

**20BS1102 / 20BS2102**  
**ENGINEERING CHEMISTRY**

<b>Course Category:</b>	Institutional Core	<b>Credits:</b>	3
<b>Course Type:</b>	Theory	<b>Lecture-Tutorial-Practice:</b>	3-0-0
<b>Prerequisites:</b>	Chemistry knowledge at Intermediate level	<b>Continuous Evaluation:</b> <b>Semester end Evaluation:</b> <b>Total Marks:</b>	30 70 100

### COURSE OUTCOMES

**Upon successful completion of the course, the student will be able to:**

<b>CO1</b>	Analyze various water treatment methods and boiler troubles.
<b>CO2</b>	Apply the concept of phase equilibrium to different materials and the knowledge of working of electrodes and batteries in various technological fields.
<b>CO3</b>	Evaluate corrosion processes as well as protection methods.
<b>CO4</b>	Apply the knowledge of conventional fuels and mechanistic aspects of conducting polymers for their effective and efficient utilisation.

### Contribution of Course Outcomes towards achievement of Program Outcomes (L - Low, M - Medium, H - High)

	PO 1	PO 2	PO 3	PO 4	PO 5	PO 6	PO 7	PO 8	PO 9	PO 10	PO 11	PO 12
<b>CO1</b>		H										
<b>CO2</b>	M											
<b>CO3</b>			H									
<b>CO4</b>					M							

### COURSE CONTENT

<b>UNIT I</b>	<b>(10 hours)</b>
<b>Water technology-I:</b> WHO standards - Water treatment for drinking purpose - sedimentation, coagulation, filtration, disinfection by chlorination, breakpoint chlorination and its significance - Desalination of brackish water - principle and process of electrodialysis and reverse osmosis, advantages and disadvantages.	
<b>Water technology-II:</b> Boiler troubles - scales-formation, disadvantages and internal conditioning methods - phosphate conditioning, calgon conditioning and sodium aluminate, caustic embrittlement- reasons, mechanism and its control,	

and boiler corrosion – causes and control.

## **UNIT II**

**(10 hours)**

**Phase rule and applications:** Definition and explanation of the terms – phase, component and degree of freedom, phase rule equation, phase equilibria of single component system – water system, two component system – silver-lead system, applications of phase rule.

**Electrochemistry:** Construction and working of Calomel electrode, silver-silver chloride electrode, and principle, construction and working of glass electrode, determination of pH using glass electrode. Chemistry of modern batteries - Li/SOCl<sub>2</sub> battery and Li<sub>x</sub>C/LiCoO<sub>2</sub> battery – construction, working and advantages. Fuel cells: General working principle of a fuel cell, examples, chemistry of H<sub>2</sub>-O<sub>2</sub> fuel cell.

## **UNIT III**

**(10 hours)**

**Corrosion principles:** Introduction, definition, reason for corrosion, examples – types of electrochemical corrosion - hydrogen evolution and oxygen absorption – corrosion due to dissimilar metals, galvanic series – differential aeration corrosion – pitting corrosion and concept of passivity.

**Corrosion control methods:** Cathodic protection- principle and types - impressed current method and sacrificial anode method, anodic protection- principle and method, corrosion inhibitors – types and mechanism of inhibition – principle, process and advantages of electroplating and electroless plating.

## **UNIT IV**

**(10 hours)**

**Conducting polymers:** Definition, examples, classification-intrinsically conducting polymers and extrinsically conducting polymers- mechanism of conduction of undoped polyacetylene, doping of conducting polymers- mechanism of conduction of p-doped and n-doped polyacetyles – applications of conducting polymers.

**Fuel technology:** Fuel-definition, calorific value- lower and higher calorific values and numericals on calculation of HCV and LCV relation, analysis of coal – proximate analysis and ultimate analysis, flue gas analysis by Orsat's apparatus, numericals based on calculation of air required for combustion.

## UNIT - I

### PART – 1

### WATER TECHNOLOGY – 1

**WHO standards for drinking water:** Following are certain specifications of drinking water as prescribed and recommended by WHO.

1. Drinking water should be colourless and odourless.
2. It should be good in taste and should not be hot.
3. It should be free from all types of pathogenic microorganisms.
4. Total hardness should not exceed 200 ppm and turbidity should be less than 10 ppm.
5. It should not be highly alkaline (pH can be 6.5-8.5).
6. Free residual chlorine can be up to 0.2 ppm and total dissolved solids up to 500 ppm.
7. It should be free from objectionable gases like  $H_2S$  and mineral salts of Pb, Cr, As and Mn.
8. The maximum limit of fluoride is 1.0 ppm, arsenic 0.01 ppm and lead 0.05 ppm.
9. Chemical oxygen demand (COD) and biological oxygen demand (BOD) limits are 20 mg/L and 5 mg/L respectively.

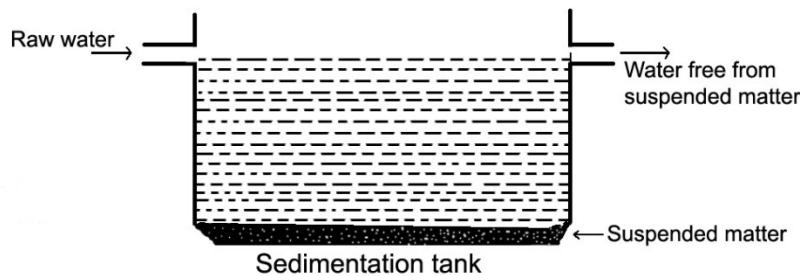
**Drinking water treatment (Municipal or domestic water treatment):** The quality of natural water from rivers, canals, etc. is not according to the required specifications of drinking water. So, water from such sources is given specific treatments to get potable water.

**1) Sedimentation:** *Sedimentation is the process of settling water for certain period of time so that most of the suspended particles heavier than water settle to bottom due to force of gravity.* The detention period in a concrete sedimentation tank ranges from 2-6 hours. Rate of sedimentation depends on amount of suspended impurities, volume of water, size, shape and weight of impurities. Heavier the impurities greater is the rate of sedimentation.

Rate of sedimentation  $\propto$  (1/Viscosity)

Temperature  $\propto$  (1/Viscosity)

$\therefore$  Rate of sedimentation  $\propto$  Temperature



**2) Coagulation:** *It is a process in which colloidal impurities are removed by adding certain chemicals called coagulants.* The dosage of coagulant required depends on extent of colloidal impurities present in water. Generally, 5 – 100 mg/L is added and stored about 1 to 2 hours.

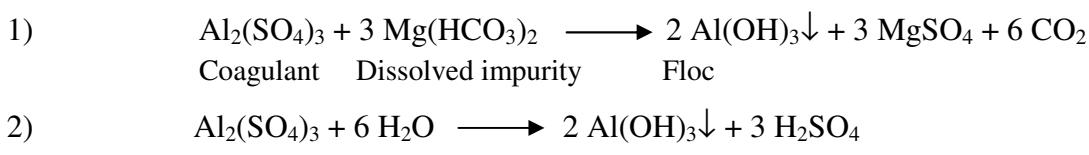
*Inorganic coagulants:*

- 1) Potash alum, common alum or alum,  $K_2SO_4 Al_2(SO_4)_3 24H_2O$
- 2) Sodium aluminate,  $NaAlO_2$
- 3) Ferrous sulphate,  $FeSO_4 \cdot 7H_2O$
- 4) Ferric sulphate,  $Fe_2(SO_4)_3$
- 5) Ferric chloride,  $FeCl_3 \cdot 6H_2O$

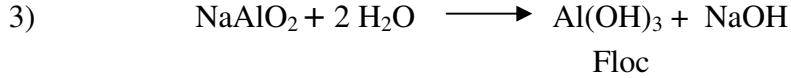
*Organic coagulants:*

- 1) Polyacrylate and 2) Polyacrylamine (PAM)

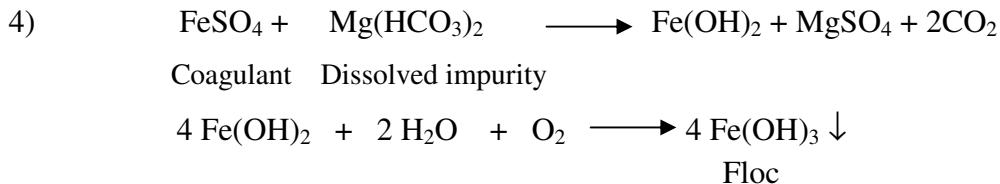
*Mechanism of coagulation:* It involves two steps. In the first step, floc is produced and in the second step, they deposit the colloidal particles. When inorganic coagulants are added to water, they react either with water or with dissolved salts of water to form flocculent and gelatinous precipitates (big in size, having porosity and large surface area).



Alum is effective in water with alkalinity. If natural alkalinity is not present, sufficient lime is added.



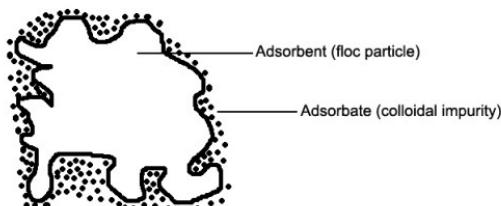
Sodium aluminate is most suited for treating water having no alkalinity ( $pH < 7$ ).



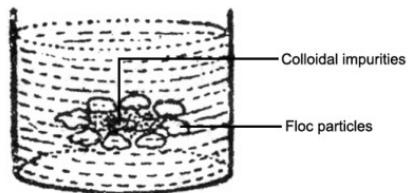
Ferrous sulphate can give good results in slightly alkaline water ( $pH > 8.5$ ).

*The flocculent precipitates settle colloidal particles by any of the following ways:*

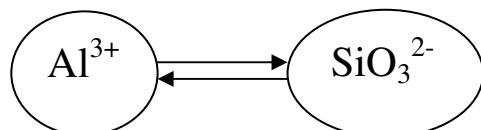
a) *Adsorption:* Some of the colloidal impurities may be adsorbed on the large surface of the precipitate particles (floc). Due to adsorption of colloidal particles on floc, the weight of the particle increases and finally it gets settled to the bottom of the tank along with colloidal particles.



b) *Mechanical entanglement:* The colloidal particles may be entrapped among the flocculent precipitate particles. Along with the precipitate the colloidal impurities also settle to the bottom of the tank.

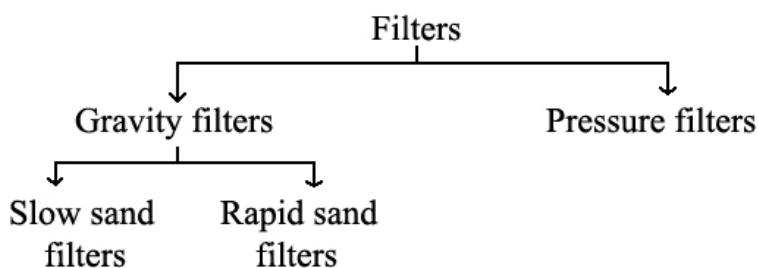


c) *Attraction towards oppositely charged ions:* If the colloidal particles are charged, then the oppositely charged ions of the coagulant attract the colloidal particles to form an insoluble compound which settles to the bottom. For example, aluminium ions of the coagulant attract silicate colloidal particles of water to form aluminium silicate which settles as suspended matter.



**3) Filtration:** In order to ensure complete removal of suspended impurities, excess of floc produced during coagulation and also certain microorganisms, water is subjected to filtration. *It is the process of removal of suspended matter from water by passing it through the porous medium or bed.*

Large quantities of water can be filtered by using sand filters. A sand filter contains three beds namely fine sand bed, coarse sand bed and gravels bed. The fine sand bed acts as the filter while the remaining two beds act as support for the fine sand bed.

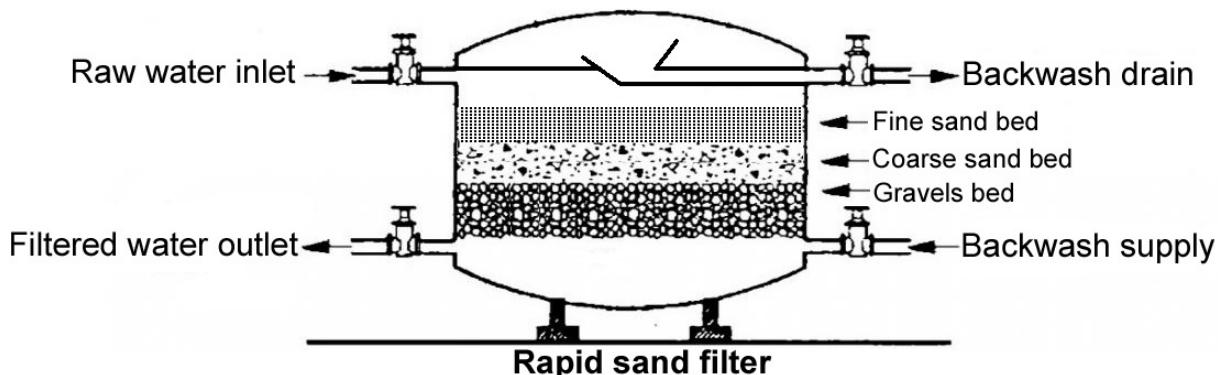


**Gravity filters:** In these filters, water flows through the filter beds by force of gravity. For municipal water treatment, gravity filters are used. These are further divided into two types – slow sand filter and rapid sand filters.

**Slow sand filters:** It is made up of a concrete tank containing the three sand beds. When water percolates through the finely graded sand bed, all the suspended matter and some bacteria are retained in the pores between sand particles. The rate of filtration is about 2 gal/sq.ft./hour. When the filter is exhausted, the working of filter is stopped and about 2-3 cm of the top fine sand layer is scrapped off and replaced with clean sand and the filter is put back into use again. Due to slow rate of filtration, slow sand filter requires large area for its construction. The overall cost of unit is high because large area of land and more quantities of materials are needed.

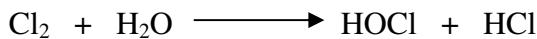
**Rapid sand filters:** The working principle of rapid sand filter is very much similar to that of a slow sand filter, except that the exhausted sand bed is regenerated by a process called reverse wash system or back wash system. When the filter is exhausted, filtration is stopped and a portion of the filtered water is forced through the filter bed in the reverse direction of filtration. This process washes off the

deposited suspended matter in the fine sand bed. Then the bed becomes ready for filtration again. They are capable of producing filtered water at the rate of 100 gal/sq.ft./hour. The overall cost of unit is low and economical.



**4) Disinfection:** The process of destruction of pathogenic microorganisms of water and making it suitable for human consumption is called disinfection and the chemicals used for this purpose are called disinfectants. Disinfection refers to the process of killing disease causing microorganisms alone, while sterilization refers to the destruction of all types of microorganisms present in water.

**Chlorination:** It is the most widely used disinfectant for water treatment. Chlorine in the form of gas or in concentrated solution form is added to water. It reacts with water to produce hypochlorous acid, which is a powerful germicide.



Hypochlorous acid attacks the enzymes present in the cells of microorganism and inactivates them. Hence, microorganisms become weak and finally destroyed. For an effective disinfection by chlorination, the pH of water should be  $\leq 6.5$ . At higher pH values above 6.5, the following equilibrium starts shifting in right hand side. The resulting hypochlorite ion ( $\text{OCl}^-$ ) cannot inactivate the enzymes of the microorganisms and hence hypochlorite ion is not a powerful germicide.



**Advantages:** The high popularity of chlorine as disinfectant is due to the following advantages.

- 1) It is readily available either in the liquid or in gaseous form.
- 2) It is effective and economical.
- 3) It is stable and does not deteriorate on storage.
- 4) It can be used at low as well as high temperatures.
- 5) It does not introduce any solid residues in water.

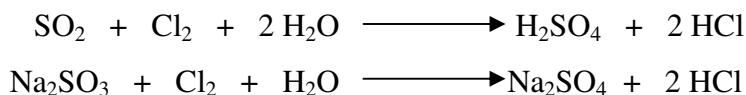
**Disadvantages:**

- 1) If excess of chlorine is added, it produces a characteristic unpleasant taste and odour.
- 2) Its excess also causes irritation on mucous membranes and to eyes.
- 3) It is less effective at higher pH above 6.5.

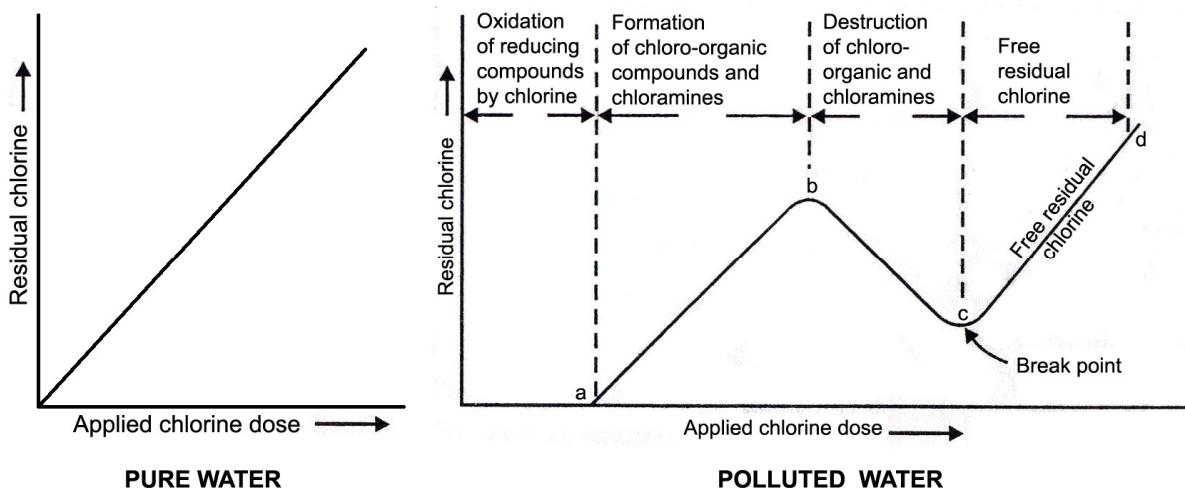
**Dechlorination:** The permitted level of residual chlorine in treated water is 0.2 ppm. Addition of chlorine to water beyond the actual required quantity produces unpleasant taste and odour. These

objectionable qualities of water can be avoided by dechlorination. *It is the process of removal of excess of chlorine (residual chlorine) present in water after disinfection.* Dechlorination can be carried out in two ways.

- After disinfection, water is passed through a bed of molecular carbon. Excess of chlorine gets adsorbed on the carbon particles. Alternatively, a small quantity of activated carbon is added directly to water, allowed some time for adsorption and then carbon is removed by filtration.
- Chlorine can also be removed by treating water with either sulphur dioxide or sodium sulphite.



**Break point chlorination:** It is the technique adapted during disinfection by chlorination of highly contaminated water. In case of highly polluted water, it is necessary to determine the exact quantity of chlorine required for 100 % disinfection without leaving residual chlorine in treated water. *Break point chlorination is the process of determining the amount of chlorine required to oxidize the organic matter, reducing substances, free ammonia and to destroy pathogenic microorganisms present in water.*



In this process, fixed quantity of chlorine is added to water, mixed thoroughly and the treated water is subjected to a titration to determine the residual chlorine. Thus, the quantity of residual chlorine is obtained after each addition of chlorine. A graph is plotted between applied chlorine and residual chlorine. In case of pure water, all the chlorine added remains as residual chlorine. In case of polluted water, the results obtained are shown graphically in the figure. The graph can be divided in to four regions.

**Region-1:** Chlorine added in this region is completely consumed for oxidation of all the reducing compounds. Hence, there will be no residual chlorine in this region.

**Region-2:** Chlorine added in this region is consumed for formation of chloroorganic compounds and chloramines.

Region-3: The chloroorganic compounds and chloramines formed in the region-2 are completely decomposed and destroyed by chlorine in this region.

Region-4: Chlorine added in this region (beyond point C) remains as residual chlorine.

The amount of chlorine corresponding to the point ‘C’ is the actual quantity of chlorine required to oxidize all organic matter, ammonia and reducing substances as well as to destroy microorganisms. This point is called break point.

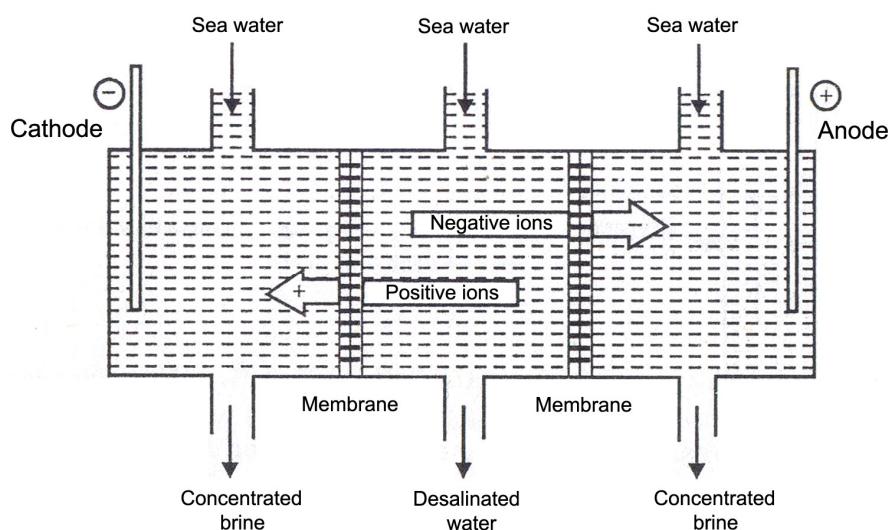
*Advantages:*

- 1) It oxidizes completely organic compounds, ammonia and reducing substances.
- 2) It removes colour, odour and unpleasant taste imparted to water due to presence of impurities.
- 3) It prevents growth of any weeds in water.
- 4) It destroys completely (100%) all the pathogenic bacteria.

