to acids, salts and any organic solvents, but it is attacked by alkalis due to the presence of- OH group.
4. It is a good anion exchanging resin, exchanges - OH group with any other anion.
5. Bakelite is an excellent electrical insulator.
6. It is a very good adhesive.
7. Bakelite has very good corrosion resistance, resistant to atmospheric conditions like O2, CO2, moisture, light, U.V.radiation etc.

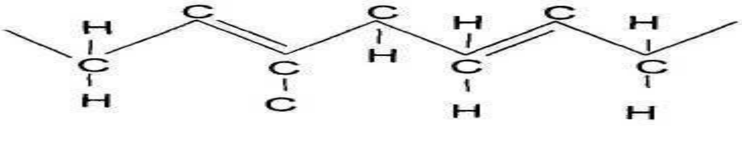
Engineering applications: Bakelite is used widely.

1. For making electrical insulator parts like switches, switch boards, heater handles etc.
2. For making moulded articles like telephone parts, cabinets for radio and television.
3. For making tarpaulins, wood laminates and glass laminates.
4. As an anion exchanger in water purification by ion exchange method in boilers.
5. As an adhesive (binder) for grinding wheels etc.
6. In paints and varnishes.
7. For making bearings used in propeller shafts, paper industry and rolling mills.

ELASTOMERS:

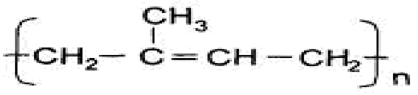
Definition: Elastomers are high polymers that undergo very long elongation (500 – 1000%) under stress, yet regain original size fully on released of stress. Those rubbers are therefore referred to as elastomers.

The property of elastomers is known as elasticity. This arises due to the coiled structure of elastomers.



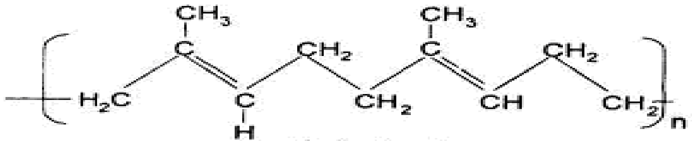
Natural rubber:

Natural rubber is found in several species of rubber trees grown in tropical countries, of these Hevea brasiliensis is the most important source of natural rubber and the rubber obtained from this is known as “Hevea” rubber. Rubber is stored in the form of white fluid called ‘latex’ behind the bark of the rubber tree.

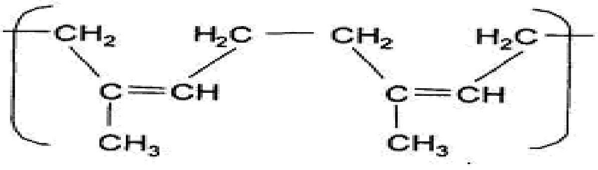


$$\left[-CH_2-\overset{CH_3}{\overset{|}{C}}=CH-CH_2-\right]_n$$

Isoprene unit of natural rubber



Coiled helix structure of trans-polyisoprene



Structure of Cis-polyisoprene

Natural rubber is a high polymer of isoprene (2-methyl-1,3-butadiene).

Polyisoprene exists in two geometric isomers cis and trans forms.

Natural rubber is soft and has cis-configuration while ‘Guttapercha’ or, ‘Ballata’ has trans configuration.

Defects (or) Disadvantages of natural rubber:

The natural rubber obtained from latex cannot be used in industries because it has some defects.

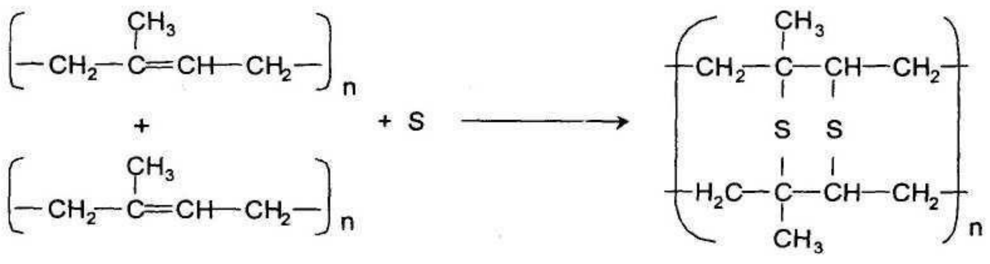
1. It becomes soft and sticky during summer and it become hard and brittle during winter.
2. It swells in water and easily attacked by organic solvents, acids bases and non – polar solvents like mineral oils, benzene and gasoline.
3. It possesses poor tensile strength.
4. Atmospheric oxygen attacks the rubber and produces epoxides which gives bad smell, stick nature to rubber.

Vulcanisation:

Some chemicals like elemental sulphur, hydrogen sulphide, sulphur dichloride, benzoyl chloride and zinc oxide are added to both natural and synthetic rubbers. The most important vulcaniser is *sulphur* which combines chemically at the *double bonds* of the different chains producing *sulphur cross linkings*, imparting *strength* increases, the brittleness also increases.

2 to 4% Sulphur addition gives soft elastic rubber.

When sulphur content is more than 30%, we get hard rubber called 'Ebonite' (or) vulcanite.

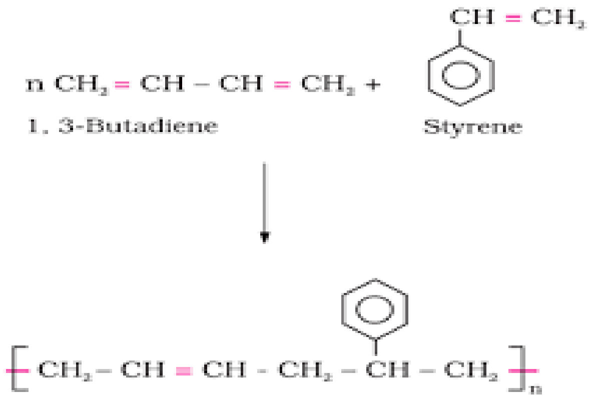


Write preparation, properties and applications of i) Buna-S ii) Thiokol

BUNA-S [or] SBR,[or] GRS) Styrene Butadiene Rubber) gov. regulated styrene rubber or *Ameripol*

BUNA - S is otherwise called styrene rubber or *GRS* (Government Rubber Styrene) or Ameripol.
BUNA - S stands for the composition of the monomers and catalyst.
BU stands for Butadiene - monomer
NA stands for Sodium - catalyst
S stands for Styrene - monomer
Buna-S is the most important synthetic rubber it is obtained by the co-polymerization of butadiene and styrene using sodium as a catalyst.

Preparation :



Butadiene - styrene copolymer

Properties:

1. Styrene rubber is a strong and tough polymer.
2. It is vulcanised by sulphur monochloride (S2CI2) or sulphur.
3. It resembles natural rubber in processing characteristics and quality of finished products.
4. BUNA - S possess excellent abrasion resistance.
5. It is a good electrical insulator.
6. It is resistant to chemicals but swells in oils and attacked by even traces of ozone, present in the atmosphere.
7. Styrene rubber possess high load bearing capacity and resilience.

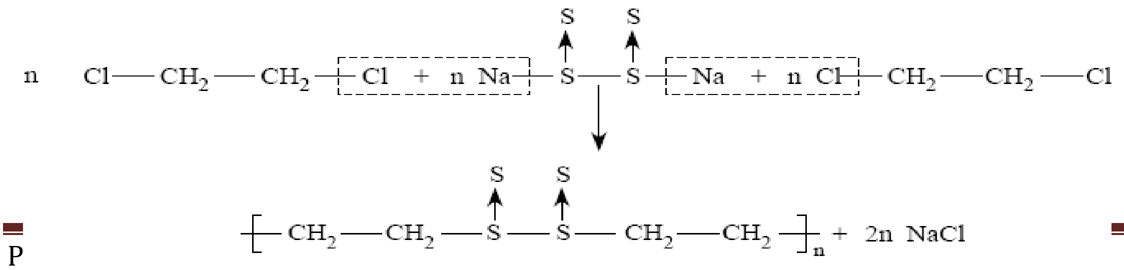
Applications:

1. Major application of styrene rubber is in the manufacture of tyres.
2. It is used in the footwear industry for making shoe soles and footwear components.
3. It is also used for making wires and cable insulations.
4. The other applications of styrene rubber are for the production of floor files, tank linings in chemical industries and as adhesives.

Thiokol (Polysulphide Rubber or GR-P):

Polysulphide rubbers are the condensation product of ethylene dichloride and sodium tetra sulphide.

Preparation :



Thiokol (yellow solid)

Properties:

Thiokol rubber possess strength and impermeability to gases.

This rubber cannot be vulcanized and it cannot form hard rubber.

Possess good resistance to mineral oils,fuels,oxygen,solvents,ozone and sunlight.

It is also resistant to the action of petrol lubricants and organic solvents

Applications:

Fabrics coated with thiokol are used for barrage balloons,life rafts and jackets.

Thiokols are used for lining for canveying gasolin and oil.

Used for making gaskets and seals for printing rolls.

Thiokol mixed with oxidizing agents in used as a fuel in rocket engine.

CONDUCTING POLYMERS:

A polymer which conducts electricity is called conducting polymer.

Eg :- Polyaniline, polyacetylene, polypyrrole, etc

They are classified into two types : 1) Intrinsically conducting polymers.
2) Extrinsically conducting polymers

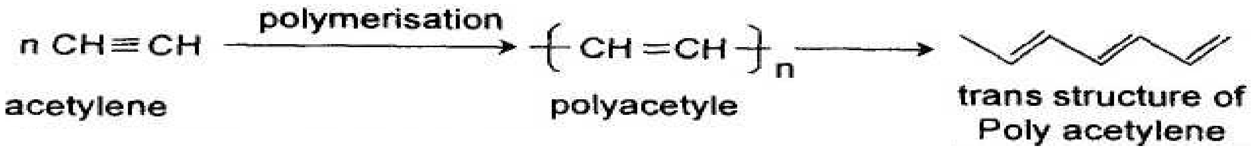
1. Intrinsically conducting polymers:

These have extensive conjugation in the backbone which is responsible for conductance. These polymers can be divided into two :

a) Conducting polymers having conjugated π – electrons in the backbone:

eg :- polyacetylene, polyaniline etc.

These type of polymers due to overlapping of conjugated π – electrons over the entire backbone results in the formation of valence bonds as well as conduction bands, which extends over the entire polymer molecule. But since the valence band and the conduction band are separated by a significant band gap, conductivity of these polymers is not very high.



