ANNAMACHARYA UNIVERSITY::RAJAMPET
(ESTD UNDER AP PRIVATE UNIVERSITIES (ESTABLISHMENT AND REGULATION) ACT, 2016)
HUMANITES AND SCIENCES

ENGINEERING CHEMISTRY (24ACHE12T)

I B.Tech. & II-Semester

Written by

Mrs. K. Umadevi

ANNAMACHARYA UNIVERSITY

EXCELLENCE IN EDUCATION; SERVICE TO SOCIETY

(ESTD, UNDER AP PRIVATE UNIVERSITIES (ESTABLISHMENT AND REGULATION) ACT, 2016)

Title of the Course: Engineering Chemistry
Category: Basic Science
Course Code: 24ACHE12T
Branch/es: CE & ME
Semester: I Semester

Lecture Hours	Tutorial Hours	Practice Hours	Credits
3	-	-	3

Course Objectives: The course aims to familiarize students with engineering chemistry and its various applications, providing a solid foundation for understanding its practical relevance. It imparts essential knowledge on hard water softening processes and the standards for drinking water. Students are also trained in electrochemistry, corrosion control, and the properties and applications of different functional materials. Additionally, the course emphasizes the importance of phase equilibria in understanding system behavior.

Course Outcomes:

At the end of the course, the student will be able to

1. explain water hardness and its treatment methods.
2. apply electrochemical principles to develop solutions for energy storage and corrosion prevention.
3. demonstrate an understanding of polymer properties and fuel technologies through practical applications.
4. differentiate the characteristics and uses of lubricants and building materials across various industries.
5. analyze the applications of the phase rule in metallurgy and nanomaterials in medicine.

Unit 1 Water technology 9

Soft and hardwater, estimation of hardness of water by EDTA method, estimation of dissolved Oxygen - Boiler troubles – Priming, foaming, scale and sludge, caustic embrittlement, industrial water treatment – specifications for drinking water, Bureau of Indian Standards (BIS) and World Health Organization (WHO) standards, ion-exchange processes - desalination of brackish water, reverse osmosis (RO) and electrodialysis.

Unit 2 Electrochemistry and corrosion 8

Electrodes – electrochemical cell, Nernst equation, cell potential calculations. Primary cells – Zinc-air battery, secondary cells – lithium-ion batteries - working principle of the batteries including cell reactions; Fuel cells - basic concepts, principle and working of Hydrogen-Oxygen fuel cell.

Corrosion: Introduction to corrosion, dry and electrochemical corrosion, differential aeration cell corrosion, factors affecting the corrosion, corrosion control - cathodic and anodic protection

Unit 3 Polymers and fuel chemistry 8

Introduction to polymers, functionality of monomers, Thermoplastics and Thermo-setting plastics, properties and applications of PVC and Bakelite.

Fibres - polyesters, mechanical requirements, crystallinity, stress strain curves. Biodegradable polymers - properties and applications of Poly Glycolic Acid (PGA), Polylactic Acid (PLA).

Fuels – types of fuels, calorific value of fuels, numerical problems based on calorific value; liquid Fuels, refining of petroleum, octane and cetane number, determination of calorific value of solids by Bomb calorimeter

Unit 4 Modern engineering materials 9

Refractories - classification, properties, factors affecting the refractory materials and applications. Lubricants - classification, functions of lubricants, mechanism, properties of lubricating oils – Viscosity index, flash point, fire point, cloud point, saponification and applications.
Building materials - manufacturing of Portland cement, constituents, setting and hardening of cement.

Unit 5 Phase rule and nanomaterials 8

Phase rule - definition of terms – phase, components, degree of freedom - derivation of Gibbs phase rule, significance and limitations of phase rule. Phase diagrams – one component system – H_2O – two component system – eutectic systems - Pb-Ag system.
Nanomaterials – classification, properties and applications of nanomaterials. Carbon based nanomaterials - CNT and Graphene - properties and applications.

Prescribed Textbooks:

1. Jain, Jain. *Engineering Chemistry.* 16th ed., Dhanpat Rai, 2013.
2. Atkins, Peter, Julio de Paula, and James Keeler. *Atkins' Physical Chemistry.* 10th ed., Oxford University Press, 2010.
3. Puri, B.R., L.R. Sharma, and M.S. Pathania. *Principles of Physical Chemistry.* 48th ed., Vishal Publishing Company, 2021.

Reference Books:

1. Taylor, H.F.W. *Cement Chemistry*. 2nd Ed., Thomas Telford Publications, 1997.
2. Billmayer, Fred W. Jr. *Textbook of Polymer Science*. 3rd Ed., Wiley, 2007.
3. Dara, S.S., and S.S. Umare. *A Textbook of Engineering Chemistry*. New Ed., S. Chand Publishing, 2004.

CO-PO Mapping:

Course outcomes	Engineering Knowledge	Problem Analysis	Design/Development of solutions	Conduct investigations of complex problems	Engineering tool usage	The engineer and the world	Ethics	Individual and collaborative teamwork	Communication	Project management and finance	Life-long learning
24ACHE12T.1	2	2	1	1	-	-	-	-	-	-	1
24ACHE12T.2	3	2	1	2	-	-	-	-	-	-	1
24ACHE12T.3	3	2	1	2	-	-	-	-	-	-	1
24ACHE12T.4	3	2	1	2	-	-	-	-	-	-	1
24ACHE12T.5	3	3	2	2	-	-	-	-	-	-	1

24ACHE12T ENGINEERING CHEMISTRY

UNIT - 1

Water Technology

Syllabus: Soft and hard water, estimation of dissolved oxygen, Boiler troubles, - priming, foaming, scale and sludge, caustic embrittlement, industrial water treatment - specifications for drinking water, Bureau of Indian standards (BIS) and World Health Organization (WHO) standards, ion - exchange process - desalination of brackish water, reverse osmosis (RO) and electrodialysis.

Introduction:

* Water is natures most wonderful, abundant and useful compound. without food, human can survive for a number of days, but water is such an essential that without it one cannot survive.
* water is essential for human beings, animals and plants, and also occupies a unique position in industries.
* water is most important, it is used as an engineering material in the steam generation.
* water is also used as coolant in power plants and chemical plants.
* water is widely distributed in nature. It has been estimated that about 75% of matter on the earth's surface consist of water, under earth water is present an average depth of three kilometers.
* The air consists of 12 to 15% volume of watervapour
* water is found in living things, the body of human beings consists of about 60% of water, plants, fruits, vegetables contain 90 to 95% of water.

Sources of water: There are two sources of water.
I) surface water
II) Underground water.

I) Surface water: There are four types.
1. Rain water
2. River water
3. Lake water
4. Sea water

1. Rain water: * It is the purest form of natural water, since it is obtained as a result of evaporation from the surface water.
* It dissolves a considerable amount of gases like CO_2, SO_2, NO_2, etc and suspended solid particles.

2. River water: River water contains dissolved minerals of the soil such as chlorides, sulphates, bicarbonates of calcium, magnesium and iron.
* It also contains organic matter derived from decomposition of plants, small particles of sand and rock in suspension, and also contains impurities.

3. Lake water: It has a more constant composition.
*It contains less amount of dissolved minerals, than well water, but it contains high quality of organic matter.

4. Sea water: It is most impure form of natural water.
* It contains 3.5% of dissolved salts, 2.6% of sodium chloride, other salts are sulphate of sodium, bicarbonates of potassium, magnesium and calcium
* It has suspended matter, it contains disease producing bacteria, it is not to be safe for consumption

Underground water:

* It is a part of rain water, which reaches the surface of the earth.
* It comes in contact with mineral salts present in the soil and dissolves some of them.
* It is clear in appearance due to the filtering action of the soil, but contains more dissolved salts. Thus water from these source contains more hardness. Usually, underground water is of high organic purity.

Types of Impurities in water:

There are three types of impurities, they are

1. physical impurities
2. chemical impurities
3. Biological impurities

1. physical impurities:-

(a) colour: Colour in water usually caused by metallic substances like salts of iron, manganese, industrial effluents etc.

(b) Turbidity: It is due to colloidal solution, such as clay, slit etc, it expresses the optical properties of water, which scatter light, rather than to transmit in straight lines.

* Turbidity in water can be eliminated by sedimentation, coagulation, filtration, etc.

(c) Taste: Bitter taste due to iron, aluminium, manganese sulphate or excess of lime, soapy taste due to large amount of sodium bicarbonate ($NaHCO_3$).

3. Biological impurities: These are algae, fungi, pathogenic bacteria, viruses, parasite worms etc.

* The source of these contamination is due to discharge of domestic and sewage wastes, etc.

2. Chemical impurities:

(a) Acidity: Surface water and ground water attain acidity from industrial wastes like acid, mine drainage, pickling liquors etc.

* Usually acidity is caused by the presence of free CO_2, mineral acids (H_2SO_4) and weakly dissociated acids. Mineral acids are released when iron and alluminium salts hydrolyse.

(b) Gases:- All natural water contains CO_2, O_2, NH_3 etc.

(c) Mineral water Matter: It has origin from rocks and industrial effluents, These include Ca^{+2}, Mg^{+2}, Na^{+}, K^{+}, fe^{+2}, CO_3^{-2}, Mn^{+2}, HCO_3^{-3} Cl^{-}, SO_4^{2-} etc.

* Types of water: There are two types of water.

(1) Soft water
(2) Hard water.

(1) Soft water: water which gives lather on shaking with soap solution, is called "Soft water."

* It does not contain dissolved calcium and magnesium salts in it.

(2) Hard water: water which does not gives lather on shaking with soap solution, but produces white precipitate, is called "hard water."

Types of Hardness:

(i) Temporary Hardness:/Carbonate Hardness:

* This temporary hardness is due to the presence of bicarbonates of calcium and magnesium.
* It can be removed by boiling.
* The bicarbonates are converted into insoluble carbonates and hydroxides, which can be removed by filtering.

$$Ca(HCO_3)_2 \longrightarrow CaCO_3 \downarrow + H_2O + CO_2$$

$$Mg(HCO_3)_2 \longrightarrow Mg(OH)_2 \downarrow + 2CO_2$$

(ii) Permanent Hardness (or) Non-Carbonate hardness

* This is due to the presence of chlorides and sulphates of calcium and magnesium.
* It can not be removed by boiling.
* It can be removed by chemical treatment.

UNITS OF HARDNESS: The following are general units used in measurement of hardness.

(i) **parts per million (ppm):** It is defined as the number of parts by weight of $CaCO_3$ equivalent hardness present per million (10^6) parts by weight of water.

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

(ii) **Milligrams per Liter (mg/l):** It is defined as the number of milligrams of calcium carbonate equivalent hardness present per liter of water.

1 mg/l = 1 mg of $CaCO_3$ equivalent hardness per liter of water.

But 1 liter of water by weight = 1 kg = 1000 gm

1000 mg × 1000 mg = 10^6 mg

1 mg/lit = 1 mg of $CaCO_3$ equivalent weight of hardness present in 10^6 mg of water

= 1 ppm

1 ppm = 1 part of $CaCO_3$ ⟶ 10^6 parts of water

1 mg/l = 1 mg of $CaCO_3$ ⟶ 10^6 parts of water

1 ppm = 1 mg/l

(iii) Clark Degree (°Cl) : It is defined as number of parts of $CaCO_3$ equivalent weight of hardness present in 70,000 parts of water.

1 ppm = 0.07°Cl

1°Cl = 1 part of $CaCO_3$ equivalent wt of hardness present in 70,000 parts of water.

$$1\ ppm = \frac{70,000}{10^6}\ °Cl$$

$$= \frac{70,000}{10,00,000}\ °Cl$$

$$= 0.07°\ Cl$$

(iv) Degree french [°Fr] : It is defined as number of parts of $CaCO_3$ eq. wt. of hardness present in 10^5 parts of water is known as Degree of french.

1 ppm = 0.1°Fr

$$1\ ppm = \frac{10^5}{10^6}\ ^\circ Fr$$
$$= \frac{100000}{1000000}$$
$$= 0.1^\circ Fr$$

$$\boxed{1\ ppm = 1\ mg/l = 0.07\ ^\circ cl = 0.1\ ^\circ Fr}$$

Degree of Hardness / Hardness of water:

The amount of hardness produced by salts present in water is known as degree of hardness.

⇒ Degree of hardness is always expressed by $CaCO_3$ equivalent weight.

⇒ Because molecular weight of $CaCO_3$ is 100. So, the calculation of degree of hardness is very easy & also $CaCO_3$ is insoluble in water.

⇒ The conversion of other hard salts to $CaCO_3$ equivalent can be achieved by the following formula.

$$\text{Degree of Hardness} = \frac{\text{wt. of salt}}{\text{M.wt. of salt}} \times \underset{CaCO_3(100)}{\text{GMW of}}$$

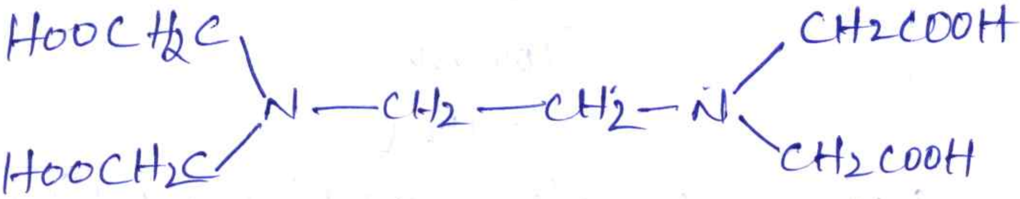
$$\text{Degree of Hardness} = \frac{\text{wt. of salt}}{\text{M.wt. of salt}} \times \underset{CaCO_3(50)}{\text{GEW of}}$$

***Estimation of Hardness by EDTA method:**

⇒ Disodium salt of Ethylene diamine tetra acetic acid [EDTA] forms stable complex with Ca^{+2} & Mg^{+2} ions in aqueous solution.

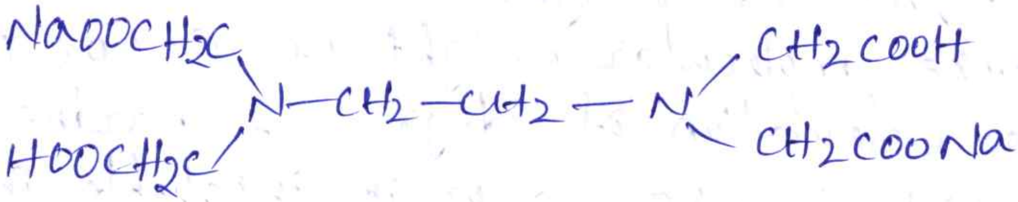
⇒ The amount of EDTA consumed in the reaction gives the amount of Calcium & Magnesium salts present in the hard water.

structure of (EDTA) EDTA:



⇒ EDTA is insoluble in water, Disodium salt of EDTA is soluble in water. So, the Disodium salt of EDTA is used as complexing agent with Ca^{+2} & Mg^{+2} ions in aqueous solution.

* **Structure of Disodium salt of EDTA:**



Principle:

When EBT (Eriochrome Black-T) indicator is added to the hard water sample, it forms wine red colour unstable complex at pH-10 with Ca^{+2} and Mg^{+2} ions. When this solution is titrated against EDTA solution. The colour of the complex changes from wine red to deep blue colour. which indicates the end point. i.e EDTA forms stable complex with Ca^{+2} & Mg^{+2} ions.

M^{2+} + EBT ⟶ [M-EBT]
unstable complex (wine red)

[$M = Ca^{+2}/Mg^{+2}$]

M-EBT + EDTA ⟶ [M-EDTA] + EBT
stable complex colourless (Blue)

⇒ NH_4OH + NH_4Cl solution (1:1 ratio) forms Buffer solution (pH=10), which resists acid - base pH range.

Procedure: Step I:

Standardisation of EDTA solution:

The Burette is rinsed and filled with EDTA Solution, 20 ml of standard hardwater is pipetted out into a clean 250 ml Conical flask. 5 ml of Ammonical buffer (NH_4Cl + NH_4OH) and few drops of EBT indicator are added and then titrated against EDTA solution until the wine red colour changes to deep blue colour, which indicates the end point. Repeat the titrations until the two Concordant titre values, are obtained.

Let the volume of EDTA Consumed, V_1 ml.

Step II: Estimation of Total Hardness:

20 ml of given sample hard water is pipette out into a clean 250 ml conical flask. 5 ml of ammonical buffer (NH_4Cl + NH_4OH for pH-10) & few drops of EBT indicator are added then titrated against EDTA solution until winered colour changes to deep blue colour, which indicates the end point. Repeat the titration until the two Concordant titre values are obtained.

Let the volume of EDTA Consumed, V_2 ml.

Step III: Estimation of permanent Hardness:

250 ml of sample hard water is taken in a beaker and evaporated nearly 50 ml (when all the bicarbonates are decomposed to insoluble $CaCO_3$ & $Mg(OH)_2$.

Filter and make up the filtrate upto 250 ml with distilled water. 20 ml of make up solution is pipetted out into a conical flask. 5 ml of ammonical buffer (buffer) and few drops of EBT indicator are added and then titrated against EDTA until the winered colour changes to deep blue colour, which indicates the endpoint. Repeat the titration until the two concordant values are obtained.

Let the volume of EDTA consumed, V_3 ml

Calculation:

Standardisation of EDTA:

1 ml of standard hard water = 1 mg of $CaCO_3$

20 ml of standard hard water = 20 mg of $CaCO_3$ Eq.

20 mg of $CaCO_3$ Eq. = V_1 ml of EDTA

$\therefore$ 1 ml of EDTA $= \frac{20}{V_1}$ mg of $CaCO_3$ Eq.

Estimation of Total hardness:

20 ml of given hard water = V_2 ml of EDTA

1 ml of EDTA $= \frac{20}{V_1}$ mg of $CaCO_3$ Eq.

20 ml of given Hard water $= V_2 \times \frac{20}{V_1}$ mg of $CaCO_3$ Eq.

1 ml of given hard water $= \frac{20}{V_1} \times \frac{V_2}{20} \times 1000$ mg of $CaCO_3$ Eq.

$\therefore$ Total hardness in 1 liter of given hardwater

$$= \frac{V_2}{V_1} \times 1000 \text{ mg/lit}$$

Estimation of permanent Hardness:

20 ml of boiled water = ____ (V_3) ml of EDTA

1 ml of EDTA consumes = $\frac{20}{V_1}$ mg of $CaCO_3$ Eq.

20 ml of boiled water = $V_3 \times \frac{20}{V_1}$ mg of $CaCO_3$ Eq.

1 ml of boiled water = $\frac{20}{V_1} \times \frac{V_3}{20}$ mg of $CaCO_3$ Eq.

1 liter of boiled water = $\frac{V_3}{V_1} \times 1000$ mg of $CaCO_3$ Eq.

permanent hardness = $\frac{V_3}{V_1} \times 1000$ mg/lit.

Calculation of temporary Hardness:

Temporary hardness = total hardness − permanent hardness

$$= \left[\frac{V_2}{V_1} \times 1000 - \frac{V_3}{V_1} \times 1000\right] = \left(\frac{V_2 - V_3}{V_1}\right) \times 1000 \text{ mg/l}$$

---

* Disadvantages of Hard water:

steam generation in boilers: For steam generation boilers are employed. If hard water is used in boilers, it may leads to the following troubles

(a) Corrosion (Boiler corrosion)

(b) Scale and sludge

(c) priming and foaming

(d) Caustic embrittlement

(a) **Boiler Corrosion:** Destruction or deterioration of boilers by a chemical or electrochemical attack by its environment is called boiler corrosion

Main sources for boiler Corrosion are

(1) Dissolved oxygen

(2) Dissolved Carbon dioxide

(3) Acids from dissolved salts.

(1) Dissolved oxygen: water usually contains about 8ml of dissolved oxygen per liter at room temperature. when this water is heated in the boilers, free oxygen attacks boilers at high temperatures.

$$2Fe + H_2O + O_2 \longrightarrow 2Fe(OH)_2$$

$$Fe(OH)_2 + O_2 \longrightarrow [Fe_2O_3 \cdot 2H_2O]$$

Removal of dissolved oxygen: Dissolved oxygen can be removed by adding calculated amount of Sodium sulphite, hydrazene and sodium sulphide.

$$Na_2SO_3 \longrightarrow Na_2SO_4$$

$$N_2H_4 + O_2 \longrightarrow N_2 + H_2O$$

$$Na_2S + 2O_2 \longrightarrow Na_2SO_4$$

when hot water is passed through hot perforated plates in a cylindrical chamber, the vacuum pump connected to its rules out the all gasses from the water.

(2) Dissolved Carbon oxide: It forms carbonic acid, which has slow corrosive effect.

$$CO_2 + H_2O \longrightarrow H_2CO_3$$

This is also produced inside the boiler, if water contains bicarbonates.

$$Mg(HCO_3)_2 \longrightarrow MgCO_3 + H_2O + CO_2$$

Removal: Dissolved CO_2 can be removed by adding calculated amount of ammonia.

$$NH_3 + CO_2 \rightarrow (NH_4)_2CO_3$$

It can also removed by mechanical deaeration.

③ **Acids from dissolved salts:**

water containing dissolved Mg salts liberate acids on hydrolysis. Mg salts dissolve in water at high temperature and form $Mg(OH)_2$ and HCl.

* The HCl attacks on Fe and corrosion occurs by liberating hydrogen gas.

$$MgCl_2 + 2H_2O \rightarrow Mg(OH)_2 + HCl$$

The liberated acid reacts with Fe.

$$Fe + 2HCl \rightarrow FeCl_2 + H_2$$

Iron also dissolved in water as $Fe(OH)_2$.

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

ⓑ **Scale and sludge:** In boilers, dissolved salts converts into precipitates.

i) **Sludge:**

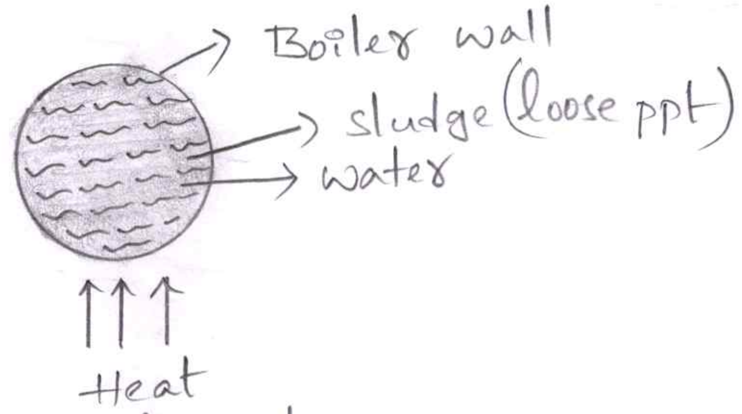


Figure: sludge formation

* sludge is a soft, non-sticky, loose, slimy precipitate formed inside the boiler.
* These are formed at cold portions of the boiler due to substances like $MgSO_4$, $MgCO_3$,

$MgCl_2$ & $CaCl_2$ since they have greater solubility hot water than in cold water.

* Disadvantages:-

(i) It is a poor conductor of heat, so a lot of energy is wasted and decrease the efficiency.
(ii) poor water circulation.
(ii) By using wire brush sludge can be removed.
(iii) By air blow down operation also deposited sludge can be removed.

prevention of sludge:

1. By using well softened water in boilers.
2. By the frequent blow-down operation.

Blow-down operation:

Drawing off a portion of the concentrated water from the boiler, when the extent of hardness in the boiler becomes alarmingly high.

ii) Scale:

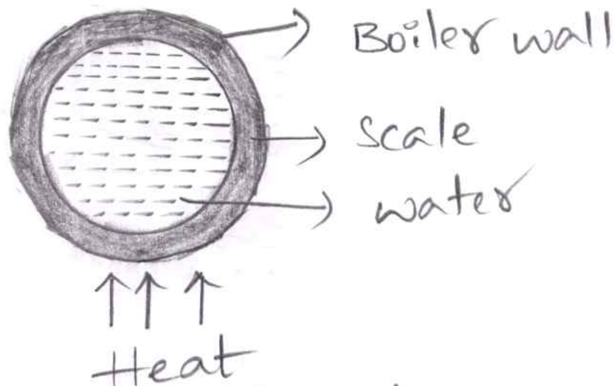


Figure: Scale formation

⇒ Scales are hard deposits, firmly sticking to the boiler. They are difficult to remove even with the help of hammer and chisel and are the main source of the boiler trouble.

⇒ The salts mainly responsible for scale formation are $CaCO_3$, $CaSO_4$, $Ca(HCO_3)_2$, Mg salts and due to the presence of silica are responsible for scale formation in boilers.

Disadvantages of scale:-

1. scales acts as bad conductor of heat.
2. Scale formation can reduce the efficiency of a boiler.
3. Due to poor Conductivity of scales, more fuel Consumption takes place i.e, wastage of fuel.
4. Lowering of boilers safety.
5. Danger of explosion.

Prevention of scales:-

1. By the usage of well softened water in boilers.
2. Using scrapes, wire brush etc, seals can be removed.
3. Using 5-10% HCl (or) EDTA solutions, scales can be removed.
4. By frequent blow-down operation, the scale formation can be avoided.

(c) Priming and foaming:

Priming: This is also known as carry over process or wet steam.

Formation of wet steam by rapid boiling of water in boilers is called priming.

Causes: priming can be caused due to

1. Rapid changes in velocity of steam.

2. High water levels.
3. Sudden boiling.
4. Improper boiler design.

prevention:

Priming can be avoided by
1) By avoiding uneven steam velocity.
2) Maintaining medium water levels.
3) By proper heating.
4) Using a good designed boiler.

Foaming:

Foaming is production of persistant bubbles or foam at the water surface in boiler, which does not break easily.

Causes: Foaming can be caused by
1. presence of oil or soapy substances (oils, alkalie substances) react to form soap which greatly lower the surface tension of water and thus increasing foaming tendency of the liquid.
2. Certain dissolved salts (NaCl, $MgSO_4$, Calcium chloride).

prevention: Foaming can be prevented by
1. By the addition of antifoaming agents like cotton seed oil and castor oil.
2. By the addition of aluminium compounds like sodium aluminate and aluminium sulphate

-which are on hydrolysis form aluminium hydroxide flocks which entrap oil drops. The flocks of $Al(OH)_3$ containing oil droplets are removed by filtration through anthrafit bed filtration.

(d) Caustic embrittlement:

Caustic embrittlement is the phenomenon with which the boiler material becomes brittle due to the accumulation of caustic substances. This type of boiler corrosion is caused by the highly alkaline water in the high pressure boilers.

* During softening of water by lime-soda process some residual Na_2CO_3 is still present in softened water. In the high pressure boilers, Na_2CO_3 decomposes to give NaOH, which makes the boiler water caustic.

$$Na_2CO_3 + 2H_2O \longrightarrow 2NaOH + H_2CO_3$$

This caustic water flows into the minute cracks present in the inner side of boiler by capillary action.

On evaporation of water the dissolved caustic soda concentration increases progressively which attacks the surrounding area, there by dissolving iron of boiler as sodium ferroate. This causes embrittlement of boiler walls more particularly stressed parts like bends, joints, rivets etc, causing even failure of boiler.

$$2NaOH + Fe \longrightarrow Na_2FeO_2 \text{ (sodium ferroate)}$$

Mechanically caustic embrittlement arises due to the setting up of a concentration cell. Iron surrounded by conc. NaOH acts as anode and the iron surrounded by dil. NaOH acts as cathode. The iron in the anodic part gets dissolved or corroded as sodium ferroate.

Iron(-) / Fe^- $\xrightarrow{+e^-}$ Iron(+) / Fe^+

Anode: Con. NaOH (Joints) — electron transfer — Cathode: Dil. NaOH (plane surface

prevention:

(i) Caustic embrittlement can be avoided by adding Na_2SO_4, tannin, lignin etc to the boiler water which block hair cracks.

(ii) By adding sodium phosphate as softening agent instead of sodium carbonate during lime - soda process.

Specification for Drinking water:

water used for drinking water should have certain quality. The following table summarizes several quality criteria and their standards for drinking water.

characteristics of drinking water:

As per the suggestion given by world health organization (WHO) and by ICMR (Indian Council of medical research), the following are the important characteristics of potable water.

(i) It should be clear, colourless, odorless and suspended impurities.

ii) It should be cool and pleasant to taste.
iii) It is free from bacteria and suspended impurities.
iv) It should be free from dissolved gases like CO_2, H_2S & NH_3.
v) Hardness should be less than 500 ppm.
vi) chloride content should be less than 250ppm
vii) Fluoride Content should be less than 1.5ppm.
viii) Total dissolved solids (TDS) Content should be less than 500ppm.
ix) pH of the potable water should be 6.5–8.5
x) Total alkalinity should be less than 250ppm

Table.

S.NO.	Parameter	WHO (mg/l)	BIS (mg/l)
1	Colour	Colour less	Colour less
2	Odour	odour less	odour less
3	Taste	tasteless	tasteless
4	PH	6.9	6.9
5	TDS	500-1500	500–2000
6	DO		3.0
7	Chloride	250	600
8	Sulphate	400	1000
9	Nitrate		45
10	Cyanide	0.2	0.01
11	Fluoride	1.5	3.0
12	chromium	0.05	0.05
13	Lead	0.05	0.1
14	Arsenic	0.05	0.2
15	Alkalinity	250	250

Industrial water treatment:

Based on the type of water, required to various industries, many methods are available for the water treatment. Untreated water may contain the following impurities.

(i) Suspended or dissolved solids like alkali metal salts, alkaline earth metal salts, Silica, Clay, organic matter etc.

ii) Lubricants such as oil, grease etc.

iii) Dissolved gases like O_2, CO_2 etc.

As we know hardness, in boiler feed water, leads to scale formation in the tubes and drums. these scales are insulators and cause damage to the boiler.

Effects of some materials:

ⓐ Effects of Fe:

water used for many industries should be free from iron because it causes the following problems.

Dry Industry: produce insoluble lakes, which give impure shades.

Paper mills: stains the paper.

Laundry work: Yellow colour to the cloth.

Removal of Iron:

(i) Iron is removed from water either by permutit or lime soda process.

(ii) Aeration: spraying the water containing iron with air.

$$2Fe(HCO_3)_2 + H_2O + O \longrightarrow 2Fe(OH)_3 + 4CO_2$$

II) Effect of Dissolved oxygen:

Dissolved oxygen boiler water helps corrosion.

$$Fe + O_2 + H_2O \longrightarrow Fe(OH)_2$$

Removal of Dissolved oxygen:

(i) It is removed by electrode polarisation.

