

**END TERM EXAMINATION  
FIRST SEMESTER (B. TECH) ETCH-113  
APPLIED CHEMISTRY-2013**

M.M.: 75

Time : 3 hrs.

**Note:** Attempt five questions including Q.no. 1 which is compulsory. Select one question from each unit.

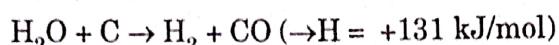
**Q.1. (a) Define the terms cetane number and octane number. (2.5 x 10)**

**Ans.** Octane number of a gasoline fuel is given by the percentage of iso-octane in a mixture of iso-octane (octane number 100) and *n*-heptane (octane number 0) that would yield the same anti-knock properties as the given fuel. Octane number is a fuel rating valid for gasoline (or petrol). Octane number describes how poor the ignition characteristics (but how good anti-knock characteristics) are. Octane number derives its name from a highly ignition-resistant liquid hydrocarbon (2,2,4-trimethylpentane) named iso-octane, which is assigned an octane number of 100 as a standard against which gasoline fuels are rated.

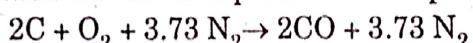
Cetane number, on the other hand, is given for a diesel fuel by the percentage of cetane in a mixture of cetane (cetane number 100) and isocetane (cetane number 15) that would give the same ignition characteristics as the given fuel. Cetane number is a rating for diesel fuel. Cetane number describes how good the ignition characteristic are. Cetane number, on the other hand, derives its name from a liquid hydrocarbon named cetane, which ignites readily under compression and hence is assigned a cetane number of 100 as a standard against which compression ignition fuels like diesel and biodiesel are rated.

**Q.1. (b) Distinguish between producer gas and water gas.**

**Ans. (1) Water gas** is a synthesis gas, containing carbon monoxide and hydrogen. It is a useful product but requires careful handling due to its flammability and the risk of carbon monoxide poisoning. The gas is made by passing steam over a red-hot carbon fuel such as coke:



**Producer gas**, also called suction gas, specifically means a fuel gas made from coke, anthracite or other carbonaceous material. Air is passed over the red-hot carbonaceous fuel and carbon monoxide is produced. and proceeds as follows:



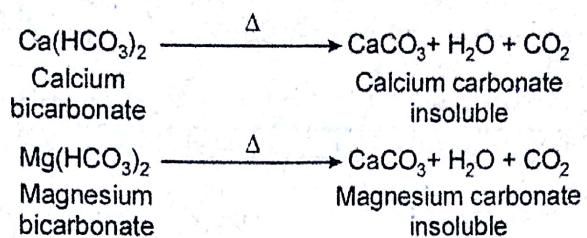
(2) Water gas reaction is endothermic, Producer gas reaction is exothermic.

(3) Producer gas is the mixture of gases produced by the gasification of organic material such as biomass at relatively low temperatures (1292° to 1832° F). Producer gas is composed of carbon monoxide (CO), hydrogen (H<sub>2</sub>), carbon dioxide (CO<sub>2</sub>) and typically a range of hydrocarbons such as methane (CH<sub>4</sub>) with nitrogen from the air. Producer gas can be burned as a fuel gas such as in a boiler for heat or in an internal combustion gas engine for electricity generation or combined heat and power (CHP). The composition of the gas can be modified by manipulation of gasification parameters

Syngas (synthesis gas) is a mixture of carbon monoxide (CO) and hydrogen (H<sub>2</sub>), which is the product of high temperature steam or oxygen gasification of organic material such as biomass. Following clean-up to remove any impurities such as tars, syngas can be used to produce organic molecules such as synthetic natural gas (SNG-methane (CH<sub>4</sub>)) or liquid biofuels such as synthetic diesel.

**Q.1. (c) Briefly explain the temporary and permanent hardness of water.**

**Ans. 1.** Temporary hardness of water is due to bicarbonates of calcium and magnesium, which:



2. Permanent hardness is due to the presence of chlorides and sulphates of calcium, magnesium, iron and other heavy metals. Permanent hardness can not be removed by boiling. It can be removed by:

- (i) Zeolite process
- (ii) Lime Soda process
- (iii) Ion exchange process

**Q.1. (d) Calculate the temporary and total hardness of a sample of water containing:  $\text{Mg}[\text{HCO}_3]_2 = 7.3 \text{ mg/l}$ ,  $\text{Ca}(\text{HCO}_3)_2 = 16.2 \text{ mg/l}$ ,  $\text{MgCl}_2 = 0.5 \text{ mg/l}$ ,  $\text{CaSO}_4 = 13.6 \text{ mg/l}$ .**

**Ans.**

| Component                   | Amount | Multiplication factor           | $\text{CaCO}_3$ equivate |
|-----------------------------|--------|---------------------------------|--------------------------|
| $\text{Mg}(\text{HCO}_3)_2$ | 7.3    | $\frac{100}{146} \times 7.3 =$  | 5 mg/L                   |
| $\text{Ca}(\text{HCO}_3)_2$ | 16.2   | $\frac{100}{162} \times 16.2 =$ | 10                       |
| $\text{MgCl}_2$             | 0.5    | $\frac{100}{95} \times 0.5 =$   | 0.5                      |
| $\text{CaSO}_4$             | 13.6   | $\frac{100}{136} \times 13.6 =$ | 10                       |

$$\begin{aligned}\text{Temporary hardness} &= \text{Mg}(\text{HCO}_3)_2 + \text{Ca}(\text{HCO}_3)_2 \\ &= 5 + 10 = 15 \text{ mg/L}\end{aligned}$$

$$\text{Total hardness} = 5 + 10 + 0.5 + 10 = 25.5 \text{ mg/L}$$

**Q.1. (e) State Gibb's phase rule.**

**Ans.** The phase rule allows one to determine the number of degrees of freedom (F) or variance of a chemical system. This is useful for interpreting phase diagrams.

$$F = 2 + C - P$$

Where F is the number of degrees of freedom, C is the number of chemical components and P is the number of phases in the system. The number two is specified because this formulation assumes that both T and P can be varied.

**Q.1. (f) Draw and explain the phase diagram of water system.**

**Ans.** Water is the only chemical compound, hence C = 1. It can exist in 3 phases i.e., solid, liquid and vapour. Which have following equilibria.

1. Single phase equilibria

(a) Solid ice—represented by area BOC

(b) Liquid  $\text{H}_2\text{O}$ —represented by area AOC

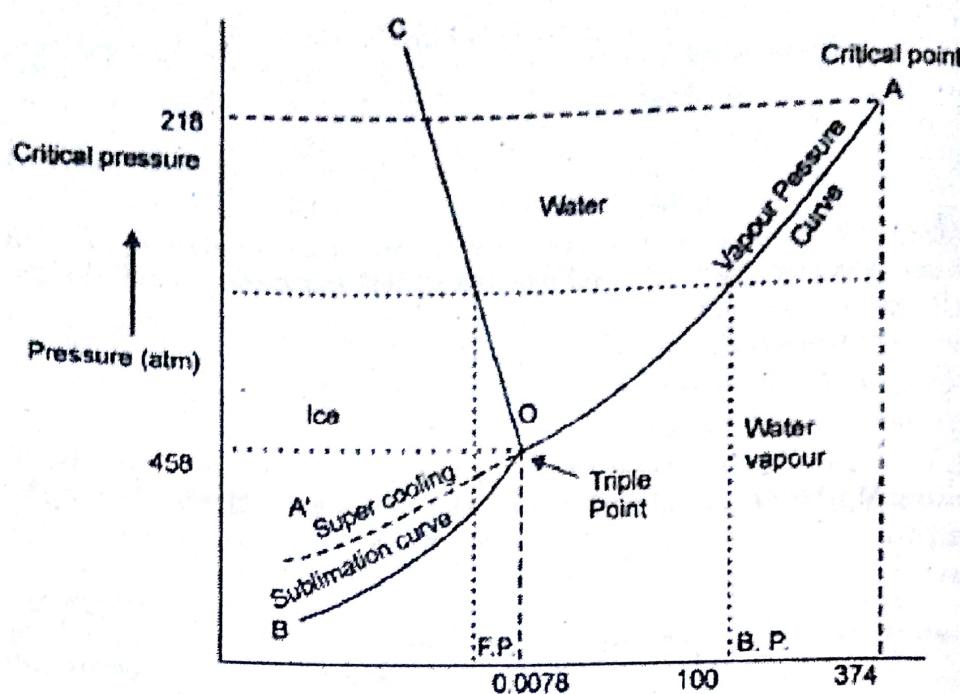
(c) Gas (vapour)—represented by area AOB

Here

$$P = 1$$

$$F = C - P + 2 \Rightarrow 1 - 1 + 2 = 2.$$

∴



System is bivariant and the both T and P must be specified to define the state of system.

### 2. Two phase equilibria:

- (a) Solid  $\rightleftharpoons$  liquid (curve OC)
- (b) Solid  $\rightleftharpoons$  Vapour (Curve OB)
- (c) Liquid  $\rightleftharpoons$  Vapour (Curve OA)

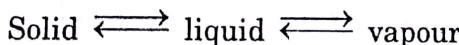
Hence,

$$P = 2$$

$$\therefore F = C - P + 2 = 1 - 2 + 2 = 1$$

System is univariant and only one variable is sufficient to describe the system state.

### 3. Three phase equilibria



$$P = 3$$

$$\therefore F = 0$$

$\Rightarrow$  System is univariant at the triplepoint 0 (0.0098°C and 4.58 mm Hg)

Since the maximum value of  $F = 2$ , this water system is represented by P-T diagram.

4. Metastable curve OA'  $\Rightarrow$  It is continuation of vapourization curve OA. It is vapour pressure curve of supercooled liquid.

**Q.1. (g) Explain the term inhibitors and poisoning agents in a catalytic reaction with suitable examples.**

**Ans. Inhibitor of Catalysis:** When the rate of reaction is retarded or diminished due to presence of a substance is called an inhibitor or negative catalyst:

Mechanism is explained by any of the following causes:

1. By poisoning or removing or counteracting the existing positive catalyst.

For e.g., : The decomposition of  $\text{H}_2\text{O}_2$  is catalyzed by traces of alkali dissolved from the glass container. Addition of an acid will destroy the alkali catalyst and retard the decomposition of  $\text{H}_2\text{O}_2$ .

**2. By breaking a chain reaction.**

For e.g.: The phenomenon of knocking in IC engines is connected with the propagation of non stationary branched chains. Anti knock materials like TEL produce metal compounds like peroxide which destroy chain carriers.

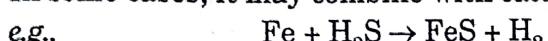
**3. By altering the surface of the walls of the reaction vessel.**

e.g.: The oxidation of liquid Benzaldehyde by O<sub>2</sub> gas is believed to be a wall reaction and walls catalyze the reaction. Inhibitors affect the nature of the wall and retard the reaction velocity.

**Poisoners:** The presence of small amount of certain substances destroys or lowers the activity of some catalysts.

e.g.: monolayer of CO on the Pt surface marks the surface unavailable for the adsorption of reactants and hence the rate of reaction decreases.

In some cases, it may combine with catalyst.



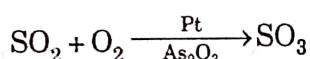
Depending on extent and strength of adsorption, it is 2 types:

**(a) Temporary Poisoning:** In this activity of the catalyst is restored when the substance responsible for poisoning is removed from the reaction.

e.g.,: (a) Combination of N<sub>2</sub> and H<sub>2</sub>, iron is used as catalyst. Water vapour or O<sub>2</sub> act as temporary poisons by uniting with Fe to form an oxide of iron. If water vapor is removed from the gas, the iron oxide is reduced to iron by H<sub>2</sub> present and its catalyst activity is restored.

**(b) Permanent Poisoning:** The poisons affect the catalyst to such an extent, that its activity is virtually changed. It is not easy to reactive.

e.g.,: Oxides of arsenic permanently poisons the catalytic power of Pt in the contact process for making SO<sub>3</sub> from SO<sub>2</sub>



**Q.1. (h) determine the number of components in a following system:**

**(i) A mixture of N<sub>2</sub>, H<sub>2</sub> and NH<sub>3</sub> gas.**

**Ans.**  $\text{NH}_4\text{Cl}(g) = \text{NH}_3(g) + \text{HCl}(g)$

$$[\text{NH}_3] = [\text{HCl}]$$

$$S = 3 \quad R = 2$$

$$C = S - R = 3 - 2 = 1 \text{ one component.}$$

$$[\text{NH}_3] = [\text{HCl}]$$

$$S = 3 \quad R = 1$$

$$C = S - R = 3 - 1 = 2 \text{ two component}$$

**Q.1. (i) What is Pilling-Bed Worth Rule?**

**Ans. Bedworth Rule-Pilling:** An oxide is protective or non-porous if the volume of the oxide is at least as great as the volume of the metal from which it is formed. If the volume of the oxide is less than the volume of the metal, the oxide layer is porous (or non-continuous) and hence non-protective because it cannot prevent the access of oxygen to the fresh metal surface below. The ratio of the volume of metal oxide to the volume of the metal is also known as specific volume ratio.

Specific Volume Ratio = MO/M; where MO = Volume of Metal Oxide, M = Volume of Metal

Smaller the specific volume ratio greater is the oxidation corrosion. Alkali and alkaline earth metals form oxide of volume less than the volume of metal, thus the oxide layer faces stress and strain, developing cracks and pores. Porous oxide scale permits free access of oxygen to the underlying metal surface for fresh action, and corrosion continue. Metal like Aluminum and Copper from oxides, whose volume is greater than

the volume of the metal, thus an extremely tightly adhering non porous layer is formed. Due to the absence of cracks or pores the rate of oxidation rapidly decreases to zero.

Example, the specific volume ratio of W, Cr and Ni is 3.6, 2.0 and 1.6 respectively, therefore the rate of corrosion of W is least even at high temperature.

**Q.1. (j) What are the conditions for dry and wet corrosion? Explain why impure metal corrodes faster than pure metal under identical conditions?**

**Ans.**

| Chemical Corrosion   | Electrochemical/Wet Corrosion  |
|--|--|
| <ol style="list-style-type: none"> <li>It occurs due to direct chemical attack of metal by environment</li> <li>It is explained by absorption mechanism</li> <li>The product of corrosion accumulate on the same spot where corrosion occurs</li> <li>It occurs on homogeneous and heterogeneous surfaces</li> <li>It is slow process</li> </ol> | <ol style="list-style-type: none"> <li>It occurs due to the formation of large number of anodic and cathodic areas in conducting medium.</li> <li>It follows the electrochemical reaction</li> <li>Corrosion occurs at anode while corrosion products gather at cathode</li> <li>It occurs only on heterogeneous metal surfaces.</li> <li>It is a fast process.</li> </ol> |

Corrosion always occurs most readily when two dissimilar metals are joined in a conducting solution, called an electrolyte. A galvanic cell forms. The second, more inert metal bleeds electrons from the anodic metal and so a continuous flow of electrons occurs if the circuit is completed. Oxidation of the anodic metal occurs and oxidation means corrosion.

Impure iron rusts more quickly than pure iron because the impurities may act as the cathode. The  $O_2$  is reduced on these impurities.

The rusting of iron is accelerated when it is in contact with a less active metal such as copper or tin because less active metals serve as the cathode.

## UNIT-I

**Q.2. (a) Differentiate between Proximate and Ultimate analysis of coal. How is coke manufactured by Otto-Hoffmann Oven?** (6.5)

**Ans. Proximate and ultimate analysis**

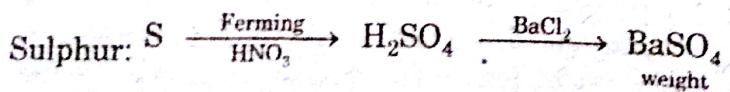
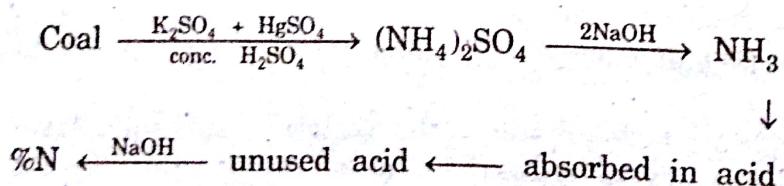
Proximate analysis is an empirical but important analysis. It determine moisture, ash, volatile member and fixed carbon of coal.

**Refer to Q.3(a) of First Term Examination 2013.**

**Ultimate analysis:** This analysis ascertain the composition of coal. Ultimate analysis estimates carbon, hydrogen, sulphur, nitrogen and oxygen.

**Carbon and hydrogen:** Coal in presence of oxygen get converted to  $CO_2$  and  $H_2O$  and passed thro'  $CaCl_2$  (which absorb  $H_2O$ ) and  $KOH$  (absorb  $CO_2$  to give  $K_2CO_3$ )

**Nitrogen:**



$$\%C = \frac{12}{44} \times \frac{\text{increase in wt.} \times 100}{\text{wt. of coal taken}}$$

$$\%H = \frac{2}{18} \times \frac{\text{increased wt. of tube} \times 100}{\text{wt. of coal taken}}$$

$$\%N = \frac{1.4 \times N_1 \times V_1}{W}$$

$N_1$  = Normality of acid

$V_1$  = Vol. of acid

$W$  = Sample taken

$$\%S = \frac{32}{233} \times \frac{W_1}{w} \times 100$$

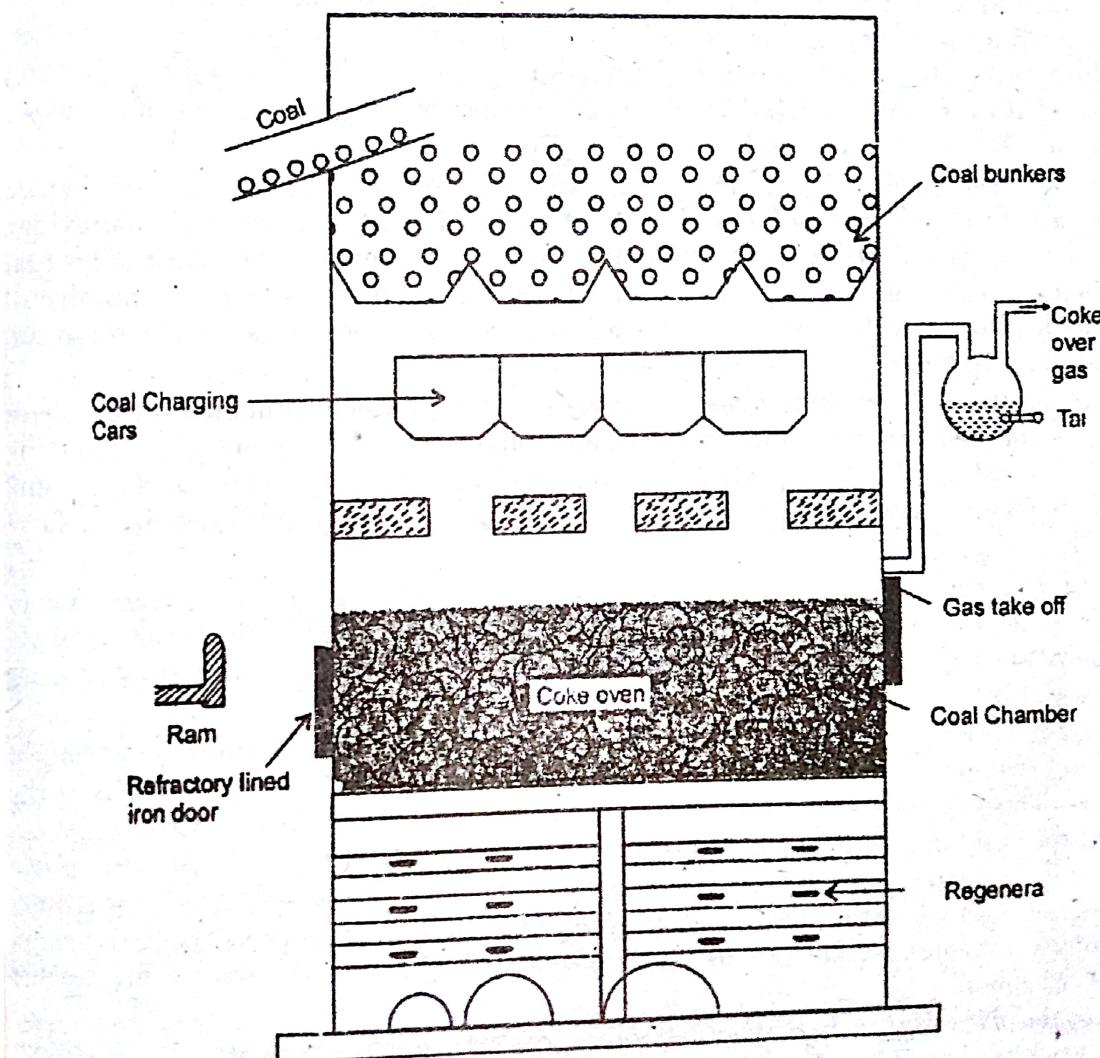
$W_1$  = weight of precipitate

$w$  = amount of coal taken

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

**Otto Hoffman:** The Otto Hoffman's Oven consists of number of narrow silica chambers. Each chamber is nearly 10-12 meter long, 3-4 in high and 0.4 - 0.45 m wide. These chambers are erected side by side with vertical flues in between them to form a sort of battery.

Each chamber is provided with a charging hole at the top, a gas off take and a refractory line cast iron door at each end for discharging coke.



Coal is charged into the chamber and the chambers are closed tightly at both the ends. The coke ovens are heated to 1200°C by burning gaseous fuels. The process of carbonization takes place layer by layer in the coal charge starting from the two side walls of the oven and moving towards the centre. As the coal adjacent to the oven walls gets heated, a plastic zone is formed which moves away from the walls towards the central zone. This moving plastic zone then heats up the central zone. There is decrease in volume as coke forms because of removal of volatile matter in the form of tar and gas at 500°C. At temperature of about 750~800°C, the plastic mass solidifies as a into hard and porous mass called coke.

**Regeneration :** It is employed to achieve economical heating. The waste gases during combustion are passed through the regenerators and then let off to the atmosphere through the chimney. These are built underneath the ovens. The flue gases pass their sensible heat to the checker brick work of regenerators until the temperature rises to 1000°C. The flow of heating flue gases is then reversed and the inlet gases used for combustion are passed through the heated checkers brick work of regenerators. After some time the flow of gases is again reversed so that the waste combustion gases again heat the checker brick work. These regenerators work on the principle of alternate heating and cooling cycles and is achieved by periodically changing the direction of flow of gases through the vertical flues every 30 minutes or so.

Carbonization of coal takes about 11-18 hours. After the process is complete, red hot coke is pushed outside by means of an electrically driven ram. The yield of coke is about 75% of coal. The coal is then sent to quenching.

**Recovery of By-products:** The gases and vapours evolved on carbonization in coke ovens are not allowed to mix with the combustion and are collected separately. The gas known as coke oven gas is treated separately for the recovery of the valuable by-products. First the gas which is at high temperature is allowed to bubble through water in the hydraulic main, which acts as a water seal preventing the passage of the gases back into the retort when it is opened.

(i) *Recovery of Tar:* The gas from the coke ovens is passed through a tower in which liquor ammonia is sprayed. Tar and dust get collected in a tank. The tank is provided with heating coils to recover back the ammonia. The ammonia is used again. The 'coal tar' is a valuable source of chemicals. The tar obtained is distilled to give a number of products like crude benzene, phenolic compounds, pyridine bases, heavy naphtha, anthracene oil etc.

(ii) *Recovery of Ammonia:* Next, the gases are then passed through a tower where water is sprayed to recover ammonia. The ammonia can also, be removed by dissolving it in H<sub>2</sub>S0<sub>4</sub> to form (NH<sub>4</sub>)<sub>2</sub>S0<sub>4</sub>, which is then used as a fertilizer. The removal of ammonia from the gas is necessary otherwise it may cause blockage of the gas pipes in the form of (NH<sub>4</sub>)<sub>2</sub>CO<sub>3</sub>.

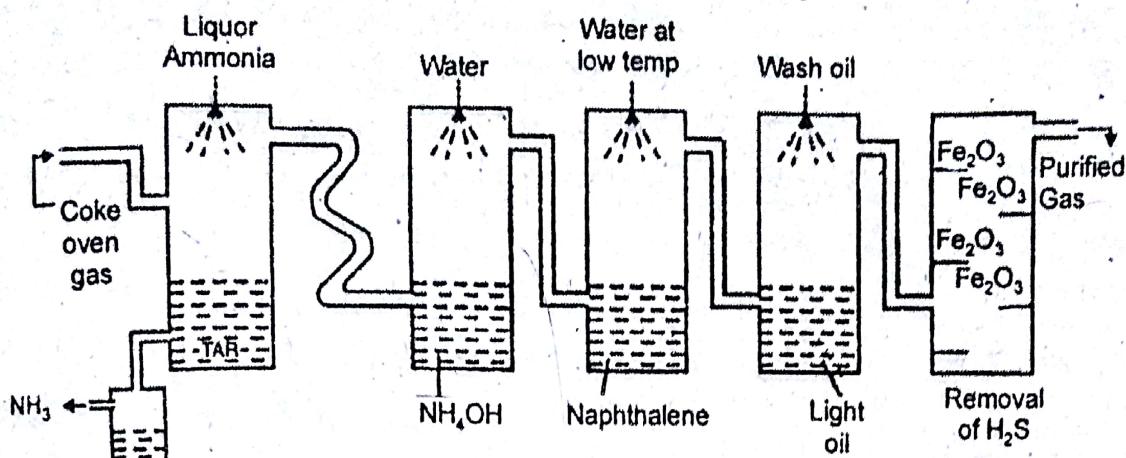
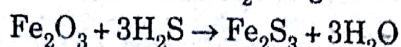
(iii) *Recovery of Naphthalene:* The gases are passed through a cooling tower, where water at a low temperature is sprayed. The gas is scrubbed with water until its temperature reduces. The naphthalene gets condensed here which is collected along with water and recovered.

(iv) *Recovery of Benzene:* The gases are then introduced into a light oil or benzene scrubber, where benzene along with its homologue is removed and is collected at the bottom. The wash oil along with the benzene homologues is known as the light oil. (Light oil is lighter than water and hence it is called light oil. It is a mixture of low boiling hydrocarbons, benzene, benzene homologues and the solvent used for washing. The solvent is a mixture of ethyl methyl benzene, trimethyl benzene etc.) Separation of different components of the light oil is carried out by distillation. The solvent is returned to the scrubber.

(v) *Recovery of H<sub>2</sub>S:* H<sub>2</sub>S and other sulphur compounds are removed, from the coke oven gas after the light oil has been separated out.