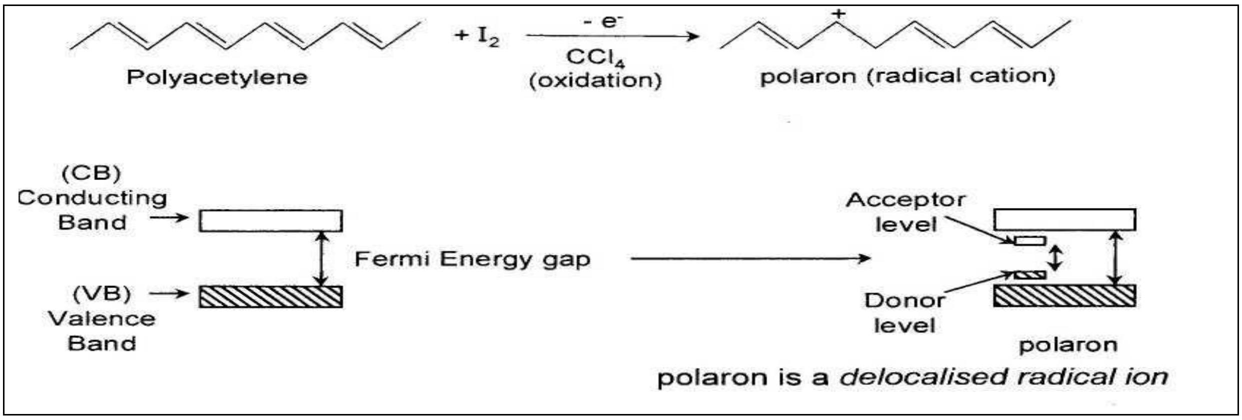
b) Doped conducting polymers:

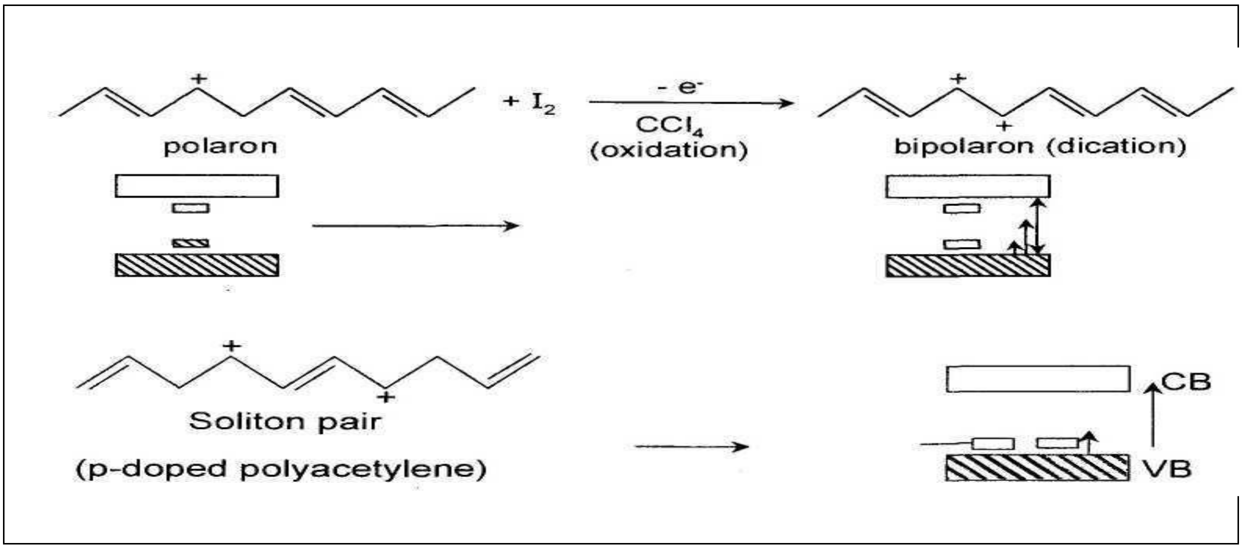
Conductivities of polymers having conjugated π – electrons in the backbone can be increased by creating either +ve or –ve charges on the polymer backbone by oxidation or reduction. This process is called doping.

It can be done in two ways :

i)Oxidative doping (P – doping):

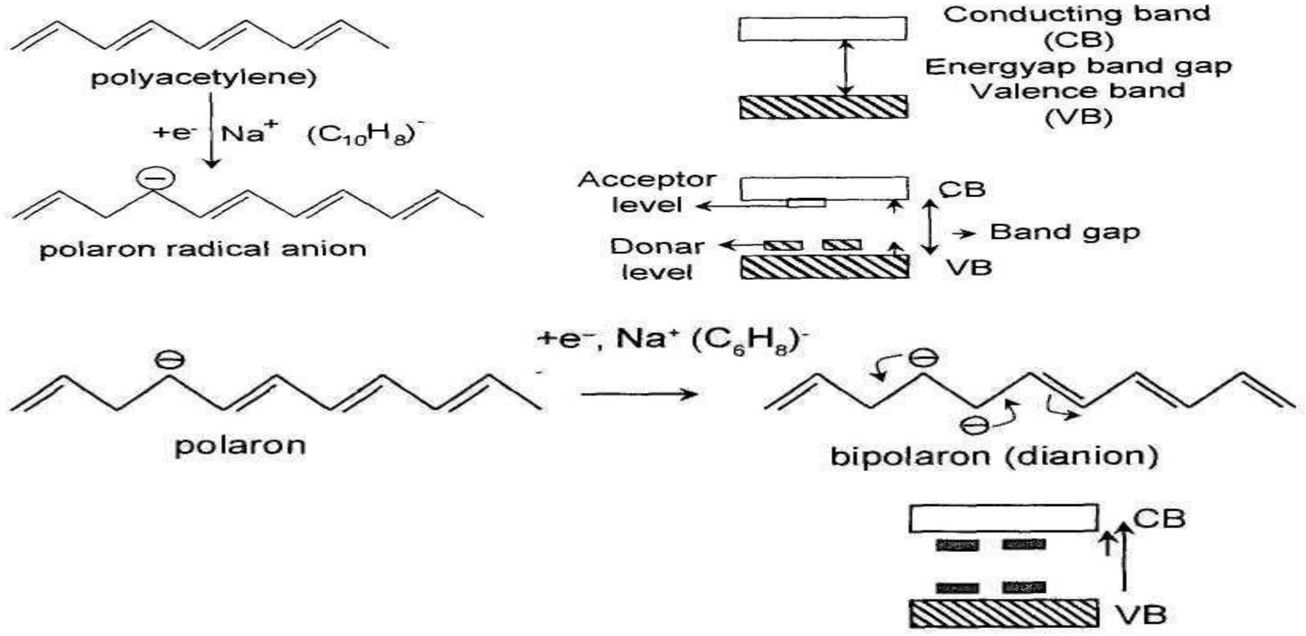
It involves treating the conjugated polymer with a Lewis acid like FeCl3 thereby oxidation takes place and +ve charges are created on the back bone.





ii) Reductive doping (n – doping):

It involves treating the polymer with a Lewis base like RNH2 thereby reduction takes place and -ve charges are created on the polymer back bone.



2.Extrinsically conducting polymers:

Some of the polymers conduct electricity due to externally added ingradients to them. They are of two types.

a) Polymers with conductive elements filled Polymers. b) Blended conducting polymers.

a).Polymers with conductive elements filled:

In these polymers, the polymer acts as a ‘binder’ and holds the conducting element added so that the polymer becomes a conductor. Examples of conductive elements are carbon black, metallic fibers, metallic oxides etc.

Minimum concentration of conductive element to be added so that the polymer becomes a conductor is called percolation threshold. The conductive elements added to create a conducting path in the polymer.

b).Blended conducting polymers:

These polymers are obtained by blending a conventional polymer with a conducting polymer.

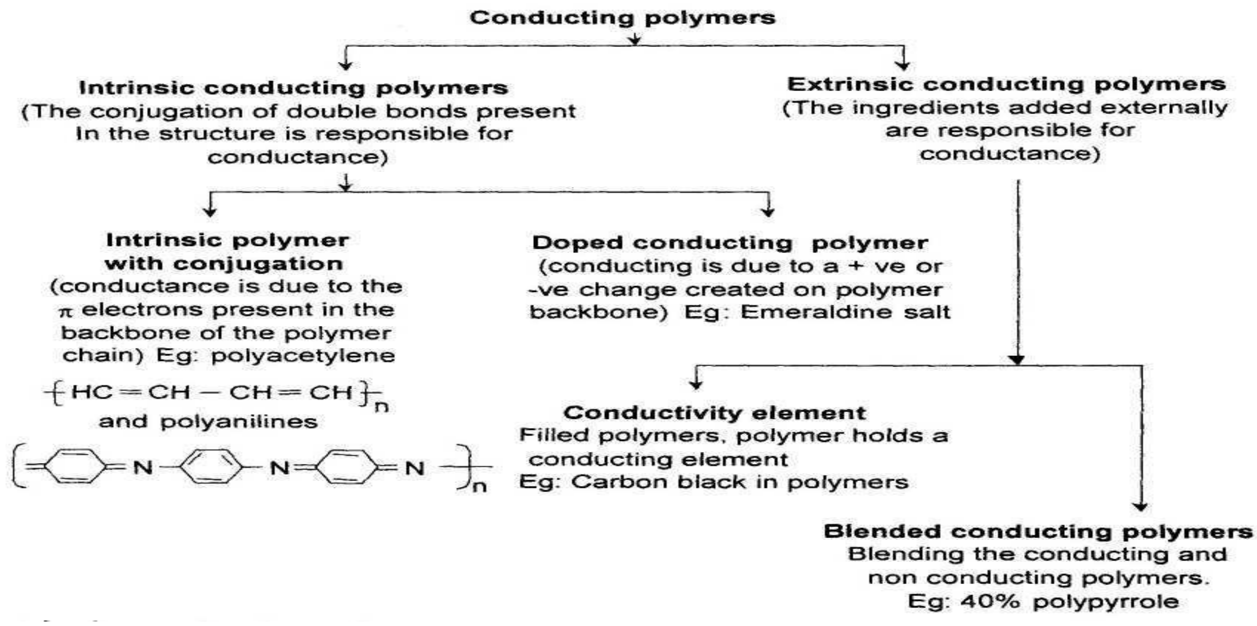
The polymer thus obtained has good chemical, physical, electrical properties and mechanical strength. Ex; 40% pyrrole when blended with a conventional polymer, the combination gives conducting polymer with good impact strength.

Applications of conducting polymers in biomedical devices:

- Conducting polymers are used in preparation of artificial devices like Heart valves, kidneys, and lungs.
- Poly methyl methacrylate is used as bone cement used for some fracture repairs.
- Poly methyl methacrylate is also used for artificial teeth.
- Used in preparation other medical devices include sutures, pins, screws used during surgery on bones, ankles, hands etc.
- They are used to prepare contact lenses which permit O_2 to the eyes. These lenses are called rigid gas permeable lenses (RGP).

Applications of conducting polymers in electronics:

- They are used in rechargeable batteries.
- They are used in analytical sensors of p^H, O_2, NO_2, SO_2, NH_3 etc.
- Used in photo voltaic cells. Ex; Al/polymer/Au.
- Used in telecommunication systems.
- Used in transistors and diodes.
- Used in solar cells.
- Used as wiring in air crafts and aerospace parts



Write a note on Biodegradable polymers.