(ii) By de-aeration method.

III) Effect of Silica:

In high pressure boilers, the water containing SiO_2 forms scale. These scales can not be removed, even by sodium zeolite exchanger/ permutit process.

Removal of Silica:

(i) A highly basic anion exchanger may be used to remove maximum SiO_2.

(ii) Coagulation process, using ferric sulphate silica can be removed.

Softening of water:

The removal of hardness causing salts from water is called Softening of water. The hardness causing salts can be removed from water by the following two ways, as

1. Internal conditioning method
2. External conditioning method

1. Internal Conditioning / Treatment:

The following are the internal conditioning methods used in boilers.

ⓐ Carbonate Conditioning:
In low pressure boilers, scale formation can be avoided by adding sodium carbonate to boiler water. In this treatment, $CaSO_4$ is converted into $CaCO_3$ in equilibrium.

$$CaSO_4 + Na_2CO_3 \longrightarrow CaCO_3 + Na_2SO_4$$

Consequently deposition of $CaSO_4$ as scale doesnot takes place and Calcium is precipitated as loose sludge of $CaCO_3$ which can be removed by blowdown Operation easily.

(b) phosphate Conditioning:
The scale formation can be avoided by high pressure boilers, by adding trisodium phosphate or other types of phosphates according to the pH of boiler water.
Added Sodium phosphate reacts with Ca & Mg Salts forming non-sticky and easily removable Soft sludge can be easily removed by blow down operation.

$$\underset{\text{(Scale)}}{3\,CaSO_4} + 2Na_3PO_4 \longrightarrow \underset{\text{(loose sludge)}}{Ca_3(PO_4)_2} + 3\,Na_2SO_4$$

$$\underset{\text{(Scale)}}{3\,MgCl_2} + 2\,Na_3PO_4 \longrightarrow \underset{\text{(loose sludge)}}{Mg_3(PO_4)_2} + 6\,NaCl$$

ⓒ Colloidal Conditioning:
Scale formation in boilers is mainly due to the crystal precipitates. chemicals like Kerosene, tannin or agar-agar when get coated on the -

-outer surface of crystalline precipitates, they form colloidal, non-sticky sludge like ppts which can be easily removed by mechanical methods or blow down operations.

(d) Treatment with Sodium Aluminate ($NaAlO_2$):-

Sodium aluminate on hydrolysis with water producing sodium hydroxide and a gelatinous precipitate of $Al(OH)_3$.

$$NaAlO_2 + 2H_2O \longrightarrow NaOH + Al(OH)_3 \downarrow$$

$$MgCl_2 + 2NaOH \longrightarrow Mg(OH)_2 + 2NaCl$$

The flocculent $Al(OH)_3$ & $Mg(OH)_2$ produce inside the boiler entraps finely suspended and Colloidal impurities including oils and silica. The loose precipitates can be easily removed from boilers by blow down operation.

(e) Calgon Conditioning:

In this process Calgon (or) sodium hexa-meta phosphate $[Na_2[Na_4(PO_3)_6]]$ is added to the boiler feed water which forms stable soluble complexes with hardness producing salts.

$$CaSO_4 + Na_2[Na_4(PO_3)_6]$$
$$\downarrow$$
$$Ca[Na_4(PO_3)_6] + Na_2SO_4$$

2. External treatment:

The external treatment of water is carried out before its entry into the boilers. This treatment prevents boiler problems. It can be done by

[ⓐ Permutit (or) Zeolite process]

ⓐ Zeolite process or permutit process

ⓑ Ion-exchange process

ⓐ Zeolite process:

This is one of the method used for removal of hardness present in water.

Zeolite is hydrated sodium alumino silicate. Its general formula is $Na_2O \cdot Al_2O_3 \cdot xSiO_2 \cdot yH_2O$.

Zeolite is of two types as natural zeolite and artificial zeolite.

Natural zeolite is non-porous & amorphous in nature. Ex:- Natrolite.

Artificial or synthetic zeolite is porous in nature and has high ion exchange capacity when compared to natural zeolite. Artificial zeolite is called as permutit.

Process: In this process, hard water is passes through a bed of zeolite at ordinary temperature. The hard water during percolation through the Na bed exchanges Ca^{+2} and Mg^{+2} ions with Na^+ ions forming magnesium and calcium-zeolite. Sodium zeolite is denoted by Na_2Ze

$$CaSO_4 + Na_2Ze \longrightarrow CaZe + Na_2SO_4$$
$$MgSO_4 + Na_2Ze \longrightarrow MgZe + Na_2SO_4$$

$CaCl_2 + Na_2Ze \longrightarrow CaZe + 2NaCl$

$MgCl_2 + Na_2Ze \longrightarrow MgZe + 2NaCl$

$Mg(HCO_3)_2 + Na_2Ze \longrightarrow MgZe + 2NaHCO_3$

$Ca(HCO_3)_2 + Na_2Ze \longrightarrow CaZe + 2NaHCO_3$

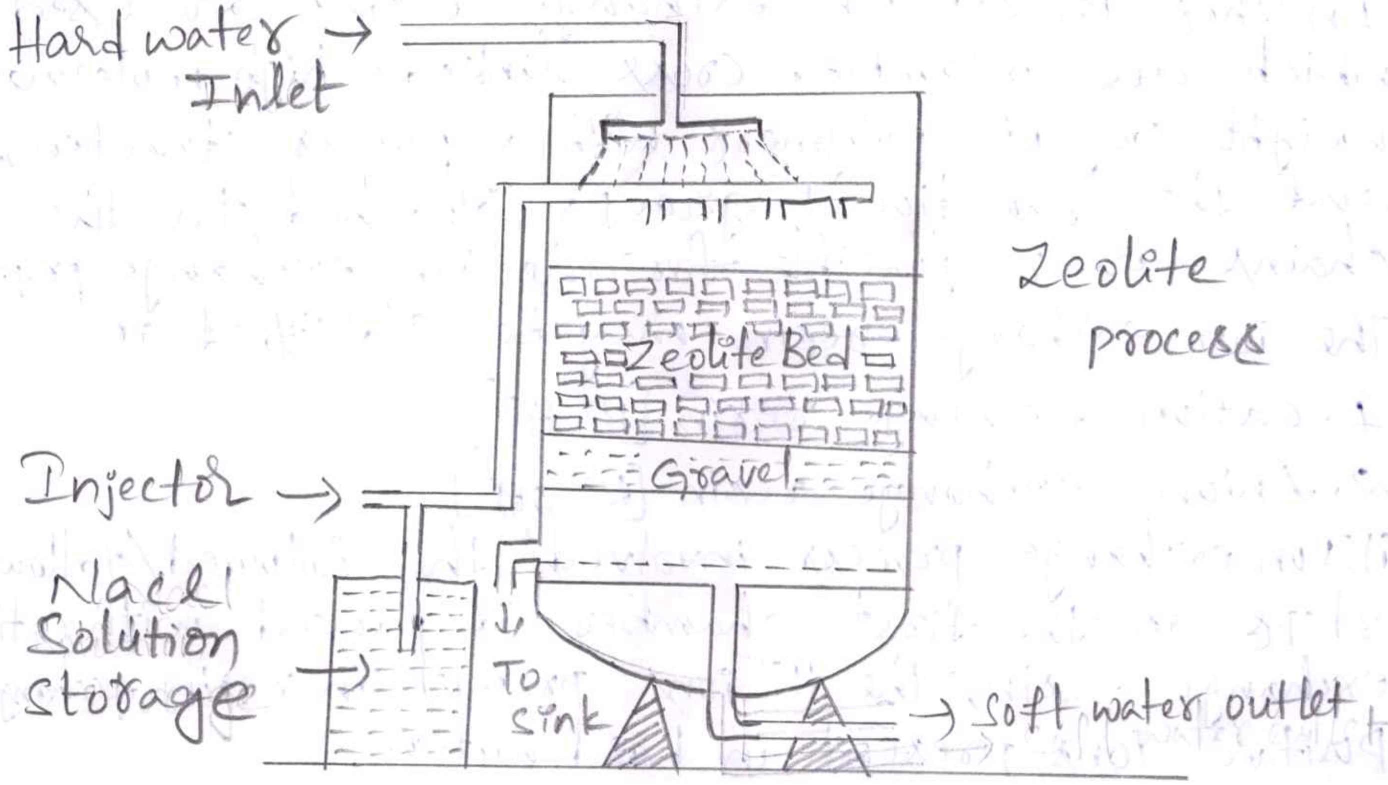
Regeneration of Zeolite:

On continuous passing of hard water through Sodium zeolite bed, it is converted calcium and magnesium zeolite which is known as exhausted bed. Hence it must be regenerated. This can be done by washing the zeolite bed with 10% NaCl solution (Brine solution).

$CaZe + 2NaCl \longrightarrow CaCl_2 + Na_2Ze$

$MgZe + 2NaCl \longrightarrow MgCl_2 + Na_2Ze$

Along with NaCl, sometimes KCl, $NaNO_3$, KNO_3 are also used but mostly NaCl is used because of low cost.



Zeolite process

Advantages:

1) The equipment is small and easy to handle.
2) It requires less time for Softening.
3) water obtained from this process contains 10 ppm hardness.
4) Easy to regenerate.
5) No sludge is formed

Disadvantages:

1) Highly turbid water can't be treated by this method.
2) water obtained from this process contains more number of sodium salts.
3) Problem of corrosion and Caustic embrittlement arises in boilers.

(b) Ion exchange process:

This is also known as demineralisation process (or) deionisation process.

In this process ion exchange resins are used which are insoluble, cross linked, high molecular weight organic polymers with a porous structure, and the functional groups attached to the chains are responsible for the ion exchange property

The ion exchange resin may be classified as

1. Cation exchange resin $[R^- H^+]$
2. Anion exchange resin $[R^+ OH^-]$

(i) Ion exchange process involved the followed/following steps as the first chamber is packed with cation exchange resin, the H^+ ions present in resin exchanges Positive ions present in hard water.

$$2R^{(-)}H^+ + Mg^{+2} \longrightarrow R_2Mg + 2H^+$$
$$2R^{(-)}H^+ + Ca^{+2} \longrightarrow R_2Ca + 2H^+$$
$$3R^{(-)}H^+ + Al^{+3} \longrightarrow R_3Al + 3H^+$$

(ii) The second chamber is packed with anion exchange resin (R^+OH^-). The water coming out of first chamber is free from positive ions expect H^+ and also contain Cl^-, SO_4^{2-}, CO_3^{2-}, HCO_3^-. Now the water is processed through anion exchange resin bed which can exchanges OH^- ions with anions like Cl^-, SO_4^{2-}, CO_3^{2-}, HCO_3^- etc.

$$R^{(+)}OH^- + Cl^- \longrightarrow RCl + OH^-$$
$$2R^{(+)}OH^- + SO_4^{2-} \longrightarrow R_2SO_4 + 2OH^-$$
$$R^{(+)}OH^- + HCO_3^- \longrightarrow RHCO_3 + OH^-$$

(iii) The H^+ ions coming out of first chamber reacts with OH^- ions released in second chamber to form water.

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

Hence water formed from the ion exchange process completely free from all cations & anions which are responsible for hardness in water.

<u>Regeneration of resins:</u>

The resins beds get exhausted when used for long period and can be regenerated by the following process.

ⓐ The exhausted cation exchange resin is regenerated by passing a solution of dilute HCl or dilute H_2SO_4.

$R_2Ca + 2HCl \longrightarrow 2R^{(-)}H^+ + CaCl_2$

$R_2Mg + 2HCl \longrightarrow 2R^{(-)}H^+ + MgCl_2$

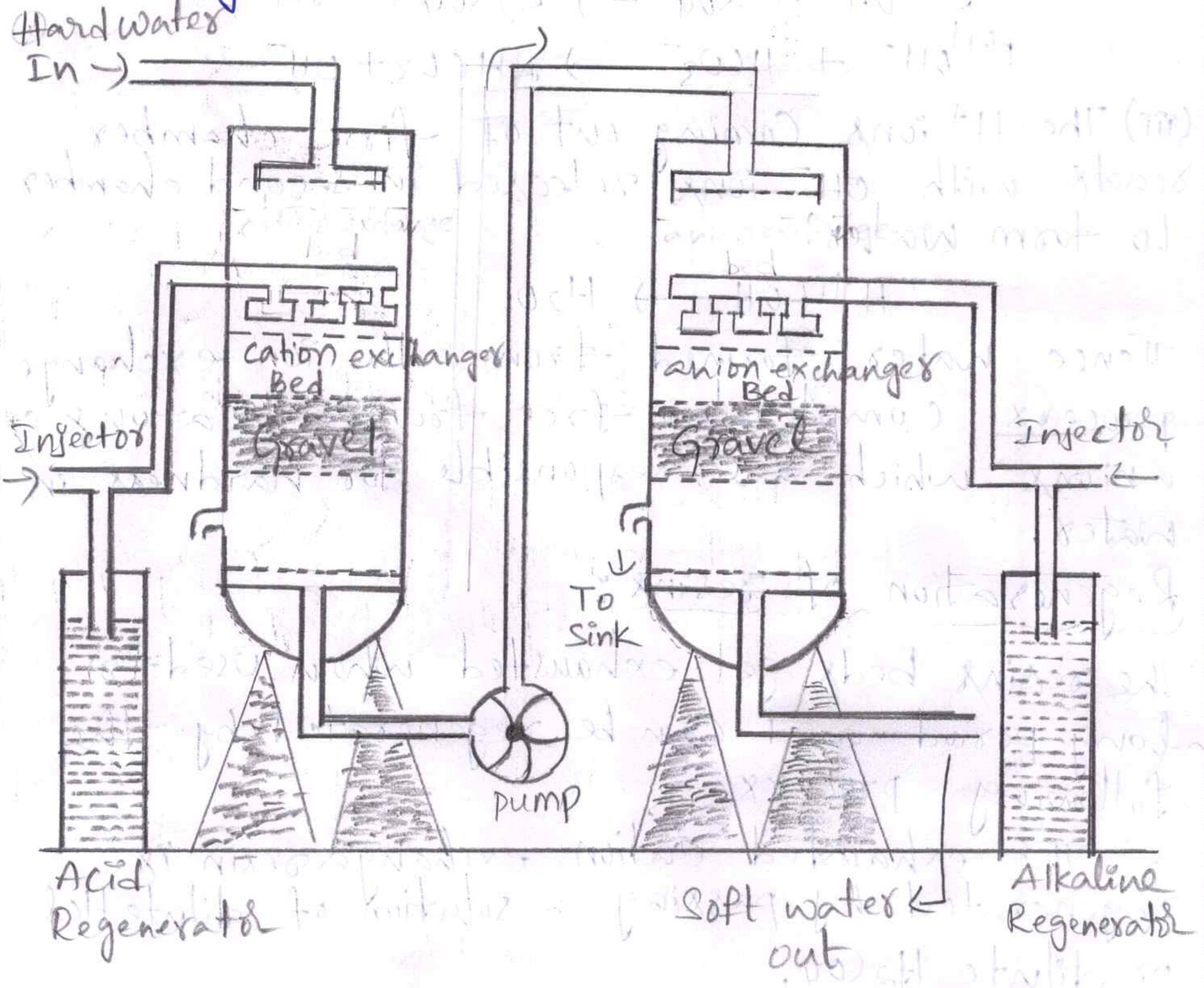
(b) similarly, the exhausted anion exchange resins is regenerated by passing a solution of dilute NaOH.

$RCl + NaOH \longrightarrow 2R^{(+)}OH^- + NaCl$

$R_2SO_4 + 2NaOH \longrightarrow 2R^{(+)}OH^- + Na_2SO_4$

$R_2CO_3 + 2NaOH \longrightarrow 2R^{(+)}OH^- + Na_2CO_3$

Then the column is washed with de-ionized water and washings is passed to sink or drain. Regenerated resins are ready for further Softening process.



Advantages:

(i) It produces very pure water of hardness nearly 2 ppm.

(ii) Highly acidic or alkaline water can be treated by this process.

(iii) The softened water is completely free from any salts and fit for use as boiler feed water.

Disadvantages:

(i) the equipment is little expensive.

(ii) Highly turbid water can not treated by this process.

Demineralization of Brackish water:

This is also known as desalination of brackish water. It involves the removal of salts from water. The alkalinity of water is nearly consiste of dissolved NaCl and to a smaller extent of other inorganic salts sea water contain an average of about 3.5 % salts (2.5 % of NaCl and 1% of other salts). This water is totally unfit for drinking and other domestic purpose. Hence this brackish water can be converted into soft water by two methods as

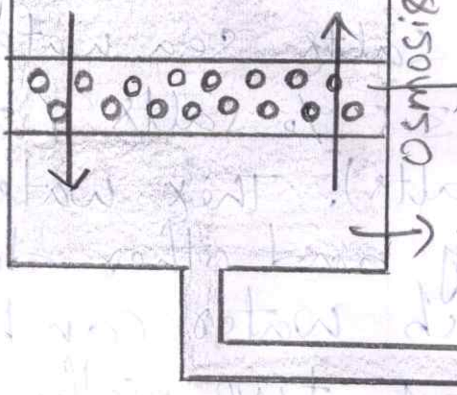
(1) Reverse Osmosis method

(2) Electro dialysis

(1) **Reverse Osmosis Method:** When a semi permeable membrane separates two solutions of different concentrations, the flow of solvent takesplace

from less concentration region to more concentrated region due to Osmosis. Mostly used semipermeable membranes are cellulose acetate, polymethyl methacrylate, polyamide polymers. Semipermeable membrane can allow only solvent (water) but not solute (salts) particulars.
If more pressure, which is high than osmatic pressure is applied, then reverse osmosis takes place i.e, flow of solvent from higher concentration to lower concentration. Using this principle drinking water is obtained from brackish water. The water molecules passes through the membrane while the salts gets concentrated in the effluent stream which can be removed.

Reverse Osmosis



Advantages:
① Colloidal SiO_2 can be removed by reverse osmosis which even can't removed by demineralization process.
② It is simple and reliable process.
③ Capital and Operating expenses are low.

(2) Electro dialysis :

This method is another efficient method used for the desalination of water. It is based on the principle that the ions migrate towards oppositely charged electrodes by passing direct current using ion select permeable membrane.

=) The cation membrane allows only cations while anion membrane allows only anions thus this process give pure water by decreasing salt Concentration.

=) The process of decreasing the concentration of salts, saline water using ion-selective membranes under the influence of a direct current is called electro dialysis.

An electro dialysis cell consists of a series of alternative cation permeable (C) and anion permeable membrane (A). Saline water is passed under pressure of about 5.6 kg m^{-2} between membrane pairs and electric field is applied across the two electrodes immersed in which the Na^+ ions move out through 'C' and Cl^- ions moves out through 'A'.

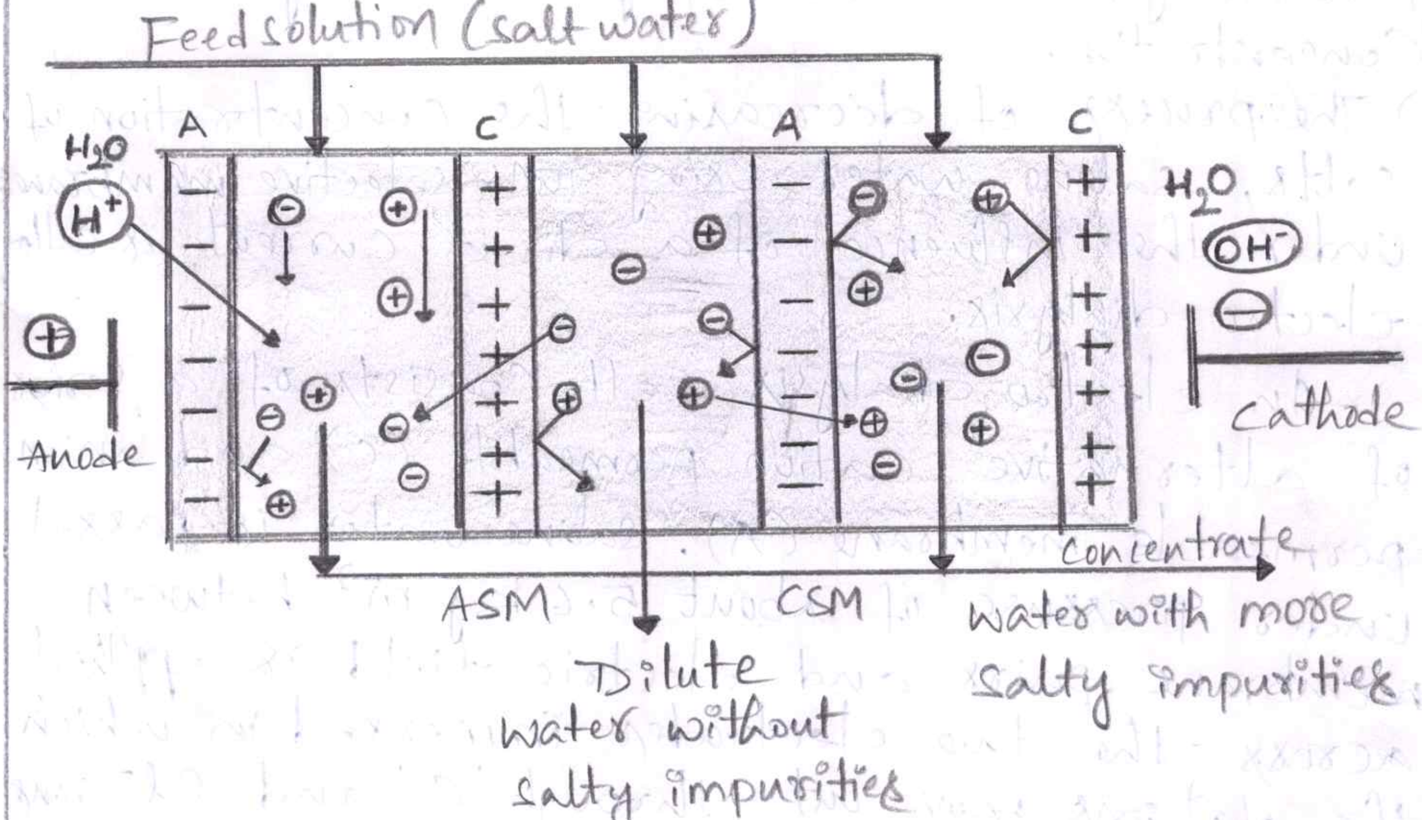
Initially CA compartment contain saline water, after movement of ions AC compartment contain saline water i.e, high salt concentrated water when compared to CA compartment. The fresh water in CA compartment is collected while the concentrated water is discharged.

Advantages :

(i) This process is economical as per the Capital cost and Operated expenses are concerned.

(ii) The unit is Compact and method is best suited.

Purification of water by Electrodialysis process:



Estimation of Dissolved oxygen:

Dissolved oxygen determination is based on the oxidation of potassium iodide (KI) by dissolved oxygen. The liberated iodine is treated against a standard sodium thiosulphate solution using starch as final indicator. However dissolved molecular oxygen in water is not capable of reacting with KI, so an oxygen (of) carrier [$Mn(OH)_2$] is used to bring about the reaction between KI and oxygen. Manganese hydroxide is produced by the action of potassium hydroxide sodium hydroxide and manganous sulphate.

$$MnSO_4 + 2KOH \longrightarrow K_2SO_4 + Mn(OH)_2$$

$$2Mn(OH)_2 + O_2 \longrightarrow 2MnO(OH)_2$$

Basic manganic oxide (Brown ppt)

$$MnO(OH)_2 + H_2SO_4 \longrightarrow MnSO_4 + 2H_2O + (O)$$

$$KI + H_2SO_4 + (O) \longrightarrow K_2SO_4 + H_2O + I_2$$

$$I_2 + starch \longrightarrow [starch - I_2] \text{ complex}$$

Blue colour

$$I_2 + 2Na_2S_2O_3 \longrightarrow 2NaI + Na_2S_4O_6$$

Procedure: Collect water sample in a 300 ml capacity of BOD bottle and add 2ml of $MnSO_4$ and 2ml of alkali-Iodide-Azide solution. Stopper the BOD Bottle immediately. Appearance of brown precipitate indicates the presence of dissolved oxygen. Mix well and allow the brown precipitate indicates the presence of dissolved oxygen

Mix well and allow the Brown precipitate, to settle down. Keep it in dark place for 5 minutes. Add 2ml of Concentrated H_2SO_4 solution along the inner side of the bottle to dissolve the brown precipitate.

100 ml of this water sample solution pipette out into a clean 250 ml conical flask add 1ml of starch solution to water sample it turns to blue colour. (is disappeared. which indicates end point.) Titrate against standard hypo ($Na_2S_2O_3$) solution present in the burette, till the blue colour is disappeared, which indicates end point. Note the volume of hypo consumed (V_1). Repeat the titration till two concordant readings are obtained.

Calculation: V_1 = volume of Hypo

N_1 = Normality of Hypo

V_2 = volume of water sample

Dissolved oxygen in the given water sample

$$= \frac{V_1 \times N_1 \times 8 \times 1000}{V_2} \text{ mg/l.}$$

UNIT - 2

Electro chemistry & Corrosion

Electrodes, electrochemical cell, Nernst equation, cell potential calculations, primary cells - Zinc air battery, secondary cells, Lithium ion batteries working principle of the batteries including cell reactions.

Fuel cells - basic concepts, principle and working of Hydrogen - oxygen fuel cell.

Corrosion: Introduction to corrosion, dry and electro chemical corrosion, differential aeration cell corrosion, factors affecting the corrosion Corrosion control - cathodic and anodic protection

Introduction:

⇒ Electrochemistry is a branch of science which deals with conversion of chemical energy into electrical energy and vice versa.

⇒ Current is said to be as flow of electrons,

⇒ Conductors:- A substance which allows electric current to pass through it is called Conductor.

Example: Metals, Aqueous solution of acids, bases, salts etc.

Conductors are of two types as

(a) Metallic Conductors: Substance which Conduct electricity but are not decomposed by it.

Ex:- Graphite, metals etc.

(b) Electrolyte: Substance which allows current to flow through it and decompose into aqueous solution is called electrolyte.

acids, bases etc.

Insulator / Non-Conductors:
Substance which does not allow the passage of Current is called "Insulator".

Ex:- Alcohols, oils etc.

In solutions, electrolyte dissociate into charged particles called Ions.

Ion carrying +ve charge is called "Cation".

Ion carrying -ve charge is called "Anion".

Electrode: A metal rod which conducts electricity is called electrode. It is of two types.

(a) cathode: Cations move towards cathode.

(b) Anode: Anions move towards Anode.

Electrolysis: The phenomenon of decomposition of electrolyte due to passage of current is called electrolysis.

Oxidation: Loss of electrons is called oxidation.

[Reduction] At Anode oxidation takes place.

$$M \xrightarrow{oxi} M^{n+} + ne^-$$

Reduction: Gain of electrons is called reduction.

At cathode reduction takes place.

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

~~Redaction~~ Reaction: Combination of oxidation and reduction is called redox reaction.

Ex:- $M \longrightarrow M^{n+} + ne^-$ ⇒ oxidation half reaction

$M^{n+} + ne^- \longrightarrow M$ ⇒ Reduction half reaction

$M \underset{Red}{\overset{oxi}{\rightleftharpoons}} M^{n+} + ne^-$ ⇒ Net reaction

Electrode potential :

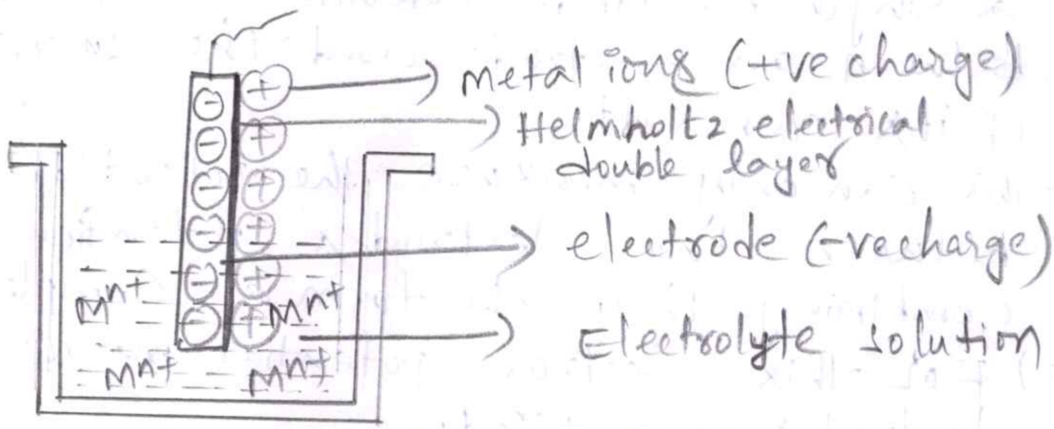
When a metal is dipped in its own salt solution metal either loss of electrons (or) gain of electrons takes place.

$$M_{(s)} \longrightarrow M^{n+}_{(aq)} + ne^- \quad \text{oxidation}$$

$$M^{n+} + ne^- \longrightarrow M \quad \text{Reduction}$$

⇒ positively charged metal ions present in the solution towards the negatively charged electrode and forms metal layer on the electrode called "Helmholtz electrical double" layer.

⇒ These reactions depends up on nature of metal, temperature and concentration of metal ions in solution.



⇒ The tendency of a metallic electrode to lose electrons or to gain electrons in its own salt solution is said to be as Electrode potential of a metal or "Single electrode potential (E)".

⇒ The tendency of metal to lose electrons and get oxidised is called "oxidation potential".

⇒ the tendency of metal to gain electrons and get reduced is called "Reduction potential."

⇒ The tendency of a metal to lose electrons or to gain electrons in its own salt solution of 1M Concentration, at 25°c, 1 atm pressure is called "standard electrode potential (E°)".

EMF (Electro motive Force):

The potential difference between two electrodes is said to be as Electro motive force (EMF) or Cell potential (E_{cell}).

E_{cell} or EMF = $E_{cathode}$ (Right) − E_{Anode} (Left)
$E^\circ_{cell} = E^\circ_{cathode}$ (Right) − E°_{Anode} (Left)

Measurement of Electrode potential:

⇒ It is impossible to know the absolute value of a single electrode potential i.e potential difference between an electrode and the sourrounding solution of its own salt.

⇒ We can only measure the potential difference between two electrodes potentiometrically by combining them to form a complete cell.

⇒ For this electrode potential measurement, Reference electrodes are used.

