

**NEW TOPICS ADDED FROM ACADEMIC SESSION 2021-22  
FIRST/SECOND SEMESTER  
APPLIED CHEMISTRY [BS 103/104]**

**POLYMERS**

**Q.1. Differentiate thermoplastic and thermosetting polymers**

**Ans. Thermoplastic :**

- Intermolecular forces are intermediary.
- Formed by addition polymerization.
- Linear polymers, no cross link.
- At room temp-hard, on heating- soft, easy moulded, on cooling-hard.

**Example:** Polyethylene, Polypropylene, polystyrene, teflon.

**Thermosetting :**

- On heating change irreversibly into hard, rigid, infusible material.
- Formed by condensation.
- Cross link, three dimensional network.
- Rigid, does not soften on heating, can not reprocessed.

**Example:** Phenol formaldehyde, Melamine formaldehyde, urea formaldehyde.

**Q.2. Give important application of Teflon.**

**Ans.** • Making valves and lining of parts.

- Used in making non sticking kitchen utensils.
- Used in making electric irons.

**Q.3. Distinguish between the following :**

**Ans.**

**Difference Between Addition and Condensation Polymers**

Addition Polymers	Condensation Polymers
Formed by addition reaction.	Formed by condensation process with elimination of small molecules like $H_2O$ .
Molecular mass is a <u>whole number</u> multiple of the monomer.	Molecular mass is not whole number multiple of the monomer units.
Generally involve <u>one monomer unit</u> .	Generally involve more than one monomer unit.
Monomers are <u>unsaturated molecules</u> .	Monomer units must have <u>two active functional groups</u> .
They are generally <u>chain growth</u> polymers.	They are generally <u>step growth</u> polymers.
They are non-biodegradable and hard to recycle.	Condensation polymers are biodegradable and can be recycled.
Addition polymerization is a rapid process.	Condensation is a slow process.

**Q.4. What are silicones? How are they prepared? Discuss their properties and uses.**

**Silicones:** synthetic organosilicon polymers containing repeated R<sub>2</sub>SiO units held together by Si-O-Si linkages.

General formula:  $(R_2SiO)_n$ , R-alkyl/aryl gp,

• Silicon polymers linear, crosslinked or cyclic.

**Preparation:** Linear silicones are obtained by hydrolysis of dialkyldichlorosilane or diaryldichlorosilane( $R_2SiCl_2$ ) yields a silanediol which undergoes condensation polymerization to form linear silicone.

**Cross linked silicones:** prepared by the hydrolysis of alkyl trichlorosilanes,  $RSiCl_3$

#### Properties:

1. Short chain (lower silicones) - oily liquid

Medium chains - viscous oil

Long chain(higher silicones) - rubbery

2. Water repellent and heat resistant.

3. Stable upto 2000 C and nonvolatile on heating.,

4. Chemically inert

5. Act as electrical insulator.

**Uses:** Used to form water resistant coatings on glass, clothes, paper, wood and wool. Silicones rubbers are used as insulating material.

#### Q.5. Write a short note on polymer composites?

**Ans. Polymer composites:** Polymer may be mixed with some other polymer or nonpolymeric material to incorporate additional properties. The resultant mix becomes more useful as compared to the original polymer is called polymer composite.

#### Three Categories

1. **Fibre reinforced plastic:** prepared by bonding fibre material + resin matrix under heat and pressure. Bonding fibre material may be glass/alumina/graphite/aromatic polyamides. Resin matrix may be polyesters/phenolic resins/silicon resin/melamine resins.

**Properties:** Strength of Glass reinforced plastic (GRP) increases with increase fibre length.

Increase in glass content in GRP increases its tensile and impact strength.

2. **Polymer blends:** Simple physical combination of two or more incompatible polymer is called polymer blend.

**Properties:** (a) Blending improves the properties like workability resistance to abrasion and impact strength.

(b) Helpful in protecting a polymer from degradation.

**Examples:** Nylon-6 polycarbonate blend, ABS plastics, Polydimethylphenylene-polystyrene blend.

3. **Polymer alloys:** "Compatible mixture of two or more polymers which interact chemically under specific sets of conditions of composition, temp and pressure." Example: ABS-PC alloys.

**Q.6. Discuss the effect of structure on properties of polymer.**

**Ans. Effect of structure on properties of polymers:**

**1. Molecular mass and degree of polymerization:** Molecular mass depends upon the number of monomer units present in a molecule referred to as degree of polymerization. Low molecular mass- soft & gummy, high molecular mass-tougher and heat resistant

**2. Shape of molecule:**

(a) Linear polymer:

- Polymeric chain stack one another.
- High densities, high tensile strength, high M.P.

**Example:** High density polyethylene

(b) Branched chain polymer :

- Side chain attached to main chain.
- Don't have packed structure.
- Low densities, low tensile strength, low M.P.

**Example:** Low density polyethylene

(c) Cross linked polymer:

- Adjacent polymeric chain link together through side chain three dimensional structure hard, brittle, rigid.

**Example:** Phenol formaldehyde, urea formaldehyde

**3. Intermolecular force of attraction:**

Strong Intermolecular force of attraction-high M.P, high tensile strength  
eg. Polyesters. Weak Intermolecular force of attraction-have stretching properties  
eg. Elastomers.

**Plastic deformation:** Thermoplastic subjected to heat, it get deformed known as plastic deformation. Linear polymers easily deformed but cross linked do not undergo plastic deformation.

**4. Crystallinity and amorphousness:**

Constituent macromolecules

- (i) In random arrangement—amorphous state.
- (ii) In definite crystalline arrangement—crystalline state.

**Example:** Polyethylene (chains are regular in zig-zag motion)-highly crystalline,  
Polystyrene (contain bulky gp)-amorphous in nature.

**5. Nature of monomer unit:** Cellulose polymer contain free OH

Cellulose acetate making thin films, nitrocellulose used as explosive Natural rubber have double bond react with ozone.

**6. Geometric arrangement of double bonds in polymeric chain:**

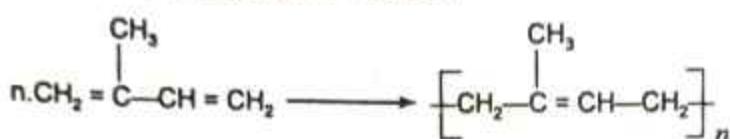
Natural rubber - cis isomer Gutta parcha- trans isomer.

**Q.7. Write note on natural rubber and synthetic rubber**

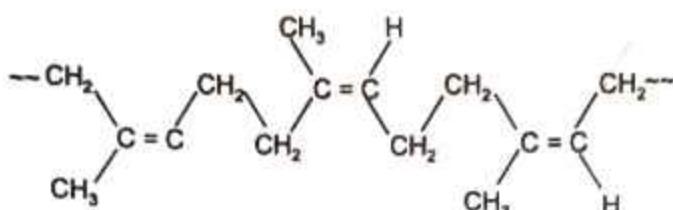
**Ans.** Natural rubber has elastic properties and it undergoes long range reversible extension even if relatively small force is applied to it. Therefore, it is also known as **Elastomer**. Natural rubber coming from latex is mostly polymerized isoprene with a

small percentage of impurities in it. This limits the range of properties available. Also, there are limitations on the proportions of cis and trans double bonds resulting from methods of polymerizing natural latex. This also limits the range of properties available to natural rubber, although addition of sulfur and vulcanization are used to improve the properties. Isoprene undergoes free radical polymerization like substituted ethylene. Isoprene polymerizes to give Polyisoprene polymer, a simple alkene having each unit still containing one double bond.

Now, polymerization of Isoprene may follow either of the two pathways; either cis-polymerization or trans-polymerization. The rubber formed from cis-polymerization is called cis-Polyisoprene or Natural Rubber. Similarly, the rubber formed from trans-polymerization is called Synthetic Rubber.



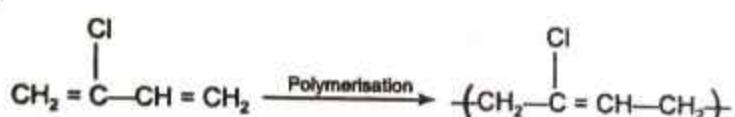
Isoprene (2-Methyl-1, 3-butadiene) undergoes cis-polymerization to form natural rubber.



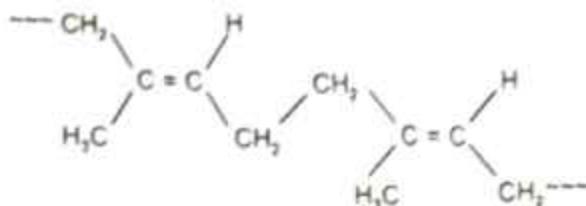
Synthetic rubber can be made from the polymerization of a variety of monomers including isoprene (2-methyl-1,3-butadiene), 1,3-butadiene, chloroprene (2-chloro-1-butadiene), and isobutylene (methylpropene) with a small percentage of isoprene cross-linking. These and other monomers can be mixed in various desirable proportions to be copolymerized for a wide range of physical, mechanical, and chemical properties. The monomers can be produced pure and the addition of impurities or additives can be controlled by design to give optimal properties.

Polymerization of pure monomers can be better controlled to give a desired proportion of cis and trans double bonds.

Chloroprene was the first commercially successful rubber substitute produced in the United States.



The properties of Rubber so formed are determined by the nature of the substituent groups. Synthetic Rubber (also known as Gutta-Percha) was obtained by the free radical polymerization of Isoprene. The rubber so formed has all trans- Configuration. As a result of this, synthetic rubber has a highly regular zig-zag chain which cannot be stretched. This accounts for non-elasticity of Synthetic Rubber.



Structure of Synthetic Rubber (trans – Polyisoprene, Gutta-percha)

**Q.8. Discuss properties and applications of fibre reinforced polymeric composites.**

**Ans. High Strength:** FRP (Fiber Reinforced Plastic) provides superior tensile, flexural and impact strength behavior. It has completely elastic behavior under stress and has no yield phenomenon.

**Light Weight:** FRP (Fiber Reinforced Plastic) component weighs roughly half its steel counterpart for bearing the same load.

**High Strength to Weight Ratio:** FRP is amongst the strongest commercial materials available. For the same weight FRP is stronger than concrete, steel and aluminium.

**Design Flexibility:** FRP can be designed in many shapes - corrugated, ribbed and contoured , in variety of shapes.

**Dimensional Stability:** FRP (Fiber Reinforced Plastic) components holds form and shape even under severe mechanical and environmental stress.

**Excellent Weatherability and Chemical Resistance:** FRP (Fiber Reinforced Plastic) has excellent resistance to moisture and chemicals over large temperature range. It does not rust, rot, corrode or swell and is maintenance free.

**Parts Consolidation:** FRP (Fiber Reinforced Plastic) structure can replace an assembly of parts and fasteners. This saves time, cuts assembling costs, facilitate the usage of lighter equipment and smaller works for installation

**Ease of Repair:** FRP is easy to repair, requiring common skill and no equipment.

**Durability:** FRP's performance under fatigue or creep is known to be superior to that of the metals, allowing longer working life.

**Applications:** Carbon steel, stainless steel, rubber-lined steel, and premium alloys, once standard materials of construction for chemical storage tanks, are more and more being replaced by fiber reinforced plastics (FRP) as engineers begin to realize the advantages of FRP, e.g. increased corrosion resistance, light weight, higher strength to weight ratio, low life cycle costs, etc.

The same advantages of FRP for chemical storage tanks apply to underground fuel storage tanks with the corrosion resistance of FRP taking particular prominence.

FRP piping is used extensively in process piping systems, stock and effluent piping in pulp bleach plants, chemical waste and municipal waste sewer piping, cooling tower piping, leach field acid piping, irrigation piping, etc.

Large diameter FRP stack liners and transport ducting for power generation stations already a proven technology for this growing application FRP impellers and fan housings are used in municipal waste water treatment plants.

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FRP is used for the storage of highly flammable sodium chlorate.

FRP has long been a material of construction for pulp washer drums used to extract residual chlorine dioxide or caustic chemical carryover from pulp.

**Q.9. Write an account of applications of polymer in electronic industry.**

**Ans.** Conductive polymers are expected to play an important role in the emerging science of molecular computers.

Organic solar cells could cut the cost of solar power by making use of inexpensive organic polymers rather than the expensive crystalline silicon used in most solar cells.

The polymers can be processed using low-cost equipment such as ink-jet printers or coating equipment employed to make photographic film, which reduces both capital and manufacturing costs compared with conventional solar-cell manufacturing.

Inexpensive polymeric substrates like polyethylene terephthalate (PET) or polycarbonate (PC) have the potential for further cost reduction in photovoltaic's.

Few except cancer researchers were interested in the electronic properties of conductive polymers, in theory applicable to the treatment of melanoma.

**Q.10. Discuss the structure, properties and applications of fullerenes.**

**Ans.** They are molecules composed entirely of carbon, in the form of a hollow sphere, ellipsoid, or tube.

Spherical fullerenes are sometimes called buckyballs, the C<sub>60</sub> variant is often compared to a typical white and black soccer football.

**Structure:** Cylindrical fullerenes are called buckytubes. Cylindrical fullerenes are often called nanotubes.

Fullerenes are similar in structure to graphite, which is composed of a sheet of linked hexagonal rings, but they contain pentagonal (or sometimes heptagonal) rings that prevent the sheet from being planar. The structure of C<sub>60</sub> is that of a truncated icosahedron, which resembles a football of the type made of hexagons and pentagons, with a carbon atom at the corners of each hexagon and a bond along each edge.



### Properties

**1. Aromaticity:** Fullerene also has aromaticity in different situations. A spherical fullerene has pibonding electrons which are free to localize or delocalize in different chemical situations.

**2. Chemistry:** According to the researchers fullerenes are considered to be the stable molecules but not fully unreactive. In certain circumstances fullerene become reactive. The reactive characteristics of fullerene is electrophilic at double bonding.

**3. Solubility:** Fullerenes are soluble in many kind of solvents. The most Common solvents for the fullerenes include carbon disulfide. Solutions of pure fullerene have a deep purple or violet color.

### Applications

- Artificial diamonds
- Antibacterial material
- Battery chemicals
- Catalysts
- Dyes
- Electronics coatings
- Fuel cells
- Industrial diamond abrasives
- Lubrican Medical antioxidants
- Pharmaceuticals
- Photovoltaic polymers
- Plastic and polymer additives
- Rubber additives
- Semiconductor processing
- Sensors
- Superconductors
- Lubricants

### **Q.11. Explain the Viscosity index and Iodine value of lubricating oils.**

**Ans. Viscosity index (VI)** is an arbitrary measure for the change of viscosity with temperature. It is used to characterize lubricating oil in the automotive industry.