- Biodegradation is the chemical breakdown of materials by physiological environment.
- Some polymers undergo degradation when exposed to moisture, heat, oxygen, ozone and micro-organism.
- These agents change the chemical structure of the polymer and lead to change in properties of polymer.
- Generally materials obtained from plants, animals and other living organism and synthetic materials similar to plant and animal material undergo degradation by microorganisms.

☑ Bio-degradable polymers:

→ Biodegradable polymers are defined as " The polymeric materials that undergoes degradation by environmental factors like, sunlight, temperature changes or by the action of micro-organisms like algae, fungi and bacteria".

→ They are easily compostable and recyclable.

→ Ex. polylactic acid, poly glycolic acid, poly vinyl alcohol etc.

☑ Types of Bio-degradable polymers:

Based on degradation they are of two types:

1. Naturally Biodegradable polymers: They are called as bio-polymers.

Ex. silk, wool, starch etc.

2. Synthetic Biodegradable polymers: They are of two sub types;

A. Biosynthetic polymers: They are produced by fermentation process by micro organisms.

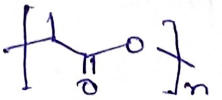
Ex. Albumin, Gelatin etc.

B. Synthetic: These polymers are derived from petroleum or biological sources. These polymers undergo degradation by micro organisms.

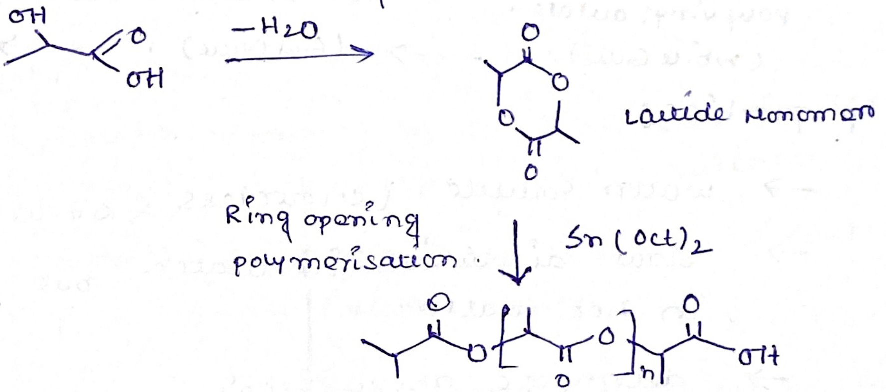
Ex. poly vinyl alcohol, PLA etc.

poly - Lactic acid (PLA):

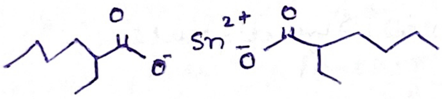
It is a biodegradable thermoplastic, aliphatic polyester derived from renewable resources such as corn-starch, tapioca products (roots, starch) and sugar cane.



(1). preparation: oligomerisation and catalytic dimerization of lactic acid results in the formation of lactide monomer, which undergoes polymerization in the presence of stannous octate catalyst to give PLA.



$Sn(Oct)_2$
≡



(2). Advantages:

(1). It is eco friendly.

(2). It has good mechanical and physical properties.

(3). It is biocompatible.

(4). It is nontoxic and can be metabolized by organisms.

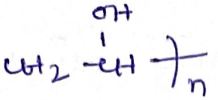
(3). Applications:

(1). PLA is used in making disposable packing materials, bottles, cups and food containers.

(2). It is widely used in orthopedic medical implants in the form of screws, plates, rods.

(3). production of biodegradable synthetic garments, hygienic products etc.

☒ Poly vinyl alcohol:

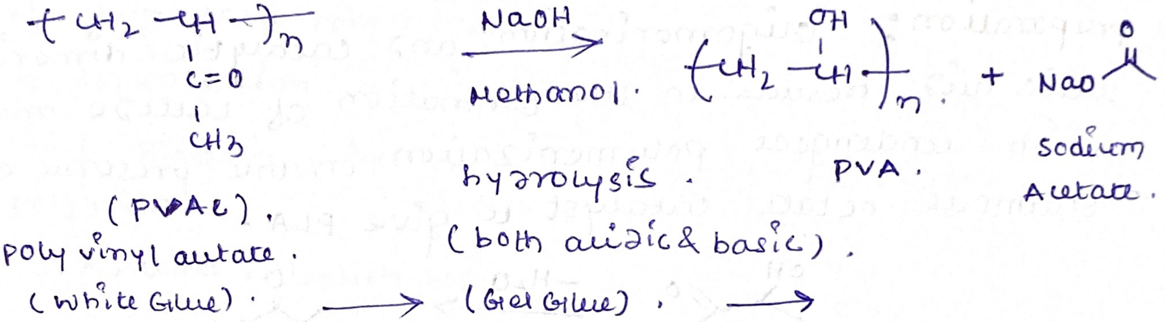


$-(CH_2-\overset{OH}{\overset{|}{CH}})_n-$

⇒ water soluble synthetic polymer.

⇒ posses excellent mechanical properties.

(1). preparation:



$-(CH_2-\underset{\underset{CH_3}{|}}{\underset{C=O}{|}}{CH})_n- \xrightarrow[\text{Methanol}]{NaOH} -(CH_2-\overset{OH}{\overset{|}{CH}})_n- + NaO\overset{O}{\overset{\|}{C}}CH_3$

(2). properties:

→ water soluble (colourless & odourless).

→ slow disolution in water but radidly disolute in hot water.

→ decompose above 250°C.

→ It is amorphous & crystalline.

(3). Applications:

(1). It is used in contact lenses.

(2). It is used in food packoging & pharmaceutical applications.

(3). used in textile industries like paper industry because of high chemical stability.

UNIT-4 Energy Resources

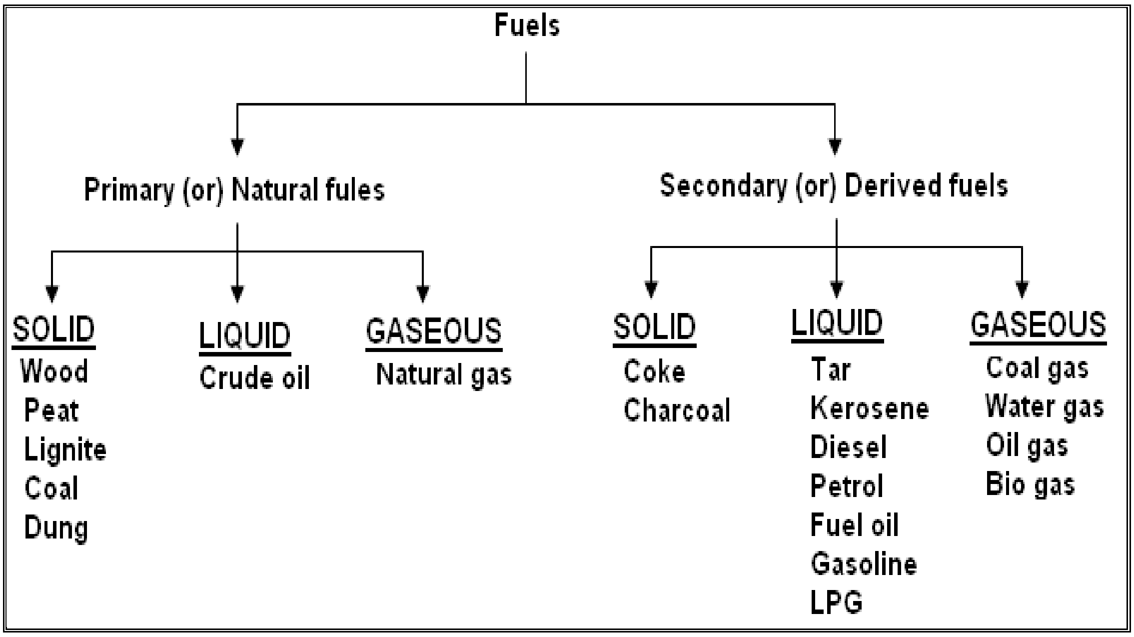
Φ Define a Fuel and Explain the classification of fuels with examples?

Fuel: Fuel is a combustible substance, containing carbon as main constituent, which on proper burning gives large amount of heat, which can be used economically for domestic and industrial purposes.

$$Fuel + O_2 \rightarrow \mathrm{Pr}oducts + Heat$$

Classification of fuels:

- ★ On the basis of occurrence fuels are classified into primary and secondary.
- ★ Again each one is divided into three types based on their physical state.
- ★ Primary fuels are found in nature. Secondary fuels are produced from primary fuels



Φ What are the characteristics of good fuel (or) Ideal fuel?

While selecting an ideal fuel for domestic or industrial purpose we should keep in mind that the fuel selected must possess the following characteristic properties.

1) It should possess high calorific value.
2) It should have proper ignition temperature. The ignition temperature of the fuel should neither be too low nor too high.
3) It should not produce poisonous products during combustion. In other words, it should not cause pollution o combustion.
4) It should have moderate rate of combustion.
5) Combustion should be easily controllable i.e., combustion of fuel should be easy to start or stop as and when required.
6) It should not leave behind much ash on combustion.
7) It should be easily available in plenty.
8) It should have low moisture content.
9) It should be cheap.
10) It should be easy to handle and transport.

Φ **Discuss comparison between solid, liquid and gaseous fuels?**

Solid fuel	Liquid fuel	Gaseous fuel
1. Slow combustion and not easy to control it	Quick combustion and can be controlled	Combustion is rapid and burning can be controlled
2. Transportation is difficult	Transportation is easy through pipelines	Transportation is easy through pipe lines and containers
3. Storage is safe	There is risk in storing	There is greatest risk in storing
4. Calorific value is comparatively low	Calorific value is comparatively higher	Calorific value is highest
5. Cannot be used in internal combustion engines	Can be used in internal combustion engines	Can be used in internal combustion engines to lesser extent
6. On burning ash and more smoke are produced.	No ash is produced but Some flue gases are produced	No ash and no smoke are produced
7. More air pollution	Less air pollution	Least air pollution

Calorific Value:

❖ **What is calorific value? Give their units?**

Calorific value: It is defined as the total amount of heat liberated, when unit mass or unit volume of the fuel is completely burnt in air or oxygen.

Units of heat:-

a) Calorie:- The amount of heat required to increase the temperature of 1 gm of water through one degree centigrade.

b) Kilocalorie:- It is equal to 1000 calories. The quantity of heat required to rise the temperature of 1 Kg of water through one degree centigrade.

1 K.cal = 1000 cals

c) British thermal unit (B.Th.U.):- The quantity of heat required to rise the temperature of 1 pound of water through one degree Farenheit.

1 B.Th.U = 252 cals = 0.252 K.cal

d) Centigrade heat unit (C.H.U):- The quantity of heat required to rise the temperature of one pound of water through one degree centigrade.

1 K. cal = 3.968 B.Th.U = 2.2 C.H.U

For solids or liquid fuel: Calorie/gm (cal/gm) (or) Kilocalorie/Kg (K.cal/Kg) (or) B.Th.U/lb

For gaseous fuels: Kilocalorie/cubic meter (K.cal/m^3) (or) B.Th.U/ft^3

- **Define HCV & LCV. Give relationship between HCV & LCV.**

HCV: [Higher Calorific Value]: It is defined as the total amount of heat liberated, when unit mass or unit volume of the fuel is completely burnt and the products of combustion are allowed to cool to room temperature.