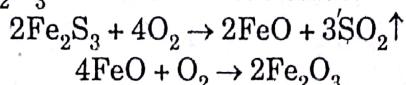
Sulphur compounds present in coal gas must be removed because sulphur along with its oxides,  $\text{SO}_2$  and  $\text{SO}_3$  aid corrosion. Moreover  $\text{H}_2\text{S}$  has offensive odour.

For the removal of sulphur and  $\text{H}_2\text{S}$  gas, the gas is passed through a chamber, packed with moist  $\text{Fe}_2\text{O}_3$ , which reacts with  $\text{H}_2\text{S}$  to give  $\text{Fe}_2\text{S}_3$ .



Schematic Diagram of Coke-Oven Gas Treatment Plant

After some time when all the  $\text{Fe}_2\text{O}_3$  is converted into  $\text{Fe}_2\text{S}_3$ , the purifier is exposed to the atmosphere when  $\text{Fe}_2\text{S}_3$  is oxidized to the oxide.



The  $\text{SO}_2$  obtained can be used for the manufacturing sulphuric acid, which can be used to absorb  $\text{NH}_3$  from the coal gas.

The purified coke oven gas is finally stored over water in holders. It is mostly used as domestic fuel in countries where coal is cheap. The main components of coal gas or coke oven gas are  $\text{CH}_4$  and  $\text{H}_2$  along with small percentage of  $\text{CO}_2$ ,  $\text{CO}$ ,  $\text{N}$ , and oxygen.

**Q.2. (b) A sample of coal was found to contain the following:** (6)

**C = 81%, H = 4%, O = 2%, N = 1.0%** the remaining being ash. Estimate the quantity of minimum air required for complete combustion of 1 kg of the sample. find the composition of dry flue gas by volume, if 40% excess air is required.

**Ans.** 1 kg of coal contain = C = 0.811g H = 0.04 kg

O = 0.02 kg N = 0.01 kg

| Constituted         | Combustion reaction   | Amount of O <sub>2</sub>           | Amount of dry producer             |
|---------------------|---|------------------------------------|------------------------------------|
| C                   | $\text{C} + \frac{1}{2}\text{O}_2 \rightarrow \text{CO}_2$          | $\frac{32}{12} \times 0.01 = 2.15$ | $\frac{44}{12} \times 0.81 = 2.96$ |
| H <sub>2</sub>      | $\text{H}_2 + \frac{1}{2}\text{O}_2 \rightarrow \text{H}_2\text{O}$ | $\frac{16}{2} \times 0.04 = 0.32$  | —                                  |
| O<br>N <sub>2</sub> | —   | —                                  | —                                  |

Oxygen required for burning 1 kg of fuel =  $[2.15 + 0.32] - 0.02 = 2.45 \text{ kg}$

$$\text{air required} = \frac{2.45 \times 100}{23} = 10.65 \text{ kg}$$

$$\text{Vol. of air required} = 10.65 \times \frac{28.94}{22.4}$$

$$= 13.75 \text{ m}^3$$

$$\text{Vol. of air supplied} = 13.75 \times \frac{140}{100} = 19.25 \text{ m}^3$$

$$\text{excess air} = 19.25 - 13.75 = 5.5 \text{ m}^3$$

$$\text{Vol. of CO}_2 = 2.96 \text{ m}^3$$

$$\text{Vol. of O}_2 = \text{excess air} \times \frac{21}{100} = \frac{5.5 \times 21}{100} = 115.5 \text{ m}^3$$

$$\text{Vol. of N}_2 = 79\% \text{ of air used} + \text{N}_2 \text{ in fuel}$$

$$= \frac{79 \times 19.25}{100} + 0.01$$

$$= 15.21 \text{ m}^3$$

$$\text{Total dry products} = 15.21 + 115.5 + 2.96$$

$$= 133.66$$

$$\% \text{ of CO}_2 = \frac{2.96}{133.6} \times 100 = 2.21\%$$

$$\% \text{ of N}_2 = \frac{15.2}{133.6} \times 100 = 11.3\%$$

$$\% \text{ of O}_2 = \frac{115.5}{133.6} \times 100 = 86.4\%$$

**Q.3. (a) Describe the bomb's calorimeter used for the determination of calorific value of fuels. Also, outline the principles involved in refining of petroleum and name of chief components separated? (6.5)**

**Ans.** Bomb calorimeter is used to find calorific value solid and non-volatile liquid fuels. It consists of following parts.

1. Steel bomb
2. Copper calorimeter → It consists of electrical stirrer and Backmann thermometer.
3. Copper calorimeter is surrounded by air and water jacket.
4. Crucible made of Ni, or fused silica.

**Working:** Given fuel is taken in silica crucible. Fine Mg wire is stretched across the electrode. Oxygen is maintained at 25 atm pressure. Bomb is placed in calorimeters having known amount of water. Initial Temperature of water is noted. The fuel is burnt using 6V battery. This heat of fuel is transferred to water. Time taken to cool the water from max. temperature to room temperature is noted. The calorific value is calculated below:

Heat gained by water =  $W \times \Delta t \times \text{Specific heat of water weight of water in calorimeter, stirrer.}$

Heat liberated by fuel =  $\propto C$

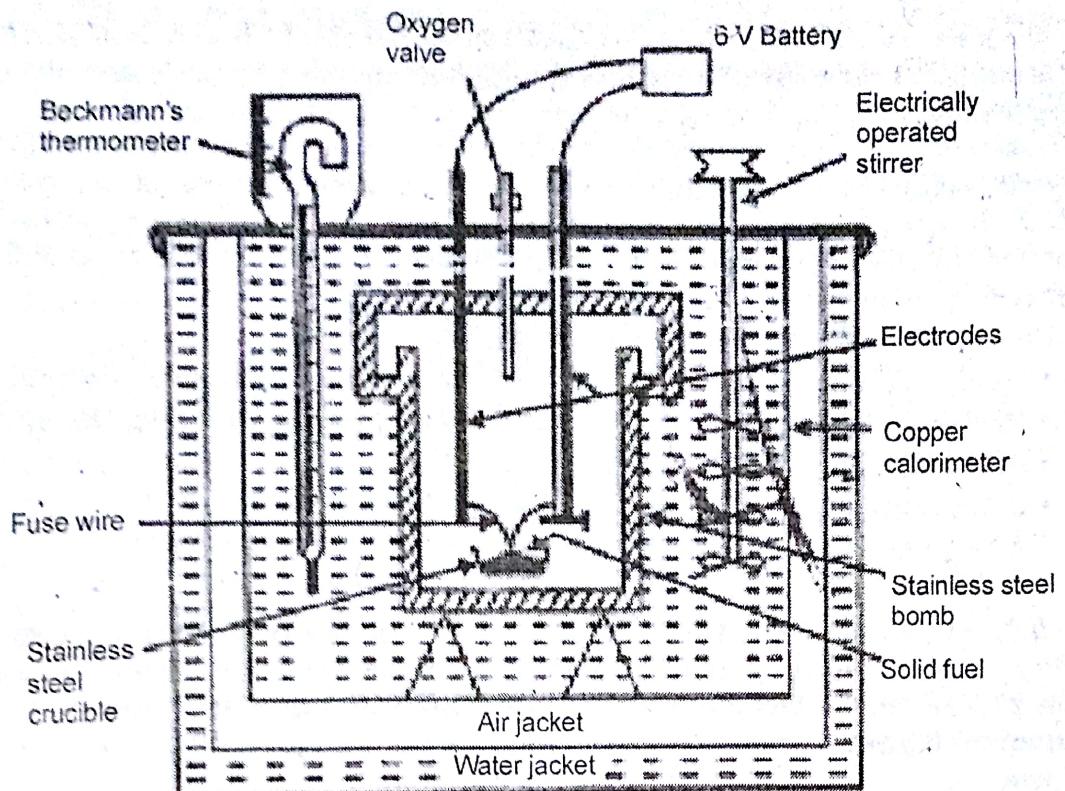
Heat liberated by fuel = Heat gained by water and calorimeter.

$$XC = (W \times w)(t_2 - t_1)$$

$$(\text{HCV}) C = \frac{(W + w)(t_2 - t_1)}{X} \text{ cal/g}$$

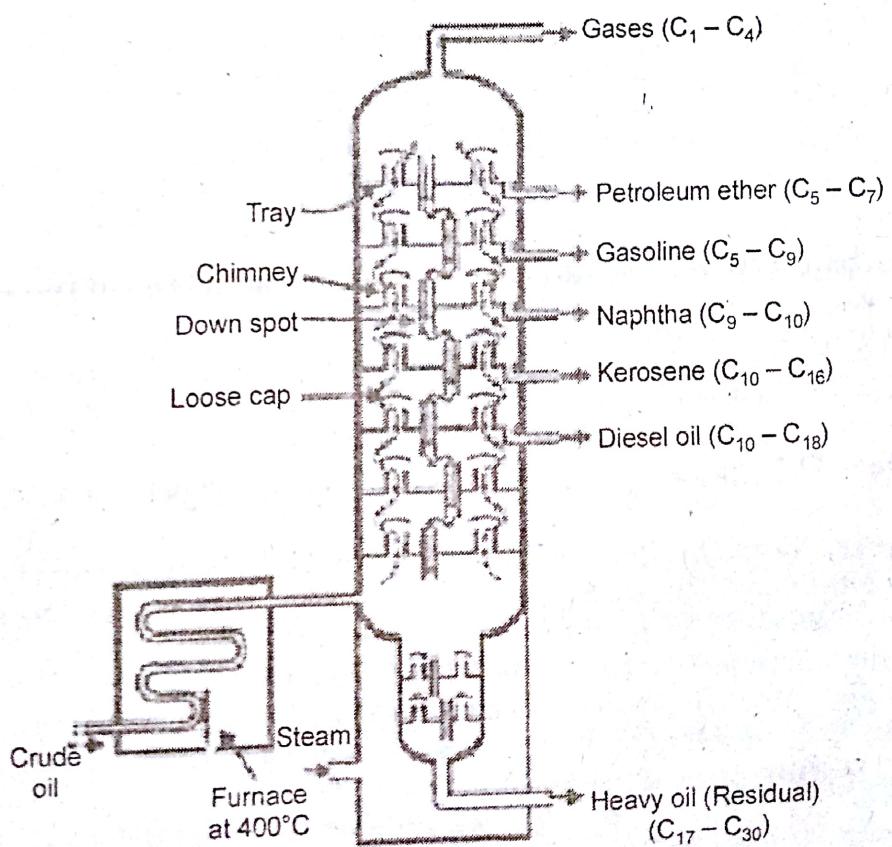
NCV = GCV - Latent heat of water formed.

C =  $0.09 H \times 58.7 \text{ Cal/g.}$



**Ans. Refining of Petroleum:** The fractional distillation of petroleum is carried out in a specially designed tall fractionating tower or column made up of steel.

The crude oil is pre-heated to 350–380°C in a specially designed tubular furnace. The hot vapours from the crude are passed through a tall fractionating column. The bubble tower consist of number of horizontal trays, provided with number of small chimneys, through which vapour rises. The chimney are covered with loose caps.



The separation of various fraction is based on the fact that hydrocarbon of petroleum boil at different temperature. The temperature in fractionating tower decreases gradually on moving upwards. As the vapour of crude oil go up they become cool and fraction condensation takes place at different heights of column. Condensation takes place at different heights of column. Higher boiler fraction condense at lower plates where as lower boiling fractions condense turn by turn at upper plates. Thus, the acid oil get separated into different fraction in order of their boiling range and are collected at different heights in the column.

Chief components of refining are:

- Liquified petroleum gas (LPG)
- Naphtha
- Diesel fuel
- Lubricating oils
- Asphalt and tar
- Sulfur.
- Gasoline (also known as petrol)
- Kerosene and related jet aircraft fuels
- Fuel oils
- Paraffin wax
- Petroleum coke

**Q.3. (b) Calculate the HCV (in kJ/kg) of 0.75 g of a fuel containing 85% of carbon, when burnt in a bomb calorimeter, increased the temperature of water from 27.5 to 29.3°C. The calorimeter contains 250 g of water and its water equivalent is 150 g.** (6)

**Ans.**

$$x = 0.75 \text{ g}$$

$$t_1 = 27.5^\circ\text{C}$$

$$t_2 = 29.3^\circ\text{C}$$

$$W = 250 \text{ g}$$

$$w = 150 \text{ g}$$

$$\begin{aligned} \text{HCV} &= \frac{(W+w)(t_2 - t_1)}{x} \\ &= \frac{(250+150)(29.3 - 27.5)}{0.75} \\ &= \frac{400 \times 1.8}{0.75} = 960 \end{aligned}$$

## UNIT II

**Q.4. (a) What is Pattinson's process for desilverisation of lead? Draw its phase diagram also.**

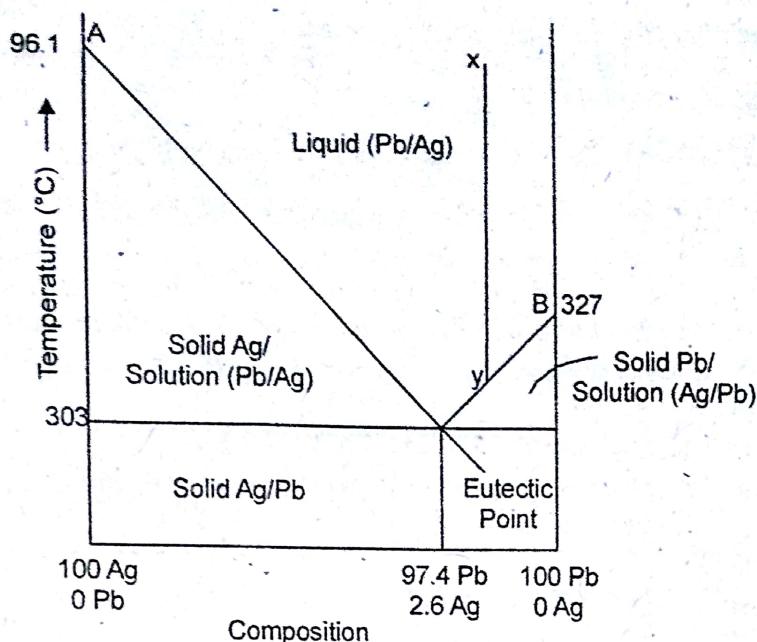
(6.5)

**Ans.** Lead-silver system is an example of eutectic system. It consists of 4 phases Ag(s), Pb(s), solution molten Pb and Ag, vapour. For this condensed phase rule is applicable  $F = C - P + 1$ . The phase diagram consists of

**1. Points:** Pt A represents the melting point of pure Pt. B represents m.pt. of pure Pb.

**2. Curves:** Curves OA represent the m.pt curve of Ag. It shows that by addition of Pb, m.pt of Ag state falling along the curve OA, till it reaches the pt O, which is a eutectic pt. The amount of Pb we added to system, the same amount of Ag will start solidifying so, of Pb. Likewise, it shows that by addition of Ag, m.pt of Pb will start falling from 327°C to 303°C. Lead will start depositing as solid, as Ag is added to it. On both these curves (i.e. OAdOB) degree of freedom is

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



**Areas:** Area above AOB is in liquid phase. The degree of freedom is two i.e. system is bivariants

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

**Eutectic Point:** At point O i.e. eutectic pt., curve OA and OB intersect. At this point, three phases present are Pb(s), Ag(s) and (Pb + Ag) melt.

$$\therefore \text{degree of freedom is } F = C - P + 1 = 2 - 3 + 1 = 0 \text{ invariant.}$$

At this pt. composition is fixed i.e. Ag = 2.6% and Pb = 97.4%. There will not be any change in composition. On further addition of Pb or Ag, or any change in temperature.

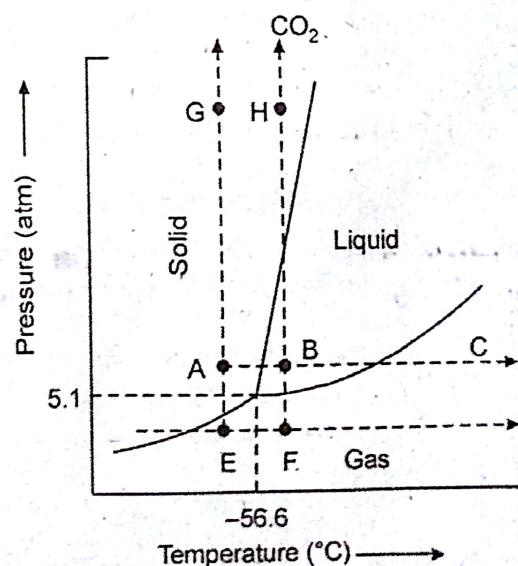
**Pattinson's Method:** The application of Pb-Ag system is in desilverisation of argenti ferrous lead. This ore contain small omt of Ag(0.1%). The ore is melted to pt. 'a'. Then it is allowed to cool along the curve xy. At pt. 'y', lead will start crystallising and solution will be richer in Ag. Now it follows the path OB. Melt will be richer in Ag till pt. O is reached. Hence the amount of Ag will increase to 2.6%.

**Q.4. (b) Draw the phase diagram of  $\text{CO}_2$  system and explain how it is different from water system. (6)**

**Ans.** The different areas of these diagrams represent conditions under which these substances are gaseous, liquid, or solid. At points 'A' and 'D', they are solid; at 'C', 'E', and 'F', gaseous; at 'B', liquid. The thick solid lines represent transitions between phases. Along these lines, two phases can exist together. At the triple point, where the lines intersect, the solid, liquid, and gas can all co-exist.

For  $\text{CO}_2$ , it falls at  $-56.6^\circ\text{C}$  and 5.1 atmospheres. The heavy dashed lines represent sequences of heating (horizontal) or squeezing (vertical):

1. Start with the ices at 'A'. Keeping the pressure constant, warm them until they reach their solid-liquid transitions. At this point the



ices melt. Further heating initially results in warmer liquids ('B'). If you warm the liquid enough, they reach their liquid-gas transitions and evaporate. Further heating results in warmer gases ('C').

2. Start with the ices at 'D'. Raising their temperature does not cause them to melt into their solid-liquid transitions, but rather into their solid-gas transitions. The ice evaporate directly into the gas phase in a process called sublimation. Further heating warms the resulting gases ('E' and 'F').

3. Start with gases at 'E'. Holding their temperature constant, squeeze them until they reach their solid-gas transitions. At this point the gases condense directly into solid ('A'). For CO<sub>2</sub> and most other materials, more pressure will not produce any additional changes ('G' on right diagram).

Difference in phase diagram of CO<sub>2</sub> and H<sub>2</sub>O:

(1) water has a negative slope due to the fact that when ice melt, the molar volume decreases. Ice actually melt at lower temperature at higher pressure. Carbon dioxide has positive slope

(2) solid carbon dioxide is called **dry ice**, because it does not go through a liquid state in its phase transition at room pressure. this is not the case for water system

(3) for water, note the triple point A (0.0098°C, 4.58 torr), the normal melting (or freezing) point B (0°C, 1 atm), the normal boiling point C (100°C, 1 atm), and the critical point D (374.4°C, 217.7 atm). In (b), for carbon dioxide, note the triple point X (-56.4°C, 5.11 atm), the normal sublimation point Y (-78.5°C, 1 atm), and the critical point Z (31.1°C, 73.0 atm).

#### **Q.5. (a) Explain the difference between the Heterogeneous and Homogeneous catalysis with suitable examples.**

**Ans. Homogenous Catalysis:**

- In homogeneous catalysis, the catalysis is in the same phase as reactants and its evenly distributed throughout this type of catalysis can occur in gas or liquid (solution) phase.

• Example

(A) In Gas Phase: Oxidation of sulphur (SO<sub>2</sub>) to sulphur trioxide (SO<sub>3</sub>) with nitric oxide (NO) as catalyst

(B) In Solution phase: Hydrolysis of cane sugar in aqueous solution in the presence of mineral acid as catalyst

- C<sub>12</sub>H<sub>22</sub>O<sub>11</sub> + H<sub>2</sub>O → C<sub>6</sub>H<sub>12</sub>O<sub>6</sub> + C<sub>6</sub>H<sub>12</sub>O<sub>6</sub> + H<sub>2</sub>SO<sub>4</sub>
- Glucose Fructose

**Heterogeneous Catalysis:**

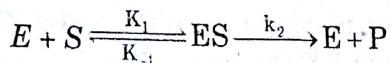
- The catalysis in which the catalyst is in a different physical phase from the reactants is termed heterogeneous catalysis, most important of such reaction are those in which the reactants are in the gas phase while the catalyst is a solid the process is called Contact Catalysis.

**Examples of Heterogeneous Catalysis:**

- (1) Heterogeneous Catalysis with gaseous reaction is (contact catalysis)
  - (A) Combination if sulphur dioxide (SO<sub>2</sub>) and oxygen in the presence of finally divided platinum or vanadium pentoxide (V<sub>2</sub>O<sub>5</sub>) (contact process for sulphuric acid)
    - 2SO<sub>2</sub> + O<sub>2</sub> + [Pt] 2SO<sub>3</sub> + Pt
    - Gas solid
  - (B) Combination of nitrogen and hydrogen to form ammonia in the presence of finally divided iron (Haber process for ammonia).
    - N<sub>2</sub> + 3H<sub>2</sub> + [Fe] 2NH<sub>3</sub> + Fe
    - Gas Gas solid

**Q.5. (b) Derive the Michaelis-Menten equation for enzyme catalysis. Explain the effect of adding an inhibitor on this equation.** (6)

**Ans. Deriving the Michaelis-Menten Equation:** In this mechanism E binds S to form an enzyme-substrate complex (ES). Michaelis and Menten therefore set out the following scheme:



The terms,  $k_1$ ,  $k_{-1}$  and  $k_2$  are rate constants

The overall rate of the reaction ( $v$ ) is limited by the step ES to E + P, and this will depend on two factors - the rate of that step (i.e.  $k_2$ ) and the concentration of enzyme that has substrate bound, i.e., [ES]. This can be written as:

$$v = k_2[ES] \quad (\text{Equation 1})$$

At this point it's important to draw your attention to two assumptions that are made in this scheme. The first is the availability of a vast excess of substrate, so that  $[S] \gg [E]$ . Secondly, it is assumed that the system is in steady-state, i.e. that the ES complex is being formed and broken down at the same rate, so that overall [ES] is constant. The formation of ES will depend on the rate constant  $K_1$  and the availability of enzyme and substrate, i.e., [E] and [S]. The breakdown of [ES] can occur in two ways, either the conversion of substrate to product or the non-reactive dissociation of substrate from the complex. In both instances the [ES] will be significant. Thus, at steady state we can write:

$$k_1[E][S] = k_{-1}[ES] + k_2[ES]$$

The next couple of steps are arrangements of this equation they are both multiplied by [ES], this given us

$$k_1[E][S] = (k_{-1} + k_2)[ES]$$

Then dividing both sides by  $(k_{-1} + k_2)$ , this becomes:

$$\frac{k_1[E][S]}{(k_{-1} + k_2)} = [ES]$$

Notice that the three rate constants are now on the same side of the equation. This new constant is termed the Michaelis constant and is written  $K_M$ .

$$\frac{(k_{-1} + k_2)}{k_1} = K_M$$

Notice that the three rate constants in the definition of  $K_M$  are actually inverted (the other way up) compared with our previous equation Substituting this definition of  $K_M$  into our previous equation now given us:

$$\frac{[E][S]}{K_M} = [ES] \quad (\text{Equation 2})$$

The total amount of enzyme in the system must be the same throughout the experiment, but it can either be free (unbound) E or in complex with substrate, ES. If we term the total enzyme  $E_0$ , this relationship can be written out:

$$[E_0] = [E] + [ES]$$

This can be rearranged (by subtracting [ES] from each side) to give:

$$[E] = [E_0] - [ES]$$

So, the [E] free in solution is equal to the total amount of enzyme minus the amount that has substrate bound. Substituting this definition of [E] back into equation 2 gives us:

$$\frac{([E_0] - [ES])[S]}{K_M} = [ES]$$

Next, multiply each side by  $K_M$ , this gives us:

$$[E_0][S] - [ES][S] = K_M[ES]$$

The collect the two  $[ES]$  terms together on the same side (you can either think of this as adding  $[ES]$   $[S]$  to both sides) This gives:

$$[E_0][S] = K_M[ES] + [ES][S]$$

$$[E_0][S] = (K_M + [S])[ES]$$

Dividing both sides by  $(K_M + [S])$  now give us:

$$\frac{[E_0][S]}{[S] + K_M} = [ES]$$

Substituting the left-hand side into Equation 1 in place of  $[ES]$  results in:

$$v = k_2 \frac{[E_0][S]}{[S] + K_M}$$

The maximum rate, which we can call  $V_{max}$ , would be achieved when all of the enzyme molecules have substrate bound. Under conditions when  $[S]$  is much greater than  $[E]$ , it is fair to assume that all  $E$  will be in the form  $ES$ . Therefore  $[E_0] = [ES]$ . Thinking again about Equation 1, we could substitute the term  $V_{max}$  for  $v$  and  $[E_0]$  for  $[ES]$ . This would give us.

$$V_{max} = k_2[E_0]$$

Notice that  $k_2[E_0]$  was present in our previous equation, so we can replace this with  $V_{max}$ , giving a final equation.

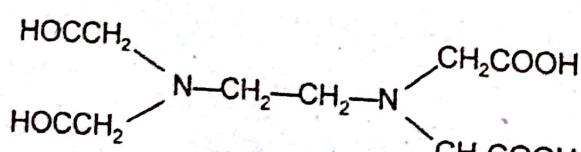
$$v = \frac{V_{max}[S]}{K_M + [S]}$$

This final equation is actually called the Michaelis-Menten equation.

### UNIT-III

**Q.6. (a) Explain the EDTA method to estimate the total hardness of water.**

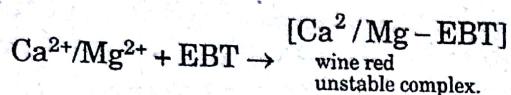
**Ans. (a)** EDTA, ethylene diamine tetroacetic acid is a strong complexing agent having structure.



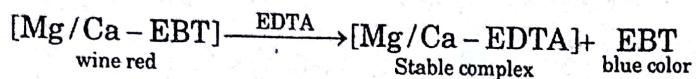
It is an hexadentate ligand and can form 4 to 6 dative bond with  $\text{Ca}^{2+}/\text{Mg}^{2+}$  It is used as disodium salt.