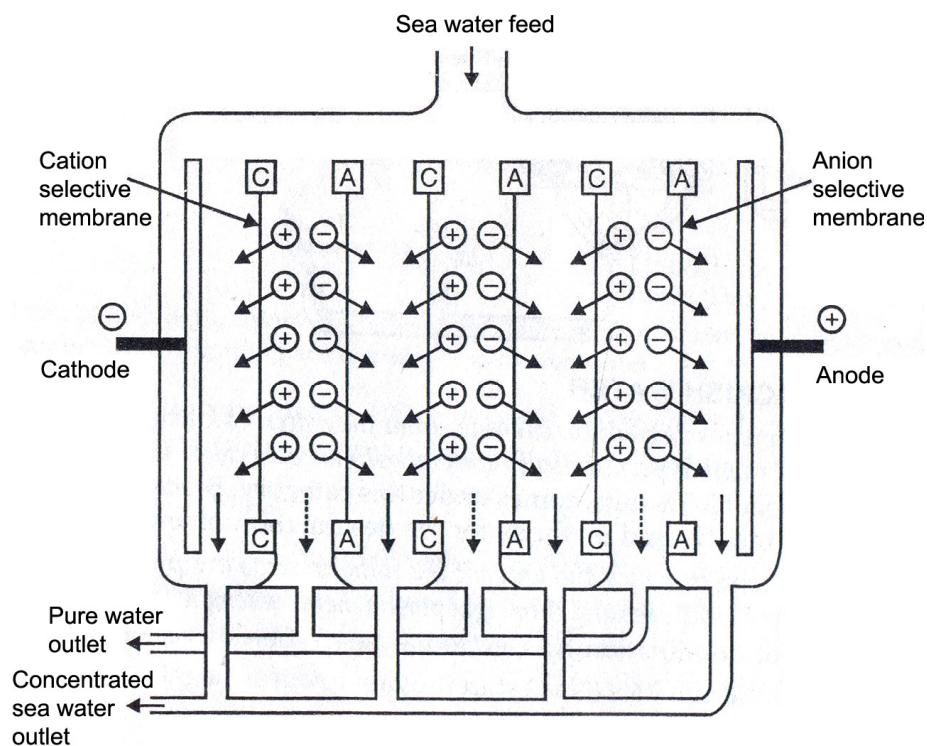
## DESALINATION

Water containing salts at very high concentrations is called saline water or brackish water. *The process of removal of dissolved salts from saline water is called desalination.* Sea water is an example for saline water. There are two important methods for desalination of brackish water.

**Electrodialysis:** *It is a method of desalination in which the ions present in water are pulled out by passing direct current through water, using electrodes and a pair of thin rigid plastic membranes.* The principle of this method can be explained by using the following figure.



When direct current is passed through saline water, positive ions start moving towards negative electrode (cathode), while negative ions start moving towards positive electrode (anode). As a result, the ions present in central compartment move to the extreme compartments. Hence, water from the central compartment becomes desalinated water, while concentrated brine is obtained from the extreme compartments.

**Method:**

In order to conduct the process for larger quantities of water, ion-selective membranes are used. An ion selective membrane has permeability for only one kind of ions with specific charge. For example, cation selective membrane allows the passage of only cations through it and does not permit the passage of anions. Cation selective membranes contain functional groups like  $\text{RCOO}^-$  or  $\text{RSO}_3^-$ , which attract cations of water and reject the anions. Similarly, anion selective membranes contain positively charged fixed functional groups like  $\text{R}_4\text{N}^+$ , which attract anions and reject cations.

An electrodialysis cell consists of a large number of ion-selective membranes. Saline water is passed under a pressure of  $\sim 5\text{-}6 \text{ kg/m}^2$  between membrane pairs and an electric field is applied in the perpendicular direction to the flow of saline water. The fixed charges inside the membrane attract the opposite charges and repel the same charges. Therefore, water in one compartment is free from ions while the salt concentration in adjacent compartments is increased. Thus, desalinated water and concentrated saline water are collected from alternate compartments.

**Advantages:**

- 1) It is a very compact unit.
- 2) The cost of installation of the plant and its operation are economical.
- 3) If electricity is available, this method is suitable for desalination.

**Disadvantages:**

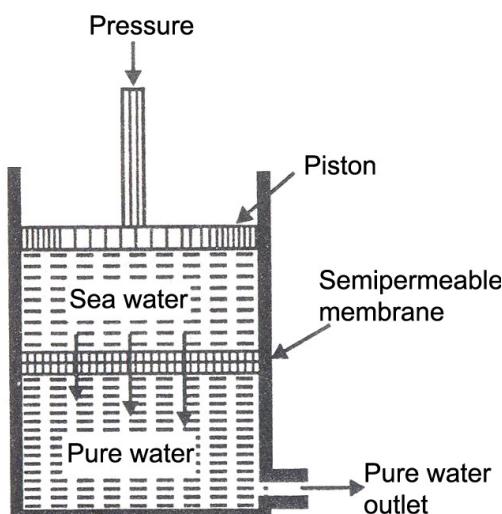
- 1) Electrical energy is essential for the process.
- 2) It cannot remove the colloidal impurities, silica and organic matter.

**Reverse osmosis (super filtration or hyper filtration):** When two solutions of unequal concentrations are separated by a semipermeable membrane, flow of solvent takes place from dilute solution side to

concentrated solution side due to osmosis. The pressure exerted by water molecules of dilute solution side on the membrane is directly proportional to difference in the concentrations of the two solutions and is called osmotic pressure.

If a hydrostatic pressure in excess of osmotic pressure is applied on the concentrated solution side, the solvent molecules start flowing from concentrated solution side to dilute solution side across the membrane. This is the basis for the reverse osmosis process. During reverse osmosis, pure water is separated from its impurities by applying a hydrostatic pressure on the contaminated water.

*Method:* Pure water and sea water are separated by a semipermeable membrane in a rectangular tank as shown in figure. A hydrostatic pressure of the order of 15-40 kg/m<sup>2</sup> is applied using a piston arrangement on sea water. This pressure is to force the water molecules of sea water to cross the membrane to enter the pure water compartment against the osmotic pressure. Thus, solvent molecules of sea water are separated from it, leaving behind all the impurities. The membrane used in this process consists of very thin films of cellulose acetate. Recently, they are replaced by superior membranes made of polymethacrylate and polyamide polymers.



#### Advantages:

- 1) It removes ionic as well as non-ionic, colloidal and organic matter.
- 2) Colloidal silica can be removed.
- 3) The maintenance cost is almost entirely on the replacement of semipermeable membrane.
- 4) Membrane can be replaced within a few minutes, thereby providing nearly uninterrupted water supply.
- 5) Due to low capital cost, simplicity, low operating cost and high reliability, this process is popular in converting sea water into drinking water and water for very high-pressure boilers.

**UNIT - I****PART – 2****WATER TECHNOLOGY – II****BOILER TROUBLES**

In industries, steam is generated by large complicated metallic structures called boilers. If hard water from natural sources is fed directly to the boilers, there arise many problems called boiler troubles.

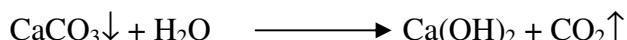
**SCALES:** *Scales are the hard deposits formed on inner surface of the boiler when hard water is used for steam generation.* They stick so strongly to inner surface of the boiler that they are difficult to remove, sometimes, even with the help of a hammer and chisel.

**Formation:** Scales are formed due to dissolved salts in water. Some of them are discussed below.

(a) *Decomposition of calcium bicarbonate:* If water contains calcium bicarbonate, it decomposes at boiler conditions to form calcium carbonate, which forms as a soft scale in low-pressure boilers.



In high-pressure boilers, calcium carbonate is hydrolysed to form calcium hydroxide soluble in water.

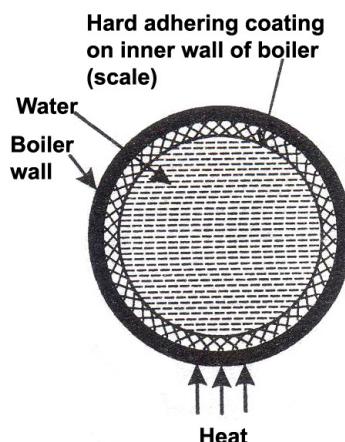


(b) *Deposition of calcium sulphate:* The solubility of calcium sulphate in water decreases with increase in temperature of water. For example, solubility of  $\text{CaSO}_4$  at  $25^\circ\text{C}$  is 3000 ppm, while it is 1660 ppm at  $100^\circ\text{C}$ . Hence, it gets separated as insoluble salt at boiler temperatures and deposited as a hard scale. It is the main cause of scales in high-pressure boilers.

(c) *Hydrolysis of magnesium salts:* Magnesium salts present in water in the dissolved form undergo hydrolysis at high temperatures in the boiler, to form magnesium hydroxide, which form a soft scale.



(d) *Presence of silica:* An important source of silica in boiler water is sand filters used for filtration. Silica reacts with calcium and magnesium salts present in water at high temperature, to give calcium or magnesium silicates ( $\text{CaSiO}_3$  or  $\text{MgSiO}_3$ ). These silicates deposit as firmly sticking hard scales.



**Disadvantages:** Boilers with scales on their inner surface have several disadvantages.

(a) *Wastage of fuel:* Scales have very low thermal conductivity. Hence, in presence of scales, the rate of heat transfer from boiler to the water inside the boiler is greatly decreased. In order to provide a

steady supply of heat to water, over-heating is done. It causes increase in fuel consumption. The wastage of fuel is directly proportional to the thickness of scale. For example, if thickness of the scale is 0.325 mm, the wastage of fuel is 10 % and if thickness increases to 12 mm, the wastage is 150 %.

(b) *Decrease of boiler safety*: In presence of scale, boilers are to be over-heated in order to maintain a constant supply of steam. Over-heating makes the boiler material softer and weaker and it causes distortion of boiler tube. Such a boiler tube is unsafe to bear the pressure of steam, especially in high-pressure boilers.

(c) *Decrease in boiler efficiency*: Sometimes scales are deposited in the valves and condensers of the boiler and choke them partially. It causes decrease in boiler efficiency.

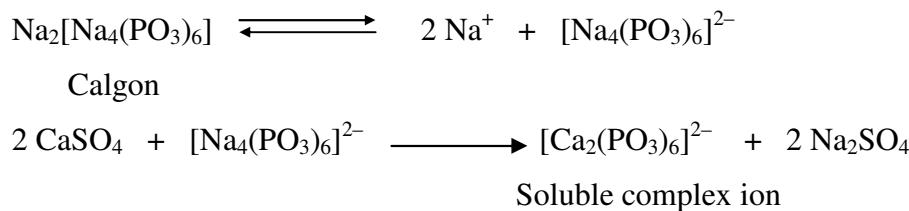
(d) *Danger of explosion*: When thick scales undergo cracking due to uneven expansion, water comes suddenly in contact with over-heated boiler surface. Hence, large amount of steam is suddenly produced. High-pressure is created due to sudden steam generation which may even cause explosion of the boiler.

**Prevention of scale formation:** Scale formation can be prevented or at least minimized by giving certain chemical treatment to boiler water. The treatment can be done in two ways.

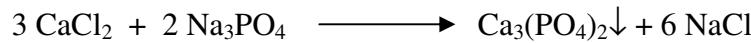
(a) *External treatment*: Methods in which water is softened before it is fed to the boilers are called external treatment methods. Examples: Lime-soda process, zeolite process and ion-exchange process.

(b) *Internal treatment (conditioning)*: Certain chemicals are added to water which prevent formation of scales in two ways: (i) by retaining the hardness-causing salts in the dissolved form, or (ii) by converting the salts into loose precipitates (sludges) which can be easily removed.

(i) *Calgon conditioning*: When calgon (sodium hexametaphosphate) is added to boiler water, it prevents the formation of scale by forming soluble complexes with hardness-causing salts of water.



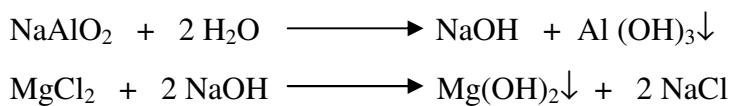
(ii) *Phosphate conditioning*: In high-pressure boilers, scale formation can be avoided by adding sodium phosphate. It reacts with calcium and magnesium salts present in boiler water to form corresponding phosphates which are non-adherent and easily removable soft precipitates (sludges). They can be removed by blow-down operation.



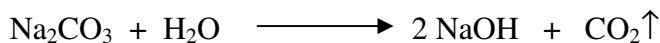
Apart from trisodium phosphate (alkaline), disodium hydrogen phosphate,  $\text{Na}_2\text{HPO}_4$  (weakly alkaline) and sodium dihydrogen phosphate,  $\text{NaH}_2\text{PO}_4$  (acidic) can be used based on the pH of water. The optimum pH for effective phosphate conditioning is 9.5-10.5 at which all calcium is precipitated.

(iii) *Treatment with sodium aluminate*: When sodium aluminate is added to boiler water, it hydrolyses to give sodium hydroxide and a gelatinous precipitate of aluminium hydroxide. The sodium

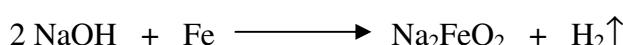
hydroxide so produced reacts with magnesium salts and produces magnesium hydroxide. Both  $Mg(OH)_2$  and  $Al(OH)_3$  produced inside the boiler form loose deposits which can be removed by blow-down process.



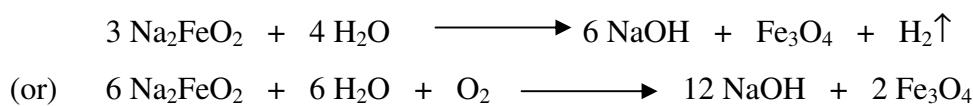
**Caustic embrittlement:** It is a type of boiler corrosion due to which sudden failure of boiler occurs by the frequent use of highly alkaline water in boilers for steam generation. During softening by lime-soda process, a small quantity of soda ( $Na_2CO_3$ ) generally remains in softened water. In high pressure boilers, it decomposes to give sodium hydroxide and carbon dioxide.



$NaOH$  produced in water enters the hair-cracks present on inner surface of the boiler through capillary action. When water evaporates, concentration of sodium hydroxide increases progressively. After reaching a certain concentration, it reacts with boiler material, iron to form sodium ferroate.



Sodium ferroate further decomposes as follows:



i.e., sodium hydroxide is regenerated, which further attacks some more iron atoms to deposit them as magnetite. Thus, boiler material slowly becomes weak at hair-cracks, joints, etc. and sudden failure of boiler occurs. This type of corrosion is an electrochemical corrosion and the cell can be indicated as

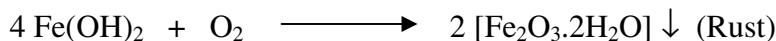
Iron at rivets, bends,joints, hair-cracks, etc.	Concentrated $NaOH$ solution	Dilute $NaOH$ solution	Iron at plane surfaces
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**Prevention:** Caustic embrittlement can be avoided by the following methods.

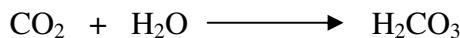
1. Using sodium phosphate as a softening agent in place of sodium carbonate in lime-soda process.
2. Adding tannin or lignin to boiler water, which block hair-cracks and prevent accumulation of  $NaOH$  in them.
3. Adding sodium sulphate to boiler water. It also blocks hair-cracks and prevents caustic soda from entering hair-cracks. However, the quantity of sodium sulphate to be added to boiler water should be as follows.  $[Na_2SO_4] / [NaOH] = 1:1, 2:1$  and  $3:1$  for the boilers working respectively at pressures upto 10, 20 and above 20 atmospheres.

**Boiler corrosion:** It is the destruction of boiler material due to chemical or electrochemical attack by the environment, i.e., chemicals present in water used in boilers for steam generation. The main reasons for boiler corrosion are described below.

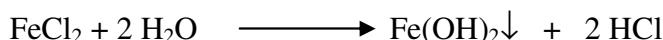
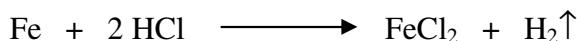
(a) *Dissolved oxygen*: At higher temperatures, dissolved oxygen attacks boiler material.



(b) *Dissolved carbon dioxide*: If boiler water contains bicarbonates, they decompose to release carbon dioxide. It produces carbonic acid, a weak acid, which has a slow corrosive effect on boiler material.



(c) *Acids from dissolved salts*: Magnesium salts present in water undergo hydrolysis at high temperatures to release acids. The acid reacts with boiler material in chain-like reactions producing the acid again and again. Hence, presence of even a small amount of magnesium salts produce large quantities of acids which corrode the boiler material to a greater extent.



#### Control methods:

(a) *Dissolved oxygen*: DO can be removed (deaeration) from water in two ways.

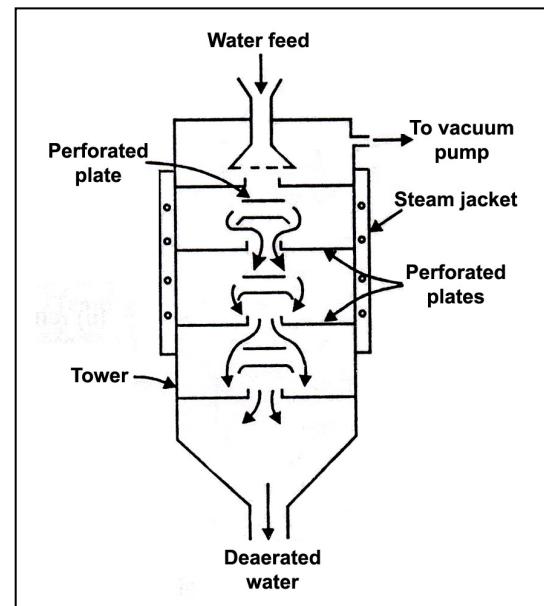
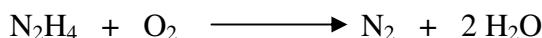
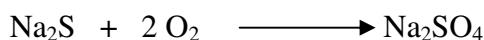
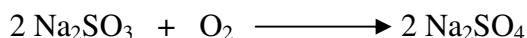
Mechanical deaeration: In this method, water is sprayed in a perforated plate-fitted tower as shown in figure. Water moving inside the tower is heated through steam jacket arranged around the tower. The tower is connected to a vacuum pump to remove the gases from the tower.

These three conditions convert the dissolved oxygen to gaseous oxygen which is removed from the tower by vacuum pump. This method removes carbon dioxide also.

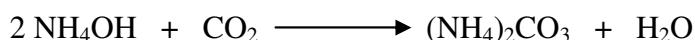
Chemical treatment: Sodium sulphite or sodium sulphide or hydrazine can chemically react with DO present in water.

Hydrazine is considered best deaerating

agent, since it removes oxygen without increasing the concentration of dissolved salts.



(b) *Dissolved carbon dioxide*: It can be removed by mechanical deaeration process or by adding calculated quantities of ammonia.



(c) *Acids from dissolved salts*: This cause of boiler corrosion can be prevented by using well-softened water in boilers.

## UNIT – II

### PART – 1

### PHASE RULE AND APPLICATIONS

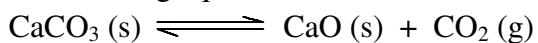
**Introduction:** The phase rule is an important generalization given by an American physicist Willard Gibbs in 1874, which deals with the behaviour of equilibria existing in heterogeneous systems. In general it may be said that with the application of phase rule, it is possible to predict qualitatively by means of a diagram the effect of changing pressure, temperature and concentration on a heterogeneous system in equilibrium.

**Terminology:** The following terms are involved in the discussion of phase rule applied to an equilibrium system.

**Phase (P):** A phase is defined as a homogeneous, physically distinct and mechanically separable portion of a system which is separated from other such parts of the system by definite boundary surfaces. A phase will have all physical and chemical properties the same throughout. A system may consist of one phase or more than one phases. The system containing a single phase is called a homogeneous system and a system containing two or more phases is called a heterogeneous system. Generally three states of matter – gas, liquid and solid are known as phases. But in phase rule, a uniform part of a system in equilibrium is termed as a phase. Thus, a liquid or a solid mixture can have two or more phases.

*Examples:*

1. A system containing a pure substance made of one chemical species only, is a one phase system (like pure water, oxygen, benzene, ice, etc.).
2. All gases mix freely to form homogeneous mixtures. Hence, any mixture of gases is a one phase system (like mixture of O<sub>2</sub> and N<sub>2</sub>).
3. If two liquids are miscible (like water and alcohol), they form one liquid phase only.
4. If two liquids are immiscible (like water and benzene), they form two separate phases.
5. A solution of a substance in a solvent is uniform throughout. Hence it is a one phase system (like aqueous solution of NaCl, sugar, etc.).
6. At freezing point, all the three forms of water (Ice, water and water vapour) coexist. Hence, it is a three phase system.
7. In a solid mixture, each solid makes up a separate phase. Hence, a mixture of solids constitutes a system with as many phases as the solids present in the mixture. For example, sulphur occurs as mixture of two allotropic forms – monoclinic and rhombic sulphur. By definition, a phase must have throughout the same physical and chemical properties. Both the allotropic forms of sulphur have same chemical properties, but their physical properties are different. Hence, mixture of two allotropes is a two phase system.
8. A mixture of two or more chemical substances contains as many phases. Each substance has different physical and chemical properties and hence each substance makes a separate phase. For example, consider the decomposition of calcium carbonate. When calcium carbonate is heated in a closed vessel, the following equilibrium is established.



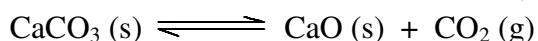
There are two solid phases and one gas phase, hence it is a three phase system.

9. In case of the equilibrium, Fe (s) + H<sub>2</sub>O (g)  $\rightleftharpoons$  FeO (s) + H<sub>2</sub> (g), there are three phases, two solid phases and a gaseous phase containing water and hydrogen.

**Component (C):** The term component can be defined as the least number of independent chemical constituents in terms of which the composition of every phase can be expressed by means of a chemical equation.