Hydrogen is present in almost all the fuels. During determination of calorific value, hydrogen is converted into steam. Higher calorific value includes the latent heat of condensation of steam. HCV is also called Gross Calorific Value. [GCV].

LCV: [Lower Calorific Value]: It is defined as the total amount of heat liberated, when unit mass or unit volume of the fuel is completely burnt and the products of combustion are allowed to escape out into atmosphere.

LCV is also called Net Calorific Value [NCV].

Relationship between HCV & LCV:

LCV = HCV – latent heat of water vapour formed

Since 1 part by mass of hydrogen produces 9 parts by mass of water.

Hence LCV = HCV – (mass of hydrogen x 9 x latent heat of steam)

$$LCV = HCV - (0.09\,H \times 587)$$

Where, H is % of Hydrogen

Latent heat of steam = 587 K.cal/Kg

- **What is Dulongs formula? Derive an expression for theoretical calculation of Calorific value of fuel?**

According to Dulong, the calorific value of fuel is the sum of the calorific values of all the elements present.

The calorific values of different elements are:

The calorific value of Carbon = 8080 cal/g
The calorific value of Hydrogen = 34500 cal/g
The calorific value of Sulphur = 2240 cal/g

The oxygen, if present in fuel, is assumed to be present in combined form with hydrogen, i.e., in the form
of fixed hydrogen [H_2O].

The amount of hydrogen available for combustion = Total hydrogen – fixed hydrogen

Dulong’s formula for calorific value from the chemical composition of a fuel is:

$$\boxed{HCV = \frac{1}{100}\left\{ 8080\,(C) + 34500\left(H - \frac{O}{8}\right) + 2240\,(S) \right\}}$$

LIQUID FUELS:

❖ What are advantages and disadvantages of liquid fuels?

Advantages:

1) They posses higher calorific value per unit mass than solid fuels.
2) They burn without dust, ash, clinkers, etc.
3) Their firing is easier and also fire can be extinguished easily by stopping liquid fuel supply.
4) They are easy to transport through pipes.
5) They can be stored indefinitely without any loss.
6) They are clean in use and economic to handle.

Disadvantages:

1) The cost of liquid fuel is relatively much higher as compared to solid fuel.
2) Costly special storage tanks are required for storing liquid fuels.
3) There is a greater risk of five hazards, particularly, in case of highly inflammable and volatile liquid fuels. They give bad odour.

❖ Explain about Refining of crude oil (or) Petroleum:

- The crude oil is separated into various fractions by fractional distillation and finally converted into desired specific products.
- The process is called "refining of crude oil" and the plants set up for the purpose, are called the oil refineries.
- The process of refining involves the following three steps:

Step-1:- Separation of water (Cottrell's process):

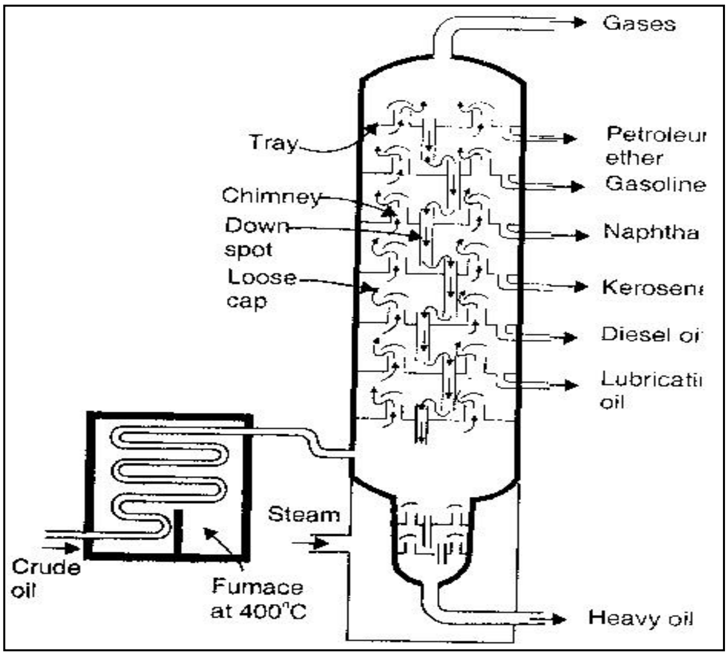
- The crude oil is in the form of stable emulsion of oil and salt water.
- Water is separated from oil by Cottrell's process.
- First the emulsified water along with salts dissolved, is removed by passing the crude oil between highly charged electrodes.
- The colloidal water droplets unite on positive electrode to form large drops which separate from oil.

Step-2:- Removal of harmful sulphur compounds:

- In this step, the oil is treated with copper oxide.
- Sulphur and its compounds are converted into solid copper sulphides.

Step-3:- Fractional distillation:

- The crude oil is then heated to about 400^{o}C in an iron retort, whereby all volatile constituents, except the residue are evaporated.
- The hot vapours are then passed up a "*fractionating column*", which is a tall cylindrical tower containing a number of horizontal stainless steel trays at short distances.
- Each tray is provided with small *chimney*, covered with a loose cap.
- As the vapours go up, they become gradually cooled and different products are obtained at different heights of the column.



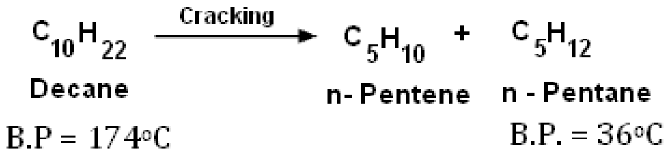
Various fractions with boiling range, approximate composition and uses :

Name of fraction	**Boiling range (°C)**	**Approximate Composition in terms of hydrocarbons containing C-atoms**	**Use**
Uncondensed gases	Below 30	$C_1 - C_4$	As domestic and industrial fuel under the name LPG
Petroleum ether	30 – 70	$C_5 - C_7$	As a Solvent
Gasoline or petrol	40 – 120	$C_5 - C_9$	Fuel for IC engines, Dry Cleaning solvent
Naphtha	120 – 180	$C_9 - C_{10}$	As solvent for paints and varnishes
Kerosene oil	180 – 250	$C_{10} - C_{16}$	Fuel for stoves, jet engine fuel and for preparing lab gas
Diesel oil	250 – 320	$C_{15} - C_{18}$	Diesel engine fuel
Heavy oil	320 – 400	$C_{17} - C_{30}$	Fuel for ships and for conversion to gasoline by cracking.

Cracking

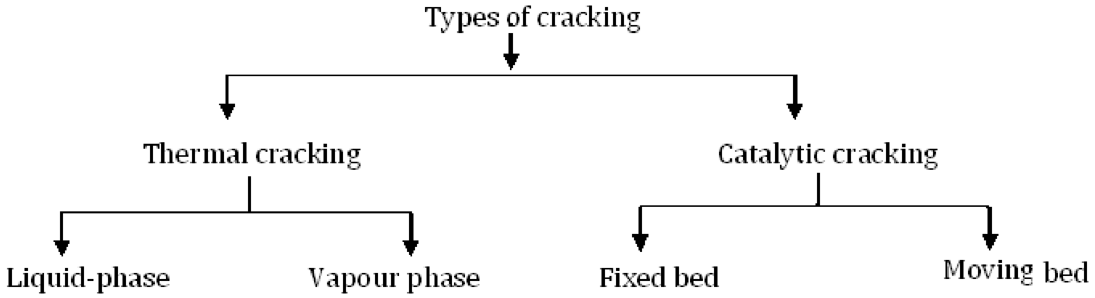
❖ **Write a note on Cracking:**

Cracking is defined as the decomposition of high molecular weight hydrocarbons of high boiling points into simpler, lower molecular weight hydrocarbons of low boiling points.



Importance:

- ✓ Of all the fractions obtained by fractionation of petroleum, gasoline has the highest demand as a motor fuel. It is called straight run gasoline.
- ✓ Also the quality of so-called 'straight-run' gasoline is not so good.
- ✓ Hence, it is used only after suitable blending.
- ✓ For instance, the petrol made by cracking has far better characteristics (as far as the IC engine is concerned) than 'straight-run' petrol.



Thermal cracking:

- ✓ When the heavy oils are subjected to high temperature and pressure in the absence of catalyst, it is called thermal cracking.
- ✓ In thermal cracking, the bigger hydrocarbon molecules break down to give smaller molecules of the paraffin, olefins plus some hydrogen.
- ✓ It is of two types' viz. liquid and vapour phase thermal cracking.

A comparative account of these two is given in the following table.

Catalytic cracking:

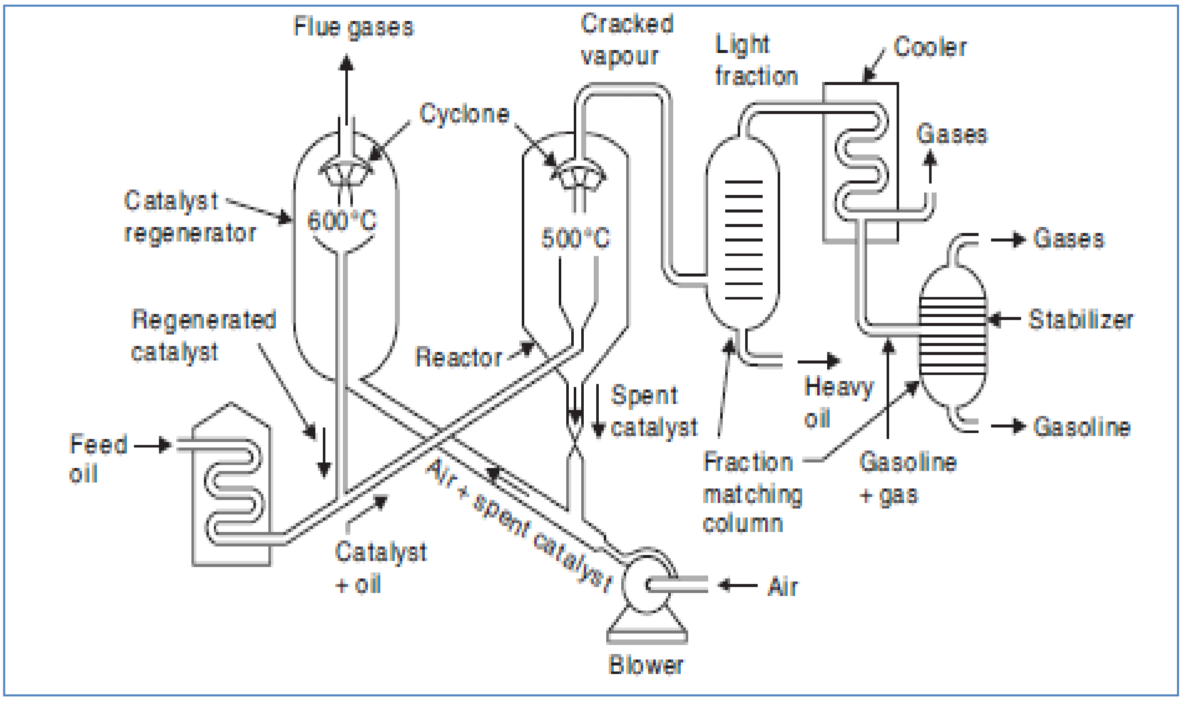
- The quality and quantity of gasoline produced by cracking can be greatly improved by using a suitable catalyst like aluminium silicate, $Al_2(SiO_3)_3$ or alumina, Al_2O_3.
- Catalytic cracking requires much lower temperatures and pressures compared to thermal cracking.
- There are two types of catalytic cracking, viz. Fixed bed and Moving bed catalytic cracking.