The viscosity of liquids decreases as temperature increases. The original scale only stretched between VI = 0 (worst oil, naphthalene) and VI = 100 (best oil, paraffin) but since the conception of the scale better oils have also been produced, leading to VIs greater than 100. He viscosity index can be calculated using the following formula:

$$V = 100 \frac{(L-U)}{(L-H)}$$

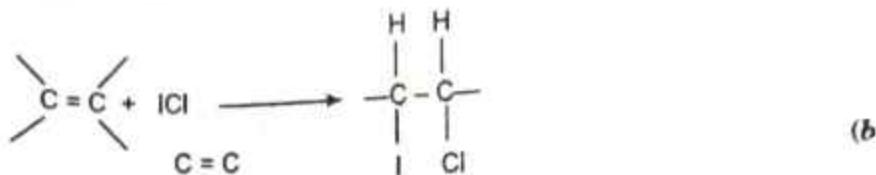
where V indicates the viscosity index, U the kinematic viscosity at 40 °C (104 °F), and L & H are various values based on the kinematic viscosity at 100 °C (212 °F)

A high viscosity index indicate small viscosity change with temperature and vice versa.

**Iodine Value:** The iodine value is the mass of iodine in grams that is consumed by 100 grams of a chemical substance. A high IV oil contains a greater number of double bonds than a low IV oil. Edible oils with high iodine value are usually less stable and more susceptible to oxidation.

The method involves the addition of Wijs solution to the sample, after which it is allowed to stand in the dark. The reaction is complete after approximately 30 min, at which time potassium iodide is added. The liberated iodine is then titrated with sodium thiosulfate, using a standard starch solution as the indicator.

Fatty acids react with a halogen [ iodine] resulting in the addition of the halogen at the C=C double bond site. In this reaction, iodine monochloride reacts with the unsaturated bonds to produce a di-halogenated single bond, of which one carbon has bound an atom of iodine.



After the reaction is complete, the amount of iodine that has reacted is determined by adding a solution of potassium iodide to the reaction product.



This causes the remaining unreacted ICl to form molecular iodine. The liberated  $\text{I}_2$  is then titrated with a standard solution of 0.1N sodium thiosulfate



Saturated fatty acids will not give the halogenation reaction. If the iodine number is between 0-70, it will be a fat and if the value exceeds 70 it is an oil. Starch is used as the indicator for this reaction so that the liberated iodine will react with starch to give purple coloured product and thus the endpoint can be observed.

**Significance:** Iodine numbers are often used to determine the amount of unsaturation in fatty acids. This unsaturation is in the form of double bonds, which react with iodine compounds. The higher the iodine number, the more C=C bonds are present in the fat.

**Q.12. Discuss the difference between fluid film lubrication and boundary lubrication.**

**Ans. Boundary Lubrication:** A state of lubrication characterized by partial contact between two metal surfaces, and partial separation of the surfaces by a fluid film of lubricant. Due to metal-metal contact, severe wear can take place during boundary lubrication. Specific additives in certain lubricants will minimize wear under boundary lubrication conditions. These additives prevent excessive friction and scoring by providing a film on the metal surface.

**Fluid Film Lubrication:** A lubrication regime characterized by a full fluid film between two moving surfaces. The most common example is the type of lubrication that occurs in oil lubricated journal bearings. The movement of one surface (the shaft or journal) "pulls" lubricating oil into the space between the journal and the bearing. This action develops a high pressure in the fluid that completely separates the two surfaces. By contrast, in boundary lubrication there is only a partial fluid film separating the two surfaces and some surface-to-surface contact occurs.

**Q.13. State flash point and fire point.**

**Ans. Flash and fire point :** Flash point of an oil is the minimum temp at which it gives sufficient vapour that ignites for a moment, when a flame is brought near the surface of oil.

Fire point of an oil is the minimum temp at which it gives sufficient vapour that appears to burn continuously for at least five seconds, when a flame is brought near the surface of oil.

**Q.14. Define Lubrication. Discuss the various mechanism through which it occurs.**

**Ans.** The process of decreasing the frictional forces between the surfaces is called lubrication.

- (a) **Solid Lubrication:** The surfaces in contact are coated with a solid substance such as graphite.
- (b) **Fluid lubrication:** A fluid is maintained between the two rubbing surfaces such as hydrocarbon oil.

### Mechanism of Lubrication

(a) **Fluid film lubrication/thick film lubrication or hydrodynamic lubrication**

- Lubricant film thickness  $1000 \text{ \AA}$
- Speed is high              • Load is light

Friction in systems with hydrodynamic or fluid film lubrication depends on:

- Thickness & viscosity of the lubricant (viscosity is not high)
- Coefficient of friction is 0.001 to 0.003 in comparison to unlubricated system.
- This type of Lubrication is generally employed in machine like sewing machine, watches, clocks etc. **Example:** Hydrocarbon oils blended with long chain polymers.

(b) **Boundary/Thin film lubrication:**

- Lubricant film thickness is less than  $1000 \text{ \AA}$
- The viscosity of oil is very low              • Heavy load
- Speed is very slow                          • Coefficient of friction is low 0.05 to 0.15

Thin layer of oil adsorbed by chemical/physical forces (oiliness)

The lubricants molecules should have

- Long chain hydrocarbon              • Polar groups to promote
- Good oiliness                          • Low pour point
- Resistance to heat and oxidation

**Example:** Mineral oil, vegetable & animal oil (liquid lubricant), graphite/Molybdenum disulphide (solid lubricant)

(c) **Extreme pressure lubrication:** When moving surfaces are working under high temp & high pressure. Special additives(extreme pressure additives) are used.

Lubricant film can withstand very high load and high temp due to their high M.P.

- Load is heavy                      • Speed is high
- Used in wire drawing, machining of tough metals
- Durable film thickness (100-10000)

**Q.15. Write a short note on cloud and pour point?**

**Ans.** Cloud point and pour point: "when a lubricating oil is cooled in a standard apparatus at a specific rate, the temp at which the oil becomes cloudy or hazy in appearance is called cloud point and the temp at which the oil ceases to flow or pour is called pour point". A good lubricating oil should possess low pour point.

**Q.16. What are additives? Discuss the various additives used in lubricants.**

**Ans. Additives for lubricants:** Compound which improve the desired qualities of lubricants are termed as additive

1. **Oiliness improvers:** increase the oiliness of lubricant and strength of oil film  
eg. fatty acid, fatty amine, vegetable oils.
2. **Viscosity index improvers:** reduce the rate of change of viscosity with temp  
eg. Polyisobutylene, polystyrene, alkyl acrylate/polyesters
3. **Antioxidants:** increase the resistance of oil toward oxidation. eg. Phenol amines, organic sulphides and phosphides.
4. **Rust and corrosion inhibitors:** used to protect bearing and other metal surface from corrosion. eg. Fatty acid and amines, metal sulphonates, metal phenolates, alkyl succinic acid.
5. **Antiwear additives:** reduce rapid wear in steel-on steel applications. eg. Zinc dithiophosphates, organic phosphates and acid phosphates.
6. **Extreme pressure additives:** adsorbed on metal surface, preventing the tearing up the metal. eg. fatty ester, acid, organic chlorine compound, organic phosphorous compound.
7. **Pour point depressants:** prevent the separation of wax from oil. eg. Phenol polymethacrylate, chlorinated wax with naphthalene.
8. **Antifoam additives:** prevent the formation of stable foam. eg. Silicon polymers, glycols, glycerols.
9. **Emulsifiers:** promote the mixing of mineral oil with water. eg. Sodium salt of carboxylic and sulphonic acid
10. **Detergents & deflocculants:** clear machine parts from dirt & dust. eg. Calcium and barium salt of sulphonates and phosphonates.
11. **Dispersants:** reduce or prevent sludge formation under low temp. eg. Alky succinimides and polymeric alkyl-thiophosphonates.

### SPECTROSCOPY

#### Q.17. What is Hooke's law?

**Ans.** IR spectroscopy based on Hooke's law, suppose two atoms or masses are connected through spring (bond), then frequency of vibration can be represented by following equation:

$$\nu = 1/2\pi \sqrt{\kappa \mu} \text{ or } \nu = 1/2\pi c \sqrt{\kappa \mu}$$

Where,  $\kappa$  is force constant of the bond,  $\nu$  is wave-number ( $\text{cm}^{-1}$ ),  $\nu$  is the frequency,  $c$  is speed of light and  $\mu$  is reduced mass ( $m_1$  and  $m_2$  are the masses of atoms)

$$\mu = m_1 \times m_2 / (m_1 + m_2)$$

#### Q.18. Discuss various types of fundamental vibrations possible in IR spectroscopy.

**Ans.** The fundamental vibrations for linear and non-linear molecules are determined by following way:

Molecule	Degree of freedom
Linear	$3n-5$
Non-linear	$3n-6$

Where, 'n' is number of atom present in the molecule

The vibrations discussed below are fundamental vibrations.

(a) **Stretching vibration:** Distance between two atoms increase and decrease but bond angle remains constant.

### **Types of stretching vibrations**

- (i) **Symmetric stretching vibration:** In this case both the atoms stretched or compressed in same direction.
- (ii) **Asymmetric stretching vibration:** In this vibration one atom undergoes stretching and other atom undergoes compression and vice versa.
- (b) **Bending vibrations:** Distance between two atom remains constant but bond angle changes. These vibrations can occur either in plane or out of plane.

### **Types of bending vibrations**

#### **1. In plane bending vibrations:**

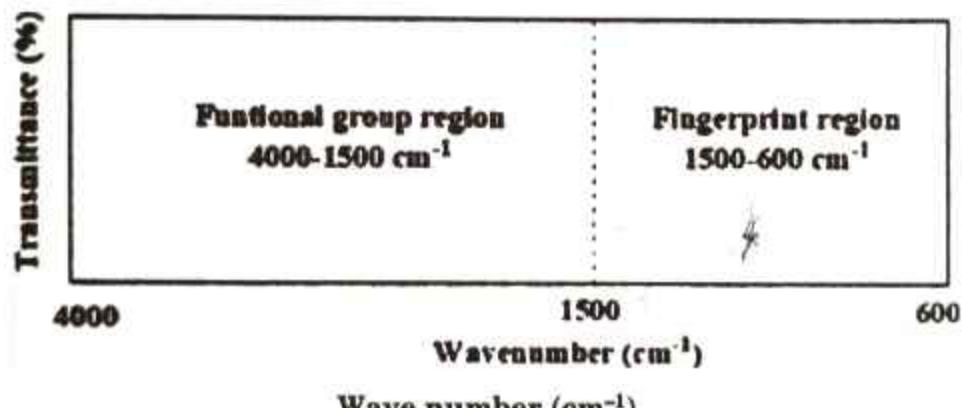
- (i) **Scissoring:** Both the atom move towards each other just like scissor.
- (ii) **Rocking:** Both the atoms move in same direction, either in left side or right side.

#### **2. Out of plane bending vibrations:**

- (i) **Wagging:** Both the atom move up and down with respect to central atom.
- (ii) **Twisting:** One atom move up and other atom move down with respect to central atom.

### **Q.19. Write a note on FINGERPRINT REGION**

**Ans.** The region from  $1500\text{--}600\text{ cm}^{-1}$  in IR spectrum is known as Fingerprint region. In this region number of bending vibration is more than the number of stretching vibration.

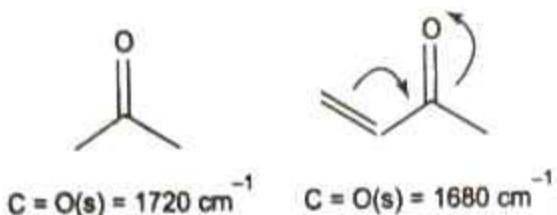


Number of molecules contains same functional group & show similar peak above  $1500\text{ cm}^{-1}$  but they show different peak in finger print region. Therefore we can say that each and every molecule have unique peak or band which is observed in finger print region, it is just like the finger print of human.

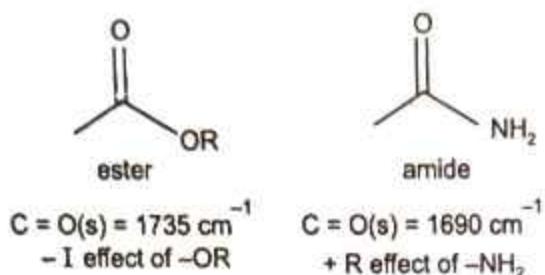
### **Q.20. What are factors effecting vibrational spectroscopy?**

#### **Ans. Factor affecting vibrational frequency**

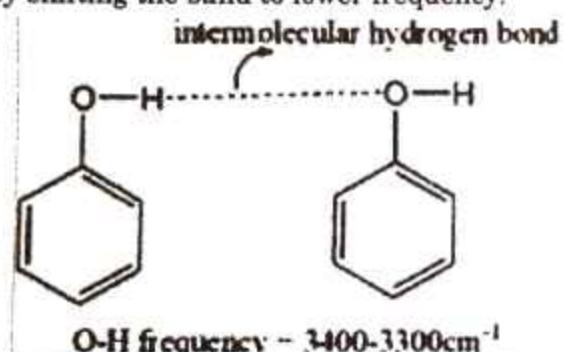
- (a) **Conjugation:** As the conjugation increase, stretching frequency decreases, because force content decrease due to conjugation.



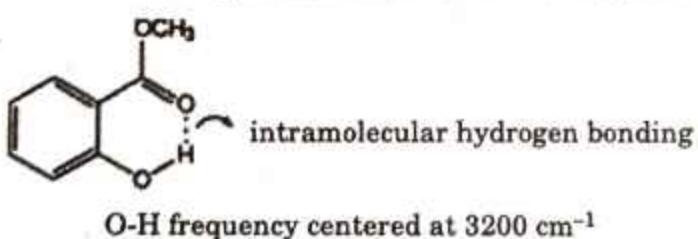
(b) **Inductive effect and resonance effect:** Oxygen is more electronegative than nitrogen, therefore nitrogen easily donate electron or lone pair of nitrogen undergoes delocalization with C=O bond. Due to delocalization double bond of C=O changes into partial double bond therefore force constant decreases which decrease the C=O stretching frequency.



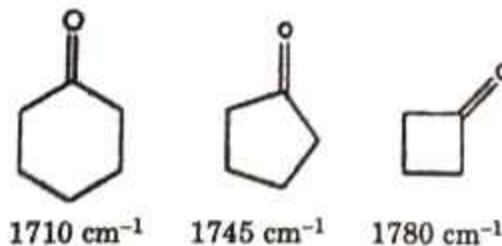
(c) **Hydrogen bonding:** Intermolecular hydrogen bonding weakens the O-H bond, thereby shifting the band to lower frequency.



Intramolecular hydrogen bonding does not change its frequency even in very dilute solution because upon dilution structure of compound does not change.



(d) **Ring strain:** As the size of the ring decrease, vibrational frequency of C=O increase. For example.