Reference Electrode: The electrode which provides a stable, reliable and reproducible potential against an indicator electrode is called "reference electrode".

⇒ These are of two types.

(a) Primary Reference Electrode

(b) Secondary Reference Electrode.

(a) Primary Reference Electrode: / Standard Hydrogen electrode

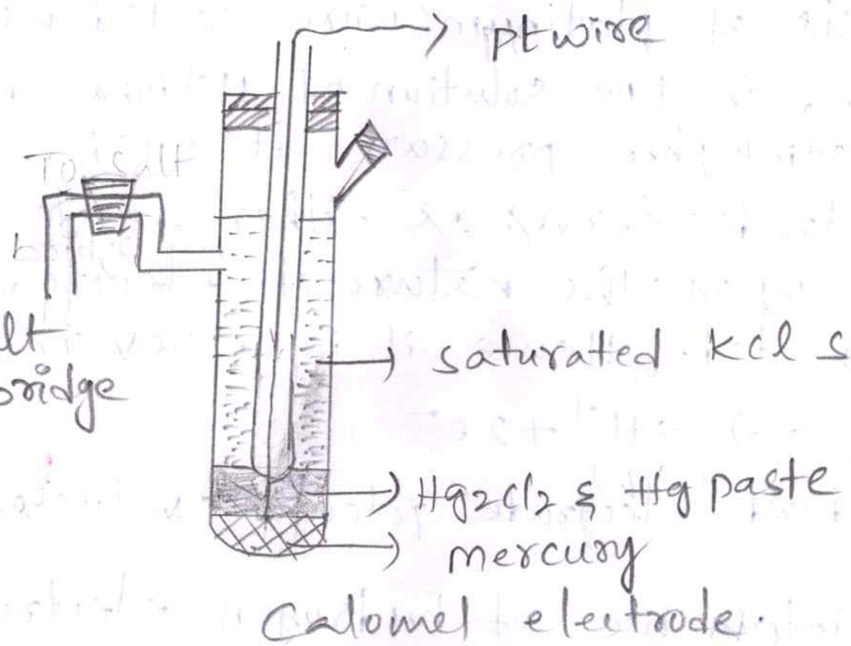
⇒ Standard hydrogen electrode (S.H.E) is used as primary reference electrode.

- electrical contact.

⇒ The potential of calomel electrode depends on the Concentration of potassium chloride (KCl) used.

⇒ This electrode is simple to construct, stable over a long period and doesnot vary with temperature

KCl Concentration	Electrode potential
0.1 N KCl	0.3335 V
1.0 N KCl	0.2810 V
Saturated KCl	0.2415 V

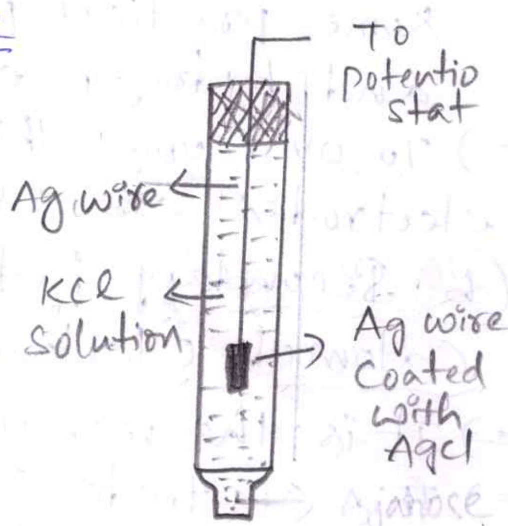


Calomel electrode.

Silver - Silver chloride electrode

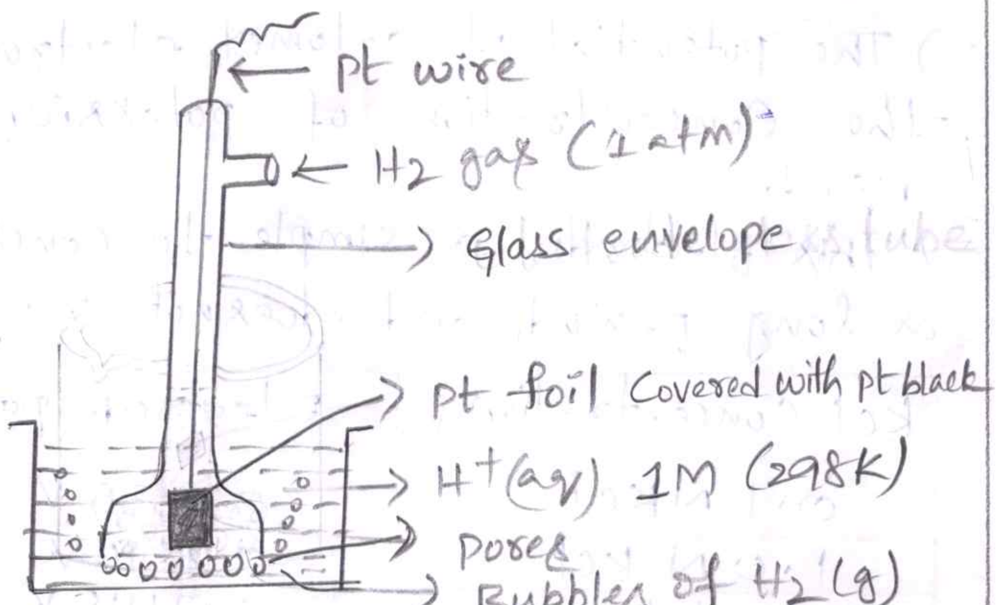
⇒ In this electrode thin layer of AgCl is deposited electronically on a silver or platinum wire & it is then immersed in solution containing chloride ions.

⇒ Based on concentration of KCl potential values vary.



KCl Conc.	Electrode Potential
0.1 N KCl	0.197 V
Saturated KCl	0.290 V

=)



Hydrogen electrode

=) It consists of platinum wire coated with platinum black dipped in 1 M solution of H^+ ions and hydrogen gas at 1 atmosphere pressure at 298K.

=) This electrode serves as either anode or cathode depending up on the nature of electrode to which it is connected. Hence it is a reversible electrode

$$H_{2(g)} \rightarrow 2H^+_{(aq)} + 2e^-$$

=) The standard electrode potential value of SHE is zero.

=) But maintenance of hydrogen electrode arises some practical problem as maintanance is difficult and hydrogen electrode is easily got poisoned.

=) To overcome this problems, secondary reference electrodes are used.

(b) Secondary Reference Electrode:

Calomel Electrode:

=) It is the mercury - mercurous chloride electrode.

=) This electrode contains small amount of mercury which is covered with a paste of solid mercurous chloride (Hg_2Cl_2). KCl solution is placed over the paste. A platinum wire is dipped into mercury layer for

Numerical problems - calculation of electrode potential using reference electrode.

1. The potential of zinc - zinc sulphate electrode is measured with respect to a saturated hydrogen electrode is -0.76 V. Find the value of standard reduction potential for the zinc - zinc sulphate electrode

Ans. Given $E^\circ_{cell} = -0.76 V$

$E^\circ_{SHE} = 0V$

we have $E^\circ_{cell} = E^\circ_{cathode} - E^\circ_{Anode}$

$$E^\circ_{cell} = E^\circ_{(Zn/ZnSO_4)} - E^\circ_{(SHE)}$$

$$E^\circ_{(Zn/ZnSO_4)} = E^\circ_{cell} + E^\circ_{(SHE)}$$

$$= (-0.76) + 0$$

$$= -0.76 \text{ V}$$

2. The potential of zinc - zinc sulphate electrode is -0.76 V and the potential of copper - copper sulphate electrode potential is +0.34 V. Find E°_{cell} potential value?

$$E^\circ_{cell} = E^\circ_{cathode\ (Cu-CuSO_4)} - E^\circ_{Anode\ (Zn-ZnSO_4)}$$

$$= +0.34 V - (-0.76)$$

$$= 1.10 V$$

3. The potential of Cu-CuSO4 electrode is +0.34V with respective to standard hydrogen electrode whose potential is zero. Find out E°_{cell} value.

$$E^\circ_{cell} = E^\circ_{cathode} - E^\circ_{Anode (SHE)}$$

$$E^\circ_{cell} = [+0.34_{[Cu/CuSO_4]} - 0] = +0.34 V$$

Electrochemical series:

⇒ The series of arrangement of reduction electrode potentials of various electrodes in increasing or decreasing order is called Electrochemical series.

⇒ Standard Reduction potential of SHE is zero.

⇒ The electrodes above hydrogen have -ve reduction potentials which indicates they undergo oxidation easily whereas electrodes below hydrogen have +ve reduction potentials which indicates they undergo reduction easily.

S.No.	Electrode Reaction	Electrode	Standard reduction potential (volts)	
1.	$Li^+(aq) + e^- \rightarrow Li(s)$	Li/Li^+	$-3.045V$ (High Anodic)	
2	$K^+(aq) + e^- \rightarrow K(s)$	K/K^+	$-2.930V$	↑ Anodic
3	$Mg^{2+}(aq) + 2e^- \rightarrow Mg(s)$	Mg/Mg^{2+}	$-2.370V$	nature
4	$Zn^{2+}(aq) + 2e^- \rightarrow Zn(s)$	Zn/Zn^{+2}	$-0.763V$	increases
5	$2H^+ + 2e^- \rightarrow H_2(s)$	H_2/H^+	$0.00V$ (Reference Electrode)	
6	$Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)$	Cu/Cu^{+2}	$+0.34V$	cathodic
7	$Ag^+(aq) + e^- \rightarrow Ag(s)$	Ag/Ag^+	$+0.79V$	nature
8	$Au^+(aq) + e^- \rightarrow Au(s)$	Au/Au^+	$+1.69V$	↓ increases
9	$F_2(g) + 2e^- \rightarrow 2F^-(s)$	$F_2/2F^{\ominus}$	$+2.87V$ (High cathodic)	

Electrochemical cells:

⇒ Cells which generate electricity by undergoing redox reactions are known as Electrochemical cells.

⇒ This device is used for conversion of electrical energy to chemical energy and chemical energy to electrical energy.

⇒ These are divided into two types.

(a) Galvanic cell / Daniel cell

(b) Electrolytic cell / Concentration cell

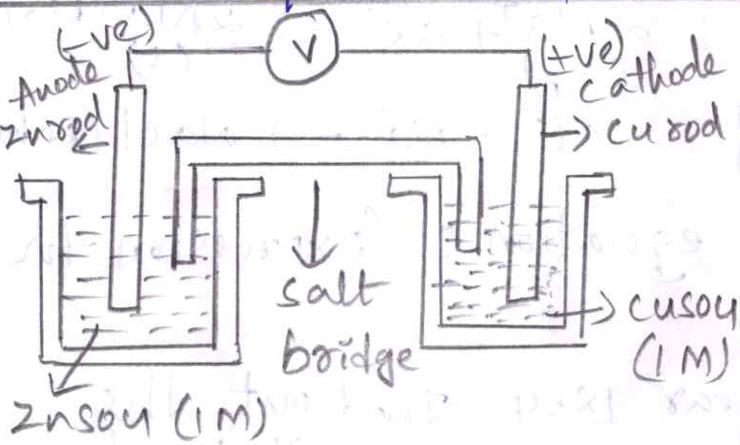
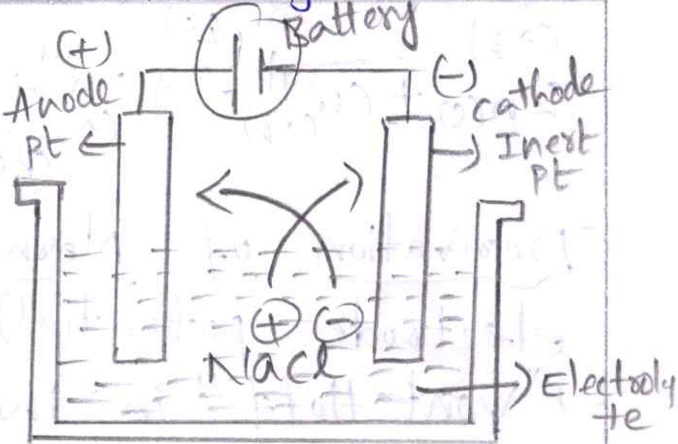
(a) Galvanic cell : (or) voltaic cell

⇒ The cell was discovered by "Luigi Galvani".

(b) Electrolytic cell : (or) ~~chemi~~ concentration cell :

⇒ The cell was discovered by Alessandro Volta

Differences between Galvanic and Electrolytic cell.

Galvanic cell	Electrolytic cell
	
⇒ The cell converts chemical energy to electrical energy.	⇒ The cell converts electrical energy to chemical energy
⇒ Zinc anode is -ve charge Copper cathode is +ve charge	⇒ Both electrodes are made up of Inert 'pt'. Anode +ve charge cathode -ve charge.
⇒ "U" shape salt bridge is present, to transfer electrons.	⇒ There is no salt bridge
⇒ Two different electrolytic solutions are there $ZnSO_4$ and $CuSO_4$	⇒ only one electrolytic solution i.e NaCl.
⇒ The redox reactions occur are spontaneous.	⇒ The redox reactions occur are non-spontaneous.
⇒ Each electrode is dipped in its own salt solution i.e Zn in $ZnSO_4$, Cu in $CuSO_4$	⇒ Only one electrolytic solution is taken.
⇒ Always Anode placed on left side, cathode right side.	⇒ Always Anode at left & Cathode at right side.

⇒ At Anode oxidation occurs, At cathode reduction occurs **At Anode:** $Zn_{(s)} \longrightarrow Zn^{+2}_{(aq)} + 2e^-$ (oxi) **At cathode:** $Cu^{2+}_{(aq)} + 2e^- \longrightarrow Cu_{(s)}$ (Red) $Zn_{(s)} + Cu^{2+}_{(aq)} \longrightarrow Zn^{2+}_{(aq)} + Cu_{(s)}$ (Redox)	⇒ At Anode oxidation occurs At cathode reduction occurs **At Anode:** $2Cl^- \longrightarrow Cl_{2(g)} + 2e^-$ (oxi) **At cathode:** $2Na^+_{(aq)} + 2e^- \longrightarrow 2Na_{(s)}$ (Red) $Cl^- + Na^+ \longrightarrow NaCl$ (Redox)

Derivation of Nernst equation: (Expression for electrode potential):

⇒ "Vont Hoff" in the year 1884 find out the derivation of nernst equation, it is also known as "Vont Hoff reaction isotherm."

⇒ This equation was derived from gibbs free free energy in thermodynamic system at constant temperature, constant pressure and one molar concentrated electrolytic solution.

⇒ This equation was used to find out "chemical shift" during the course of redox reaction in an electrolytic solution.

⇒ It is used for calculating single electrode potentials

⇒ Consider a general redox reaction

$$\underset{\text{Reactant}}{M^{n+}_{(aq)}} + ne^- \rightleftharpoons \underset{\text{product}}{M_{(s)}}$$

⇒ For a reversible reaction, the free energy change is given by

$$\Delta G = -RT\ln k + RT\ln\frac{[P]}{[R]} \rightarrow (1)$$

$$\Delta G^{\circ} = -RT\ln k \quad , \quad \Delta G = \Delta G^{\circ} + RT\ln\frac{[P]}{[R]} \rightarrow (2)$$

$$M^{n+} + ne^- \xrightarrow{Red} M$$

$$\Delta G = -nFE \rightarrow (3)$$

$$\Delta G^{\circ} = -nFE^{\circ} \rightarrow (4)$$

Substitute eq (3) & (4) in eq (2)

$$-nFE = -nFE^{\circ} + RT\ln\left[\frac{M}{M^{n+}}\right] \quad \therefore M = 1M$$

$$-nFE = -nFE^{\circ} + RT\ln\frac{1}{[M^{n+}]}$$

$\therefore$ formula $\ln\frac{1}{x} = -\ln x$

$$-nFE = -nFE^{\circ} - RT\ln[M^{n+}] \rightarrow (5)$$

Divide both sides with $-nF$

$$\frac{-nFE}{-nF} = \frac{-nFE^{\circ}}{-nF} - \frac{RT}{-nF}\ln[M^{n+}]$$

$$E = E^{\circ} + \frac{RT}{nF}\ln[M^{n+}]$$

$$E = E^{\circ} + \frac{0.0591}{n}\log[M^{n+}] \rightarrow (6)$$

Reduction potential

$$E = E^{\circ} - \frac{0.0591}{n}\log[M^{n+}] \rightarrow (7)$$

oxidation potential.

Notations:

ΔG = Gibbs free energy

ΔG° = standard Gibbs free energy

ΔE = Electrode potential

ΔE° = standard Electrode potential

$T = 298 K$ $R = 8.314 J$

$P = 1 atm$ $\ln = 2.303 \log$

$F = 96,500 C$ $M = 1 M$

Calculation : $\frac{8.314 \times 298}{96,500} \times 2.303 = 0.0591$

Applications of Nernst equation :

⇒ Nernst equation is used to study the effect of electrolyte concentration on electrode potential.

⇒ It is also used for calculation of potential of a cell under non-standard conditions.

⇒ It is used for finding the valency of an ion or the number of electrons involved in the reaction.

⇒ It is used to determine the unknown concentration of one of the ionic species in a cell provided with E°_{cell} and concentration of other ionic species.

Numerical problems :

1. calculate the EMF of a daniel cell at 25°C when the concentration of $ZnSO_4$ and $CuSO_4$ are 0.001M and 0.01 M respectively. The standard potential of the cell is 1.1 volts.

Ans. Given $E^{\circ}_{cell} = 1.1$ volts

$[Zn^{2+}] = 0.001M; [Cu^{+2}] = 0.01M$

$$E_{cell} = E^{\circ}_{cell} - \frac{0.0592}{n} \log \frac{[Zn^{2+}]}{[Cu^{2+}]}$$

$$= 1.1 - \frac{0.0592}{2} \log \left(\frac{0.001}{0.01}\right)$$

$$= 1.1 - (0.0296 \log (0.1))$$

$= 1.1 - (0.0296 \times -1)$
$= 1.1296 V$

2. Find the EMF of the following cell at 25°C given standard electrode potentials of zinc and copper are −0.76V & 0.34 V respectively.

$$Zn/Zn^{+2}(1M) \,//\, Cu^{+2}(1M)/Cu$$

"/" indicates potential difference arises between electrode and electrolyte

"//" represents salt bridge in a galvanic cell, used for electrolytic contact between the two half cells.

This is known as "representation of galvanic cell."

Ans: $Zn^{+2} = 1M$; $Cu^{+2} = 1M$

$E^{\circ}_{Cu} = 0.34 V$; $E^{\circ}_{Zn} = -0.76V$

$$E_{cell} = (E^{\circ}_{Cu} - E^{\circ}_{Zn}) - \frac{0.0592}{n} \log \frac{[Cu][Zn]^{2+}}{[Zn][Cu]^{2+}}$$

$$= [0.34 - (-0.76)] - \frac{0.0592}{2} \log\left(\frac{1}{1}\right)$$

$$= [0.34 + 0.76] - 0$$

$$= 1.1 V$$

Batteries:

⇒ A battery is a device which convert chemical energy to electrical energy (or)
Several electrochemical cells connected in series that can be used as a source of direct electric current at constant voltage.

⇒ A single electrochemical cell consists of cathode, anode, electrolyte are connected in a series forms battery.

=) Batteries acts as portable source of electrical energy.

=) In general batteries are of two types.

(1) primary battery (2) Secondary Battery

Primary Battery/Dry	Secondary Battery/wet
=> These cells are not designed to be recharged.	=> These cells are designed for repeated use.
=> The cell reaction is Irreversible.	=> The cell reaction is reversible.
=> Reactants → products chemical energy → Electrical energy	=> Reactants $\underset{charge}{\overset{Discharge}{\rightleftharpoons}}$ products chemical energy ⇌ electrical energy
=> Ex:- Dry cell, Zinc-air Battery	Ex:- Ni-cd, Lithium ion, mercury battery.
=> when all the reactants are converted into products no electricity produced.	=> Reactions are reversed by passing direct electric current in opposite direction
=> Battery becomes dead.	=> These can be used a large no. of cycles by discharging & charging process.
=> High resistance	=> Low resistantance.

1. Primary Cell: Ex:- Zinc - Air Battery:

=) It is a non rechargable metal - air battery.

=) The major components in Zinc-air battery are

Anode : Granulated Zinc powder

Cathode : Porous carbon supplied with oxygen

Electrolyte : Aqueous solution of KOH (Alkaline medium)

Separator : made up of poly vinyl Alcohol.

Construction & working principle:

⇒ A loose granulated powder of Zinc mixed with KOH electrolyte acts as Zinc anode material.

⇒ The outer covering acts as the cathode of the battery and a plastic gasket insulates the anode active materials.

⇒ The production of electrochemical energy is due to the use of oxygen from the atmosphere, the diffused oxygen acts as a cathode reactant in the battery.

⇒ Since the air cathode has infinite life, the electrical capacity of the cell is determined by the anode capacity, produce 1.6 V of power.

⇒ Cell reactions!

At Anode: oxidation

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

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

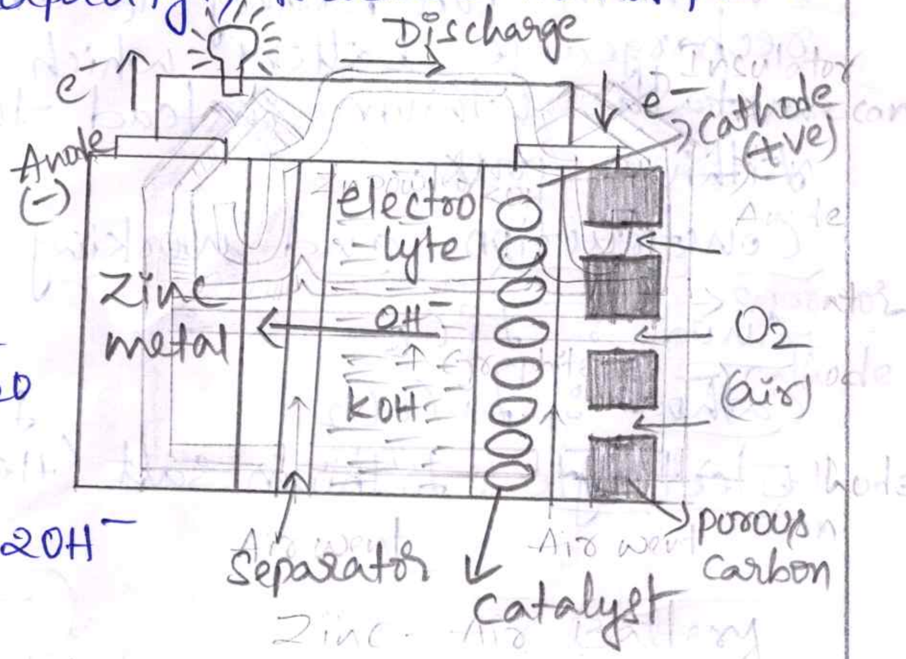
$Zn(OH)_2 \rightarrow ZnO + H_2O$

Cathode: Reduction:

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

Net Reaction:

$Zn + \frac{1}{2} O_2 \rightarrow ZnO$



Zinc air Battery

Advantages:

⇒ High energy density.

⇒ Flat discharge voltage.

⇒ Long shelf life.

⇒ No ecological problems.

⇒ Low cost, independent of temperature.

Disadvantages:-

⇒ High self - discharging nature.

⇒ CO_2 from air forms carbonate, which reduces conductivity.

Applications:-

⇒ Commonly used for watches, hearing aids.

⇒ Larger size cells are used in Cylindrical cells for telecoms and railway remote signalling

⇒ safety lamps for roads etc.

② Secondary Battery : Ex:- Lithium ion Battery

⇒ Lithium has the most negative electrode potential (-3.05V) hence it usually acts as anode.

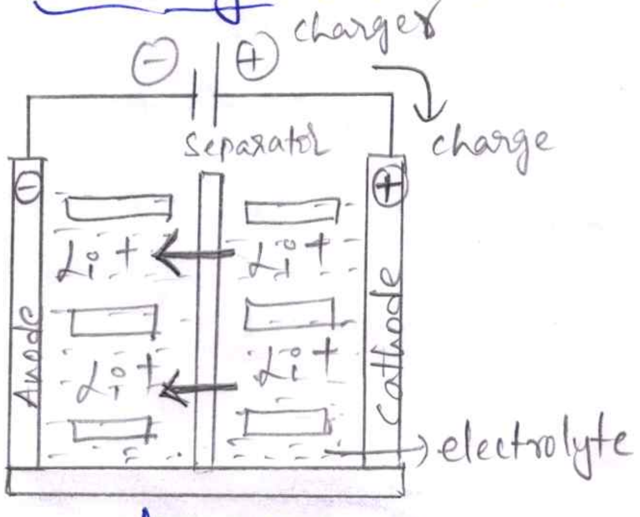
⇒ Lithium - ion battery is an example for rechargeable battery which doesnot contain metallic lithium instead these batteries contain Lithium ions.

Construction and working principle:

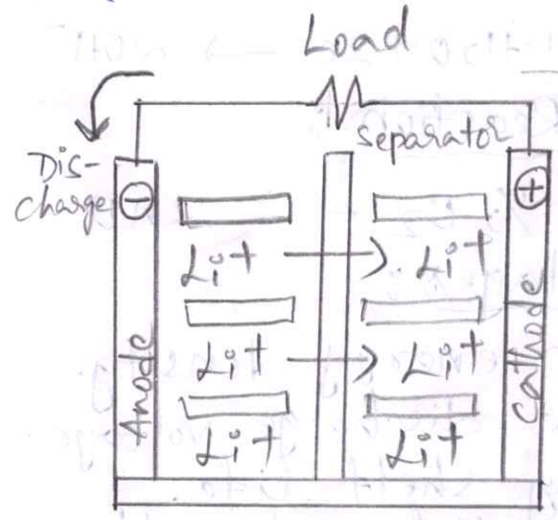
Anode : LiC_6

Cathode : $LiCoO_2$

Electrolyte : Lithium salt (Lithium - Hexafluorophosphate)



Charging (store energy)



Discharge (using energy)

⇒ Inside Lithium ion battery oxidation takes place at the anode. There, the graphite intercalation compound LiC_6 forms graphite (C_6) and lithium ions.

At Anode: Half cell reaction is oxidation. It is "not true oxidation" $LiCoO_2 + \text{graphite}(C_6) \rightarrow Li_{1-x}CoO_2 + Li_xC_6$

⇒ Reduction takes place at cathode. There cobalt-oxide combines with lithium ions to form Lithium cobalt oxide ($LiCoO_2$).

At cathode: Half cell reaction is reduction. It is "not true reduction". $Li_{1-x}CoO_2 + Li_xC_6 \rightarrow Li_{1-x+y}CoO_2 + Li_{x-y}C_6$

⇒ Here is the cell reaction left to right discharging, right to left charging, cycle, simply sweep Li^+ ions back & forth between two electrodes with electrons.

⇒ When the Lithium ion battery in mobile is powering it, positively charged Lithium ions move from the negative anode to positive cathode, by moving the electrolyte until they reach positive electrode. There, they are deposited. The electrons on the other hand move from anode to cathode.

Advantages:

⇒ High energy density.
⇒ Wide operating temperature range.
⇒ High discharge rates.
⇒ Low Cost.

Applications: power tools, Cameras, smart phones, Tablets, Laptops, medical equipments, vaccum-cleaners, Electronic bikes.

Fuel cells :

=) Fuel cell is an electrochemical cell, which converts chemical energy to electrical energy by oxidising fuel.

=) Fuel cell converts 75% of available chemical energy into electrical energy.

=) Fuel cells are said to be as primary cells which are capable of supplying current as long as the reactants are supplied.

=) These cells are free of noise, vibrations & thermal pollution.

Basic principle :

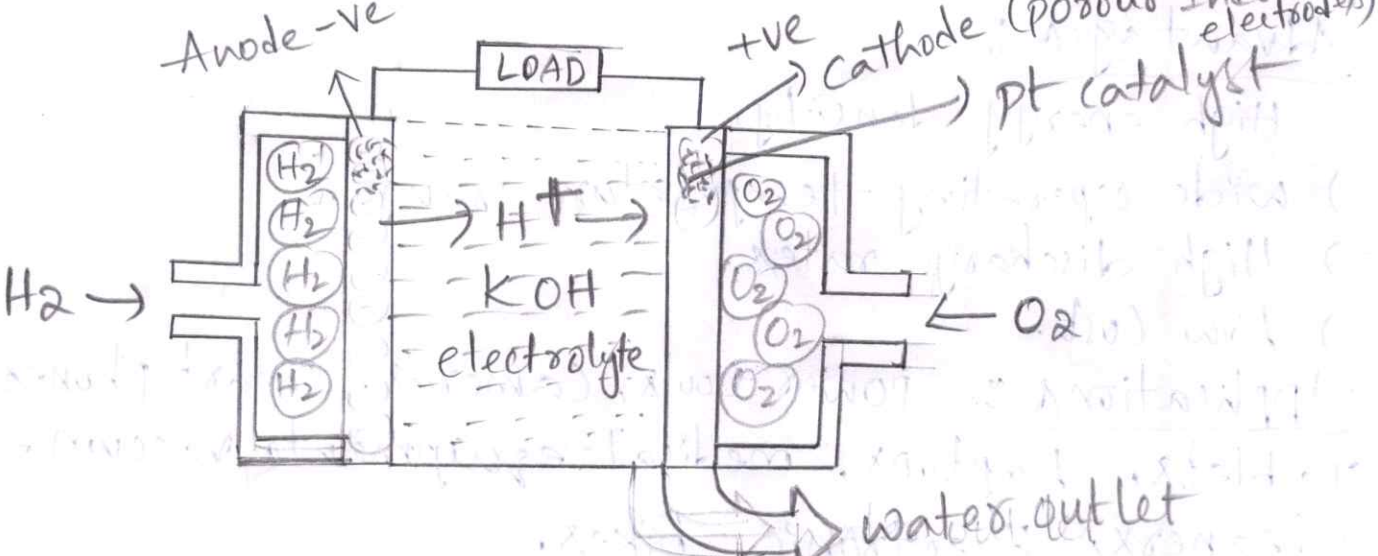
=) In fuel cells, chemical energy undergo oxidation in presence of oxidant, which is stored outside the cell.

Fuel + oxygen ⟶ products + Energy

$C + O_2 \longrightarrow CO_2 + Energy.$

Ex:- Hydrogen-oxygen fuel cell
Methanol - oxygen fuel cell.