*Examples:*

1. In the water system, ice, water and water vapour are in equilibrium (three phase system). The composition of all the three phases can be expressed in terms of one chemical  $\text{H}_2\text{O}$ . Hence it is a one component system.
2. A mixture of gases, say  $\text{N}_2$  and  $\text{O}_2$ , is a single phase system. Its composition can be expressed by two chemical substances  $\text{N}_2$  and  $\text{O}_2$  (Gaseous mixture =  $x \text{ N}_2 + y \text{ O}_2$ ). Hence it is a two component system. In general, the no. of components of a gaseous mixture is given by the number of individual gases present.
3. An aqueous solution of sodium chloride is a one phase system. Its composition can be expressed in terms of two chemicals, sodium chloride and water (Aq. sodium chloride solution =  $x \text{ NaCl} + y \text{ H}_2\text{O}$ ). Hence, an aqueous solution of any solute is a two component system.
4. When calcium carbonate is heated in a closed vessel, the following equilibrium is established.



It is a three phase system, containing  $\text{CaCO}_3$ ,  $\text{CaO}$  and  $\text{CO}_2$ . The composition of each phase can be expressed in terms of any two of the three chemical substances in equilibrium.

For example, if we consider  $\text{CaCO}_3$  and  $\text{CaO}$ , then all the three phases can be expressed as follows.

$$\text{Phase CaCO}_3 = \text{CaCO}_3 + 0 \text{ CaO}$$

$$\text{Phase CaO} = 0 \text{ CaCO}_3 + \text{CaO}$$

$$\text{Phase CO}_2 = \text{CaCO}_3 - \text{CaO}$$

Hence, it is a two component system.

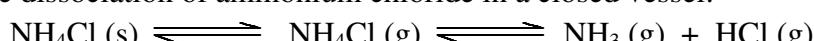
5. The sulphur system consists of four phases, namely rhombic, monoclinic, liquid and vapour sulphur. The chemical composition of all the phases is S. Hence, it is a one component system.

6. Potassium chlorate dissociates in a closed vessel with the following equilibrium:



It has three phases and each phase can be expressed in terms of any two components in an equation. Hence the number of components is two.

7. Consider the dissociation of ammonium chloride in a closed vessel:

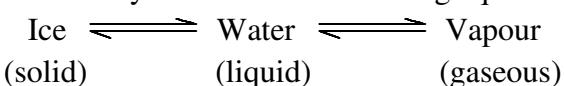


Here the proportions of  $\text{NH}_3$  and  $\text{HCl}$  are equivalent and hence, the compositions of both the phases (solid  $\text{NH}_4\text{Cl}$  and gaseous  $\text{NH}_4\text{Cl}$ ) can be expressed in terms of  $\text{NH}_4\text{Cl}$  alone. Hence, it is a one component system. But, if either  $\text{NH}_3$  or  $\text{HCl}$  is in excess, then it becomes a two component system.

**Degree of Freedom (F):** It is the least number of variable factors like concentration, temperature and pressure, which must be arbitrarily specified so that the remaining variables are fixed automatically and the system is completely defined. The systems with  $F = 0, 1$  and  $2$  are said to be having no degree of freedom (nonvariant), one degree of freedom (univariant) and two degree of freedom (bivariant) respectively.

*Examples:*

1. Consider the water system with the following equilibrium:



It is a three phase and one component system. In order to describe the system, no condition is required to be specified, as the three phases can be in equilibrium only at a particular temperature and

pressure. Therefore, the system is non-varient. If any condition (temperature or pressure) is altered, one of the three phases disappears and equilibrium will not remain.

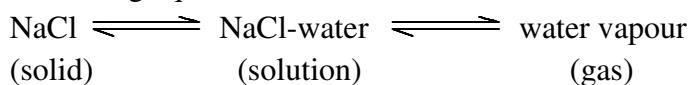
**2.** Consider the equilibrium, Water  $\rightleftharpoons$  Water vapour  
(liquid)  $\rightleftharpoons$  (gaseous)

It is a two phase and one component system. In order to describe the state of the system, either temperature or pressure is to be specified. Hence, degree of freedom is one or the system is univariant.

**3.** For a system consisting of water phase alone, we must specify both temperature and pressure in order to describe the system completely. Hence, it has two degrees of freedom or the system is bivariant.

**4.** For any given sample of a pure gas,  $PV = RT$ . If the values of pressure and temperature are specified, volume can have only one definite value. That is the volume (the third variable) is fixed automatically. Hence, a system containing a pure gas has two degrees of freedom.

**5.** Consider the following equilibrium.



This is a three phase and two component system. It can be completely defined if we specify temperature alone. The other two variables i.e., composition of NaCl-solution (solubility) and vapour pressure have a definite value at a fixed temperature. Hence, the system has one degree of freedom.

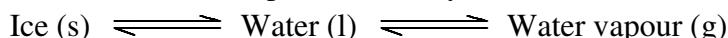
**Gibb's Phase Rule:** It can be stated as “*provided the equilibrium between any number of phases is not influenced by gravity, or electrical, or magnetic forces, or by surface action, and only by temperature, pressure and concentration, then the number of degrees of freedom (F) of the system is related to the number of components (C) and of phases (P) by the phase rule equation,*

$$F = C - P + 2$$

*for any system at equilibrium at a definite temperature and pressure.* In other words, the sum of the number of phases and number of degrees of freedom of any heterogeneous system is greater than the number of components by two.

## PHASE EQUILIBRIUM OF ONE COMPONENT SYSTEM – WATER SYSTEM

The water system consists of three phases, namely, ice, water and water vapour.



Since  $\text{H}_2\text{O}$  is the only chemical compound involved in the equilibrium, it is a single component system.

∴ According to Phase rule equation,  $F = C - P + 2$

$$\begin{aligned} F &= 1 - P + 2 \\ &= 3 - P \end{aligned}$$

i.e., the degree of freedom depends on the number of phases present at equilibrium.

*A phase diagram is a plot showing the conditions of pressure and temperature under which two or more physical states can exist together in a state of dynamic equilibrium.* The phase diagram (PT-diagram) of the water system is shown in figure. It consists of areas, curves and triple point.

**AREAS:** The diagram is divided in to three areas, BOC, AOC and AOB, which represent the existence of ice, liquid water and water vapour. Applying phase rule to the system when only one phase is present, we get

$$\begin{aligned} F &= C - P + 2 \\ &= 1 - 1 + 2 \end{aligned}$$

$$= 2$$

i.e., each single phase has two degrees of freedom. Within these single phase areas, the system is bivariant, because to locate any point in an area, temperature and pressure coordinates are to be known.

**CURVES or LINES:** The three areas are separated from each other by three curves joining at the point O. Each curve represents existence of equilibrium between two phases. In order to locate any point on any line, either temperature or pressure coordinate must be specified. If one of them is specified, the other one is automatically fixed. i.e., any point on boundary line has one degree of freedom. This also follows from phase rule equation,

$$\begin{aligned} F &= C - P + 2 \\ &= 1 - 2 + 2 \\ &= 1 \end{aligned}$$

- i) *Curve OA:* Along this curve, the two phases water and water vapour co-exist in equilibrium and it is called vapour pressure curve of liquid water. At any given temperature, there is one and only one pressure at which water vapour is in equilibrium with liquid water. This curve terminates at point A, called critical point (218 atm and 374 °C) when the liquid and vapour are indistinguishable from each other and there exists only one phase.
- ii) *Curve OB:* It is called sublimation curve of ice. Along this curve, there is equilibrium between solid ice and water vapour. This curve has a natural limit at point B at which the temperature is –273 °C, beyond which the phases merge together.
- iii) *Curve OC:* It is called fusion curve of ice. Along this curve, there exists an equilibrium between solid ice and liquid water. It indicates the effect of pressure on melting point of ice. This curve slightly slopes to the left indicating that the melting point of ice decreases with increase of pressure. At 1 atm pressure, the melting point of ice is 0 °C.

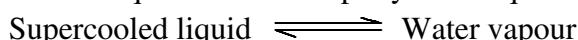
**THE TRIPLE POINT, O:** The curves OA, OB and OC meet at the point O, called triple point. At this point, all the three phases solid, liquid and gas co-exist in equilibrium. It occurs at 0.0098 °C and 4.58 mm Hg pressure. Since there are three phases and one component at this point,

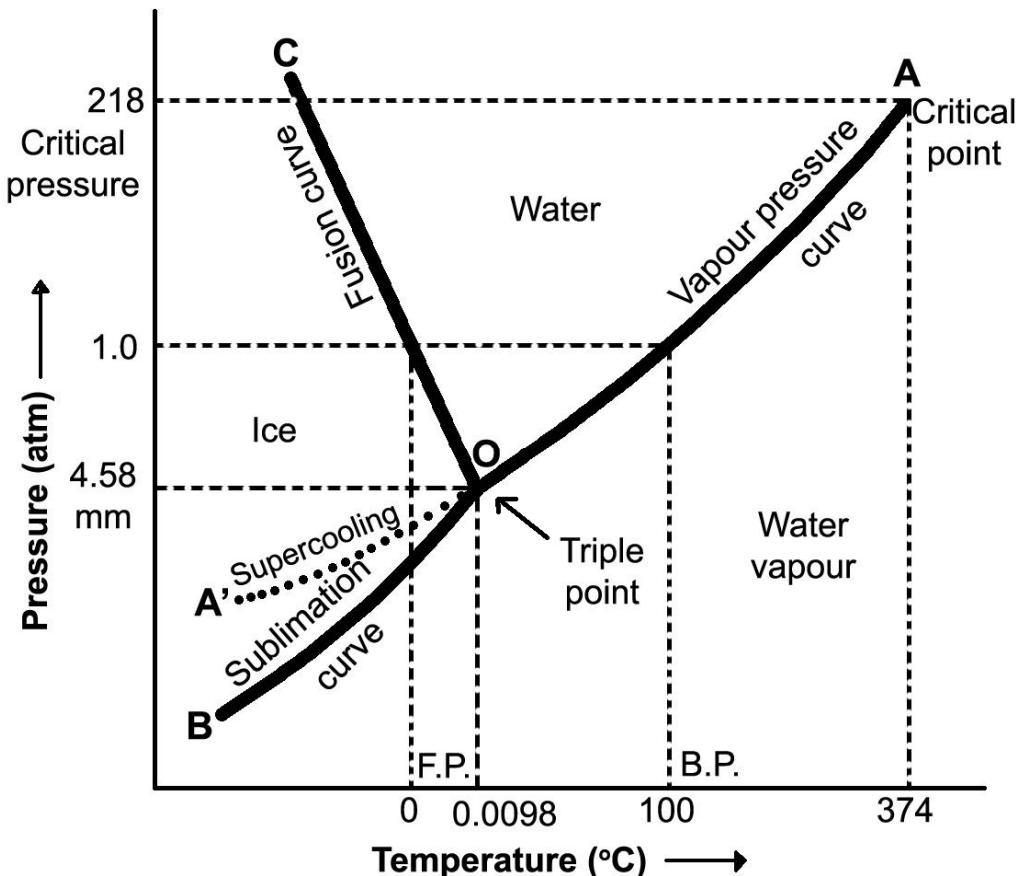
$$\begin{aligned} F &= C - P + 2 \\ &= 1 - 3 + 2 = 0 \end{aligned}$$

i.e., the system at the triple point is nonvariant or has no degrees of freedom.

Thus, if either pressure or temperature is changed even slightly at the triple point, it causes disappearance of one of the phases.

**Metastable curve, OA':** The vapour pressure curve AO terminates at O where the liquid starts freezing or solidifying. However, by careful cooling of the liquid, the curve AO can be extended to A'. This means that the liquid can be cooled far below the freezing point (supercooled) without formation of crystals. But the supercooled liquid is in an unstable condition. On the slightest disturbance, the entire liquid solidifies rapidly. This equilibrium can be represented as,





This metastable equilibrium is shown in figure, as dotted curve OA'. This curve is above the normal sublimation curve OB. i.e., the vapour pressure of metastable phase is always higher than that of the stable phase at any given temperature.

**Reduced Phase Rule:** When a single phase is present in a two-component system, the degree of freedom is 3 ( $F = C - P + 2 = 2 - 1 + 2 = 3$ ). That means three variables must be specified in order to describe the system. In case of such system, concentration of one of the components must be given, in addition to temperature and pressure. In order to represent graphically, three coordinate axes at right angles to each other are required. Hence, the phase diagram obtained would be a (three-dimensional) solid model.

In order to have a simple plane diagram, we generally consider only two variables, the third one being a constant. For example, for a solid/liquid equilibrium, the gas phase is usually absent and the effect of pressure on equilibrium is very small. Hence, in such a system, temperature and concentration are considered as variables while the pressure variable is neglected. Such systems are generally studied under atmospheric pressure. For these systems, reduced phase rule is applied instead of the original phase rule equation.

*Reduced (condensed) phase rule is the phase rule applied to discuss certain systems with degrees of freedom reduced by one.*

$$F' = C - P + 1$$

## PHASE EQUILIBRIUM OF TWO COMPONENT SYSTEMS

### SILVER – LEAD SYSTEM:

This system has two components and four phases. The phases are solid silver, solid lead, solution of molten silver & lead and vapour. The boiling points of silver and lead being very high, the vapour phase is practically absent. Hence Ag/Pb system is a condensed system with three phases.

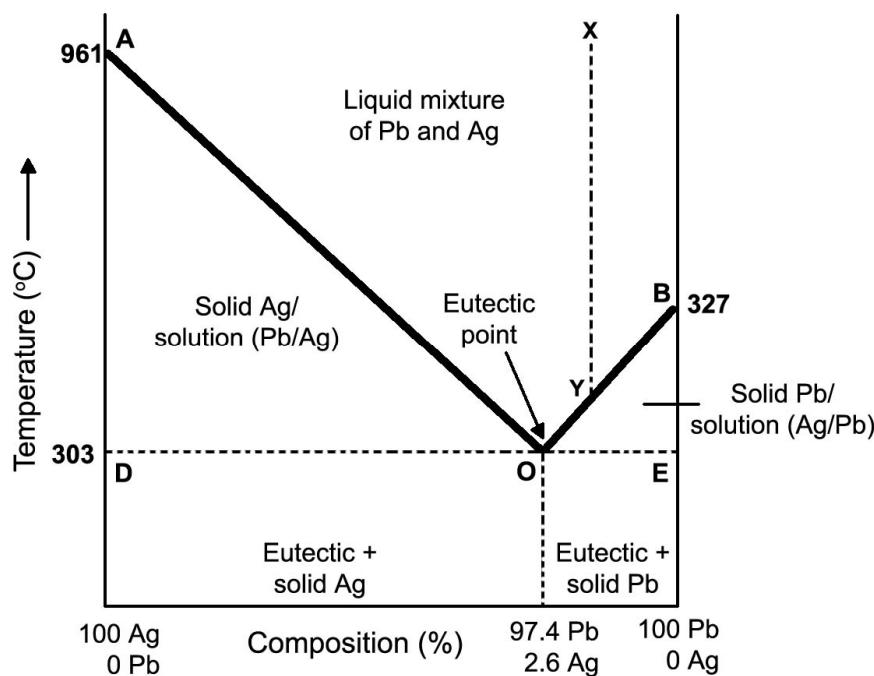
Hence, we consider only temperature and concentration in the phase diagram (TC-diagram). The phase diagram consists of

- (i) Two curves AO and BO,
- (ii) Three areas: area above AOB, area below AO and area below BO,
- (iii) Eutectic point, O.

*Curve AO* (Freezing point curve of Ag): It shows the effect of addition of lead on freezing point of silver. The curve starts at A with composition 100 % Ag and temperature 961 °C (melting point of pure silver). This point corresponds to an equilibrium between pure solid Ag and liquid Ag. From figure, it is clear that with gradual addition of lead to silver, the melting point of silver decreases gradually along the curve up to point O (303 °C). At this point the composition of the mixture is 97.4 % Pb and 2.6 % Ag. Beyond this point, if lead is further added, it cannot go into the solution and separates as solid phase.

Along the curve AO, the number of phases,  $P = 2$ , the number of components,  $C = 2$

$$\therefore \text{Degree of freedom, } F' = C - P + 1 \\ = 2 - 2 + 1 = 1, \text{ i.e., the system is univariant.}$$



*Curve BO* (Freezing point curve of Pb): It shows the effect of addition of silver on freezing point of lead. The curve starts at B with composition 100 % Pb and temperature 327 °C (melting point of pure lead). This point corresponds to an equilibrium between pure solid Pb and liquid Pb. With gradual addition of silver to lead, the melting point of lead decreases gradually along the curve up to point O (303 °C). At this point the composition of the mixture is 2.6 % Ag and 97.4 % Pb. Beyond this point, if silver is further added, it cannot go into the solution and separates as solid phase. Along this curve also, the system is univariant.

#### *The Eutectic point, O:*

A binary system consisting of two substances, which are miscible in all proportions in the liquid phase, but which do not react chemically, is known as the eutectic system. Silver-lead system is an example of such system. *A solid solution of two or more substances having the lowest freezing point*

of all the possible mixtures of the components is called eutectic mixture. Two or more solid substances capable of forming solid solutions with each other have a property of lowering each other's freezing point. The minimum freezing point attainable corresponding to eutectic mixture is termed as eutectic point.

In case of Ag-Pb system, point 'O', where the two curves AO and BO meet, is the eutectic point. At this point, three phases are in equilibrium – solid Ag, solid Pb and their solution. According to condensed (reduced) phase rule equation,

$$F' = C - P + 1 = 2 - 3 + 1 = 0$$

i.e., the system at eutectic point is nonvariant. All the three phases co-exist at specific temperature and composition only. The temperature corresponding to point O is 303 °C (eutectic temperature) and the composition is 97.4 % Pb and 2.6 % Ag (eutectic composition). No mixture of lead and silver can have a melting point lower than the eutectic temperature. Below this temperature both the components are crystallized simultaneously (area below the line DOE).

*Area above AOB:* This area represents the single phase containing solution of molten silver and molten lead.

$$F' = C - P + 1 = 2 - 1 + 1 = 2$$

i.e., the system is bivariant in this area.

Consider a liquid mixture corresponding to the point 'X' in this area (as shown in figure) with concentration of silver less than 2.6 %. If the mixture is cooled gradually, the temperature decreases without any change in composition along the line XY until it reaches point 'Y' on the curve BO. On further lowering of temperature, lead begins to separate out and the composition varies along the curve BO till the point O is reached. On further cooling, the whole mass solidifies en-block to the eutectic composition.

The area below curve AO and BO contain two phases each and hence the system is univariant. Similarly, the area under the line DOE, with two phases, is also univariant.

*Application to Pattinson's process:* The principle explained above is used in the Pattinson's process of desilverization of lead. If a sample of argentiferous lead, containing < 2.6 % Ag, is allowed to cool gradually, lead starts separating out as solid from the solution and the solution will become progressively richer in silver, till the percentage 2.6 of Ag is reached, and on further cooling, the whole mass will solidify as such. On the other hand, if lead-silver alloy containing Ag greater than 2.6 % is allowed to cool, then pure silver starts separating out as solid along the curve AO, till the eutectic composition at O is reached. This process of increasing the relative proportion of silver in the alloy is known as pattinson's process.

#### **Applications of Phase Rule:**

1. Phase rule is useful for studying and controlling various processes such as phase separation, solidification of metals, changes in the structures during heat treatment, etc.
2. It is used in metallurgical industry for separation of precious metal, silver from argentiferous lead alloy.
3. Eutectic mixtures are used in preparing solders for joining two metallic materials together in electronics and electrical fields. For example, lead-tin alloy used for soldering electrical connections, sealing tin cans and joining lead pipes.
4. Phase rule is useful in the preparation of safety fuse making alloys. For example, Wood metal containing 50% Bi, 25% Pb, 12.5% each of Sn and Cd, with melting point 70 °C, is used for making fire-alarms, automatic sprinklers, safety plugs in cookers, electric fuses and boiler fuses.

## U N I T - II

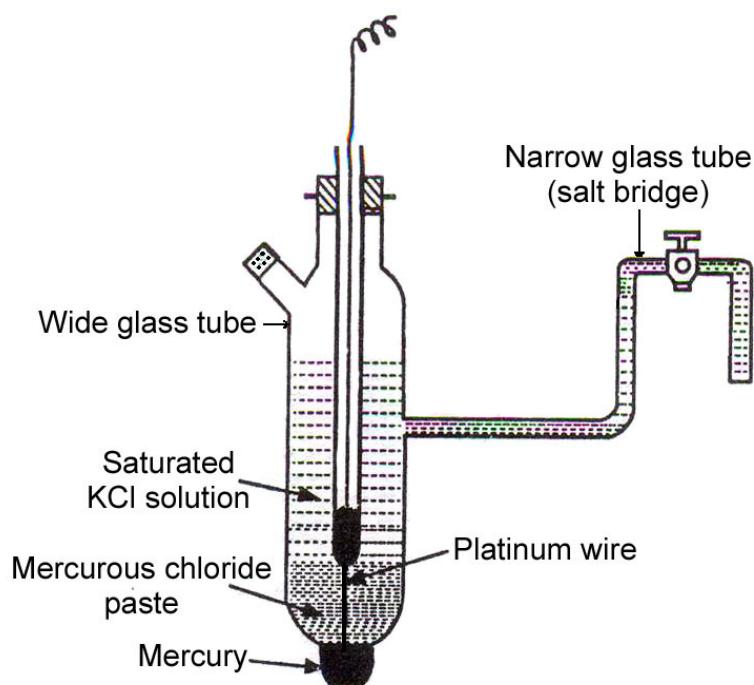
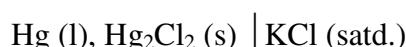
### PART - 2      ELECTROCHEMISTRY

**Reference electrodes:** Electrode potential of a metal is the measure of tendency of the metal to undergo oxidation. It is impossible to measure the value of single electrode potential by using a voltmeter or potentiometer. Hence, it is necessary to assemble first a cell by coupling the given electrode with another electrode, whose potential is either exactly known or arbitrarily fixed. *This type of electrode of standard potential, with which it is possible to compare the potentials of all other electrodes, is called a reference electrode.*

The reference electrode used is standard (normal) hydrogen electrode (SHE or NHE). By convention, electrode potential of SHE at standard conditions (25°C temperature and 1M electrolyte) is taken as zero. However, in view of the limitations of the electrode, several other subsidiary reference electrodes are also constructed. Such electrodes are called secondary reference electrodes while hydrogen electrode is called primary reference electrode.