**Q.21. Give reasons why spectroscopic techniques are better than classical methods.**

**Ans.** Cheap and fast compared to things like NMR. It also works for a wide variety of samples and can detect things very strongly, whereas similar techniques like Raman spectroscopy are weaker.

Spectroscopic techniques such as UV-Vis, fluorescence, FTIR/FT Raman, and Near-UV CD, are used for qualitative and quantitative analysis of conformational structure of proteins and their behavior in solution as a function of solution composition.

They are rapid, do not require reagents and are non-destructive.

With this method a single analysis of one sample takes 3 hours and requires several millilitres of different pollutant reagents.

In addition to the health and environmental aspects of the use of these products, it is important to add the cost generated by the adequate treatment of the chemical waste.

The time required for a single determination using a classical technique (i.e., the titrimetric or chromatographic method) is 30–60 minutes following the procedure chosen, whereas a spectroscopic determination takes about 5 minutes.

Other analytical characteristics of infrared and Raman spectrometers are that they require no (or limited) sample preparation, that sample form and size are not a restriction and that they can be used for analyzing samples in almost any physical state infrared and Raman Spectrometers are relatively economic as they are considerably less demanding in terms of time and the use of reagents than traditional methods.

Spectra allow us explore a population before we determine what we should measure by classical technique.

### **Q.22. Define Lambert Beer's Law**

**Ans. Lambert-Beer law:** "Rate of decrease of the intensity of incident radiation with respect to the thickness of the medium is proportional to the product of intensity and conc."

$$-dI/dx = k.c.l,$$

K is constant called absorption coefficient.

$$\epsilon' = 1/x, \epsilon' - \text{molar}$$

extinction coefficient defined as equal to reciprocal of the thickness of the of 1M solution which reduces the intensity of light to one tenth of its original value.

### **Q.23. Write the applications of UV – vis spectroscopy and IR spectroscopy?**

#### **Ans. Application of IR spectroscopy:**

1. Identification of an organic compound.
2. Detection of functional group.
3. In detection of impurities in a sample.
4. Studying the progress of the reaction.
5. Presence of hydrogen bonding in a molecule.
6. Presence of water in a sample.

#### **Application of UV-Vis spectroscopy:**

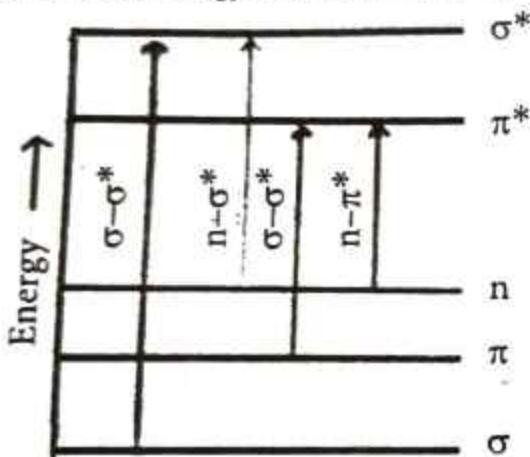
1. In qualitative analysis.
2. Detection of functional group.
3. Extent of conjugation.

4. In quantitative analysis.
5. In the detection of impurities.
6. In chemical impurities.

**Q.24. What type of transitions are possible in uv spectra.**

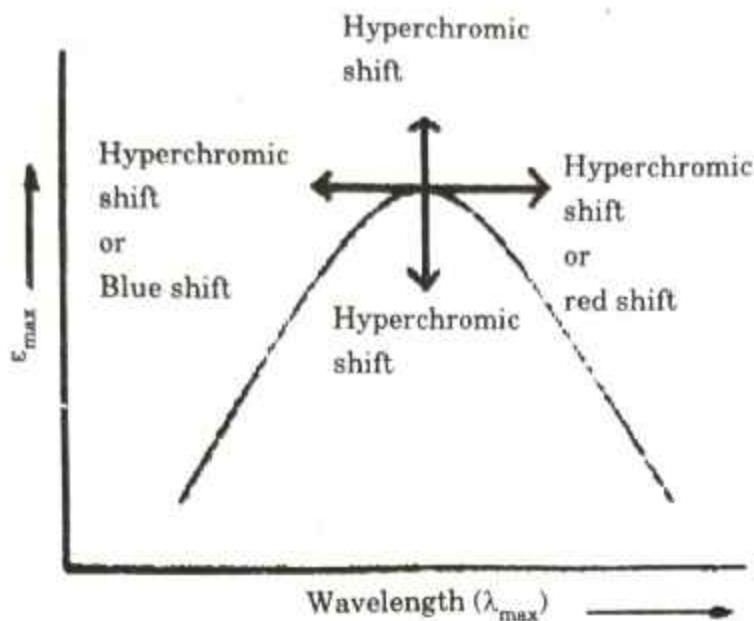
**Ans. Types of electronic transitions**

- (a)  **$\sigma - \sigma^*$  Transition:** transition of an electron from bonding sigma orbital to anti-bonding sigma orbital ( $\sigma^*$ ), is represented by  $\sigma - \sigma^*$  transition. example, alkanes because in alkane all the atoms are held together with  $\sigma$  bond.
- (b)  **$\pi - \sigma^*$  &  $\pi - \pi^*$  Transition:** Transitions from non-bonding molecular ( $n$ ) orbital to anti-bonding sigma orbital or anti-bonding pi orbital ( $\pi^*$ ), are represented  $\pi - \sigma^*$  or  $\pi - \pi^*$  transition respectively. These transition required less energy than  $\sigma - \sigma^*$  transition. For example, alkyl halide, aldehydes, ketones etc.
- (c)  **$\pi - \pi^*$  Transition:** This type of transition generally show in unsaturated molecules like alkenes, alkynes, aromatics, carbonyl compounds etc. transition required less energy as compare to  $n - \sigma^*$  transition.



**Q.25. Discuss various type of shifts possible in UV spectroscopy.**

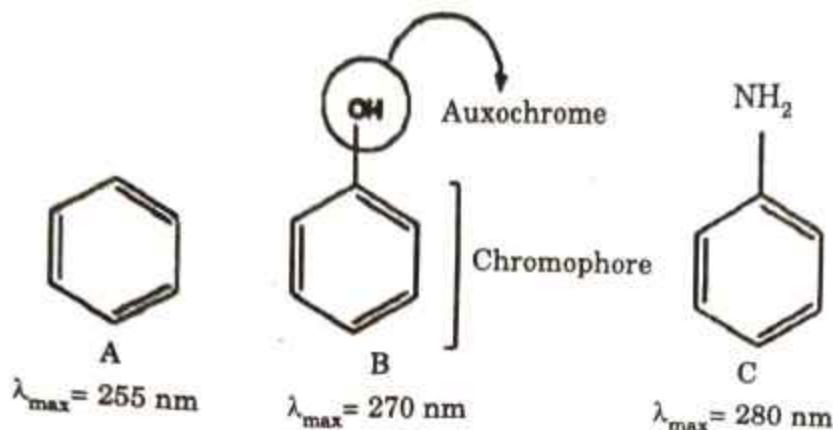
- (a) **Bathochromic shift:** It is also known as Red shift, in this absorption shift towards longer wavelength ( $\lambda_{max}$ ).
- (b) **Hypsochromic shift:** It is also known as Blue shift, in this case absorption shift towards shorter wavelength ( $\lambda_{max}$ ).
- (c) **Hyperchromic shift:** Intensity of absorption maximum ( $\epsilon_{max}$ ) increases.
- (d) **Hypochromic shift:** Intensity of absorption maximum ( $\epsilon_{max}$ ) decrease.



#### Q.26. What are chromophores and auxochromes?

**Ans. Chromophore:** A covalently unsaturated group responsible for absorption in the UV or visible region is known as a chromophore. For example, C=C, C-C, C=O, C N, N=N, NO<sub>2</sub> etc. If a compound absorbs light in the visible region (400-800 nm), only then it appears coloured. Thus, a chromophore may or may not impart colour to a compound depending on whether the chromophore absorbs radiation in the visible or UV region. Chromophores like C=C or C-C having  $\pi$  electrons undergo  $\pi \pi^*$  transitions and those having both  $\pi$  and non-bonding electrons, e.g. C=O, C N or N=N, undergo  $\pi \pi^*$ , n  $\pi^*$  and n  $\delta^*$  transitions. Since the wavelength and intensity of absorption depend on a number of factors, there are no set rules for the identification of a chromophore.

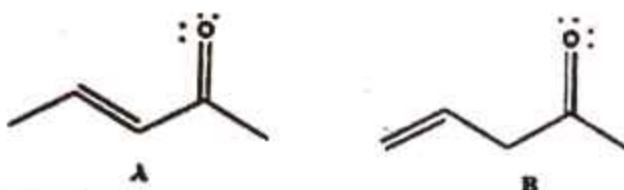
**Auxochrome:** A covalently saturated group which, when attached to a chromophore, changes both the wavelength and the intensity of the absorption maximum is known as auxochrome, e.g. NH<sub>2</sub>, OH, SH, halogens etc. Auxochromes generally increase the value of  $\lambda_{\max}$  as well as  $\epsilon_{\max}$  by extending the conjugation through resonance. These are also called colour enhancing groups. An auxochrome itself does not show absorption above 200 nm. Actually, the combination of chromophore and auxochrome behaves as a new chromophore having different values of  $\lambda_{\max}$  and  $\epsilon_{\max}$ . For example, benzene shows  $\lambda_{\max}$  256 nm,  $\epsilon_{\max}$  200, whereas aniline shows  $\lambda_{\max}$  280 nm,  $\epsilon_{\max}$  1430 (both increased).

**Absorption & Intensity Shift**

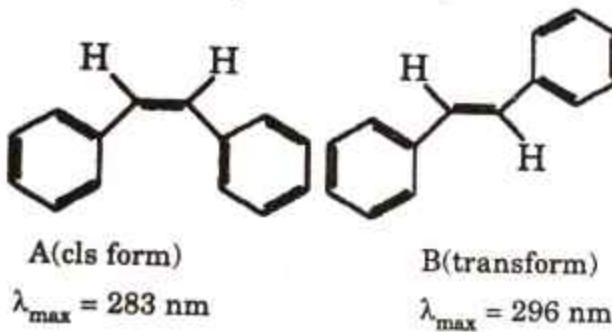
**Q.27. Discuss application of UV spectroscopy.**

**Ans. Application of UV spectroscopy**

- (i) **Extent of conjugation:** As the double bond increase, absorption shift towards longer wavelength.



- (ii) **Distinction between conjugated and non conjugated compounds:** Both the above compound A & B are isomer of each other. Due to  $n - \pi^*$  transition, compound A appear at longer wavelength than compound B.



- (iii) **Study of geometric isomerism:** In isomer A, due to steric hindrance absorption shift towards lower wavelength. We know that, steric hindrance destabilize the compound means energy of the molecule increase which decreases the wavelength.

- (iv) **Used in the detection of impurities:** Due to presence of impurities in the compound, give additional peaks are observed in UV spectrum.

**Q.28. What is NMR? Discuss it's principle.**

**Ans.** Nuclear magnetic resonance spectroscopy is one that studies the spin change at the nuclear level. This spin change occurs when a radio frequency energy is absorbed by the nucleus in the presence of a magnetic field.

Sample cell  
provide uniform :  
revolutions per se

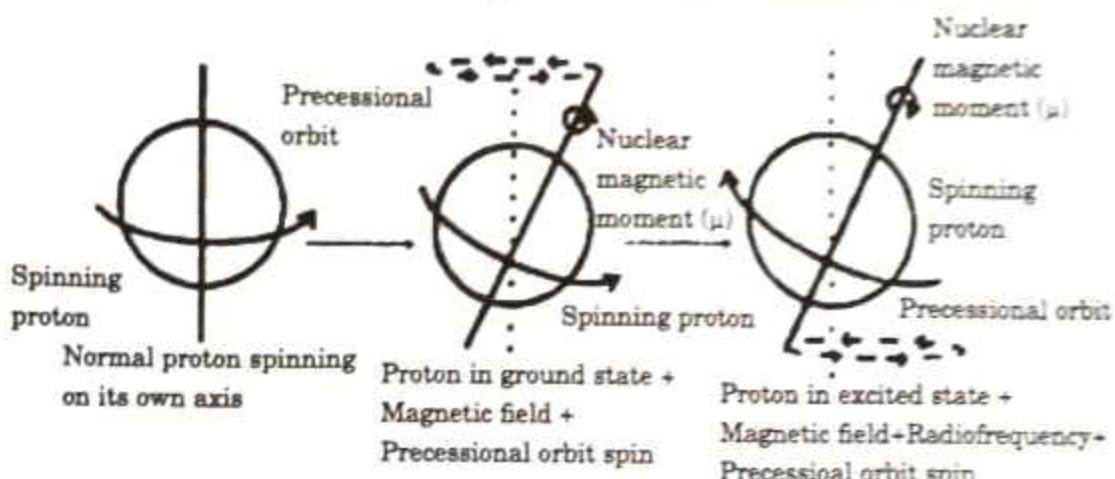
RF transmit  
can apply a frequ  
of the instrument.

### Principle of NMR Spectroscopy

In an atom with an odd mass number, the proton (nucleus) spins on its own axis. When an external magnetic field is applied, the spin shifts to precessional orbit with a precessional frequency. But still, the nuclei are in the ground state with its spin aligned with the externally applied magnetic field.

To this atom, if radio-frequency energy is applied such that the applied frequency is equal to precessional frequency, then the absorption of energy occurs leading to an NMR signal.

Since the energy is absorbed, the nucleus moves from the ground state to the excited state with its spin oriented in the opposite or anti-parallel direction.

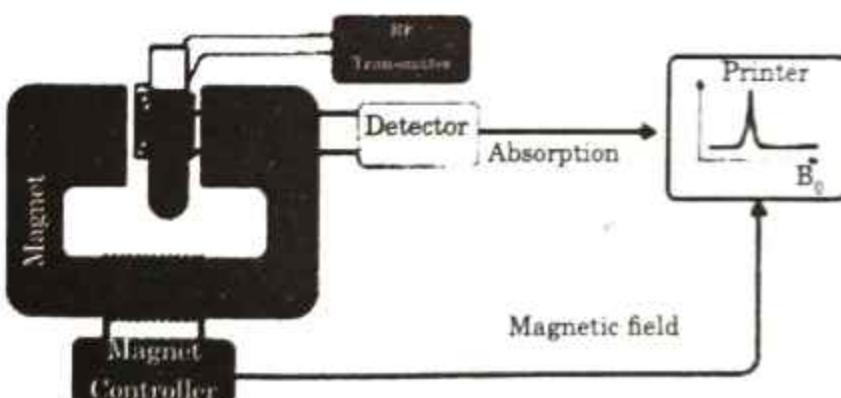


If the application of radio frequency energy is stopped, then the nucleus returns to the ground state with parallel orientation spinning is precessional orbit.

If even the magnetic field is removed, the nucleus will return to its normal spin on its own axis instead of precessional orbit.