① Hydrogen - oxygen fuel cell :



Construction and working principle:

⇒ This is one of the simplest and successful fuel cell.

⇒ At Anode, hydrogen gas is diffused through a porous carbon electrode containing pt (or) Pd catalyst.

⇒ The two electrodes are separated by aqueous KOH electrolyte solution (20%).

⇒ At cathode, oxygen is diffused through a porous carbon electrode containing Pt (or) Ag catalyst.

⇒ Hydrogen at anode undergoes oxidation to form H^+ ions which further reacts with OH^- which are liberated from electrolyte to form water.

⇒ Released electrons from anode flow towards cathode where O_2 undergo reduction to form OH^- ions. OH^- ions formed at cathode migrate into electrolyte thus retaining the electrolytic solution.

⇒ EMF generated from this cell is 1.23V.

At Anode: oxidation:

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

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

At electrolyte:

$$KOH \longrightarrow K^+ + OH^-$$

$$2H_2 + 4OH^- \longrightarrow 4H_2O + 4e^-$$

At cathode: Reduction:

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

Net reaction: $2H_2 + O_2 \longrightarrow 2H_2O$

Advantages: (or) Applications:

⇒ High efficiency
⇒ Light in weight
⇒ The water produced in fuel cell is used as drinking water for austronauts.
⇒ Used as auxillary energy source in space vehicles, submarines, military vehicles etc.

Dis advantages:

⇒ production of H_2 gas is costly.
⇒ storage of highly flammable Hydrogen is problematic.
⇒ Life time is not accurately known.

Corrosion

⇒ Corrosion is defined as "gradual disintegration of meal from its surface due to unwanted chemical or electrochemical attack by its environment."
⇒ Corrosion is also said to be as eating away of metal from its surface.
⇒ Reverse process of the metal extraction is called corrosion.

$$\boxed{\text{Ore}} \underset{\text{Corrosion}}{\overset{\text{extraction}}{\rightleftharpoons}} \boxed{\text{Metal}}$$

⇒ The extent of corrosion depends on the chemical affinity between the metal surface and environment and also on nature of corrosion product.

Ex:- Rusting of Iron.

$$O_2 + Fe + H_2O \longrightarrow \underset{\text{(Rust)}}{Fe_2O_3 H_2O}$$

Types of corrosion:

On the basis of environment to which it is exposed Corrosion is divided into two types.

(A) Dry (or) chemical corrosion

(B) Wet (or) Electrochemical Corrosion

(A) Dry/chemical Corrosion:

Dry corrosion occurs mainly through the direct chemical action of atmospheric gases (CO_2, SO_2, H_2S, halogens) and anhydrous inorganic liquids with metal surface in its immediate proximity in absence of water.

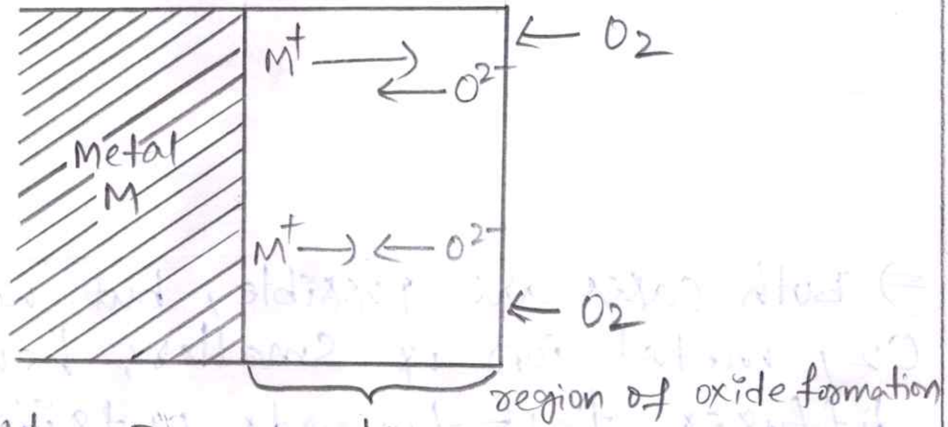
In Dry corrosion, there are three methods

1. Oxidation Corrosion
2. Corrosion by other gases
3. Liquid metal corrosion.

1. Oxidation corrosion:

⇒ This corrosion is carried out by direct action of O_2 on metals at low (or) high temperature generally in absence of moisture.

⇒ Generally, at normal or low temperatures, metals are shortly attacked by O_2 where as alkali and alkaline earth metals are rapidly oxidised.



Metal - oxide Preparation

⇒ At high temperatures, except Ag, Au, Pt all other metals rapidly oxidised.

$M \longrightarrow M^{2+} + 2e^-$ (oxidation) (loss of e^-)

$\frac{1}{2}O_2 + 2e^- \longrightarrow O^{2-}$ (Reduction) (gain of e^-)

$M + \frac{1}{2}O_2 \longrightarrow M^{2+} + O^{2-} \longrightarrow$ (MO metal oxide)

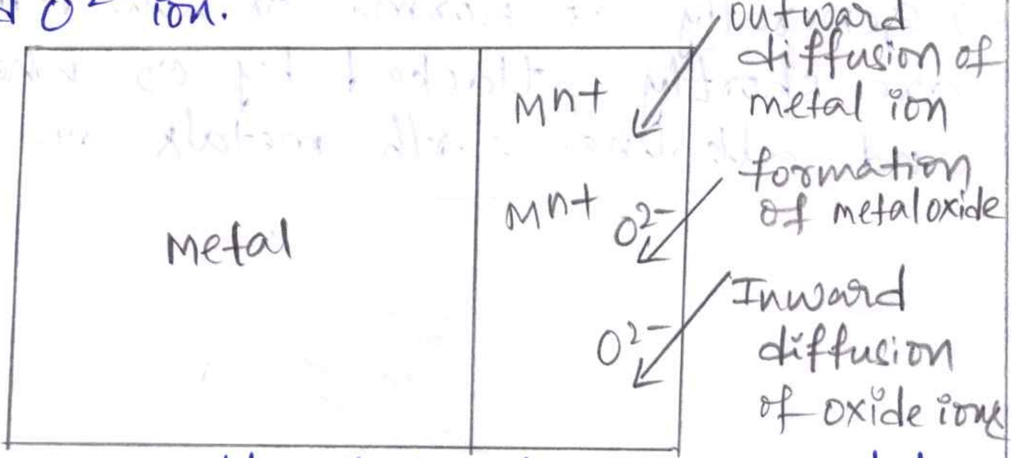
⇒ At the surface, metal in presence of oxygen undergo oxidation to form metal oxide.

⇒ Metal oxide formed at the surface acts as a barrier between metal and oxygen which reduces further corrosion process.

⇒ To continue oxidation of metal, either metal diffuses outward through the barrier or O_2 diffuses inward through the barrier.

⇒ When metal diffuses outward it reacts with outward O_2 and form metal oxide when O_2 diffuses inwards, O_2 reacts with underlying metal and form metal oxide inside the metal.

(1) Outward diffusion of metal ion through scale.
(2) Inward diffusion of O^{2-} ions through scale.
(3) Metal oxide scale formed by direct reaction of metal ion and O^{2-} ion.



⇒ Both cases are possible, but when compared to O_2, metal ion is smaller, hence metal ion diffuses fast towards outside when compared -

to O_2 diffusion. Hence metal oxide formation is more on outward when compared to inward.

⇒ Nature of metal oxide formed on the metal surface play an important role in deciding further action of metal.

If the film formed is

Stable: Impermeable and tightly adhering. when stable layer is formed on the metal surface it doesnot allow oxygen to penetrate into the metal thus stops the corrosion process. Hence stable film acts as a protective coating for inner metal.

Ex:- Cu & Al oxide film.

Unstable: If the formed layer is unstable, it decomposes back to metal and oxygen, thus no oxidation corrosion occurs.

Ex:- Ag, Al & Pt don't undergo oxidation corrosion

Volatile: The moment it is formed, it get volatile, thus underlying metal easily exposes to oxygen and further corrosion process continuous. Excessive corrosion occurs.

Ex:- Molybdenum undergo excessive corrosion.

Porous: It forms layer is porous, oxygen easily pass through the pores into the underlying metal and hence corrosion continuous till entire metal converts to oxide.

Ex:- Alkaline and Alkaline earth metal.

Pilling Bed worth Rule:

According to this rule, "If the volume of oxide is less than the volume of metal, the oxide layer is porous or non-Continuous and hence non-protective".

$$\text{Specific volume ratio} = \frac{\text{Volume of metal oxide}}{\text{volume of metal}}$$

Alkaline and alkali earth metals like Li, Na, K forms oxides of volume less than the volume of metal, Consequently the oxide layer faces stress there by developing cracks & pores on the structure, this layer can't prevent the access of oxygen to fresh metal surface below.

Metals like Al forms oxides, whose is greater than the volume of metal (Al) Consequently an extremely, tightly adhering non-porous layer is formed, thus the rate of oxidation rapidly decreases to '0' (zero).

Smaller the specific ratio, greater the oxidation Corrosion.

$$\text{Specific ratio} \propto \frac{1}{\text{oxidation Corrosion}}$$

2. Corrosion by Other gases:

⇒ This type of corrosion when the metals directly attacked by the gases like SO_2, H_2S, CO_2, Cl_2, F_2 etc. in absence of moisture (other than O_2).

⇒ The extent of Corrosion effect metal and depends on involved gas & chemical affinity, between them.

⇒ The intensity of attack depends on the formation of protective or non protective films on the metal surfaces.

⇒ If the film formed is protective or non-porous or stable the extent of attack decreases.

Ex:- AgCl stable layer formed due to attack of Cl_2 on Ag.

⇒ If the film formed is protective non-protective or porous, the whole metal is gradually destroyed due to increase in corrosion rate.

Ex:- AgCl stable layer formed due to attack of Cl_2 on Ag.

If the film formed is non-protective or porous the whole metal is gradually destroyed due to increase in corrosion rate.

Ex:- Dry Cl_2 gas attacks on Sn film forming volatile $SnCl_4$ layer which volatises, immediately leaving fresh metal to further attack.

3. <u>Liquid metal corrosion</u>:

⇒ This is due to chemical action of flowing liquid metal at high temperature on solid metal (or) alloy.

⇒ This type of corrosion occurs in devices used for nuclear power.

⇒ The corrosion reaction involves either

(i) Dissolution of a solid metal by the liquid metal

(ii) Internal penetration of the liquid metal into solid metal, either of this method

lowers the solid metal nature. Coolant (Na) causes 'Cd' corrosion in nuclear reaction.

(B) Wet Corrosion (or) Electrochemical Corrosion :

Wet or Electrochemical corrosion is a type of corrosion where

(i) Conducting electrolytic Liquid dipped is in Contact with metal (or)

(ii) Metals are dipped in contact with conducting liquid. (Two dissimilar metals)

(iii) Metals are dipped in solution.

⇒ Metal acts as anode, where oxidation takesplace with the liberation of electrons, where actual corrosion takesplace.

⇒ Another part of metal acts as cathode where reduction takes place with absorption of electrons liberated from anode.

⇒ The rate of electrochemical corrosion depends upon the following factors

1. If the corrosion product goes into solution without any difficulty.

2. It is readily soluble in environment, the rate of corrosion is maximum.

3. If the corrosion product is an insoluble in environment covering metal surface, the rate of corrosion is maximum.

Mechanism of Wet or electrochemical Corrosion :

This Corrosion involves flow of electrons between anode and cathode through conducting medium.

⇒ During corrosion reaction at anode, M^{n+} ions are formed and at cathode O^{2-} and OH^- are formed. The metallic and non-metallic ions are

- formed diffuses through conducting medium and forms a corrosion product somewhere between anode and cathode.

Gain of electrons takes place by

1. Evolution of Hydrogen
2. Absorption of Oxygen

① Evolution of Hydrogen:

⇒ This type of corrosion mostly occurs in acidic medium containing two dissimilar metals.

⇒ They themselves acts as Anode and cathode.

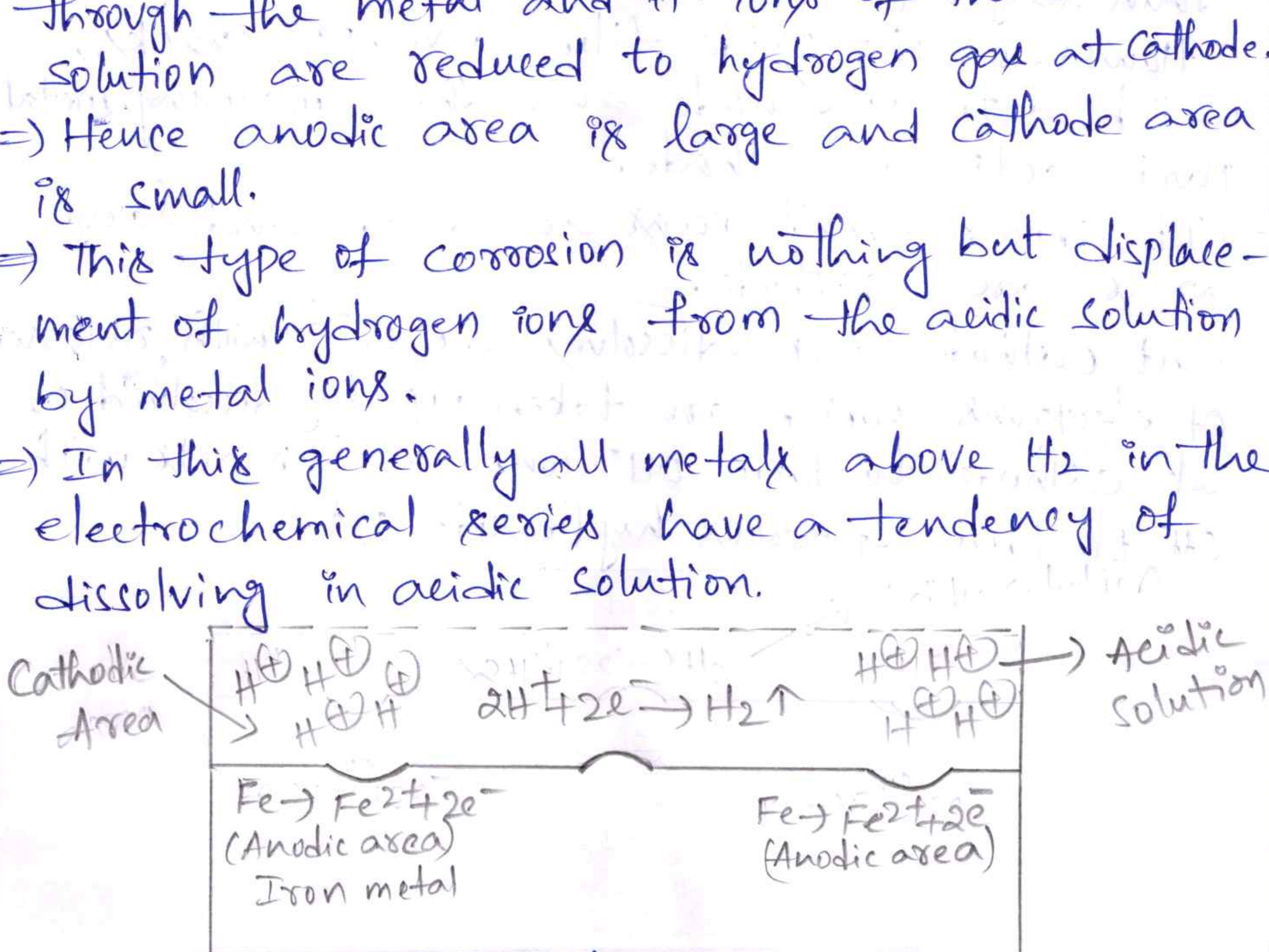
⇒ In case of iron metal, iron undergoes oxidation to form Fe^{+2} ions with liberation of electrons

⇒ These electrons flow from anode to cathode through the metal and H^+ ions of the acidic solution are reduced to hydrogen gas at cathode.

⇒ Hence anodic area is large and cathode area is small.

⇒ This type of corrosion is nothing but displacement of hydrogen ions from the acidic solution by metal ions.

⇒ In this generally all metals above H_2 in the electrochemical series have a tendency of dissolving in acidic solution.



Evolution of Hydrogen gas

At Anode: $Fe \longrightarrow Fe^{+2} + 2e^-$ (oxidation larger area)

At cathode: $2H^+ + 2e^- \longrightarrow H_2\uparrow$ (Reduction - smaller area)

$$Fe + 2H^+ \longrightarrow Fe^{+2} + H_2\uparrow$$

2. Absorption of oxygen:

when the metals are in contact with slightly alkaline or neutral solutions with some amount of dissolved oxygen, this type of corrosion takes place.

Ex:- Rusting of Iron.

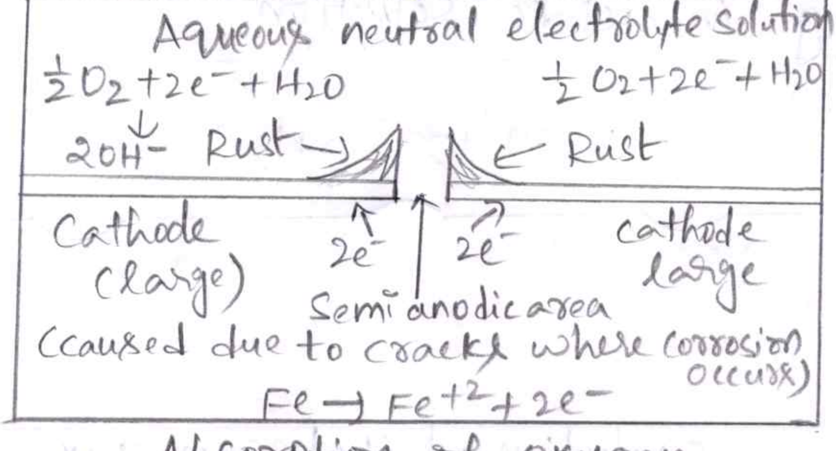
⇒ In this type, metal acts as anode and cathode and the environment acts as electrolyte through which electrons flow from anode to cathode.

⇒ The surface of iron is usually coated with a thin layer of iron oxide.

⇒ However the oxide film develops cracks, which acts as anode and the remaining metal part acts as cathode.

⇒ It shows small areas are anode and large areas are cathode.

⇒ At cathode, iron dissolves as Fe^{+2} with release of electrons which are taken up by dissolved O_2 at cathode to form OH^- ions. Fe^{+2} reacts with OH^- to form ferrous hydroxide ppt.



Absorption of oxygen

At Anode : $Fe \longrightarrow Fe^{+2} + 2e^-$ (oxidation - smaller area)

At cathode : $\frac{1}{2}O_2 + H_2O + 2e^- \longrightarrow 2OH^-$ (Reduction - larger area)

$$Fe + \frac{1}{2}O_2 + H_2O \longrightarrow Fe^{+2} + 2OH^- \} \; Fe(OH)_2 \downarrow$$

Ferrous hydroxide

$$2Fe(OH)_2 + \frac{1}{2}O_2 \longrightarrow Fe_2O_3 \cdot 2H_2O \text{ (Rust)}$$

$$4Fe(OH)_2 + O_2 + 2H_2O \longrightarrow 4Fe(OH)_3 \text{ (Ferric hydroxide)}$$

If O_2 is available in excess, $Fe(OH)_2$ is converted to $Fe(OH)_3$ which is yellow rust, correspons to $Fe_2O_3 \cdot XH_2O$, which further converts to black anhydrous magnatite (Fe_3O_4). Hence corrosion occurs at anode and rust formation takesplace at cathode.

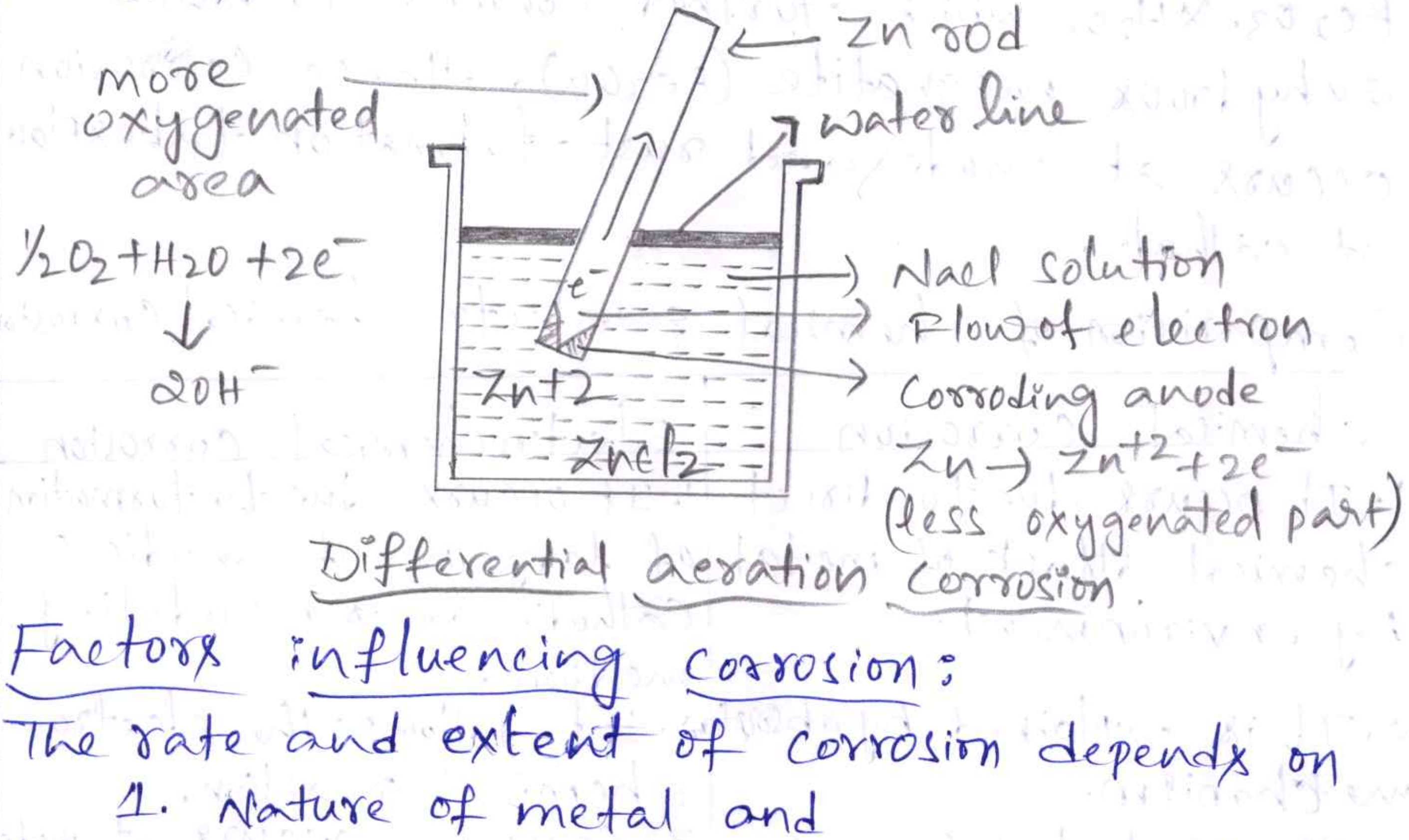
Comparision of chemical & electro chemical corrosion

Chemical corrosion	Electrochemical corrosion
1. It occurs due to direct chemical attack of metal by environment.	1. It occurs due to formation of large no. of anodic & cathodic areas in conducting medium.
2. It is explained by absorption mechanism.	2. It follows the electro-chemical reaction.
3. The product of corrosion accumulate on the same spot where corrosion occurs.	3. Corrosion occurs at anode while corrosion product gathers at cathode.
4. It occurs at homogeneous and heterogeneous surfaces	4. It occurs only at heterogeneous metal surfaces.
5. It is a slow process.	5. It is a fast process.
6. In this type of corrosion large areas are anode & small areas are cathode.	6. In this type of corrosion, large areas are cathode and small areas are anode.

Differential aeration or Concentration cell corrosion

⇒ This type of corrosion occurs when a metal is exposed to varying concentration of oxygen (or) any electrolyte on the surface of the base metal.

⇒ If a metal is partially immersed in a conducting solution, the metal part above the solution is more aerated and hence become cathodic. On the other hand the metal part inside the solution is less aerated and thus becomes anodic and suffers corrosion.



Differential aeration corrosion.

Factors influencing corrosion:

The rate and extent of corrosion depends on

1. Nature of metal and
2. Nature of environment

1. Nature of metal:

ⓐ Position in Galvanic series:

Higher the metal in galvanic series, higher is the corrosion rate.

⇒ When two metals are in electrical contact in presence of electrolyte, the highest metal in series undergoes oxidation.

Greater the difference in the position of the metal higher is a corrosion rate at anode.

(b) purity of metal:

The rate & extent of corrosion increases with the increasing rate of purity.
Hence as the purity of metal is more corrosion rate is less.

Ex:- when pb/Fe imurity is present in zinc, zinc undergoes fastest corrosion when compared to pure zinc.

(c) physical state of metal:

Rate of corrosion is influenced by physical state of metal that is size, orientation of crystal, stress etc.

→ smaller the grain size of metal greater is its solubility hence greater will be its corrosion moreover stressed areas in metal also undergo corrosion easily.

(d) Passive character of metal:

passivity means the metal undergo low corrosion than the expected from their Galvanic cell, Hence as the passive character of metal increases corrosion rate decreases.
Thus Stainless steel which show more passive character is mostly used in utensils.

(e) Nature of Surface film:

If the formed Surface film is stable non-porous it decreases the corrosion rate further, greater the specific volume ratio, lesser is the oxidation corrosion.

(f) solubility of corrosion product: If the corrosion product is soluble in the corroding medium the Corrosion proceeds at faster rate. Hence corrosion product acts as physical barrier for proceeding further corrosion.

(g) volatility of corrosion product:

If the corrosion product is volatile it's easily evaporates into the environment hence corrosion process proceeds further. Thus formation of volatile product increases the corrosion rate & fast the rate.

(h) Over voltage:

Decrease in over voltage of the metal increases the corrosion rate.

Ex:- Initially zinc in sulphuric acid undergoes slow corrosion, when copper is added to it fast the corrosion rate, because copper addition decreases the voltage.

2. Nature of Environment:

(a) Temperature: Rate of corrosion increases when temperature of environment increases.

(b) Humidity of air: In the presence of humidity in environment corrosion rate increases, generally humidity of air is the deciding factor in atmospheric corrosion.

(c) presence of impurities in atmosphere:- presence of corrosive gases such as sulphur dioxide, Carbon dioxide, oxygen etc. in atmosphere increases acidic nature thus increases corrosion-rate.

(d) presence of suspended particles in atmosphere:
The suspended particles in atmosphere may be chemically active or inactive.
If the suspended particles are chemically active they absorb moisture and fastly involves in corrosion process.
If suspended particles are chemically inactive they absorb sulphur gases and moisture which is slowly involved in corrosion process.

(e) Influence of pH: Corrosion is higher in acidic medium when compared to basic and neutral medium. Hence by increasing pH value we can decrease in corrosion rate.
Ex:- Zinc rapidly undergo corrosion in acidic medium and shows minimum corrosion at pH = 11.

(f) Conductance of corroding medium:
Conductance of dry sandy soil is slower when compared to clay and mineralised soils.
Stray currents will cause more serious damage to metallic structures.

Control of Corrosion:
⇒ The method used to protect the metal from corrosion mainly operates by preventing corrosion reaction from taking place.
⇒ Various preventive measures include modification of environment, modification of properties of metal, use as a protective coating and cathodic protection

Cathodic protection:

Generally metal undergoes corrosion by oxidation process that is metal behaves as anode, the main principle involved in this process is to force the metal to behave like cathode, so that corrosion doesn't occur as there is no anodic area.

Cathodic protection is of two types.

1. Sacrificial anodic protection
2. Impressed current cathodic protection.

1. Sacrificial anodic protection:

⇒ It is also known as galvanic protection.

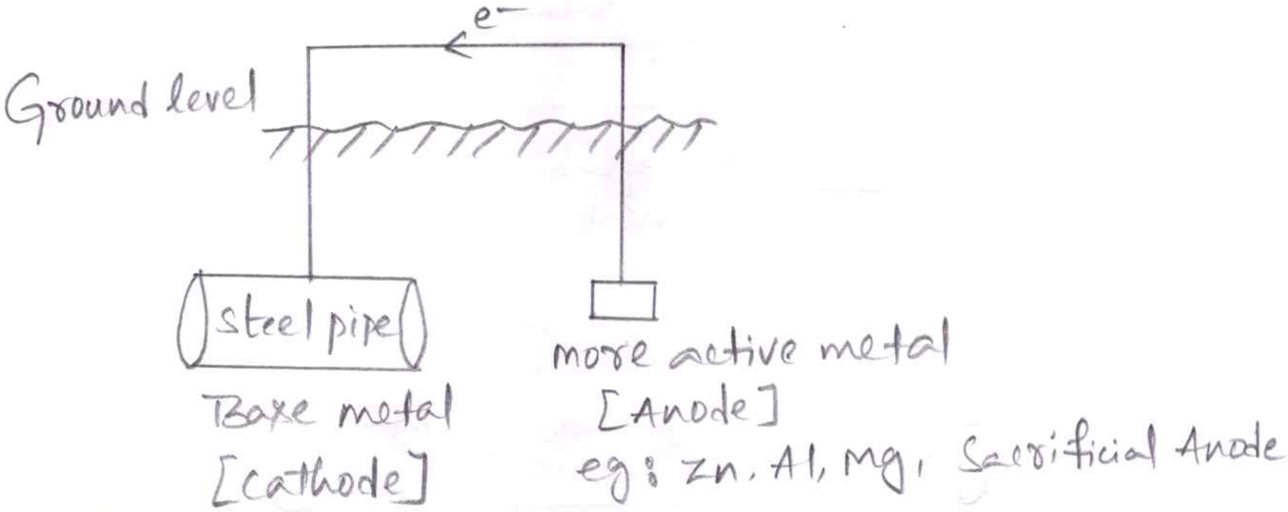
⇒ The metal surface can be saved from corrosion by connecting it with wire to a more active metal that is more anodic metal.

⇒ So that all the corrosion is concentrated at the more active metal thus saving the metal surfaces ~~from~~ corrosion.

⇒ As this more active metal is sacrified in the process of saving metal from corrosion it is called sacrificial anode.