#### **Calomel electrode (Mercury-Mercurous chloride electrode)**

**Construction:** The electrode consists of a wide glass tube connected to a narrow glass tube that acts as a salt bridge. The wide glass tube consists of mercury at the bottom, covered by mercurous chloride paste. Above the  $\text{Hg}_2\text{Cl}_2$  paste, potassium chloride solution is filled in the tube which acts as electrolyte. A platinum wire dipped up to the mercury layer is used for electrical contact. The wide and narrow glass tubes can be filled with 0.1 N or 1.0 N or saturated KCl solution. The saturated calomel electrode can be represented as

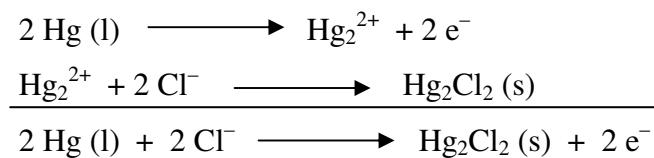


*Working:* Calomel electrode can act as either anode or cathode depending upon the nature of the electrode connected to it. The potential of calomel electrode can be determined by connecting it to the standard hydrogen electrode. When calomel is connected to SHE, hydrogen electrode acts as anode and calomel acts as cathode. The cell containing these two electrodes can be represented as follows:

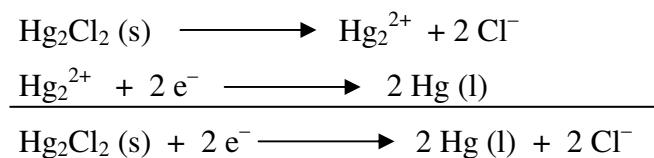


Following are the reactions occurring on calomel electrode during its working in any cell.

If calomel electrode acts as anode,



If calomel electrode acts as cathode,



The reduction potentials of calomel electrode measured by using hydrogen electrode at 298 K and at various concentrations of KCl are as shown below.

Electrode type	Decinormal (DNCE)	Normal (NCE)	Saturated (SCE)
Concentration of KCl	0.1 N	1.0 N	Saturated
Reduction potential ( $E^\circ$ )	+ 0.3335 V	+ 0.2810 V	+ 0.2422 V

The potential of calomel electrode depends on concentration of chloride ions in contact with the electrode and is given by Nernst equation as below.

$$E = E^\circ - 0.0591 \log [\text{Cl}^-]$$

Calomel electrode is a common reference electrode used in place of hydrogen electrode in potential determinations in many areas of electrochemistry.

*Advantages:*

1. It is a robust electrode and relatively of low cost.
2. It is simple to construct.
3. The results are reproducible and stable over a long period.

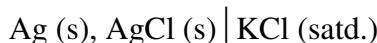
*Disadvantages:*

1. Solubility of KCl is sensitive to change in temperature.
2. It involves use of toxic metal - mercury.

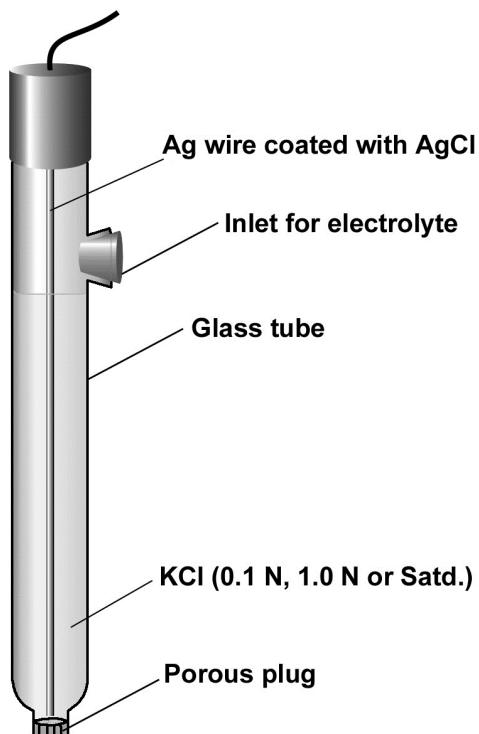
### Silver – Silver chloride electrode ( $\text{Ag}/\text{AgCl}$ electrode)

*Construction:* It is a common reference electrode based on the redox couple between Ag and AgCl. It consists of a glass tube in which a silver wire coated with silver chloride is immersed in a solution of KCl at desired concentration. At the end of the glass tube, there is a porous plug which acts as salt

bridge. The commonly used electrolyte concentrations are saturated, 3.5 N, 0.1 N or 1.0 N. The electrode is denoted in cell notation as,

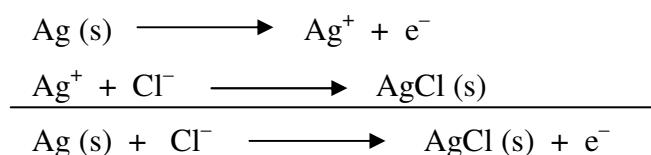


*Working:* Ag/AgCl electrode can act as either anode or cathode depending upon the nature of the electrode connected to it. The potential of Ag/AgCl electrode can be determined by connecting it to either standard hydrogen electrode or calomel electrode. When Ag/AgCl electrode is connected to SHE, hydrogen electrode acts as anode and Ag/AgCl electrode as cathode. The cell containing these two electrodes can be represented as follows:

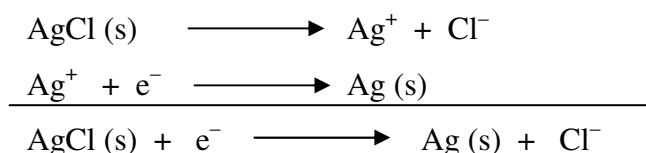


Following are the reactions occurring on Ag/AgCl electrode during its working in any cell.

If Ag/AgCl electrode acts as anode,



If Ag/AgCl electrode acts as cathode,



The reduction potentials of Ag/AgCl electrode measured using hydrogen electrode at 298 K and at various concentrations of KCl are mentioned below.

Concentration of KCl	0.1 N	1.0 N	3.5 N	Saturated
Reduction potential ( $E^\circ$ )	+ 0.2894 V	+ 0.2368 V	+ 0.2050 V	+ 0.1976 V

The potential of Ag/AgCl electrode depends on concentration of chloride ions in contact with the electrode and is given by Nernst equation as below.

$$E_{\text{Ag}/\text{AgCl}} = E^{\circ}_{\text{Ag}/\text{AgCl}} - 0.0591 \log [\text{Cl}^-]$$

Ag/AgCl electrode is a common reference electrode used in place of hydrogen electrode or calomel electrode. It also acts as an ion-selective electrode with respect to chloride ion. *An ion selective electrode is the one which selectively responds to a specific ion in a mixture and the potential developed at the electrode is a function of concentration of that ion.*

*Advantages:*

1. Construction of this electrode is easy.
2. It can be used over a relatively wide range of temperatures.
3. It can be used in non-aqueous solutions also.

*Disadvantages:*

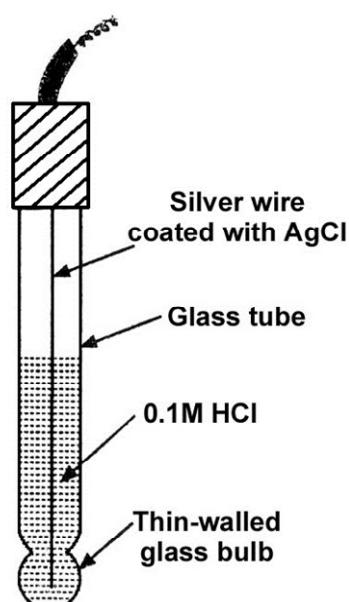
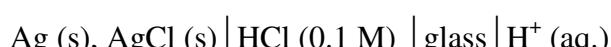
1. It is more temperature-sensitive with saturated KCl solution than with unsaturated KCl solution.
2. It cannot act as chloride ion-selective electrode in presence of some ions like  $\text{Br}^-$ ,  $\text{I}^-$ ,  $\text{SCN}^-$ , etc. which also can form insoluble compounds with silver ions.

### Glass electrode

*Principle:* When two solutions of different concentrations of  $\text{H}^+$  ions are separated by a thin glass membrane, there develops a potential difference between two surfaces of the membrane. This potential difference is directly proportional to the difference in the concentrations of  $\text{H}^+$  ions in both the solutions. The development of potentials on the surfaces of the membrane is due to the existence of an equilibrium between sodium ions of the glass material and hydrogen ions of the solution.

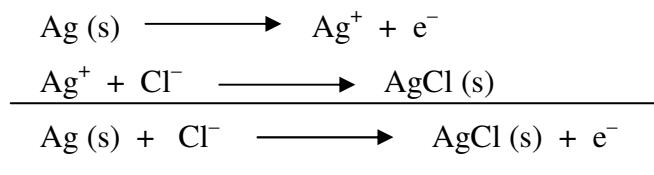
*Construction:* It consists of a glass tube made of an ordinary glass.

At the bottom of glass tube, a thin-walled glass bulb made of a special glass (with relatively low m.p. and high electrical conductivity) is connected. Both the glass bulb and glass tube are filled with 0.1 M HCl solution. A silver wire coated with silver chloride is immersed in the solution. This electrode works as internal reference electrode, and also serves for the external electrical contact. The 0.1 M HCl is preferred as electrolyte because Ag/AgCl electrode possesses low temperature coefficient in this solution. The glass electrode is dipped in a solution containing  $\text{H}^+$  ions. The electrode can be represented as follows.

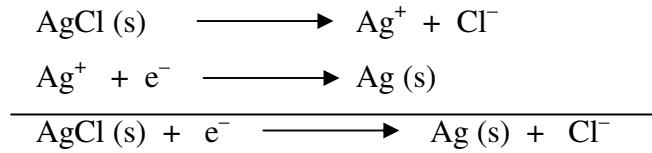


*Working:* Glass electrode is an example of ion-selective electrode. It responds to the presence of  $\text{H}^+$  ions in the solution. The Ag/AgCl electrode acts as an internal reference electrode. Following are the reactions occurring on Ag/AgCl electrode during working of glass electrode in any cell.

If glass electrode acts as anode, Ag/AgCl electrode acts as anode.



If glass electrode acts as cathode, Ag/AgCl electrode acts as cathode.



The potential of glass electrode is composed of three factors.

$$E_G = E_b + E_{\text{ref}} + E_{\text{asy}}$$

Here,  $E_b$  is the boundary potential developed on glass membrane due to difference in concentration of  $\text{H}^+$  ions in both the solutions in contact with the two surfaces of membrane.

$E_{\text{ref}}$  is the potential of internal reference electrode, Ag/AgCl.

$E_{\text{asy}}$  is a small asymmetry potential generated based on the nature and composition of the glass with which the glass bulb is prepared.

Applying Nernst equation to the glass electrode,

$$E_G = E_G^\circ - (2.303RT/nF) \log (1/\text{[H}^+])$$

On substituting the values of R, T, F and n=1,

$$E_G = E_G^\circ - 0.0591 \log (1/\text{[H}^+]) = E_G^\circ - 0.0591 \text{ pH}$$

*Advantages:*

1. It is simple and can easily be used.
2. Equilibrium is rapidly achieved and results are accurate.
3. It is not easily poisoned.
4. It can be used in turbid solutions as well as coloured solutions.

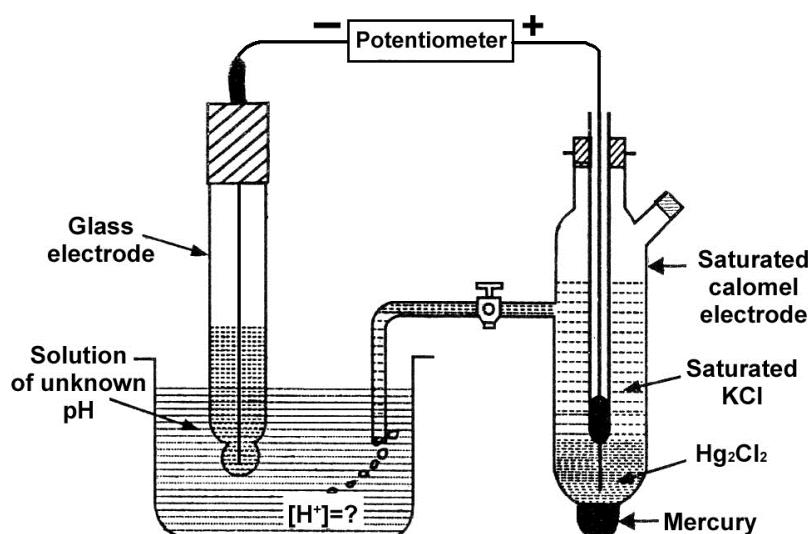
*Disadvantages:*

1. It can be used in solutions with pH up to 10. Electrodes made of special glasses can be used for solutions up to pH 12. Above pH 12, cations of solution affect the glass interface and make the electrode useless.
2. Although special glass material is used for glass electrodes, it offers very high resistance of the order of 10-100 million ohms. In presence of such high resistance, ordinary potentiometers are to be replaced by special electronic potentiometers for emf measurements.

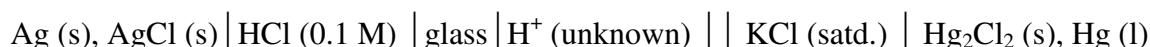
## Determination of pH using glass electrode:

**Principle:** When two solutions of different concentrations of  $\text{H}^+$  ions are separated by a thin glass membrane, there develops a potential difference between two surfaces of the membrane. The potential difference developed is directly proportional to the difference in the concentrations of hydrogen ions in both the solutions. The potentials are developed on the surfaces of the membrane due to existence of an equilibrium between  $\text{Na}^+$  ions of the glass material and  $\text{H}^+$  ions of the solution.

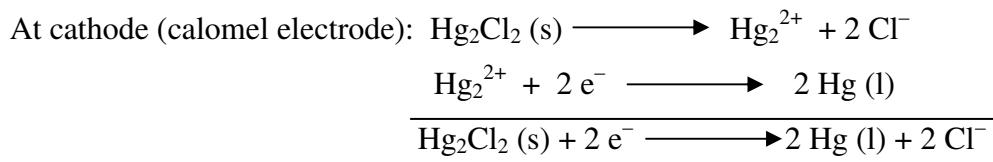
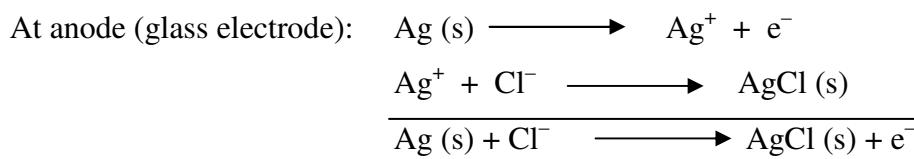
**Construction:**



In order to determine pH of a given solution, glass electrode is immersed in the given solution and connected it to a reference electrode like calomel electrode to produce an electrochemical cell. Both these electrodes are connected with a metallic conductor through a special electronic potentiometer. The electrolytic contact is established by immersing the narrow glass tube of calomel electrode in the solution of unknown pH as shown in figure. The resulting cell can be represented in cell notation as



**Determination:** In the cell constructed as above, glass electrode acts as anode and calomel electrode acts as cathode in normal pH range. Hence, the following reactions occur in the cell.



Potential of anode (glass electrode) is given by

$$E_{\text{anode}} = E_G = E^{\circ}_G - (2.303RT/nF) \log (1/\text{[H]})$$

On substituting the values of R, T, F and n=1,

$$\begin{aligned} E_G &= E^{\circ}_G - 0.0591 \log (1/[H^+]) \\ E_G &= E^{\circ}_G - 0.0591 \text{ pH} \end{aligned} \quad \text{----- (1)}$$

Potential of cathode (saturated calomel electrode) at standard conditions is

$$\begin{aligned} E_{\text{cathode}} &= E_{\text{SCE}} = +0.2422 \text{ V} \\ \therefore E_{\text{cell}} &= E_{\text{cathode}} - E_{\text{anode}} \\ &= E_{\text{SCE}} - E_G \\ &= 0.2422 - (E^{\circ}_G - 0.0591 \text{ pH}) \quad (\text{from eq.1}) \\ &= 0.2422 - E^{\circ}_G + 0.0591 \text{ pH} \\ \Rightarrow 0.0591 \text{ pH} &= E_{\text{cell}} + E^{\circ}_G - 0.2422 \end{aligned}$$

$$\boxed{\therefore \text{pH} = \frac{E_{\text{cell}} + E^{\circ}_G - 0.2422}{0.0591}}$$

$E^{\circ}_G$  of the glass electrode can be determined by immersing it in a solution of known pH (buffer solution), connecting it to the calomel electrode, measuring emf of the cell and substituting it in the above equation.

### CHEMISTRY OF MODERN BATTERIES

One of the most important applications of electrochemistry is in designing electrochemical energy systems. They are the devices producing electrical energy due to some spontaneous chemical reactions. These systems include both batteries and fuel cells.

*A battery is an electrochemical cell or a combination of number of electrochemical cells connected in series, which can produce direct current at constant voltage.*

Discharging: Discharging is the process of complete conversion of reactants of a battery into products with simultaneous generation of electrical energy. During discharging, the battery works as a galvanic cell (conversion of chemical energy to electrical energy).

Charging: It is the process conducted after discharging of a battery. It involves supply of electrical energy to the products of a discharged battery in order to get back its reactants. During charging, the battery works as an electrolytic cell (conversion of electrical energy to chemical energy).

Primary batteries (Irreversible cells): They are the electrochemical cells in which the cell reaction cannot be reversed by passing electrical energy back through the cell. They are discarded after a single discharge.

Secondary batteries (Reversible cells): They are the electrochemical cells in which the cell reaction can be reversed by passing electrical energy infinitesimally greater than the emf generated by the cell, in opposite direction of emf. i.e., reactants can be regenerated so that the battery can be used again for discharge. Thus, a number of cycles of discharging and charging are possible in case of these

batteries. The number of such possible cycles in case of a secondary battery is called its cycle life. These batteries are also called storage batteries or electric accumulators.

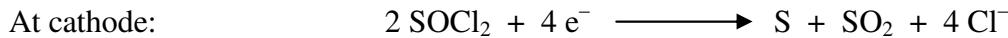
**Fuel cells (Flow batteries):** They are simple electrochemical cells which produce electrical energy until a fuel is provided to the device. They are also irreversible in nature.

**Lithium Batteries:** It refers to a large family of batteries with a common feature of having lithium as anode material. Lithium metal offers an attractive option of using it as anode material because of its low weight, high electrode potential and good conductivity. This group of batteries has both primary and secondary cells. Lithium-thionyl chloride battery is an example of a lithium primary battery. Different lithium ion batteries form a group of lithium secondary batteries.

### **Lithium-Thionyl chloride (Li/SOCl<sub>2</sub>) battery**

The cell contains lithium metal as anode and carbon rod as cathode. The active cathode materials is thionyl chloride (SOCl<sub>2</sub>). The electrolyte is LiAlH<sub>4</sub> dissolved in thionyl chloride. SOCl<sub>2</sub> acts as both active cathode materials and solvent for electrolyte.

The following reactions take place during discharge of the battery.



The battery exhibits an emf of 3.6 V. Since one of the products SO<sub>2</sub> is a gas, it facilitates the forward reaction leading to complete use of reactant. It is a primary battery as charging cannot be done due to unavailability of SO<sub>2</sub> for charging. These batteries find use in electronic circuit boards as well as military and space applications.

#### *Advantages:*

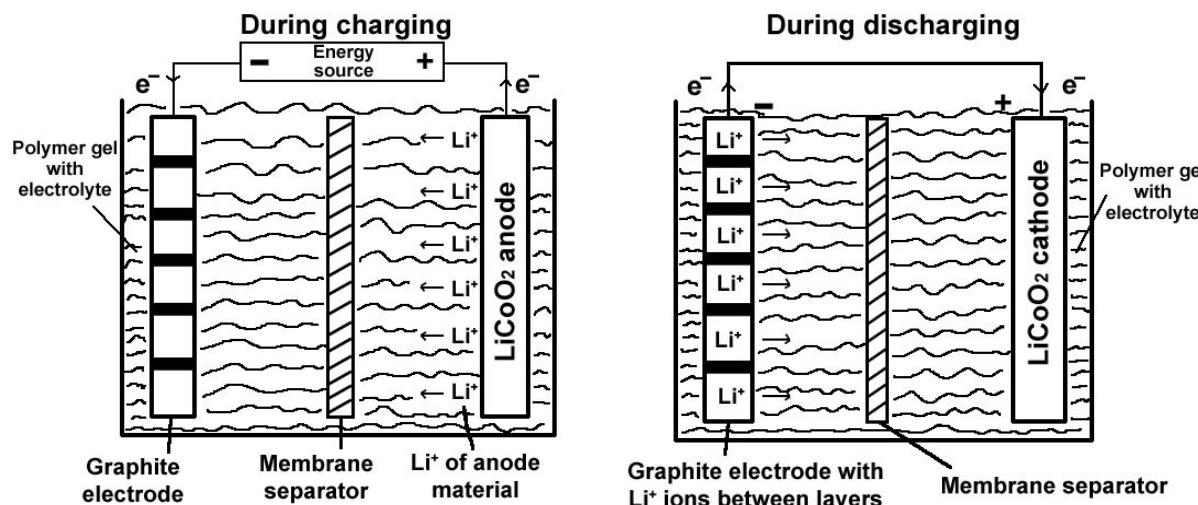
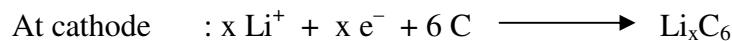
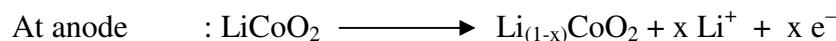
1. Unlike other batteries producing gaseous products, it has limited emission of gas.
2. It can be used in a wide temperature range of -55°C to +85 °C.

**Lithium cobalt oxide battery:** It is one of the commercially important lithium ion batteries. It is a rechargeable battery which operates based on movement of lithium ions from one electrode to the other. It consists of graphite rod as anode and an intercalated lithium compound, namely lithium cobalt oxide (LiCoO<sub>2</sub>) as cathode material. The electrolyte is a polymer gel containing lithium salt, lithium phosphorous hexafluoride (LiPF<sub>6</sub>) dissolved in ethylene carbonate. Both the half-cells are separated by a membrane separator. It allows only lithium ions from one half-cell to the other.