Principle and titration involved is

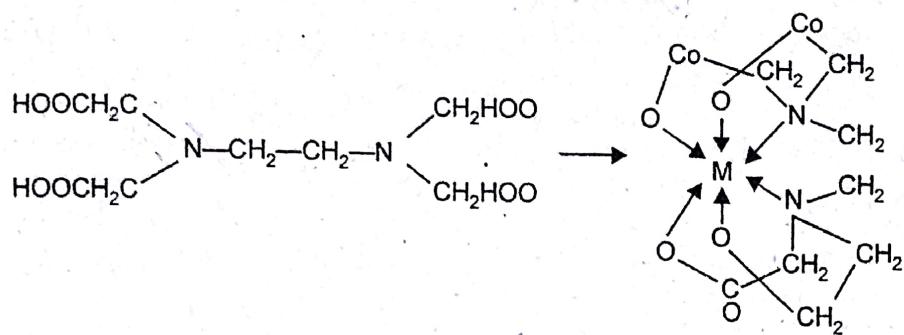
1. Prepare a standard solution of known strength.
2. To this a buffer i.e.  $\text{NH}_4\text{Cl}-\text{NH}_4\text{OH}$  is added. This buffer is added to maintain the pH between 9–10. In this pH range predominant form of Indicator is  $\text{HIn}^{2-}$  i.e. blue color.
3. Now eriochrome black-T (EBT), a blue coloured dye is added to it. On addition solution turns wine red as indicator complexes with metal ion. This complex is an unstable complex.



As this solution is titrated with EDTA, the free  $\text{Ca}^{2+}/\text{Mg}^{2+}$  ion in water form stable metal-EDTA complex.



This complex is stable because EDTA makes dative bond and cage like structure. This chelation makes the complex stable.



EDTA is again pH sensitive. It predominantly exist in  $\text{H}_2\text{Y}^{2-}$  when  $\text{pH} \approx 5$ .

**Q.6. (b) Explain the carbonate and phosphate conditioning methods for water softening. (3.5)**

**Ans. Carbonate conditioning:** In this process,  $\text{Na}_2\text{CO}_3$  is added to the boiler water.  $\text{Na}_2\text{CO}_3$  reacts with  $\text{CaSO}_4$  leading to formation of  $\text{CaCO}_3$  which can be removed by blow down operation.



**Phosphate Conditioning:** In this method  $\text{Na}_3\text{PO}_4$  is used to remove  $\text{CaSO}_4$  scale.  $3\text{CaSO}_4 + 2\text{Na}_3\text{PO}_4 \rightarrow \text{Ca}_3(\text{PO}_4)_2 + 3\text{Na}_2\text{SO}_4$ . This method is applicable in high pressure boilers. The choice of phosphate depends on alkalinity of water.

$\text{NaH}_2\text{PO}_4$  — acidic

$\text{Na}_2\text{HPO}_4$  — weakly alkaline

$\text{ab}_3\text{PO}_4$  — alkaline

**Q.6. (c)** A sample of ground water has 150 mg/l of  $\text{Ca}^{2+}$  and 60 mg/L of  $\text{mg}^{2+}$ . Find the total hardness expressed in milliequivalents per litre and mg/L in terms of  $\text{CaCO}_3$ . (3)

**Ans.**

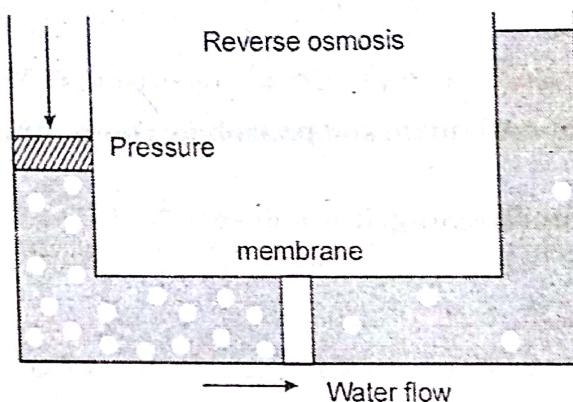
| Component        | Amount factor | Multiplication equivalent      | $\text{CaCO}_3$ |
|------------------|---------------|--------------------------------|-----------------|
| $\text{Ca}^{2+}$ | 150           | $\frac{100}{40} \times 150$    | 375 mg/L        |
| $\text{Mg}^{2+}$ | 60            | $\frac{100}{24} \times 60$     | 250 mg/L        |
| Total hardness   | =             | $375 + 250 = 625 \text{ mg/L}$ |                 |

**Q.7. (a) What is the principle of reverse osmosis? Name the membranes employed in it. Also, state the advantages of this process.** (4)

**Ans. Reverse osmosis:** As spontaneous process, "the flow of solvent from the concentrated solution to dilute soln are separated by a semi permeable membrane when a pressure greater than the osmotic pressure is applied on the more concentrated solution side, the solvent is forced to move from the more conc. soln to dilute soln. This phenomenon is called reverse osmosis."

**Principle:** Its useful for the desalination of brackish or sea water. Brackish water or sea water contain many dissolved salts and is more conc as compared to fresh water. If sea water kept in contact with fresh water through semi permeable and pressure of order 15-40 kg/cm<sup>2</sup> is applied on sea water, reverse osmosis will and water will be forced to flow from sea water to fresh water side leaving behind the dissolved salt.

**Process:** Desalination of sea water/ brackish water is carried out in a reverse osmosis cell. In this cell saline water is separated from the fresh water through semi permeable membrane made of very thin films of cellulose acetate affixed to side of a perforated plate or tube, pressure of the order 15-40 kg/ cm<sup>2</sup> is applied to sea water. Reverse osmosis take place. Advantage: 1. The process removes ionic as well as nonionic dissolved salt. It is also effective in removing colloidal impurities.



1. The process involves a very low capital and operating cost. It is suitable for converting sea water into drinking water
2. The water obtained by his process may be used in high pressure boilers
3. It removes colloidal silica which is not removed by demineralization.
  - (a) eliminates 95 to 99% of TDS (total dissolved solids), reverse osmosis is the best technology today for getting clean water free of contaminants.
  - (b) R/O systems remove salt, dissolved minerals, nitrates, pesticides, metals, and microorganisms from the water.
  - (c) R/O systems provide such diverse uses as drinking water, rinse water, car wash, water reclamation, pharmaceutical production, ice-making, laboratory and other biomedical applications, farming, and providing clean water to so many other industries that use it.
  - (d) R/O provides water for the kitchen counter in a private home as well as water for use in space.

**Q.7. (b) A 50 ml of a sample of hard water consumes 32.5 ml of 0.01 M EDTA what will be the hardness of water.** (2.5)

**Ans.** 1 ml of 0.01 M EDTA = 1 mg of CaCO<sub>3</sub>

18 ml of 0.01 M EDTA = 18 mg of CaCO<sub>3</sub>

50 ml of Hard water = 18 mg of CaCO<sub>3</sub>

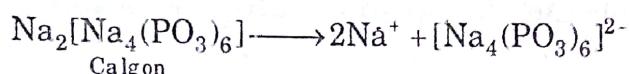
$$1 \text{ ml of Hard water} = \frac{18}{50}$$

$$1000 \text{ ml of Hard water} = \frac{18}{50} \times 1000 = 360 \text{ mg/L}$$

**Q.7. (c) Define the following: (i) Calgon conditioning, (ii) Priming and foaming, (iii) Electrodialysis.** (6)

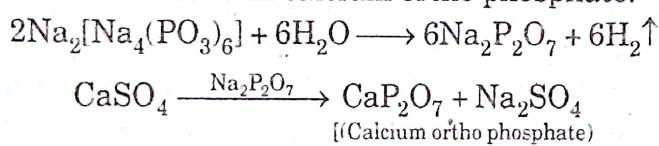
**Ans. (i) Calgon Conditioning:** Calgon conditioning involves addition of sodium hexa meta phosphate known as calgon to boiler water to prevent scale and sludge formation.

It converts the scale forming impurity like  $\text{CaSO}_4$  into soluble complex, compound, which are harmless to boiler.



- At low temperature and pressure, it forms quite stable and soluble complexes with calcium salts.

- At high temperature and pressure, calgon is converted into sodium ortho phosphate which reacts with calcium salts to form calcium ortho phosphate.



$\text{CaP}_2\text{O}_7$  appears as loose sludge and can be removed by blow down operation.

**(ii) Priming:** The phenomenon of formation of wet steam i.e. steam associated with water droplets is called priming. It is caused by the high steam velocity, high water level, sudden steam demand, faulty boiler design and presence of impurities in water. Priming can be avoided by

- Keeping water level low
- Efficient softening and filtration of boiler feed water.
- Good boiler design.

**Foaming:** is formation of small persistent bubbles at the surface of water in boiler. Foaming occurs due to presence of oil/gases in water. Foaming can be avoided by

- Using antifoaming chemicals e.g. castor oil.
- Removing oil from boiler water.

#### Disadvantage of Priming and Foaming

- dried salts deposits on engine valve thereby decreases life of machine
- water droplet presence leads to corrosion.

**(iii) Electrodialysis:** Refer to Q3(a) Second Term Examination, 2013.

## UNIT IV

**Q.8. (a) Describe the different types of corrosion and discuss the factors that affect the corrosion.** (6.5)

**Ans.** There are different types of corruptions based on the reactions and physical states.

It has been seen that there are several types of corrosion. They are:

- (a) Galvanic Corrosion
- (b) Pitting Corrosion

- (c) Stress Corrosion
- (d) Crevice Corrosion
- (e) Erosion Corrosion
- (f) Soil Corrosion
- (g) Micro-biological Corrosion
- (h) Water-line Corrosion
- (i) Differential aeration Corrosion
- (j) Intergranular corrosion

Discuss the important factors which influence the rate and extant of corrosion of the metal.

Factors affecting corrosion: (A) Nature of the metal (B) Nature of the environment

**(A) Nature of the metal :** 1. Position in galvanic series: "Higher the position of metal in the series, more its activity and greater is its tendency to undergo corrosion". More active metal – anode & larger the difference in position of two metals in galvanic series- higher is rate of corrosion of more active metal.

2. Overvoltage : "The difference between the voltage required for an electrode reaction to occur and that expected theoretically is referred to as overvoltage. Anodic metal having small overvoltage corrodes much faster as compared to that having a higher overvoltage. For example: when Zn is placed in 1N  $H_2SO_4$ , the rate of rxn is slow due to high overvoltage (0.70 V) inspite of high activity of Zn. On addition of  $CuSO_4$ , the rate of reaction becomes fast due to small overvoltage( 0.33 V) forming minute cathodes.

3. Relative area of the cathodic to anodic parts: Rate of corrosion increases with increase in ratio of cathodic to anodic part. e.g. Small steel pipe fitted in large Cu tank undergoes localized, rapid & severe corrosion.

4. Purity of the metal: Presence of impurities in metal accelerates its corrosion. Eg. Impurity of Pb or Fe or C is present in Zn, tiny electrochemical cells are set up, & Zn corroded.

5. Physical state of the metal : Grain size-The rate of corrosion increases with a decrease in grain size. orientation-Corrosion rate of copper is not uniform at all the faces. Stress- Area under stress is more anodic and undergo corrosion.

6. Nature of oxide film : In case of Aluminium oxide, lead oxide, tin oxide, volume of the oxide is greater than the volume of metal consumed. On the other hand Alkali & Alkaline earth metal Li, Na, K, Mg, Ca, Sn the volume of oxide is less than the volume of the metal.

7. Solubility of the corrosion products: If Corrosion product soluble -corrosion rate increases. On the other hand, if corrosion product is insoluble eg.  $PbSO_4$  in case of Pb in medium of  $H_2SO_4$ , it forms a protective layer on the metal surface and inhibits further corrosion.

**(B) Nature of the corroding environment:** 1. Temperature: Rate of corrosion increases with rise in temp eg. Intergranular corrosion such as caustic embrittlement take place at high rate.

2. Presence of moisture: Presence of moisture accelerates the rate of corrosion. Rusting of iron increases rapidly when humidity of air is 60-80% in comparison to dry air.

3. Presence of corrosive gases in the atmosphere: The rate of corrosion increases with the presence of  $CO_2$ ,  $H_2S$ , fumes of  $HCl$ ,  $H_2SO_4$  gases due to acidity of the liquid.

4. Nature of the ions present : Presence of chloride ion in the medium destroy the passive film and increases the rate of corrosion. on the other hand presence of silicate ions inhibit corrosion as they form an insoluble reaction product(silica gel).

5. Presence of suspended particles in the atmosphere: chemically active suspended particles like  $\text{NaCl}$ ,  $(\text{NH}_4)_2\text{SO}_4$  form strong electrolytes, increases the rate of corrosion. whereas chemically inactive suspended particles such as charcoal absorbs  $\text{H}_2\text{S}$ ,  $\text{SO}_2$  & moisture slowly increases the rate of reaction.

6. Conductance of the corroding medium: The flow of corrosion current depends on the conductance of medium. For eg. Conductance of clay and mineralized soils is much higher than those of dry sandy soils, that's why metal structure buried under clay and mineralized soils are damaged to larger extent.

#### 7. pH of the medium:

Media pH corrosion

Acidic pH  $< 7$  more

Alkaline pH  $> 7$  Less than acidic

Alkaline pH = 7 Less than acidic

#### 8. Concentration of oxygen and formation of oxygen conc. cells:

Differential aeration sets up conc. cells which enhance the rate of reaction.

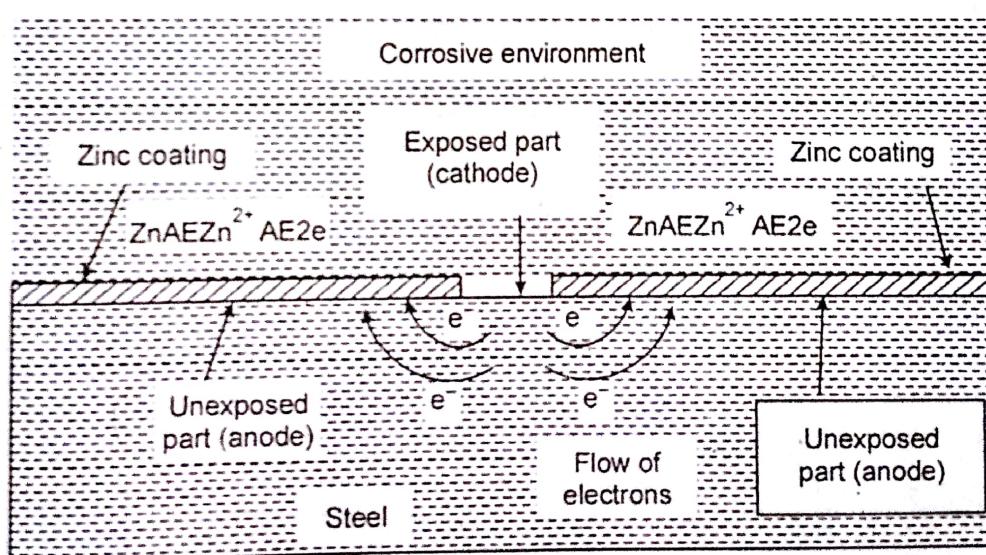
**Q.8. (b) Explain the following protective measures for corrosion:** (6)

(i) Galvanizing and tinning (ii) Cathodic protection (iii) Electroplating

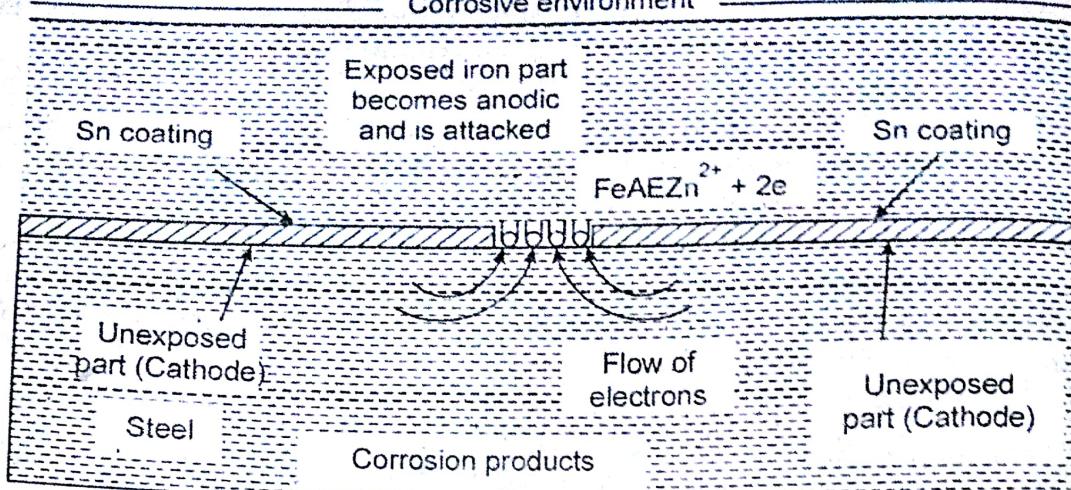
**Ans.** (i) Coating of zinc over iron is anodic coating and this process has its special name galvanisation. Zinc occupies a position before iron. In this process base metal is immersed in molten coating metal. The base metal should be very clear. Anodic coating of iron is done by Al and Cd also. If any crack or pit is formed on the coated metal, Zn will act as anode and Fe as cathode and hence Fe will not corrode (Fig. 2.8).

Since Zn is toxic, galvanised utensils are not used for cooking or food storing. Zinc coating protects iron sacrificially.

Galvanised iron is used for buckets, tubes, wires, roof sheets etc.

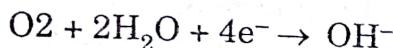
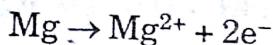


(ii) Cathodic coating of a base metal (say iron) is done by another metal which occupies a position below it in electrochemical series but it will be higher corrosion resistant. Coating of Sn over iron (tinning) is an example of cathodic protection. Cathodic protection of iron is successful only when there is no pit or crack formation on the surface of metal. Coating of tin is called tinning. Tin-coated iron is used for cooking as well as storage purposes.



**Cathodic protection (Electrical protection):** For the structures immersed in soils, **Metal to be protected-cathode**

**1. Sacrificial anode protection (galvanic protection):** more reactive(electropositive) metal - sacrificial anode Used for the protection of underground pipes and tanks, underground cables, marine structure . Reactive metal Zn/ Mg buried inside the pipe &connected by a wire. Mg- anode(oxi), Fe cathode(red) reduce  $O_2$  to  $OH^-$



**2. Impressed current cathodic protection:** Metal structure (protected) cathode(by applying an impressed current form D.C source in opposite direction. Impressed current reverse the direction of corrosion current, so metal act as cathode instead of anode.)

**(iii)** Electroplating is a process that uses electrical current to reduce dissolved metal cations so that they form a coherent metal coating on an electrode. The process used in electroplating is called electrodeposition. It is analogous to a galvanic cell acting in reverse. The part to be plated is the cathode of the circuit. In one technique, the anode is made of the metal to be plated on the part. Both components are immersed in a solution called an electrolyte containing one or more dissolved metal salts as well as other ions that permit the flow of electricity. At the cathode, the dissolved metal ions in the electrolyte solution are reduced at the interface between the solution and the cathode.

These coatings are used in particular for tribological applications, for example friction reduction and improved wear resistance. To refine metallic surfaces, various electrochemical processes are regularly used, in which for example the surfaces are electroplated with chrome or nickel. Zinc and zinc alloys are often used for corrosion resistant coatings. Well-known examples include the decorative chrome plating of plastic components in vehicles or household objects.

**Q.9. (a) Explain the term "passivity". what are the factors which affect corrosion?** (6.5) seri

**Ans.** The process in which a metal exhibits higher corrosion resistance is called passivity. When a very thin, invisible and highly protective film is formed on the surface of a metal or an alloy, it is called passivity. This film is insoluble and non-passive. A metal is passive in a certain environment if its corrosion rate is very low. By the change of the environment, the passivity of a metal may change and may become active toward corrosion. The formation of a passive film on the metal surface is determined by the

Pourbaix diagram, which depends on the electrode potential and pH of the medium. Low carbon steel does not corrode in conc.  $\text{HNO}_3$  due to protection effect of passive film. However, in dil.  $\text{HN}_3$  does not form a stable passive film and therefore dissolves steel. Passive film is formed on the surface of aluminium, Cr, Si, Ti in air, water and dilute acids. There is a good corrosion and oxidation resistance of stainless oxide passive layer.

A damage of passive film may cause intensive localised corrosion (pitting corrosion). Passive oxide layers are dissolved in electrolytes containing  $\text{SO}_4^{2-}$  and chloride. Phosphate and chromate ions stabilise passive films, promoting the regain of its defects.

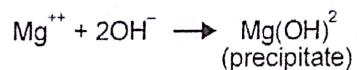
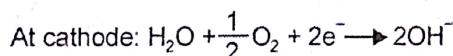
**Q.9. (b) Write short notes on the following:**

**(i) Corrosion inhibitors (ii) Galvanic corrosion (iii) Electroless plating**

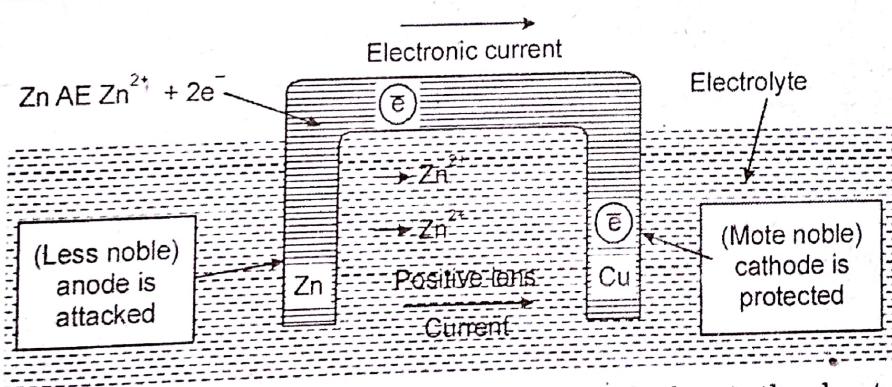
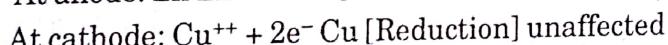
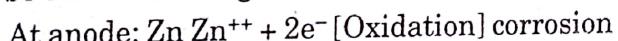
**Ans. (i)** There are some chemicals which reduce the rate of corrosion. These chemicals are called corrosion inhibitors. They are of two types, anodic and cathodic. Phosphate, chromate, tungstate protect anode.

They form sparingly soluble products which are adsorbed on the surface of metal and hence check corrosion. Cathodic protection is done by organic amines, mercaptans, thiourea and substituted urea. The above chemicals retard reduction reaction taking place at cathode.

Also, by the use of salts of Mg, Zn or Ni, the insoluble hydroxides of Mg, Zn, Ni are deposited preventing corrosion.



**(ii) Galvanic corrosion:** This type of electrochemical corrosion is also called bimetallic corrosion. When two dissimilar metals are connected and exposed to an electrolyte, they will form a galvanic cell. The anodic metal will be oxidised and it will undergo corrosion. Zinc and copper metals connected with each other in an electrolyte medium form a galvanic cell. Zinc acts as anode and undergoes corrosion while cathode will be unaffected (Fig. 2.3).



1. Galvanic corrosion can be avoided by coupling metals close to the electrochemical series.

2. Fixing insulating material between two metals.

3. By using larger anodic metal and smaller cathodic metal.

Example of galvanic corrosion: 1. Steel screws in brass marine hardware,

2. steel pipe connected to copper plumbing, 3. steel propeller shaft in bronze bearing,

4. zinc coating on mild steel, 5. lead-tin solder around copper wires.

(iii) Electroless plating is also a widely used technique to protect the base metal from the corrosion. It is also called displacement plating or Immersion coating/plating. It involves base metal to be immersed in a bath of noble metal salt used for plating. The noble metal ion is displaced from this salt solution by the base metal ion and forms a thin uniform deposit on the base metal article. The better example for electroless plating is nickel plating.

The base metal to be protected from corrosion, is immersed in a bath containing sodium hypophosphate and nickel sulphate at pH 4.5 – 5.0 and maintain bath temperature of about 100°C. The hypophosphate reduces nickel ion to metal nickel and finally converts into nickel phosphide. An alloy of nickel and nickel phosphide is deposited on the base metal article surface forming a strong adherent non-porous coating with high corrosion resistance.

**FIRST SEMESTER [B. TECH.]**  
**END TERM EXAMINATION [2014]**  
**APPLIED CHEMISTRY [ETCH-113]**

Time : 3 hrs.

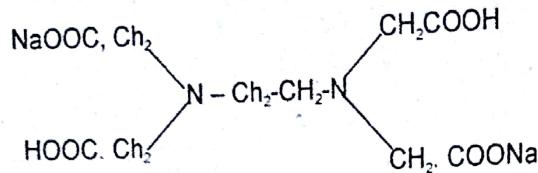
Note: Attempt any five questions including Q.No. 1 which is compulsory. Select one question from each unit.

M.M.: 70

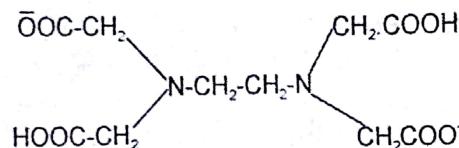
**Q.1.(a) Explain how the hardness of water is removed by EDTA method.**  
**Ans.** This is a complexometric method. Ethylene diamine tetraacetic acid (EDTA) in the form of its sodium yields the anion.

**Theory**

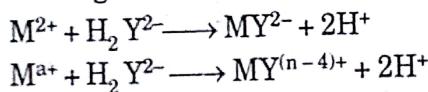
The disodium salt of ethylenediamine tetraacetic acid (EDTA)



ionises in water to give  $2\text{Na}^+$  ions and a strong chelating agent



which for simplicity can be represented by  $\text{H}_2\text{Y}^{2-}$ . It forms complexes with  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  and other divalent or higher valent cations represented by the reactions:



The dissociation of these complexes is governed by the pH of the solution and the complexes with hardness causing divalent ions are stable in alkaline medium (pH range 8-10).

When a small amount of the indicator solution is added to a hard water sample whose pH has been controlled by the addition of the buffer solution, the indicator reacts with  $\text{Mg}^{2+}$  to produce.



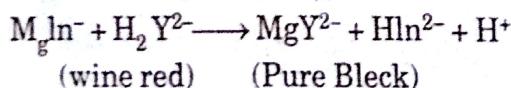
wine red colour. As EDTA ( $\text{H}_2\text{Y}^{4-}$ ) is added,  $\text{Ca}^{4+}$  ions are first complexed to  $\text{CaY}^{2-}$  this being the most stable complex:



Free  $\text{Mg}^{2+}$  ions then react to give Mg-EDTA complex which is less



stable than Ca-EDTA complex but more stable than Mg-indicator complex. Therefore, if an extra drop of EDTA is added after all the free  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  ions have been complexed, EDTA takes up  $\text{Mg}^{2+}$  from the weak Mg-indicator complex to form stable Mg-EDTA complex simultaneously liberating the indicator in the free form:



Completion of the above reaction makes the end-point of the titration.