❖ **Explain with a neat diagram Moving bed catalytic cracking?**

- ➤ In moving bed catalytic cracking, the feed oil is first passed through a preheater.
- ➤ The pre-heated oil vapours along with very finely powdered catalyst are then passed in a reactor which is maintained at a temperature of 500°C for catalytic cracking.
- ➤ The cracked oil vapours are then passed to the fractionating column where heavy oil is separated.
- ➤ The vapours are then passed through the cooler where gasoline condenses along with some gases.
- ➤ This is then sent to a stabilizer where the dissolved gases are removed and pure gasoline is recovered.

- The main components along with their functions are discussed with the help of the figure.

1. Cyclone allows only the cracked oil vapours to pass on to the ‘fractionating column’, but retains all the catalyst powder in the reactor itself.
2. The catalyst powder gradually becomes heavier, due to coating with carbon, and settles to the bottom, from where it is forced by an air blast to regenerator (maintained at 600°C).
3. In regenerator, carbon is burnt and the regenerated catalyst then flows through stand-pipe for mixing with fresh batch of incoming cracking oil.



- **What are the Advantages of catalytic cracking over thermal cracking?**

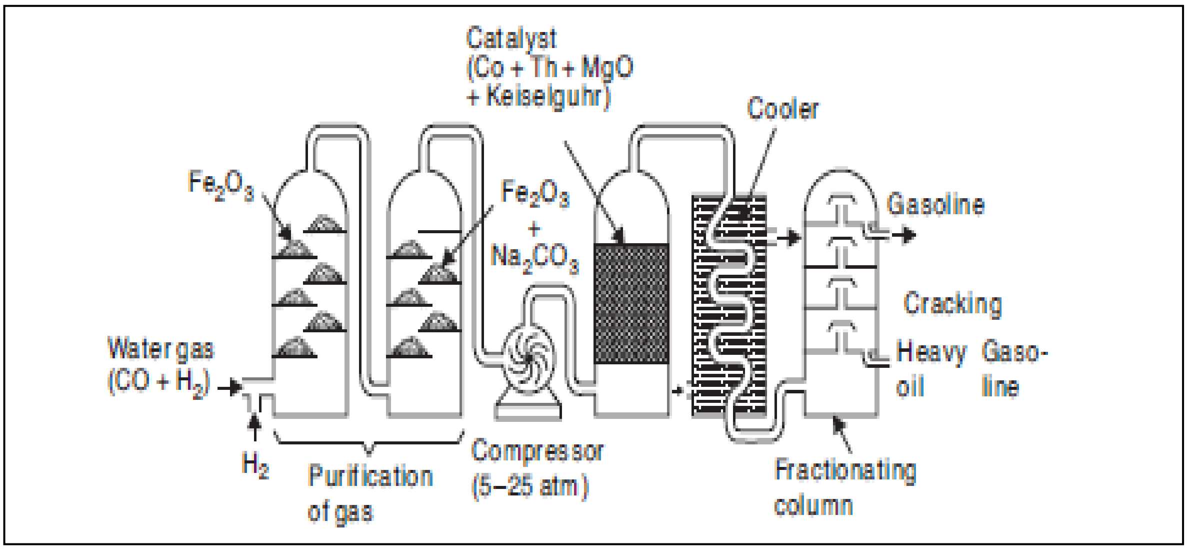
Catalytic cracking has a number of advantages:

1. The production cost is very less since high temperatures and high pressures are not needed.
2. The yield of petrol is higher.
3. The quality of petrol produced is better.
4. No external fuel is necessary for cracking. The heat for cracking is derived by burning the carbon deposited on the catalyst.
5. The product contains less sulphur compounds.
6. The percentage of gum and gum forming compounds is very low.

The octane number of cracked gasoline is higher compared to straight-run gasoline. It is due to presence of branched paraffins and aromatic hydrocarbons in cracked gasoline.

❖ Discuss Fischer-Tropsch method of manufacture of Synthetic Petrol?

Water gas (CO+H 2), produced by passing steam over preheated (at 1200 C) hard coke, is mixed with hydrogen. The gas is purified by passing through FeO (to remove H2S)and then into a mixture of Fe2O3 + Na2CO3 (to remove organic sulphur compounds). The purified gas is compressed to pressure of 30 atmospheres and then led through a convertor containing a catalyst, which is a mixture of 100 parts of cobalt, 5 parts of thoria, 8 parts of magnesia, and 200 parts of keiselguhar-earth, maintained at about 200-300 ° C. A mixture of saturated and unsaturated hydrocarbons results: The reaction is exothermic as such the hot gaseous mixture is led to a cooler, where a liquid resembling crude oil is obtained. The crude oil thus obtained is then fractionated to yield: (i) gasoline, and (ii) high- boiling heavy oil. The heavy oil is reused for cracking to get more gasoline.



KNOCKING

- ✓ The characteristic rattling sound produced in internal combustion engine due to immature ignition is known as knocking.
- ✓ This situation occurs when compression ratio exceeds certain limit.
- ✓ Fuel mixture is heated to beyond ignition temperature which leads prior combustion than the sparking ignition.

Influence of chemical structure on fuel knocking:

- ★ As the length of the carbon chain increase, knocking tendency increases.
  Ex: n- butane < n – pentane < n – hexane < n – heptane
- ★ Straight chain paraffins have more knocking property than branched chain alkanes.
  Ex: 2, 2 – dimethyl pentane < 2- methyl hexane < n- heptane
- ★ Aromatic compounds like benzene and toluene have poor knocking property.
- ★ In general, the order of knocking property of various compounds is
  Aromatic < Cyclo paraffins < Olefins < Branched alkanes < Straight chain alkanes.

16) Explain about Petrol Knocking : [Gasoline knocking]:

The performance of motor car is measured in terms of Km/L of petrol, which depends on the quality of the fuel.

Important method of obtaining more power from petrol is increasing the compression ratio of the engine.

Compression ratio of engine = Intial volume of petrol and air mixture sucked into cylinder / Final volume of petrol and air mixture after compression.

Increase in the compression ratio of the engine, increases the efficiency of the engine. Knocking is defined as the production of shock wave in an IC engine due to explosive combustion of mixture of petrol and air which increases compression ratio beyond a certain value leading to rattle sound.

17) Explain about Diesel knocking?

Knocking in diesel engine occur due to ignition delay which is caused by the chemical nature of hydrocarbons in diesel i.e; straight chain hydrocarbons have shorter ignition delay than branched and aromatics hydrocarbons.

Ignition delay is caused because time is required for vapourization of fuel and raising the temperature of the vapour to its ignition temperature i.e; accumulation of of fuel in the engine which leads to explosive combustion. This is called diesel knocking.

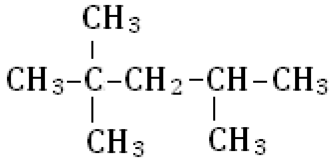
❖ Define Octane number? Explain in detailed.

- Anti knocking property of a fuel is expressed in terms of octane number.
- n – Heptane knocks very badly and an anti knocking property value zero is assigned to it where as iso octane has very high anti knocking property. So, its value is assigned as 100.

$CH_3-CH_2-CH_2-CH_2-CH_2-CH_2-CH_3$

n - heptane

Anti knocking value = 0



$$CH_3-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-CH_2-\underset{\underset{CH_3}{|}}{CH}-CH_3$$

Iso octane

Anti knocking value = 100

- **Octane number is defined as the percentage of iso octane in a mixture of iso octane and n- heptane which has same knocking characteristics as that of test fuel under same set of conditions.**
  Ex: Octane number of test petrol is supposing 77. It means that the knocking properties of the test petrol are similar to that of a fuel which contains 77% iso octane and 23% n – heptane.
- Higher the octane number, greater is the anti knocking property of fuel (good fuel).

Example	Octane number
Benzene	106
Iso pentane	90
Cyclo hexane	77
n – pentane	62
n – hexane	26

20) Define Cetane number? Explain in detailed.

- Quality of diesel is expressed in terms of Cetane number.
- If the diesel undergoes ignition as soon as it is injected, it is good fuel.
- It should have very short interval between injection and ignition.

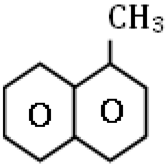
- The hydrocarbon Cetane (n – hexa decane) has a very short ignition delay and an arbitrary value of 100 has been assigned to it where as α – methyl naphthalene has very long ignition delay and hence 0 value is assigned to it.

$CH_3-(CH_2)_{14}-CH_3$

n - hexa decane

Cetane

Anti knocking value = 100



α - Methyl Naphthalene

Anti knocking value = 0

- **Cetane number of a diesel fuel may be defined as the percentage of Cetane in a mixture of Cetane and α – methyl naphthalene which has same ignition characteristics of test fuel under same set of conditions.**
- Cetane number of various hydro carbons is in the following order.
  Aromatics < Branched chain alkanes < Alkenes < Cyclo paraffins < n- alkanes
- The hydrocarbon with good Cetane number has poor octane number. A good fuel to diesel engine is a bad fuel to petrol engine.

Φ Differentiate Octane number and Cetane number.

	Octane number		Cetane number
1.	Octane referred for petrol	1.	This is referred for diesel
2.	Petrol with straight chain alkanes has lower octane number.	2.	Diesel with straight chain alkanes has higher cetane number.
3.	Low octane petrol in petrol engine produces loud cracking noise.	3.	Low cetane diseal in diesel/engine produces rattling metals noise and intese vibrations.
4.	Sudden combustion of hydrocarbons produces knocking in petrol engine.	4.	Delay in combustion causes knocking in diesel engine.
5.	Combustion decreasing chemicals are added in petrol to increase octane number.	5.	Combustion rate increasing chemicals added in diesel to increase cetane number.
6.	Octane number is considered to lower mol. wt. alkanes	6.	This is considered for mainly higher mol.wt. alkanes.

Gaseous fuels:

Gaseous fuels occur in nature, besides being manufactured from solid and liquid fuels.

❖ What are the advantages and disadvantages of gaseous fuels ?

Gaseous fuels due to ease and flexibility of their applications, possess the following advantages over solid or liquid fuels :

1) They can be conveyed easily through pipelines to the actual place of need, thereby eliminating manual labour in transportation.
2) They can be lighted at ease.
3) They have high heat contents and hence help us in having higher temperatures.
4) They can be pre-heated by the heat of hot waste gases, thereby affecting economy in heat.
5) Their combustion can readily by controlled for change in demand like oxidizing or reducing atmosphere, length flame, temperature, etc.
6) They are clean in use.
7) They do not require any special burner.