⇒ Metals commonly used as sacrificial anode are zinc, aluminium, magnesium and their alloys

Ex:- Zinc is used as sacrificial anode in good electrolyte such as sea water.



Applications:

⇒ protection of underground cables and pipelines from soil corrosion.

⇒ protection of ships from marine corrosion. sheets of magnesium and zinc are hang around the ship hull, these sheets being anodic to iron, these are corroded when consumed completely, they are replaced by fresh ones. Formation of rusty water is prevented by insertion of magnesium sheets into water boilers or tanks.

Impressed Current Cathodic protection:

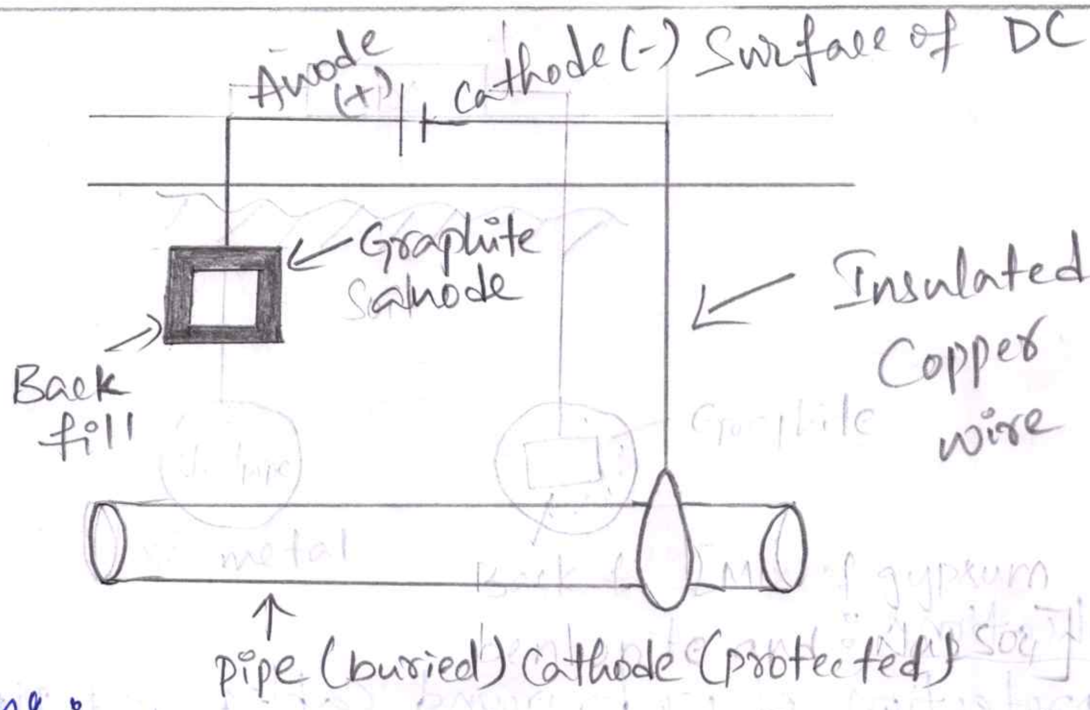
In this method, current from external source is applied in opposite direction to nullify the corrosion current.

Thus, converting an anode to cathode.

Once the metal becomes cathodic it is protected from corrosion.

The anode used may be graphite, carbon, steel, High silica. These are inert materials which are to be replaced periodically.

This insoluble anode buried in soil is connected to metallic structure to be protected. This anode buried is used to increase electrical contact with the surrounding soil



Applications :

This method is useful when electrolyte resistivity and current requirement are high. It is well suited for large structures.

UNIT - III

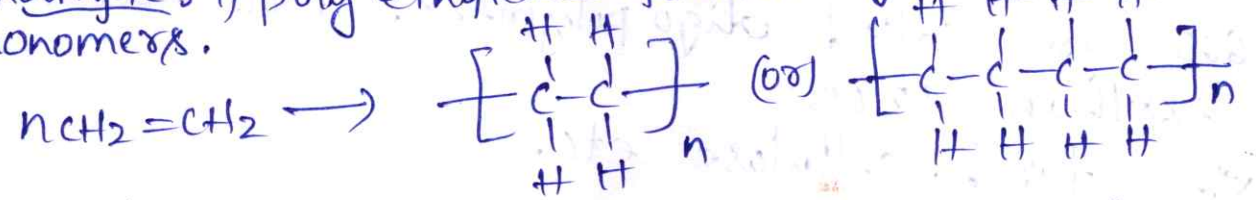
Polymers and fuel chemistry

Syllabus:
Introduction to polymers, functionality of monomers, thermoplastics and thermo setting plastics, properties and applications of Bakelite & PVC.
Fibres: Polyesters, mechanical requirements for fibres - crystallinity, stress strain curves.
Biodegradable polymers - properties & applications of poly glycolic acid (PGA), poly lactic acid (PLA).
Fuels: Types of fuels, calorific value of fuels, numerical problems based on calorific value.
Liquid fuels, refining of petroleum, octane and cetane number, determination of calorific value of solids by bomb calorimeter.

Polymers: Polymers are macromolecules (or) giant molecules made by linking together a large number of small molecules called monomers.

In greek "poly" means "many"
mers means "units" or "molecules"

Example: 1) poly ethylene formed by no. of ethylene - monomers.



Example(2): Poly styrene formed by no. of styrene - monomers.

Polystyrene

Monomers: The small molecules which combines with each other to form polymer molecules are called as "monomers."

Molecules are termed as monomers, if they have atleast two bonding sites.

$$\underset{\text{molecule}}{M} \longrightarrow \underset{\text{Monomer.}}{-M-}$$

Degree of polymerization (D.P.):

The number of repeating units in a polymer chain is known as "Degree of polymerization."

Molecular weight of polymer = M.wt. of monomer × DP

Based on degree of polymerization, polymers are divided into two types.

(1) High polymers

(2) oligo polymers.

(1) **High polymers:-** polymers have high D.P. i.e >600 are called high polymers. Molecular weight ranges from 10,00,000.

Ex:- PVC, Polyethylene, etc.

(2) **oligo polymers:-** polymers having less D.P. i.e <600 are called oligo polymers. Molecular weight is less than 10,000.

Ex:- starch, cellulose etc.

Classification of polymers:-

polymers may consist of identical monomers (or) monomers of different chemical structures. According to this, polymers are classified into two types, (i) homo & hetero or Copolymers.

(a) Homo polymer :- polymers in which monomers are identical (or) belongs to only one chemical compound.

$$-M-M-M-M-M-M-$$

(b) Co-polymers :- polymers in which monomers are not identical, they belongs to two or more chemical compounds.

$$-M-M_1-M_2-M_3-M-M_1-M_2-M_3-$$

(c) Hetero polymers :- The polymer chain is made up of different series of atoms is called hetero polymers.

$$-C-C-O-C-C-O-C-C-O-$$

Functionality of monomers :-

For a substance to act as a monomer, it must have atleast two reactive sites (or) bonding sites.

"The no. of bonding sites in a monomer is referred to functionality."

Based on functionality, monomers are classified into three types.

(1) Bifunctional
(2) Trifunctional
(3) poly functional

(1) Bifunctional : Monomers with two bonding sites.

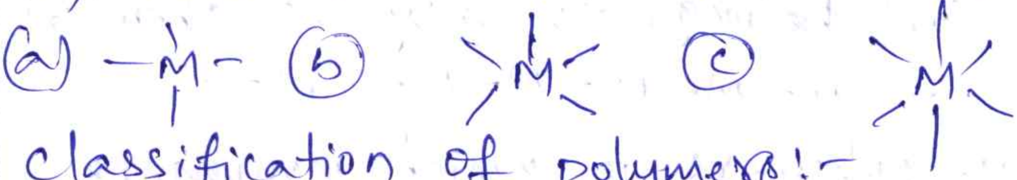
$-M-$ (or) XMX

(2) Trifunctional : Monomers with three bonding sites.

$-\overset{|}{M}-$ (or) $X\overset{X}{M}X$

(3) poly functional :- Monomers with more than three bonding sites

(a) Tetra functional (b) Penta & (c) Hexa functional



<u>Classification of polymers:-</u>

Polymers are with different chemical structure, physical properties, mechanical behaviour, thermal behaviour etc. So they can be classified into different types.

① Natural and synthetic ② organic & Inorganic
③ Thermo & Thermosetting ④ plastics, Elastomers, Fibers & liquid resins.

<u>① Natural & Synthetic polymers:-</u>

Depending on origin, polymers are classified into two types as natural and synthetic polymers.

Natural polymers:- These polymers are isolated from natural materials.

Ex:- Cotton silk, Wool, Rubber etc.

Synthetic polymers:- These polymers are prepared from laboratory techniques.

Ex:- Poly ethene, PVC, Teflon etc.

<u>② Organic and Inorganic polymers:-</u>

Based on chemical structure polymers are classified into two types, as Organic & Inorganic.

<u>Organic polymers:-</u> polymers whose back bone is made up of carbon atoms are called organic polymers. The side valencies are filled by usually hydrogen, oxygen, nitrogen etc.

Ex:- polythene, PVC etc.

Inorganic polymers:-
Inorganic polymers generally contain no carbon atoms in their backbone chain.
Ex:- Glass and Silicone rubber.

(3) Thermo and thermo setting plastics: Based on thermal behaviour, these are classified into two types.

Thermoplastics:- polymers which soften on heating and harden on cooling are termed as thermoplastics. Ex:- polythene, polystyrene etc.

Thermo setting plastics:- polymers on heating sets into infusible mass, once it set cannot be reshaped
Ex:- Bakelite, polyesters etc.

(4) plastics, Elastomers, Fibers and Liquid resins
Depending on its ultimate form and use, polymers can be classified as plastics, elastomers, fibers, resins
⇒ A polymer is shaped into hard and tough utility articles by the application of heat and pressure it is used as plastic.
Ex:- polystyrene, PVC, polythene etc.
⇒ when vulcanized into rubbery products exhibiting good strength and elongation, polymers are used as elastomers.
Ex:- Natural rubber, Synthetic rubber etc.
⇒ If drawn into long filaments like materials whose length is atleast 100 times greater to its diameter polymers are said to have been converted into fibres. Ex:- Nylon, and Terylene

⇒ polymers used as adhesives in liquid form are described as liquid resins. Ex:- Epoxy resins

plastics :-

⇒ These are the high polymers, which can be moulded into any desired form by applying heat & pressure in presence of catalyst.

⇒ plastics attained great importance in every day life because of their unique properties like.

1) Light weight
2) Good thermal and electrical insulation
3) High corrosion resistance
4) High chemical Inertness
5) Low maintainance cost.
6) Toughness and water resistance.
7) Easy fabrication and remarkable colour change.
8) Easy work ability like moulding, casting etc.

Differences between thermo & thermo setting plastics

Thermo plastics	Thermosetting Plastics
1) which are soften on heating and harden on cooling.	1) These are harden during moulding and cannot be soften by heating.
2) weak vanderwaals forces of attraction between them.	2) strong covalent bonds between them.
3) these are formed by addition polymerisation	3) These are formed by condensation polymerisation.
4) They are generally long chain linear polymers.	4) They have three dimensional cross linked structures.
5) They can be reclaimed from waste	5) They can not be reclaimed from waste.

6. They dissolve in some organic solvents.	6. They are not easily soluble in organic solvents.
7. The scrap of the plastic can be reused.	7. The scrap of plastic can not be reused.
8. There is no chemical change in chemical composition during moulding process	8. They undergo chemical changes during moulding process.
9. They are soft, weak, less brittle.	9. They are hard, strong, more brittle.
10. Ex:- polyethylene, PVC etc.	10. Bakelite, Nylon 6,6 etc.

Properties and applications of PVC (poly vinyl chloride):

Synthesis: By the combination of 'n' number of vinyl chloride monomers, in presence of peroxide, under pressure, by addition polymerization, polyvinyl chloride is formed.

$$n\ CH_2=\underset{\underset{Cl}{|}}{CH} \xrightarrow[\text{pressure}]{\text{peroxide}} \left[CH_2-\underset{\underset{Cl}{|}}{CH} \right]$$

Vinyl chloride   Poly vinyl chloride (PVC)

Properties: ① PVC is a colourless & odourless powder.
② It is a chemically inert material.
③ It has high softening point at 148°c
④ It is soluble in chlorinated hydro carbons, like Ethyl chloride etc.
⑤ It has high resistance to light, acids, alkalis and ethyl chloride etc.

Applications: ① PVC is used for making rain coats, table cloths, curtains, coatings for electric wire, radio, TV components etc.

(2) Rigid PVC (or) unplasticized PVC has high rigidity and high chemical inertness. It is mainly used for making sheets, tanks etc.

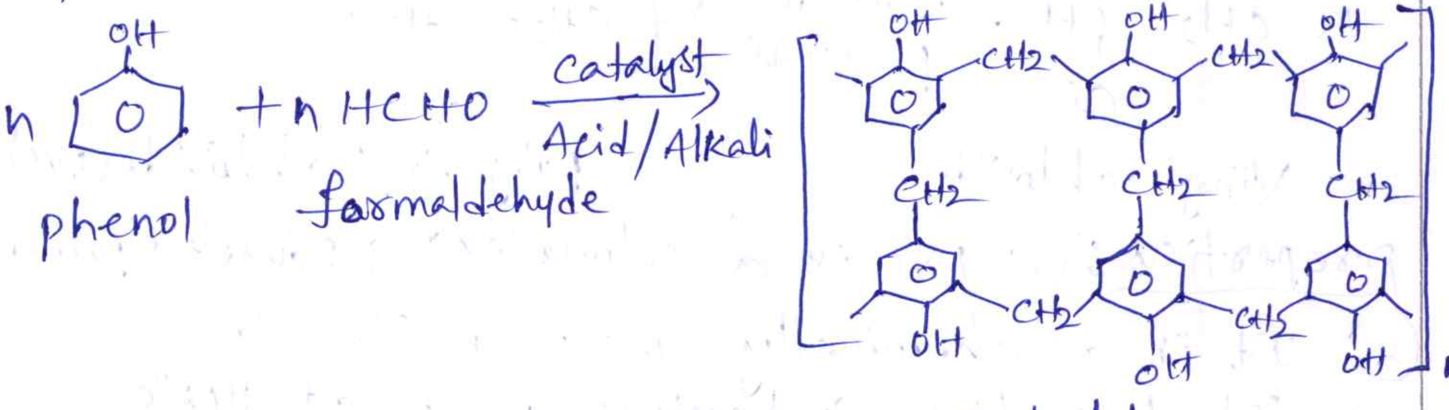
(3) It is also used for making refrigerator components, trays, cycle and motorcycle mudguards etc.

(4) It is used for window frames, PVC pipes, wire insulation, door profiles etc.

Properties and Applications of Bakelite:

Synthesis:- Bakelite is earliest thermosetting resin, named after Belgian scientist, an american scientist Baekeland.

⇒ Bakelite is formed by condensation polymerisation of phenol and formaldehyde in presence of an acid (or) alkali catalyst.



Bakelite.

Properties:

(1) Out standing heat resistance.

(2) Dimensional resistance & stability to scratches.

(3) Excellent electrical insulating character.

(4) Resistant to acids, salts, most organic solvents

(5) Easily attacked by alkalies.

Applications:-

① It is used for making electrical equipments like switches, plugs, holders, heater handles etc.

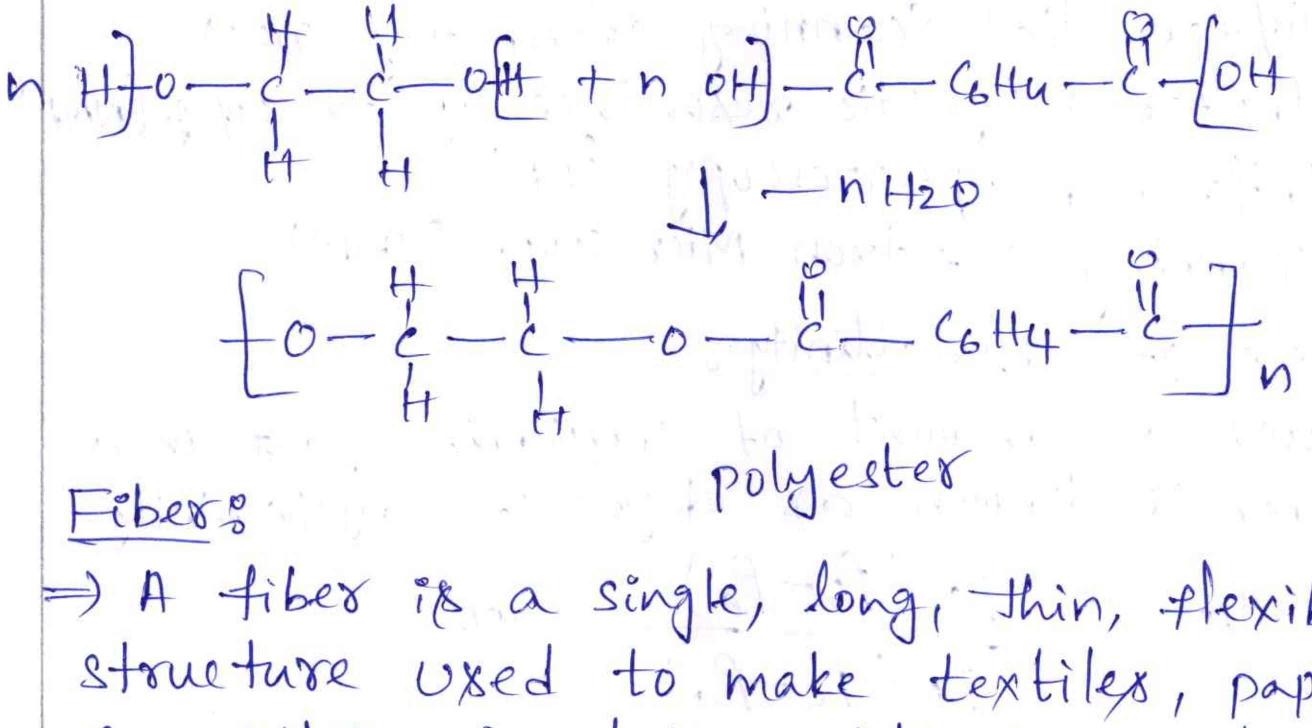
② Making telephone parts, radio, T.V. cabinets.

③ paints & varnishes.

④ Production of ion-exchange resins.

⑤ Brake linings, abrasive wheels and sand-papers etc.

Poly ester: Ethylene glycol monomers and terephthalic acid monomers reacts with eachother by condensation polymerisation to form polyester.



polyester

Fiber:

⇒ A fiber is a single, long, thin, flexible structure used to make textiles, papers, composites, insulation, filtration, sutures etc.

Types of fibers:-

① Natural fibres ⇒ ⓐ plant – cotton, flax (plant)
ⓑ Animal – wool, silk
ⓒ mineral – Asbestos

② Synthetic fibres ⇒ polyester, Nylon, PVC, polystyrene

(3) Semi synthetic fibres:- Rayon, modal, bamboo [extracted from wood pulp.

Crystallinity of polyester/polymer:

The degree of structural regularity with in the polymer chain is known as crystallinity of polymer.

(1) Amorphous (non-crystalline)
(2) Semi crystaline (partial crystalline)
(3) Crystalline (highly crystalline)

Methods to measure crystallinity:

1. X-ray diffraction (XRD)
2. Differential Scanning colorimetry (DSC)
3. Nuclear magnetic resonance spectroscopy. (NMR)
4. Infrared Spectroscopy (IR)
5. Scanning Electron Microscope (SEM)

Degree of crystallinity:

Measure of amount of crystalline part in a polymer is known as degree of crystallinity.

$$\% C = \frac{\rho_c(\rho_s - \rho_a)}{\rho_s(\rho_c - \rho_a)} \times 100$$

where ρ_c = crystalline density
ρ_a = amorphous density
ρ_s = polymer density

properties:

→ A crystalline solid has sharp melting point, amorphous do not have a sharp melting point.

⇒ Crystalline solid has a definite shape with orderly arranged ions, atoms, (or) molecules in a 3-D pattern, known as Crystal lattice with a uniform intermolecular forces.
⇒ The density of crystalline polymer is greater than that of non-crystalline polymer because of more effective packing.

Applications:-

1) Textiles – clothing
2) packaging – Bottles, Containers
3) films – photographic, magnetic films
4) Fibres – Industrial technical fibres
5) Composites – Reinforced materials.

Stress – strain (or) Load elongation curves of polyester:/ Mechanical requirements for fibres

⇒ Mechanical properties of fibres are determined from load elongation curves in which a progressively increasing load or stress is applied to fibre and the resulting deformation is determined.
⇒ Elasticity: Ability of a material to return to its original shape after deformation (rubber).
⇒ Plasticity: Ability of a material to undergo permanent deformation without breaking (spring)

Stress (σ): Force per unit area applied to a material (pascal/ mega pascal).

Strain: Measure of deformation due to stress.

Tensile strength: Maximum stress a material can with stand without breaking (Pa/MPa).

Young's (or) Initial modulus (E):
Ratio of stress to strain within limits.

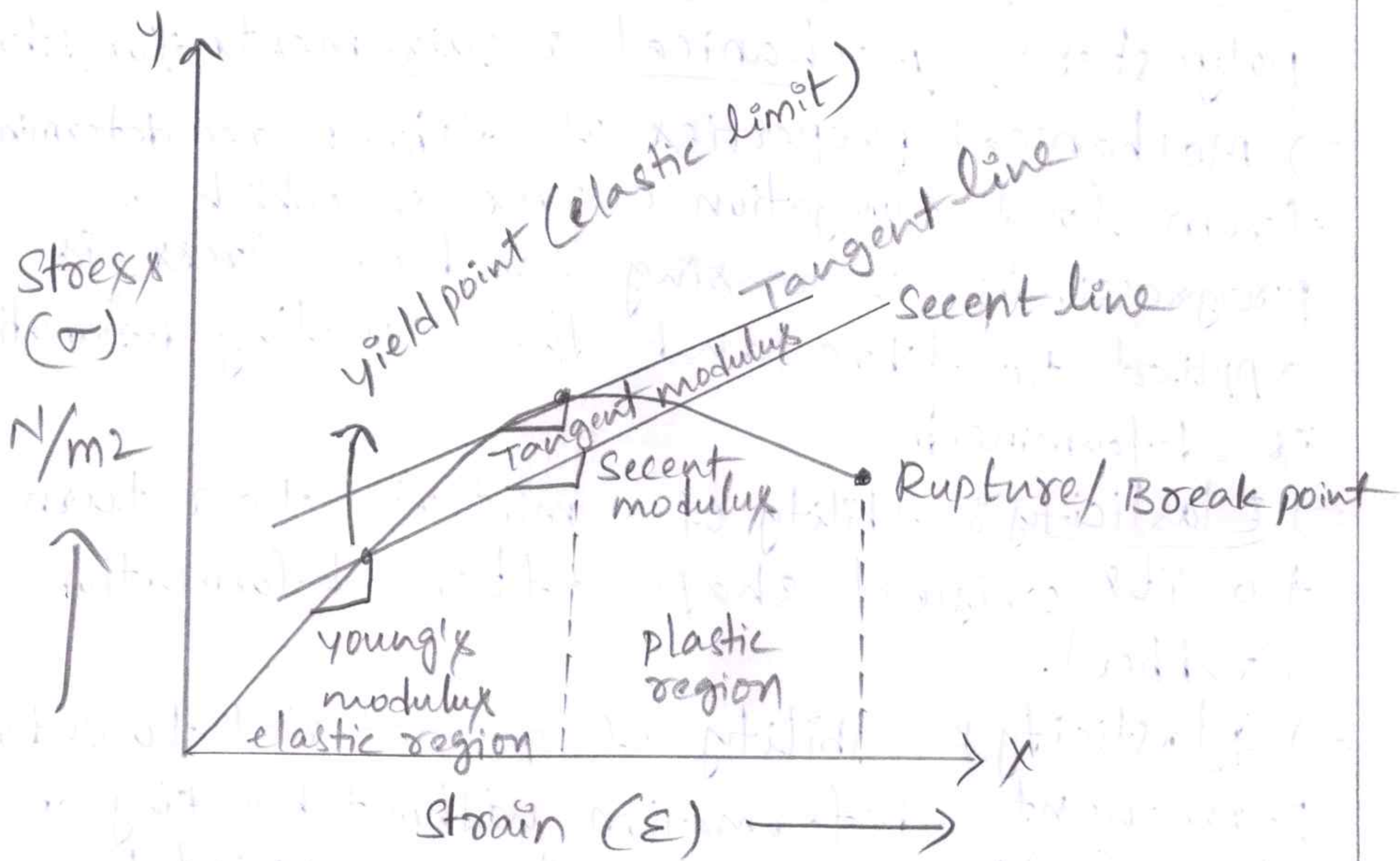
$$E = \frac{\Delta \sigma}{\Delta \varepsilon}$$

Tangent modulus: Rate of change of stress with strain.

Secent modulus:- Average rate of change of stress with respect to strain between two points.

Tangent line:- Touches the curve at a point.

Secent line:- Connects two points on the curve.



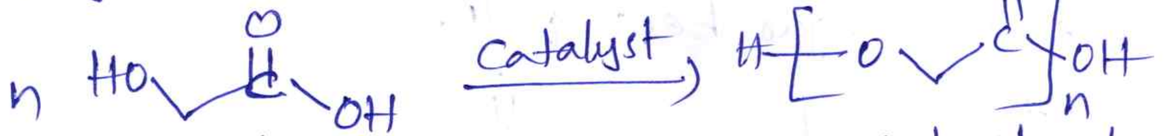
Bio degradable polymers :

⇒ These polymers can be decomposed by natural processes, through the action of micro organisms like bacteria and fungi, into simpler substances such as CO_2, H_2O and biomass.

Examples : ① Poly Glycolic Acid (PGA)
② Poly Lactic Acid (PLA)

① Poly Glycolic Acid : (PGA)

⇒ PGA is formed by direct condensation polymerisation of glycolic acid.



Glycolic acid — Poly Glycolic acid

Properties:-

⇒ It is a crystalline polymer with 46~52% of crystallinity.

⇒ Density of 1.5 – 1.64 g/cm3.

⇒ Glass transition temperature of 36°c.

⇒ Melting point is 224°c.

⇒ Good mechanical properties, high molecular weight.

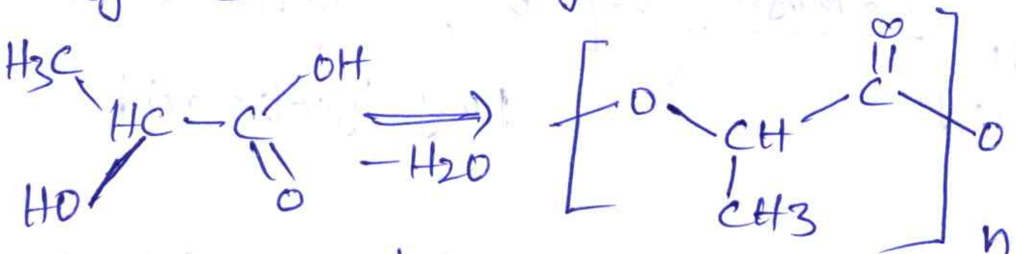
⇒ Dense crystalline polymer, insoluble in all organic solvents except hexafluoroisopropanol.

Applications:- ① PGA is used as suture material for nerve conduits when the limitations of silicone tubes were observed.

⇒ Most widely used synthetic degradable polymer in medicine.
⇒ Surgical sutures made of PGA tend to lose their mechanical strength over a period of 2-4 weeks post implantation.
⇒ It is much less reactive, able to resist infection from contaminating bacteria.
⇒ It is used for subcutaneous sutures, intra-cutaneous closures, abdominal, thoracic surgeries

Poly Lactic Acid (PLA):

⇒ It is made from fermented plant starch such as from corn, cassava, tapioca roots, sugar cane or sugar beet pulp.



Lactic acid   poly lactic acid

Properties:-

⇒ Degree of crystallinity is 37%
⇒ Glass transition temperature is 60-65
⇒ melting temperature 173−178°C
⇒ Tensile modulus is 2.7 − 16 GPa
⇒ Good optical properties, biocompatible.

Applications: ① Drug release, bone fixation.
② pesticides, fertilizers, composite bags.
③ Disposable plates, cups, food service items.
④ Textiles ⑤ 3D printing filaments.

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

Ex:- wood, charcoal, coal, kerosene, petrol, diesel, producer gas etc.

Combustion:- Burning of a substance in presence of air (or) oxygen is known as "Combustion". Combustion is an exothermic chemical reaction, which is accompanied by development of heat and light at rapid rate, so that temperature rises considerably. During Combustion of fuels, atoms of C and H etc., combine with oxygen with simultaneous liberation of heat. The new products formed are CO_2, H_2O etc., the energy is liberated due to the rearrangement of valency electrons". So the energy liberated during the process of Combustion is the difference in the energy of the reactants (C, H, O) and that of the products (CO_2, H_2O) formed.

Fuels + oxygen ⟶ products + Heat
(more heat energy contents) (Less heat energy contents)

For proper combustion, the fuel must be pre-heated to reach ignition temperature which is defined as the" minimum temperature at which the substance ignites and burns without further addition of heat from outside".

Classification (or) Types of fuels:-

Fossil fuels have been classified according to 1. occurance 2. state of aggregation.