**Q.29. Write note on instrumentation of NMR spectroscopy?**

**Ans. Instrumentation for NMR Spectroscopy:** An NMR spectrometer consists of 5 main



**Sample cell:** This a test tube like glass apparatus placed in the sample cavity. To provide uniform magnetic exposure to the sample, the cell is rotated at a speed of 30 revolutions per second.

**RF transmitter:** This is used to apply radio-frequency radiation to the sample. It can apply a frequency of 60, 90, 100, 220, 300 and 400MHz depending on the resolution of the instrument.

**RF detector:** It is meant to determine the unabsorbed radio-frequency radiation.

**Sweep generator:** This is not one which applies a magnetic field. But it is one which helps to modify the strength of the applied magnetic field.

**Recorder:** It helps to record the NMR signal received by the RF detector.

### **Q.30. Discuss application of NMR spectroscopy.**

**Ans.** Applications of NMR-Spectroscopy: NMR-applications are as follows:

1. It is used for quantitative analysis of mixtures of compounds.
2. It is used for quality control.
3. It is used to determine the molecular structure of compounds.
4. It is used to check the purity of samples.
5. It is used in food science.
6. It is used in the study of drugs.
7. It is used in the study of biofluids, cells and nucleic acids.

### **Q.31. What is the principle of Raman spectroscopy. Also write its application?**

**Ans. Principle of Raman Spectroscopy:** The principle behind Raman spectroscopy is that the monochromatic radiation is passed through the sample such that the radiation may get reflected, absorbed, or scattered. The scattered photons have a different frequency from the incident photon as the vibration and rotational property vary. This results in the change of wavelength, which is studied in the IR spectra.

The difference between the incident photon and the scattered photon is known as the Raman shift. When the energy associated with the scattered photons is less than the energy of an incident photon, the scattering is known as Stokes scattering. When the energy of the scattered photons is more than the incident photon, the scattering is known as anti-Stokes scattering.

### **Applications of Raman Effect**

- Raman amplification: this is based on the Raman scattering where the low-frequency photons are pumped to a high-frequency regime with a surplus amount of energy. This method is applicable to telecommunications.
- Supercontinuum generation: In optics, supercontinuum is formed using the Raman spectra, which results in smooth spectra as the initial spectra are built spontaneously which is later amplified to higher energy.
- Raman spectroscopy works on the basis of Raman effect and finds applications in various fields like in nanotechnology to understand the structure of nanowires, biology and medicine where the low-frequency DNAs and proteins are studied in chemistry to understand the structure of molecules and their bonds.
- Raman scattering is used in remote sensing and planetary exploration.
- Raman scattering is used to sense the minerals in Mars.

### **Q.32. Define Raman scattering?**

**Ans.** Raman scattering is defined as the scattering of photons by the excited molecules that are at higher energy levels.

### **Q.33. What are the types of Raman's Spectroscopy?**

**Ans.** Resonance Raman Spectroscopy (RRS), Surface-enhanced Raman Spectroscopy (SERS), Micro-Raman Spectroscopy, Non-linear Raman Spectroscopic Techniques, biocatalyst.

### **Q.34. What do you mean by biocatalyst? Are enzymes called biocatalysts?**

**Ans.** Biocatalysis refers to the use of living (biological) systems or their parts to speed up (catalyze) chemical reactions. In biocatalytic processes, natural catalysts, such as enzymes, perform chemical transformations on organic compounds.

Enzymes may be defined as biocatalysts synthesized by living cells. They are protein in nature w (exception - RNA acting as ribozyme), colloidal and thermolabile in character, and specific in their action.

**Q.35. How will you classify biocatalyst?**

**Ans. Classification of Biocatalyst:**

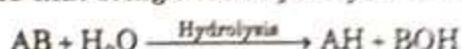
**1. Oxidoreductases:** Enzymes involved in oxidation-reduction reactions.



**2. Transferases:** Enzymes that catalyse the transfer of functional groups.



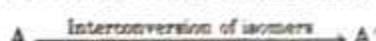
**3. Hydrolases:** Enzymes that bring about hydrolysis of various compounds.



**4. Lyases:** Enzymes specialised in the addition or removal of water, ammonia,  $\text{CO}_2$  etc.



**5. Isomerases:** Enzyme involved in all the isomerization reactions.



**6. Ligases:** Enzymes catalysing the synthetic reactions (Greek: ligate to bind) where two molecules are joined together and ATP is used.

Condensation (usually dependent on ATP)



**Q.36. Explain application of biocatalyst?**

**Ans. Applications of Biocatalyst**

- In Textile Industry
- Detergent Biocatalyst
- Biocatalyst to Convert Sugars from Starch
- Bioindicators
- Production of Biodiesel
- Bioremediation
- Waste management
- In Food Industry

### GREEN CHEMISTRY

**Q.37. Discuss the principle of green chemistry.**

**Ans.** Twelve principle of green chemistry:

**1. Prevention:** It is better to prevent waste than to treat or clean up waste after it has been created.

**2. Atom Economy:** Synthetic methods should be designed to maximize the incorporation of all materials used in the process into the final product.

**3. Less Hazardous Chemical Syntheses:** Wherever practicable, synthetic methods should be designed to use and generate substances that possess little or no toxicity to human health and the environment.

**4. Designing Safer Chemicals:** Chemical products should be designed to attain their desired function while minimizing their toxicity.

**5. Safer Solvents and Auxiliaries:** The use of auxiliary substances (e.g., solvents, separation agents, etc.) should be made unnecessary wherever possible and innocuous when used.

**6. Design for Energy Efficiency:** Energy requirements of chemical processes should be recognized for their environmental and economic impacts and should be minimized. Synthetic methods should be conducted at ambient temperature and pressure.

**7. Use of Renewable Feedstocks:** A raw material or feedstock should be renewable rather than depleting whenever technically and economically practicable.

**8. Reduce Derivatives:** Unnecessary derivatization (use of blocking groups, protection/ deprotection, temporary modification of physical/chemical processes) should be minimized or avoided if possible, because such steps require additional reagents and can generate waste.

**9. Catalysis:** Catalytic reagents (as selective as possible) are superior to stoichiometric reagents.

**10. Design for Degradation:** Chemical products should be designed so that at the end of their function they break down into innocuous degradation products and do not persist in the environment.

**11. Real-time analysis for Pollution Prevention:** Analytical methodologies need to be further developed to allow for real-time, in-process monitoring and control prior to the formation of hazardous substances.

**12. Inherently Safer Chemistry for Accident Prevention:** Substances and the form of a substance used in a chemical process should be chosen to minimize the potential for chemical accidents, including releases, explosions, and fires.

### **Q.38. What are innocuous reagent?**

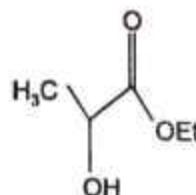
**Ans.** Chemicals that are less hazardous to human health and the environment are called innocuous reagents. Characteristics are:

- Less toxic to organisms
- Less damaging to ecosystems
- Not persistent or bioaccumulative in organisms or the environment
- Inherently safer to handle and use because they are not flammable or explosive

### **Q.39. What are green solvents/ alternative solvents?**

**Ans.** Green solvents are environmentally friendly solvents or biosolvents, which are derived from the processing of agricultural crops. The use of petrochemical solvents are the key to the majority of chemical processes but not without severe implications on the environment.

For example Ethyl lactate, for example whose structure is shown, is a green solvent derived from processing corn.



Ethyl lactate is the ester of lactic acid. Lactate esters solvents are commonly used solvents in the paints and coatings industry and have numerous attractive advantages.

including being 100% biodegradable, easy to recycle, non-corrosive, non-carcinogenic and non-ozone depleting.

Ethyl lactate is a particularly attractive solvent for the coatings industry as a result of its high solvency power, high boiling point, low vapour pressure and low surface tension. It is a desirable coating for wood, polystyrene and metals and also acts as a very effective paint stripper and graffiti remover. Ethyl lactate has replaced solvents including NMP, toluene, acetone and xylene, which has resulted in the workplace being made a great deal safer.

The hazardous organic solvents need replacements. The ecofriendly reaction media are water, polyethylene glycol room temperature ionic liquids, supercritical water, super critical carbon dioxide etc. microwave assisted organic reactions in such green solvents are playing important roles in green chemistry. Organic synthesis in aqueous media is becoming increasingly popular. Different organic reactions in aqueous media coupled with microwave/ultrasonic irradiation have now been established. Supercritical water in which organic compounds are more soluble compound to water at ordinary condition is also a potential alternative.

#### **Q.40. Explain designing of safer chemicals**

**Ans. Designing safer chemicals:** Chemical products to be synthesized should be safe to use. Thalidoimide presents an example of a typically unsafe drug, used for reducing the nausea and vomiting in pregnant women. The children born to such women suffered birth defects, which necessitated the ban on the use of this drug. Manipulation of molecular structures has helped in lot in the design of safer chemicals.

A well-known example of retrometabolic design is that of ethylene glycol, which is used as an antifreeze and has been replaced by propylene glycol which is less hazardous. Ethylene glycol once ingested in to body gets converted in to glyceraldehyde, glyoxylic acid and oxalic acid which are toxic to body, as against propylene glycol which gets metabolized into normal body metabolites like lactic and pyruvic acid.

#### **Q.41. What is fermentation? Outline the fermentation process?**

**Ans.** Fermentation is a metabolic process in which an organism converts a carbohydrate, such as starch or a sugar, into an alcohol or an acid. For example, yeast performs fermentation to obtain energy by converting sugar into alcohol. Bacteria perform fermentation, converting carbohydrates into lactic acid. The study of fermentation is called zymology.

**Fermentation process:** Fermentation is usually divided into three stages: primary, secondary, and conditioning (or lagging). Fermentation is when yeast produce all of the alcohol and aroma and flavor compounds found in beer. Manipulation of temperature, oxygen levels, and pitch rate as well as yeast strain selection will all dramatically affect the production of aroma and flavor compounds produced during fermentation.

**(a) Primary Fermentation:** The primary stage of fermentation begins when the yeast is introduced into cooled, aerated wort. The yeast quickly utilize the available oxygen to produce sterols, a vital compound for culture expansion. When the oxygen is gone, the yeast switch to the anaerobic phase where the majority of wort sugars are reduced to ethanol and  $\text{CO}_2$ . Yeast growth occurs during primary fermentation. The extent and rate of yeast growth is directly related to the production of aroma and flavor compounds.

**(b) Secondary Fermentation:** The secondary stage of fermentation refers to the stage of fermentation after the majority of the wort sugars have been consumed and there is a sharp decrease in the rate of fermentation. During this period, most of the final sugars are depleted and some secondary metabolites are converted by the yeast. Yeast flocculation and settling begins to occur due to the increase in alcohol

content and the depletion of sugar and nutrients. Diacetyl reduction takes place during secondary fermentation and during the diacetyl rest that some brewers incorporate into the secondary stage of fermentation.

**Q.42. Discuss properties of nanomaterial?**

**Ans.** The main parameters of interest with respect to nanoparticle safety are:

**Physical properties**

- Size, shape, specific surface area, aspect ratio
- Agglomeration/aggregation state
- Size distribution
- Surface morphology/topography
- Structure, including crystallinity and defect structure
- Solubility

**Chemical properties**

- Structural formula/molecular structure
- Composition of nanomaterial (including degree of purity, known impurities or additives)
- Phase identity
- Surface chemistry (composition, charge, tension, reactive sites, physical structure, photocatalytic properties, zeta potential)
- Hydrophilicity/lipophilicity

**Q.43. List various nanoparticle characterization techniques.**

**Ans.** The various Nano-particle characterization techniques are as follows

- Spectroscopic Analysis (UV-Visible Spectroscopy)
- Transmission Electron Microscopy (TEM)
- Dynamic Light Scattering (DLS)
- Zeta Potential
- Inductively Coupled Plasma Mass Spectrometry (ICP-MS)
- Dark Field Microscopy
- Aerodynamic Particle Sizer (APS)
- Scanning Mobility Particle Sizer (SMPS)
- Matrix-assisted Laser Desorption/Ionization Mass Spectrometry (MALDI-MS)

**Q.44. Explain various applications of Nanoparticles.**

**Ans.** Everyday Materials and Processes

- Nanoscale additives to or surface treatments of fabrics can provide lightweight ballistic energy deflection in personal body armor, or can help them resist wrinkling, staining, and bacterial growth.
- Clear nanoscale films on eyeglasses, computer and camera displays, windows and other surfaces can make them water- and residue-repellent, antireflective, self-cleaning, resistant to ultraviolet or infrared light, antifog, antimicrobial, scratch-resistant, or electrically conductive.
- Nanoscale materials are beginning to enable washable, durable "smart fabrics" equipped with flexible nanoscale sensors and electronics with capabilities for health monitoring, solar energy capture, and energy harvesting through movement.
- Lightweighting of cars, trucks, airplanes, boats, and space craft could lead to significant fuel savings. Nanoscale additives in polymer composite materials are being

used in baseball bats, tennis rackets, bicycles, motorcycle helmets, automobile parts, luggage, and power tool housings, making them lightweight, stiff, durable, and resilient.

- Nano-bioengineering of enzymes is aiming to enable conversion of cellulose from wood chips, corn stalks, unfertilized perennial grasses, etc., into ethanol for fuel.

### **Electronics and IT Applications**

- Transistors, the basic switches that enable all modern computing, have gotten smaller and smaller through nanotechnology.
- Using magnetic random access memory (MRAM), computers will be able to "boot" almost instantly.
- Ultra-high definition displays and televisions are now being sold that use quantum dots to produce more vibrant colors while being more energy efficient.
- Flexible, bendable, foldable, rollable, and stretchable electronics are reaching into various sectors and are being integrated into a variety of products, including wearables, medical applications, aerospace applications, and the Internet of Things.
- Ultra-high definition displays and televisions are now being sold that use quantum dots to produce more vibrant colors while being more energy efficient.

### **Medical and Healthcare Applications**

- Better imaging and diagnostic tools enabled by nanotechnology are paving the way for earlier diagnosis, more individualized treatment options, and better therapeutic success rates.
- Nanotechnology is being studied for both the diagnosis and treatment of atherosclerosis.
- Nanotechnology researchers are working on a number of different therapeutics where a nanoparticle can encapsulate or otherwise help to deliver medication directly to cancer cells and minimize the risk of damage to healthy tissue.
- use of nanotechnology for regenerative medicine spans several application areas, including bone and neural tissue engineering.
- nanotechnology can improve vaccines, including vaccine delivery without the use of needles.

### **Energy Applications**

- Nanotechnology is improving the efficiency of fuel production from raw petroleum materials through better catalysis.
- Nanotechnology can be incorporated into solar panels to convert sunlight to electricity more efficiently, promising inexpensive solar power in the future.
- Nanotechnology is already being used to develop many new kinds of batteries that are quicker-charging, more efficient, lighter weight, have a higher power density, and hold electrical charge longer.
- An epoxy containing carbon nanotubes is being used to make windmill blades that are longer, stronger, and lighter-weight than other blades to increase the amount of electricity that windmills can generate.