8) They burn without any shoot, or smoke and ashes.
9) They are free from impurities found in solid and liquid fuels.

Disadvantages:

1) Very large storage tanks are needed.
2) They are highly inflammable, so chances of fire hazards in their use is high.

Φ Write a short note on Natural gas.

- ✓ Natural gas is obtained from wells dug in the oil bearing regions .
- ✓ When natural gas occurs along with petroleum in oil wells it is called '*wet gas'*.
- ✓ The wet gas is treated to remove propane, propene , butane and butene which are used as LPG.
- ✓ On the other hand when the gas is associated with crude oil, it is called as '*dry gas'*.
- ✓ The natural gas is purified to remove objectionable ingredients such as water, dust, H_2S, CO_2, N_2 and heavier liquefiable hydrocarbons.
- ✓ The approximate composition of natural gas is CH_4 = 70-90%; C_6H_6 = 5-10%; H_2 = 3%; and the remainder = $CO+CO_2$
- ✓ Calorific value =12000-14000 Kcal/m^3

Uses:

- ✓ It is an excellent domestic fuel and can be conveyed over very large distances in pipe lines .
- ✓ A large number of chemicals are synthesized from natural gas
- ✓ It is also used as raw material for the manufacture of carbon black and hydrogen
- ✓ Synthetic proteins is obtained by micro biological fermentation of methane

❖ Write a short note on CNG (Compressed natural gas).

- CNG is natural gas compressed to a high pressure of about 1000 atmospheres.
- It is an odour less , non toxic gaseous mixture .
- CNG is measured in units of Gasolin Gallon Equivalent (GGE).
- The composition of CNG is CH_4 (90%), Other constituents are ethane ,propane , gases like N_2, CO etc..

Propreties:

- Light wight ,gaseous fuel. It mixes with air easily .
- It has a high auto-ignition temperature (540^0C) and narrow range of flammability.
- CNG does not contaminate with lubricating oils, thus increases the life of the IC engine .
- It requires more space for storage .
- The calorific value of CNG is 900KJ/mole

Uses:

1. Majorly used as fuel in automobiles like cars,autos,trucks,buses etc..
2. It is also used as fuel for locomotive diesel generators to generate electricity, that drive the motors of trains.

❖ Write a short note on LPG (Liquified petroleum gas).

- It is also called as Bottled Gas (or) Refinery Gas.
- LPG is obtained as a by-product during the cracking of heavy oils or from natural gas.
- The main constituents of LPG are n-butane, iso-butane, butylene and propane
- LPG is supplied under pressure in containers under the trade name like Indane, Bharat gas, H.P etc..
- LPG is dehydrated and desulphurised.
- Its Calorific value is about 27800 Kcal/m^3.
- LPG consists of hydrocarbons of such volatility that they can exist as gas under atmospheric pressure but can be readily liquefied under pressure.

Uses:

1. The largest use is as domestic fuel.
2. This is also used widely as an industrial fuel
3. LPG is used as a fuel in certain class of vehicles like trucks and tractors.
4. LPG leaded with tetramethyl lead can be used as the railway diesel locomotives

Disadvantage: Handling has to be done extremely carefully to avoid hazards.

- **Write a note on Biodiesel?**

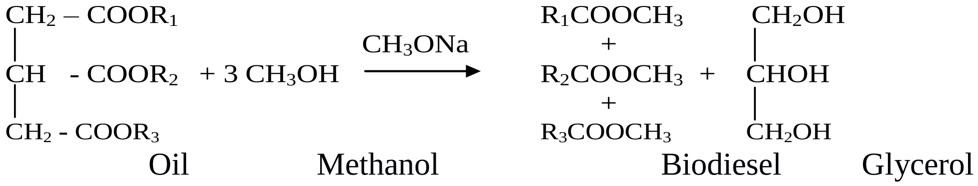
Definition :

Chemically biodiesel is the mixture of methyl esters of long chain carboxylic acids. Biodiesel is obtained by transesterification of vegetable oil or animal fats with methyl alcohol using catalyst sodium metal or sodium methoxide. (Transesterification is the process of converting one ester to another ester).

Reaction for Biodiesel Formation :

During the chemical conversion of vegetable oil to biodiesel we get water soluble glycerol and a small amount of sodium soaps. The water soluble part can be easily separated from biodiesel by washing the mixture with water. The alkaline sodium methoxide catalyst, saponifies some small amount of oil to give soap.

Vegetable Oil + Methanol + Catalyst ⇌ Biodiesel + Glycerol



$$\begin{array}{l} CH_2-COOR_1 \\ | \\ CH\ -COOR_2 \\ | \\ CH_2-COOR_3 \end{array} + 3\,CH_3OH \xrightarrow{CH_3ONa} \begin{array}{c} R_1COOCH_3 \\ + \\ R_2COOCH_3 \\ + \\ R_3COOCH_3 \end{array} + \begin{array}{l} CH_2OH \\ | \\ CHOH \\ | \\ CH_2OH \end{array}$$

Compounds present in biodiesel are like,

methyl palmitate	$H_3C - (CH_2)_{14} - COOCH_3$
methyl stearate	$H_3C - (CH_2)_{16} - COOCH_3$
methyl oleate	$H_3C - (CH_2)_7 - CH = CH - (CH_2)_7 - COOCH_3$
methyl linoleate	$H_3C - (CH_2)_5 - (CH = CH)_2 - (CH_2)_7 - COOCH_3$

Advantages of Biodiesel :

1) Biodiesel is cheaper, as it is manufactured from cheap, nonedible or waste oil or animal fats.
2) It has high cetane numbers 46 to 54 and high C.V. of about 40 kJ/gm.
3) It is regenerative and environment friendly.
4) It does not give out particulate and CO pollutants, as 0 atoms in biodiesel help for complete combustion.
5) It has certain extent of lubricity, due to higher oiliness of the esters.
6) Its use provides good market to vegetable oils and reduces our dependence on diesel on foreign countries, saving currency.
7) It is clean to use biodiesel in diesel engines.

SMART MATERIALS AND LUBRICANTS

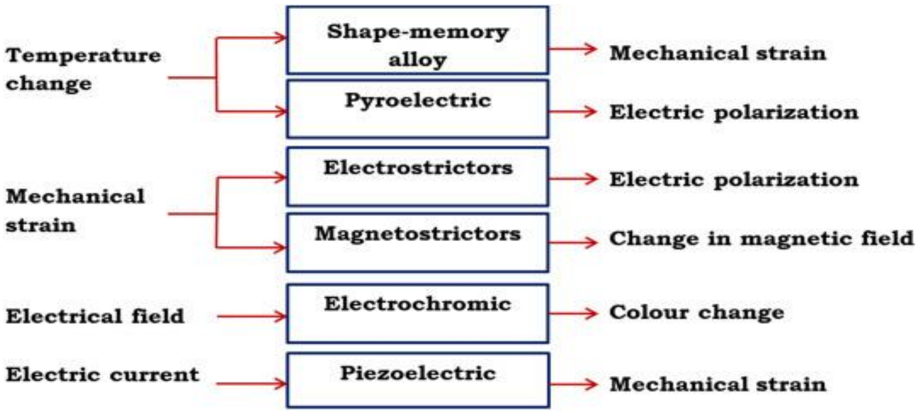
Smart materials: these materials are also called intelligent or responsive materials. Smart materials are those in which properties can be significantly changed in a controlled fashion by external stimuli, such as stress, moisture, electric or magnetic fields, light temperature, PH, chemical or biological components.

(**Stimulus** —stress, strain, light, electric field, temperature and pressure, etc.

Response —motion or change in optical properties, modulus, surface tension, piezoelectricity etc.)

- Five common fundamental characteristics were defined as distinguishing a smart material from the more traditional materials such as transiency, immediacy, self-actuation, directness and selectivity.
- Smart materials are either passive or active.
- The active smart materials have intrinsic ability to transducer energy, where as passive do not.
  Eg: Piezoelectric materials are active smart materials while fibre optic is passive.
- Generally sensor and actuator are fundamental functions of smart structures for sensing and controlling purposes.
- **Sensor:** Sensor is a device used for the conversion of physical events or characteristics into the electric signals. This is a hardware device that takes input from environment and gives to the system by converting it.
  Eg: a thermometer takes the temperature as physical characteristic and then converts it into electric signals for the system.
- **Actuator:** Actuator is a device that converts the electric signals into the physical events or characterstics. It takes the input from the system and gives output to the environment.
  Eg: Motors and heaters are some of the commonly used actuators.

Some smart materials:

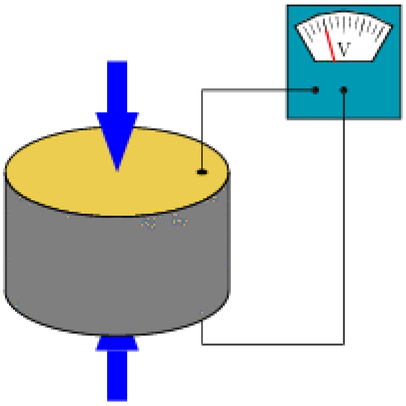


1) **Piezoelectric materials :** the materials that produce a voltage when stress is applied are called piezoelectric materials. Since this effect also applies in the reverse manner, a voltage across the sample will produce stress within the sample. Suitably designed structures made

from these materials can therefore be made that bend, expand or contract when a voltage is applied.

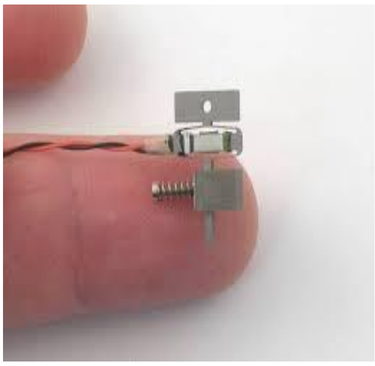
Example: Quartz, BaTiO3,GaPO4

The piezoelectric effect describes the relation between a mechanical stress and an electrical voltage in solids.



Applications of Piezo electric effect:

In lighters or portable sparkers with a piezofuzea sudden and strong pressure is used to produce a voltage. The spark then ignites the gas.



2) Shape memory alloys:

Shape memory alloys and shape memory polymers are thermoresponsive materials where deformation can be induced and recovered through temperature changes.

Example: Nickel Titanium alloy that “remembers” its original, cold- forged shape By heating it returns back to their deformed shape.