**Q.1.(b) Define the terms thermal cracking and anti knocking agents.**

**Ans.** Thermal cracking is a process in which hydrocarbons such as crude oil are subjected to high heat and temperature to break the molecular bonds and reduce the molecular weight of the substance being cracked. This process is used to extract usable components, known as fractions, which are released during the cracking process. It is one among several cracking methods used in the petroleum industry to process crude oil and other petroleum products for commercial use. In the thermal cracking process, the compound to be cracked is subjected to high heat and pressure. Sometimes a catalyst is added to control the chemical reactions which occur during the process

An **antiknock agent** is a gasoline additive used to reduce engine knocking and increase the fuel's octane rating by raising the temperature and pressure at which auto-ignition occurs. Tetraethyl lead ( $(C_2H_5)_4Pb$ ) is a main additive and is a common antiknock compound. A small quantity of tetraethyl lead (TEL) improves the anti-knock quality of the gasoline.

**Q.1. (c) What is power alcohol? How is it manufactured from starchy material?**

**Ans.** Alcohol has been used as a fuel for internal combustion engines. The alcohols become more like petroleum fuels as their chemical weights increase. Therefore, an engine burning methyl alcohol would produce the most power. It also is possible to take advantage of the higher octane ratings of methyl (and ethyl) alcohol and increase the engine compression ratio. This would increase the efficiency of converting the potential combustion energy to power. Finally, alcohols burn more completely, thus increasing combustion efficiency. Mixing alcohol with gasoline produces gasohol or power alcohol

Corn (maize) is the most important cereal grain employed; it is produced worldwide. Potatoes have been used in distilled spirits production primarily in central Europe; in the tropics, other starchy roots are employed.

#### Milling and pressing

The purpose of milling and pressing is to make the starch or sugar more available for enzyme action. In milling, grains are reduced to a meal to allow wetting of their starch cells. The grinding action of the rollers is mainly a shearing action.

**Mashing:** The purpose of the mashing operation is to (1) mix the proper proportions of grains, (2) increase the availability of the starch for enzyme action, and (3) convert the starches into fermentable sugars.

#### Fermenting and distilling

In grain-based products, yeast cells are grown in grain mixtures. The mash is sterilized, then inoculated with lactic-acid bacteria to increase acidity. When the desired acidity is reached, the mixture is again sterilized and a pure yeast culture is added.

The previously prepared yeast is then added, and final dilution of the mixture is made. The final concentration of sugars is adjusted so that the yeast fermentation will produce a finished fermented mixture containing between 7 and 9 percent alcohol.

#### Distillation

As mentioned above, the difference in the boiling points of alcohol and water is utilized in distillation to separate these liquids from each other.

**Q.1.(d) 100 ml of  $H_2O$  sample when titrated against  $\frac{N}{50} H_2SO_4$  Using**

**phenolphthalein as an indicator, gave the end point with 10 ml of acid. Another 100 ml of the sample also required 10 ml of the acid to obtain methyl orange end point. What type of alkalinity is present in the sample and what is its magnitude?**

**Ans.** 100 ml of water upto phenolphthalein

$$\text{end pt.} = 10 \text{ ml of } \frac{N}{50} \text{ H}_2\text{SO}_4$$

$$100 \text{ ml} \times N_p = 10 \text{ ml} \times \frac{N}{50}$$

$$N_p = \frac{10 \times 1}{50 \times 100} = \frac{1}{500} N$$

Strength of alkalinity upto phenol-phthalein end pt.

$$(P) = \frac{1}{500} \times 50 \text{ g/L} = 0.1 \text{ g/L} = 100 \text{ mg/L}$$

100 ml of water upto methyl orange end point = 10 ml of  $\frac{N}{50}$  H<sub>2</sub>SO<sub>4</sub>

$$100 \text{ ml} \times N_M = 10 \text{ ml} \times \frac{N}{50}$$

$$N_M = \frac{10}{100} \times \frac{1}{50} = \frac{1}{500} N$$

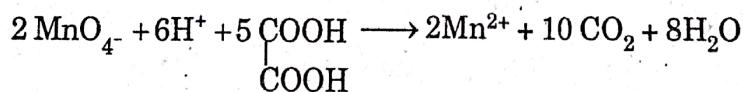
strength of alkalinity upto methyl orange end pt

$$(M) = \frac{1}{500} \times 50 = 0.1 \text{ g/L} = 100 \text{ mg/L}$$

Since P = M, only OH<sup>-</sup> ions are present P = M = 100 mg/L

#### Q.1.(e) Explain what is autocatalysis?

**Ans.** A single chemical reaction is said to have undergone **autocatalysis**, or be **autocatalytic**, if the reaction product itself is the catalyst for that reaction. In autocatalysis, the reaction is catalysed by one of its products. One of the simplest examples of this is in the oxidation of a solution of oxalic acid by an acidified solution of potassium manganate(VII) (potassium permanganate).



The reaction is very slow at room temperature. It is used as a titration to find the concentration of potassium manganate(VII) solution and is usually carried out at a temperature of about 60°C. Even so, it is quite slow to start with.

The reaction is catalysed by manganese(II) ions.

#### Q.1. (f) Derive Gibb's phase Rule.

**Ans.** The principle we extract here is that

$$\text{variance} = \text{number of variables} - \text{number of equations} \geq 0$$

Let us now apply this principle to phase equilibrium. Consider a system which is composed of *c* components. That is,

$$c = \text{number of components.}$$

We define the number of components as the **minimum** number of independent substances (compounds and/or elements) required to form the system. If you can make one substance out of the others you can't count it!

Number the components 1, 2, 3, ... c.  
Let

$$p = \text{number of phases.}$$

Enumerate the phases by lower case Greek letters,  $\alpha, \beta, \gamma, \delta, \dots, \zeta$ . Let's now count the number of variables and the number of equations. We will get the variance from

$$v = \text{variables} - \text{equations}$$

Our variables are  $T, p$ , (pressure) and the mole fractions of the components in each phase.

|                 |              |
|-----------------|--------------|
| T,              | P,           |
| $X_{1\alpha}$   | $X_{1\beta}$ |
| $X_{2\alpha}$ , | $X_{2\beta}$ |
| :               | :            |

Notice that there are  $p$  columns and  $c$  rows in the array of mole fraction variables. That is, there are  $cp$  mole fraction variables. This gives a total of  $2 + cp$  variables.

Now let's count the equations. First of all the mole fractions in each phase must sum to unity. That is

$$\begin{aligned} X_{1\alpha} + X_{2\alpha} + X_{3\alpha} + \dots &= 1 \\ X_{1\beta} + X_{2\beta} + X_{3\beta} + \dots &= 1 \\ &\vdots \end{aligned}$$

Since there is one such equation for each phase this gives  $p$  equations. Next, the chemical potential of each component must be the same in every phase. (In the following we designate  $\zeta$  as the last phase, that is the phases are denoted  $\alpha, \beta, \gamma, \dots, \zeta$ .)

$$\begin{aligned} \mu_{1\alpha} &= \mu_{1\beta} & \mu_{2\alpha} &= \mu_{2\beta} & \dots & \mu_{c\alpha} = \mu_{c\beta} \\ \mu_{1\beta} &= \mu_{1\gamma} & \mu_{2\beta} &= \mu_{2\gamma} & \dots & \mu_{c\beta} = \mu_{c\gamma} \\ &\vdots & &\vdots & &\vdots \end{aligned}$$

$$\mu_{1(\zeta-1)} = \mu_{1\zeta}, \quad \mu_{2(\zeta-1)} = \mu_{2\zeta}, \quad \dots, \quad \mu_{c(\zeta-1)} = \mu_{c\zeta}$$

(Note that there is no row of the form  $\mu_{1\zeta} = \mu_{1\alpha}$ , etc. Equations of this form are not linearly independent because they can be deduced from the other  $p - 1$  equations.) So for this array of chemical potential equations there are  $c$  columns and  $p - 1$  rows, which yields  $c(p - 1)$  equations. The total number of equations is then  $p + c(p - 1)$ . If, as we have argued above, the variance is given by

$$v = \text{variables} - \text{equations}$$

we get,

$$v = 2 + cp - p - c(p - 1)$$

$$v = 2 + c - p.$$

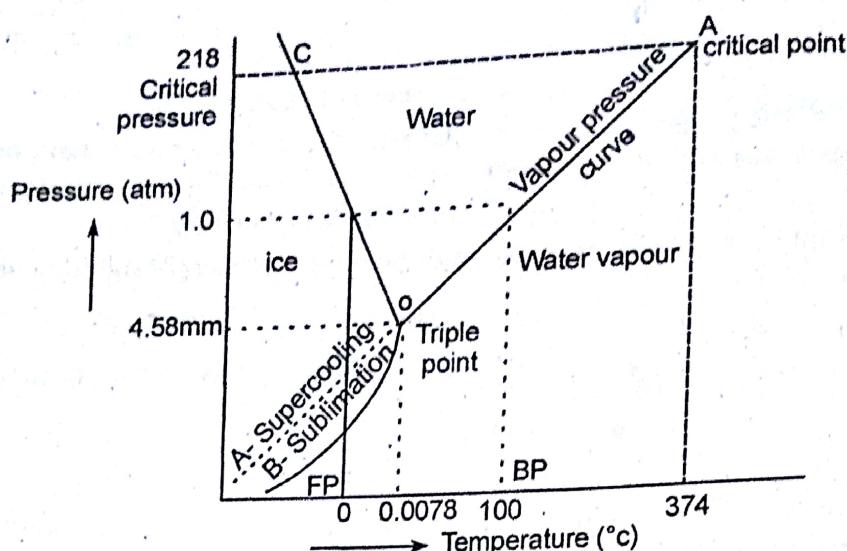
Equation 17 is called the Gibbs phase rule and it is a generally valid thermodynamic equation. That is, it contains no approximations.

**Q.1.(g) Draw the phase diagram of water system and explain the importance of a triple point.**

**Ans.** Phase diagram of water system

Refer to end term 2013 Q1(f)

**Triple point:** The point 0 where all the three curves CC, CA and OB meet is known as triple point. At the triple point all the three phases of water system namely solid ice, liquid water and gas vapour are in equilibrium. The equilibrium in three phases is attained at  $0.0076^{\circ}\text{C}$  temperature and 4.58 mm Hg pressure.



### The phase diagram of water system

Since there are 3 phases and one component present in the system, the degree of freedom will be

$$F = C - P + 2$$

$$F = 1 - 3 + 2 = 0$$

Hence the system is non various. If either the temperature or the pressure or both are changed, the three phases would no longer coexist and at least one of them would disappear.

### Q.1.(h) What is pilling-Bedworth Rule.

#### Ans. Pilling-Bedworth Rule

An oxide is protective or non-porous if the volume of the oxide is at least as great as the volume of the metal from which it is formed. If the volume of the oxide is less than the volume of the metal, the oxide layer is porous (or non-continuous) and hence non-protective because it cannot prevent the access of oxygen to the fresh metal surface below. The ratio of the volume of metal oxide to the volume of the metal is also known as specific volume ratio.

$$\text{Specific Volume Ratio} = MO/M$$

$$= \text{Volume of Metal Oxide, } M = \text{Volume of Metal}$$

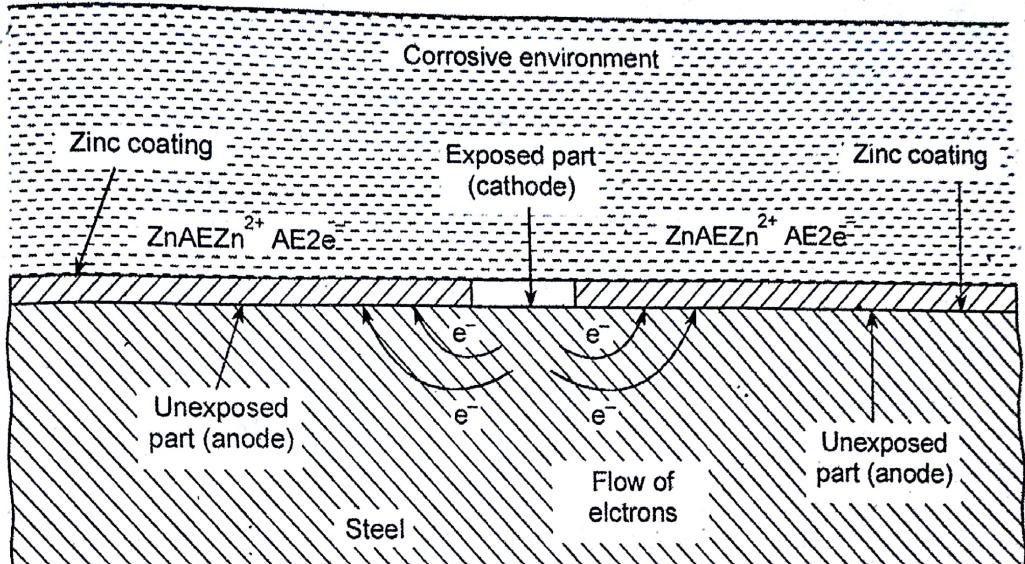
Smaller the specific volume ratio greater is the oxidation corrosion. Alkali and alkaline earth metals form oxide of volume less than the volume of metal, thus the oxide layer faces stress and strain, developing cracks and pores. Porous oxide scale permits free access of oxygen to the underlying metal surface for fresh action, and corrosion continue. Metal like Aluminum and Copper form oxides, whose volume is greater than the volume of the metal, thus an extremely tightly adhering non porous layer is formed. Due to the absence of cracks or pores the rate of oxidation rapidly decreases to zero. Example, the specific volume ratio of W, Cr and Ni is 3.6, 2.0 and 1.6 respectively therefore the rate of corrosion of W is least even at high temperature.

### Q.1.(i) What is galvanization and explain how it is done.

Ans. Coating of zinc over iron is anodic coating and this process has its special name galvanization. Zinc occupies a position before iron. In this process base metal is immersed in molten coating metal. The base metal should be very clear. Anodic coating of iron is done by Al and Cd also. If any crack or pit is formed on the coated metal, Zn will act as anode and Fe as cathode and hence Fe will not corrode.

Since Zn is toxic, gawanised utensils are not used for cooking or food storing. Zinc coating protects iron sacrificially.

Galvanised iron is used for buckets, tubes, wires, roof sheets etc.



#### **Q.1. (j) Explain the use of inhibitors and promoters in a catalytic reaction.**

**Ans. Inhibitor of Catalysis:** When the rate of reaction is retarded or diminished due to presence of a substance is called an inhibitor or negative catalyst:

Mechanism is explained by any of the following causes:

1. By poisoning or removing or counteracting the existing positive catalyst.

For e.g., : The decomposition of  $H_2O_2$  is catalyzed by traces of alkali dissolved from the glass container. Addition of an acid will destroy the alkali catalyst and retard the decomposition of  $H_2O_2$ .

2. By breaking a chain reaction.

For e.g.: The phenomenon of knocking in IC engines is connected with the propagation of non stationary branched chains. Anti knock materials like TEL produce metal compounds like peroxide which destroy chain carriers.

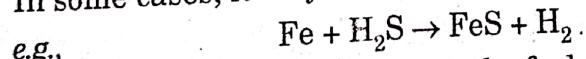
3. By altering the surface of the walls of the reaction vessel.

e.g.: The oxidation of liquid Benzaldehyde by  $O_2$  gas is believed to be a wall reaction and walls catalyze the reaction. Inhibitors affect the nature of the wall and retard the reaction velocity.

**Poisoners:** The presence of small amount of certain substances destroys or lowers the activity of some catalysts.

e.g.: monolayer of CO on the Pt surface marks the surface unavailable for the adsorption of reactants and hence the rate of reaction decreases.

In some cases, it may combine with catalyst.



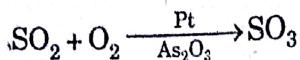
Depending on extent and strength of adsorption, it is 2 types:

(a) **Temporary Poisoning:** In this activity of the catalyst is restored when the substance responsible for poisoning is removed from the reaction.

e.g., (a) Combination of  $N_2$  and  $H_2$ , iron is used catalyst. Water vapour or  $O_2$  act as temporary poisons by uniting with Fe to form an oxide of iron. If water vapor is removed from the gas, the iron oxide is reduced to iron by  $H_2$  present and its catalyst activity is restored.

(b) Permanent Poisoning: The poisons affect the catalyst to such an extent, that its activity is virtually changed. It is not easy to reactive.

e.g., Oxides of arsenic permanently poisons the catalytic power of Pt in the contact process for making  $\text{SO}_3$  from  $\text{SO}_2$



### Promoters

**Catalytic Promotors:** Catalytic promotor is defined as a substance which promotes the activity of the catalyst to which it is added in small amounts and this process is called activation.

For e.g., In  $\text{NH}_3$  manufacture by Haber's process, finely devided Fe acts a catalyst while Mo acts as a promoter.

Promoters improve one or more of the following properties which are:

1. **Activity Enhancement:** An alkali metal can directly increase the rate of synthesis.

2. **Selectivity Enhancement:** A promoter may change pathway of a reaction to enhance the rate of formation of the selective product.

3. **Increased catalyst life time:** Sometimes a promoter can appear to have little effect on the initial performance of a catalyst, but can keep it operating longer.

This can be due to either reduction in the build-up of an irreversible poison on the surface with time, due to alteration of surface chemistry or a reduction of the sintering time.

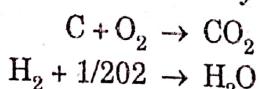
**Q.2. (a) Explain what is ultimate analysis of coal? How one can fine the % Composition of C, H, N & S using it?**

Ultimate Analysis Of Coal And Coke Is Defined In Astm D 3176 as the determination of the carbon and hydrogen in the material, as found in the gaseous products of its complete combustion, the determination of sulphur, nitrogen, and ash in the material as a whole, and the estimation of oxygen by difference. The carbon determination includes that present in the organic coal sub-stance and any originally present as mineral carbonate. The hydrogen determination includes that in the organic materials in coal and in all water associated with the coal.

Carbon and Hydrogen

The carbon is

converted to carbon dioxide and the hydrogen to water.

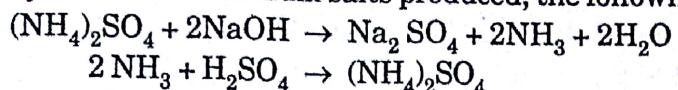


inorganic carbonates contribute to the carbon value in coal as it is normally determined. Hydrogen values also are usually high, due to the inclusion of the various forms of moisture that are present in coal.

### Nitrogen

The Kjeldahl-Gunning method is an analysis that has been widely used for determining nitrogen. In this method, any nitrogen present in the sample is converted into ammonium salts in a hot mixture of concentrated sulfuric acid and potassium sulphate. After the digestion mixture has been made alkaline with sodium or potassium hydroxide, ammonia is expelled by distillation, condensed, and absorbed in an excess of boric acid. The ammonia in the boric acid solution is then titrated with a standard acid

In the analysis of the ammonium salts produced, the following reactions take place.



### Sulphur

The sulphur content is an important value to consider in the utilization of coal and coke for most purposes.

The sulphate in the residue is extracted with hot water, treated with a  $BaCl_2$  solution to form insoluble  $BaSO_4$ . A  $BaSO_4$  precipitate that is easily filtered is to add the  $BaCl_2$  precipitant rapidly to the hot solution and stir the mixture vigorously.

### Oxygen

In an ultimate analysis, it is calculated by subtracting the sum of the as-determined percentages of C, H, N, S, and ash from 100.

$$Ox = 100 - [C + H + N + S + ash]$$

**Q.2. (b)** 2.16 g of coal was kjeldalized and  $NH_3$  gas thus evolved was absorbed in 25 ml of 0.1  $NH_2SO_4$ . After absorption, the excess acid required 12.5 ml of 0.1 N NaOH for exact neutralization. Determine the percentage of N in sample of coal.

**Ans.** 12.5 ml of 0.1 N NaOH = 25 ml of 0.1  $NH_2SO_4$

Volume of  $H_2SO_4$  used to neutralize  $NH_3$  evolved = 25 ml of 0.1 N - 12.5 ml of 0.1 N  $H_2SO_4$

$$= 12.5 \text{ ml of } 0.1 \text{ N } H_2SO_4$$

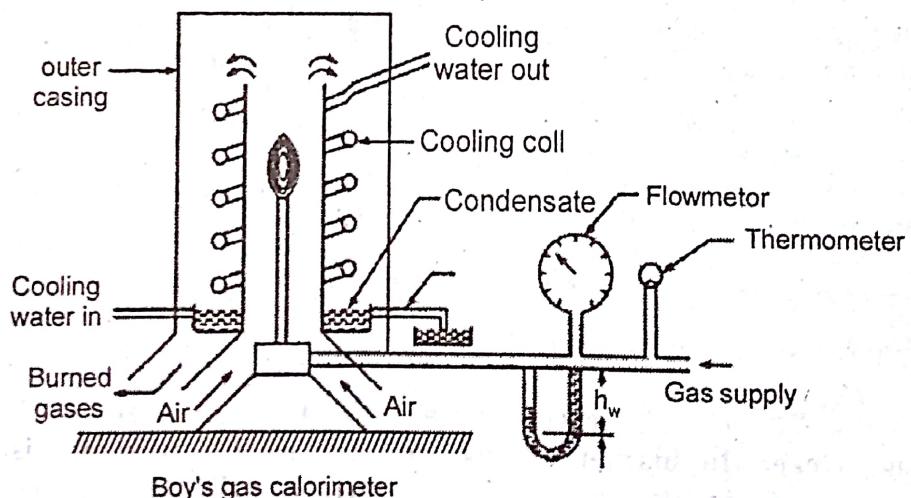
$$\%N = \frac{\text{Volume of } H_2SO_4 \times N \times 1.4}{\text{weight of coal sample}}$$

$$= \frac{12.5 \times 0.1 \times 1.4}{2.16}$$

**Q 3(a)** How the calorific value of a fuel can be determined by Boy's gas calorimeter? Explain with the help of a neat diagram.

### Ans. Boy's Gas Calorimeter

The calorific value of liquid and gaseous fuels can be determined by Boy's Gas calorimeter. The apparatus is shown in



### Boy's Gas Calorimeter

**Construction:** The apparatus consists of a suitable gas burner in which a known volume of gas at known pressure can undergo combustion at a uniform rate of 3-4 litres

per minute. Around the burner, there is a combustion chamber with a copper tube coiled inside as well as outside. Water is passed through this coil at constant rate continuously. To determine the calorific value correctly, the whole system is kept insulated.

Total

**Function:** A definite volume of gas is taken in the gas burner at definite pressure. The gas is burnt at constant rate to produce a large amount of heat. The rise in temperature in the water circulation is recorded accurately with the help of thermometer. When the steady situation with respect to rate of fuel burning and water circulation is attained, then the following observations are taken.

- The volume of gas burnt in a given time
- The quality of water circulated through the coil
- Mass of water condensed during that time
- The rise in temperature

Q.4.

Pattinson

Ans.

Q.4.

the follo

Ans

of glucose

(1)

**Calculation:** (i) Using the above observations, we can calculate HCV and LCV of liquid fuels and gaseous fuels as follows :

$$V = \text{volume of gas burnt in time } t.$$

$$W = \text{mass of water circulated in time } t.$$

$T_1$  and  $T_2$  are initial and final temperatures of water, respectively.

$L$  = Higher calorific value of fuel (cal/gm)

$m$  = mass of water condensed in time  $t$ .

(ii) Heat given by the combustion of fuel =  $V \times L$

(iii) Heat taken by the circulated water =  $W(T_2 - T_1)$

Assuming that there is no loss of heat, we can say that

$$\text{Heat given} = \text{Heat taken}$$

$$VL = W(T_2 - T_1)$$

$$\text{Gross calorific value (L)} = \frac{W(T_2 - T_1)}{V}$$

$$\text{LCV} = \text{HCV} - \text{Latent heat of water produced}$$

Weight of water condensed per m<sup>3</sup> of gas =  $m/V$

$$\text{Latent heat of steam} = (m \times 587)/V \text{ k cal}$$

$$\text{Net calorific value} = \text{GCV} - (m \times 587)/V$$

**Q.3. (b)** The % analysis by volume of producer gas is  $\text{H}_2 = 18.3\%$ ,  $\text{CH}_4 = 3.4\%$ ,  $\text{CO} = 25.4\%$ ,  $\text{CO}_2 = 5.1\%$ ,  $\text{N}_2 = 47.8\%$ . Calculate the volume of air required per m<sup>3</sup> of the gas.

(6)

Ans.

| Constituent     | Amount | Reaction  | Vol. of O <sub>2</sub> required |
|-----------------|--------|---|---------------------------------|
| H <sub>2</sub>  | 18.3   | $\text{H}_2 + \frac{1}{2}\text{O}_2 \rightarrow \text{H}_2\text{O}$<br>mole y <sub>2</sub> mole | $0.183 \times \frac{1}{2}$      |
| CH <sub>4</sub> | 0.034  | $\text{CH}_4 + \text{O}_2 \rightarrow 2\text{H}_2\text{O}$<br>1 mole 1 mole                     | $0.0915$                        |
| CO              | 0.254  | $\text{CO} + \frac{1}{2}\text{O}_2 \rightarrow \text{CO}_2$<br>1 mole y <sub>2</sub> mole       | $0.034$                         |
| CO <sub>2</sub> | 0.051  |   | $0.254 \times \frac{1}{2} =$    |
| N <sub>2</sub>  | 0.478  |   | 0.127                           |

$$\begin{aligned}\text{Total volume of O}_2 \text{ required} &= 0.0915 + 0.034 + 0.127 \\ &= 0.2525 \text{ m}^3\end{aligned}$$

$$\text{Volume of air required} = 0.2525 \times \frac{100}{21} = 1.20^3 \text{ m}$$

**Q.4. (a) Draw and explain the phase diagram of Pb-Ag system. What is Pattinson's Process?**

**Ans.** Refer to Q.4(a) of End Term Examination 2013.

**Q.4. (b) Find out the number of phases, component and degree of freedom in the following:**

**Ans.** (i)  $\text{NH}_3(\text{g})$  at  $42^\circ\text{C}$  (ii) Crystal of  $\text{Cu SO}_4 \cdot 5\text{H}_2\text{O}$  (iii) An aqueous solution of glucose.