### **Environmental Remediation**

- Nanotechnology could help meet the need for affordable, clean drinking water through rapid, low-cost detection and treatment of impurities in water.
- Engineers have developed a thin film membrane with nanopores for energy-efficient desalination.

- Nanoparticles are being developed to clean industrial water pollutants in ground water through chemical reactions that render the pollutants harmless.
- Nanotechnology-enabled sensors and solutions are now able to detect and identify chemical or biological agents in the air and soil with much higher sensitivity than ever before.

## THERMODYNAMICS

**Q.45. How many laws of thermodynamics are there?**

**Ans.** There are four laws of thermodynamics and are given below:

- Zeroth law of thermodynamics
- First law of thermodynamics
- Second law of thermodynamics
- Third law of thermodynamics

**Zeroth Law of Thermodynamics:** The Zeroth law of thermodynamics states that if two bodies are individually in equilibrium with a separate third body, then the first two bodies are also in thermal equilibrium with each other.

**First Law of Thermodynamics:** First law of thermodynamics, also known as the law of conservation of energy, states that energy can neither be created nor destroyed, but it can be changed from one form to another.

**Second Law of Thermodynamics:** Second law of thermodynamics states that the entropy in an isolated system always increases. Any isolated system spontaneously evolves towards thermal equilibrium—the state of maximum entropy of the system.

**Third Law of Thermodynamics:** Third law of thermodynamics states that the entropy of a system approaches a constant value as the temperature approaches absolute zero.

**Q.46. Discuss various Thermodynamic processes.**

**Ans. Thermodynamic Process:** A system undergoes a thermodynamic process when there is some energetic change within the system that is associated with changes in pressure, volume and internal energy.

There are four types of thermodynamic process that have their unique properties, and they are:

- **Adiabatic Process** – A process where no heat transfer into or out of the system occurs.
- **Isochoric Process** – A process where no change in volume occurs and the system does no work.
- **Isobaric Process** – A process in which no change in pressure occurs.
- **Isothermal Process** – A process in which no change in temperature occurs.

**Q.47. What are various laws of thermo chemistry?**

**Ans. Laws of thermochemistry**

1. **Lavoisier and Laplace law:** In accordance to this law enthalpy of decomposition of the compound is numerically equal to the enthalpy of formation of that specific compound with opposite sign,
2. **Hess's law (law of the constant heat summation):** This law was presented by Hess in the year 1840. According to this law If a chemical reaction can be made to take place in a number of ways in one or in several steps, the total enthalpy change (total heat change) is always the same, that is the total enthalpy change is no dependent on the intermediate steps involved in the change.

**Q.48. Write kirchoff's equation?**

**Ans.** Kirchoff's law describes the variation of enthalpy of a reaction with the change in temperature. And at constant pressure, if the heat capacities ( $c_p$ ) do not vary with temperature then the change in enthalpy is a function of the difference in temperature and the heat capacities.

$$\Delta H_2 = \Delta H_1 + \Delta c_p(T_2 - T_1)$$

So, equations C and D are the form of the above equation.

The equation B)  $dH = TdS + VdP$  is derived from the second law of thermodynamics.

**Q.49. What is Joule-Thomson Effect?**

**Ans.** The Joule-Thomson effect also known as Kelvin-Joule effect or Joule-Kelvin effect is the change in fluid's temperature as it flows from a higher pressure region to lower pressure.

The Joule-Kelvin effect can be explained best by considering a separate gas packet placed in the opposite flow of direction for restriction. For the gas packet to pass through, the upstream gas needs to perform some work to push through the packet. The work equals the volume of the packet multiplied by the times of upstream pressure.

$$W_1 = V_{\text{packet}} \times P_1$$

As the packet goes through the restriction, it has to make some room by displacing a considerable amount of the downstream gas. It includes performing the work which equals the product of packet volume and downstream pressure.

$$W_2 = V_{\text{packet}} \times P_2$$

Due to the different effects of compressibility, the work performed upstream is not equal to the amount of work done downstream for real gases. Since depressurizing is viewed as an adiabatic process, it reveals that any gas does not exchange work or heat by its surroundings, any change in internal energy has to follow the first law of thermodynamics.

$$U_2 - U_1 = W_1 - W_2$$

Gas molecules are subjected to repulsive and attractive forces, (Van der Waals forces) as they are in random motion. When the gas pressure is lowered, i.e., the average distance between the molecules increases, the attractive forces become dominant for many gases at ambient temperature which results in an elevation in potential energy.

Most of the real gases need more work downstream at ambient temperature, due to the effects of compressibility.

$$P_1 \times V_1 < P_2 \times V_2$$

This indicates that the internal energy decreases when the gas passes through the restriction.

**Joule Thomson Coefficient**

$$\mu JT = (\partial T / \partial P)H$$

**Applications of Joule-Thomson Effect**

- The cooling produced in the Joule-Thomson expansion has made it a very valuable tool in refrigeration.
- The effect is applied in the Linde technique in the petrochemical industry, where the cooling effect is used to liquefy gases.
- It is also used in many cryogenic applications. For example for the production of liquid nitrogen, oxygen, and argon.
- The effect can also be used to liquefy even helium

**Q.50. Derive Gibbs Helmholtz equation.**

**Ans.** The Gibbs-Helmholtz equation is a thermodynamic equation used for calculating changes in the Gibbs energy of a system as a function of temperature.

It is named after Josiah Willard Gibbs and Hermann von Helmholtz.

Equation the equation is

$$\left( \frac{\partial(G/T)}{\partial T} \right)_p = \frac{H}{T^2},$$

where H is the enthalpy, T the absolute temperature and G the Gibbs free energy of the system, all at constant pressure p.

The equation states that the change in the G/T ratio at constant pressure as a result of an infinitesimally small change in temperature is a factor  $H/T^2$ .

We know that

$$\Delta_r G^\circ = \Delta_r H^\circ - T \Delta_r S^\circ$$

derivative of G with respect to T

$$\left( \frac{\partial G}{\partial T} \right)_p = -S.$$

If we apply Equation 1 to  $\Delta_r G^\circ = G^\circ_{\text{products}} - G^\circ_{\text{reactants}}$  we get,

$$\begin{aligned} \left( \frac{\partial \Delta_r G^\circ}{\partial T} \right)_p &= \left( \frac{\partial G^\circ_{\text{products}}}{\partial T} \right)_p - \left( \frac{\partial G^\circ_{\text{reactants}}}{\partial T} \right)_p \\ &= -S^\circ_{\text{products}} - (S^\circ_{\text{reactants}}) \\ &= \Delta_r S^\circ. \end{aligned}$$

Equation shows that if  $\Delta_r S^\circ$  is positive  $\Delta_r G^\circ$  decreases with temperature, but if  $\Delta_r S^\circ$  is negative  $\Delta_r G^\circ$  increases with temperature. This will tell us whether  $\Delta_r G^\circ$  increases or decreases with increasing temperature

The Gibbs-Helmholtz equation can be presented in two different, but equivalent forms.

$$\left( \frac{\partial \left( \frac{G}{T} \right)}{\partial \left( \frac{1}{T} \right)} \right)_p = H,$$

and

$$\left( \frac{\partial \left( \frac{G}{T} \right)}{\partial T} \right)_p = -\frac{H}{T^2}. \quad \dots(3e)$$

Or, applying the procedure we used in Equations 2a, b, and c, we can write,

$$\left( \frac{\partial \frac{\Delta G}{T}}{\partial \frac{1}{T}} \right)_p = \Delta H, \quad \dots(3e)$$

and

$$\left( \frac{\partial \left( \frac{\Delta G}{T} \right)}{\partial T} \right) = -\frac{\Delta H}{T^2}.$$

### Q.51. What is clausius clapeyron equation?

**Ans.** When the system is in a state of equilibrium, i.e., thermal, mechanical and chemical equilibrium, the temperature of the two phases has to be identical, the pressure of the two phases has to be equal and the chemical potential also should be the same in both the phases.

Representing in terms of Gibbs free energy, the criterion of equilibrium is:

$$d\hat{g} = 0 \text{ at constant } T \text{ and } P$$

$$\text{or } d\hat{g} = \hat{s}dT + \hat{v}dP = 0$$

Consider a system consisting of a liquid phase at state 1 and a vapour phase at state 1° in a state of equilibrium.

Let the temperature of the system is changed from  $T_1$  to  $T_2$  along the vaporization curve.

For the phase transition for 1 to 1°:

$$d\hat{g} = -\hat{s}_f dT + \hat{v}_f dP = 0$$

$$\text{or } \hat{g}_{\text{liquidphase}} = \hat{g}_{\text{vaporphase}}$$

$$\text{or } \hat{g}_1 = \hat{g}_2$$

In reaching state 2 from state 1, the change in the Gibbs free energy of the liquid phase is given by:

$$\hat{g}_2 - \hat{g}_1 = -\hat{s}_f dT + \hat{v}_f dP$$

Similarly, the change in the Gibbs free energy of the vapour phase in reaching the state 2 from state 1 is given by:

$$\hat{g}_2 - \hat{g}_1 = -\hat{s}_g dT + \hat{v}_g dP$$

$$-\hat{s}_f dT + \hat{v}_f dP = -\hat{s}_g dT + \hat{v}_g dP$$

Therefore,

$$\text{or } \left( \frac{\partial P}{\partial T} \right)_{\text{sat}} = \frac{\hat{s}_g - \hat{s}_f}{\hat{v}_g - \hat{v}_f}$$

Where the subscript sat implies that the derivative is along the saturation curve.

The entropy change associated with the phase transition:

$$\hat{s}_g - \hat{s}_f = \frac{\hat{h}_g - \hat{h}_f}{T} = \frac{\hat{h}_{fg}}{T}$$

$$\text{Hence, } \left( \frac{\partial P}{\partial T} \right)_{\text{sat}} = \frac{\hat{h}_{fg}}{T\hat{v}_{fg}} = \frac{\Delta \hat{h}}{T\Delta \hat{v}}$$

which is known as the **Clapeyron equation**.

Consider the liquid-vapour phase transition at low pressures. The vapour phase may be approximated as an ideal gas.

The volume of the liquid phase is negligible compared to the volume of the vapour phase ( $\gg$ ) and hence  $\hat{v}_{fg} = \Delta\hat{v} = \hat{v}_g - \hat{v}_l = RT/P$ .

The Clapeyron equation becomes:

$$\left(\frac{\partial P}{\partial T}\right)_{sat} = \frac{\hat{h}_{fg}P}{RT^2}$$

$$\text{or } \frac{d \ln P}{dT} = \frac{\hat{h}_{fg}}{RT^2}$$

which is known as the **Clausius-Clapeyron equation**.

Assume that  $\hat{h}_{fg}$  is constant over a small temperature range, the above equation can be integrated to get,

$$\ln \frac{P_2}{P_1} = \frac{\hat{h}_{fg}}{R} \left( \frac{1}{T_1} - \frac{1}{T_2} \right)$$

$$\text{or } \ln P = \frac{\hat{h}_{fg}}{RT + \text{constant}}$$

Hence, a plot of  $\ln P$  versus  $1/T$  yields a straight line the slope of which is equal to  $(\hat{h}_{fg}/R)$ .

### Q.52. Derive Maxwell's relation of thermodynamics

**Ans.**

$$F(T, V, N) = U(S, V, N) - TS$$

$$dF = dU - d(TS) = dU - TdS - SdT,$$

$$dU = TdS - pdV + \mu dN$$

$$dF = TdS - pdV + \mu dN - TdS - SdT$$

$$dF = -SdT - pdV + \mu dN.$$

$$\left(\frac{\partial F}{\partial T}\right)_{V,N} = -S, \left(\frac{\partial F}{\partial V}\right)_{T,N} = -p, \left(\frac{\partial F}{\partial N}\right)_{T,V} = \mu.$$

Thus, we have  $F = F(T, V, N)$  as desired. We continue as above to generate the definitions and the Maxwell relations

$$\left(\frac{\partial S}{\partial V}\right)_{T,N} = \left(\frac{\partial p}{\partial T}\right)_{V,N}, \left(\frac{\partial S}{\partial N}\right)_{T,V} = -\left(\frac{\partial \mu}{\partial T}\right)_{V,N} \left(\frac{\partial p}{\partial N}\right)_{T,V} = \left(\frac{\partial \mu}{\partial V}\right)_{T,N}$$

### Q.53. What is the Criteria to attain equilibrium?

**Ans.** Entropy is a universal criteria of spontaneity. This means for any process if  $(dS) > 0$ , the process is spontaneous. Most of the chemical process take place at constant temperature and pressure.

During course of every spontaneous process, Gibb's function decreases.

$$(dG)TP < 0$$

If a process is allowed to run spontaneously, eventually it attain equilibrium.

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

Time 1.30 hrs.

M.M.: 30

**Q.1. (a) What type of coke is produced from high temperature carbonization and low temperature carbonization?**

**Ans.** High temperature carbonization produces hard coke which is mechanically strong. it is used for metallurgically purpose

Whereas low temperature carbonization produces soft coke which is mechanically weak. it is used for domestic purpose

**Q.1. (b) Hydrocarbons that are poor gasoline fuel are quite good dieses fuels, Explain.**

**Ans.** Straight chain hydrocarbons have low cetane number but they have high octane number. Thus in petrol engines they knock badly. However they don't knock at all in diesel engines. Thus hydrocarbons that are poor gasoline fuel are quite good diesel fuel.

**Q.1. (c) What are the advantages of catalytic cracking over thermal craking?**

Advantage of catalytic cracking over thermal cracking

1. The yield of petrol is high because catalyst are selective in nature
2. The quality of petrol is better
3. No external fuel is required for cracking
4. A much lower pressure is needed in catalytic cracking
5. The cracking process can be easily controlled, so the desired product can be obtained
6. The percentage of gum forming compound is very low.

**Q.1. (d) Differentiate between positive and negative catalysis with suitable example.**

**Ans.** POSITIVE CATALYST: The catalyst which increases the rate of reaction is called positive catalyst. eg. 1. Decomposition of potassium chlorate in the presence of small amount of  $\text{MnO}_2$ .

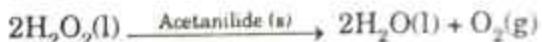


2. Manufacture of ammonia by Haber's process using finely divided iron as a catalyst

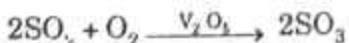


**Negative Catalyst:** The catalyst which decreases the rate of reaction is called negative catalyst. eg.

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.1. (e) Give the condition when GCV = NCV.**

**Ans.** If the does not contain hydrogen (e.g. pure carbon, sulphur etc.), then GCV=NCV.

**Q.2. (a) Describe the otto-Halfman's process for preparing coke. What are its advantages over earlier method?**

Ans2 (a) Refer Q.No 3(a) of Prac I, Pg No 1015 (Page No 13-2015)

**Q.2. (b) A sample of coal was found to have the following percentage composition C= 73% H = 5.2%, O= 12.1%, N=3.2%, Ash = 4.5%**

(i) Calculate the minimum air required for complete combustion of 1 Kg. of coal.