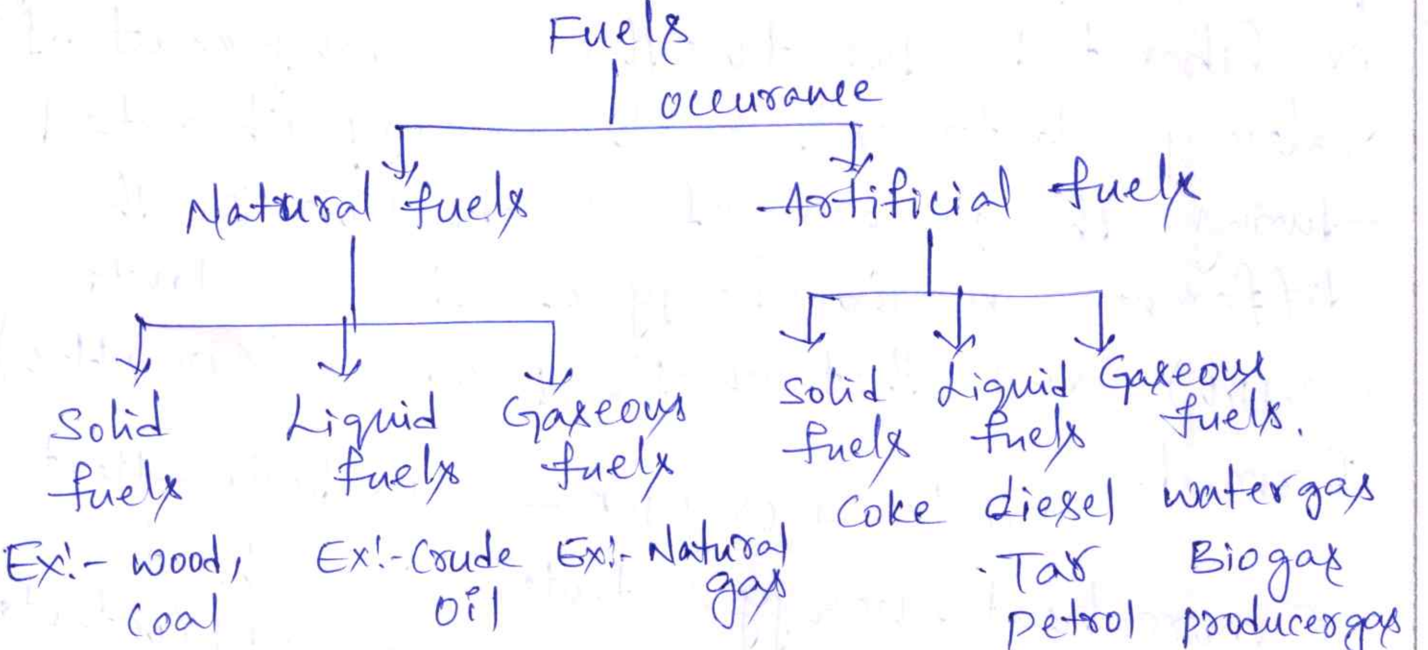
1. classification based on occurance:

(a) Natural fuels / primary fuels:- These fuels occur in nature as wood, petroleum, natural gas, coal etc.

(b) Artificial / secondary fuels:- These fuels are prepared from primary fuels as charcoal, coke, kerosene oil, diesel oil, coal gas, producer gas

2. classification based on physical state:

(a) solid fuels (b) Liquid fuels (c) Gaseous fuels



Characteristics of a good fuel:

A good and ideal fuel should contain the following characteristics.

(1) A good fuel should posses high calorific value, since the amount of heat liberated and temperature attained depends upon the property of the fuel.

(2) Moderate Ignition temperature: Ignition temperature is the lowest temperature at which the fuel must be preheated so that it starts burning smoothly. Hence an ideal fuel must have moderate ignition temperature

(3) Low moisture Content: Moisture content of the fuel reduces the heating value which leads to loss of money. Hence an ideal fuel must have low moisture content

(4) Low non-Combustible matter:- It remains after combustion like ash, clincker. Presence of non-combustible matter reduces heating value and increases the cost of storage, handling and disposal of waste products produced Thus a good fuel should have low non-Combustible matter.

(5) moderate velocity of combustion

(6) cheap in cost, easy to handle & transport.

(7) should burn in air with out smoke.

(8) should not undergo Spontaneous Combustion.

Comparision between solid, liquid and gaseous fuels			
Fuel characteristics	Solid fuels	Liquid fuels	Gaseous fuels
Cost	Easily available and cheap	More costly than solid fuels but cheap in countries of origin	Except natural gas other gaseous fuels are costly.
Storage & transportation	Transportation storage & handling is easy	Easily transported through pipes but care must be taken to store them.	Must be stored in leak proof storage containers.
Risk of fire hazards	Least risk of fire hazards	High risk of fire hazards	very high risk
Rate of combustion	Combustion is slow process	Quick combustion	Rapid combustion takes place
Control of combustion	Can't be controlled easily	Can be controlled (or) stopped when needed	possible by controlling air supply
Handling cost	High	Low	Low
By products	Ash & smoke is always produced as by product	No ash problem smoke is by product	No smoke no ash is produced as by product
Requirements of air	Requires excess of air for combustion	Requires slight excess of air	Burn in slight air
Use in Internal combustion engine fuel	Can't be used as internal engine fuel	Can be used as interal engine fuel.	can be used as internal engine fuel.
w/w calorific value	Low calorific value	High calorific value	Calorific value is highest
Thermal efficiency	Thermal efficiency is least	Thermal efficiency is high	Thermal efficiency is highest
Examples	Coal, coke etc	petrol, diesel etc.	Natural gas Coal gas etc.

Calorific value :

the efficiency of fuel is expressed in terms of calorific value.

Calorific value is defined as "the total quantity of heat liberated by burning a unit mass (or) volume of fuel completely".

Units of Heat :

The units of heat are
1. Calorie (cal)
2. kilo calorie (K.cal)
3. British thermal unit (B.Th.U)
4. centigrade Heat unit (C.H.U)

(1) Calorie (or) Gram calorie : The amount of heat required to raise the temperature of 1 gram of water through 1°C is called calorie.

$$1 \text{ cal} = 4.185 \text{ Joules} = 4.185 \times 10^{7} \text{ ergs}$$

(2) kilocalorie (or) kilogram calorie (K.cal): The amount of heat required to raise the temperature of 1 kilogram of water through 1°C is called kilo calorie.

$$1 \text{ K.cal} = 1000 \text{ cal}$$

(3) British Thermal Unit (B.Th.U.) : The amount of heat required to raise the temperature of 1 pound of water through 1°F is called British Thermal unit.

$$1 \text{ B.Th.U} = 252 \text{ cal} = 1054.6 \text{ Joules} = 1054.6 \times 10^{7} \text{ ergs.}$$

(4) Centigrade Heat Unit (C.H.U.) : The amount

of heat required to raise the temperature of 1 pound of water through 1°C is called Centigrade Heat Unit.

1 K.cal = 1000 cal = 3.968 B.Th.U. = 2.2 C.H.U

<u>Units for calorific value:</u>

It is generally expressed in terms of Calorie/gm or K.cal/kg (or) B.Th.U/lb in case of solid (or) liquid fuels.

In case of gaseous fuels, the units are K.cal/m3 (or) B.Th.U/ft3.

classification of calorific value of fuels:-

(i) Higher (or) Gross Calorific value (HCV (or) GCV)

(2) Lower (or) Net Calorific of fuel (LCV or NCV)

<u>(1) Higher or Gross Calorific value (HCV or GCV):</u>

The total amount of heat produced when unit mass (or) volume of a fuel has been burnt Completely and the products of combustion have been cooled to room temperature. Hydrogen is found in almost all fuels.

<u>(2) Lower (or) Net calorific value (LCV) or (NCV):</u>

The amount of heat liberated when a unit of fuel is completely burnt and the Combustion products are allowed to escape is called Net calorific value.

NCV = GCV − latent heat of water vapour formed

$$NCV = GCV - 9 \times \frac{H}{100} \times 587$$

$$NCV = GCV - 0.09 \times H \times 587$$

(or)

$$LCV = HCV - 0.09 \times H \times 587$$

where 587 = latent heat of stem
H = % of hydrogen in fuel

Problem: 1. Calculate the gross and net calorific value of a coal which analyses: C 74%, H 6%, N 1%, O 9%, S 0.8%, moisture 2.2% and ash 8%

Ans:

$$GCV = 339 \times \%C + 1427\,(\%H - \%O/8) + 22 \times \%S = 32060.2 \text{ KJ/Kg}$$

$$NCV = GCV - 24.44\,(9 \times \%H + \%M) = 30630.26 \text{ KJ/kg}$$

Thus NCV = 0.955 times GCV in this case.

Liquid fuels:

The liquid fuels can be classified as follows.

(a) Natural fuels − Ex:- Crude oil

(b) Artificial (or) manufactured fuels
Ex:- Petrol, diesel etc.

Advantages / Applications:-

⇒ They possess high calorific value than liquid fuels.

⇒ They burn without forming dust, ash, clinker etc

=) they are easy to transport through pipes.
=) clean in use and economic labour.
=) Loss of heat is low.
=) They require optimum air for complete Combustion.
=) They can be used as internal Combustion fuel.
=) Their firing is easier and fire can be extinguished by stopping liquid fuel Supply.

=) Dis advantages:-
=) The cost of liquid fuel is much higher than solid fuels.
=) Costly and Special storage tanks are required to store liquid fuels.
=) Greater risk of fire hazards.
=) They have bad odour.
=) Specially designed burners and sprayers are required for effective combustion.

Ex:- petroleum and synthetic petrol.

Petroleum or Crude oil:
(1) In Latin petro = rock, oleum = oil.
(2) Petroleum is a dark, greenish, brown coloured viscous oil float between the layers of natural gas and brine solution, inside the earth.
(3) It is a complete complex mixture of hydro-carbons (straight chain paraffins, cyclo paraffin or naphthalene, olefins, aromatic hydro carbons) along with small amounts of organic compounds

oxygen, nitrogen and sulphur.

4. Its average composition is C = 79.5 – 87.1%, H = 11.5 – 14.8%, S = 0.1 – 3.5%, N + O = 0.1 – 0.5%.

Refining of petroleum:

① The separation of crude oil into various useful fractions by fractional distillation is called "Refining of crude oil".

② The plants which perform this process are called "oil refineries".

③ Refining of petroleum involves three steps.

They are a. Separation of water
b. Removal of harmful sulphur compounds
c. Fractional distillation

① Separation of water:

Crude oil extracted from oil-well is a stable emulsion of salt water in oil. The emulsions are stabilized because of the procedure of emulsifying agents or sodium salts or naphthalen-ic acids and sulpho acids and finely dispersed clay, metal oxides.

The water is separated by placing two stable electrodes in the bulk of crude oil and sending higher voltage of alternating current. As a result (a black precipitate of copper sulphide is obtained which) water droplets accumulate to form large drops which separate out from the oil.

2. Removal of harmful sulphur compounds:-

The crude oil obtained in above step is then treated with copper oxide, as a result a black precipitate of copper sulphide is obtained which is then removed by filtration.

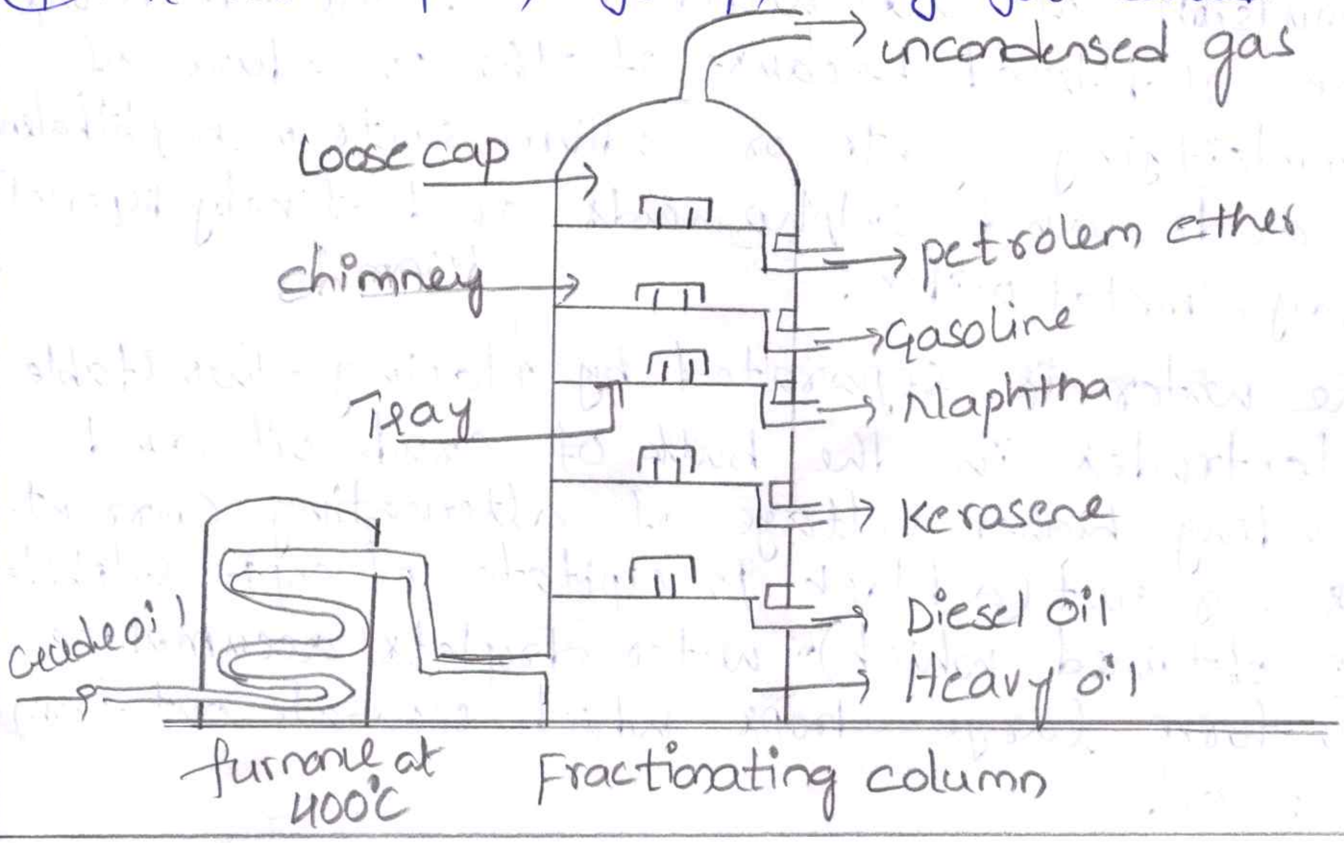
Fractional Distillation:

(1) The crude oil obtained from step-2 then heated to 400°c in an iron retort.

(2) Here the liquid content is evaporated and the solid residue like tar, asphalt, petroleum coke is separated.

(3) The hot vapours are then passed into a fractional distillation column which a tall cylindrical tower is containing a number of horizontal stainless-steel trays provided with small chimneys covered with loose caps.

(4) As the vapours go up, they got cooled.



S.NO.	Name of the fraction	Boiling range	Carbon Compounds	Uses
1.	Uncondensed Petroleum gas	Below 30°C	C1 – C4	As domestic or industrial fuel under name L.P.G
2.	Petroleum ether	30°C – 70°C	C3 – C7	As a solvent
3.	petrol (or) gasoline (or) motor split	40° – 120°C	C5 – C9	As motor fuel, solvent & in dry cleaning
4.	Naphtha oil (or) Solvent spirit	120 – 180°C	C9 – C10	As solvent & in dry cleaning
5.	kerosene oil	180 – 250°C	C10 – C16	As an illuminent engine fuel for preparing laboratory gases
6.	Diesel oil (or) Fuel oil/Gas oil	250 – 320°C	C15 – C18	As diesel engine fuel
7.	Heavy oil	320 – 400°C	C17 – C30	For setting gasoline by cracking process as lubricant

a) Lubricating oil – as Lubricant
b) Petroleum Jelly (or) vaseline – as lubricant in cosmetics
c) Grease – as lubricant
d) Paraffin wax – in candles, boot polishes, wax paper

8.		Residue	> 400°C	C30 and above

a) Asphalt or tar – water proofing of roofs & for road making
b) Petroleum Coke – as a fuel and in moulding arc for rods

<u>Octane Number</u>: The most common way of expressing the knocking characteristics of a fuel are by octane number, Introduced by Edgerin 1972.
Branched chain compounds produce low knocking while straight chain compounds produce high knocking

N-heptane knock is very bad hence octane number = 0, but isooctane gives very less knocking so its anti-knocking value has been given 100. octane number off fuel is defined as the percentage volume of iso octane in a mixture of octane and n-heptane blend.

Cetane Number:

The most common way of expressing the knocking characteristics of diesel by cetane number. The efficiency of diesel fuel is determined by its cetane value, cetane number of diesel is defined as the mixture of n-cetane and 2-methyl naphthalene. It has been found that hexadecane (cetane) gives less knocking and its anti-knocking values taken as 100.

On the other hand 2-methylnaphthalene knocks very badly and its anti-knocking value is taken as zero. Cetane number of diesel is defined as the percentage volume of n-cetane in mixture of n-cetane and 2-methyl naphthalene

⇒ straight chain compounds undergo easy compression ignition cetane is chosen as upper limit of cetane number = 100.

⇒ Branched chain compounds do not undergo compression ignition readily readily and 2-methylnaphthalene is chosen as lower limit of cetane number = 0.

Determination of Calorific value of solids by bomb Calorimeter:

Bomb calorimeter is used to find the calorific value of solid and liquid fuels.

Construction: A simple sketch of bomb calorimeter is shown in fig.1.

It consists of a strong cylindrical stainless steel bomb in which the combustion of fuel is made to takesplace.

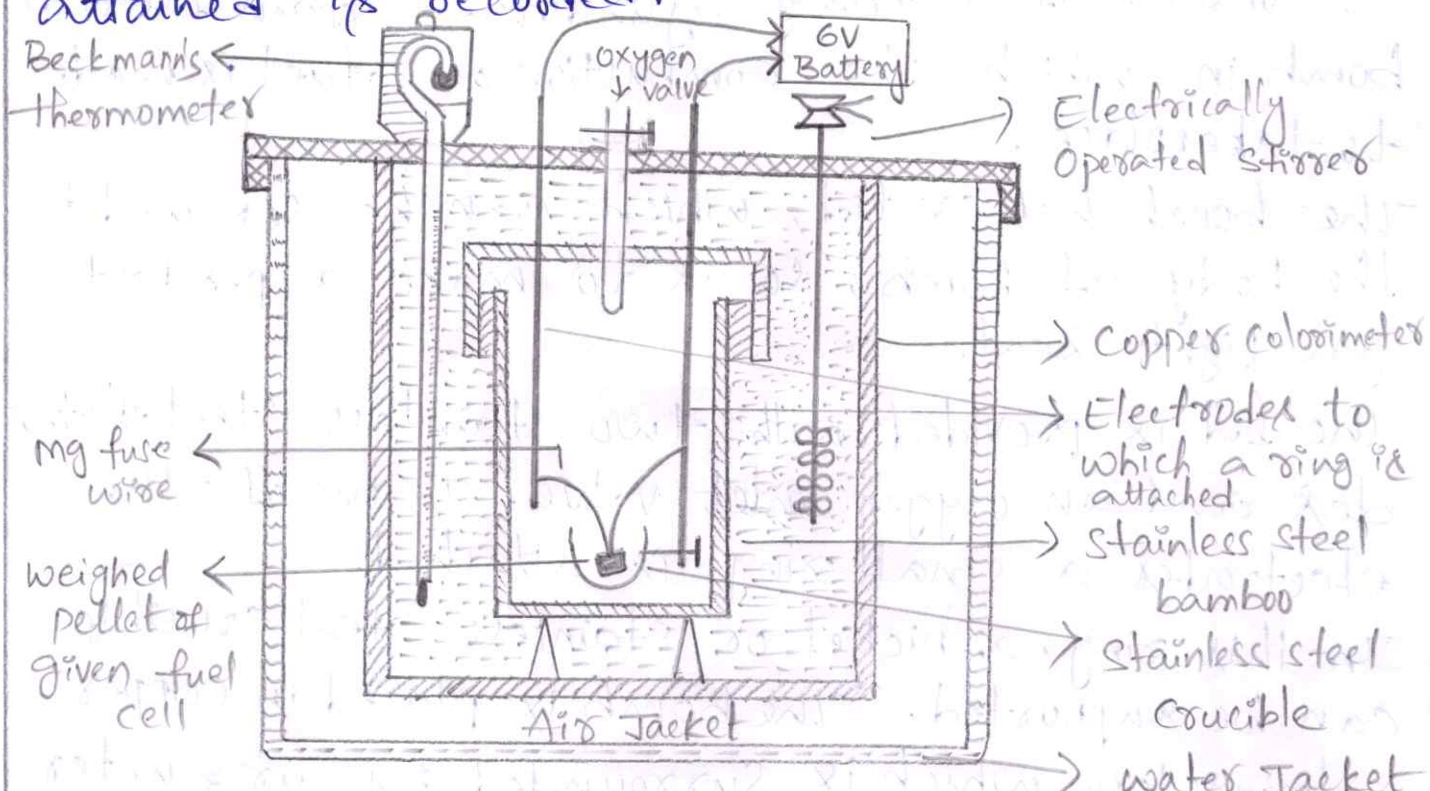
The bomb has a lid, which can be screwed to the body of bomb, so as to make a perfect gas tight seal.

The lid is provided with two stainless steel electrodes and an oxygen inlet valve. To one of the electrodes a small ring is attached.

In this ring, a nickel or stainless steal crucible can be supported. The bomb is placed in copper calorimeter, which is surrounded by air & water jacket to prevent heat loss due to radiation.

⇒ The calorimeter is provided with an electrically operated stirrer and Beckmann's thermometer, which can read accurately temperature difference up to 1/100 th of a degree.

Working: A known mass of the given fuel is taken in clean crucible. The crucible is then supported over the ring. A fine magnesium wire, touching the fuel sample, is then stretched across the electrodes. The bomb lid is tightly screwed and bomb filled with oxygen to 25 atmospheric pressure the bomb is then lowered into copper calorimeter containing a known mass of water. The stirrer is worked and initial temperature of the water is noted. The electrodes are then connected to 6-volt battery and circuit completed. The sample burns and heat is liberated. Uniform stirring of water is continued and the maximum temperature attained is recorded.



Bomb Calorimeter

Calculation : Let x = mass in g of fuel sample taken in crucible ; W = mass of water in the calorimeter w = water equivalent in g, stirrer, thermometer, bomb etc. t_1 = initial temperature of water, t_2 = final temperature of water, L = Higher calorific value in fuel in cal/g.

∴ Heat liberated by burning of fuel $= xL$

Heat absorbed by water & apparatus $= (W+w)(t_2-t_1)$

But heat liberated by the fuel = Heat absorbed by water, apparatus.

$xL = (W+w)(t_2 - t_1)$

$$L = \frac{xL}{x} = \frac{(W+w)(t_2-t_1)}{x} \text{ cal/g (or kcal/kg)}$$

(HCV of fuel)

Benzoic acid HCV = 6,325 kcal/kg

Naphthalene HCV = 9688 kcal/kg

H = percentage of hydrogen in fuel, then

$\frac{9H}{100}$ g = Mass of H_2O from 1 g of fuel = 0.09 H(g)

Heat taken by water in forming steam

= 0.09 H × 587 cal

∴ LCV = HCV − Latent heat of water formed

= (L − 0.09 H × 587) cal/g (or kcal/kg)

To get more accurate results, the following corrections are applied.

Corrections : (i) fuse wire correction

(ii) Acid correction

(iii) Cooling correction

(i) Fuse wire Correction: The heat liberated, as measured above, includes the heat given out by ignition of the fuse wire used.

(ii) Acid Correction:- Fuels containing S and N are oxidised, under high pressure and temperature of ignition, to H_2SO_4 and HNO_3 respectively

$$S + 2H + 2O_2 \rightarrow H_2SO_4 + \text{Heat}$$

$$2N + 2H + 3O_2 \rightarrow 2HNO_3 + \text{Heat}$$

Formation of these acids are exothermic reactions. H_2SO_4 alone is determined by precipitation as $BaSO_4$.

The correction for 1mg of S is 2.25 cal.

1ml of N/10 HNO_3 formed is 1.43 cal.

(iii) Cooling correction:

Time taken to cool the water in calorimeter from maximum temperature to room temperature is noted.

From the rate of cooling (dt°/minute) and the actual time taken for cooling (t minutes), the Cooling Correction of dt × t is added to the rise in temperature.

$$L = \frac{(W+w)(t_2 - t_1 + \text{cooling correction}) - (\text{Acid} - \text{fuse corrections})}{\text{Mass of fuel } (x)}$$

UNIT-IV
MODERN ENGINEERING MATERIALS

Refractories – Classification, Properties, Factors affecting the refractory materials and Applications. Lubricants – Classification, Functions of lubricants, Mechanism, Properties of lubricating oils – Viscosity index, Flash point, Fire point, Cloud point, Saponification and Applications.
Building materials – Manufacturing of portland Cement, Constituents, Setting and Hardening of Cement.

REFRACTORIES

* Refractory is "any material that can withstand high temperature without softening (or) suffering a deformation in shape.
* Refractories are the essential materials of construction in metallurgy, engineering and chemical industries and without their use, it is impossible to maintain required high temperature.
* The main objective of refractory is to resist loss of heat and at the same time to resist the abrasive and corrosive action of molten metals, slags and gases at high operating temperatures, without undergoing softening (or) distortion in shape.

CLASSIFICATION OF REFRACTORIES

Basing on their chemical properties, refractories are classified into three main types. They are
1) Acid refractories, 2) Basic refractories, 3) Neutral refractories.

1. ACID REFRACTORIES :-

These refractories are made of acid materials like alumina (Al_2O_3), Silica (SiO_2) Etc. They Can withstand acidic materials but are easily attacked by basic materials.

Ex:- Alumina, Silica and fine Clay refractories.

2. BASIC REFRACTORIES :-

These refractories are made up of lime (CaO), Magnesia (MgO) etc. They are resistant to basic materials but easily attacked by acidic medium.

Ex:- Magnesite and dolomite refractories.

3. NEUTRAL REFRACTORIES :-

These refractories are made up of acidic / basic materials like Carbon, Chromite and Zinc. They are not attacked by either acidic (or) basic materials

Ex:- Graphite, Chromate, Zirconia (ZrO_2) and Carborundum (SiC), refractories.

PROPERTIES OF REFRACTORIES

Important Characteristics of refractories are

1) Refractoriness, 2) Refractoriness stability, 3) Chemical inertness 4) Dimensional stability 5) Thermal spallings, 6) Porosity 7) Thermal Expansion 8) Thermal Conductivity 9) Abrasion resistance. 10) Electrical Conductivity.

1. REFRACTORINESS :-

* It is the ability of a refractory material to withstand the heat without appreciable Softening (or) deformation Under given Service Conditions.

* It is generally measured by the softening temperature of the refractory.
* The softening temperature of a refractory material is usually determined by pyrometric test (or) Seger cones test.
* A good refractory should have high refractoriness.
* Generally the refractoriness is measured in terms of Pyrometric Cone Equivalence (PCE) number.

Ex:- Silica bricks → PCE no. = 32 → Softening temp - 1710°C

Magnetic brick → PCE no = 38 → Softening temp - 1850°C

In these two magnetite brick acts as good refractory when compared to silica brick.

2. REFRACTORINESS UNDER LOAD (RUL) (or) STRENGTH:-

* Refractories should have high mechanical strength to with- -stand the load applied under operating temperatures, without breaking.
* Thus a refractory should have high load bearing capacity which can be measured by RUL test.

RUL - is expressed as the temperature at which 10% deformation takes place under a load at 3.5 kg/cm² in presence of temperature refractory specimen having 5 cm² size and 75 cm height with rise of 10°C / minute in carbon resistance furnace.

3. CHEMICAL INERTNESS:-

The refractory selected for a specific purpose should chemically inert and should not react with the slages, furnace gases etc. It is always advisable not to employ an acidic refractory in contact with an alkaline product and the basic refractory in contact with an acidic product.

4. DIMENSIONAL STABILITY:-

* Dimensional stability is the resistance of material to any volume changes which may occur on its exposure to high temperature on prolong heating, these dimensional changes may be permanent (or) reversible.
* A good refractory should have high dimensional stability.

5. THERMAL SPALLING:-

* It is the property of braking, cracking (or) fracturing of a refractory under high temperature.
* So a good refractory should show a high resistance to thermal spalling.
* Thermal spalling can be controlled by following factors.
  a) Low porosity and low coefficient of expansion.
  b) By avoiding sudden changes in temperature.
  c) By modification of furnace design.

6. POROSITY:-

* Refractories generally contain pores either due to manufacturing defects (or) incorporation of saw dust etc. during manufacture.
* Porosity is defined as the ratio of its porous volume to the bulk volume.

$$P = \frac{W-D}{W-A} \times 100$$

where P = Porosity, W = Weight of saturated specimen (with water)
D = Weight of dry specimen
A = Weight of saturated specimen with air.

* Porosity is an important property of refractory because it affects many other properties like strength, thermal conductivity and abrasion resistance.

Advantages :-

1) Highly porous refractory reduce thermal spalling.
2) Highly porous refractory can be used for lining in furnace, ovens, retorts etc.

Disadvantages :-

- Highly porous refractory reduces.

a) strength, b) the resistance to corrosion, c) resistance to abrasion

7. THERMAL EXPANSION :-

* The refractory tends to expand when temperature increases and contract when temperature decreases. Thermal expansion affects all dimensions of body.
* So a good refractory should have less thermal expansion.

8. THERMAL CONDUCTIVITY :-

* It depends upon the chemical composition and degree of porosity of refractory.
* Most of the furnaces are lined inside with refractory material of low thermal conductivity in order to reduce heat loses to outside by radiation.
* However, in muffle furnace, retorts etc., thermal conductivity refractories are employed.

9. ABRASION RESISTANCE :-

* A good refractory should resist the abrasion of flue gases, flames, slages etc.

10. ELECTRICAL CONDUCTIVITY :-

* Generally, refractories are poor conductors of electricity (except graphite). So refractories should have low electrical conductivity.

Applications :-

* Refractories are used for lining in furnaces, ovens, retorts etc.
* They are used as lining for crucibles which are used during manufacture of cement, metals, glass, ceramics etc.
* Silica refractory bricks are used as roofs for open-hearth furnaces, eletrical furnaces, etc.

LUBRICANTS

* In all types of machines, the surfaces of moving, sliding (or) rolling parts rub against eachother. This mutual rubbing of one part against another, generates frictional force which offers resistance to the relative motion of these surfaces wear results when the resistance over come by applied forces.
* Hence friction causes alot of wear and tear of surfaces of moving / sliding / rolling parts which consequently require repeated replacement.
* Friction also generates heat which gets dissipated thereby causing loss in the efficiency of the machine.

→ The study of wear and tear, machismo of friction between two surfaces and lubrication is called "Tribology"

→ The main aim of tribology is to minimize the friction there by reducing the loss of material due to wear.