(1)  $\text{NH}_3(\text{g})$  at  $42^\circ\text{C}$

$$P = 1 \quad C = 1$$

$$\begin{aligned}F &= C - P + 1 \quad (\text{as temperature is Constant}) \\ &= 1 - 1 + 1 = 1 \text{ univariant}\end{aligned}$$

(2) Pure crystal of  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$

$$P = 1 \text{ (crystal)}$$

$$C = 1 (\text{CuSO}_4 \cdot 5\text{H}_2\text{O})$$

$$F = C - P + 2$$

$$= 1 - 1 + 2 = 2 \text{ (bivariant)}$$

(3) An aqueous solution of glucose

$$P = 1 \text{ (solution)}$$

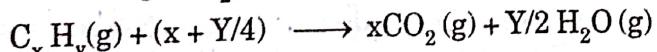
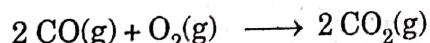
$$C = 2 \text{ (water + glucose)}$$

$$F = C - P + 2$$

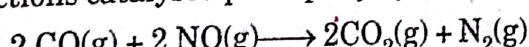
$$= 2 - 1 + 2 = 3 \text{ Invariant.}$$

**Q.5.(a) What is criteria for choosing the catalyst for industrial process? Explain the application of catalyst in industry by taking suitable example.**

**Ans.** Motor vehicles are fitted with catalytic converters. These consist of a metal casing in which there are two metals, palladium and rhodium, dispersed very finely on the surface of a ceramic support. The exhaust gases contain carbon monoxide and unburned hydrocarbons that react with the excess oxygen to form carbon dioxide and water vapour, the reaction being catalysed principally by the palladium:



The exhaust gases also contain nitrogen(II) oxide (nitric oxide, NO), and this is removed by reactions catalysed principally by the rhodium:



The accepted mechanism for the oxidation of carbon monoxide to carbon dioxide involves the chemisorption of both carbon monoxide molecules and oxygen molecules on the surface of the metals. The adsorbed oxygen molecules dissociate into separate atoms of oxygen. Each of these oxygen atoms can combine with a chemisorbed carbon monoxide molecule to form a carbon dioxide molecule.

Each of these steps has a much lower activation energy than the homogeneous reaction between the carbon monoxide and oxygen.

**Q.5. (b) Write short note on the following:**

**(i) Wilkinson's catalyst.**

**Ans.** Refer to Q.4(a) of First Term Examination 2014.

**(ii) Heterogeneous Catalysis and Homogeneous Catalysis**

**Ans. Homogenous catalysis**

- In homogenous catalysis, the catalysis is in the same phase as reactants and its evenly distributed throughout this type of catalysis can occur in gas, liquid(solution)phase.
- Example
- A) In Gas Phase :
- Oxidation of sulphur ( $\text{SO}_2$ ) to sulphur trioxide( $\text{SO}_3$ ) with nitric oxide ( $\text{NO}$ ) as catalyst.
- B) In Solution Phase:
- I. Hydrolysis of cane sugar in aqueous solution in the presence of mineral acid as catalyst.
- $\text{C}_{12}\text{H}_{22}\text{O}_{11} + \text{H}_2\text{O} \rightarrow \text{C}_6\text{H}_{12}\text{O}_6 + \text{C}_6\text{H}_{12}\text{O}_6 + \text{H}_2\text{SO}_4$
- Glucose Fructose

**Heterogenous Catalysis:**

- The catalysis in which the catalyst is in a different physical phase from the reactants is termed heterogeneous catalysis, most important of such reactions are those in which the reactants are in the gas phase while the catalyst is solid the process is called Contact Catalysis.

**Examples of Heterogeneous Catalysis:**

- I) Heterogeneous Catalysis with gaseous reaction is (contact catalysis)
- (A) Combination of sulphur dioxide ( $\text{SO}_2$ ) and oxygen in the presence of finely divided platinum or vanadium pentoxide( $\text{V}_2\text{O}_5$ ) (contact process for sulphuric acid).
- $2\text{SO}_2 + \text{O}_2 + [\text{Pt}] \rightarrow 2\text{SO}_3 + \text{Pt}$
- Gas Gas solid
- (B) Combination of nitrogen and hydrogen to form ammonia in the presence of finely divided iron (Haber process for ammonia).
- $\text{N}_2 + 3\text{H}_2 + [\text{Fe}] \rightarrow 2\text{NH}_3 + \text{Fe}$
- Gas Gas solid

**Q.6. (a) Explain the following terms:**

- (i) Reverse Osmosis (ii) Electro dialysis (iii) Priming & foaming.**

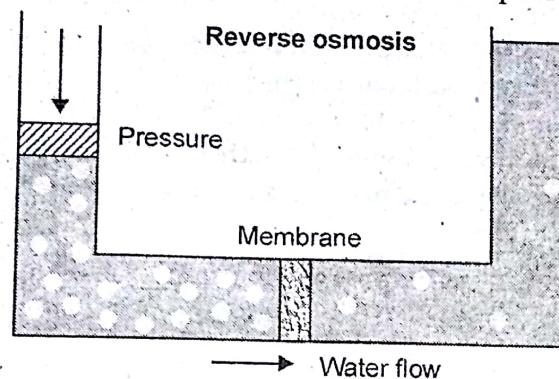
**Ans. (i) Reverse Osmosis**

**Ans. Reverse osmosis:** Spontaneous process, "the flow of solvent from the concentrated solution to dilute soln are separated by a semi permeable membrane when a pressure greater than the osmotic pressure is applied on the more concentrated solution side, the solvent is forced to move from the more conc. solution to dilute solution. This phenomenon is called reverse osmosis."

**Principle:** Useful for the desalination of brackish or sea water. Brackish water or sea water contain many dissolved salts and is more concentration as compared to fresh water. If sea water kept in contact with fresh water through semi permeable and pressure

of order 15-40 kg/cm<sup>2</sup> is applied on sea water, reverse osmosis will and water will be forced to flow from sea water to fresh water side leaving behind the dissolved salt.

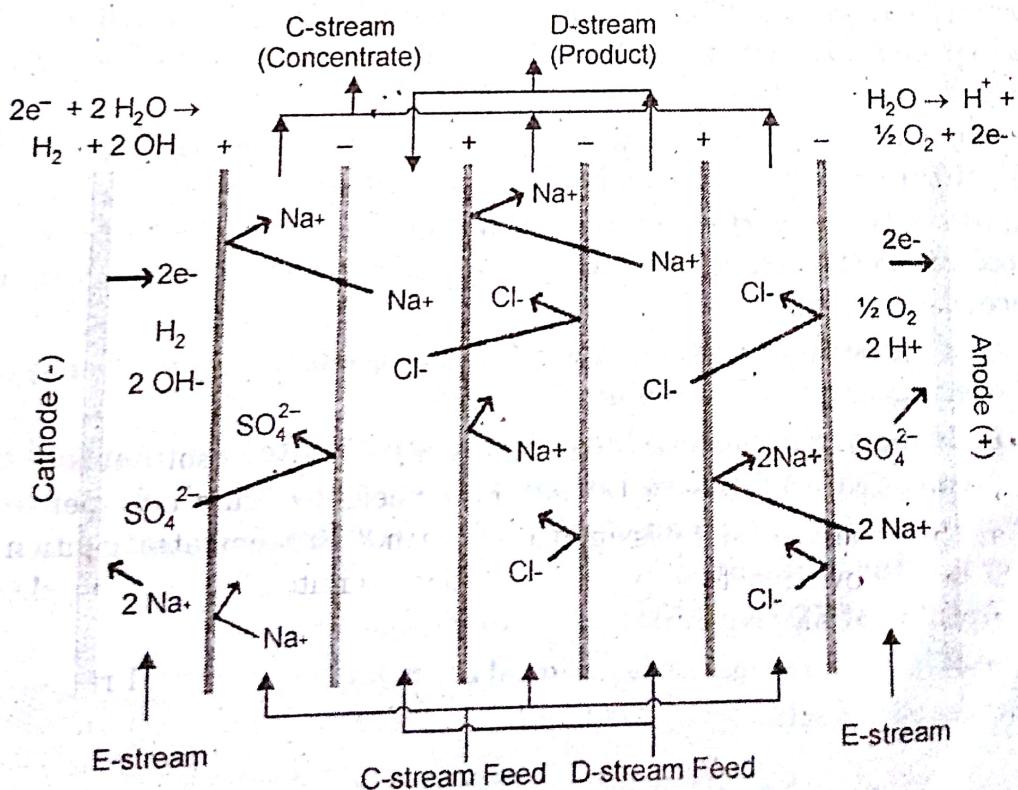
**Process:** Desalination of sea water/ brackish water is carried out in a reverse osmosis cell. In this cell saline water is separated from the fresh water through semi permeable membrane made of very thin films of cellulose acetate affixed to side of a perforated plate or tube, pressure of the order 15-40 kg/cm<sup>2</sup> is applied to sea water. Reverse osmosis take place. Advantage: 1. The process removes ionic as well as nonionic dissolved salt. It is also effective in removing colloidal impurities.



1. The process involves a very low capital and operating cost. It is suitable for converting sea water into drinking water
2. The water obtained by this process may be used in high pressure boilers
3. It removes colloidal silica which is not removed by demineralization.

#### Q.6.(a) (ii) Electro dialysis

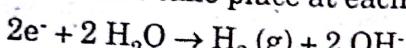
**Ans.** Electro dialysis (ED) is used to transport salt ions from one solution through ion-exchange membranes to another solution under the influence of an applied electric potential difference. This is done in a configuration called an electrodialysis cell. The cell consists of a feed (dilute) compartment and a concentrate (brine) compartment formed by an anion exchange membrane and a cation exchange membrane placed between two electrodes.



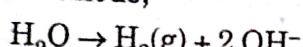
In an electrodialysis stack, the diluate (D) feed stream, brine or concentrate stream, and electrode (E) stream are allowed to flow through the appropriate compartments formed by the ion exchange membranes. Under the influence of electrical potential difference, the negatively charged ions (e.g., chloride) in the dilute stream migrate toward the positively charged anode. These ions pass through the positively charged anion exchange membrane, but are prevented from further migration toward the anode by the negatively charged cation exchange membrane and therefore stay in the C stream, which becomes concentrated with the anions. The positively charged species (e.g., sodium) in the D stream migrate toward the negatively charged cathode and pass through the negatively charged cation exchange membrane. These cations also stay in the C stream, prevented from further migration toward the cathode by the positively charged anion exchange membrane. As a result of the anion and cation migration, electric current flows between the cathode and anode. Only an equal number of anion and cation charge equivalents are transferred from the D stream into the C stream and so the charge balance is maintained in each stream. The overall result of the electrodialysis process is an ion concentration increase in the concentrate stream with a depletion of ions in the diluate solution feed stream.

### Reaction

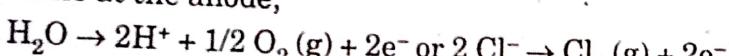
Reactions take place at each electrode. At the cathode,



while at the anode,



while at the anode,



Small amounts of hydrogen gas are generated at the cathode and small amounts either oxygen or chlorine gas at the anode.

### Q.6.(a) (iii) Priming and foaming

**Ans. Priming and foaming:** When a boiler is producing steam rapidly, some particles of the liquid water are carried along with steam. This process of wet steam formation is called priming. It occurs due to presence of large amount of dissolved solid or due to high steam velocities, sudden boiling or due to sudden increase in the rate of steam production.

Priming can be avoided by removing sludge or scales, maintaining low levels in boilers, By fitting mechanical steam purifiers, using softened water.

Foaming is the production of foam or bubbles in the boilers which do not break easily. It occurs due to presence of substances like oils or dissolved matter which decrease the surface tension of water.

Foaming can be avoided by adding anti foaming agents like castor oil or by removing oil from boiler water by adding sodium aluminate.

**Q.6. (b) 50 ml of a sample of hard water was titrated against 0.01 EDTA, it required 15 ml of EDTA for titration. 50 ml of the same hard water after boiling and filtering etc. required 5 ml of EDTA for titration. Calculate the total and temporary hardness of water.**

**Ans. Titration of EDTA solution with sample of lead water sample of hard water heat water EDTA solu.**

$M_1 V_1 M^{22}$ 

$$M_1 \times 50 = 0.01 \times 15$$

$$M = \frac{0.01 \times 15}{50} = 3 \times 10^{-3} M.$$

$$\begin{aligned}\text{Total hardness} &= M \times \text{Molar mass of } \text{CaCO}_3 \\ &= 3 \times 10^{-3} \times 100 \text{ g/L} \\ &= 3 \times 10^{-3} \times 100 \times 1000 = 300 \text{ mg/L} \\ &= 300 \text{ PPM}\end{aligned}$$

Titration of EDTA with boiled water

$$M_1 V_2 = M_2 V_2$$

$$M_1 \times 50 = 0.01 \times 5$$

$$M_1 = \frac{0.01 \times 5}{50} = 1 \times 10^{-3} M$$

$$\begin{aligned}\text{Permanent hardness} &= 1 \times 10^{-3} \times 100 \times 1000 \\ &= 100 \text{ PPM}\end{aligned}$$

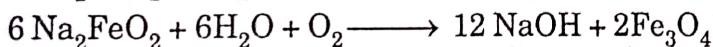
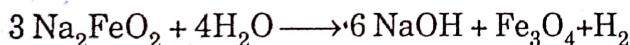
$$\begin{aligned}\text{Temp. Hardness} &= \text{Total - permanent. Hardness} \\ &= 300 - 100 \\ &= 200 \text{ PPM}\end{aligned}$$

#### **Q.7. (a) What is caustic embrittlement? Explain its causes and prevention.**

**Ans.** It is actually a special type of boiler corrosion and is caused by the use of highly alkaline water in the boiler. During softening of hard water by soda-lime process free sodium carbonate ( $\text{Na}_2\text{CO}_3$ ) is usually present in small proportion in the softened water. In high-pressure boilers,  $\text{Na}_2\text{CO}_3$  decomposes to give sodium hydroxide and  $\text{CO}_2$ ,



The formation of NaOH makes the boiler water caustic. The caustic water flows into the minute hair crack parts (like bends, joints, rivets etc.) inside the boiler by the capillary action. Water evaporates and the concentration of NaOH increases slightly. This caustic soda attacks the surrounding area and iron of boiler is dissolved into NaOH to form sodium ferroate which decomposes and forms rust magnetite ( $\text{Fe}_3\text{O}_4$ )



This causes the formation of irregular intergranular cracks on the boiler metal, which is known as embrittlement. It always occurs particularly at highly stressed parts like joints, rivets etc. It is actually electrochemical phenomenon and may be explained as:

|                                      |                               |                         |                                    |
|--------------------------------------|-------------------------------|-------------------------|------------------------------------|
| Iron at rivets<br>joint etc. (anode) | Concentrated NaOH<br>solution | Dilute NaOH<br>Solution | Iron at plane<br>surface (cathode) |
|--------------------------------------|-------------------------------|-------------------------|------------------------------------|

By the electrochemical action the point of high local stress gets corroded. Here the iron surface surrounded by dilute NaOH acts as cathode whereas iron cracks surrounded by concentrated NaOH acts as anode.

#### **Preventions**

It is prevented by the following:

1. Adding tannin or lignin to boiler water because these block the hair cracking inside to boiler.

2. Using  $\text{Na}_2\text{SO}_4$  to the boiler water.  $\text{Na}_2\text{SO}_4$  also blocks the hair cracking inside boiler. It has been observed that in boiler if the ratio of  $\text{Na}_2\text{SO}_4$ :  $\text{NaOH}$  concentration is 3:1 then the boiler works smoothly at 20 atmospheric pressure and above.
3. Using sodium phosphate as softening reagent instead of  $\text{Na}_2\text{CO}_3$  during softening of hard water in lime-soda process.

#### **Q.7.(b) What are the methods of water softening by external treatment?**

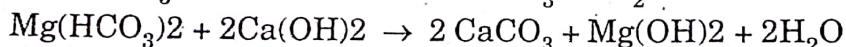
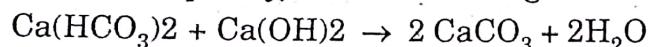
**Ans.** Softening of water (Removing of the dissolved salt) – The process of removing the hardness causing salts from the water called softening of water.

##### **Lime-soda process:**

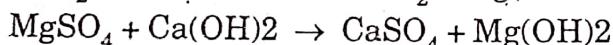
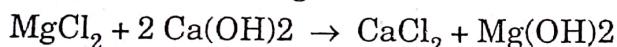
**1. Lime-soda process:** Principle : Conversion of all the soluble hardness causing salts into insoluble precipitate by the addition of soda and lime which can be easily removed by settling and filtration In this method, the soluble calcium and magnesium salts in water are converted chemically into insoluble compounds by adding calculated amounts of lime [ $\text{Ca}(\text{OH})_2$ ] and soda [ $\text{Na}_2\text{CO}_3$ ]. Precipitates of calcium carbonate [ $\text{CaCO}_3$ ] and magnesium hydroxide [ $\text{Mg}(\text{OH})_2$ ] formed are filtered off.

Function of lime: lime removes temporary Ca and Mg hardness, permanent Mg, Fe hardness and dissolved  $\text{CO}_2$  and  $\text{H}_2\text{S}$  gases and free mineral acid present in water. Lime does not react with  $\text{CaCl}_2$  and  $\text{CaSO}_4$  so it cannot remove calcium permanent hardness.

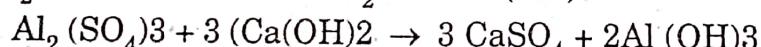
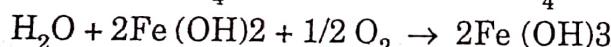
##### **(a) Removal of temporary, calcium and magnesium hardness:**



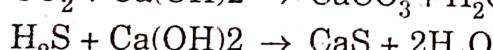
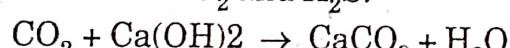
##### **(b) Removal of permanent magnesium hardness:**



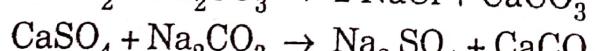
##### **(c) Removal of dissolved iron, aluminium salts:**



##### **(d) Removal of dissolved $\text{CO}_2$ and $\text{H}_2\text{S}$ :**



##### **Function of soda:**



## UNIT IV

#### **Q.8.(a) What happens and why?**

- (i) Iron Sheets gets corroded, when riveted with copper rivets.
- (ii) An iron pole is partly buried under earth.
- (iii) Zinc plate fixed below the shit.

**Ans.** Galvanic corrosion occurs with an electrolyte like seawater. Metals have different values of electrical potentials. When they become electrically connected and put in an electrolyte; the more active metal which has a high negative potential becomes the anode. Due to its high negative potential, it corrodes fast. But the less active metal becomes the cathode. In this case, two metals of different nobility (copper and iron)

immersed in an electrolyte (sea water), created an electrolytic, or galvanic, cell. more active, or less noble(iron), a metal is the more likely it will form an anode in an electrolytic environment. While the more noble (copper)metal is, the more likely is will form a cathode when in the same environment. The anode metal, as a result, corrodes more quickly than it otherwise would, while the cathode metal corrodes more slowly.

(ii) In Soil, presence of moisture, bacteria electrolyte of differential aeration are responsible for corrosion of iron pole. Lead pipeline passes through clay then through sand. Since clay is less acreted than sand, hence, corrosion of lead pipelines takes place in clay.

### **(iii) Zinc plate fixed below the ship.**

Ship gets protected from marine corrosion when Zn plate is fixed below the ship. Zn plate is anodic to iron, so the corrosion is concentrated at this more active Zn metal. When Zn plate is consumed due to corrosion they must be replaced by fresh one. There wise corrosion of iron will also starts.

### **Q.8.(b) Write a short note on soil corrosion and its control.**

**Ans.** Soil corrosion is a geologic hazard that affects buried metals and concrete that is in direct contact with soil or bedrock. Soil corrosion is a complex phenomenon, with a multitude of variables involved. Pitting corrosion and stress-corrosion cracking (SCC) are a result of soil corrosion, which leads to underground oil and gas transmission pipeline failures.

In some respects, corrosion in soils resembles atmospheric corrosion Corrosive soils contain chemical constituents that can react with construction materials, such as concrete and ferrous metals, which may damage foundations and buried pipelines. Both the soil and the climate influence the groundwater composition.

Factors that influence soil corrosion are:

- Porosity (aeration)
- Electrical conductivity or resistivity
- Dissolved salts, including depolarizers or inhibitors
- Moisture
- pH

Each of these variables may affect the anodic and cathodic polarization characteristics of a metal in soil.

Sandy soils are high on the resistivity scale and therefore considered the least corrosive. Clay soils, especially those contaminated with saline water are on the opposite end of the spectrum.

Soil corrosion can be controlled by:

- Using organic and inorganic coatings
- Applying metallic coatings
- Alteration of soil
- Cathodic protection

### **Q.9. Write short note on the following:**

**(i) Electroplating.**

**(ii) Electroless plating.**

**(iii) Corrosion inhibitors.**

**(iv) Cathodic protection.**

**(v) Galvanic corrosion.**

**Ans.** Refer to Q.8(b)(iii) of End Term Examination 2013.

**(ii) Electroless plating**

**Ans.** Electroless plating is also a widely used technique to protect the base metal from the corrosion. It is also called displacement plating or Immersion coating plating. It involves base metal to be immerse in a bath of nobel metal salt used for plating. The noble metal ion is displaced from its salt solution by the base metal ion and forms thin uniform deposit on the base metal artical. The better example for electroless plating is nickel plating.

The base metal to be protected from corrosion, is immersed in a bath containing sodium hypophosphate and nickel sulphate at pH 4.5-5.0 and maintain bath temperature of about 100°C. The hypophosphate reduces nickel ion to metal nickel and finally converts into nickel phosphide. An alloy of nickel and nickel phosphide is deposited on the base metal article surface forming a stron adherent non-porous coating with high corrosion resistance

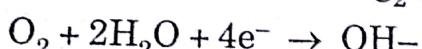
**(iii) Corrosion inhibitors**

**Ans.** Refer to Q.9(b)(i) of End Term 2013.

**(iv) Cathodic protection:** Cathodic protection (Electrical protection): For the structures immersed in soils.

**Ans. Metal to be protected-cathode**

1. Sacrificial anode protection (galvanic protection): more reactive(electropositive) metal-sacrificial anode Used for the protection of underground pipes and tanks, underground cables, marine structure . Reactive metal Zn/ Mg buried inside the pipe & connected by a wire. Mg- anode(oxi), Fe cathode(red) reduce O<sub>2</sub> to OH<sup>-</sup>

**2. Impressed current cathodic protection:**

Metal structure (protected)- cathode(by applying an impressed current form D. source in opposite direction .Impressed current reverse the direction of corrosion current so metal act as cathode instead of anode.

**(v) Galvanic Corrosion**

**Ans.** Refer to Q.9(b)(ii) of End Term Examination 2013.

**END TERM EXAMINATION [DEC. 2015]  
FIRST SEMESTER [B.TECH]  
APPLIED CHEMISTRY [ETCH-113]**

**Time: 3 Hours**

**Note: Attempt any five Questions including Q. No. 1 which is compulsory.**

**M.M.: 75**

**(3x5=15)**

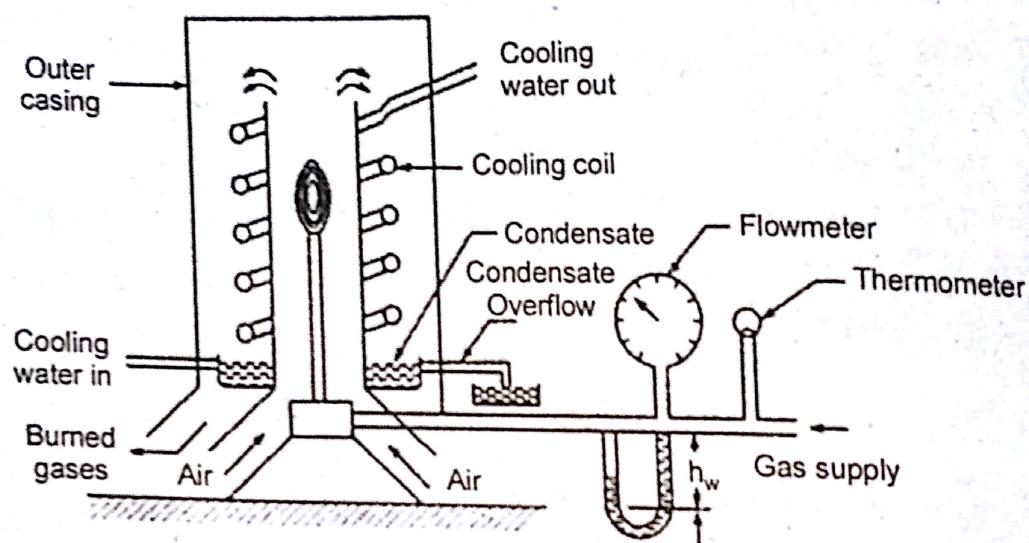
**Q.1. (a) Explain Octane and Cetane number by chemical structure.**

**Ans.** Refer Q.2. First Term Examination 2015.

**Q.1. (b) Explain the determination of calorific value by Boy's calorimeter.**

**Ans.** Boy's Gas Calorimeter

The calorific value of liquid and gaseous fuels can be determined by Boy's Gas calorimeter. The apparatus is shown below.



**Boy's Gas Calorimeter**

**Construction:** The apparatus consists of a suitable gas burner in which a known volume of gas at known pressure can undergo combustion at a uniform rate of 3-4 litres per minute. Around the burner, there is a combustion chamber with a copper tubing coiled inside as well as outside. Water is passed through this coil at constant rate continuously. To determine the calorific value correctly, the whole system is kept insulated.

**Function:** A definite volume of gas is taken in the gas burner at definite pressure. The gas is burnt at constant rate to produce a large amount of heat. The rise in temperature in the water circulation is recorded accurately with the help of thermometer. When the steady situation with respect to rate of fuel burning and water circulation is attained, then the following observations are taken.

- (i) The volume of gas burnt in a given time
- (ii) The quality of water circulated through the coil
- (iii) Mass of water condensed during that time
- (iv) The rise in temperature.

**Calculation:**

- (i) Using the above observations, we can calculate HCV and LCV of liquid fuels and gaseous fuels as follows:

$V$  = volume of gas burnt in time ' $t$ '.

$W$  = mass of water circulated in time ' $t$ '.

$T_1$  and  $T_2$  are initial and final temperatures of water, respectively.

$L$  = Higher calorific value of fuel (cal/gm)

$m$  = mass of water condensed in time ' $t$ '.