(ii) Also calculate the GCV and NCV of coal sample (using Dulong's formula)

$C = \frac{75}{100} \times 1000 = 750 \text{ g}$	Reaction	$O_2 \text{ required}$
$H = \frac{5.2}{100} \times 1000 = 52 \text{ g}$	$\text{C}_{12} + \text{O}_{32} \longrightarrow \text{CO}_{24}$	$\frac{32}{12} \times 750 = 2000 \text{ g}$
$O = \frac{12.1}{100} \times 1000 = 121 \text{ g}$	$\text{H}_2 + \text{Y}_{16} \text{O}_2 \longrightarrow \text{H}_2\text{O}_{18}$	$\frac{16}{2} \times 52 = 416 \text{ g}$
$N = \frac{3.2}{100} \times 1000 = 32 \text{ g}$		
$\text{Ash} = \frac{4.5}{100} \times 1000 = 45 \text{ g}$		

$$\text{Total } O_2 = 2000 + 416 \text{ g} = 2416 \text{ g}$$

$$O_2 \text{ present in fuel} = 121 \text{ g}$$

$$\text{Net } O_2 \text{ required} = 2416 - 121 = 2295 \text{ g}$$

air required for complete combustion of 1 kg of coal

$$= 2295 \times \frac{100}{23} = 9978 \text{ g}$$

$$\text{GCV} = \frac{1}{100} \left[ 8080C + 34500 \left( 4 - \frac{0}{8} \right) + 22405 \right] \text{ cal}$$

$$= \frac{1}{100} \left[ 8080 \times 75 + 34500 \left[ 5.2 - \frac{12.1}{8} \right] \right]$$

$$= \frac{1}{100} \times [606000 + 127218]$$

$$= 7332.18 \text{ cal/g}$$

$$\text{WCV} = \text{GCV} - 0.09H \times 587$$

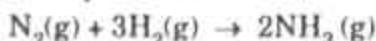
$$= (7332 - 0.09 \times 5.2 \times 5.87)$$

$$= 7057 \text{ cal/g}$$

**Q.3. (a) Write short note on (i) Promoters (ii) Catalytic poisons.**

**Ans. (i) Catalytic promoters:** Certain substances were found to increase the activity of catalyst, although they are not considered as catalyst. These substances are called promoters or activators.

Eg. 1. In the Haber's process for the manufacture of  $\text{NH}_3$  from  $\text{H}_2$  and  $\text{N}_2$ , Mo and ( $\text{Al}_2\text{O}_3 + \text{K}_2\text{O}$ ) is used as a promoter.



Fe and  $\text{Mo}/\text{Al}_2\text{O}_3$ ,  $\text{K}_2\text{O}$  act as catalyst.

2. In the Bosch's process, for the manufacture of hydrogen from the water gas, finely divided iron is used as catalyst and metallic copper is used as a promoter.

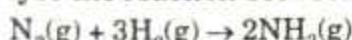
Mechanism of Action of catalytic promoters:

**Active centers:** Surface of the catalyst is not uniform, there are a number of edges, peaks and cracks. The catalytic activity at these sites is relatively high due to the presence of more residual forces at these spots.

**Ans. (a) (ii) Catalytic Poisons:** Any substance which inhibit or destroy the catalytic activity to accelerate the reaction is called catalytic poison.

Eg. 1. In contact process for the manufacture of  $\text{H}_2\text{SO}_4$ , catalytic poison  $\text{AS}_2\text{O}_3$  absorbs on the active site of Pt forming  $\text{PtS}$  on the surface of the Pt reducing the catalytic activity of Pt.

2. In Haber's process for the manufacture of ammonia, the iron catalyst used to catalyse the reaction between  $\text{H}_2$  and  $\text{N}_2$  is poisoned by the presence of  $\text{H}_2\text{S}$ .



Fe, poisoned by  $\text{H}_2\text{S}$

#### Type of Catalytic Poison:

1. **Temporary poisoning:** In which the catalyst regains its activity when the poison is removed from the reactants.

eg. In the reaction between  $\text{H}_2$  and  $\text{N}_2$  catalysed by Fe catalyst in Haber's process, water vapour and  $\text{O}_2$  acts as temporary poison.

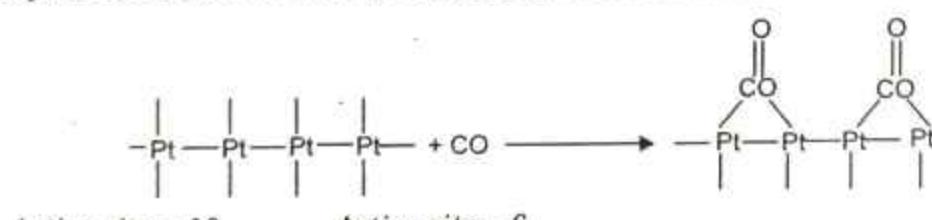
2. **Permanent poisoning:** In which the catalyst cannot regains its activity even by removing the poison.

eg.  $\text{AS}_2\text{O}_3$  poison permanently the Pt powder catalyst in contact process for the manufacture of  $\text{SO}_3$  from  $\text{SO}_2$  and  $\text{O}_2$

Mechanism of catalytic poisoning:

1. By preferential adsorption of catalytic poison on the surface of solid catalyst.

eg. A monolayer of CO on the Pt surface makes the surface unavailable for further adsorption of reactants. Thus the rate of reaction decreases.



Active site = 10      Active site = 6

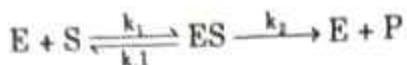
2. The catalyst combine with chemically with the catalytic poison eg. Poisoning of iron catalyst by  $\text{H}_2\text{S}$



**Q.3. (b) Deduce Michaelis-Menten Equation and give conditions under which an Enzyme catalyzed reaction changes its order.**

#### 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 is 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 rearrangements of this equation they are both multiplied by  $[ES]$ , this gives 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 gives 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:

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

This can now be rearranged in several steps

$$\frac{[E_0][S] - [ES][S]}{K_m} = [ES]$$

Then 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:

$$\begin{aligned}[E_0][S] &= K_M[ES] + [ES][S] \\ [E_0][S] &= (K_M + [S])[ES]\end{aligned}$$

Dividing both sides by  $(K_m + [S])$  now gives us:

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

Substituting this 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:

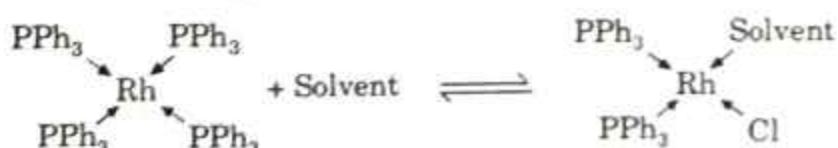
$$V = \frac{V_{max}[S]}{K_M[S]}$$

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

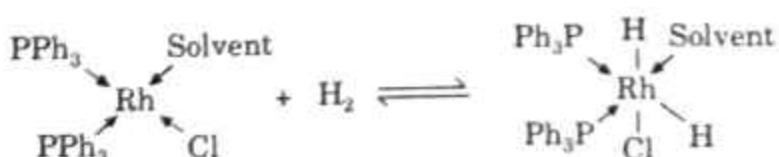
#### **Q.4. (a) Explain Catalysis by metal salts (Wilkinson's Catalyst).**

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

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

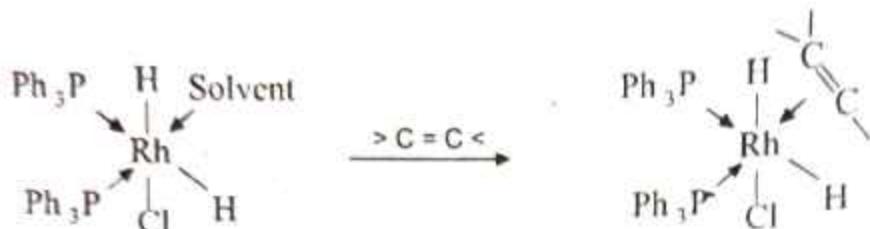


2. The reactant, alkene and molecular  $H_2$  are brought close to catalysis. The H-H bond breaks and each  $H_2$  attack separately to Rh.

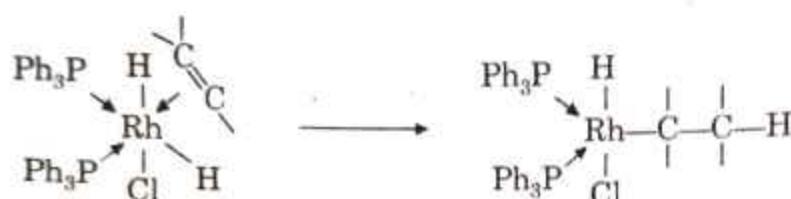


Phodium changes from oxidation state (I) to (III)

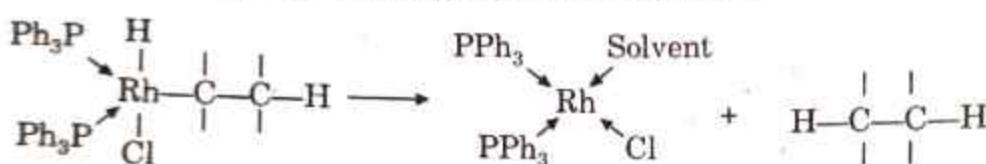
3. Alkene react with catalyst replacing a solvent molecule. The bonding occurs by overlapping of an empty orbital of metal with  $\pi$ -cloud of alkene.



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



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



**Q.4. (b)** 1.56g of a sample of coal was kjeldahlized and ammonia gas thus evolved was absorbed in 50ml of 0.1N  $H_2SO_4$ . After absorption the excess acid required 6.2ml of 0.1 N, NaOH for exact neutralization. Calculate percentage of nitrogen.

**Ans.** Amount of  $H_2SO_4$  used to neutralise the ammonia evolved

$(0.1 \times 50 - 0.1 \times 6.25)$  milli equivalence

$$\frac{0.1(15 - 6.25)}{1000} \text{ equivalent}$$

$$\text{wt. of nitrogen} = \frac{0.1(15 - 6.25)}{1000} \times 14$$

$$\% \text{ of N} = \frac{\text{wt. of nitrogen}}{\text{wt. of coal sample}} \times 100$$

$$= \frac{0.1(15 - 6.25)}{1000} \times \frac{14}{1.56} \times 100 = 0.78\%$$

**Q.4.(c) What are the limitations of intermediate compound formation theory?**

**Ans.** This theory fails to explain

1. The action of promoters as catalytic poison
2. The function of catalyst in heterogenous reaction, where intermediate compound formation is not possible.

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

Time : 1.30 hrs.

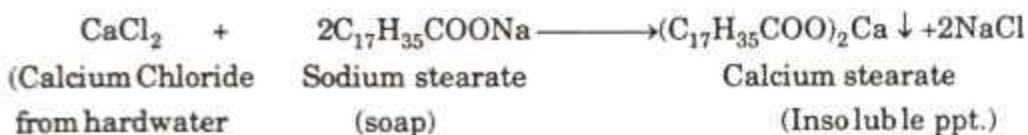
M.M. : 30

**Note:** Attempt Three Questions. Q. No. 1 is compulsory.

**Q.1. Attempt any five:**

**(a) What is Hardness of water? Differentiate between Temporary and permanent Hardness of water.**

**Ans.** Hardness of water is due to the presence of some dissolved salts in it. When hard water is treated with soap, it does not produce lather rather soap gets precipitated in the form of insoluble salts of calcium and magnesium. Let us consider the following case



Temporary hardness is due to the presence of bicarbonate ions of calcium and magnesium. It is also called carbonate hardness or alkaline hardness. It can be removed by mere boiling of water

Permanent hardness is due to the presence of sulphates and chlorides of calcium and magnesium. It is also called non-carbonate hardness and cannot be removed by boiling

i.e. single component system

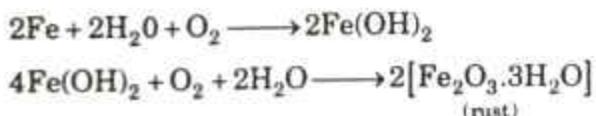
**Q1(b) Why phosphate Conditioning is better than Carbonate Conditioning.**

This is so because even if carbonate conditioning forms soft scale, but it is a SCALE phosphate conditioning forms soft sludge, which can be removed by blow down operation. So its better than carbonate conditioning. Phosphate can be chosen according to quality of boiler feed water i.e. alkaline, weakly alkaline, acidic.

**Q.1 (c) How do you remove dissolved Oxygen from water? Explain**

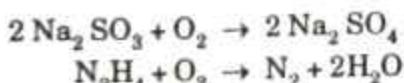
**Ans. Removal of dissolved oxygen**

Dissolved oxygen in water is mainly responsible for the corrosion of a boiler. The dissolved oxygen in water attacks the boiler material at high temperatures.



Hydrazine is found to be an ideal compound for removing dissolved oxygen since the products are water and inert  $\text{N}_2$  gas. It removes oxygen without increasing the concentration of dissolved salts.

Dissolved oxygen can be removed from water by chemical and mechanical means. Sodium sulphite, hydrazine etc. are some of the chemicals used for removing oxygen.



**Q.1.(d) Explain the term Eutectic mixture and Eutectic point.**

**Ans. Eutectic mixture:** A solid solution of two component system which has lowest freezing point of all the possible mixtures of the components is called eutectic mixture.

**Eutectic point:** Minimum freezing point attainable corresponding to the eutectic mixture is called eutectic point (means lowest melting point). The eutectic mixture has a definite composition and a sharp melting point. In this respect it resembles a compound. However, it is not a compound for the components are not present in stoichiometric proportions.

**Q.1. (e) Explain the  $\text{NH}_4\text{Cl}$  in equilibrium with its dissociation product in one component system.**

**Ans.**  $\text{NH}_4\text{Cl}$  is equilibrium with its dissociation product.



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

Here

$$S = 3 (\text{NH}_4\text{Cl}, \text{NH}_3, \text{HCl})$$

$$R = 2 \text{ (from above equation)}$$

$$C = S - R = 3 - 2 = 1$$

i.e., single component system.