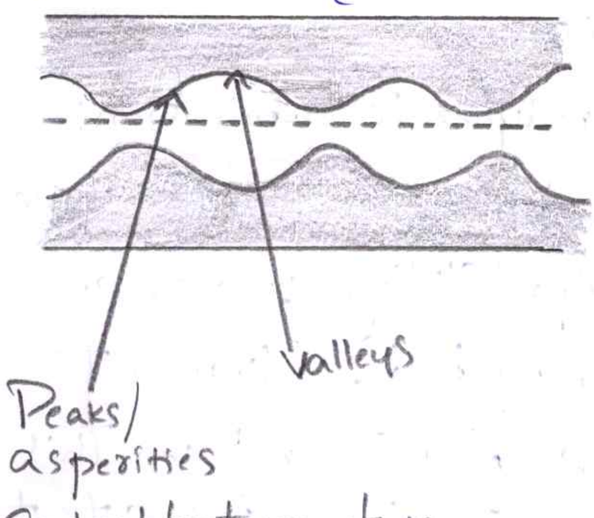
→ During the motion of sliding surface, a considerable amount of frictional heat is evolved at the rubbing surfaces due to frictional resistance. As a result, high local temperature even under relatively light loads, speeds are crushed and undergo plastic deformation.

→ Further the temperature of surfaces raises near to the melting point of the materials there by causing the formation of welding junctions.

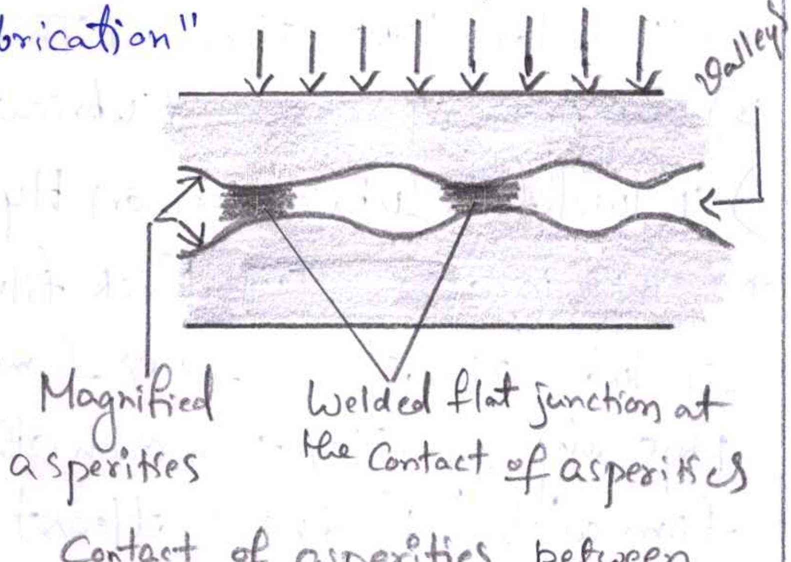
→ Strong welds may form between hard surfaces causing considerable physical damage on both the surfaces.

→ These drawbacks of frictional resistance can be minimized by applying a thin film (or) layer of certain substances known as "Lubricants"

→ "A lubricant may be defined as a substance which reduces the friction when introduced between two surfaces and the phenomenon is called lubrication"



Contact between two Surfaces and roughness



Contact of asperities between Two Surfaces at high load.

FUNCTIONS OF LUBRICANTS:—

Important function of lubricants which enhances the efficiency of a machine and life of the material as follows.

* Reduces frictional resistance.
* Reduces wear, tear, Surface deformation because direct Contact between Surfaces is avoided
* Acts as Coolent by reducing heat loss.
* Improves efficiency of machine.
* Prevents rust formation and Corrosion which reduces maintance and running Cost of machine.
* As they Cover the moving parts of the machine, they acts as seal in many Cases.
* Reduces noise by absorbing shock between bearing and other engine parts.

MECHANISM OF LUBRICATION :—

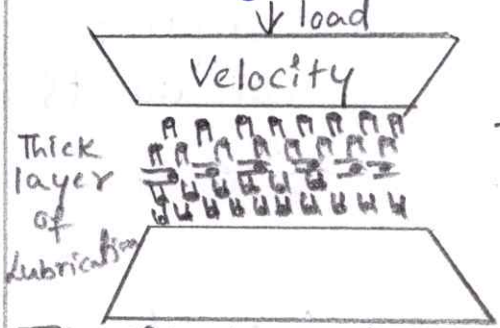
Lubrication mechanisms Can be Classified into 3 types as.

1) Fluid film Lubrication (or) Hydrodynamic Lubrication.
2) Boundary Lubrication (or) Thin-film Lubrication.
3) Extreme pressure Lubrication.

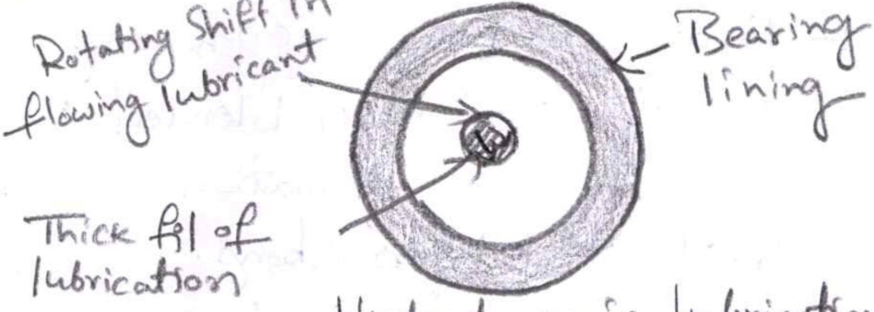
1) Fluid film lubrication (or) Hydrodynamic Lubrication:-

* This is also called thick film lubrication. In this type of lubrication, two Surfaces of moving / Sliding Surfaces are physically Seperated from each other by bulk of lubricant film with a thickness atleast 1000 A° between them. This bulk lubricant film can prevent metal-to-metal Contact

- So that small peaks and Valleys don't interlock Consequently it will reduce friction and prevents wear. This Condition is known as fluid film lubrication.



Fluid film lubrication.



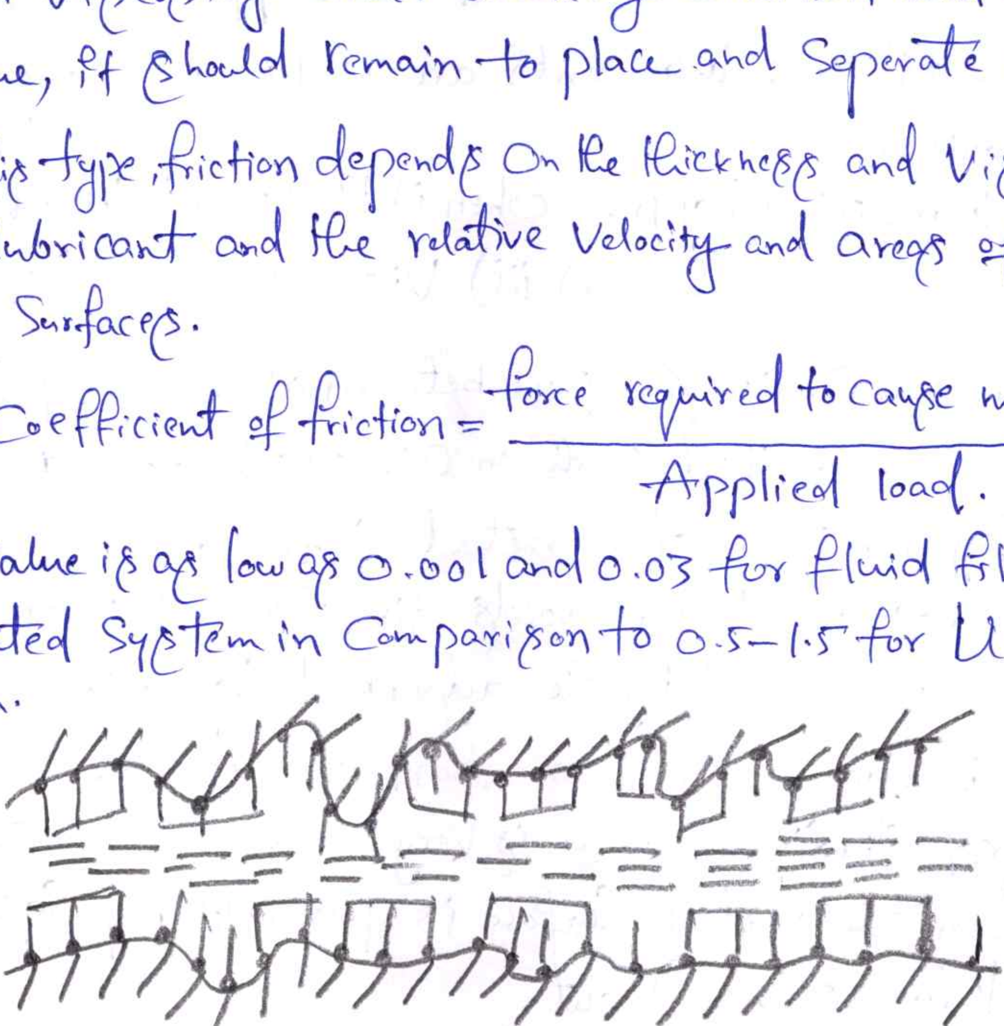
Hydrodynamic lubrication in journal bearing

* The small friction (if any) mainly due to the internal resistance between the particles of lubricant moving over each other. It is also known as hydrodynamic lubrication based on the theory of hydrodynamics. In this types, lubricant used should have minimum Viscosity under working Condition and at the same time, it should remain to place and seperate the surface.

* In this type, friction depends on the thickness and viscosity of the lubricant and the relative velocity and areas of moving/ Sliding Surfaces.

$$\text{Coefficient of friction} = \frac{\text{force required to cause motion}}{\text{Applied load.}}$$

* This Value is as low as 0.001 and 0.03 for fluid film lubricated System in Comparison to 0.5–1.5 for Unlubricated System.



Mechanism of a boundary lubrication.

* This type of lubrication is generally found in delicate instruments, light machines like guns, Sewing machines, watches, Scientific instruments etc.

Ex:- Hydrocarbon oils are generally suitable for hydro--dynamic lubrication blended with some antioxidants to prevent gummy formation as well as oxidation of Unsaturated hydrocarbons.

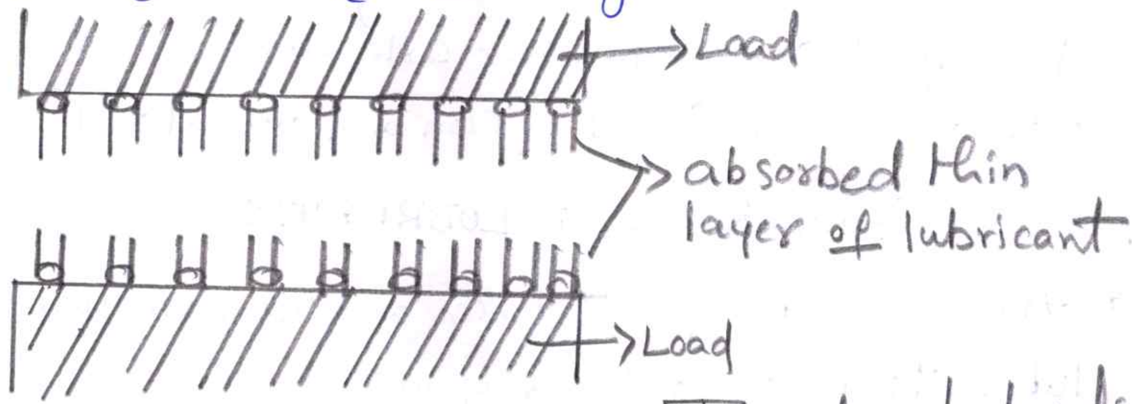
2. Boundary Film Lubrication (or) Thin Film Lubrication:-

* It is alone in Systems whenever, a Continuous fluid film of lubrication Can't be maintained.
* when the lubricant is not enough Viscous to generate a Sufficient thickness of film to Separate the Surface of heavy loads, friction may yet to be reduced with application of proper lubricants such lubricants are used in boundary film mechanism.
* This lubrication happens when i) the Speed is Very low (or) ii) the load is very high (or) iii) Viscosity of the oil is too low
* Under such Conditions, Space between the moving / Sliding Surfaces is lubricated with an Oil, which get adsorbed as thin layer between two metal Surfaces.
* This adsorbed layer avoids direct metal-to-metal Contact. The load is Carried by the adsorbed layers.
* In boundary film lubrication, the distance between moving / Sliding Surface is Very small. The Contact between the metal Surface is possible by Squeezing the lubricating oil out.

* When this occurs, the load would be taken on the high spots of the journal and the bearings, and the two surfaces tend to become welded together by the appreciable head that is generated. As two surface adhere together, motion of metal is prevented. This is known as "Seizure"
* If motion continues with the removal of some metal from one of the surfaces, the result is known as "Scuffing"
* The practice, Seizure and Scuffing are generally delayed by the fact of applying lubricating oil.

For boundary lubrication, the lubricant should have 1) Long hydrocarbon chains, 2) lateral attraction between the chains, 3) High viscosity index, 4) Good oiliness 5), Low pour and oxidation, 6) Resistance to heat and oxidation.

Ex:- Graphite, Mineral oils, Vegetable and animal oils and their soaps are mostly used as lubricants in boundary lubrication.



Boundary Lubrication

3) Extreme Pressure Lubrication :-

* When the moving / sliding surfaces are under very high speed and pressure, a high local temperature is attained and under such conditions, liquid lubricants fail to stick and may decompose and even vaporurize.

* To meet these extreme pressure Conditions, Special additives are added to mineral oils, these are called "Extreme - Pressure additives"
* Due to these additives, a thick film capable of withstanding very high loads and high temperature is formed on metal surface.

Ex:- Important additives are Chlorine (as Chlorinated esters), Sulphur (as sulpharized oils), phosphorous (as tricresyl-phosphate)

* These Compounds react with metallic Surfaces, at high temperatures, to form metallic Chlorides, Sulphates (or) phosphides.
* These metallic Compounds posses high melting point and serves as good lubricant under extreme pressure and extreme-temperature Conditions.

Application of extreme pressure additives :-

Mostly these additives are used in.

1) Wire drawing of titanium.
2) In cutting fluids in machining of tough metals.
3) For hypoid gear used in rear axle drive of cars which have both longitudinal sliding motion and normal rolling movement.

PROPERTIES OF LUBRICANTS

* A large number of substances are available to be utilized as lubricants in various types of machines.
* The selection of a lubricant for a specific application is based on the properties of the lubricant some of the important properties of lubricant are.

1) Viscosity 3) Flash and Fire points 4) Cloud and pour points 2) Viscosity Index.

1. Viscosity :-

* Viscosity is One of the important properties of a lubricating oil.
* It is the Property of a fluid that determines its resistance to flow Viscosity is measured in terms of Viscosity coefficient. The Viscosity coefficient is defined as "force per Unit area required to maintain a Unit Velocity gradient between two Parallel layers"
* The Unit of Velocity is "Poise"

Viscosity Index :-

A good lubricating oil Should not change with operating temperature. It is found that Viscosity decreases with increasing temperature.

"The rate at which the Viscosity of an oil Changes with temperature is measured by an arbitrary scale called Viscosity Index.

High Viscosity index shows small Change in Viscosity with temperature low Viscosity index shows high change in Viscosity with temperature.

The pennsylvanian Oil Consisting mainly of paraffin is is arbitrarily assigned a Viscosity Index (VI) Value of "100". Gulf oil Shows Viscosity Index (VI) Value as "0"

$$VI = \frac{L-U}{L-H} \times 100.$$

where VI → Viscosity index of oil Under test.

L → Viscosity of gulf oil at 100F and also having Some Viscosity at 210F

H → Viscosity of Pennsylvanian oil at 100F having VI same Viscosity at at 210 F.

U → Viscosity of Oil Under test at 100 F.

The Viscosity of lubricating oils can be increased with addition of certain polymers which are partially soluble in oils.

Flash and Fire point :-

* "The minimum temperature at which oils give of enough Vapour to ignite for a moment, when a tiny flame is brought near it is called Flash point"
* The lowest temperature at which vapours of the oil burn continuously for atleast 5 seconds when a tiny flame is brought near it is called fire point.
* A good lubricant should have flashpoint above the operating temperature.
* A good lubricant should not be volatile in working temperature.

Cloud and pour point :-

* Cloud point is the temperature at which the lubricating oil forms turbid (or) cloudy nature.
* Pour Point is the temperature at which oil ceases to flow (or) Pour.
* The cloud and pour points reveal the stability of lubrication oil in low temperature.
* The lubricant should have low cloud and pour point at the working conditions.

Differences between thick film lubrication and thin film lubrication.

Thick film lubrication.	Thin film lubrication.
1. It is also known as fluid film lubrication (or) hydrodynamic lubrication	It is also known as boundary film lubrication.
2. Moving / Sliding surfaces are separated by a thick fluid film.	Moving / Sliding surfaces are separated by a thin film of lubricant.
3. Mostly light oils are used as lubricants	Heavy oils are used as lubricants.
4. Two moving / Sliding surfaces are far away from each other.	Two moving / Sliding surface are nearer to each other.
5. This lubrication is mostly done in high speed, low load machines.	Thin lubrication is mostly done in low speed, high load machines.
6. Coefficient of friction is low as 0.001 – 0.03.	Coefficient of friction is high as 0.05 – 0.15.
7. Low viscous oils are used as lubricants. Ex:– HydroCarbon oils.	High viscous oils are used as lubricants. Ex:– Vegetable oils, glycerides of fatty acids.
8. Oils used in this lubrication have low sticky nature (adhesion (or) oiliness.	Oils used in this lubrication have high sticky nature.
9. Thickness of oil used in this lubrication is 1000 A°	Thickness of oil is
10. This type of mechanism is mostly seen in sewing machines, gun machines, scientific machines etc.	This type of mechanism is seen in heavy machines in industries.

SAPONIFICATION AND APPLICATIONS

Saponification is the chemical process where a fat (or) oil react with a base (like Sodium hydroxide or potassium hydroxide) to produce soap and glycerol. This reaction is essentially a hydrolysis of triglycerides, breaking them down into their constituent fatty acid salts and alcohol, Saponication has several practical applications including soap and detergent manufacturing biodiesel production, and even in some fire extinguishers.

Mechanism:

Saponification involves the nucleophilic acyl substitution of an ester (the fat or oil) with a hydroxide ion, resulting in the formation of a carboxylate salt (soap) and alcohol (Glycerol).

Base:

The base used in Saponification determines the type of soap produced. Sodium hydroxide (NaOH) typically yields hard soaps, while potassium hydroxide (KOH) produces soft soaps.

Applications:

Soap and Detergent production:

Saponification is the fundamental process for making soap, a mixture of fatty acid salts used for cleaning. It also plays a role in the synthesis of some detergents.

Biodiesel production:

The process is related to transesterification, a key step in producing biodiesel from vegetable oils or animal fats.

Food industry:

It is used to determine the amount of free fatty acids in food products.

Textile Manufacturing

It helps remove oils and greases from textiles.

BUILDING MATERIALS

Building materials are used for construction purpose. These are of two types.

i) Naturally occuring material: Steel, Lime, Clay, Rocks, Sand, wood etc.

ii) Man-made materials : Brick, Cement, Paints.

The Selection of raw materials is the first and most important step to achieve economy in construction. The building materials to be achieve their properties like strength, durability, appearance, etc.

The characteristics of building materials.

i) They must be impervious to Biological and Chemical attack for long Period.

ii) They must be strong.

iii) They must resist wear and tear.

PORTLAND CEMENT

Cement is defined as an inorganic binding material possessing adhesive and cohesive properties and capable of bonding materials like stones, brick, building blocks etc. Cement is obtained by heating the mixture clay and lime. It hardness under water. It is mixed with gypsum. It possesses quick setting and hardening property. As it resembles Portland stone in colour, it is called portand cement.

Chemical Composition (or) Analysis of portland Cement.

Good Sample of portland Cement has the Composition of

Lime (CaO) = 60 - 69%

Silica (SiO_2) = 17 - 25%

Alumina (Al_2O_3) = 3 - 8%

Magnesia (MgO) = 1 - 5%

Ferric Oxide (Fe_2O_3) = 2-4%.

Sulphur trioxide (SO_3) = 1-3%.

Sodium Oxide (Na_2O) }
Potassium Oxide (K_2O) } = 0.3 - 1.5%.

Composition of Ordinary portland Cement shall Satisfy the following Conditions.

1) Ratio of Percentage of lime (CaO) to that of Silica (SiO_2) alumina (Al_2O_3) and iron Oxide (Fe_2O_3), Shall not be less than 0.66 and more than 1.02

According to the formula $\frac{CaO - 0.7\,SO_3}{2.8\,SiO_2 + 1.2\,Al_2O_3 + 0.65\,Fe_2O_3}$.

Ratio of Al_2O_3 percentage to that of Fe_2O_3 shall not be less than 0.66.

→ Weight of MgO Should not be more than 6%.
→ Insoluble material Should be within 2%
→ Total Sulphur Contents (as in SO_3) Shall not be more than 2.75%.
→ Total loss on ignition Should be with in 4%.
→ Alkali Oxides (Na_2O, K_2O) Should be with in 0.3% to 1.5%.

Manufacture of Portland Cement :-

Raw materials :-

1) Calcarious materials, rich in lime Ex:- Limestone, Chalk Etc.
2) Argillaceous materials rich in Silica Al_2O_3 Ex:- clay, Slate
3) Powdered Coal (or) Fuel Oil.
4) Gypsum ($CaSO_4 \cdot 2H_2O$)

The following steps are involved in manufacture of portland Cement.

STEP I :- Mixing of raw materials :-

This can be done either by wet (or) dry process.

Dry Process :-

* The dry process produces a fine ground powder.
* In this process initially limestone is crushed into pieces and then it is mixed with clay in the proportion 3:1.
* In this process mixture is pulverised to fine powder, & stored in storage bins for fed into a rotary kiln.

Wet process :-

* The limestone is crushed, powdered & stored in big storage tanks.
* The clay is mixed with water in wash mills to make it free from other soluble impurities & stored.
* Powdered lime stone & washed wet clay in right proportions introduced to grinding mills to from slurry on mixing.
* The slurry contains about 40% water & is stored in tanks for fed into rotary kiln.

STEP : II : Burning in a rotary kiln :-

The upper part of kiln temperature is 400°C but the temperature gradually increases upto 1750°C at the bottom.

$$3CaO + Al_2O_3 \longrightarrow Ca_3Al_2O_6$$

Tri calcium aluminate (C_3A)

$$4CaO + Al_2O_3 + Fe_2O_3 \longrightarrow Ca_4Al_2Fe_2O_{10}$$

Tetracalcium alumino ferrite (C_4AF)

The fusion Product of aluminates & Silicates of Calcium is Called Clinkers which are Small, hard and grayist Stones.

These Clinkers are Very hot & fed into another Small rotary Kiln where as Cool air is admitted for Cooling the Clinkers.

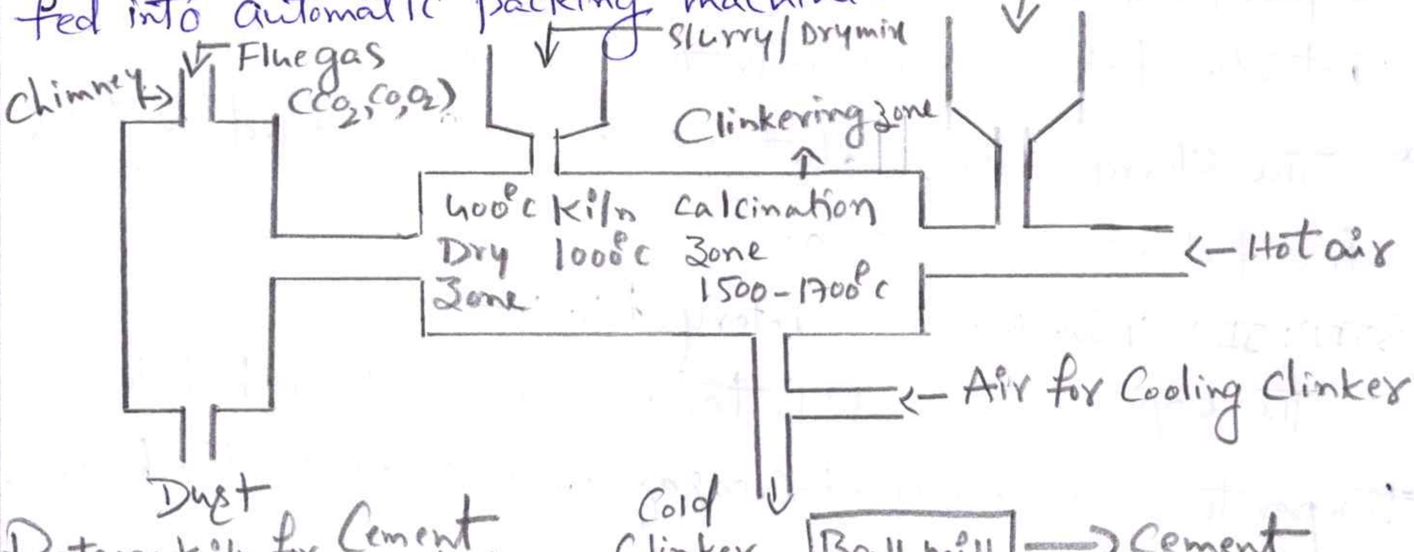
STEP III: Grinding:

The Cooled Clinkers are Collected and then grinded with addition of 2-3% of Gypsum in ball mills.

The mixture of Clinkers and Gypsum powder is Called Portland Cement.

STEP: IV Packing:-

The Ground Cement is Stored in Silos, from which it is fed into automatic packing machine.



Rotary kiln for Cement manufacture.

The raw Slurry from the wet process (or) the powder from the dry Process is Passed into the rotary Kiln through the upper end.

Hot flames are introduced into the Kiln through the Lower End.

The following reactions takes place in the rotary kiln

i) Dry zone:

* This is present in the upper part of kiln, where the temperature is around 400°C
* In this zone most of the water in the slurry get evaporated (Dried)
* The clay is broken as Al_2O_3, SiO_2 & Fe_2O_3.

$$Al_2O_3 \cdot 2SiO_2 \cdot Fe_2O_3 \cdot 2H_2O \longrightarrow Al_2O_3 + 2SiO_2 + Fe_2O_3 + 2H_2O.$$

ii) Calcination / Decarbonation zone:

It is the centre part of the kiln, where as the temperature is around 1000°C

Limestone of dry mix (or) slurry undergoes decomposition and forms quick lime $CaO + CO_2$

$$CaCO_3 \longrightarrow CaO + CO_2 \uparrow$$

iii) Clinkering zone:

It is the lower part of the rotary kiln, where the temperature between 1500°C to 1700°C

Here lime & clay combine to form calcium aluminates and calcium silicates.

$$2CaO + SiO_2 \longrightarrow Ca_2SiO_4$$

Dicalcium Silicate (C_2S)

$$3CaO + SiO_2 \longrightarrow Ca_3SiO_5$$

Tri Calcium Silicate (C_3S)

SETTING AND HARDENING OF PORTLAND CEMENT:

When water is added to Cement, a paste is formed which bind the inert particles to form a rock like materials.

* This is the process of Solidification which Comprises of Setting then hardening.
* Setting means the formation of a rigid (or) Stiffening of the Plastic mass due to initial gel formation.
* Hardening means the development of strength due to Crystallization in the interior of the mass.
* After Setting, hardening starts, due to the gradual progress of Crystallization in the interior of the mass.
* The strength developed by Cement Paste at any time, depends upon the amount of gel formed and extent of Crystallization.

Setting of Cement [Initial Setting]:-

Initial Setting of Cement paste is due to hydration of tricalcium aluminate and gel formation of tetra calcium alumino ferrite.

$$3CaO \cdot Al_2O_3 + 6H_2O \longrightarrow Ca_3Al_2O_3 \cdot 6H_2O + 880\,kJ/kg$$

$$C_3H + 6H_2O \longrightarrow C_3A \cdot 6H_2O + 880\,kJ/kg$$

Tricalcium Aluminate — Hydrated Tricalcium aluminate (Crystalline)

$$4CaO \cdot Al_2O_3 \cdot Fe_2O_3 + 7H_2O \longrightarrow 3CaO \cdot Al_2O_3 \cdot 6H_2O + CaO\,Fe_2O_3 \cdot H_2O + 420\,kJ/kg$$

Crystalline (gel)

$$C_4AF + 7H_2O \longrightarrow C_3A \cdot 6H_2O + CF \cdot H_2O + 420\,kJ/kg + 420\,kJ/kg$$

Crystalline — Gel.

$2[2CaO \cdot SiO_2] + 7H_2O \rightarrow 3CaO \cdot 2SiO_2 \cdot 6H_2O + Ca(OH)_2 + 250\ kJ/kg$

Dicalcium Silicate — Tobermonite gel — Crystalline

$2C_2S + 7H_2O \rightarrow C_3S_2 \cdot 6H_2O + Ca(OH)_2 + 250\ kJ/kg.$

Final Setting & Hardening:

This is due to the formation of tobermonite gel & Crystallized Calcium hydroxide.

$2(3CaO \cdot SiO_2) + 6H_2O \rightarrow 3CaO \cdot 2SiO_2 \cdot 3H_2O + 3Ca(OH)_2 + 500\ kJ/kg$

(TriCalcium Silicate)

Flow Chart:

Unhydrated Cement
↓ $+H_2O$
Hydration (plastic mass)
↙ Metastable gel ↓ Stable gel → Crystalline products
↘ [Crystalline] Hydration products ↓ Crystalline products

Cement + water paste —1 day→ Hydration of C_3A and C_4AF —7 days→ Gelation of C_3S —28 days→ Gelation of C_2S & C_3S & Crystallization of $Ca(OH)_2$

Merits & Demerits of Dry & Wet Processes.

Dry Process	Wet process
* It is adopted when the raw materials are quite hard	* It can be used for any type of raw materials.
* Fuel Consumption is low	* Fuel Consumption is higher
* Process is Slow	* Process is Comparitively fast.
* The Process is Costly	* The Process is Cheaper.
* Cost of production of Cement is less.	* Cost of production of Cement is Somewhat higher.

UNIT - 5

PHASE RULE AND NANO MATERIALS

Phase Rule - Definition of terms - phase - Components - degree of freedom - derivation of Gibbs phase rule - significance and limitations of phase rule. phase diagrams - One component system - H_2O - Two component system - Eutectic systems - Pb-Ag systems.
Nano materials - classification, properties and applications of nano materials.
Carbon based nano sized materials - CNT and Graphene - properties and applications

Introduction :

⇒ phase rule is an important "generalisation" which deals with the behaviour of hetero-geneous system.