#### *Working:*

**During charging:** During charging, lithium compound acts as anode and graphite rod as cathode. In presence of energy source, lithium ions present in the lithium compound are pulled to graphite rod through the electrolyte. These ions are occupied in the layered structure of graphite. The electroneutrality of graphite is maintained by the occupation of same number of electrons in between

the layers. When the transport of  $\text{Li}^+$  ions occurs from  $\text{LiCoO}_2$ , the compound is stabilized by the oxidation of  $\text{Co}^{3+}$  ion to  $\text{Co}^{4+}$ .



**During discharging:** After charging of the battery, the graphite rod consists of lithium ions in between its layers. During discharging, the energy source is removed from the circuit and both the electrodes are directly connected through a conductor. Now, lithium ions start moving spontaneously towards the lithium compound through the electrolyte and electrons start moving from graphite rod to lithium compound through external conductor. Lithium ions and electrons enter the lithium compound and produce the original compound,  $\text{LiCoO}_2$ .



Thus, lithium-ion batteries can perform a number of cycles of charging and discharging by the movement of lithium ions between the two electrodes. The  $\text{LiCoO}_2$  battery can produce an emf of about 3.7 V.

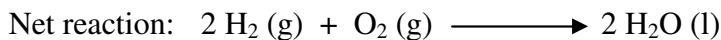
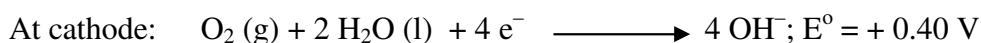
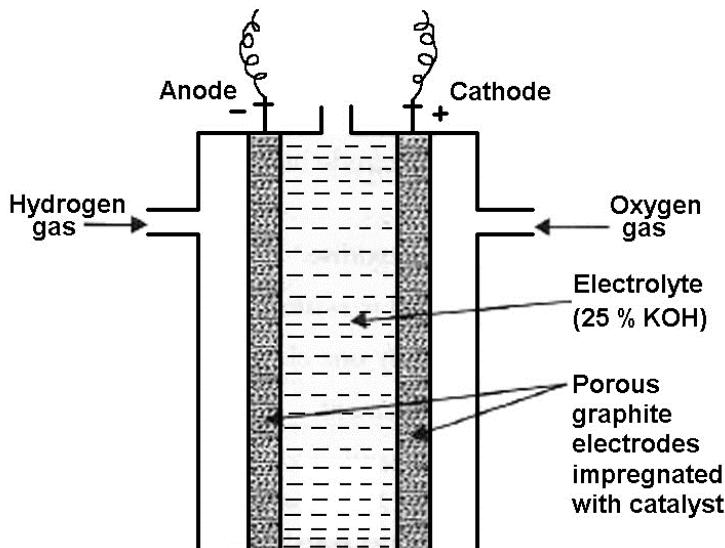
**Advantages:**

1. It exhibits high energy density and high cycle life (1000+).
2. Self-discharge is low (~ 5% per month).
3. Its low-temperature performance is good (up to -30 °C).
4. It has no memory effect and requires no maintenance.
5. Low environmental-toxic effects compared with conventional batteries.

**Fuel cells:** Fuel cells are the electrochemical cells in which electrochemical reactions occur between a conventional fuel/gas and oxygen of air to produce electrical energy. It can be considered as a type of primary cells.



**Hydrogen-oxygen fuel cell:** One of the simplest and most successful fuel cell is hydrogen-oxygen fuel cell. It consists of two inert porous electrodes made up of graphite. The electrolyte filled between the two electrodes is 25 % KOH solution. Hydrogen and oxygen gases are bubbled through anode and cathode respectively through separate inlets.



$$\begin{aligned} E_{\text{cell}} &= E_{\text{cathode}} - E_{\text{anode}} \\ &= +0.40 - (-0.83) = 1.23 \text{ V} \end{aligned}$$

At anode, hydrogen undergoes oxidation to produce  $\text{H}^+$  ions. The hydroxyl ions from electrolyte combine with hydrogen ions at anode to form water. The electrons transfer from anode to cathode through external circuit and participate in the reduction of oxygen at cathode to form hydroxyl ions. In practice, the emf of the cell is about 1.0 V. Usually, a large number of such cells are connected together in series to make a battery. The electrodes used in the fuel cell should exhibit catalytic activity and must not be consumed during working.

#### Advantages:

1.  $\text{H}_2\text{-O}_2$  fuel cell is an excellent energy source in space vehicles, submarines and military vehicles. The weight of the fuel cell sufficient for 15 days in space is about 250 kg. This is very less compared to several tonnes of materials required in case of other storage systems to produce same quantity of energy.
2. The only product produced in these fuel cells is water. It is treated as highly pure water and used by astronauts.
3. It does not cause any pollution or toxicity to environment.

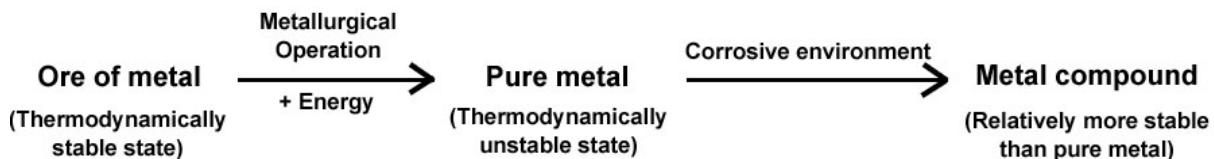
## UNIT – III

### PART – 1

### CORROSION PRINCIPLES

**Introduction:** Most of the metals (except noble metals such as Au, Pt, etc.) exist in nature in combined forms as their oxides, carbonates, chlorides, etc. During extraction, they are reduced to their metallic states from their ores. During extraction of metals, considerable amounts of energy are required. Consequently, isolated pure metals can be regarded in a higher energy state than their corresponding ores, and they have a natural tendency to revert back to combined state (or lower energy state). Hence, when metals are put into use, they are exposed to environment and the surface begins to decay (i.e. conversion to more stable metal compounds). Hence, destruction or deterioration of the metal starts at the surface of the metal.

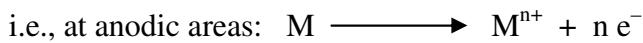
**Definition:** Destruction and consequent loss (of useful properties) of metals or alloys through unwanted chemical or electrochemical attack starting at their surface by its environment is called corrosion. Corrosion process can be considered as a process of reverse of extraction of metals.



*Examples:*

1. Most well-known example of corrosion is rusting of iron. When iron is exposed to atmospheric conditions, a layer of reddish scale and powder of oxide is formed. The rust is composed of oxides and hydroxides of iron.
2. Formation of green film or basic carbonate  $[CuCO_3 + Cu(OH)_2]$  on the surface of copper exposed to moist air containing carbon dioxide is another example.

**Electrochemical corrosion:** Corrosion of a metal in an aqueous solution is an electrochemical phenomenon involving flow of electrons between the anodic and cathodic areas. The anodic reaction involves in dissolution of metal as corresponding metallic ions with the liberation of free electrons.

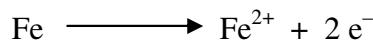


Electrons released in this reaction are consumed at cathodic areas by some reduction reaction. Several cathodic reactions are possible during wet corrosion based on the nature of the environment.

There are two important cathodic reactions that frequently occur during electrochemical corrosion. With reference to these reactions, mechanism of electrochemical corrosion is discussed as follows.

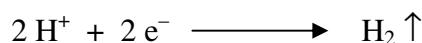
a) *Hydrogen evolution corrosion:* This type of corrosion occurs in acidic environments like industrial wastewaters and solutions of non-oxidizing acids like HCl. Consider a metal like Fe in the acidic environment. Suppose that a portion of the metal surface possesses high concentration of hydrogen ions relative to the rest of the surface. This portion becomes cathodic area and the rest of the surface anodic.

At anodic areas, the reaction is



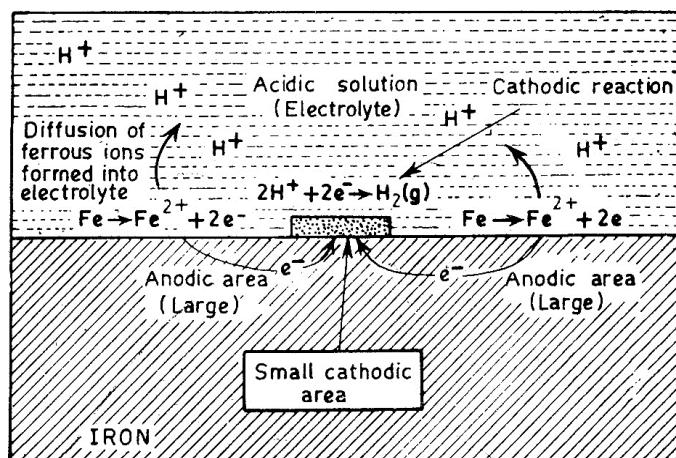
These electrons flow through the metal from anode to cathode.

At cathode,  $\text{H}^+$  ions of the acidic medium undergo reduction to evolve as hydrogen gas.

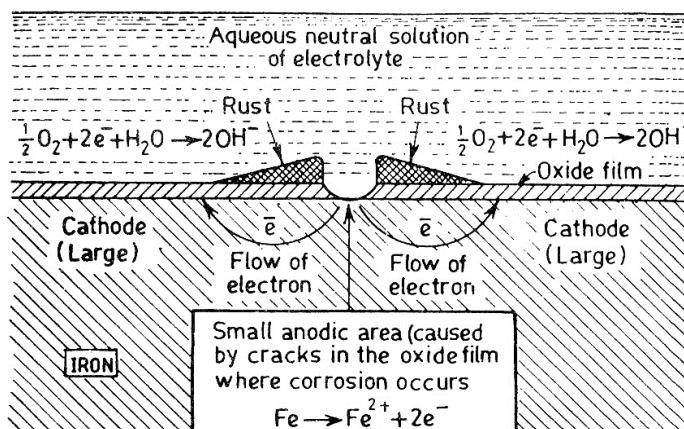


Thus the overall reaction is  $\text{Fe} + 2 \text{H}^+ \longrightarrow \text{Fe}^{2+} + \text{H}_2 \uparrow$

This type of corrosion occurs in case of the metals present above hydrogen in the electrochemical series.



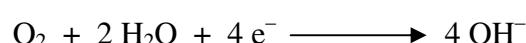
*b) Oxygen absorption corrosion:* This type of corrosion occurs when the corrosive environment is either neutral or alkaline in nature. Rusting of iron in such media is an example of this type of corrosion. Usually, there will be an oxide film on iron due to initial corrosion. But when some cracks are formed in the oxide layer, they become anodic areas leaving behind the remaining areas as cathodic. Thus, the anodic areas are smaller when compared with cathodic areas.



At anodic areas, iron dissolves as ferrous ions with liberation of electrons.



The liberated electrons flow from anodic to cathodic areas through iron metal where electrons are consumed by dissolved oxygen as follows:



The  $\text{Fe}^{2+}$  ions at anodic areas and  $\text{OH}^-$  at the cathodic areas diffuse and when they meet, they precipitate as ferrous hydroxide:



The two reactants  $\text{Fe}^{2+}$  and  $\text{OH}^-$  originate from the anode and cathode respectively, but their combination occurs, more commonly at cathode because of the fast diffusion of  $\text{Fe}^{2+}$  ions than hydroxide ions (due to smaller size of ferrous ion). Hence, corrosion product is deposited at the cathode.

If enough oxygen is present in the medium, ferrous hydroxide is easily oxidized to ferric hydroxide.

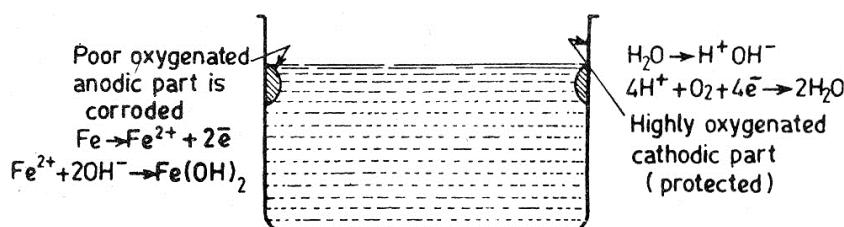


This product is called yellow rust.

If the supply of oxygen is limited, the corrosion product may be even black anhydrous magnetite,  $\text{Fe}_3\text{O}_4$ .

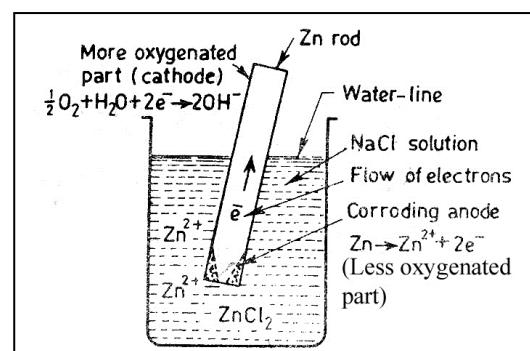
**Concentration Cell Corrosion:** The electrochemical attack on the metal surface exposed to an electrolyte of varying concentrations or of varying aeration is called concentration cell corrosion. It may be due to local difference in ion concentration or inadequate agitation or slow diffusion of metal ions produced by corrosion.

*Differential aeration corrosion:* It is the most common type of concentration cell corrosion. It is also called oxygen concentration cell corrosion. It occurs due to exposure of different parts of a metal to different concentrations of oxygen. It causes difference in potential between differently aerated areas. Poor-oxygenated parts are anodic, while more-oxygenated parts are cathodic. It causes a flow of electrons from poor-oxygenated parts to more-oxygenated parts. *Waterline corrosion* is an example of differential aeration corrosion. Here corrosion of metal takes place just below the waterline, when the metal is partially immersed in a solution.

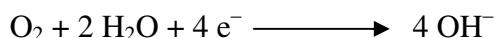


If a metal (say zinc) is partially immersed in a dilute solution of a neutral salt (say  $\text{NaCl}$ ) and the solution is not agitated properly, then the part above and closely adjacent to the waterline are more aerated and it becomes cathodic. The part of the metal immersed to greater depth, which has less access to oxygen, becomes anodic. Hence, difference of potential is created, which causes a flow of current between the two differently-aerated areas of the same metal.

Then, oxidation of zinc takes place at anodic areas,

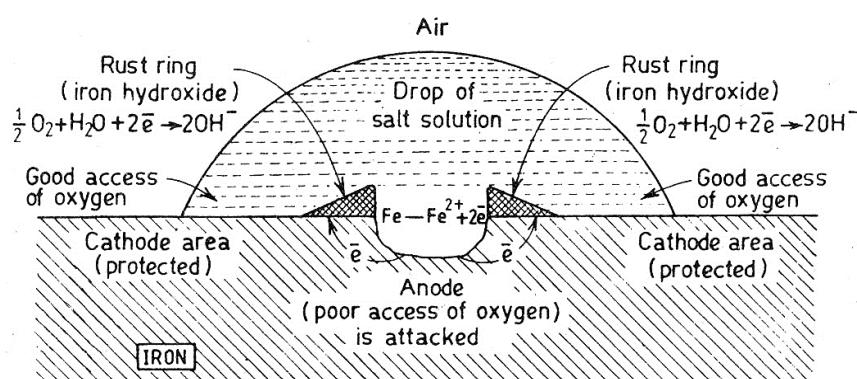


and reduction of oxygen takes place at cathodic areas,



The flow of electrons takes place through the metal and migration of ions takes place through the electrolyte.

Another example of differential aeration corrosion is the corrosion of iron under the drops of water (or salt solution). Here, areas covered by droplets are less-oxygenated parts and become anodic, while the surrounding parts are more-oxygenated and become cathodic. The corrosion starts at the metal under the droplet. Similarly, corrosion is accelerated at the places where the access to oxygen is less. The oxygen-deficient parts serve as anodes and hence cracks and crevices are formed at those places.



*Practical examples for differential aeration corrosion:*

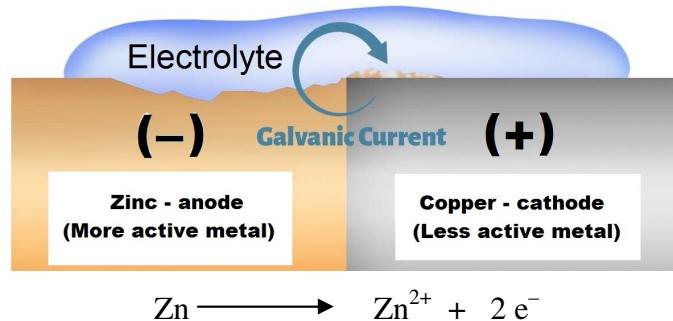
- 1) Part of nail inside the wall
- 2) Window rods inside the frame
- 3) Paper pins inside the paper
- 4) Partially buried pipelines in soil

**Corrosion due to dissimilar metals (Galvanic corrosion or bimetallic corrosion):** When two different metals (e.g. zinc and copper) are placed in contact or electrically connected, there exists a potential difference, due to which electrons flow takes place between them. The more active metal will become anodic and undergoes severe corrosion while the less active metal becomes cathodic and is protected. This type of corrosion is called galvanic corrosion or bimetallic corrosion. The rate of galvanic corrosion depends on the difference in the nature of the two metals towards oxidation.

Examples of galvanic corrosion:

1. Steel screws in a brass marine structure
2. Steel pipe connected to copper plumbing.

The nature of the corrosive environment decides the type of cathodic reactions. In acidic solution, the corrosion occurs by the hydrogen evolution process, while in neutral or slightly alkaline solution, oxygen absorption occurs. The electron-current flows from the anodic metal, zinc to the cathodic metal, copper. Thus, it is evident that the corrosion occurs at the anodic metal, while the cathodic part is protected from the attack.



**Galvanic series:** In order to know the nature of metals and alloys (important engineering materials) towards their corrosion tendency, a list of these materials was prepared based on potential measurements and galvanic corrosion tests in unpolluted seawater. The list of metals and alloys arranged in the decreasing order of their corrosion tendency in unpolluted seawater is called galvanic series. Some of them are listed in the order as they are in galvanic series:

Magnesium and its alloys  
 Zinc  
 Commercially pure Aluminium  
 Cadmium  
 Lead  
 Tin  
 Nickel (active)  
 Brasses (Cu-Zn)  
 Copper  
 Bronzes (Cu-Sn)  
 Nickel (passive)  
 Chromium stainless steel  
 Silver  
 Titanium  
 Gold  
 Platinum

A lot of information related to corrosion of metals and alloys can be obtained from galvanic series. It is easy to assess the anode in the given combination of the two materials with the help of galvanic series. The material that comes first in the series is more active and acts as anode when compared with the other material which comes later in the series. The severity of corrosion depends on the difference in the corrosion tendencies of the two materials. Hence, in order to minimize bimetallic corrosion, it is always suggested that the two materials selected for construction should be as close together as possible in the series.

#### *Control of galvanic corrosion:*

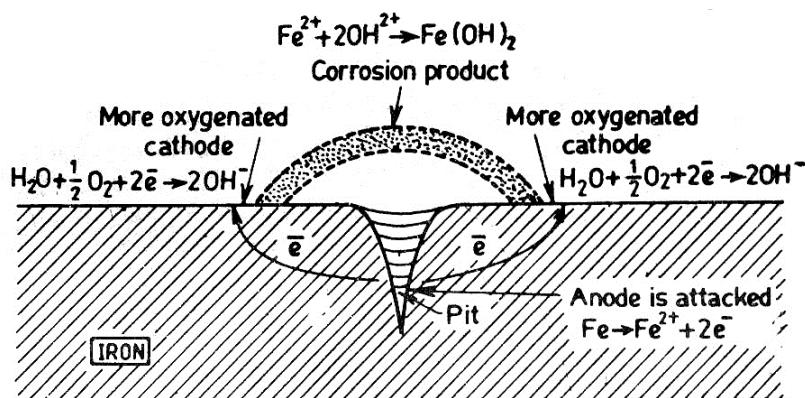
1. Avoiding the use of dissimilar metals during the construction of a metallic structure.
2. If the use of dissimilar metals is unavoidable, the combination of metals is to be selected such that they are as close together as possible in the galvanic series.
3. The unfavorable area effect of small anode and large cathode is to be avoided.
4. Wherever applicable, the dissimilar metals are to be insulated.

5. A third metal, which is anodic to both the metals, can be connected (cathodic protection).

**Pitting corrosion:** It is a localized accelerated attack resulting in the formation of cavities around which the metal is relatively unattacked. Thus, pitting corrosion results in the formation of pinholes, pits and cavities in the metal. Because of the formation of these pinholes, etc. which may penetrate deep into metal, pitting is very destructive.

Pitting is usually the result of the breakdown or cracking of the protective film on a metal at specific points. This gives rise to the formation of small anodic and large cathodic areas. In a suitable environment, this produces corrosion current. Breakdown of the protective film may be caused by various mechanical factors such as surface roughness or non-uniform finish, scratches or cut edges, local straining of metal due to non-uniform stresses, etc.

Breakdown of the protective film may also be caused by a particular type of chemical attack. Thus, metals owing their corrosion-resistance to their passive state show a marked pitting under all conditions, which lead to the destruction of their passivity. Stainless steel and aluminium show characteristic pitting in chloride solution.



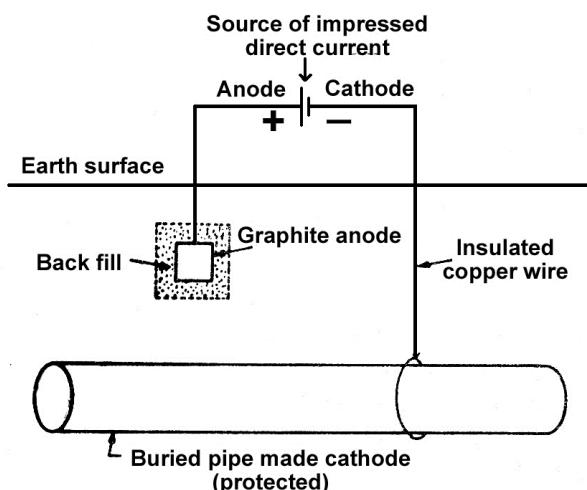
**Passivity:** Passivity is a property by which a metal or alloy shows high corrosion resistance due to the formation of a highly protective, very thin (about 0.0004 mm thick) and quite invisible surface film. Passivation of metal takes place only in certain environments, which tend to maintain protective film on the surface. For example, Ti, Cr, Al and Cr-containing stainless steel alloys exhibit outstanding corrosion resistance in the presence of oxygen. This is due to the formation of a thin, protective oxide film on their surfaces. Whenever any damage occurs, this film is automatically repaired in oxidizing environments. But in reducing environments, the passive metals and alloys become chemically active and are rapidly corroded.