(ii) Heat given by the combustion of fuel =  $V \times L$

(iii) Heat taken by the circulated water =  $W(T_2 - T_1)$

Assuming that there is no loss of heat, we can say that Heat given = Heat taken

5

$$VL = W(T_2 - T_1)$$

)

$$\text{Gross calorific value } (L) = W(T_2 - T_1)/V$$

$$\text{LCV} = \text{HCV} - \text{Latent heat of water produced}$$

$$\text{Weight of water condensed per m}^3 \text{ of gas} = m/V$$

$$\text{Latent heat of steam} = (m \times 587)/V \text{ k cal}$$

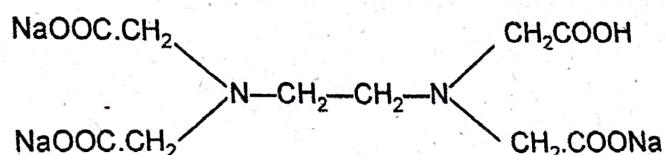
$$\text{Net calorific value} = \text{GCV} - (m \times 587)/V$$

**Q.1. (c) Write principle of EDTA method of determination of hardness of water.**

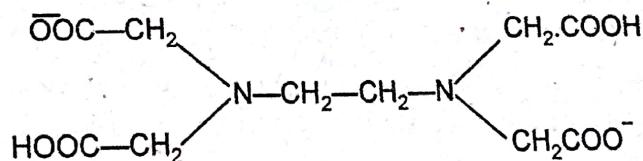
**Ans.** This is a complexometric method. Ethylene diamine tetraacetic acid (EDTA) in the form of its sodium yields the anion.

### Theory

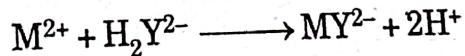
The disodium salt of ethylenediamine tetra acetic acid (EDTA).



ionises in water to give  $2\text{Na}^+$  ions and a strong chelating agent

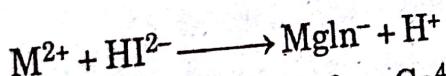


which for simplicity can be represented  $\text{H}_2\text{Y}^{2-}$ . It forms complexes with  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  and other divalent or higher valent cations represented by the reactions:

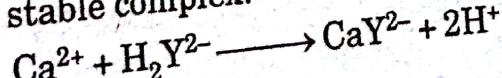


The dissociation of these complexes is governed by the pH of the solution and the complexes with hardness causing divalent ions are stable in alkaline medium (pH range 8-10).

When a small amount of the indicator solution is added to a hard water sample whose pH has been controlled by the addition of the buffer solution, the indicator reacts with  $\text{Mg}^{2+}$  to produce



Wine red colour. As EDTA ( $\text{H}_2\text{Y}^{4-}$ ) is added, free  $\text{Ca}^{2+}$  ions are first complexed to  $\text{CaY}^{2-}$ , this being the most stable complex:

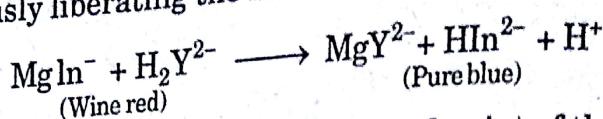


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Free  $Mg^{2+}$  ions then react to give  $Mg$ -EDTA complex which is less acidic than  $Mg$  indicator conc.

$$M^{2+} + H_2Y^{2-} \longrightarrow MY^{2-} + 2H^+$$

stable than Ca-EDTA complex but more stable than Mg-indicator complex. Therefore, if an extra drop of EDTA is added after all the free  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  ions have been complexed, EDTA takes up  $\text{Mg}^{2+}$  from the weak Mg-indicator complex to form stable Mg-EDTA complex simultaneously liberating the indicator in the free form:



(Wine red)  
Completion of the above reaction makes the end-point of the titration.

**Q.1. (d) OH<sup>-</sup> and HCO<sub>3</sub><sup>-</sup> cannot present together in a water sample, Why?**  
**Explain with reaction.**

**Ans.** But it can never be due to the presence of  $\text{OH}^-$  and  $\text{HCO}_3^-$  together because they combine to form  $\text{CO}_3^{2-}$  and  $\text{H}_2\text{O}$ .



Q.1. (e) Define the terms Phase, Component and Degree of Freedom.

**Ans.** PHASE may be defined as any particular portion of a system, which is physically homogeneous, has a specific composition, and can be mechanically removed or separated from any other phase in the system. A system consisting of one phase only is homogeneous system. A system consisting of two or more phases is heterogeneous system.

**Component:** A component is the smallest number of independent variable chemical constituents necessary to define any phase in the system by means of a chemical equation.

For example, experiments carried out in the  $\text{H}_2\text{O}$  system, show that the phases which appear over a wide temperature and pressure range are ice, liquid water and water vapour. The composition of each phase is  $\text{H}_2\text{O}$  and only one chemical parameter or component is required to describe the composition of each phase.

**Degree of Freedom: (or Variance of a System):** The least number of independent variables (concentration, pressure and temperature) which must be arbitrarily fixed in order to define a system completely.

For considering a system consisting of water vapour phase only both temperature and pressure should be stated in order to define the system. Then the system is bivariant.

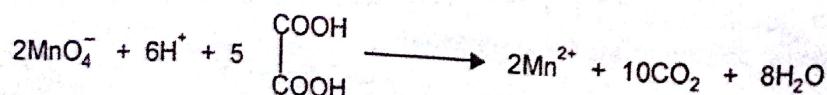
**Q.1. (f) Discuss the effect of Temperature and pH on the activity of Enzymes.**  
**Ans.** Maximum efficiency at optimum temperature—The rate of enzyme catalysed reaction is maximum at optimum temperature. Above this temperature the enzyme gets denatured, losing its activity.

Maximum efficiency at optimum pH → The rate of enzyme catalysed reaction generally increases with pH until the optimum pH is reached and then decreases with further increase of pH.

**Q.1. (g) What do you mean by autocatalysis? Explain.**

**Q.1. Q.) What do you mean by autocatalysis? Explain with example.**

**Ans.** A single chemical reaction is said to have undergone **autocatalysis**, or be **autocatalytic**, if the reaction product itself is the catalyst for that reaction. In autocatalysis, the reaction is catalysed by one of its products. One of the simplest examples of this is in the oxidation of a solution of oxalic acid by an acidified solution of potassium manganate(VII) (potassium permanganate).



The reaction is very slow at room temperature. It is used as a titration to find the concentration of potassium manganate(VII) solution and is usually carried out at a temperature of about 60°C. Even so, it is quite slow to start with.

The reaction is catalysed by manganese(II) ions.

**Q.1. (h) Write short note on Pilling Bedworth ratio.**

**Ans.** Refer Q.1. (i) Pre. University Examination 2015.

**Q.2. (a) Describe the manufacture of metallurgical coke by Otto Hoffmann method.**

**Ans.** Refer Q. 3. (a) of Pre. University Examination 2015. (6)

**Q.2. (b) What is the significance of Ash, Moisture and Volatile matter present in a coal sample?**

**Ans. Significance of proximate analysis:** It provides the following valuable information in assessing the quality of coal. (4)

(i) **Moisture content:** Moisture lowers the effective calorific value because considerable amount of heat is wasted in evaporating the moisture during combustion. Hence lesser the moisture content, better the quality of coal as a fuel.

(ii) **Volatile matter:** It may be combustible gases ( $H_2$ ,  $CO$ ,  $CH_4$  etc.) or non-combustible gases ( $CO_2$ ,  $N_2$ ). The presence of non-combustible gases is undesirable since they do not add to the heat value.

The volatile matter content of coal influences the furnace design. Higher the content, larger is the combustion space required. The % of volatile matter in coal denotes the proportion of coal which will be converted into gas and tar products by heat. Hence high volatile matter content is preferable in coal gas manufacture and carbonization plants. Low volatile matter and high fixed carbon is preferred for manufacture of metallurgical coke.

(iii) **Ash:** It is the non-combustible, useless matter that is left behind when all the combustible matter is burnt off from coal. Hence lesser the ash content better is the quality of coal.

(iv) **Fixed carbon:** Higher the percentage of fixed carbon, greater is its calorific value and better the quality of coal.

**Q.2. (c) Calculate the minimum amount of air required for complete combustion of 100 kg of coal sample having the following composition: C = 84%; H = 9%, N = 2%, S = 1.5% and O = 3.5%.** (5)

**Ans.**

| Constituent | Reaction   | Weight of $O_2$ required         |
|-------------|--|----------------------------------|
| C           | $C + O_2 \longrightarrow CO_2$<br>12    32                 | $\frac{32}{12} \times 84 = 224$  |
| H           | $H_2 + \frac{1}{2}O_2 \longrightarrow H_2O$<br>2        16 | $\frac{16}{2} \times 9 = 72$     |
| S           | $S + O_2 \longrightarrow SO_2$<br>32    32                 | $\frac{32}{32} \times 1.5 = 1.5$ |
| N           | —  | —                                |
| O           | —  | —                                |

Theoretical  $O_2$  required for 100 kg of fuel

$$= 224 + 72 + 1.5 = 297.5 \text{ kg of } O_2$$

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

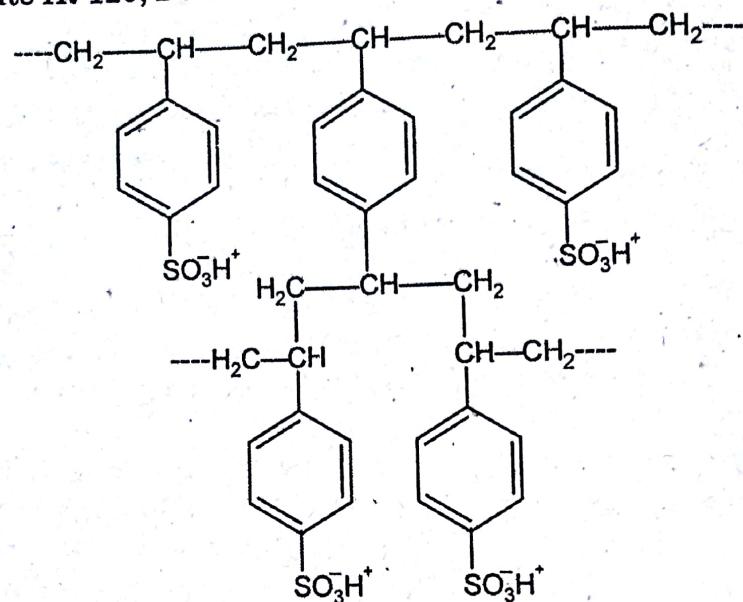
$$= 297.5 - 3.5 = 294.0 \text{ kg}$$

$$\text{Air required} = \frac{194}{1} \times \frac{100}{23} = 127.8 \text{ kg}$$

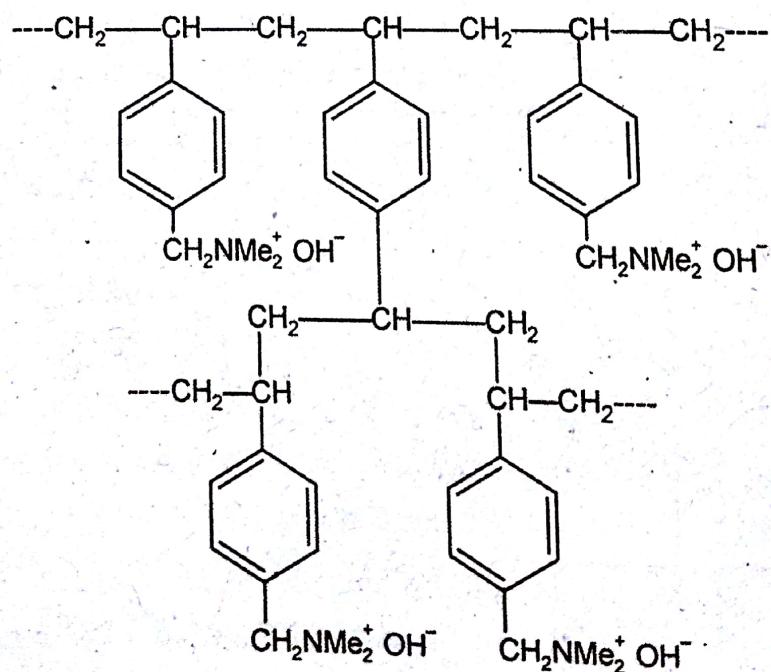
**Q.3. (a)** What are ion-exchange resins? How are they used for softening of water, explain with reactions and diagram? How can they be regenerated after getting exhausted?

**Ans. Ion Exchange Process:** Ion exchange resins are high molecular mass insoluble cross linked organic polymers which are capable of exchanging cations and anions from hard water. They are of two types:

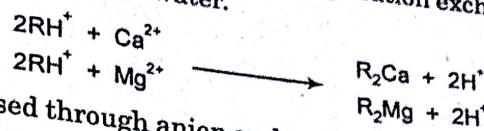
1. Cation Exchange Resins contain functional groups like  $-\text{COOH}$ ,  $-\text{SO}_3\text{H}$  etc. which are capable of exchanging their H ions with the cations. They are denoted as RH. They are mainly carboxylate or sulphonated styrene and divinyl benzene copolymers e.g. Zeocarb, Amberlite IR-120, Dowex-50, Duolite etc.



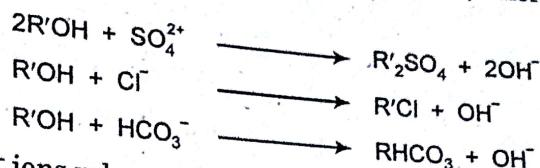
2. Anion Exchange Resins contain basic functional group like  $-\text{NH}_2$ ,  $=\text{NH}$  etc. as hydrochloride or hydroxide which are capable of exchanging their  $\text{OH}^-$  ion with anions present in hard water. They are represented as ROH. They are mainly styrene divinyl benzene or amine-formaldehyde copolymers. e.g. Amberlite-400, Dowex-3.



**Principle:** When hard water is passed through cation exchange column  $H^+$  ion are replaced by cations present in hard water.



Then water is passed through anion exchange column, where anions are removed from water.

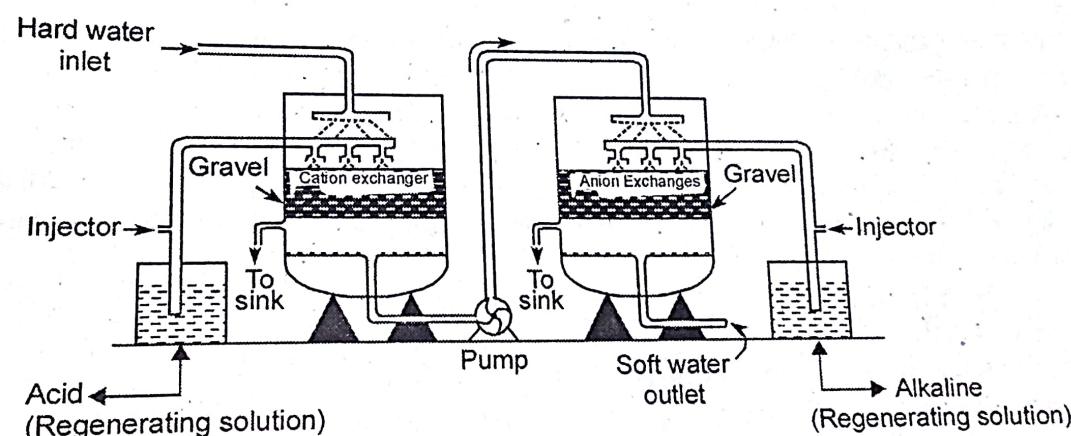


The  $H^+$  and  $OH^-$  ions released will combine to form water.

**Regeneration:** As the cation and anion exchangers are used continuously they loose their ion exchanging capacity and become exhausted. They are treated with dil.  $H_2SO_4$  and dil.  $NaOH$ .



**Mixed bed deioniser/demineraliser:** It consists of cation exchanger and anion exchanger in a single unit. The hard water is passed through it. Soft water obtained by this method is free from both cations and anions.



#### Demineralisation of water

**Q.3. (b)** Calculate the lime (84% pure) and soda (92% pure) required for treatment of 50000 liters of water containing  $Ca(HCO_3)_2 = 40.5$  ppm,  $Mg(HCO_3)_2 = 36.5$  ppm,  $MgSO_4 = 30.0$  ppm,  $CaSO_4 = 34$  ppm,  $CaCl_2 = 27.75$  ppm and  $NaCl = 10.0$  ppm. (8)

**Ans.**

| Constituent   | Amount | Multiplication factor | $CaCO_3$ equivalence |
|---------------|--------|-----------------------|----------------------|
| $Ca(HCO_3)_2$ | 40.5   | $\frac{100}{162}$     | 25                   |
| $Mg(HCO_3)_2$ | 36.5   | $\frac{100}{146}$     | 25                   |

|          |       |                   |    |
|----------|-------|-------------------|----|
| $MgSO_4$ | 30.0  | $\frac{100}{120}$ | 25 |
| $CaSO_4$ | 34.0  | $\frac{100}{136}$ | 25 |
| $CaCl_2$ | 27.75 | $\frac{100}{111}$ | 25 |
| $NaCl$   | —     |                   |    |

Lime requirement

$$\begin{aligned}
 &= \frac{74}{100} [Ca(HCO_3)_2 + 2 \times Mg(HCO_3)_2 + MgSO_4] \\
 &= \frac{74}{100} [25 + 2 \times 25 + 25] \times 50,000 \times \frac{100}{84} \\
 &= 4.404 \text{ kg.}
 \end{aligned}$$

Soda requirements

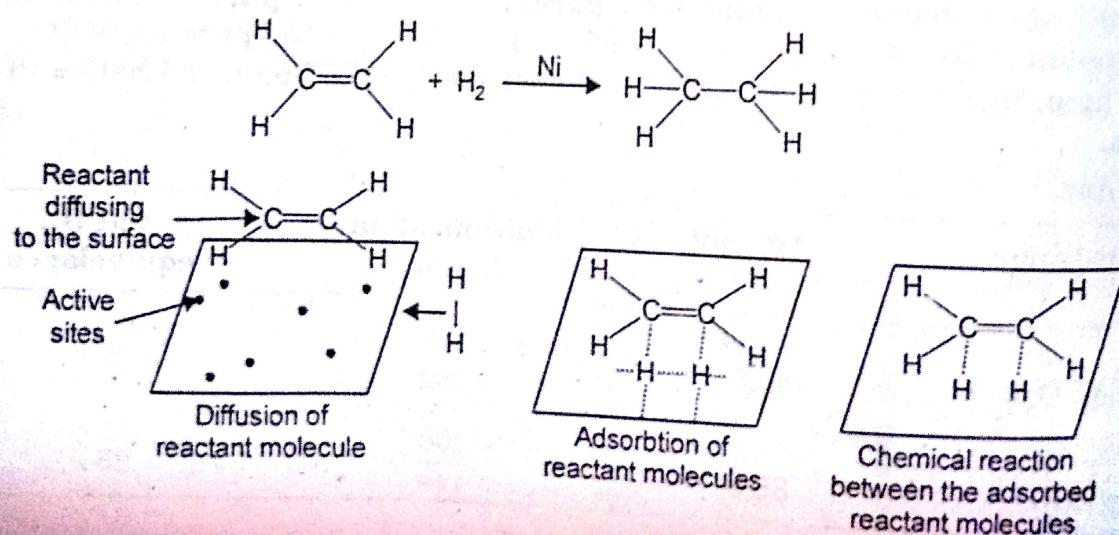
$$\begin{aligned}
 &= \frac{106}{100} [MgSO_4 + CaSO_4 + CaCl_2] \\
 &= \frac{106}{100} [25 + 25 + 25] \times 50,000 \times \frac{100}{92} \\
 &= 4.320 \text{ kg}
 \end{aligned}$$

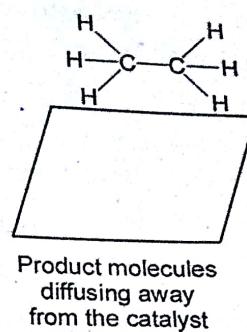
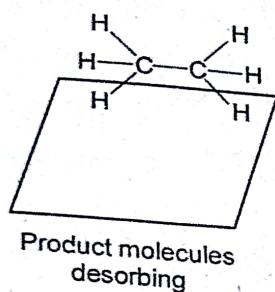
**Q.4. (a) Explain Adsorption theory of catalysis. Which step is the rate determining step?** (5)

**Ans.** Mechanism of heterogenous catalysis: According to the mechanism a gaseous reaction on the surface of the solid catalyst takes place through the following steps.

- The reactant molecules are diffused to the surface of the catalyst.
- Reactant molecules are absorbed on the surface of the catalyst, which results in stretching and weakening of the bonds.
- Chemical reaction of the absorbed molecules on the surface of the catalyst forming product.
- Product molecules are desorbed from the surface.
- The product molecules diffuse away from the surface.

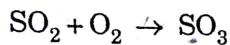
The above sequence is illustrated by hydrogenation of ethylene in the presence of hydrogen.





Any of the steps mentioned above may be slowest and hence becomes rate determining. Diffusion of the reactants towards the surface of the catalyst and diffusion of the products away from the catalyst viz, step (i) and (v) are considered very fast. Absorption of the reactants and desorption of the products i.e. step (ii) and (iv) are faster than the step (iii). Therefore step (iii) i.e. the chemical reaction at the surface is the slowest and rate determining step.

i.e.

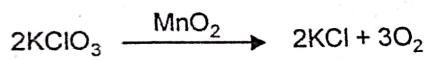


Catalyst = Pt

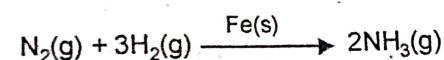
Poison =  $\text{As}_2\text{O}_3$ .

**Q.4. (b) Define positive and negative catalyst and give examples of each. (3)**

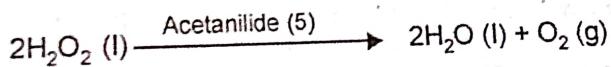
**Ans. Positive Catalyst:** The catalyst which increases the rate of reaction is called positive catalyst. e.g. 1. Decomposition of potassium chlorate in the presence of small amount of



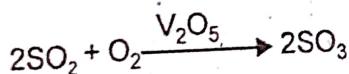
2. Manufacture of ammonia by Haber's process using finely divided iron as a catalyst



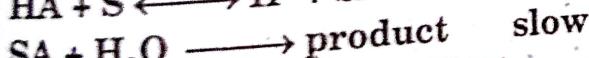
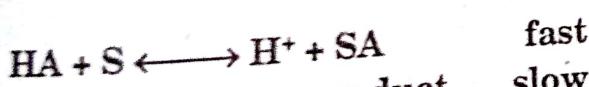
**Negative Catalyst:** The catalyst which decreases the rate of reaction is called negative catalyst. e.g. 1. Decomposition of  $\text{H}_2\text{O}_2$  is retarded in the presence of acetanilide



2. In the contact process, the rate of combination of  $\text{SO}_2$  and  $\text{O}_2$  is slowed down by arsenic compound or  $\text{V}_2\text{O}_5$  as a catalyst

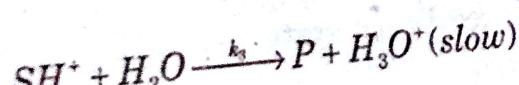
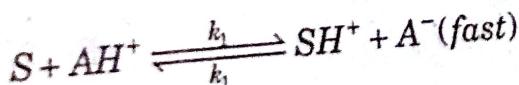


**Q.4. (c) Derive the rate expression for the following acid catalyst reaction. (4)**



Where  $\text{H}_2\text{O}$  is the solvent. Discuss different cases.

**Ans.**



Eq. 2 is slow and hence rate determining step  
 $\therefore$  Rate of rxn. is given by

$$r = \frac{-d[S]}{dt} = k_3[SH^+] \quad \dots(3)$$

by applying steady state approximation.

$$\begin{aligned} \frac{d[SH^+]}{dt} &= 0 = k_1[S][AH^-] - k_2[SH^+][A^-] - k_3[SH^+] \\ k_1[S][AH^+] &= k_2[SH^+][A^-] + k_3[SH^+] \\ &= [k_2[A^-] + k_3][SH^+] \\ [SH^+] &= \frac{k_2[S][AH^+]}{k_2[A^-] + k_3} \end{aligned}$$

Substitute in equation (3)

$$r = \frac{k_3 k_1 [S][AH^+]}{k_2[A^-] + k_3}$$

If  $k_3 \gg k_2[A^-]$ , then ignore  $k_2[A^-]$

$$r = k_1[S][AH^+]$$

This is general acid catalysis.

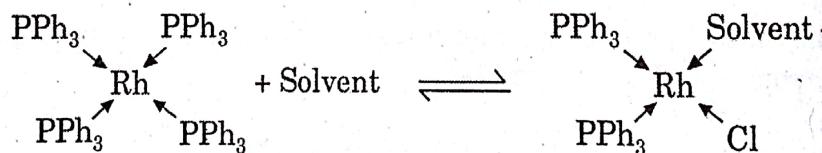
If  $k_2(A^-) \gg k_3$ , ignore  $k_3$

$$r = \frac{k_1 k_2 [S][AH^+]}{k_2[A^-]}$$

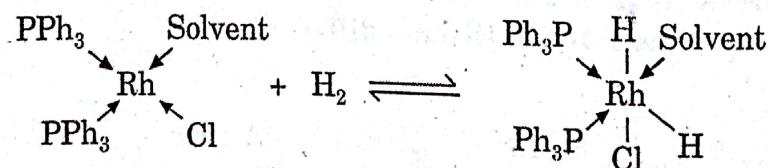
**Q.4. (d) Explain the mechanism of hydrogenation of alkenes by using Wilkinson catalyst.**

**Ans. Catalysis by Metal Salts:** The mechanism of catalysis by metal salt is illustrated by wilkinson's catalysis. It is used for homogeneous hydrogenation.

1. The complex  $RhCl(PPh_3)_3$  exchange one of its  $PPh_3$  for a solvent molecule, reversibly



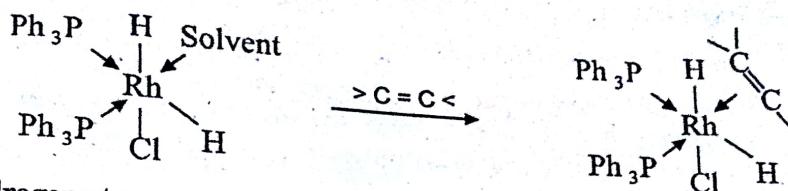
2. The reactant, alkene and molecular  $H_2$  are brought close to catalysis. The H-H bond breaks and each  $H_2$  attack separately to Rh.