⇒ The phase rule was first discovered by an American physicist namely "J. Willard Gibbs" in 1874.

phase rule : which explains about the equilibrium existing in heterogeneous system.

The equilibrium between number of phases is not influenced by gravity (or) electrical (or) magnetic forces, but it is

- influenced by temperature, pressure and concentration. Then the no. of degrees of freedom (F) of the system is related to the no. of components (C), no. of phases (P), by the phase rule equation.

$$F = C - P + 2$$

Different terms in phase rule:

System: In chemical equilibrium, the process involved are changes in chemical composition or in the physical state or in both. The material that undergoes these changes constitute the system.

Systems are divided into two types. They are (a) Homogeneous system
(b) Hetero geneous system

(a) Homogeneous system:

This is a system, which exhibits identical physical and chemical properties throut out is known as a "homogeneous system".

Ex:- The solution of NaCl in water.

(b) Heterogeneous system: It is a system, which consists of parts with different physical properties.

Ex:- Ice-water-vapour system constitues heterogeneous -system.

phase rule is an important tool used for the quantitative treatment of systems in equilibrium.

① **phase:** A phase is defined as homogeneous physically distinct, mechanically Separable part of a system with well defined boundaries.

A system which is in equilibrium may Consists of one phase or more than one phase.

Ex:- ① water Consists of three phases

$$\underset{(\text{Solid})}{\text{Ice}} \rightleftharpoons \underset{(\text{Liquid})}{\text{water}} \rightleftharpoons \underset{(\text{gas})}{\text{vapour}}$$

② A gaseous mixture being thoroughly miscible in all proportions which Constitute one phase i.e a mixture of N_2 & H_2 forms one phase.

③ If two liquids are immiscible. They will form two separate phases.

Ex:- Carbon tetra chloride and water.

④ If two liquids are miscible, they will form one liquid phase only.

Ex:- water + Alcohol ⟶ one phase

Benzene + chloroform ⟶ One phase.

(5) The decomposition of Calcium carbonate into CO_2 & CaO.

$$\underset{(s)}{CaCO_3} \rightleftharpoons \underset{(s)}{CaO} + \underset{(g)}{CO_2}$$

This is three phase system.

(6) Similarly a system of finely divided rhombic sulphur, monoclinic sulphur, Liquid sulphur, vapour contains four phases of "S".

Components (C): The number of components of a system at equilibrium is defined as the smallest number of independent variables taking part in the state of equilibrium by means of which the composition of each phase can be expressed in the form of chemical equation.

Ex:- (i) water exists in three phases i.e,

$$\underset{(s)}{Ice} \rightleftharpoons \underset{(l)}{water} \rightleftharpoons \underset{(g)}{water\ vapour}$$

The composition of each phase can be expressed in terms of H_2O. Hence it is one component system.

(ii) sulphur exists in four phases namely rhombic, mono clinic, liquid and vapour. The composition of all phases is "sulphur". Hence it is one component system.

(iii) A system of saturated solution of NaCl Consists of solid salt solution and water vapour. The composition of all phases (is "Sulphur"! Hence it is one component system) is NaCl and H_2O, hence it is two Component system.

Example: ① NaCl + H_2O

② $CaCO_3 \rightleftharpoons CaO + CO_2$ – Two Component system.

Degree of freedom:

The maximum no. of independently variable factors such as temperature, pressure & Composition of the phases, which must be arbitrarily specified in order to represent perfectly the conditions of a system.

① In case of water system:

Ice $\rightleftharpoons$ water $\rightleftharpoons$ water vapour

If all the three phases are present in equilibrium at particular temperature & pressure. It has no degree of freedom. Therefore the system is invarient (or) non-variant (or) zero varient.

A system in equilibrium is affected by factors such as pressure, temperature, Composition of phases.

(1) A pure gas :- A pure gas is completely describle by just knowing the temperature and pressure.

$$F = C - P + 2$$
$$F = 1 - 1 + 2$$
$$= 2$$

So, the system is bivarient.

(2) Ice- water- vapour: All the three phases of water i.e Ice, water, vapour are at equilibrium at a temperature of 0.0098°c, pressure 4.58 mm of Hg.

Any change in temperature & pressure disturbs the three phases equilibrium & we get one or two phases.

$C = 1, P = 3$ $\quad F = C - P + 2$
$F = 1 - 3 + 2$
$F = 0$ non- varient system.

PHASE RULE EQUATION or GIBBS PHASE RULE

DERIVATION :

The phase rule was put forward by an american physicist Willard Gibbs (1874) & is known as "Gibbs phase rule".

Mathematically it may be written as

$$\boxed{F = C - P + 2}$$

With the help of phase rule, the effect of pressure, temperature and composition may be predicted for a heterogeneous system at equilibrium.

Derivation of phase rule:/ Gibbs phase rule:

A heterogeneous system having 'p' phases and 'c' components.

The degree of freedom (F) of the system is minimum no. of independent variables, these variables must be fixed arbitrarily to define the system completely.

The number of these variables is equal to the total number of variables minus (−) the number of relations between them at equilibrium.

F = Total no. of independent variables − Number of relationships between these variables.

Calculation of total number of independent variables:

(1) **Temperature:** At equibriom, temperature of every phase is same, so there is only one temperature variable for the entire system. i.e T = 1.

(2) **Pressure:** At equilibrium, each phase has the same pressure, so there is only one pressure

variable for the entire system. i.e $p=1$

(3) Concentration: Concentration of each components is generally expressed in terms of mole fractions.

⇒ As a rule, the no. of composition variables required for each phase are $(c-1)$.

⇒ If we have 'c' components, we must know the concentrations of $c-1$ components.

⇒ So, for 'p' phases the total composition variables are $p(c-1)$.

Hence total no. of variables

$= 1$ (for temperature) $+ 1$ (for pressure) $+$

$p(c-1)$ (for composition)

$$= p(c-1)+2$$

Number of relations at equilibrium:

For a system, in a thermodynamic equilibrium the chemical potential (μ), which is related to Concentrations of component in all particular components 'i', we have at equilibrium.

$$[\mu_i]_\alpha = [\mu_i]_\beta = [\mu_i]_\gamma$$

⇒ If there are three phases. Hence for 'p' phases, the number of such relationships for each component are $(p-1)$, Consequently for 'c' components, such relationships will be $c(p-1)$

Degree of freedom F = Total no. of independent variables − No. of relationships between these variables.

$$F = [P(C-1)+2] - [C(P-1)]$$

$$F = [(PC - P)+2] - [CP - C] \Rightarrow PC - P + 2 - PC + C$$

$$F = C - P + 2$$

$$\boxed{F = C - P + 2}$$

⇒ This is "mathematical statement" of phase rule.

ONE COMPONENT SYSTEM : (WATER SYSTEM)

The water system consists of three phases, ice, water, water vapour.

$$\text{Ice (s)} \rightleftharpoons \underset{(l)}{\text{water}} \rightleftharpoons \underset{(g)}{\text{water vapour}}$$

Here H_2O is the only one chemical compound involved, So, it is one component system.

According to phase rule $c = 1$, $P = 3$

$$F = C - P + 2$$
$$F = 1 - 3 + 2$$
$$F = 0$$ system is non varient

Ice (s) $\xleftrightarrow{\text{fusion}}$ Liquid water (l)

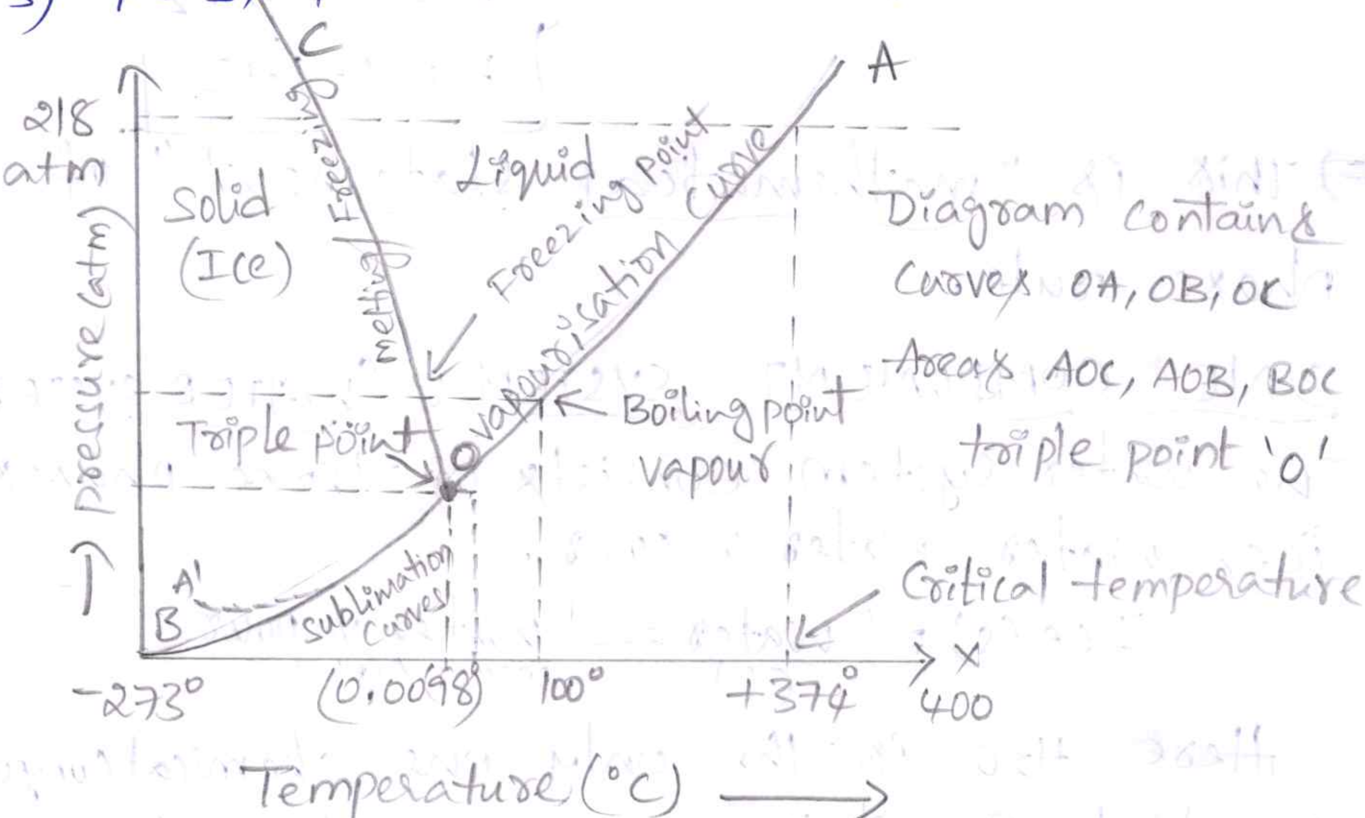
Ice (s) $\xleftrightarrow{\text{Sublimation}}$ water vapour (g)

liquid water (l) ⟷ water vapour (g)

Ice (s) ⟷ liquid water (l) ⟷ water vapour (g)

⇒ the degree of freedom depends up on the number of phases present at equilibrium. Here, three different cases are possible.

1) P=1, F=2 (Bivarient system)
2) P=2, F=1 (Univarient system)
3) P=3, F=0 (invarient system)



<u>Curve 'OA'</u> : <u>Vapour pressure curve of water</u> :

It represents the vapour pressure of liquid water at different temperatures.

- Above this curve, the liquid water alone exists, below it, only water vapour exist.
- Along this curve OA, the two phases water & water vapour co-exist in equilibrium.
- The curve OA terminates at A, the critical point i.e. 218 atm, temp 374°c where liquid & vapour

are indistinguishable from each other. i.e

$$F = C - P + 2$$
$$F = 1 - 2 + 2$$
$$\boxed{F = 1}$$

The system is mono varient.

Curve OB: Sublimation Curve of Ice: The curve represents the equilibrium between ice & water vapour. It is also called as vapour pressure curve of Ice.

⇒ This curve separates the ice region from vapour region. i.e above it lies ice and below it the vapour.

⇒ The two phases, solid ice & vapour co-exist in equilibrium along this curve.

⇒ At the lower limit the curve OB terminates at absolute zero (−273°C) where no vapour exists.

$$\therefore F = C - P + 2$$
$$F = 1 - 2 + 2$$
$$\boxed{F = 1}$$

∴ The system at curve is "monovarient".

Curve OC: Melting/fusion curve: The 'OC' curve represents melting point curve or fusion curve.

⇒ This curve divides the solid ice region from the liquid water region.

⇒ This curve is inclined towards the pressure axis, which indicates the melting point of ice is lowered by increase of pressure.

∴ Along these curve OC, there are two phases in equilibrium and one component, According to the phase rule.

$$F = C - P + 2$$
$$= 1 - 2 + 2 = 1$$
$$\boxed{F = 1}$$

Hence each two phase system i.e OA, OB, OC has one degree of freedom i.e "mono varient".

2) Areas AOC, AOB, BOC: The areas (or) regions between the curves shows the conditions of temperature & pressure under which a single phase – ice/water/vapour is capable of stable existance. Thus area 'AOC' represents conditions for the one phase system of water

⇒ Area 'AOB' represents conditions for the one phase system of water vapour

⇒ Area 'BOC' represents conditions for the one phase system of Ice.

⇒ In all these areas there is one phase & one component system. we have

$$F = C - P + 2$$
$$= 1 - 1 + 2$$
$$\boxed{F = 2}$$

⇒ Thus, each system, water, water vapour or Ice has '2' degree of freedom i.e the system is bivarient.

③ Triple point 'O': The curves OA, OB, & OC meet at the triple point 'O', where all the three phases water / ice / vapour are in equilibrium. This occurs at 0.0098°C and a vapour pressure of 4.58 mm Hg.

$$\therefore \quad F = C - P + 2 = 1 - 3 + 2 = 0$$

$$\boxed{F = 0}$$

i.e the system at the triple point is non-varient (or) invarient. Thus, if either pressure or temperature is changed, the three phases are not exist.

Unstable curve OA' (or) metastable curve:
Water does not always freeze at 0°C, if the vessel containing water & vapour is clean & free from dust, it is possible to super-cool several degrees below its freezing point 'O'.
The curve OA' is continuation of vapourisation curve 'OA', represents the vapour pressure curve of super cooled water. This curve represents a metastable system.

metastable is the state of super cooled water.

Triple point : The three curves OA, OB, OC meet at the triple point 'O'. At this point the three phases liquid, ice, and vapour are in equilibrium. This occurs at 0.0098°C and vapour pressure at 4.58 atm. They are three phases and one component.

Hence $F = C - P + 2$

$= 1 - 3 + 2$

$\boxed{F = 0}$ the system at triple point is invarient.

Eutectic system: A binary system consisting of two system which are miscible in all proportions in the liquid phase, but which do not react chemically is known as the "Eutectic system". Eutectic mixture is a solid solution of two (or) more substances, having the lowest freezing point of all the possible mixtures of the components.

Eutectic point: Eutectic means easy melting. Two or more solid substances capable of forming solid solutions & have the property of lowering each others freezing point & the minimum freezing point (attainment) attainable corresponding to the eutectic mixture is termed as eutectic point (C) [Lowest melting point].

Lead silver system / Two component / Heterogeneous system:

It is a two component system with four possible phases - solid Ag, solid Pb, solution of Ag and solution of Pb.

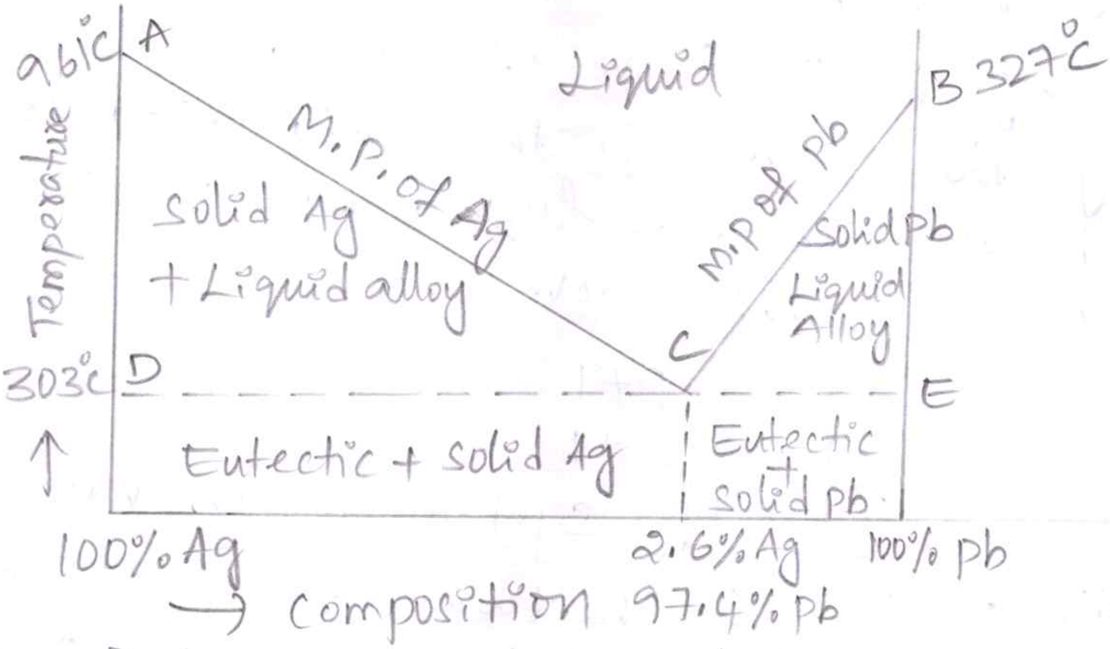
*Vapour pressure has nearly no effect on equilibrium, so the system can be conveniently represented by a temperature - concentration diagram at atmospheric pressure.

* The gaseous phase is practically absent & one variable is neglected.

In this condensed phase rule is applicable.

$$F = C - P + 1$$

This system is also known as "Condensed system"



[T-C diagram of heterogeneous system]

In this two compent system curves are AC & BC.

Areas ACB, ACD & BCE.

Curve AC: Point 'A' represents the melting point (961°C) of pure silver. when increasing the quantities of pure lead are added, the freezing of silver lowers along the curve AC. This curve is also known as freezing point curve of silver.

The solid silver is in equilibrium with liquid-melt along the curve AC. so, there are two phases.

$$F = C - P + 1$$
$$F = 2 - 2 + 1$$
$$\boxed{F = 1}$$ system is monovarient.

Curve BC: point 'B' represents the melting point of lead (327°C). when increasing the quantities of pure silver are added to the lead, the freezing point of lead lowers along the curve BC. Therefore this curve may be called freezing point curve of lead.

Along the curve BC, the solid lead is in equilibrium with the liquid melt. so the no. of phases along the curve is two.

$$F = C - P + 1$$
$$F = 2 - 2 + 1$$
$$\boxed{F = 1}$$ system is mono varient.

Eutectic point "C": The two curves AC & BC intersect at the point 'c', this point is called eutectic point & the temperature at this point is 303°c, this temperature is called Eutectic temperature. The composition at this point is 2.6% of Ag & 97.4% of Pb. This is called Eutectic composition.

All the three phases i.e solid Ag, solid pb, solutions of Ag & pb are co-exist at equilibrium, so, Degree of freedom $F = C - P + 1$
$F = 2 - 3 + 1$ $\boxed{F = 0}$

F=0, so system is non-varient.

Area ACB: In this area only liquid melt is exist. So, there is only one phase.

$$F = C - P + 1$$
$$F = 2 - 1 + 1$$
$$\boxed{F = 2}$$ system is bivarient.

Area ACD: In this area, solid silver is in equilibrium with eutectic mixture / liquid melt. So, there is two phases. $\boxed{F=1}$

Area BCE: In this area, solid Lead is in equilibrium with eutectic mixture, so, there is two phases. $\boxed{F=1}$ system is monovarient.

Advantages of phase rule: / Applications:

⇒ It gives a simple method of classifying equilibrium states of systems.

⇒ It predicts the behaviour of systems when subjected to changes in variables such as pressure, temperature and volume.

⇒ It is applicable to physical as well as to chemical phase reactions.

Limitations / disadvantages of phase rule:

⇒ As the phase rule is applicable to heterogeneous system in equilibrium, it is therefore of no use for such systems which are slow in reaching the equilibrium state.

⇒ As the phase rule is applicable to a single equilibrium state, it never tells about the-number of other equilibrium possible in the system.

⇒ All the phases in the system must be present under the same pressure & temperature.

⇒ No liquid or solid phases should be finely divided otherwise their vapour pressures will differ from their normal values.

⇒ In phase rule, temperature, pressure & composition variables are considered but do not consider electrical, magnetic & gravitational forces. If such variables are considered, the factor 2 of the phase rule has to be adjusted accordingly.

<u>Significance of phase rule:</u>

The phase rule, a concept in thermodynamics, is significant because it provides a framework for understanding the behaviour of multi phase systems and predicting the conditions under which phase transitions occur.

It helps in determine the no. of degrees of freedom (independent variables) needed to define a system at equilibrium.

NANOMATERIALS

Nanomaterials - Classification, Properties and application of nanomaterials. Carbon based nanosized materials - CNT and Graphene - Properties and applications.

Nanomaterials :-

The term nanoscale refers to the dimension of 10-9 meters. It is the One billionth part of a meter. So, the particles whose any of the external dimensions or internal structure dimension or Surface structure dimension lies in the range of 1nm to 100nm are Considered as Nanomaterials.

These materials are invisible to the naked eye. The material Science-based approach of nanotechnology is Considered for nano materials. At this Scale, these materials have Unique optical, Electronic, mechanical and quantum properties Compared to their molecular-Scale behavior.

1. Classifications of Nanomaterials based on Morphology and Dimensions:

* Zero-dimensional nanomaterials: Here, all dimensions (x, y, z) are at nanoscale, i.e., no dimensions are greater than 100nm. It includes nanospheres and nanoclusters.
* One-dimensional nanomaterials :- Here, two dimensions (x, y) are at nano scale and the other is outside the nano scale, This leads to needle shaped nanomaterials. It includes nanofibres, nanotubes, nanorods, and nanowires.
* Two-dimensional nanomaterials: Here, One dimension (x) is at nanoscale and the other two are outside the nano scale. The 2D nanomaterials exhibit plate like shapes. It includes nanofilms, nanolayers, nanoCoatings with nano meter thickness.

* Three-dimensional nanomaterials: These are the nanomaterials that are not Confined to the nanoscale in any dimension. It includes dispersion of nanoparticles, bundles of nanowires and nanotubes as well as multinano layers (polycrystals)

Classifications of Nanomaterials based on Composition:

i) Carbon based materials:
These are Composed of Carbon, taking the form of hollow Spheres, ellipsoids or tubes. The Spherical and ellipsoidal forms are referred as fullerenes, while Cylindrical forms are Called nanotubes.

ii) Metal based materials:
These include quantum dots, nanogold, nanosilver and metal Oxides like TiO_2. A quantum dot is a closely packed Semi Conductor Crystal Comprised of hundreds or thousands of atoms, whose Size is on the order of a few nanometers to a few hundred nanometers.

iii) Dendrimers:
These nanomaterials are nanosized polymers built from branched Units. The Surface of a dendrimer has numerous Chain ends, which can perform Specific Chemical functions.

iv) Composites:
Composites are Combination of nanoparticles with other nanoparticles or with larger, bulk-type materials, Nano-particles like nanosized clays are added to products (auto parts, Packaging materials, etc) to enhance mechanical, thermal, and flame-retardant properties.

Applications of Nanomaterials:

i. Medicine:

NPs have drawn increasing interest from every branch of medicine for their ability to deliver drugs in the optimum dosage range often resulting in increased therapeutic efficiency of the drugs, weakened side effects and improved patient compliance. Iron oxide particles such as magnetite (Fe_3O_4) or its oxidized from magnetic (Fe_2O_3) are the most commonly employed for biomedical applications.

ii) Enviromental applications:

Nano Sensor applications that can continuously measure and give warnings and alarms in case of deviation from the given threshold values are becoming widespread in order to monitor air, water and environment pollution.

iii) Automobile:

Nanomaterials will play a critical role in efforts to reduce vehicle weight, higher strength and more flexible structures. with nano technology, scratch-resistant, dirt-free and self-repairing vehicle paints can be applied on the exterior of the vehicle. This is done with nanoparticle flexible, fast-adhering, corrosion-resistant and antimicrobial layers in the nanocoating technique.

iv Electronics:

Ultra-high definition displays and televisions are now beings sold that use quantum dots to produce more vibrant colors while beings more energy efficient.

v. Mechanical:

Nanoparticles can offer many applications in mechanical industries especially in Anti-corrosive coating, lubricants and adhesive applications.

Carbon Nano Tube (CNT)

A Carbon nanotube is a tube-Shaped materials, made ups of Carbon, having a diameter ranging from <1 nm to 50 nm. Simply we can say, Carbon nanotubes (CNT) are Cylinders of one or more layers of graphene (lattice)

Types of CNT:

Single-wall nanotubes (SWNT):

These may be Zigzag, armchair and Chiral depending on the manner in which the grapheme sheets are rolled. The diameter of Single-walled Carbon nanotubes is 2nm. The length of Single-walled Carbon nanotubes is around 2 micrometers. They exist in a One-dimensional Structure. Therefore, it is also known as a nanowire

Electronics Can miniaturized by Using a Single-walled Carbon nanotube. Their band gap varies from 0-2 Electron volts (eV). They Show Conductivity like a Semiconductor. Therefore, they exhibit both metallic and Semiconductivity behaviour.

Multi-wall nanotubes (MWNT):

It Consists of Several Single walled nanotubes with different diameters. A multi-wall nanotube is Shown in Fig.

The outer diameter of Multi-walled Carbon nanotubes is around 2-20 nanometers. The inner diameter of Multi-walled Carbon nano-tubes is 1-3 nm. The length of Multi-walled Carbon nanotubes is around 5-6 micrometers.

Properties of CNT:

i) Electrical Conductivity: Carbon nanotubes (CNTs) are electrically and Conductive and have a high mechanical Strength.

ii) Strength And Elasticity: It terms of tensile strength and elastic modulus, Carbon nanotubes are the strongest and stiffest materials yet found.

iii) Thermal Conductivity and Expansion: The Carbon bond's rigidity aids in the transmission of vibrations throughout the nanotube, resulting in excellent heat conductivity.

iv) Electrical Conductivity: They have high Electrical Conductivity because each Carbon atom is Connected to three other Carbon atoms by Strong Covalent bonds, Carbon nanotubes have an extremely high melting point. This also leaves a spare electron on each Carbon atom, resulting in a sea of delocalized electrons within the tube, allowing nanotubes to Conduct electricity.

V. Corrosion resistant: Carbon nanotubes are chemically neutral. So, they are chemically stable. Therefore, Carbon nanotubes resist Corrosion.

Applications:

Carbon nanotube technology Can be Used for a wide range of new and existing applications, which are as follows:

i) Nanotubes Can potentially replace indium tin Oxide in Solar Cells to generate photocurrent.

ii) SWNTs are Used in transistors and Solar panels.

iii) MWNTs are Used in lithium ion batteries to enhance cycle life.

iv) Parallel CNTs have been Used to Create loudspeakers.

v) CNTs Can Serve as a multifunctional Coating material.

vi) CNTs Can be Used to produce nanowires.

vii) CNTs are also Used for applications in energy storage, automotive parts, boat hulls, water filters, thin-film electronics Coating, ultra-capacitors, biosensors for harmful gases, extra strong fibers, etc.

Graphine

Structure of Graphene :-

-Graphene (G) is a two-dimensional allotrope of Carbon Consisting of a Single, flat layer of Carbon atoms just one atom thick bonded together in a hexagonal, honeycomb lattice.

Carbon atoms have a total of 6 electrons: 2 in the inner Shell and 4 in the outer, Valence Shell, Each Carbon atom is bonded to three other Carbon atoms with very Strong Covalent - (Sigma) bonds which are difficult to break, leaving one of the four Electrons in each Carbon atom's Outer Valence Shell available for Conduction and free to "Wander" Or to interact with other atoms or molecules. These highly mobile electrons are Called π (pi) electrons or π Orbitals (π and π*) are located above and below the graphene Sheet. The Pi Orbitals overlap and help to enhance the Carbon to Carbon bonds in graphene. The electronic properties of graphene are dictated by the bonding of these π Orbitals.

Different forms of graphene: (a) graphene oxide (b) pristine graphene (c) functionalized graphene (d) graphene quantum dot, and (e) reduced graphene oxide.

Graphene properties:

* High thermal Conductivity and Electrical Conductivity.
* High elasticity and flexibility.
* High hardness and High resistance.
* Graphene is approximately 200 times Stronger than Steel, Similar to diamond resistance, but much lighter.

* Ionizing radiation is not affected.
* Able to generate electricity by exposure to Sunlight.
* Transparent material.
* High density which doesn't let Helium atoms pass, but it does alow the passage of water, which evaporates at the Same Speed as if it were in an open Container.
* Antibacterial effect. Bacteria are not able to grow in it.
* Low Joule effect, heating when Conducting electrons.
* Low electricity Consumption Compared to Other Compounds.

Applications of Graphene:

1. Sensors:
Graphene Could be Used in Sensors in Various fields including bio-Sensors, diagnostics, field effect transistors, DNA Sensors, to name a few.

2. Batteries:
Graphene Can be incorporated into both the anode and the Cathode in Various battery Systems to increase the efficiency of the battery and improve the Charge / discharge cycle rate

3. Biomedical:
Graphene applications in biomedicine are numerous and Can be Classified into Several main areas: transport (delivery) System, Sensors, tissue engineering and biological agents (for Example antimicrobials)

4. Rust-free future:
By Combining graphene with paint, a Unique graphene Coating is formed with Could Signal the end of the deterioration of Ships and Cars through rust.

5. Electronics:
Graphene Can be Used as Coating to improve Current touch Screens for phones and tablets.

Properties of Nanomaterials:

* The magnetic properties increases with decrease in size of materials.
* Melting point of the Nanomaterials increases when compared with other material depending on size of particles.
* Solubility of nanomaterials is more than others materials due to decreased size.
* Colour: The physical property colour is again size dependent
* Transparency: Transparency of nanomaterials is more than other materials.
* Catalytic Behaviour: Due to increased surface area, the catalytic activity of nanomaterials is more than other materials.
* Chemical Reactivity: Nanoparticles possess high chemical reaction.
* The Nanomaterials exhibit and dispersibility.
* The nanomaterials can be used as good conducting semiconducting & insulating materials.