*Examples:* (1) Aluminium is not attacked by conc.  $\text{HNO}_3$ . (2) Iron rapidly undergoes corrosion even by dil.  $\text{HNO}_3$ , whereas stainless steel, due to the presence of Cr in it, maintains protective oxide film so exhibits high corrosion resistance in  $\text{HNO}_3$  solution over a wide range of concentrations.

UNIT - III**PART – 2****CORROSION CONTROL METHODS**

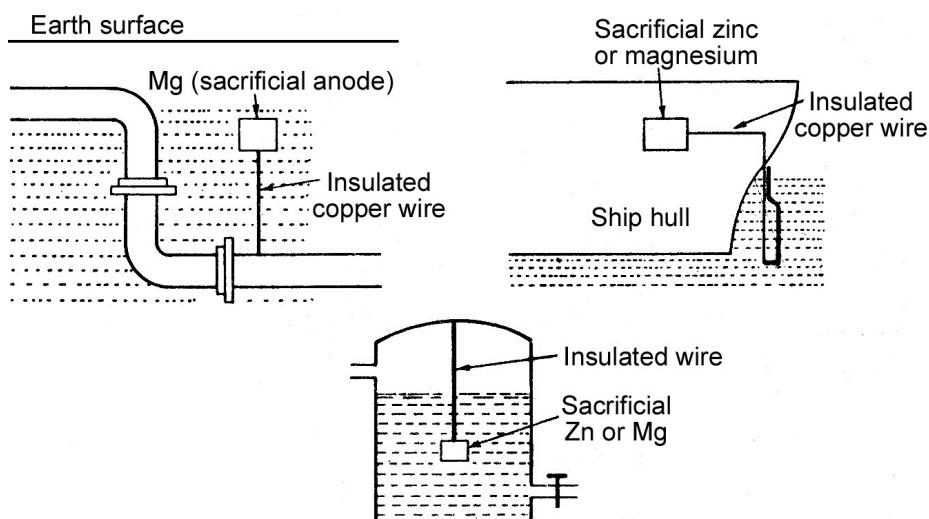
**Cathodic Protection:** Cathodic protection involves forcing the metal to be protected to behave like a cathode so that corrosion does not occur. This is based on the principle that during electrochemical corrosion, cathodic areas are not affected by corrosion. The base metal can be forced to behave as cathode by using two methods.

i) *Impressed current method:* In this method, an impressed current is applied in opposite direction to nullify the corrosion current, and convert the corroding metal from anode to cathode. Impressed current can be derived from a DC source with an insoluble anode like graphite, high silica iron, scrap iron, stainless steel or platinum.



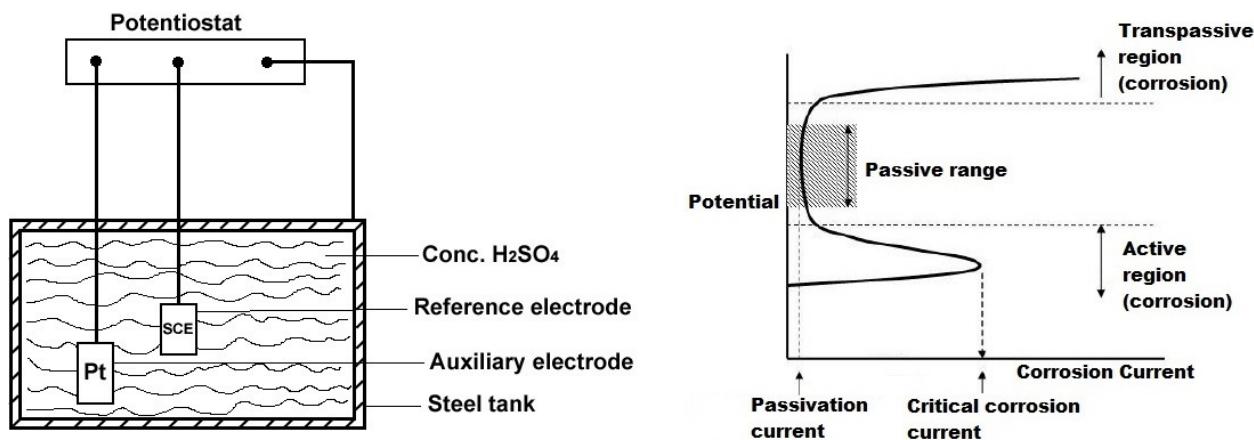
Usually, a sufficient D. C. current is applied to an insoluble anode, buried in the soil (or immersed in the corroding medium) and connected to the metallic structure to be protected. The anode is usually in backfill (composed of coke breeze or gypsum) so as to increase the electrical contact with the surrounding soil. This method has been applied to water tanks, buried oil or water pipes, condensers, transmission line towers, marine piers, laid-up ships, etc. This kind of protection technique is particularly useful for large structures for long-term operation.

ii) *Sacrificial anode method:*



In this method, the metallic structure to be protected, is connected to a more anodic (active) metal so that entire corrosion is concentrated on this more-active metal. The more active metal itself gets corroded, while the parent structure (which becomes cathode) is protected. The more-active metal so employed is called sacrificial anode. The corroded sacrificial anode block is replaced by a fresh one, when consumed completely. Metals commonly employed as sacrificial anodes are magnesium, zinc, aluminium and their alloys. Important applications of sacrificial anodic method include protection of buried pipeline, underground cables, marine structures, ship-hulls, water-tanks, etc.

**Anodic protection (Anodization):** This method is based on the formation of protective film on metals by externally applied anodic currents. This method is useful for active-passive metals like Cr, Fe, Ni, Ti and their alloys.



If carefully controlled anodic currents are applied to these metals, they get passivated and the rate of material dissolution decreases. For this purpose, a device called potentiostat is used. It is an electronic device, which maintains a metal at a constant potential w.r.t. the reference electrode. It has three terminals, one connected to the base metal (eg. steel tank), other to the reference electrode (Calomel electrode) and the third to an auxiliary electrode (platinum). This method is based on the principle that a protective oxide surface film is formed on metal/alloy by the application of anodic current on the appliance in a suitable oxidizing environment. From electrochemical measurements, the optimum potential is determined for protection. The required potential for protecting the metal can be obtained from its ‘potential-current curve’.

When the potential of the base metal is gradually increased, corrosion current increases from A to B reaching a maximum,  $I_{\text{crit}}$  (critical current). Above this potential ( $E_{\text{crit}}$ ), current decreases drastically and suddenly and maintains at  $I_p$  (passivation current), due to attainment of passive state. The corresponding potential required is called passivation potential. Until this minimum current,  $I_p$  is maintained by the potential,  $E_p$ , the object will be in its passive state. This method is mainly used for stainless steel containers used for storing or transporting corrosive chemicals like concentrated acids by maintaining the structures at their passivation current. This method is applicable to only those metals/alloys that exhibit passivity and are present in the oxidizing environment.

**Corrosion inhibitors:** A corrosion inhibitor is a substance which when added in small quantities to the aqueous corrosive environment, effectively decreases the rate of corrosion. They get dissolve in corroding medium, but capable of forming a protective layer either at anode or at cathode.

a) *Anodic inhibitors:* (Chromates, phosphates, tungstates and other transition metal compounds possessing high content of oxygen): These inhibitors control corrosion process by controlling the following reaction taking place at anodic areas.



These inhibitors are soluble in the corrosive medium. The anions of the inhibitor are migrated towards anode and combine with the metal ions produced at anode due to initial corrosion and form insoluble/sparsely soluble metal compound, which forms as a protective film by adsorption and reduces corrosion rate. Although these inhibitors are effective, they are dangerous, if used in inadequate quantities. If certain areas are unprotected by the depletion of inhibitor layer, severe localized corrosion occurs.

b) *Cathodic inhibitors:*

(i) *In acidic solutions:* The predominating cathodic reaction in acidic media is



Rate of this reaction can be reduced by controlling the diffusion of  $H^+$  ions to the cathodic sites. This can be achieved by organic inhibitors like amines, ureas, thioureas, mercaptans, heterocyclic nitrogen compounds, which adsorb at the metal surface. In order to control the above reaction, antimony and arsenic oxides can be used. They get deposited as metallic antimony or arsenic in the form of adherent film thereby increases hydrogen over voltage.

(ii) *In neutral or alkaline solutions:* The predominating cathodic reaction in these media is



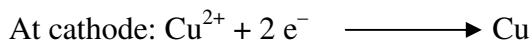
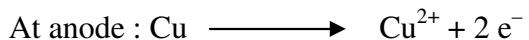
The rate of this reaction can be reduced in two ways:

1. By eliminating oxygen from the medium by deaeration or deactivation (hydrazine, etc.).
2. By retarding the diffusion of oxygen to cathodic areas. This can be achieved by adding salts of Mg, Zn or Ni. They release corresponding metal ions into the medium, which diffuse to cathodic sites and react with hydroxide ions produced during the above reaction to form insoluble metal hydroxides. These hydroxides deposit on cathodic sites as protective film.

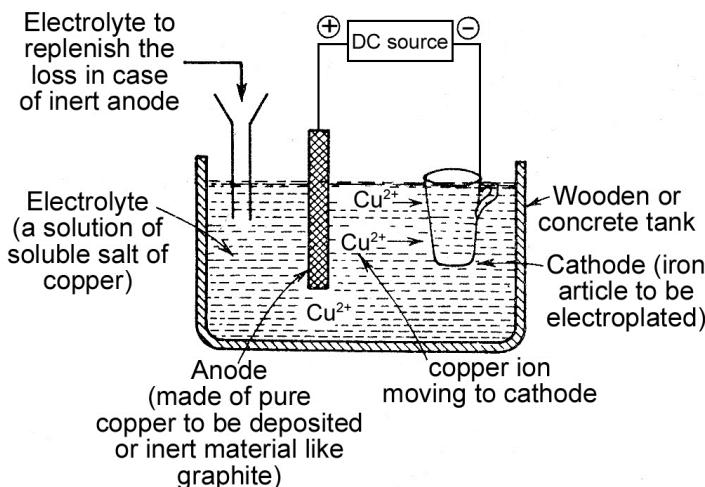
### **Electroplating (Electrodeposition)**

*Principle:* Electroplating or electrodeposition is the process by which the coating metal is deposited on the base metal by passing a direct current through an electrolytic solution, containing the soluble salt of the coating metal.

*Process:* In case of copper electroplating on iron article, copper metal bar is to be taken as anode and iron article as cathode. When these two electrodes are dipper in an electrolytic solution containing copper ions and connected to a d.c. source, the following reactions will occur at the electrodes:



The deposited copper on the iron article produces as a thin layer to protect the base metal iron. The thickness of the copper deposit depends on the concentration of the electrolyte, power provided to the electrodes, current density, time of plating, etc.



#### *Conditions for electroplating of copper:*

Plating bath composition (per Litre): 200 – 250 g of Copper sulphate, 50-75 g of sulphuric acid and the balance water, Anode: P contained rolled Copper

Additives: Gelatin or dextrin, sulphur-containing brightener, sulphonic acid.

Temperature ( $^{\circ}\text{C}$ ): 20 – 40, Current density ( $\text{mA.cm}^{-2}$ ): 20 – 50, Current efficiency (%): 95 – 98 and

Throwing power: low

*Surface preparation:* In order to ensure the effective electroplating, proper cleaning of the surface to be plated is a very important step. Surface preparation can be done by the following methods:

- Solvent cleaning:* It is used to remove oils, greases and fatty substances. This process involves cleaning the surfaces by the application of organic solvents like naphtha, chlorinated hydrocarbons like  $\text{CCl}_4$ , toluene, xylene or acetone.
- Alkali cleaning:* It is used for the removal of old paint coating from metal surfaces. Alkali cleaning agents are trisodium phosphate along with soaps and wetting agents like caustic soda. An alkali treatment is always to be followed by a very thorough rinsing with water and then immersion in a slightly acid solution of 0.1 % chromic acid (or sodium or potassium chromate) to remove the last traces of alkalies.
- Mechanical cleaning:* It removes loose rust and other impurities from the surface. This is generally done by using bristle brush and some abrasive like sand paper and detergent like soap. Impact tools like dull chisels, knife scrapers, wire brushes, grinding wheels and cutters are also used for removing strongly adhering scales, etc.

- d) *Sand-blasting*: It is used for removing oxide scales, particularly when a slightly roughened surface is desired. This method is especially suitable for large steel surfaces. The process consists in introducing the sand into an air stream under pressure of 25 to 100 atmospheres.
- e) *Pickling*: Acid pickling is more convenient method of scale removal in many cases than mechanical cleaning or sand-blasting. It is usually accomplished by immersing the metal in an acid pickling solution. In case of aluminium, pickling is done in alkaline solution.

**Electroless plating:** *Deposition of a metal from its salt solution on a catalytically activated surface by a suitable reducing agent without the aid of electrical energy is known as electroless plating.* Metal ions are reduced to the metal with the help of reducing agents. Once the metal atoms are formed, they get plated over a catalytic surface.

Metal ions + Reducing agent  $\longrightarrow$  Metal plated on a catalyst surface + Oxidized products

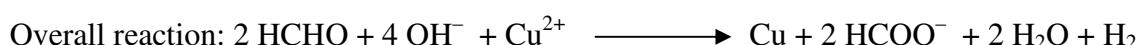
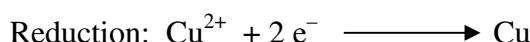
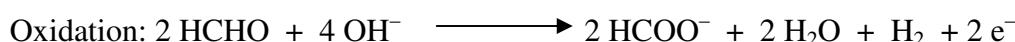
The following techniques are used for the preparation of the surface of the object so that an active surface is obtained.

Etching (acid treatment) and treatment of surface with stannous chloride and palladium chloride alternately for non-conducting surfaces such as plastics and printed circuit boards.

#### *Electroless plating of copper:*

The surface to be treated is degreased and etched in acid. On gold, silver, platinum, palladium, rhodium, iron, cobalt and nickel, electroless copper gets deposited spontaneously in presence of reducing agents. But insulators like plastics, printed circuit boards and glass are activated by dipping first in stannous chloride and then in palladium chloride.

A solution of copper sulphate (12 g/L), formaldehyde (8 g/L) as reducing agent, sodium hydroxide (15 g/L) and Rochelle salt (14 g/L) as buffer, EDTA as complexing agent (20 g/L) acts as plating bath solution for copper plating. For an effective plating of copper, the pH and temperature to be maintained are 11.0 and 25 °C respectively. The following reactions occur during plating:



Cupric ions and formaldehyde consumed during plating are replenished periodically.

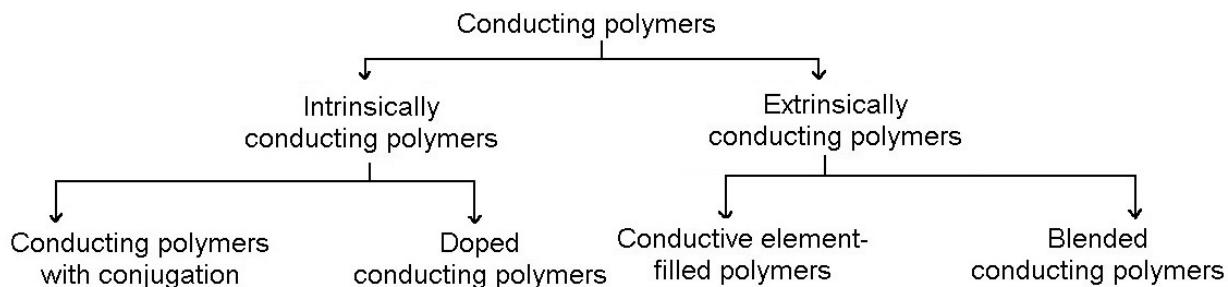
#### *Advantages of electroless plating:*

1. Use of electrical contacts or electrical power is eliminated.
2. Throwing power of electroless bath is better so intricate parts with irregular shapes can be uniformly coated.
3. Plastics and other insulators and semiconductors can also be plated by electroless plating.
4. Resulting deposits have unique chemical, mechanical and magnetic properties.

**UNIT - IV****PART – 1****CONDUCTING POLYMERS**

A polymer material which can conduct electricity through it is termed a conducting polymer. Previously, it was thought that polymers are electrical insulators. But the concept of conductivity in polymers was originated in 1906, and now we have several commercially useful conducting polymers. They exhibit good electrical properties along with useful range of mechanical properties and thermal properties.

**Classification:** Based on mechanism of conductivity, conducting polymers are classified as follows:

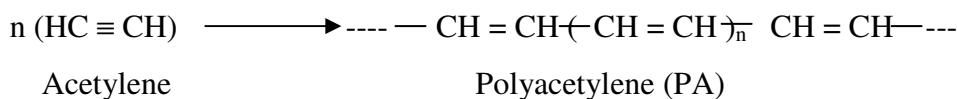


**Intrinsically (Inherently) conducting polymers (ICPs):** These polymers show conductivity due to presence of an extensive conjugation in the backbone of their structures. They can be classified into two types.

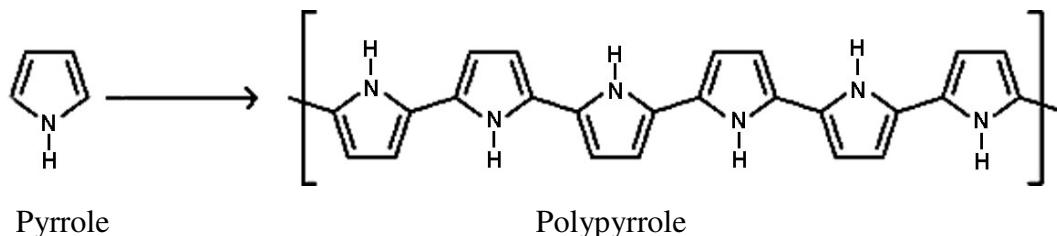
(a) *Conducting polymers with conjugation:* These polymers contain conjugated  $\pi$ -electrons in the backbone, which increase their conductivity to a large extent. Overlapping of the orbitals containing conjugated  $\pi$ -electrons over the entire backbone forms valence band and conduction band with significant band gap. Hence, electrical conduction occurs only when electrons are excited by thermal or photolytic activation. This excitation causes electrons to get sufficient energy to jump from valence band to lower levels of conduction band.

*Examples:*

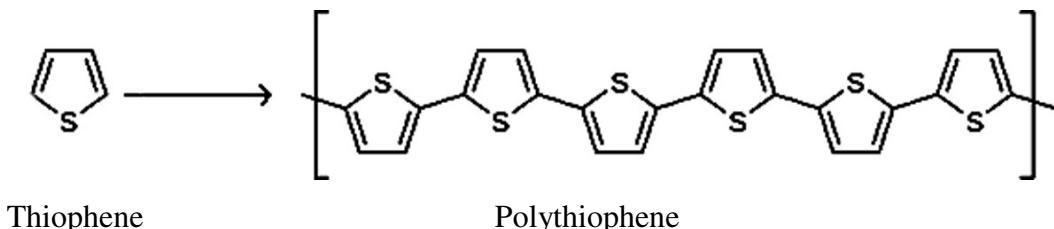
1. Polyacetylene (PA)



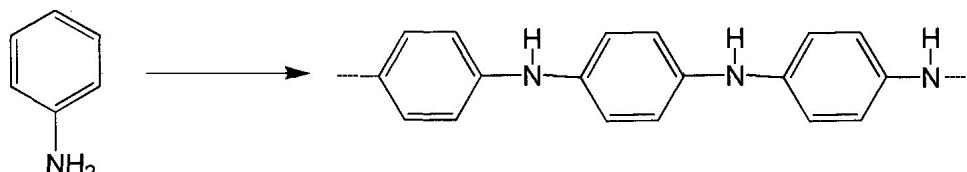
2. Polypyrrole (PPy)



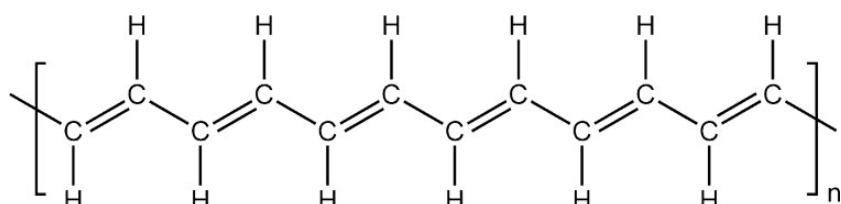
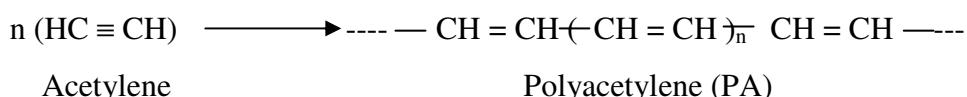
3. Polythiophene (PTh)



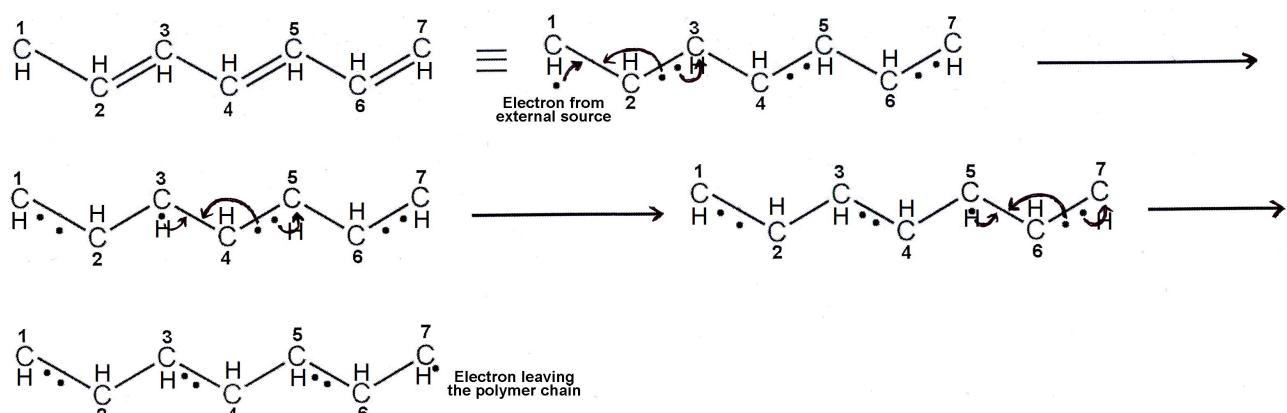
#### 4. Polyaniline (PANI)



*Mechanism of conduction in Polyacetylene:* Polyacetylene is obtained by polymerization of acetylene. During this reaction the polymer gets conjugation (alternate double bonds), which is the fundamental reason for conductivity of certain polymers. (Polymers like polyethylene act as insulators due to absence of conjugation in their structures).