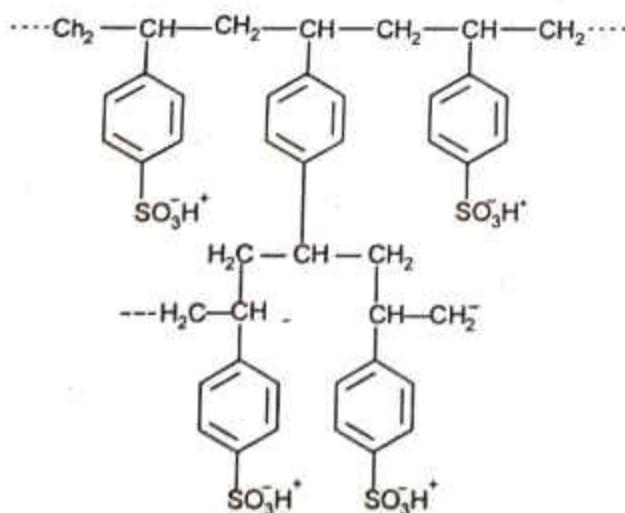
**Q1(f) What is pilling bedworth rule?**

**Ans.** Pilling-Bedworth ratio: "When the volume of the oxide is greater than the volume of metal then the oxide layer is tightly adherent, nonporous, and protective eg. Aluminium oxide, lead oxide, tin oxide. If the volume of oxide is less than the volume of the metal, the oxide layer is porous, non continuous, non protective eg. Alkali & Alkaline earth metal".

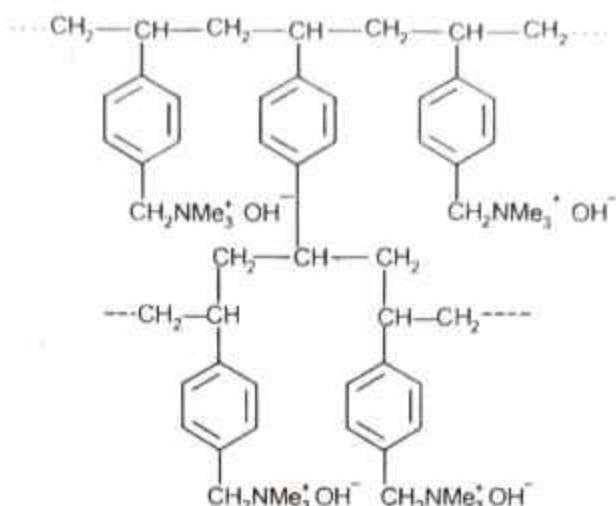
**Q.2.(a) Describe Demineralization method for water softening. Give chemical equations wherever necessary.**

**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 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  $\text{H}^+$  ion are replaced by cation present in hard water.

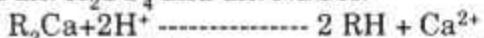


Then water is passed through anion exchange column, where anions are removed from water.

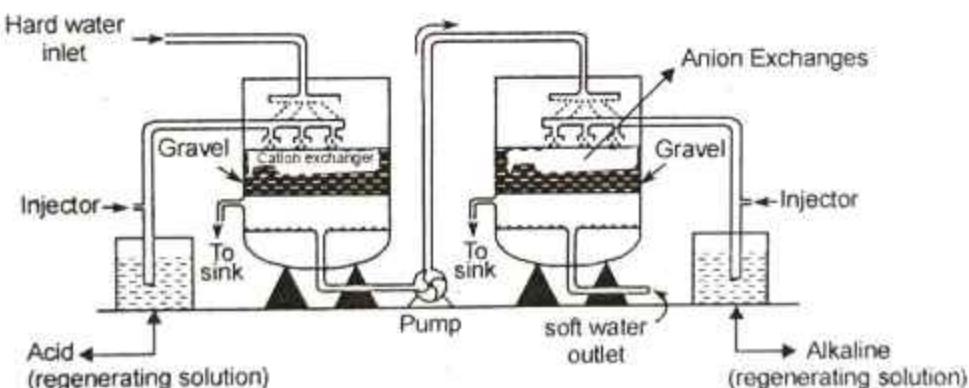


The  $\text{H}^+$  and  $\text{OH}^-$  ions released will combine to form water.

**Regeneration:-** As the cation and anion exchangers are used continuously they lose their ion exchanging capacity and become exhausted. They are treated with dil.  $\text{HCl}$ /dil.  $\text{H}_2\text{SO}_4$  and dil.  $\text{NaOH}$ .



**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.



**Q.2.(b)** Calculate the amount of Lime (90% pure) and Soda (94% pure) required for treatment of 30000 liters of water whose analysis is as follows:  
 $\text{Ca}(\text{HCO}_3)_2 = 40.5 \text{ ppm}$ ;  $\text{Mg}(\text{HCO}_3)_2 = 36.5 \text{ ppm}$ ;  $\text{MgSO}_4 = 60 \text{ ppm}$ ;  $\text{CaSO}_4 = 68 \text{ ppm}$ ;  $\text{CaCl}_2 = 27.75 \text{ ppm}$ ; and  $\text{NaCl} = 10 \text{ ppm}$ . Also Calculate Temporary and Permanent Hardness.

**Ans.**

$$\begin{array}{lll} \text{Ca}(\text{HCO}_3)_2 & 40.5 & 40.5 \times \frac{100}{162} = 25 \end{array}$$

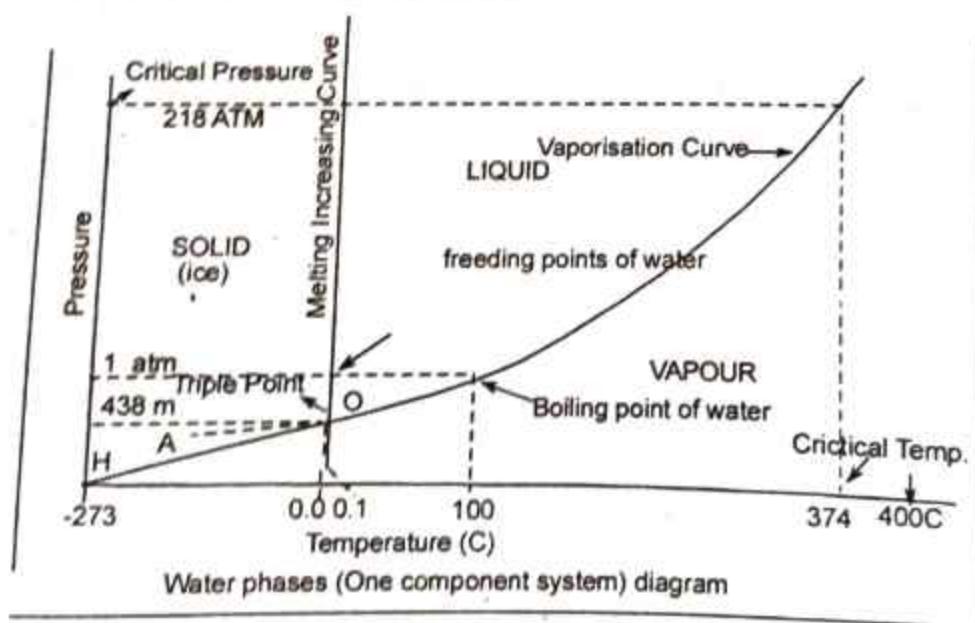
$Mg(HCO_3)_2$	36.5	$36.5 \times \frac{100}{146} = 25$
$MgSO_4$	60	$60 \times \frac{100}{120} = 50$
$CaSO_4$	68	$68 \times \frac{100}{136} = 50$
$CaCl_2$	27.75	$27.75 \times \frac{100}{151} = 25$
$NaCl$	10	-
Lime	=	$\frac{74}{100} [Ca(HCO_3)_2 + 2(Mg(HCO_3)_2 + MgSO_4)] \times \text{Vol.} \times \text{purity factor}$
	=	$\frac{74}{600} [25 + 2 \times 25 + 50] \times 30000 \times \frac{100}{90} \text{ mg} = 3.08 \text{ kg}$
Soda	=	$\frac{106}{100} [MgSO_4 + CaSO_4 + CaCl_2] \times \text{volume} \times \text{purity factor.}$
	=	$\frac{106}{100} [50 + 50 + 25] \times 30000 \times \frac{100}{94} \text{ mg}$
	=	$\frac{106}{100} \times 125 \times 30000 \times \frac{100}{94} \times 10^6 \text{ kg} = 4.2 \text{ kg}$

**Q.3.(a)** Give a labeled phase diagram of water system and discuss the important of triple point.

**Ans. The Water system:** Water can exist in three possible phases, namely solid, liquid and vapour. Hence there can be three equilibriums:

1. Liquid      Vapour
2. Solid      Vapour
3. Solid      Liquid

Each equilibrium involves two phases.



### The Curve OA

It is called the vapourization curve of water; it represents the equilibrium between liquid water and vapour. At any point on the curve the following equilibrium will exist.

Liquid water vapour

The degree of freedom of the system is one i.e., univariant. This is predicted by the phase rule.

$$F = C - P + 2; \quad F = 1$$

This equilibrium will extend up to the critical temperature  $370^{\circ}\text{C}$ . Beyond the critical temperature, the equilibrium will disappear only water vapour will exist.

### The curve OB

It is called the sublimation curve of ice. It represents the equilibrium between ice and vapour. At any point on the curve the following equilibrium will exist.

Ice                  Vapour

The degree of freedom of the system is one i.e., univariant. This is predicted by the phase rule.

$$F = C - P + 2; \quad F = 1 - 2 + 2; \quad F = 1$$

This equilibrium will extend up to the absolute zero.

### Triple point

The vaporization curve (OA) and the sublimation curve (OB) meet at point C where three phases, namely solid, liquid and vapour will coexist. Such a point is known as the "Triple point". Temperature and pressure at the triple point of water are  $0.0198$  and  $4.58\text{mm}$  respectively. according to phase rule, the degree of freedom is zero i.e., in invariant.

$$F = C - P + 2 \quad F = 1 - 3 + 2; \quad F = 0$$

### The curve OC

It is called the fusion curve of ice; it represent the equilibrium between ice and water. At any point, on the curve the following equilibrium will exist.

Ice                  water

The curve OC shows how is the melting point of ice increased by increasing pressure. The degree of freedom of the system is one, i.e., univariant.

### The curve OA\*

It is called vapour pressure curve of the super-cool water (or) metastable equilibrium. Some times water can be cooled below  $0^{\circ}\text{C}$  without the formation of ice. this water is known as super-cool water. The super-cool water can be preserved if the system is not subjected to stirring (or) "Seeding" by solid. At any point on the curve the following equilibrium will exist.

Super-cool water      Vapour

The degree of freedom of the system is one i.e., univariant.

**Area :** AOB, AOC and BOC contain vapour, liquid and ice phases respectively, within these areas, the system is bivariant. This is predicted by the phase rule.

$$F = C - P + 2 \quad F = 1 - 1 + 2; \quad F = 2$$

To locate any point in an area, temperature and pressure needs to be known.

### Q.3. (b) What are the Advantages and Limitations of Phase Rule?

#### Advantages of Gibbs Phase Rule

This equation gives the phase rule given by Willard Gibbs, the fundamental relation controlling the equilibria in heterogeneous systems. Advantages of phase rule:

- (a) It gives a simple method of classifying equilibrium states of systems.
  - (b) It confirms that the different systems having the same number of degrees of freedom behave in like manner.
  - (c) It predicts the behavior of systems when subjected to changes in the variables such as pressure, temperature and volume.
  - (d) The phase rule is applicable to macroscopic systems. Therefore, it is not necessary to take into account about their molecular structures.
  - (e) It is applicable to physical as well as chemical reactions.
- Limitations of Phase Rule**
- (a) As the phase rule is applicable to heterogeneous systems in equilibrium, therefore of no use for such systems which are slow in reaching the equilibrium state.
  - (b) As the phase rule is applicable to a single equilibrium state, it never tells about the number of other equilibria possible in the system.
  - (c) In phase rule, various variables are temperature, pressure and composition. This phase rule does not consider the electric or magnetic influences. If such variables are considered, the factor 2 of the phase rule has to be adjusted accordingly.
  - (d) All the phases in the system must be present under the same pressure, temperature and gravitational force.
  - (e) No liquid or solid phases should be finely divided otherwise their vapor pressures will differ from their normal values.

**Q.3. (c) Explain Condensed Phase Rule with explanation of terms involved** (4 + 4 + 4)

**Ans. Condensed phase rule / reduced phase rule:**

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

For a two component system,

$$C = 2 \text{ then } F = 2 - P + 2 = 4 - P$$

The minimum number of phases at equilibrium is one.

$$\text{Then } F = 4 - 1 = 3.$$

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

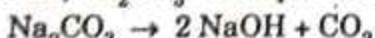
$$F = C - P + 1 \text{ (Two component system)}$$

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

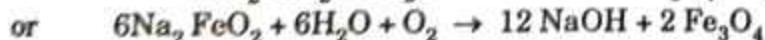
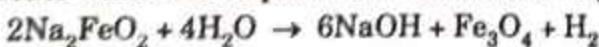
This is the reduced/condensed form of the phase rule.

**Q.4. (a) What are the factors that lead to Caustic Embrittlement in boiler? How can this be prevented?**

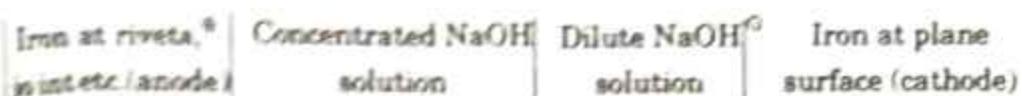
**Ans.** It is actually a special type of boiler corrosion and is caused by the use of highly alkaline water in the boiler. During softening of hard water by soda-lime process free sodium carbonate ( $\text{Na}_2\text{CO}_3$ ) is usually present in small proportion in the softened water. In high-pressure 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 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  $\text{Na(OH)}_2$  to form sodium ferroate which decomposes and forms rust magnetic ( $\text{Fe}_3\text{O}_4$ ).



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



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

#### Preventions:

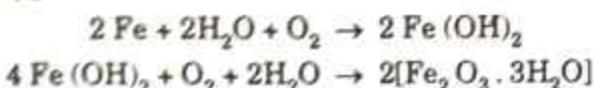
It is prevented by the following:

1. Adding tanning or ligning 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 the 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.

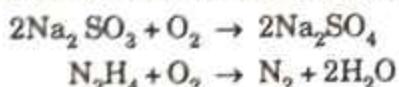
#### Boiler corrosion

##### 1. Removal of dissolved $\text{O}_2$

Dissolved oxygen in water is mainly responsible for the corrosion of a boiler. The dissolved oxygen in water attacks the boiler material at high temperatures.



Dissolved oxygen can be removed from water by chemical and mechanical means. Sodium sulphite, hydrazine, etc. are some of the chemicals used for removing oxygen.



Hydrazine is found to be an ideal compound for removing dissolved oxygen since the products are water and inert  $\text{N}_2$  gas. It removes oxygen without increasing the concentration of dissolved salts.