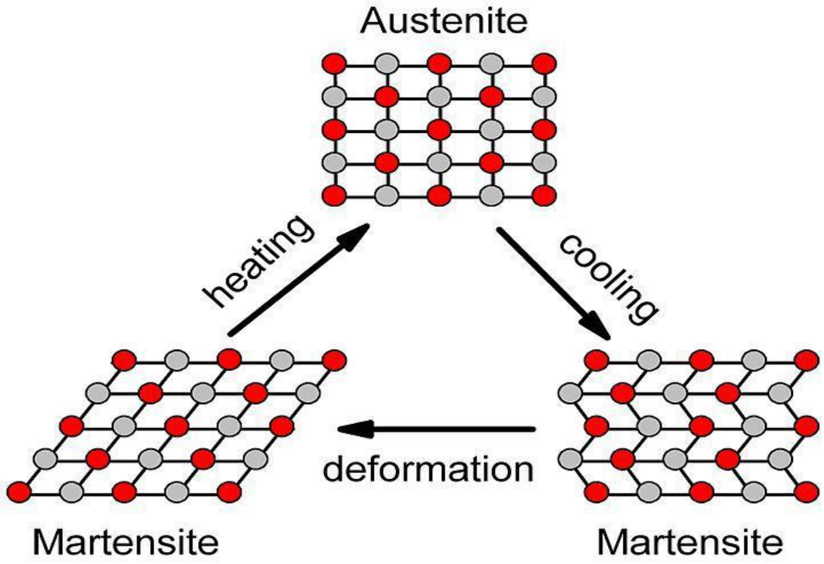
SMAs are materials which can revert back to original shape & size on cooling by undergoing phase transformations.

Examples: NiTiNOL (thermal),
NiMnGa, Fe-Pd, Terfenol-D (Magnetic)

Applications:

Dental Implants (healing of broken bones; misaligned teeth)

Shape Memory Alloys (SMAs) are a unique class of metal alloys that can recover apparent permanent strains when they are heated above a certain temperature.



3) Magnetostrictive materials:

Magneto striction is a property of ferromagnetic materials that causes them to change their shape or dimensions during the process of magnetization.

Ex: Fe, Co, Terfenol–D (UStransducers, sonar, soundbug)

Actuators and Sensors: Magnetostrictive transducers -Convert magnetic energy in to mechanical energy

4) Electro strictive materials: In the presence of electric field, these materials experience a strain (mechanicalchange) which is proportional to strength of electric field.

Eg: Lead Lanthanum Zirconate Titanate (PLZT), Lead Magnesium Niobate (PMN)

5) Thermoelectric materials: These materials when subjected to any temperature difference; they producechange in voltage and vice versa

6) Rheological materials: Materials which can change state instantly through the application of an electric ormagnetic charge/field.

Eg: Silicates, Food additives etc;

7) Chromic materials: These materials have very excellent property to change their color when subjected toexternal impetus (temperature, lights, electric field).

Eg: A variety of dyes, pigments, oxides, organic molecules, conjugated conducting polymers etc;

showchromic phenomenon.

Types: Photochromic, Thermochromic; Electrochromic, Magnetochromic, piezo chromic etc

8) **pH sensitive materials:** This kind of smart materials have properties to change their color when their will be the change in the acidity of the liquid. These kind of smart materials can be use to indicates the corrosionby mixing it with the paint.

TYPE OF SMART MATERIAL	INPUT	OUTPUT
Piezoelectric	**Bending**	**Potential difference**
Electrostrictive	**Potential difference**	**Deformation**
Magnetostrictive	**Magnetic field**	**Deformation**
Thermoelectric	**Temperature**	**Potential difference**
Shape memory alloys	**Temperature**	**Deformation**
Chromic materials	**Radiation**	**Color change**
Rheological materials	**Electric or magnetic field**	**Physical state change**
pH sensitive materials	**pH**	**Color change**

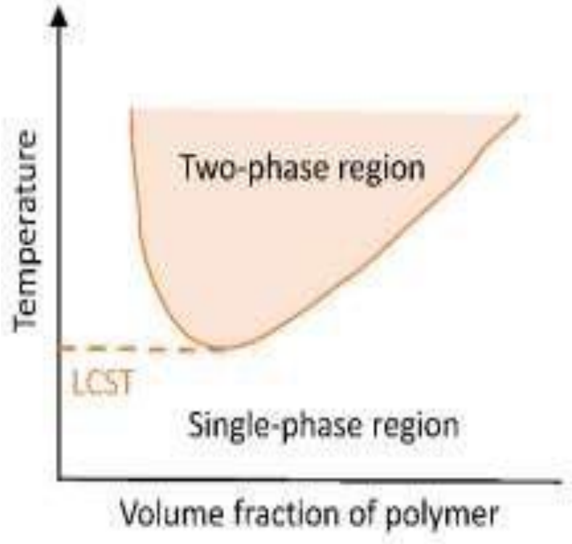
Applications of smart materials:

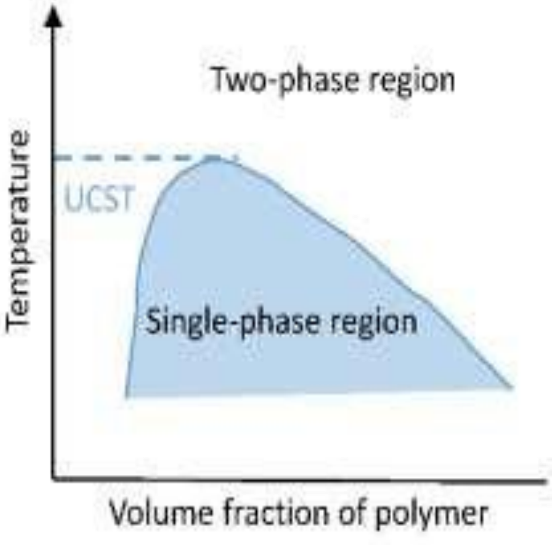
- Some major field of application of smart materials are:
- **Aeronautics:** In aircraft or automotive structure to reduce the vibrations we use piezoelectric materials andshape memory alloy to control the spatial goal.
- **Structural Health Monitoring:** The embedding smart sensors within the structure to monitor the damage and stress and can reduce the repairing cost and can increase their life.

- **In Nuclear industries:** Smart materials and smart structure offers great range of application to the nuclear filed from enhancing safety measures life-cycle cost reduction and performance improvement.
- **In the Civil Engineering:** Smart materials are able to detect the cracks in concrete structure, vibration of tall buildings, to predict the choc waves in the concrete and metallic structure. Can analyze innovative seismic retrofit of buildings and bridges.
- **In Medical field:** For artificial muscle application, polyelectrolyte gels are used, in which a polymer matrix swollen with a solvent that can expand or contract when exposed to an electric field.

Thermo responsive polymers (Temperature-responisve)

- The polymers which exhibit drastic and discontinuous changes in their physical properties with temperature are called thermoresponsive polymers
- These are contrast to temperature –sensitive materials which change their properties continuously with environmental conditions.
- Usually, the temperature responsive term is concerned with solubility property in a given solvent, but not only limited to solubility.
- Based on miscibility gap of the polymers in the phase diagram, polymers can have either lower critical solution temperature (LCST) or upper critical solution temperature (UCST).
- The polymers which are miscible (Single phase) below the phase transition temperature and immiscible (two phases) above the phase transition temperature come under LCST type.
- The polymers which are immiscible (two phases) below the phase transition temperature and miscible (Single phase) above the phase transition temperature come under UCST type.

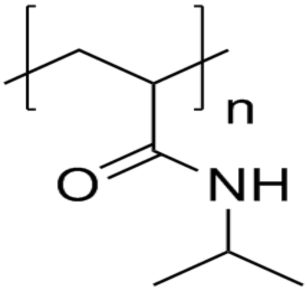




❖ POLY ACRYLAMIDE:

- The most commonly studied and first reported thermoresponsive polymer in aqueous solution is Poly (N-isopropyl acryl amide) (PNIPAM).
- PNIPAM is considered to be the gold standard of thermoresponisve polymers, especially for biomedical applications.

Structure:



Poly(N-isopropyl acryl amide)

Preparation:

- Free radical polymerization of N-isopropyl acryl amide monomers using radical initiator (azo bis-isobuytronitrile)

Advantages:

- LCST lies between body and room temperature i.e., ~32°C, suitable for biological applications.
- Robust phase behaviour.
- LCST of PNIPAM does not depend on chain length or Environmental such as P^H.

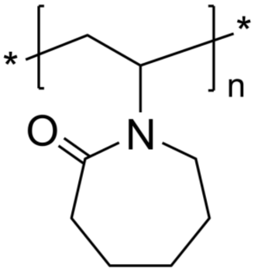
Disadvantages:

- Very high glass transition temperature (~140^OC to 150^OC) may lead to vitrification of high concentrated polymers.

❖ POLYVINYL AMIDE:

- This class of thermo-responsive polymers are second most explored polymer
- Poly N-Vinyl caprolactum (PVCL) is the best example of this category.

Structure of Poly N-Vinyl caprolactum:



- It can be prepared by free radical polymerisation of N-Vinyl caprolactum by using azo bis-isobutyronitrile as free radical initiator,

Advantages:

- Low critical solution temperature (LCST) of this polymer lies in between body and room temperature (~31°C).
- LCST of PNIPAM does not depend on chain length or Environmental such as P^H.

Disadadvantages:

- Very high glass transition temperature (~130^{O}C to 140^{O}C) may lead to vitrification of high concentrated polymers.

<u>Applications of thermosreponsive polymers</u>:

- Drug delivary
- Tissue engineering
- Liquid chromatography
- Bio separation

LUBRICANTS

❖ **Define lubricant? What are the functions of a good lubricants.**

Def: Lubricant is a substance used in between two moving surfaces to reduce the friction. Lubrication is a process of reducing friction and wear between two moving surfaces by adding lubricant in between them.

Criteria of a good lubricant:- A good lubricant must have the following functions:

1) The first and foremost function is to reduce friction.
2) It reduces surface deformation, wear and tear because the direct contact between the rubbing surfaces is avoided.
3) It reduces waste of energy. Hence the efficiency of the machine is enhanced.
4) It reduces expansion of metal by local frictional heat.
5) It avoids seizure of moving surfaces as the lubricant minimises the liberation of frictional heat.
6) It avoids unsmooth relative motion of moving parts.
7) It reduces the maintenance and running cost of machine, by preventing rust and corrosion.
8) It also acts as a seal.

❖ **Discuss the Classification of Lubricants**?

Classification of Lubricants:Lubricants may be broadly classified as follows:

1) Solid lubricants : Eg:(a) Graphite, (b) Molybdenum disulphide , (c) Talc, (d) Mica.
2) Semi – solid Lubricants: (a) Greases (b) Vaseline's
3) Liquid lubricants:
(a) Vegetable oils – eg: palm oil & castor oil
(b) Animal oils - eg: Whale oil & lard oil
(c) Mineral oils – eg: petroleum fractions.
(d) Blended or compounded oils: Eg:Mineral oils with various additives to induce desired properties.
(e) Synthetic oils – eg: Silicones.