Polyacetylene is represented as  $(\text{CH})_x$ . Each carbon in the backbone structure of PA is  $\text{sp}^2$  hybridized. It exhibits geometrical isomerism, i.e., it has cis- and trans- isomers. Trans-polyacetylene shows high conductivity due to uniform distribution of delocalized  $\pi$ -electron cloud. When an electron from external source enters  $\pi$ -electron cloud, it moves through the chain of C – C bonds as shown below.

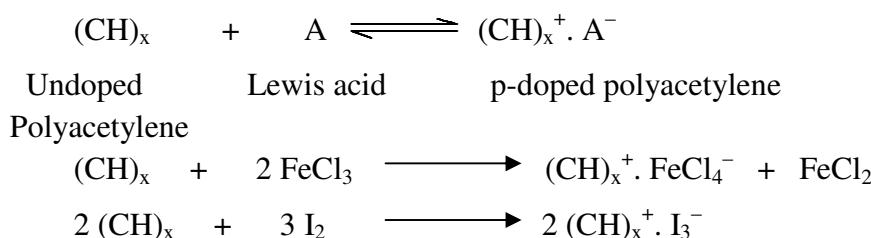


The conductivity of polymers with conjugation is measurable but not sufficient for their use in different fields commercially.

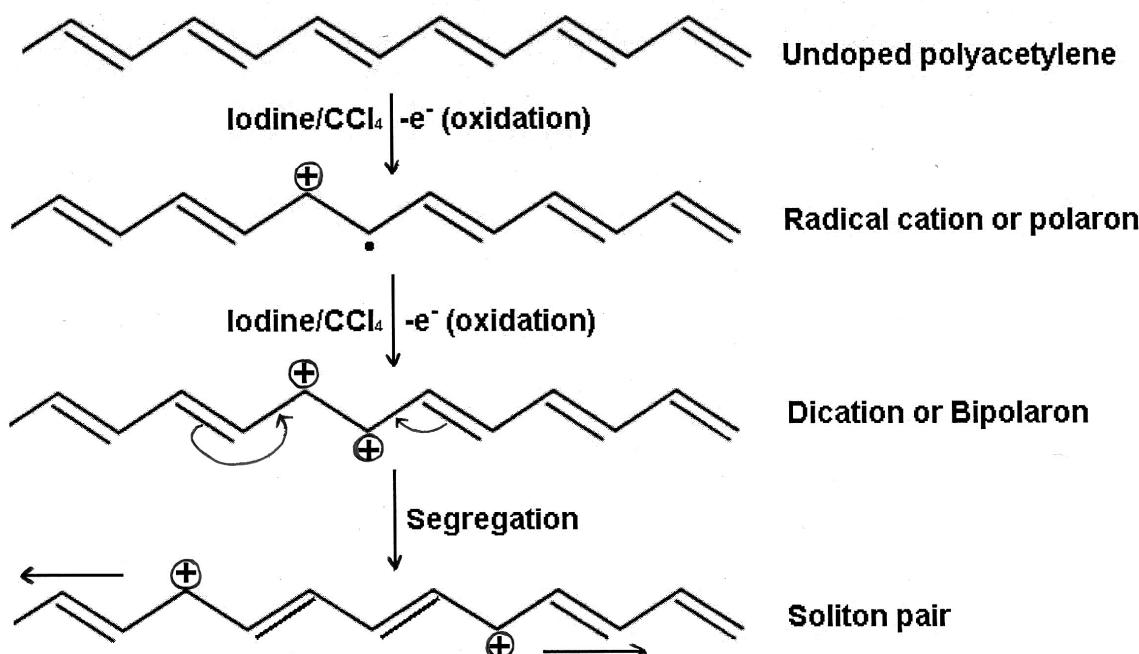
(b) *Doped conducting polymers*: ICPs are proved to be the most useful conducting polymers due to possibility of their ‘doping’. Addition of electron donors or acceptors to ICPs causes dramatic electronic changes in them, which results in increase in conductivity almost to metallic range. Hence, ICPs are also known as synthetic metals.

Conducting polymers with conjugated structures can be easily oxidized or reduced due to their low ionization potentials and high electron affinities. By oxidation or reduction, positive or negative charges are created on polymer backbone and thus conductivity increases. For example, conductivity of undoped polyacetylene is  $< 10^{-7}$  S/cm, while its conductivity after doping is in the range  $10 - 10^5$  S/cm. By analogy with semiconductor technology, it is referred to as doping and is of two types.

**p-doping (Oxidative doping):** It is the process of improving conductivity of conducting polymers with conjugation by treating with a suitable Lewis acid (A). Some Lewis acids used for this purpose are  $I_2$  in  $CCl_4$ ,  $FeCl_3$ ,  $AlCl_3$ , etc.



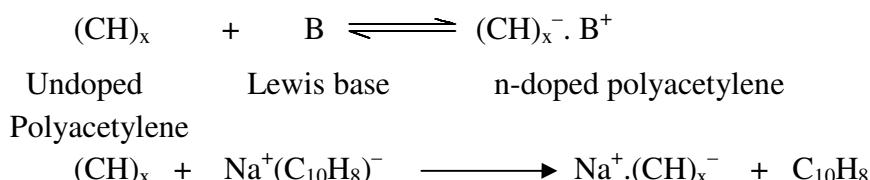
During p-doping, the polymer is partially oxidized by a suitable oxidizing agent. The oxidizing agent removes an electron from the polymer  $\pi$ -backbone leading to the formation of radical cation (polaron). Oxidation of polaron further forms a dication or bipolaron. Bipolaron contains two positive charge carriers, which are mobile. Segregation of these positive charges produces soliton pairs. These soliton pairs are responsible for increase of conductivity in conducting polymers with conjugation.



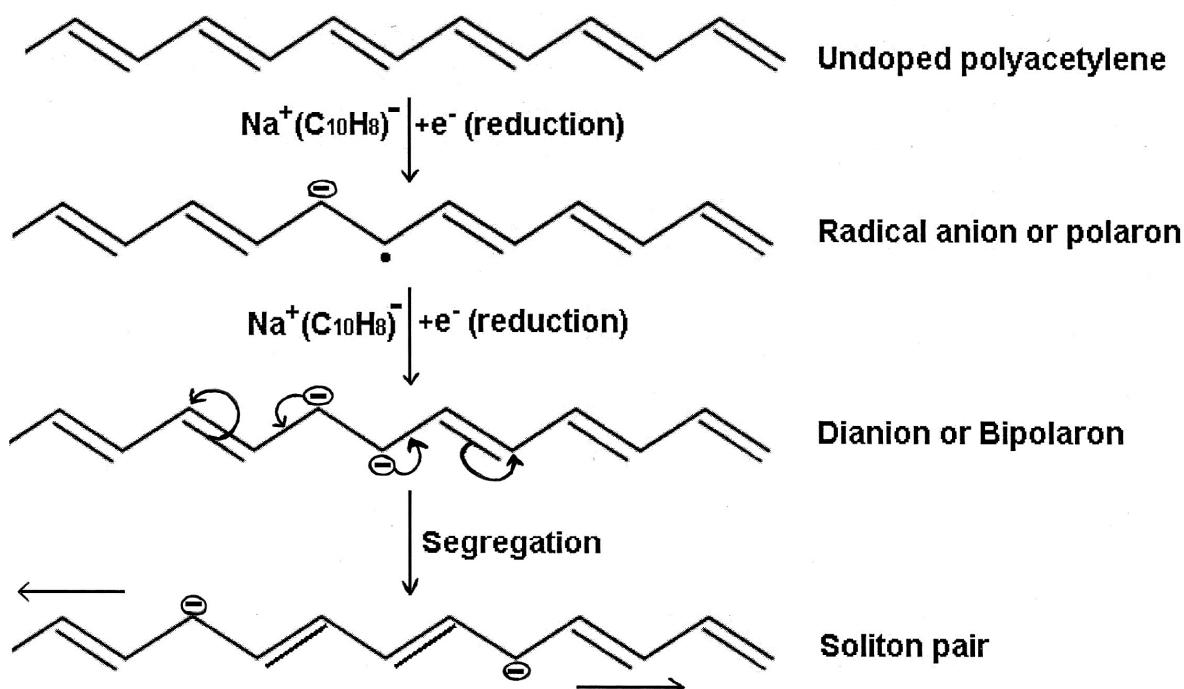
*Explanation based on band theory:*

- In trans-polyacetylene, valence band (VB) and conduction band (CB) are separated by a significant band gap. Hence, conductivity of undoped polymer is very low.
- The radical cation formed has a hole in between VB and CB. The dication has two holes in between these two bands. Thus, there is formation of a new energy level by the holes between VB and CB.
- Segregation of the positive charges through the carbon backbone generates soliton pairs which facilitate facile jumping of electrons from VB to these holes and then to the CB. Thus, more electrons are available in CB and hence, conductivity increases enormously after doping.

**n-doping (Reductive doping):** It is the process of improving conductivity of conducting polymers with conjugation by treating with a suitable Lewis base (B) like sodium naphthalide.



During n-doping, the polymer is reduced by the addition of electrons using a reducing agent like sodium naphthalide. The reducing agent adds an electron to the polymer  $\pi$ -backbone leading to the formation of delocalized radical anion (polaron). Reduction of polaron further forms a dianion or bipolaron. Bipolaron contains two negative charge carriers, which are mobile. Segregation of these negative charges produces soliton pairs. These soliton pairs are responsible for increase of conductivity in conducting polymers with conjugation.



### *Explanation based on band theory:*

- In trans-polyacetylene, valence band (VB) and conduction band (CB) are separated by a significant band gap. Hence, conductivity of undoped polymer is very low.
- The radical anion and bipolaron have an intermediate electronic state within the band gap. The added electrons occupy this electronic state.
- Segregation of the negative charges through the carbon backbone generates soliton pairs which facilitate facile jumping of electrons from VB to the intermediate electronic state and then to the CB. Thus, more electrons are available in CB and hence, conductivity increases enormously after doping.

**Extrinsically conducting polymers:** These polymers show conductivity due to the presence of an externally added chemical in them. They are further classified into two types.

(a) *Conductive element-filled polymers:* These polymers are obtained by adding a conductive material to a conventional (non-conducting) polymer. The conventional polymer acts as binding material to hold the conductive material like metal powders, metal oxides, carbon black, etc. together in the solid entity. The minimum concentration of conductive filler required so that the polymer starts conducting is called percolation threshold, at which a conducting path is produced in the polymeric material.

These polymers are of low cost, exhibit good conductivity, light in weight, mechanically strong and durable, and are easily processed in different forms, sizes and shapes.

(b) *Blended conducting polymers:* They are obtained by blending a conventional polymer with a conducting polymer. Such polymers possess better physical, chemical, mechanical and electrical properties and they can be easily processed. In case of conductive element-filled polymers, the addition of even 10 % of carbon black drastically reduces the tensile strength. But in case of blended polymers, for example, when a polymer is mixed with upto 40% of polypyrrole (a conducting polymer), the tensile strength is affected to only a very small extent.

### **Applications of conducting polymers:**

1. *In rechargeable batteries:* They are used in light weight rechargeable batteries. The polymer battery such as polypyrrole-lithium cell operates by the oxidation and reduction of the polymer backbone. These batteries are more environmentally friendly.
2. *In analytical sensors:* They are used in the preparation of various sensors, which can detect O<sub>2</sub>, SO<sub>2</sub>, NH<sub>3</sub>, oxides of nitrogen, etc. For example, polypyrrole acts as a gas sensor.
3. *For making ion-exchangers:* Membranes made up of conducting polymers can show selective permeability for ions, gases, etc. Hence, they can be used for ion-exchangers and controlled release of drugs. With this, regular injection or oral ingestion of the drug is no longer needed. This technique can be used for cancer chemotherapy.

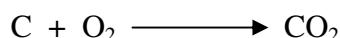
4. *In corrosion protection:* The metals like Cu, Ag used in microelectronics for wiring can undergo corrosion at high temperatures and applied potentials. Conducting polymer like polyaniline can cover the metal surface with good adhesion and protect them from corrosion.
5. *In aircraft structures:* Weight is at a premium for aircraft and spacecraft. The use of polymers with a density of about 1g/cc rather than 10g/cc for metals is attractive. Modern planes are often made with light-weight polymer composites.
6. *For artificial nerves:* Due to biocompatibility of some conducting polymers, they can be used to transport small electrical signals through the body. i.e., they act as artificial nerves.
7. *As conductive adhesive:* A monomer is placed between two conducting surfaces and allowed to polymerise, so that it sticks them together. Thus the polymer exhibits both conduction and adhesion.
8. *In Printed Circuit Boards:* PCBs are epoxy resins coated with copper. The copper conducting lines are produced by electroless plating in order to connect various devices. But this method is an expensive multistage process and adhesion is poor. Copper can be replaced by conducting plastic. This is much cheaper, easy and quick to do and possess good adhesion.
9. *In electromagnetic shielding:* Many electrical devices like computers generate electromagnetic radiation, often microwave and radio frequencies. This can cause malfunctions in nearby electrical devices. Plastic casing provided is transparent to such radiation. Hence, by coating the inner side of the plastic casing with conductive plastics, it can absorb such radiation and protects the devices.
10. *Prevention of static electricity:* By coating an insulator with a very thin layer of conducting polymer, it is possible to prevent the built up of static electricity. Such a discharge can be dangerous in an environment with flammable gases and liquids and in explosive industry. In the computers, the sudden discharge of static electricity can damage microcircuits. The insulating plastic is modified by adding a conducting plastic which gives protection against electrostatic discharge.

**UNIT - IV****PART – 2****FUEL TECHNOLOGY**

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

Examples: Wood, charcoal, kerosene, petrol, diesel, producer gas, oil gas, etc.

Carbon compounds have been used for many centuries as the sources of heat energy due to strong exothermic nature of the following reaction.



During the process of combustion of a fuel, the atoms of carbon, hydrogen, etc. combine with oxygen to liberate heat at a rapid rate along with formation of new compounds like  $\text{CO}_2$ ,  $\text{H}_2\text{O}$ , etc.



(High energy content) (Low energy content)

The primary sources of fuels are coals and petroleum oils. These are stored fuels available in earth crust and are generally called fossil fuels.

**Units of Heat:** Calorie (cal) and kilocalorie (kcal) are the two most commonly used units to express the amount of heat in fuel technology.

1. Calorie (cal): It is the amount of heat required to raise the temperature of one gram of water through one degree Centigrade ( $15$  to  $16$  °C).
2. Kilocalorie (kcal): It is the amount of heat required to raise the temperature of one kilogram of water through one degree Centigrade ( $15$  to  $16$  °C).

$$1 \text{ kcal} = 1000 \text{ cal}$$

**Calorific value of a fuel:** The most important property of a fuel to be taken in to account is its calorific value which indicates the capacity of the fuel to supply heat. It can be defined as *the total quantity of heat liberated when unit mass (or volume) of the fuel is burnt completely*. Calorific value of a fuel can be expressed in two ways.

**(a) Gross or Higher Calorific Value (HCV):** All fuels contain some hydrogen and during combustion, it converts to steam. Hence, during experimental determination of calorific value of a fuel, if products of combustion are condensed to the room temperature ( $15$  °C or  $60$  °F), latent heat of condensation of steam also gets included in the measured heat. So, *gross or higher calorific value is the total amount of heat produced, when unit mass/volume of a fuel has been burnt completely and the products of combustion have been cooled to room temperature (i.e.,  $15$  °C or  $60$  °F)*.

**(b) Net or Lower Calorific Value (LCV):** In practical application of any fuel, the water vapour and moisture, etc. produced during combustion are not condensed and they escape as such along with hot combustion gases. Hence, in such cases, less amount of heat is available compared with HCV. So, *net*

or lower calorific value is the amount of heat produced, when unit mass/volume of a fuel has been burnt completely and the products are permitted to escape.

$\therefore \text{LCV} = \text{HCV} - \text{Latent heat of water vapour formed}$

$$= \text{HCV} - \text{Mass of hydrogen} \times 9 \times \text{Latent heat of steam}$$

Note: 1 part by mass of hydrogen produces 9 parts by mass of water. The latent heat of steam is 587 kcal/kg of water vapour formed at room temperature ( $15^\circ\text{C}$ ).

**Analysis of Coal:** Coal is a highly carbonaceous matter that has been formed as a result of alteration of vegetable matter like plants under certain favourable conditions. It is mainly composed of C, H, N and O along with some non-combustible inorganic matter. The parent material for coal is wood which gradually undergoes alteration to form different types of coals (also called rank of coal) mentioned as follows.

Wood  $\longrightarrow$  Peat  $\longrightarrow$  Lignite  $\longrightarrow$  Bituminous coal  $\longrightarrow$  Anthracite

The transformation of wood to anthracite results in decrease in moisture content, H, O, N, S, volatile matter and increase in carbon content and calorific value.

Hence, the quality of a coal can be assessed by the analysis of the coal sample in two ways.

**(1) Proximate Analysis:** It involves determination of moisture, volatile matter, ash content and fixed carbon in the coal sample. This analysis provides valuable information related to quality of coal.

**(a) Moisture content:** About 1 g of finely powdered air-dried coal sample is weighed in a crucible. The crucible is placed inside an electric hot air-oven maintained at  $105\text{-}110^\circ\text{C}$  for about 1 hour. Then it is taken out, cooled in a desiccator and weighed. Loss in weight is reported as moisture on percentage scale.

$$\text{Moisture (\%)} = \frac{\text{Loss in weight}}{\text{Weight of coal taken}} \times 100$$

Moisture in coal evaporates during burning of coal and it takes some of the liberated heat in the form of latent heat of evaporation. Therefore, moisture lowers the effective calorific value of coal. Further, it quenches the fire in the furnace. Hence, lesser the moisture content, better the quality of coal as a fuel.

**(b) Volatile matter:** The dried sample of coal left in the crucible after determination of moisture content is then covered with a lid and placed in an electric furnace (muffle furnace) maintained at  $925 \pm 20^\circ\text{C}$  for about 7 minutes. Then it is taken out, cooled first in air, then in a desiccator and weighed. Loss in weight is reported as volatile matter on percentage scale.

$$\text{Volatile matter (\%)} = \frac{\text{Loss in weight due to removal of volatile matter}}{\text{Weight of coal taken}} \times 100$$

A high volatile matter content in a coal means that a high proportion of fuel will distill over as vapour, a large portion of which escapes unburnt. A coal sample may contain volatile matter as high as 50 %, which includes combustible gases like methane, hydrogen, carbon monoxide, other

hydrocarbons as well as non-combustible gases like carbon dioxide, nitrogen, etc. Higher volatile content in coal is undesirable. Lesser the volatile matter, better the rank of the coal.

**(c) Ash content:** The residual sample left in the crucible after determination of moisture content and volatile matter is heated without lid in a muffle furnace at  $700 \pm 50$  °C for half-an-hour. The crucible is then taken out, cooled first in air, then in desiccator and weighed. The process of heating, cooling and weighing is repeated till a constant weight is obtained. The residue is reported as ash content on percentage scale.

$$\text{Ash (\%)} = \frac{\text{Weight of ash left}}{\text{Weight of coal taken}} \times 100$$

Ash is a useless, non-combustible matter, which reduces the calorific value of a coal. Also, it causes the hindrance to the flow of air and heat. Hence, lower the ash content, better the quality of coal.

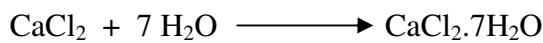
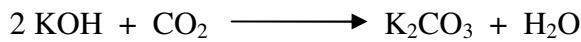
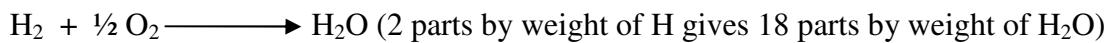
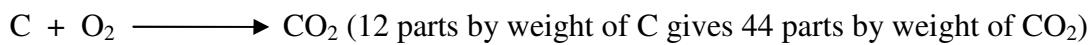
**(d) Fixed carbon:** Percentage of fixed carbon is calculated using the following expression.

$$\text{Fixed carbon (\%)} = 100 - \% \text{ of (moisture + volatile matter + ash)}$$

Fixed carbon represents the quantity of carbon available for combustion. Higher the percentage of fixed carbon, greater is its calorific value and better the quality of coal.

**(2) Ultimate Analysis:** It involves determination of elemental composition of the coal. The elements analysed are carbon, hydrogen, nitrogen, sulphur, oxygen as well as ash content.

**(a) Carbon and Hydrogen:** About 1-2 grams of accurately weighed coal sample is burnt in a current of oxygen in a combustion apparatus. Carbon and hydrogen of the coal are converted into CO<sub>2</sub> and H<sub>2</sub>O respectively. These gaseous products of combustion are absorbed respectively in KOH and CaCl<sub>2</sub> tubes of known weights. The gain in weights of these tubes is determined to calculate percentages of C and H.