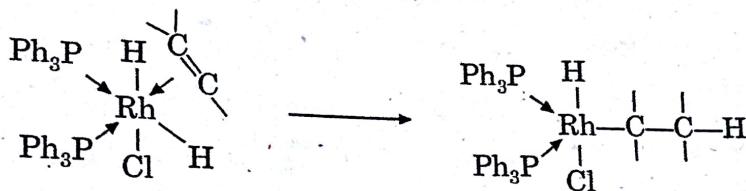
Platinum changes from oxidation state (I) to (III)

3. Alkene react with catalyst replacing a solvent molecule. The bonding occur by overlapping of an empty orbital of metal with  $\pi$ -cloud of alkene.

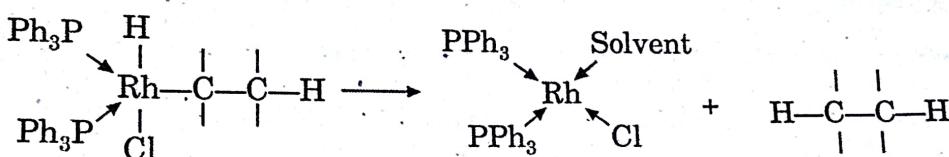
... (3)



4. A hydrogen atom migrate from one C-atom of alkene, whereas other attaches itself to metal alkyl



5. Now, the second hydrogen migrate from metal to carbon.



**Q.5. (a) What is corrosion of metals? Describe the mechanism of electrochemical corrosion by hydrogen evolution and by oxygen absorption. (7)**

**Ans.** Corrosion is a natural process, which converts a refined metal to a more stable form, such as its oxide, hydroxide, or sulfide. It is the gradual destruction of materials (usually metals) by chemical reaction with their environment.

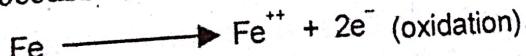
It is a common type of corrosion of metal in aqueous corrosive environment. This type of corrosion occurs when the metal comes in contact with a conducting liquid or when two dissimilar metals are immersed or dipped partly in a solution. According to this theory, there is the formation of a galvanic cell on the surface of metals. Some parts of the metal surface act as anode and rest act as cathode.

The chemical in the environment and humidity acts as an electrolyte. Oxidation of anodic part takes place and it results in corrosion at anode, while reduction takes place at cathode. The corrosion product is formed on the surface of the metal between anode and cathode.

Let us take the example of corrosion of iron.

Oxidation of metal takes place at anode while the reduction process takes place at cathode. By taking rusting of iron as an example, the reaction can be explained as that it may occur in two ways: (i) evolution of hydrogen and (ii) absorption of oxygen.

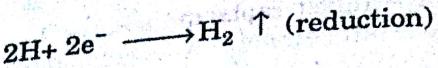
At anode: oxidation occurs.



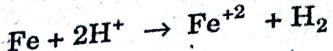
At cathode:

Case I: Evolution of  $\text{H}_2$

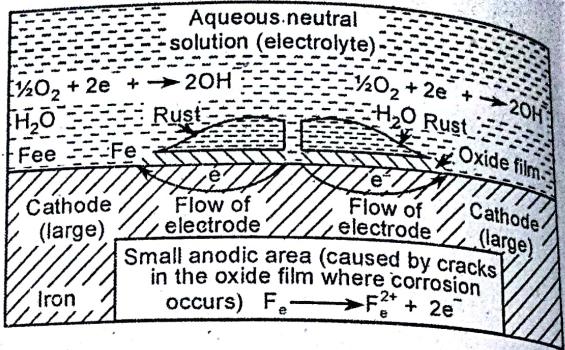
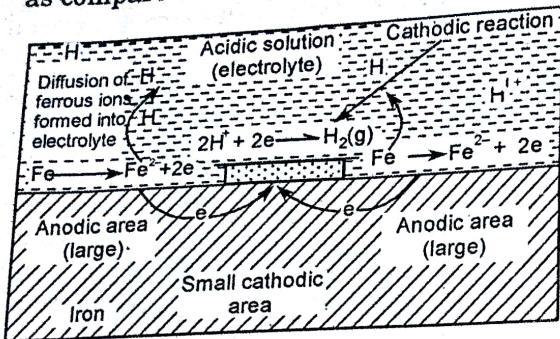
The hydrogen ions ( $\text{H}^+$ ) are formed due to the acidic environment and the following reaction occurs in the absence of oxygen



The overall reaction is

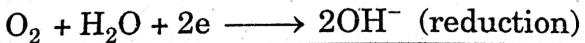
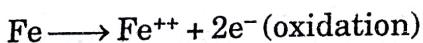


In this case, metals react in the acidic environment and are dissolved (undergo corrosion) to release  $H_2$  gas. All metals above hydrogen in electrochemical series can show this type of corrosion. In hydrogen evolution type of corrosion, anodic area is large as compared to its cathodic area

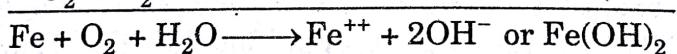


**Case II: Absorption of  $O_2$ .** This type of corrosion takes place in neutral or basic medium in the presence of oxygen. The small scratch on the surface creates small anodic area and rest of the surface acts as cathodic area. The following chemical reactions occur at anode and cathode.

At anode



At cathode



Ferric hydroxide is actually hydrated ferric oxide,  $Fe_2O_3 \cdot H_2O$ , which is yellowish rust. Anhydrous magnetite,  $Fe_3O_4$  [a mixture of  $(FeO + Fe_2O_3)$ ], is also formed, which is brown-black in colour.

**Q.5. (b) Impure metals corrode faster than pure metal under identical conditions. Give reason.** (3)

**Ans.** Corrosion always occurs most readily when two dissimilar metals are joined in a conducting solution, called an electrolyte. A galvanic cell forms. The second, more inert metal bleeds electrons from the anodic metal and so a continuous flow of electrons occurs if the circuit is completed. Oxidation of the anodic metal occurs and oxidation means corrosion. Impure iron rusts more quickly than pure iron because the impurities may act as the cathode. The  $O_2$  is reduced on these impurities. The rusting of iron is accelerated when it is in contact with a less active metal such as copper or tin because less active metals serve as the cathode.

**Q.5. (c) Write short note on electroplating and electroless plating.** (5)

**Ans.** Electroplating is a process that uses electrical current to reduce dissolved metal cations so that they form a coherent metal coating on an electrode. The process used in electroplating is called electro deposition. It is analogous to a galvanic cell acting in reverse. The part to be plated is the cathode of the circuit. In one technique, the anode is made of the metal to be plated on the part. Both components are immersed in a solution called an electrolyte containing one or more dissolved metal salts as well as other ions that permit the flow of electricity. At the cathode, the dissolved metal

ions in the electrolyte at the cathode.

These coatings reduce friction and electrochemical protection is provided by electroplated with resistant coatings.

Electroless plating reduces the corrosion. It involves base metal and noble metal ion in a thin uniform deposit is nickel plating.

The base metal sodium hypophosphate temperature of a finally converts iron on the base metal to high corrosion resistance.

**Q.6. (a) Write component system.**

**Ans.**

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**Q.6.**

**Ans**

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ions in the electrolyte solution are reduced at the interface between the solution and the cathode.

These coatings are used in particular for tribological applications, for example friction reduction and improved wear resistance. To refine metallic surfaces, various electrochemical processes are regularly used, in which for example the surfaces are electroplated with chrome or nickel. Zinc and zinc alloys are often used for corrosion-resistant coatings. Well-known examples include the decorative chrome plating of plastic components in vehicles or household objects.

Electroless plating is also a widely used technique to protect the base metal from corrosion. It is also called displacement plating or Immersion coating/ plating. It involves base metal to be immersed in a bath of noble metal salt used for plating. The noble metal ion is displaced from its salt solution by the base metal ion and forms a thin uniform deposit on the base metal article. The better example for electroless plating is nickel plating.

The base metal to be protected from corrosion, is immersed in a bath containing sodium hypophosphate and nickel sulphate at pH 4.5-5.0 and maintain bath temperature of about 100°C. The hypophosphate reduces nickel ion to metal nickel and finally converts into nickel phosphide. An alloy of nickel and nickel phosphide is deposited on the base metal article surface forming a strong adherent non-porous coating with high corrosion resistance.

**Q.6. (a) Write condensed Phase rule and explain why is it used for two component systems.**

**Ans.**

**Condensed phase rule / reduced phase rule:**

The phase rule equation is  $F = C - P + 2$

For a two component system,  $C = 2$

Then  $F = 2 - P + 2 = 4 - P$

The minimum number of phase at equilibrium is one.

Then  $F = 4 - 1 = 3$ .

Hence the maximum number of degree of freedom is three and temperature, pressure and composition are required to define the system. This leads to 3D figures which cannot be explained on a paper. Hence one of the three variable is to be kept constant.

So pressure is kept constant.

$F = C - P + 1$  (Two component system)

$F = 2 - P + 1 = 3 - P$

This is the reduced / condensed form of the phase rule.

**Q.6. (b) Discuss the applications of Eutectic mixtures. (atleast 3).**

(3)

**Ans. Applications of Eutectic system.**

1. The Eutectic is used in preparation of alloy such as various type of solders in electric fuses.

2. Alloy of Bi, Pb, Sn + Cd is called wood metal alloy. It has m.pt. of 65°C. In case of fire, base melts and water is released automatically.

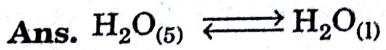
3. A system at eutectic point can maintain its temp. Over long period and such system are used as constant temp bath.

4. In Pattinson's method for desil/verisation of an gentiferrous lead.

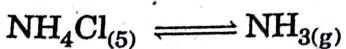
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Q.6. (c) Determine the number of components and number of phases for the following: (i)  $\text{H}_2\text{O}_{(5)} \rightleftharpoons \text{H}_2\text{O}_{(1)}$  (ii)  $\text{NH}_4\text{Cl}_{(5)} \rightleftharpoons \text{NH}_3_{(g)}$ , if  $\text{NH}_3$  is in excess. (4)



No. of component = 1      no. of phases = 2



No. of component = 2      no. of phases = 1

Q.6. (d) If 50 ml of sample of hard water consumed 15ml of 0.01M EDTA. What is the hardness of water? (5)

Ans. 1ml of 0.01 MEDTA = 1mg of  $\text{CaCO}_3$

$$15 \text{ ml of } 0.01 \text{ M EDTA} = \frac{1 \times 15}{0.01} \times 0.01 \text{ mg of } \text{CaCO}_3 \\ = 150 \text{ mg of } \text{CaCO}_3$$

50 ml of water contain 150 mg of  $\text{CaCO}_3$

$$\therefore \text{Hardness} = \frac{150}{50} \times 1000 = 3000 \text{ mg/L} \\ = 3000 \text{ PPM.}$$

**END TERM EXAMINATION**  
**FIRST SEMESTER B.TECH. [DEC. 2016]**  
**APPLIED CHEMISTRY (ETCH-113)**

**Time : 3 hrs.**

**Note:** Attempt any five questions including Q. no. 1 which is compulsory select one question from each unit.

M.M. : 75

**Q.1. (a) Define HCV and GCV.**

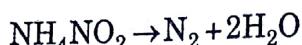
**Ans.** Higher or Gross Calorific Value (HCV): Refer Q. 1. (a) of First Term 2016. (2.5)

**Q.1. (b) Define order and molecularity of a reaction with suitable example.** (2.5)

**Ans.** The molecularity of a reaction is defined as the number of molecules or ions that participate in the rate determining step. A mechanism in which two reacting species combine in the transition state of the rate-determining step is called bimolecular. If a single species makes up the transition state, the reaction would be called unimolecular. In a unimolecular reaction, a single molecule shakes itself apart or its atoms into a new arrangement.

**Example**

Decomposition of  $\text{NH}_4\text{NO}_2$  to  $\text{N}_2$  and  $2 \text{H}_2\text{O}$



Bimolecular reactions involve the collision of pair of molecules. Bimolecular reactions are common order is the sum of powers raised on concentration terms in the rate expression. Order of reaction with respect to a given substance (such as reactant, catalyst or product) is defined as the exponent, to which its concentration term in the rate equation is raised. For the typical rate equation of form where  $[A]$ ,  $[B]$ , ... are concentrations, the reaction orders are  $x$  for substance A,  $y$  for substance B, etc. The overall reaction order is the sum  $x + y + \dots$ . For many reactions, the reaction orders are *not* equal to the stoichiometric coefficients.

For example, the chemical reaction between mercury (II) chloride and oxalate ion has the observed rate equation

$$r = k[\text{HgCl}_2]^1[\text{C}_2\text{O}_4^{2-}]^2$$

In this case, the reaction order with respect to the reactant  $\text{HgCl}_2$  is 1 and with respect to oxalate ion is 2; the over all reaction order is  $1 + 2 = 3$ .

**Q.1. (c) What is biodiesel?**

(2.5)

**Ans.** Biodiesel is an alternative fuel similar to conventional or 'fossil' diesel. Biodiesel can be produced from straight vegetable oil, animal oil/fats, tallow and waste cooking oil. The process used to convert these oils to Biodiesel is called transesterification. The largest possible source of suitable oil comes from oil crops such as rapeseed, palm or soybean. The result is Biodiesel produced from waste vegetable oil can compete with fossil diesel.

#### **Biodiesel Production**

As mentioned above Biodiesel can be produced from straight vegetable oil, animal oil/fats, tallow and waste oils. There are three basic routes to biodiesel production from oils and fats:

- Base catalyzed transesterification of the oil.
- Direct acid catalyzed transesterification of the oil.

- Conversion of the oil to its fatty acids and then to biodiesel.

Biodiesel has many environmentally beneficial properties. The main benefit of biodiesel is that it can be described as 'carbon neutral'. This means that the fuel produces no net output of carbon in the form of carbon dioxide ( $\text{CO}_2$ ). This effect occurs because when the oil crop grows it absorbs the same amount of  $\text{CO}_2$  as is released when the fuel is combusted. Biodiesel is rapidly biodegradable and completely non-toxic, meaning spillages represent far less of a risk than fossil diesel spillages.

#### **Q.1. (d) State Gibb's phase rule.**

(2.5)

**Ans.** It is defined as the minimum number of the independently variable factors such as the temperature, pressure and composition of the phases which must be arbitrarily specified in order to represent perfectly the condition of a system. The phase rule allows one to determine the number of degrees of freedom (F) or variance of a chemical system. This is useful for interpreting phase diagrams.

$$F = C - P + 2$$

Where F is the number of degrees of freedom, C is the number of chemical components and P is the number of phases in the system. The number two is specified because this formulation assumes that both T and P can be varied

#### **Q.1. (e) What is Pilling-Bed-Worth rule?**

(2.5)

#### **Ans. Pilling Bedworth Rule**

An oxide is protective or non-porous if the volume of the oxide is at least as great as the volume of the metal from which it is formed. If the volume of the oxide is less than the volume of the metal, the oxide layer is porous (or non-continuous) and hence non-protective because it cannot prevent the access of oxygen to the fresh metal surface below. The ratio of the volume of metal oxide to the volume of the metal is also known as specific volume ratio.

$$\text{Specific Volume Ratio} = \text{MO}/\text{M}$$

$$\text{MO} = \text{Volume of Metal Oxide}, \text{M} = \text{Volume of Metal}$$

Smaller the specific volume ratio greater is the oxidation corrosion. Alkali and alkaline earth metals form oxide of volume less than the volume of metal, thus the oxide layer faces stress and strain, developing cracks and pores. Porous oxide scale permits free access of oxygen to the underlying metal surface for fresh action, and corrosion continue.

Metal like Aluminum and Copper form oxides, whose volume is greater than the volume of the metal, thus an extremely tightly adhering non porous layer is formed. Due to the absence of cracks or pores the rate of oxidation rapidly decreases to zero.

Example, the specific volume ratio of W, Cr and Ni is 3.6, 2.0 and 1.6 respectively therefore the rate of corrosion of W is least even at high temperature.

#### **Q.1. (f) What is an eutectic mixture?**

(2.5)

**Ans.** Solid solution of two components having the lowest melting point of all possible mixtures of the components is called an eutectic mixture and binary mixture forming an eutectic mixture at a particular composition is called an eutectic system

#### **Q.1. (g) Explain what is happening at the triple point of water. How many phases are there in the system at this point?**

(2.5)

**Ans. Triple point:** The point O where all the three curves OC, OA and OB meet is known as triple point. At the triple point all the three phases of water system namely

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solid ice, liquid water and gas vapour are in equilibrium. The equilibrium in three phases is attained at  $0.0076^{\circ}\text{C}$  temperature and 4.58 mm Hg pressure.

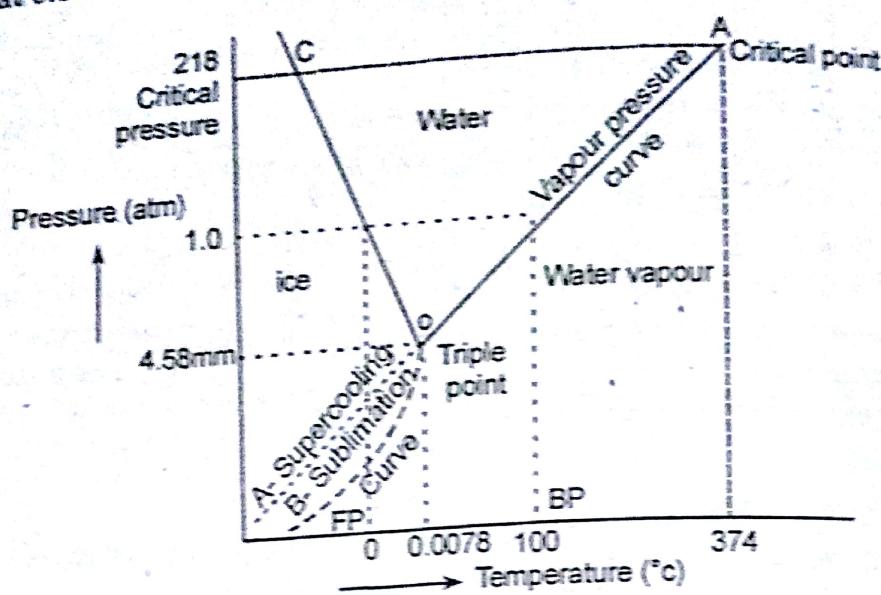


Fig. The phase diagram of the water system.

Since there are 3 phases and one component present in the system, the degree of freedom will be

$$F = C - P + 2$$

$$F = 1 - 3 + 2 = 0$$

Hence the system is non-variant. If either the temperature or the pressure or both are changed, the three phases would no longer coexist and at least one of them would disappear.

**Q.1. (h) What is synthetic petrol?** (2.5)

**Ans.** Synthetic fuel or synfuel is a liquid fuel, or sometimes gaseous fuel, obtained from syngas, a mixture of carbon monoxide and hydrogen, in which the syngas was derived from gasification of solid feedstocks such as coal or biomass or by reforming of natural gas.

Common methods for manufacturing synthetic fuels include the Fischer Tropsch conversion, methanol to gasoline conversion, or direct coal liquefaction. The three most popular sources of syncrude are extra-heavy oil, oil shale and oil sands. Each of those materials occurs naturally just like conventional oil, but they have different physical properties and amounts of impurities. For example, oil shale is a rock, and oil sands are a tarry mixture of sand and the oil-containing substance bitumen. These syncrude feedstocks are exposed to various levels of heat, pressure, and physical manipulation to produce a substance with the same arrangement of hydrocarbons as naturally occurring crude oil.

**Q.1. (i) Name the catalyst used for the following reactions/processes:-** (5)

- (a) Fischer Tropsch process: Co or Fe catalyst.
- (b) Contact process: Vanadium(V) oxide  $\text{V}_2\text{O}_5$
- (c) Zeigler Natta polymerisation:  $\text{TiCl}_3 + (\text{C}_2\text{H}_5)_3\text{Al}$
- (d) Haber's process: Fe
- (e) Homogeneous hydrogenation reaction: Ni or Pt

**UNIT-I****Q.2. (a) Differentiate the following:**

(i) Chemical fuel and nuclear fuel

(2.5×4=10)

**Ans.** Nuclear fuel is a substance that is used in nuclear power stations to produce heat to power turbines. Heat is created when nuclear fuel undergoes nuclear fission.

Most nuclear fuels contain heavy fissile elements that are capable of nuclear fission, such as uranium-235 or plutonium-239. When the unstable nuclei of these atoms are hit by a slow-moving neutron, they split, creating two daughter nuclei and two or three more neutrons. These neutrons then go on to split more nuclei. This creates a self-sustaining chain reaction that is controlled in a nuclear reactor, or uncontrolled in a nuclear weapon.

The processes involved in mining, refining, purifying, using, and disposing of nuclear fuel are collectively known as the nuclear fuel cycle.

**Chemical fuel**

The Principal fuel used in internal combustion engines (automobiles, diesel, and turbojet) and in the furnaces of stationary power plants are organic fossil fuels. These fuels, and others derived from them by various refining and separation processes, are found in the earth in the solid (coal), liquid (petroleum), and gas (natural gas) phases.

Special fuels to improve the performance of combustion engines are obtained by synthetic chemical procedures.

**Q.2. (a)(ii) High temperature and low temperature carbonization****Ans.**

| Characteristics   | Low temperature carbonization | High carbonization temperature |
|---|-------------------------------|--------------------------------|
| 1. Heating temperature  | 500-700°C                     | 900-1200°C                     |
| 2. Yield of coke  | 75-80%                        | 65-75%                         |
| 3. Volatile matter content  | 5-15%                         | 1-3%                           |
| 4. Mechanical strength  | Poor                          | Good                           |
| 5. Calorific value  | 6500-9500 kcal/m <sup>3</sup> | 5400-6000 kcal/m <sup>3</sup>  |
| 6. Quantity of by-product gases   | 130-150 m <sup>3</sup> /tonne | 300-390 m <sup>3</sup> /tonne  |
| 7. Coke produced  | Soft                          | Hard                           |
| 8. Smoke produced   | Smokeless                     | Smoky                          |
| 9. In gas, percentage of<br>(a) Aromatic hydrocarbons<br>(b) Aliphatic hydrocarbons | Lower<br>Higher               | Higher<br>Lower                |
| 10. Uses  | Domestic                      | Metallurgy                     |

**Q.2. (a)(iii) Fixed and Fluidized bed catalytic cracking.**

**Ans.** In fixed bed catalyst is in granular form. its position is fixed in catalyst tower. Catalyst stop working after 10-11 hrs as carbon deposites in carbon so catalyst has to be regenerated.

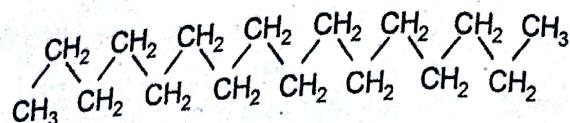
In this reactor catalyst remains in fluidized form and it cracks the gas oil molecules into lighters like naphtha and LPG. In this process regeneration occur within reactor so process does not stop

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**Q. 2. (a) (iv) Octane and cetane number**

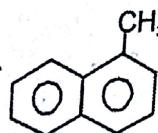
**Ans.** Octane number of a gasoline fuel is given by the percentage of isoctane in a mixture of isoctane (octane number 100) and n-heptane (octane number 0) that would yield the same anti-knock properties as the given fuel. Octane number describes how poor the ignition characteristics are. Octane number derives its name from a highly ignition-resistant liquid hydrocarbon (2,2,4-trimethylpentane) named isoctane, which is assigned an octane number of 100 as a standard against which gasoline fuels are rated.

**n-Hexadecane**



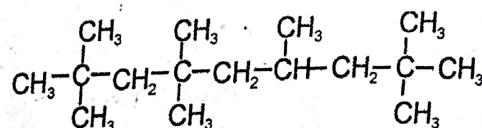
Hexadecane (cetane), cetane number = 100

**1-Methylnaphthalene**



1-Methylnaphthalene, cetane number = 0

**Heptamethylnonane**



2,2,4,4,6,8,8- Heptamethylnonane (Isocetane), cetane number = 15

Cetane number, on the other hand, is given for a diesel fuel by the percentage of cetane in a mixture of cetane (cetane number 100) and isocetane (cetane number 15) that would give the same ignition characteristics as the given fuel. Cetane number is a rating for diesel fuel. Cetane number describes how good the ignition characteristic are. Cetane number, on the other hand, derives its name from a liquid hydrocarbon named cetane, which ignites readily under compression and hence is assigned a cetane number of 100 as a standard against which compression ignition fuels like diesel and biodiesel are rated.

**Q.2. (b) What is sweetening of petrol?**

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**Ans.** The sweetening process is an industrial chemical process for converting mercaptans in sour gasoline into disulfides. Sulfur compounds darken gasoline, give it an offensive odor and increase toxic sulfur dioxide engine emissions. However, this process only reduces the odor.

These sulfur compounds can be removed with the following chemical reactions (sour gasoline)  $2\text{RSH} + \text{Na}_2\text{PbO}_2 + \text{S} \rightarrow \text{R-S-S-R} + \text{PbS} + 2\text{NaOH}$  (alkyl disulfide)

**Q.3. (a) Explain how the calorific value of a fuel can be determined by Bomb's calorimeter with the help of a neat diagram.**

**Ans.** Refer Q.2. (a) of First Term Exam. 2016

**Q. 3. (b) Calculate GCV and NCV of a gaseous fuel from the following data obtained from calorimeter experiment.**

Volume of gaseous fuel burnt at STP =  $0.08\text{m}^3$

Temperature of inlet water =  $26^\circ\text{C}$

Temperature of Outlet water =  $32^\circ\text{C}$

Weight of water produced by steam condensation =  $0.01\text{ kg}$ .

Late heat of steam =  $587\text{ Kcal/kg}$

Ans.

$$W = 20\text{ kg } t_2 = 32^\circ\text{C}, t_1 = 26^\circ\text{C}$$

$$V = 0.08\text{ m}^3, m = 0.01\text{ kg}$$

$$\text{GCV} = \frac{W(t_2 - t_1)}{v}$$

$$= \frac{20 \times (32 - 26^\circ\text{C})}{0.08} = \frac{20 \times 6}{0.05} = 1500\text{ kcal/m}$$

$$\text{NCV} = \text{GCV} - \frac{m}{v} \times \text{lateat heat of condensation}$$

$$= 1500 - \frac{0.01}{0.08} \times 587$$

$$= 1500 - 73.37 = 1426.6\text{ kcal/m}^3$$

## UNIT-II

Q.4. (a) What is "degree of freedom" of a system? Calculate degrees of freedom of the following systems:- (10)

(i) Water (liquid)  $\leftrightarrow$  water vapour at 1 atm.

Ans. Degree of freedom- It is defined as the minimum number of the independently variable factors such as the temperature, pressure and composition of the phases which must be arbitrarily specified in order to represent perfectly the condition of a system.