❖ **Explain the different theories of the mechanism of lubrication.**

Mechanism of lubrication:-

There are mainly three types of mechanisms by which lubrication takes place. They are:

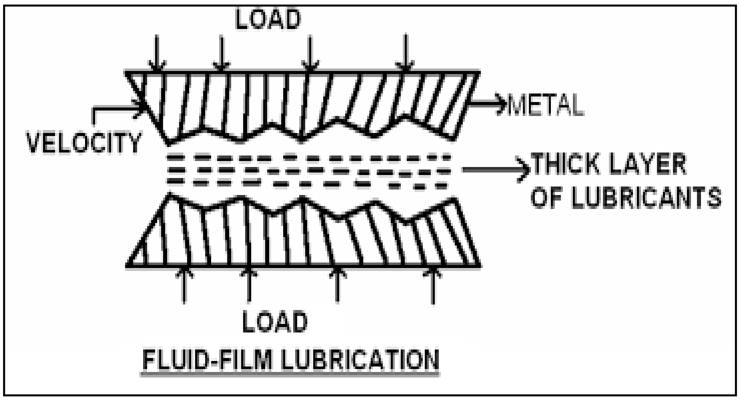
1) Fluid-film lubrication (Thick-film lubrication).
2) Boundary lubrication (Thin-film lubrication).
3) Extreme pressure lubrication.

1) Fluid-film lubrication:

It is known as thick film lubrication or hydrodynamic lubrication. It is done by lubricants which are liquid in nature. The thickness of lubricants in this case is about 1000 A0, hence the name 'Thick-Film lubrication'

In this type of lubrication, the moving or sliding surfaces are separated from each other by a thick film of fluid, so that there is no direct contact between them. The lubricant film covers the irregularities of the surfaces and reduces friction and wear and tear. The resistance to movement of sliding or moving parts is due to internal resistance between the particles of the lubricant moving over each other. For this, the lubricant should have minimum viscosity under working conditions. It should remain in place and separate thesurfaces.

This type of lubrication is used in delicate and light machines like watches, clocks, guns, sewing machines and in heavy machines like turbines, submarines etc. Fluid film lubrication is satisfactory done by hydrocarbon oils. Hydrocarbon oils used are generally mixed with long chain polymers in order to maintain the viscosity of the oil constant in all the season of the year.



2) Boundary lubrication: (Thin-film lubrication):

It is also known as thin-film lubrication because the thickness of the lubricant used in this type may not exceed one or two molecular layers. Boundary lubrication is necessary when fluid film lubrication fails to maintain the lubrication.

This type of lubrication occurs when a continuous film of lubricant cannot persist and direct metal to metal is possible. In these conditions, the space between the moving or sliding surfaces is lubricated so that a thin layer of lubricant is adsorbed on the metallic surfaces due to physical or chemical forces. This adsorbed layer helps to avoid the direct metal to metal contact between the rubbings surfaces. This load is carried by the layers of adsorbed lubricant on both the metal surfaces.

The coefficient of friction varies from 0.05 to 0.15.

For boundary lubrication, the lubricant molecules should have;

1. Long hydrocarbon chains.
2. Polar groups to promote wetting or spreading over the surface.
3. Lateral attraction between the chains.
4. Active functional groups which can form chemical bonds with metals or other surfaces.
5. High viscosity index,
6. Good oiliness,
7. Resistance to heat and oxidation.

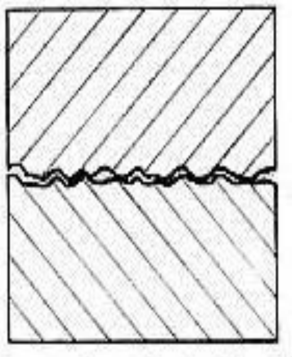


Figure 1: Boundary Lubrication

Solid lubricants, greases and oils with proper additives function as lubricants in this type of lubrication. For example, graphite, molybdenum disulphide, mineral oils with additives of fatty acids or fatty oils, vegetable and animal oils and their soaps. These materials form films on the metal surfaces having internal friction. So they can bear compression and high temperatures.

3)Extreme Pressure lubrication:

When the moving or sliding surfaces are under high pressure and speed, a special type of lubricants is used called high pressure lubricants.They withstand high temperatures generated due to friction.When moving surfaces are working under very high temperature and pressure, the ordinary liquid lubricants either vaporises or decomposes. In such cases, extreme pressure lubrication is done.

For this, special additives are used along with the liquid lubricants. Chlorinated esters, sulphurized oils and tricrysl phosphates are some examples. These additive compounds combine with the metallic surfaces at high temperatures and form metallic chlorides, sulphides or phosphides in the form of a durable film. These films can withstand very high loads and temperatures due to their high melting point.

Extreme pressure lubricants have great advantages:

i) They are used in wire drawing machining of tough metals etc.
ii) In cutting fluids in machining of tough metals.

❖ **Write short notes on the following properties of lubricants: (a) Cloud and Pour point (b) Flash and Fire point. (c) Viscosity and Viscosity index.**

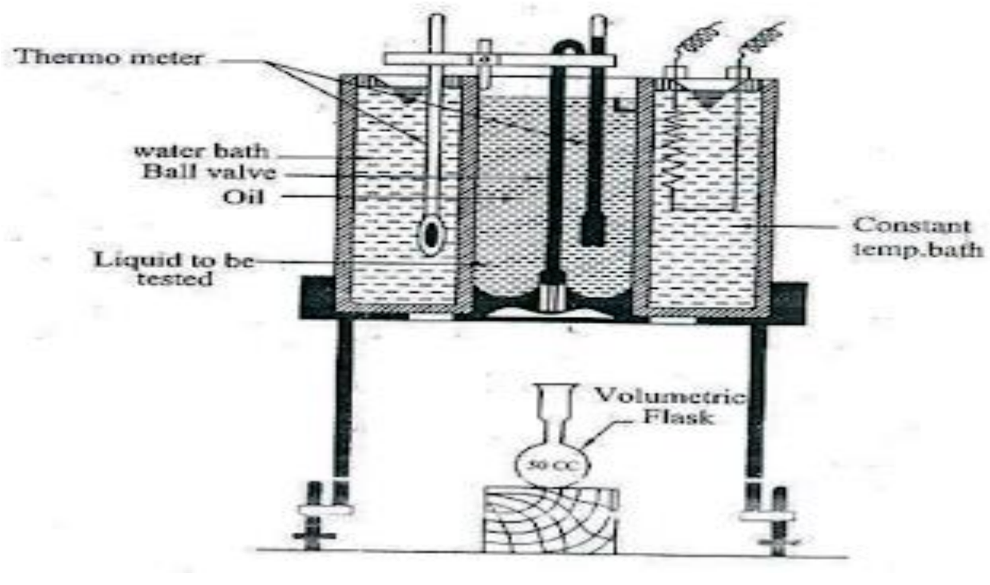
The properties of lubricants:

1. Viscosity
2. Flash and Fire Point
3. Cloud and Pour Point

1.Viscosity:

Viscosity of lubricating oil is the property which creates internal resistance to its flows. Good lubricating oil should always have moderate viscosity. Lower the viscosity, greater the flow ability. If the viscosity of the lubricating oil is high, then restriction of moving or sliding parts of a machine will occur leading towear and tear. Lubricating oil with low viscosity will not be able to form a film and it will be squeezed out of the machine leading to a friction.

Viscosity of oil can be determined with the help of red wood viscometer or sayboltz viscometer. Viscosity of oil is inversely proportional to its temperature.

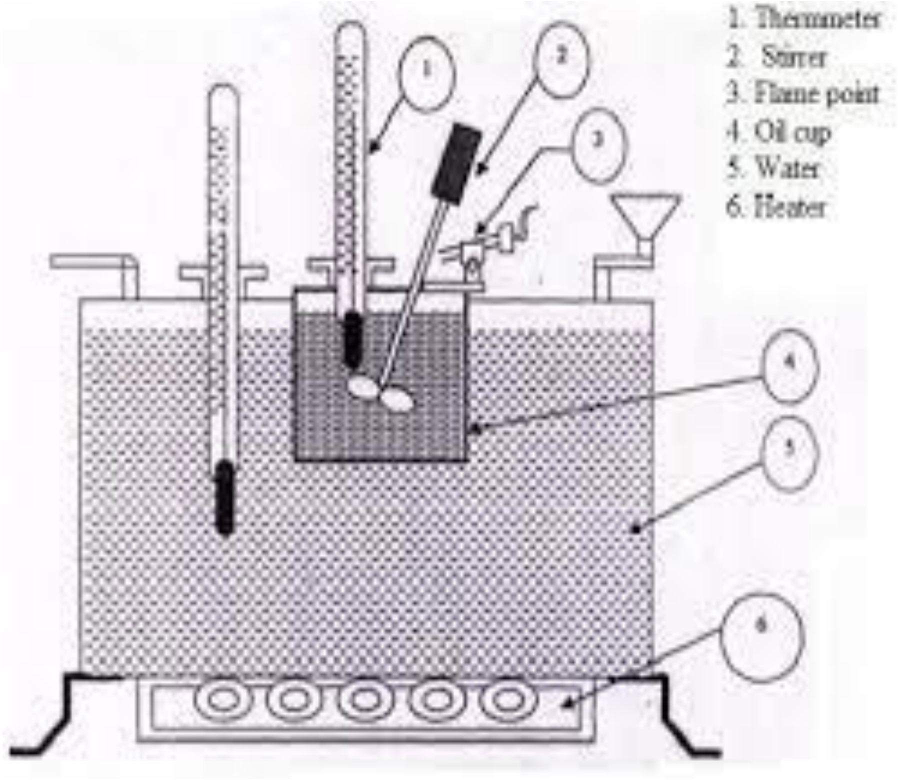


Significance:

Viscosity helps in the selection of good lubricating oil. Viscosity helps in the selection of good lubricating oil. Light oils have low densities and easy flow abilities and are used on parts moving a high speed. Heavy oils are used on parts moving at slow speed under heavy loads.

2. **Flash and Fire point:**
    - Flash point is the lowest temperature at which vapours of the oil ignite for a moment when flame is brought near it.
    - Fire point is the lowest temperature at which vapours of the oil burn for few seconds when a small flame is brought near it.
    - Generally fire point is 5 – 30°C higher than flash point.

    Significance:
    - A good lubricant must have higher flash point than working temperature of a machine.
    - The knowledge of flash point and fire point helps in selecting the suitable oil and maintaining necessary conditions to prevent fire accidents while storing or transportation.

    Determination:
    - Flash and fire points are determined with the help of Pensky – Marten's apparatus.
    - Oil is heated in a standard cup with certain rate, the vapours are exposed to flame at certain intervals till fire point and flash points are identified.
    - 

3. **Cloud and Pour point:**
    - Cloud point is the temperature at which the oil becomes hazy when it is cooled.
    - The cloudiness or haziness developed in the oil is due to presence of impurities.
    - When the oil is cooled, the impurities become solidified which appears as cloud.
    - Pour point is the temperature at which the oil cann't flows when cooled to low temperature.

    Determination:
    - Oil is taken in a flat bottomed tube and cooled to low temperature by using freezing mixture.
    - The cloud point and pour points are determined one after another.

    Significance:
    - Cloud point and pour point are due to presence of impurities.

- These two help in deciding the suitability of a lubricant to the machines working at low temperatures.
- A good lubricant must have low cloud and pour points.