Increase in weight of KOH tube is due to CO<sub>2</sub> produced during combustion and hence it gives percentage of carbon in the coal. Similarly, increase in weight of CaCl<sub>2</sub> tube is due to H<sub>2</sub>O produced and hence it corresponds to percentage of hydrogen.

$$\text{Carbon (\%)} = \frac{\text{Increase in weight of KOH tube} \times 12 \times 100}{\text{Weight of coal sample taken} \times 44}$$

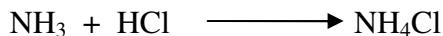
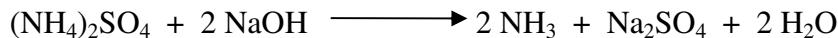
$$\text{Hydrogen (\%)} = \frac{\text{Increase in weight of CaCl}_2 \text{ tube} \times 2 \times 100}{\text{Weight of coal sample taken} \times 18}$$

Higher the percentages of carbon and hydrogen, better the quality of coal and higher its calorific value. Percentage of carbon is helpful in assessing the rank of the coal.

**(b) Nitrogen:** Nitrogen present in a coal sample is determined by the Kjeldahl method. About 1 gram of the finely powdered coal sample is heated with conc.  $\text{H}_2\text{SO}_4$  along with the catalyst  $\text{K}_2\text{SO}_4$  in a long necked flask called Kjeldahl flask. Nitrogen in the coal gets converted to ammonium sulphate and a clear solution is obtained.



Then it is heated with excess of  $\text{NaOH}$  and liberated ammonia is distilled over and absorbed in a known volume of standard acid solution.



The unused acid is then determined by back titration with standard  $\text{NaOH}$  solution, from which acid neutralized by the liberated ammonia is calculated. From this, percentage of nitrogen in coal is calculated as follows.

$$\text{Nitrogen (\%)} = \frac{\text{Volume of acid used} \times \text{Normality of acid} \times 1.4}{\text{Weight of coal taken}}$$

Nitrogen does not contribute to calorific value of coal and hence its presence is undesirable in coal. Hence, good quality coal has less nitrogen content.

**(c) Sulphur:** Sulphur present in a coal sample is determined by Eschka method. In this method, sulphur present in coal is converted into soluble (sodium) sulphate by incinerating known weight of coal with a 1:2 mixture of  $\text{Na}_2\text{CO}_3$  and calcinated  $\text{MgCO}_3$  in a bomb calorimeter. The washings obtained from bomb are treated with barium chloride solution so that sulphates are precipitated as  $\text{BaSO}_4$ . The precipitate is filtered, washed and heated to constant weight.

$$\text{Sulphur (\%)} = \frac{\text{Weight of BaSO}_4 \text{ obtained} \times 32 \times 100}{\text{Weight of coal sample taken in bomb} \times 233}$$

Sulphur increases the calorific value of coal. But, it produces acidic combustion products ( $\text{SO}_2$  and  $\text{SO}_3$ ) which have corrosion effects on metallic equipment as well as these harmful gases cause air pollution. Good quality coal contains low sulphur content.

**(d) Ash content:** Determination of ash content is carried out as in proximate analysis.

**(e) Oxygen:** It is obtained by subtracting percentages of all the elements and ash content determined above, from 100.

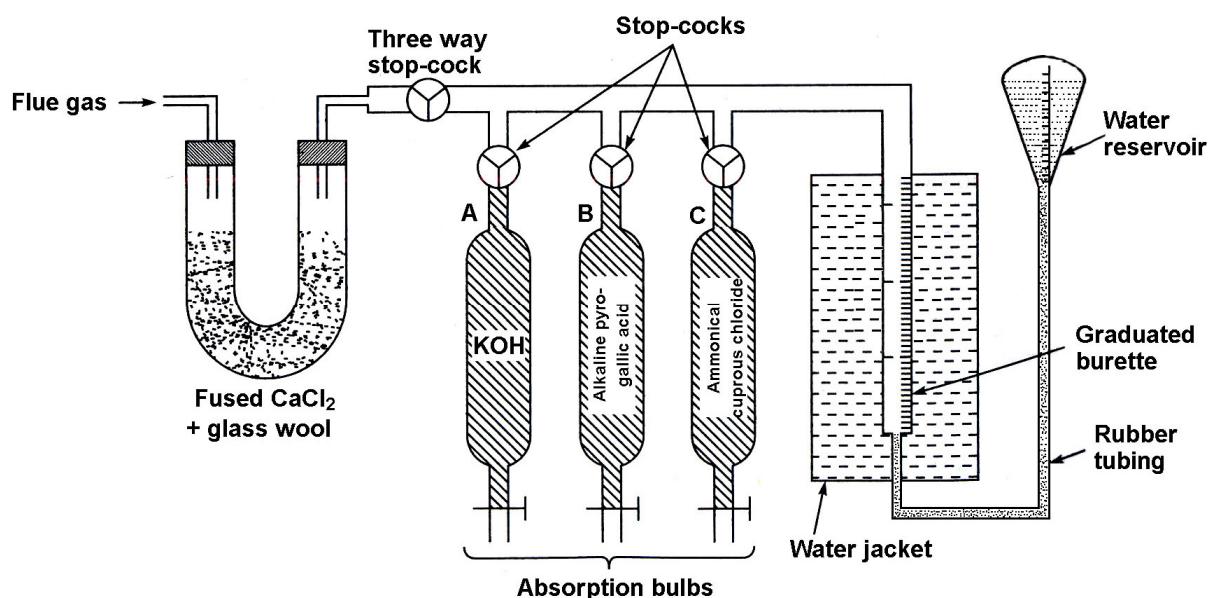
$$\text{Oxygen (\%)} = 100 - \% \text{ of (C + H + S + N + ash)}$$

Coals containing high oxygen content are characterized by high inherent moisture and low calorific value. As oxygen is present in combination with hydrogen, in the form of water, hydrogen available for combustion is lesser than actual one. Thus, a good quality coal has low percentage of oxygen.

**Analysis of flue gas by Orsat's apparatus:** The mixture of gases liberating out of the combustion chamber is called flue gas. The mixture mostly consists of CO<sub>2</sub>, CO and O<sub>2</sub>. Analysis of flue gas is carried out with the help of Orsat's apparatus.

**Construction:** It consists of a horizontal tube. At one end of this tube, there is a three way stop-cock and the other end is connected to a graduated gas burette (up to 100 ml). Gas burette is surrounded by water jacket to maintain constant temperature. The burette is further connected to a water reservoir by means of a rubber tube. The water level in the burette is raised or lowered by raising or lowering the water reservoir. The burette is connected in series to a set of three absorption bulbs, each through a separate stop-cock. The three bulbs A, B and C contain KOH, alkaline pyrogallic acid and ammonical cuprous chloride to absorb CO<sub>2</sub>, O<sub>2</sub> and CO respectively. The other end of the horizontal tube connected to three way stop-cock is further connected to a U-tube. The U-tube is packed with fused CaCl<sub>2</sub> and glasswool for drying flue gas before analysis and avoiding the incoming smoke particles respectively.

**Working:** Before starting the analysis, the entire apparatus is thoroughly cleaned, stoppers greased and tested for air-tightness. The three absorption bulbs are filled with their respective solutions and their stop-cocks are closed. Firstly, the three way stop-cock is opened to atmosphere and air is excluded from the burette by raising the water reservoir till the burette is completely filled with water. Then, the three way stop-cock is opened to flue gas to be analysed and is drawn in to the apparatus by lowering the water reservoir. For accurate results, the process of sucking and expelling the flue gas is repeated by lowering and raising the reservoir repeatedly. It ensures complete removal of air from the apparatus.



Finally, 100 ml of flue gas is carefully sucked in to the burette for analysis and the three way stop-cock is closed. Now, the stop-cock of bulb A is opened and the flue gas is forced to enter the bulb by raising the water reservoir. KOH present in bulb A absorbs CO<sub>2</sub>. Flue gas is sent to the bulb

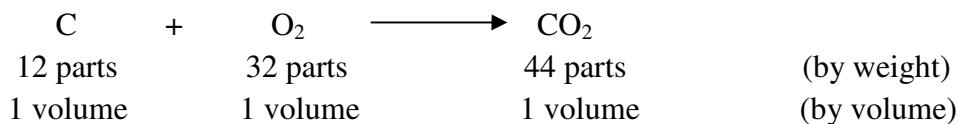
A 2 or 3 times by raising and lowering the water reservoir repeatedly so that all the CO<sub>2</sub> present in flue gas is completely absorbed in bulb A.

The unabsorbed gas is now taken back in to the burette by lowering the reservoir and the stop-cock of bulb A is closed. The levels of water in the reservoir and the burette are equalized and the volume of residual gas is noted. The decrease in volume corresponds to the volume of CO<sub>2</sub> present in 100 ml of flue gas sample. The volumes of O<sub>2</sub> and CO are also determined by passing the flue gas through absorption bulbs B and C respectively. The gas remaining after the absorption of CO<sub>2</sub>, O<sub>2</sub> and CO is taken as nitrogen.

Significance: Analysis of flue gas from a furnace or an exhaust gas from an engine gives information about efficiency of the combustion process. For example, if the flue gas contains considerable amount of CO, it indicates that incomplete combustion is occurring and there is shortage in supply of oxygen required for combustion. If flue gas contains considerable amount of oxygen, it indicates that O<sub>2</sub> supply is in excess than required for combustion. An excess of oxygen (air) results in the loss of heat.

**Numerical problems on combustion:** The amount (weight or volume) of oxygen and air required for the complete combustion of a given quantity of fuel can be calculated by taking the following points into consideration.

1. Carbon undergoes combustion in presence of oxygen as per the following reaction.



2. The other most common reactions taking place during combustion of a fuel are

- (a) H<sub>2</sub> + ½ O<sub>2</sub> → H<sub>2</sub>O
- (b) S + O<sub>2</sub> → SO<sub>2</sub>
- (c) CO + ½ O<sub>2</sub> → CO<sub>2</sub>
- (d) CH<sub>4</sub> + 2 O<sub>2</sub> → CO<sub>2</sub> + 2 H<sub>2</sub>O

Nitrogen, ash and CO<sub>2</sub> present, if any, in the fuel or air are incombustible and hence they do not consume oxygen during combustion.

3. Total or theoretical amount of oxygen required for complete combustion of a fuel is the sum of the amounts of O<sub>2</sub> required by the individual combustible constituents present in the fuel. But,

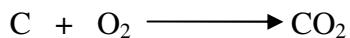
Net or minimum O<sub>2</sub> required = Theoretical O<sub>2</sub> required – O<sub>2</sub> present in the fuel

4. The amount of oxygen present in air is 23 % by weight and 21 % by volume.

∴ Minimum air required (by weight) = (100/23) × minimum oxygen required  
and Minimum air required (by volume) = (100/21) × minimum oxygen required

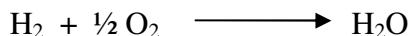
1. Calculate the minimum weight of air required for the complete combustion of 1 kg of coal having the following composition by weight. C=90%, H<sub>2</sub>=3.5%, S=0.5%, O<sub>2</sub>=3%, N<sub>2</sub>=0.5% and ash 1.5%.

**Solution:** As per the data, 1 kg of coal contains 0.9 kg of carbon, 0.035 kg of hydrogen, 0.005 kg of sulphur, 0.03 kg of oxygen, 0.005 kg of nitrogen and 0.015 kg of ash.



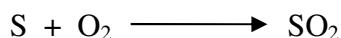
According to the balanced chemical equation, 12 kg of carbon requires 32 kg of oxygen.

∴ 0.9 kg of carbon requires (32/12) × 0.9 = 2.4 kg of oxygen



*2 kg of hydrogen requires 16 kg of oxygen.*

$\therefore 0.035 \text{ kg of hydrogen requires } (16/2) \times 0.035 = 0.28 \text{ kg of oxygen}$



*32 kg of sulphur requires 32 kg of oxygen.*

$\therefore 0.005 \text{ kg of sulphur requires } (32/32) \times 0.005 = 0.005 \text{ kg of oxygen}$

Nitrogen and ash do not undergo combustion and they do not consume oxygen.

Theoretical O<sub>2</sub> required =  $2.4 + 0.28 + 0.005 = 2.685 \text{ kg}$

$\therefore \text{Net amount of oxygen required for 1 kg of fuel}$

$$= \text{Theoretical O}_2 \text{ required} - \text{O}_2 \text{ present in fuel}$$

$$= 2.685 - 0.03 = 2.655 \text{ kg}$$

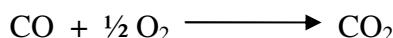
23 kg of oxygen is supplied by 100 kg of air.

$\therefore 2.655 \text{ kg of oxygen is supplied by } (100/23) \times 2.655 = 11.54 \text{ kg of air}$

$\therefore \text{Minimum weight of air required for complete combustion of 1 kg of coal} = \mathbf{11.54 \text{ kg}}$

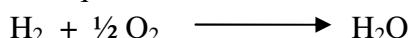
**2.** Calculate the minimum volume of air required for the complete combustion of 1 m<sup>3</sup> of a gaseous fuel of the following composition by volume. CO=23%, H<sub>2</sub>=12%, CH<sub>4</sub>=3%, CO<sub>2</sub>=5%, N<sub>2</sub>=55% and O<sub>2</sub>=2%.

**Solution:** 1 m<sup>3</sup> of the fuel contains 0.23 m<sup>3</sup> of CO, 0.12 m<sup>3</sup> of H<sub>2</sub>, 0.03 m<sup>3</sup> of CH<sub>4</sub>, 0.05 m<sup>3</sup> of CO<sub>2</sub>, 0.55 m<sup>3</sup> of N<sub>2</sub> and 0.02 m<sup>3</sup> of O<sub>2</sub>.



According to the balanced chemical equation, 1 vol. of CO requires 0.5 vol. of oxygen.

$\therefore 0.23 \text{ m}^3 \text{ of CO requires } 0.23 \times 0.5 = 0.115 \text{ m}^3 \text{ of oxygen}$



*1 vol. of hydrogen requires 0.5 vol. of oxygen.*

$\therefore 0.12 \text{ m}^3 \text{ of hydrogen requires } 0.12 \times 0.5 = 0.06 \text{ m}^3 \text{ of oxygen}$



*1 vol. of CH<sub>4</sub> requires 2 vol. of oxygen.*

$\therefore 0.03 \text{ m}^3 \text{ of CH}_4 \text{ requires } 0.03 \times 2 = 0.06 \text{ m}^3 \text{ of oxygen}$

CO<sub>2</sub> and N<sub>2</sub> do not participate in combustion process.

Theoretical O<sub>2</sub> required =  $0.115 + 0.06 + 0.06 = 0.235 \text{ m}^3$

$\therefore \text{Net volume of O}_2 \text{ required for complete combustion of 1 m}^3 \text{ of fuel}$

$$= \text{Theoretical O}_2 \text{ required} - \text{O}_2 \text{ present in fuel}$$

$$= 0.235 - 0.02 = 0.215 \text{ m}^3$$

21 m<sup>3</sup> of O<sub>2</sub> is supplied by 100 m<sup>3</sup> of air

$\therefore 0.215 \text{ m}^3 \text{ of O}_2 \text{ is supplied by } (100/21) \times 0.215 = 1.02 \text{ m}^3 \text{ of air}$

$\therefore \text{Volume of air required for complete combustion of 1 m}^3 \text{ of gaseous fuel} = \mathbf{1.02 \text{ m}^3}$

**3.** Calculate the weight and volume of air required for complete combustion of of 1 kg of coke.



*12 kg of carbon requires 32 kg of oxygen*

$\therefore 1 \text{ kg of coke requires } (32/12) \times 1 = 2.67 \text{ kg of O}_2$

It is known that 23 kg of O<sub>2</sub> is supplied by 100 kg of air.

$\therefore 2.67 \text{ kg of O}_2 \text{ is supplied by } (100/23) \times 2.67 = 11.6 \text{ kg of air}$

At STP conditions, 32 kg of O<sub>2</sub> occupies 22.4 m<sup>3</sup> of volume.

$\therefore \text{Volume occupied by } 2.67 \text{ kg of O}_2 = (2.67 \times 22.4)/32 = 1.87 \text{ m}^3$

Since  $21 \text{ m}^3$  of  $\text{O}_2$  is supplied by  $100 \text{ m}^3$  of air,

$1.87 \text{ m}^3$  of  $\text{O}_2$  is supplied by  $(100/21) \times 1.87 = 8.9 \text{ m}^3$

Weight of air required for combustion of 1 kg of coke = 11.6 kg

Volume of air required for combustion of 1 kg of coke =  $8.9 \text{ m}^3$

**4.** 1000  $\text{m}^3$  of a producer gas having the volumetric composition  $\text{CO} = 22\%$ ,  $\text{CO}_2 = 4\%$ ,  $\text{CH}_4 = 2\%$ ,  $\text{H}_2 = 14\%$ ,  $\text{N}_2 = 56\%$  and  $\text{O}_2 = 2\%$  has to be burnt for heating a furnace. Calculate the minimum quantity of air required for the complete combustion. *(Answer: 952.38  $\text{m}^3$ )*

**5.** The percentage composition of a sample of anthracite coal was found by weight to be  $\text{C} = 90$ ,  $\text{H} = 3.3$ ,  $\text{O} = 3.0$ ,  $\text{N} = 0.8$ ,  $\text{S} = 0.9$  and ash 2.0. Calculate the minimum weight of air required for the complete combustion of 1 kg of this fuel. *(Answer: 11.49 kg)*

**6.** Calculate the volume of air at STP needed for the complete combustion of 1 kg of methane.

*(Answer: 13.33  $\text{m}^3$ )*

**7.** A gaseous fuel has the following composition by volume.  $\text{H} = 40\%$ ,  $\text{CH}_4 = 40\%$ ,  $\text{C}_2\text{H}_6 = 6\%$  and  $\text{N} = 8\%$ . Calculate the volume of air required for the combustion of 1  $\text{m}^3$  of the fuel.

*(Answer: 6.05  $\text{m}^3$ )*

**8.** On analysis, an oil was found to have the following percentage composition.  $\text{C} = 48\%$ ,  $\text{H} = 12\%$  and  $\text{O} = 4\%$ . Calculate the weight of air required for the complete combustion of 1 kg of this oil.

*(Answer: 9.57 kg)*

**9.** A sample of coal was found to contain the following.  $\text{C} = 81\%$ ,  $\text{H} = 4\%$ ,  $\text{O} = 2\%$ ,  $\text{N} = 10\%$ ,  $\text{S} = 2\%$  and the remaining being ash. Estimate the quantity of minimum air required for the complete combustion of 1 kg of the sample. *(Answer: 10.78 kg)*

**10.** Calculate the volume of air required for the complete combustion of 1  $\text{m}^3$  of the gaseous fuel having the following composition by volume.  $\text{H} = 50\%$ ,  $\text{CH}_4 = 36\%$ ,  $\text{N} = 1.5\%$ ,  $\text{CO} = 6\%$ ,  $\text{C}_2\text{H}_4 = 4\%$  and water vapour = 2.5%. *(Answer: 5.33  $\text{m}^3$ )*

**VELAGAPUDI RAMAKRISHNA  
SIDDHARTHA ENGINEERING COLLEGE, VIJAYAWADA  
(AUTONOMOUS)  
DEPARTMENT OF CHEMISTRY**

I/IV B.Tech. DEGREE EXAMINATIONS, JULY, 2021  
**ENGINEERING CHEMISTRY (20BS1102)**

Time: 3 hours

Max. Marks: 70

**P A R T - A**

10 x 1 = 10 marks

- a) List the WHO standards of drinking water.
- b) Sodium aluminate conditioning is the best internal treatment method. Justify the statement.
- c) Explain the importance of break-point chlorination.
- d) List any two advantages of reverse osmosis.
- e) Mention the advantages of modern batteries over conventional batteries.
- f) Define corrosion.
- g) What is cathodic protection?
- h) Define passivity.
- i) Give relation between higher and lower calorific values.
- j) List two common n-dopants.

**U N I T - I**

2. a) An expert committee requested to investigate the reason for unpredicted explosion in a steam generating boiler in an industry. Later, the committee visited the industry and collected the MgCO<sub>3</sub>, MgCl<sub>2</sub>, Ca(HCO<sub>3</sub>)<sub>2</sub>, CaCl<sub>2</sub>, CaSO<sub>4</sub>, CaSiO<sub>3</sub>, MgSiO<sub>3</sub>, NaOH and Na<sub>2</sub>CO<sub>3</sub> deposits from the boiler pieces. Looking at this data, the committee discussed how boiler has suffered before explosion. Can you write the report discussing the attributes for explosion? (9 marks)
2. b) What is desalination? Explain the use of electrodialysis for desalination of water, with the help of a neat diagram. (6 marks)

(OR)

3. a) What is potable water? Outline the purification process of water for domestic use. (9 marks)
3. b) Discuss the boiler corrosion. How is it controlled? (6 marks)

**U N I T - II**

4. a) Apply the phase rule to explain water system. (7 marks)
4. b) Outline the working principle of a fuel cell with a diagram and write the chemistry involved in H<sub>2</sub> – O<sub>2</sub> fuel cell. (8 marks)

(OR)

5. a) Make use of phase diagram to explain triple point and eutectic point. (7 marks)
5. b) Discuss the construction and working of Calomel electrode. (8 marks)

**U N I T - III**

6. a) Applying various methods for the protection of underground pipeline from corrosion. Discuss your answer. (8 marks)
6. b) Explain hydrogen evolution type corrosion. (7 marks)

(OR)

7. (a) Giving two examples of each, explain the difference between galvanic corrosion and pitting corrosion. (6 marks)  
7. b) Define electroplating. Explain the principle, process and advantages of electroplating. (9 marks)

#### **U N I T - IV**

8. a) What is the significance of ultimate analysis of coal? How this analysis is carried out in the laboratory? (9 marks)  
8. b) How does polyacetylene become conductive? Discuss your answer. (6 marks)

(OR)

9. a) Distinguish between gross and net calorific values of fuel. Calculate the gross and net calorific value of coal having the following compositions. Carbon = 85%, Hydrogen = 8%, Sulphur = 1%, Nitrogen = 2%, ash = 4%. The latent heat of steam is 587 cal/g. (7 marks)  
9. b) What are conducting polymers? List their uses in the present days. (8 marks)
-