(i) Water (l) = water (g)

Ans. No. of component : 1

No. of phases : 2

$$F = C - P + 2$$

$$1 - 2 + 2 = 1 \text{ (univariant)}$$

(ii)  $S_p \leftrightarrow S_m \leftrightarrow S_l \leftrightarrow S_v$

Ans. No. of component : 1

No. of phases : 4

$$F = C - P + 2$$

$$1 - 4 + 2 = -1$$

Negative degree of freedom means four phases cannot exist together

(iii) An aqueous solution of glucose

Ans. No. of component : 2 (glucose and water)

No. of phases : 1

$$F = C - P + 2$$

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$$2 - 1 + 2 = 3$$

(iv) Pure crystals of  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$

Ans. No. of component : 1

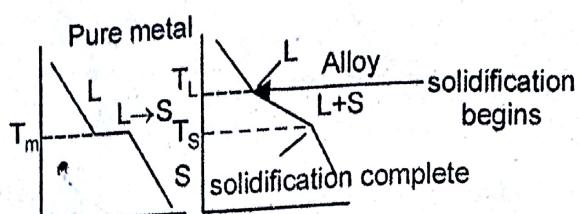
No. of phases : 1

$$F = C - P + 2$$

$$1 - 1 + 2 = 2 \text{ (bivalent)}$$

**Q.4. (b) What are cooling curves?**

Ans. A cooling curve is a graphical plot of the changes in temperature with time for a material over the entire temp range through which it cools. Cooling curve for a pure metal is



In this method alloys with different composition are melted and then temp of the mixture is measured at a certain interval while cooling back to room temp.

**Q.5. (a) Explain Langmuir Hinshelwood mechanism of catalysis in detail.**

(6)

Ans. Langmuir-Hinshelwood has proposed a mechanism for adsorption of gases on the surface of solid. The surface reaction is assumed to occur in the following steps:

1. Diffusion of the reactants on the surface of the solid adsorbent.
2. Adsorption of the reactants at the surface.
3. Chemical reaction at the surface.
4. Desorption of the products from the surface.
5. Diffusion of the products from the surface of the adsorbent.

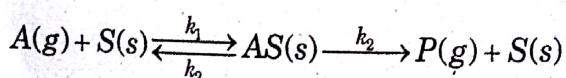
Step 1 and 5 are generally very fast and step 2 and 4 are generally faster than 3. Thus step 3 is the rate determining step in the surface reaction, i.e., chemisorption of the reactants on the surface of the solid adsorbent.

**Two feature of this type of surface reaction:**

1. Chemisorption plays a very important role in such type of adsorption.
2. The reaction rate per unit surface area is proportional to the fraction of total surface covered with adsorbed gas molecule.

Langmuir Hinshelwood mechanism of catalysis/ Heterogenesis catalysis

Many gas-phase reactions are catalyzed on a solid surface. For a first-order, unimolecular reaction, the reaction mechanism can be written as



where the first step is reversible adsorption of the gas molecule, A, onto active sites on the catalyst surface, S, to form a transition state, AS, and the second step is the conversion of adsorbed A molecules to species B.

Applying the steady-state approximation to species AS, we can write

$$\frac{d[AS]}{dt} = k_1[A][S] - k_{-1}[AS]_{ss} - k_2[AS]_{ss} = 0 \quad \dots(1)$$

Because the concentration of total active sites on the catalyst surface is fixed at  $[S]_0$ , the concentration of adsorbed species on the catalyst surface,  $[AS]$  can be written as

$$[AS] = \theta [S]_0 \quad \dots(2)$$

and  $[S]$  can be written as

$$[S] = (1 - \theta)[S]_0 \quad \dots(3)$$

where  $\theta$  is the fractional surface coverage of species A on the catalyst surface.

We can now write Equation (1) as

$$k_1 - [A](1 - \theta)[S]_0 - (k_{-1} + k_2)\theta [S]_0 = 0 \quad \dots(4)$$

Rearranging the above equation in terms of  $\theta$  yields

$$\theta = k_1[A]/(k_1[A] + k_{-1} + k_2) \quad \dots(5)$$

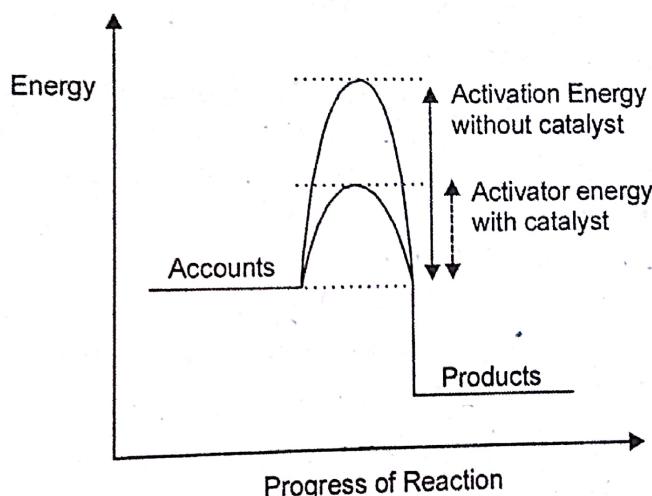
The rate of production of P can be written as

$$d[P]/dt = k_2[AS]ss = k_2\theta[S]_0 = k_1k_2[A][S]_0/(k_1[A] + k_{-1} + k_2) \quad \dots(6)$$

From the above equation, we can observe the importance of having high surface areas for catalytic reactions.

**Q.5. (b) How does a catalyst increase the rate of reaction by affecting the reaction pathway? Will it affect the rate of backward reaction in case of a reversible reaction? Also describe auto catalysis with suitable example. (6.5)**

**Ans.** Catalysts increase the rate of reaction without being used up. They do this by lowering the activation energy needed. With a catalyst, more collisions result in a reaction, so the rate of reaction increases. Different reactions need different catalysts. every reaction has a specific "Activation energy" which is the energy needed for the reaction to take place, what the catalyst does is decreasing this activation energy like shown in the figure below:



A catalyst speeds up both forward/backward reactions of a reversible reaction. The idea is that the activation energies are lowered for both the forward and backward reactions. the activation energy is lowered by exactly the same amount in each direction.

### Autocatalysis

In certain reactions, one of the products acts as a catalyst. In the initial stages the reaction is slow but as soon as the products come into existence the reaction rate increases. This type of phenomenon is known as auto-catalysis. Some examples are as follows,

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(i) The rate of oxidation of oxalic acid by acidified potassium permanganate increases as the reaction progresses. This acceleration is due to the presence of  $Mn^{3+}$  ions which are formed during reaction. Thus  $Mn^{3+}$  ions act as auto-catalyst.

$$5C_2H_2O_4 + 2kMnO_4 + 3H_2SO_4 \rightarrow 2MnSO_4 + K_2SO_4 + 10CO_2 + 8CO_2$$

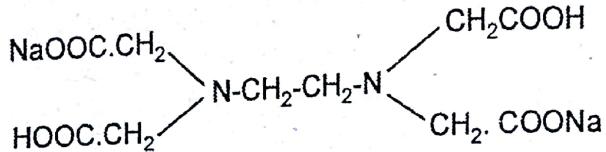
## UNIT-III

**Q.6. (a) Describe the principle and theory of EDTA method for determination of hardness of water.** (6.5)

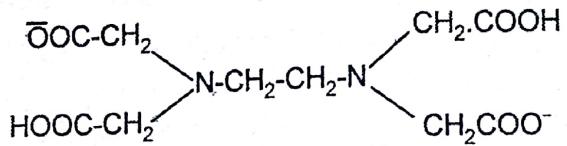
**Ans.** This is a complexometric method. Ethylene diamine tetraacetic acid (EDTA) in the form of its sodium yields the anion.

## Theory

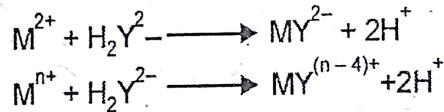
The disodium salt of the ethylenediamine tetraacetic acid (EDTA)



ionises in water to give  $2Na^+$  ions and a strong chelating agent

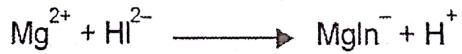


which for simplicity can be represented by  $H_2Y^{2-}$ . It forms complexes with  $Ca^{2+}$  and  $Mg^{2+}$  and other divalent or higher valent cations represented by the reactions.



The dissociation of these complexes is governed by the pH of the solution and the complexes with hardness causing divalent ions are stable in alkaline medium (pH range 8–10).

When a small amount of the indicator solution is added to a hard water sample whose pH has been controlled by the addition of the buffer solution, the indicator reacts with  $Mg^{2+}$  to produce



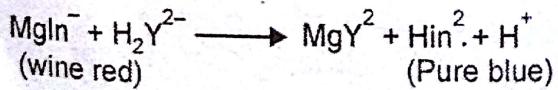
wine red colour. As EDTA ( $H_2Y^{2-}$ ) is added, free  $Ca^{2+}$  ions are first complexed to  $CaY^{2-}$ , this being the most stable complex.



Free  $Mg^{2+}$  ions then react to give Mg-EDTA complex which is less



stable than Ca-EDTA complex but more stable than Mg-indicator complex. Therefore, if an extra drop of EDTA is added after all the free  $Ca^{2+}$  and  $Mg^{2+}$  ions have been complexed, EDTA takes up  $Mg^{2+}$  from the weak Mg-indicator complex to form stable Mg-EDTA complex simultaneously liberating the indicator in the free form:



Completion of the above reaction makes the end-point of the titration.

ml req  
titr  
ten

**Q.6. (b)** 1 g of  $\text{CaCO}_3$  was dissolved in dil. HCl and solution dilute to 1 litre. 50 ml of this solution required 42 ml of EDTA solution while 50 ml of sample water required 15 ml of EDTA. On the other hand when 50 ml of boiled water sample titrated against EDTA consumed 9 ml of solution. Calculate total permanent and temporary hardness of water in ppm. (6)

**Ans.** Strength of standard heat water (SHW) = 1 g/L = 1 mg/l  
**Strength of EDTA**

$$\begin{aligned} 42 \text{ ml of EDTA} &= 50 \text{ ml of SHW} \\ &= 50 \text{ mg of } \text{CaCO}_3 \end{aligned}$$

$$1 \text{ ml of EDTA} = \frac{50}{42} \text{ mg of } \text{CaCO}_3$$

### Total hardness

50 ml of samples required = 15 ml of EDTA

$$= 15 \times \frac{50}{42} \text{ ml of } \text{CaCO}_3$$

$$1000 \text{ ml/1L sample required} = 15 \times \frac{50}{42} \times \frac{1000}{50}$$

$$= 357.14 \text{ PPM}$$

### Temp. hardness

50 ml of boiled water required = 9 ml of EDTA

$$= 9 \times \frac{50}{42} \text{ ml of } \text{CaCO}_3$$

$$1000 \text{ ml of boiled water required} = 9 \times \frac{50}{42} \times \frac{1000}{50} = 214.28 \text{ PPM}$$

$$= 214.28 \text{ PPM}$$

Permanent hardness = Total hardness – Temp. hardness

$$= 357.14 - 214.28$$

$$= 142.86 \text{ PPM.}$$

### Q.7. Explain the following:-

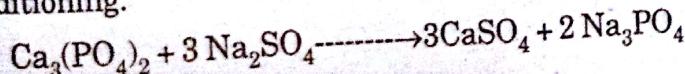
(a) Carbonate and Phosphate conditioning. (6)

**Ans. Carbonate Conditioning:** Scale formation can be avoided by adding  $\text{Na}_2\text{CO}_3$  to the boiler water. It is used only in low pressure boilers. The scale forming salt like  $\text{CaSO}_4$  is converted into  $\text{CaCO}_3$ , which can be removed easily.



### Phosphate conditioning:

Used for high pressure boiler. No risk of  $\text{CO}_2$  liberation. It is better than carbonate conditioning.



Three types of Phosphate salts are used:

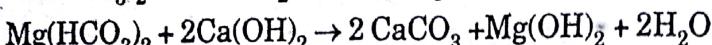
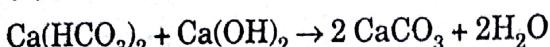
| S.No. | Salt                      | Name                           | Used for treating     |
|-------|---------------------------|--------------------------------|-----------------------|
| 1     | $\text{Na}_3\text{PO}_4$  | (Tri sodium Phosphate)         | highly acidic water   |
| 2     | $\text{Na}_2\text{HPO}_4$ | (Di sodium hydrogen Phosphate) | slightly acidic water |
| 3     | $\text{NaH}_2\text{PO}_4$ | (Sodium di hydrogen phosphate) | highly alkaline water |

### Q.7. (b) Lime soda process

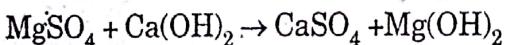
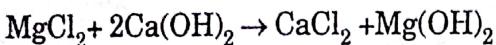
**Ans. Principle :** Conversion of all the soluble hardness causing salts into insoluble precipitate by the addition of soda and lime which can be easily removed by settling and filtration. In this method, the soluble calcium and magnesium salts in water are converted chemically into insoluble compounds by adding calculated amounts of lime  $[\text{Ca}(\text{OH})_2]$  and soda  $[\text{Na}_2\text{CO}_3]$ . Precipitates of calcium carbonate  $[\text{CaCO}_3]$  and magnesium hydroxide  $[\text{Mg}(\text{OH})_2]$  formed are filtered off.

**Function of lime:** Lime removes temporary Ca and Mg hardness, permanent Mg, Al, Fe hardness and dissolved  $\text{CO}_2$  and  $\text{H}_2\text{S}$  gases and free mineral acid present in water. Lime does not react with  $\text{CaCl}_2$  and  $\text{CaSO}_4$  so it cannot remove calcium permanent hardness.

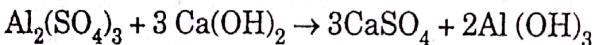
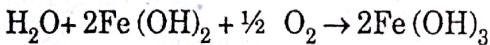
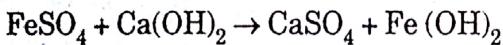
#### (a) Removal of temporary, calcium and magnesium hardness:



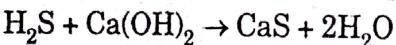
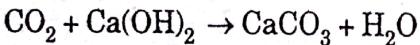
#### (b) Removal of permanent magnesium hardness:



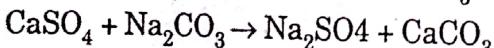
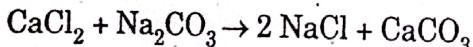
#### (c) Removal of dissolved iron, aluminium salts:



#### (d) Removal of dissolved $\text{CO}_2$ and $\text{H}_2\text{S}$ :



#### Function of Soda:



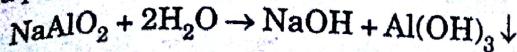
**(a) Cold lime soda process:** can be carried at room temperature water + soda + lime + coagulant  $\rightarrow$  insoluble ppt (in the form of sludge settle down and taken out through outlet at the bottom)  $\rightarrow$  softened water (filtered by wood fibre) and taken out from an outlet provided at the top.

The softened water contain residual hardness of about 50-60 ppm.

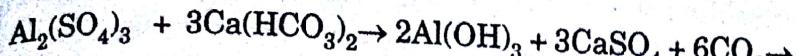
#### (i) Cold lime-soda process:

In this method, calculated quantity of lime and soda are mixed with water at room temperature. At room temperature, the precipitates formed are finely divided so they do not settle down easily and cannot be filtered easily. Hence, small amounts of coagulants like alum, aluminium sulphate, sodium aluminate etc, that hydrolyse to flocculent,

gelatinous precipitate of aluminium hydroxide and entraps the fine precipitates. Sodium aluminate as a coagulant helps the removal of silica as well as oil. Cold Lime-soda process provides water having a residual hardness of 50-60ppm.



Sodium aluminate



Coagulant calcium bicarbonate

(hardness in water)

### **(ii) Hot Lime-soda process:**

The process involves in treating water with softening chemicals at a temperature of 94-1006. since hot process is operated at a temperature close to the boiling point of the solution. So-

- The reaction proceeds faster.
- The softening capacity of hot process is increased to many fold.
- No coagulants are needed as the precipitate and sludge formed settle down rapidly.
- Most of the dissolved gases are driven out of the water.
- Filtration of water becomes much easier as the viscosity of softened water is lower.

This in turn increases the filtering capacity of filters. Hot lime-soda process produces water of comparatively lower residual hardness of 15-30ppm.

Hot lime-soda plant consists of mainly 3 parts.

- (a) a “reaction tank” in which raw water, chemicals and steam are thoroughly mixed.
- (b) a “Conical sedimentation vessel” in which the sludge settles down.
- (c) a “sand filter” that ensures complete removal of sludge from the softened water.

## UNIT-IV

**Q.8. (a) Define the factors affecting the corrosion rate.**

(6.5)

**Ans. The Factors affecting corrosion rate are:**

### **(A) Nature of the metal**

**1. Position in galvanic series:** “Higher the position of metal in the series, more its activity and greater is its tendency to undergo corrosion”. More active metal – anode and larger the difference in position of two metals in galvanic series- higher is rate of corrosion of more active metal.

**2. Overvoltage :** “The difference between the voltage required for an electrode reaction to occur and that expected theoretically is referred to as overvoltage. “ Anodic metal having small overvoltage corrodes much faster as compared to that having a higher overvoltageFor example: when Zn is placed in 1N  $\text{H}_2\text{SO}_4$ , the rate of rxn is slow due to high overvoltage( 0.70 V) inspite of high activity of Zn. On addition of  $\text{CuSO}_4$ , the rate of reaction become fast due to small overvoltage( 0.33 V) forming minute cathodes .

**3. Relative area of the cathodic to anodic parts:** Rate of corrosion increases with increase in ratio of cathodic to anodic part. e.g. Small steel pipe fitted in large Cu tank undergoes localized, rapid and severe corrosion.

**4. Purity of the metal:** Presence of impurities in metal accelerate its corrosion. Eg. Impurity of Pb or Fe or C is present in Zn, tiny electrochemical cells are set up, and Zn corroded.

**5. Physical state of the metal :** Grain size-The rate of corrosion increases with a decrease in grain size, orientation-Corrosion rate of copper is not uniform at all the faces , Stress- Area under stress is more anodic and undergo corrosion.

**6. Nature of oxide film :** In case of Aluminium oxide, lead oxide, tin oxide, volume of the oxide is greater than the volume of metal consumed. On the other hand Alkali and Alkaline earth metal Li, Na, K, Mg, Ca, Sn the volume of oxide is less than the volume of the metal.

**7. Solubility of the corrosion products:** If Corrosion product soluble -corrosion rate increases. On the other hand, if corrosion product is insoluble eg.  $Pb_3O_4$  in case of Pb in medium of  $H_2SO_4$ , it forms a protective layer on the metal surface and inhibits further corrosion.

#### (B) Nature of the corroding environment:

**1. Temperature:** Rate of corrosion increases with rise in temp eg. Intergranular corrosion such as caustic embrittlement take place at high rate.

**2. Presence of moisture:** Presence of moisture accelerates the rate of corrosion. eg. Rusting of iron increases rapidly when humidity of air is 60-80% in comparison to dry air.

**3. Presence of corrosive gases in the atmosphere:** The rate of corrosion increases in the presence of  $CO_2$ ,  $H_2S$ , fumes of HCl,  $H_2SO_4$  gases due to acidity of the liquid .

**4. Nature of the ions present :** Presence of chloride ion in the medium destroy the passive film and increases the rate of corrosion. on the other hand presence of silicate ions inhibit corrosion as they form an insoluble reaction product(silica gel).

**5. Presence of suspended particles in the atmosphere:** chemically active suspended particles like  $NaCl$ ,  $(NH_4)_2SO_4$  form strong electrolytes, increases the rate of corrosion. whereas chemically inactive suspended particles such as charcoal absorbs  $H_2S$ ,  $SO_2$  and moisture slowly increases the rate of reaction.

**6. Conductance of the corroding medium:** The flow of corrosion current depends on the conductance of medium. For eg. Conductance of clay and mineralized soils is much higher than those of dry sandy soils, that's why metal structure buried under clay and mineralized soils are damaged to larger extent.

#### 7.pH of the medium:

Media pH corrosion

Acidic pH < 7 more

Alkaline pH > 7 Less than acidic

Alkaline pH= 7 Less than acidic

#### 8. Concentration of oxygen and formation of oxygen conc. cells:

Differential aeration sets up conc. cells which enhance the rate of reaction.

#### Q.8. (b) Explain with reasons:-

##### (i) Stainless steel is resistant to atmospheric conversion

**Ans.** Steel is an alloy of iron and carbon. Contrary to carbon steel, the presence of a minimum of 10.5 % chromium in the stainless steel gives it the property of corrosion resistance. Indeed, on contact with oxygen, a chromium oxide layer is formed on the surface of the material. This passive layer protects it and has the particular ability to self repair.

**Q.8.(a)(ii) Iron in contact with copper corrodes more rapidly than lead.**

**Ans.** When placed in an electrolyte dissimilar metals in electrical contact with one another form an electrochemical cell, like a battery. An oxidation chemical reaction occurs at the more electronegative terminal of the cell (e.g. iron turns to iron oxide or rust when in contact with a more noble metal than itself like copper) while reduction i.e. the addition of electrons takes place at the more noble electrode i.e. the more electropositive electrode.

**Q.8. (b)(iii) Cr anodes are not used in chromium plating**

**Ans.** Chromium anode is not used in chrome plating as it readily undergoes corrosion

**Q.9.(a) Describe the “Electrochemical theory of corrosion”. (6.5)**

**Ans. Electrochemical theory of corrosion.**

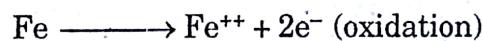
It is a common type of corrosion of metal in aqueous corrosive environment. This type of corrosion occurs when the metal comes in contact with a conducting liquid or when two dissimilar metals are immersed or dipped partly in a solution. According to this theory, there is the formation of a galvanic cell on the surface of metals. Some parts of the metal surface act as anode and rest act as cathode.

The chemical in the environment and humidity acts as an electrolyte. Oxidation of anodic part takes place and it results in corrosion at anode, while reduction takes place at cathode. The corrosion product is formed on the surface of the metal between anode and cathode.

Let us take the example of corrosion of iron.

Oxidation of metal takes place at anode while the reduction process takes place at cathode. By taking rusting of iron as an example, the reaction can be explained as that it may occur in two ways: (i) evolution of hydrogen and (ii) absorption of oxygen.

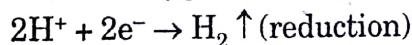
**At anode:** oxidation occurs.



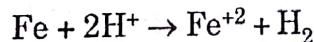
**At cathode:**

**Case I: Evolution of H<sub>2</sub>**

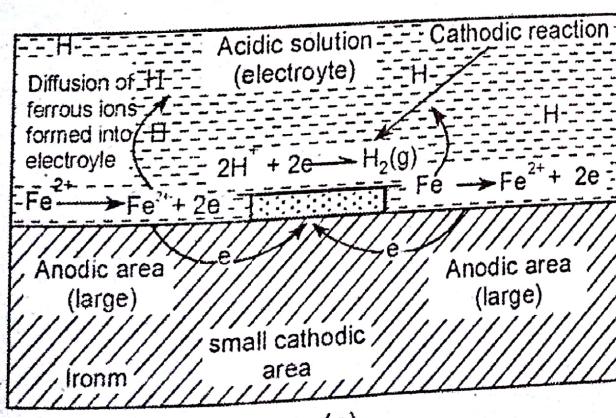
The hydrogen ions (H<sup>+</sup>) are formed due to the acidic environment and the following reaction occurs in the absence of oxygen



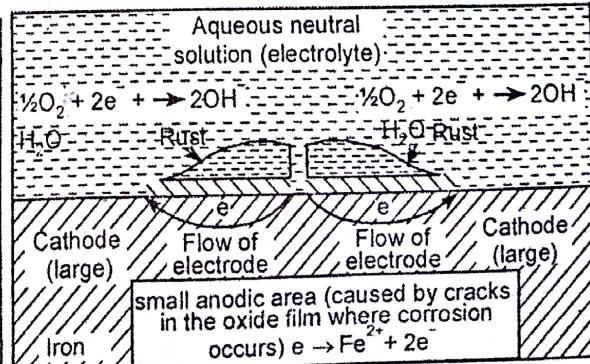
The overall reaction is



In this case, metals react in the acidic environment and are dissolved (undergo corrosion) to release H<sub>2</sub> gas. All metals above hydrogen in electrochemical series can show this type of corrosion. In hydrogen evolution type of corrosion, anodic area is large as compared to its cathodic area.



(a)



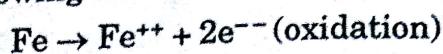
(b)

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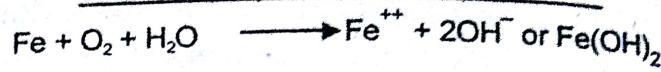
**Case II: Absorption of O<sub>2</sub>**

This type of corrosion takes place in neutral or basic medium in the presence of oxygen. The small scratch on the surface creates small anodic area and rest of the surface acts as cathodic area. The following chemical reactions occur at anode and cathode.

At anode



At cathode



Ferric hydroxide is actually hydrated ferric oxide,  $\text{Fe}_2\text{O}_3 \cdot \text{H}_2\text{O}$ , which is yellowish rust. Anhydrous magnetite,  $\text{Fe}_3\text{O}_4$  [a mixture of  $(\text{FeO} + \text{Fe}_2\text{O}_3)$ ], is also formed, which is brown-black in color.

**Q.9. (b) Write short note on soil corrosion and its control.**

(6)

**Ans.** Soil corrosion is a geologic hazard that affects buried metals and concrete that is in direct contact with soil or bedrock. Soil corrosion is a complex phenomenon, with a multitude of variables involved. Pitting corrosion and stress-corrosion cracking (SCC) are a result of soil corrosion, which leads to underground oil and gas transmission pipeline failures.

In some respects, corrosion in soils resembles atmospheric corrosion. Corrosive soils contain chemical constituents that can react with construction materials, such as concrete and ferrous metals, which may damage foundations and buried pipelines. Both the soil and the climate influence the groundwater composition.

Factors that influence soil corrosion are:

- Porosity (aeration)
- Electrical conductivity or resistivity
- Dissolved salts, including depolarizers or inhibitors
- Moisture
- pH

Each of these variables may affect the anodic and cathodic polarization characteristics of a metal in soil.

Sandy soils are high on the resistivity scale and therefore considered the least corrosive. Clay soils, especially those contaminated with saline water are on the opposite end of the spectrum.

**Soil corrosion can be controlled by:**

- Using organic and inorganic coatings
- Applying metallic coatings
- Alteration of soil
- Cathodic protection