Dissolved oxygen can also be removed by mechanical deaeration.

##### 2. Dissolved $\text{CO}_2$ in water produces carbonic acid which is corrosive in nature.



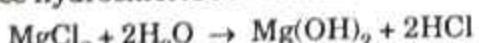
$\text{CO}_2$  can be removed from water by chemical or mechanical means. In the chemical method  $\text{CO}_2$  is removed from water by the addition of a calculate quantity of  $\text{NH}_4\text{OH}$ .



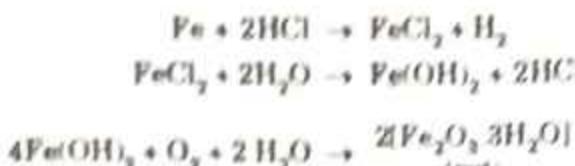
Dissolved  $\text{CO}_2$  along with oxygen can be removed by mechanical deaeration.

##### 3. Removal of acids

Acids produced from salts dissolved in water are also mainly responsible for corrosion of boilers. Certain salts like  $\text{MgCl}_2$  and  $\text{CaCl}_2$  on hydrolysis at higher temperatures produce hydrochloride acid which corrodes the boiler.



The liberated acid can produce rust in the following way.



#### Q.4. (b) Explain the Electrochemical Theory of Corrosion.

**Ans.** It is a common type of corrosion of metal in aqueous corrosive environments. 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 at 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 it may occur in two ways: (i) evolution of hydrogen and (ii) absorption of oxygen.

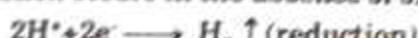
At anode: oxidation occurs.



At cathode:

#### Case I: Evolution of H<sub>2</sub>

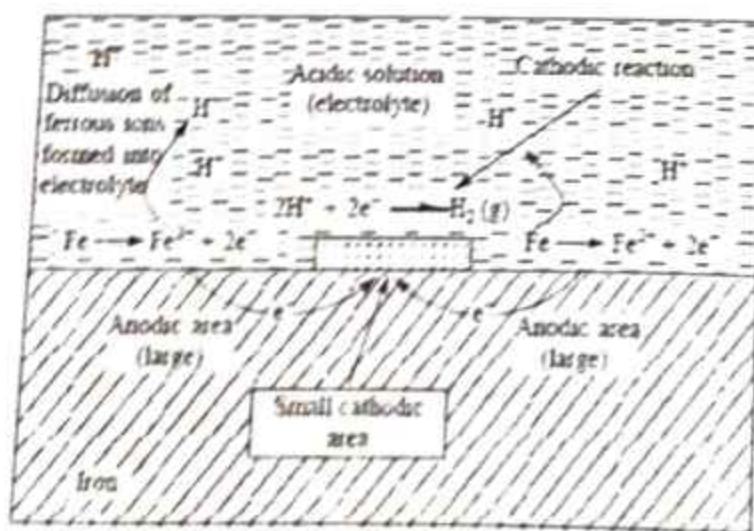
The hydrogen ions (H<sup>+</sup>) are formed due to the acidic environment and the following reaction occurs in the absence of oxygen

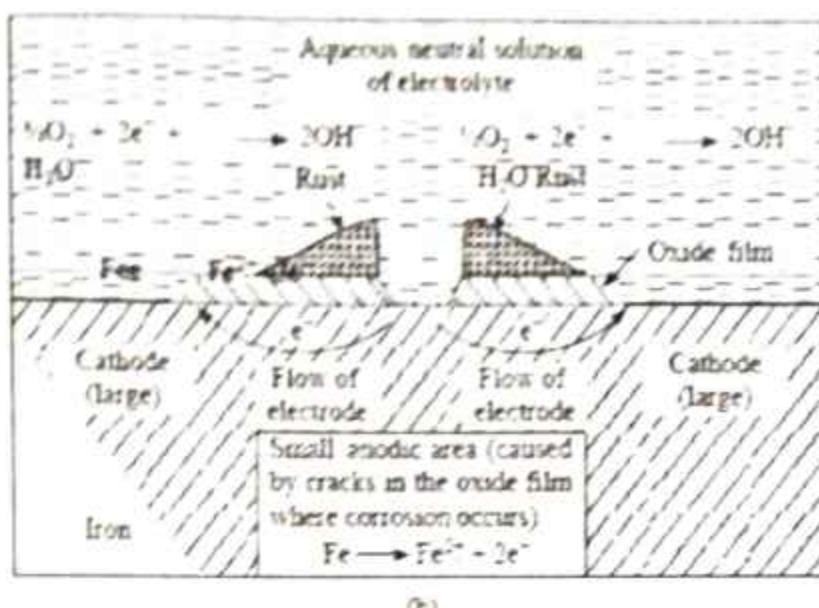


The overall reaction is



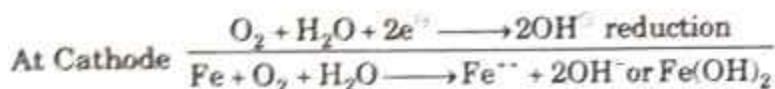
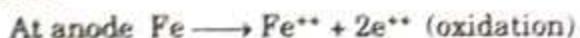
In this case, metals react in the acidic environment and are dissolved (under corrosion) to release H<sub>2</sub> gas. All metals above hydrogen in electrochemical series show this type of corrosion. In hydrogen evolution type of corrosion, anodic area is large as compared to its cathodic area





### 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.



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.4. (c) Calculate the degree of freedom of the following systems:**

(i) **An aqueous solution of  $\text{NaCl}_2$  and  $\text{Na}_2\text{SO}_4$**

(ii) **Solid Iodine in equilibrium with its Vapours,  $\text{I}_2(\text{s}) \rightleftharpoons \text{I}_2(\text{v})$**

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

$$C = 3 (\text{NaCl}, \text{Na}_2\text{SO}_4, \text{H}_2\text{O})$$

$$F = C - P + 2$$

$$= 3 - 1 + 2 = 4$$

$$(ii) \quad \text{I}_2(\text{s}) = \text{I}_2(\text{v})$$

phase (p) = 2 (solid, vapour)

$$C = 1 (\text{I}_2)$$

$$F = C - P + 2$$

$$= 1 - 2 + 2 = 1 \text{ i.e. univariant.}$$

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

M.M.

Time : 3 hrs.

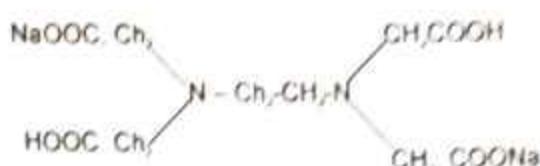
**Note:** Attempt any five questions including Q.No. 1 which is compulsory. Select one question from each unit.

**Q.1.(a) Explain how the hardness of water is removed by EDTA method.**

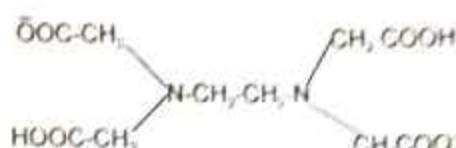
**Ans.** This is a complexometric method. Ethylene diamine tetraacetic acid (EDTA) in the form of its sodium yields the anion:

**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:



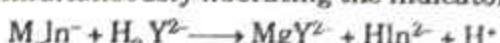
wine red colour. As EDTA ( $\text{H}_2\text{Y}^{4-}$ ) is added,  $\text{Ca}^{2+}$  ions are first complexed to  $\text{CaY}^{4-}$  this being the most stable complex:



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:



(wine red) (Pure Bleck)

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  $\frac{N}{50}$   $\text{H}_2\text{SO}_4$

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

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

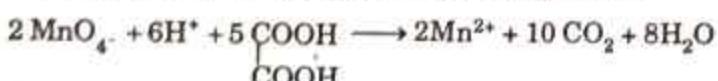
strength of alkalinity upto methyl orange end pt

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

Since P = M, only  $\overline{\text{OH}}^-$  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,  $\alpha, \beta, \gamma, \delta, \dots$ . 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.

$T,$	$P,$			
$X_{1\alpha}$	$X_{1\beta}$	$X_{1\gamma}$	—	
$X_{2\alpha}$	$X_{2\beta}$	$X_{2\gamma}$	—	
:	:	:	:	:

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  $\alpha, \beta, \gamma, \dots, \zeta$ .)

$$\mu_{1\alpha} = \mu_{1\beta}, \quad \mu_{2\alpha} = \mu_{2\beta}, \dots, \quad \mu_{c\alpha} = \mu_{c\beta}$$

$$\mu_{1\beta} = \mu_{1\gamma}, \quad \mu_{2\beta} = \mu_{2\gamma}, \dots, \quad \mu_{c\beta} = \mu_{c\gamma}$$

$$\vdots \quad \vdots \quad \vdots \quad \vdots \quad \vdots \quad \vdots$$

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

(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,

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

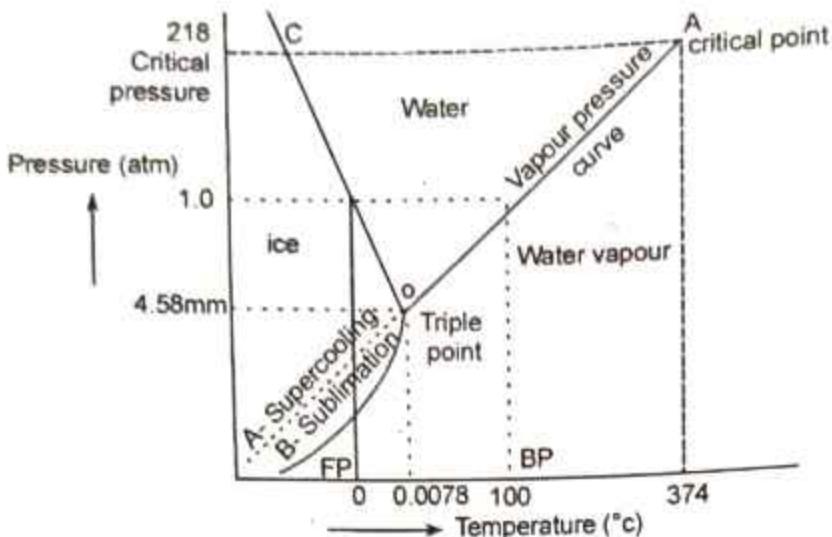
$$v = 2 + c - p.$$

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 1(g)** . Phase diagram of water system: Refer Q.No.4(a) of Pre -University Exam 2015 (Pg.No. 17-2015)

**Triple point:** The point O 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-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 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.

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

$$= \frac{\text{Volume of Metal Oxide}}{\text{Volume of Metal}}$$

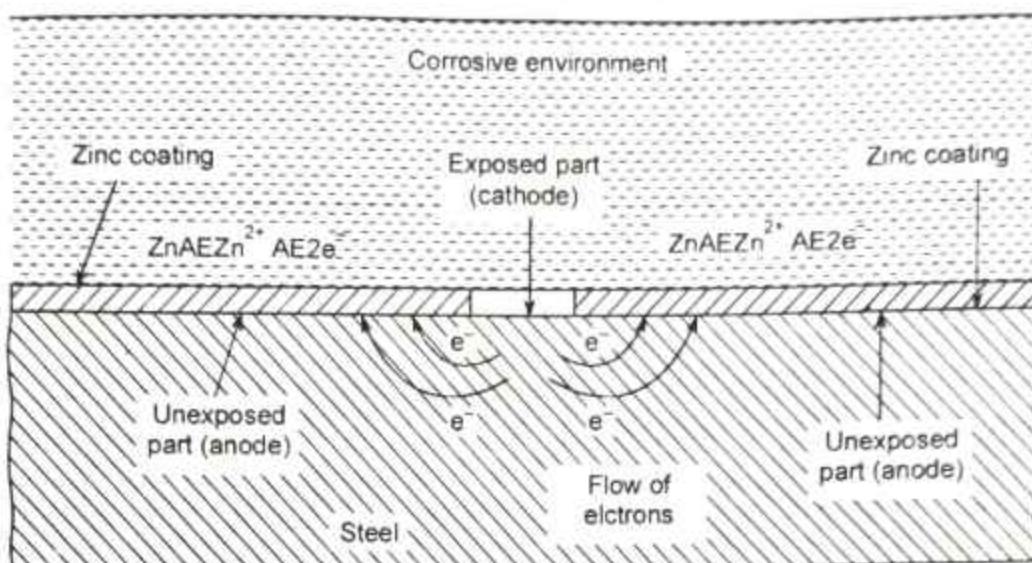
Smaller the specific volume ratio greater is the oxidation corrosion. Alkali and alkaline earth metals form oxide of volume less than the volume of metal, thus the oxide layer faces stress and strain, developing cracks and pores. Porous oxide scale permits free access of oxygen to the underlying metal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



**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.

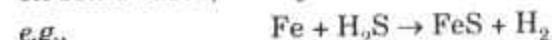
3. By altering the surface of the walls of the reaction vessel.

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.



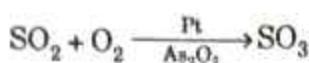
Depending on extent and strength of adsorption, it is 2 types:

**(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, 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 process for making  $\text{SO}_3$  from  $\text{SO}_2$



### Promoters

**Catalytic Promoters:** 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 called activation.

For e.g., In  $\text{NH}_3$  manufacture by Haber's process, finely divided 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.

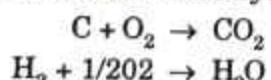
**Q.2. (a) Explain what is ultimate analysis of coal? How one can find the % Composition of C, H, N & S using it?**

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 substance 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.

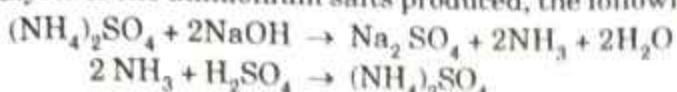


inorganic carbonates contribute to the carbon value in coal as it is normally determined. Hydrogen values also are usually high, due to the inclusion of the various forms of moisture that are present in coal.

#### 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 solution.

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  $\text{BaCl}_2$  solution to form insoluble  $\text{BaSO}_4$ . A  $\text{BaSO}_4$  precipitate that is easily filtered is to add the  $\text{BaCl}_2$  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.

$$\text{Ox} = 100 - [\text{C} + \text{H} + \text{N} + \text{S} + \text{ash}]$$

**Q.2. (b)** 2.16 g of coal was kjeldalized and  $\text{NH}_3$  gas thus evolved was absorbed in 25 ml of 0.1  $\text{NH}_2\text{SO}_4$ . 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.**  $12.5 \text{ ml of } 0.1 \text{ N NaOH} = 25 \text{ ml of } 0.1 \text{ NH}_2\text{SO}_4$

Volume of  $\text{H}_2\text{SO}_4$  used to neutralize  $\text{NH}_3$  evolved = 25 ml of 0.1 N – 12.5 ml of 0.1 N  $\text{H}_2\text{SO}_4$

$$= 12.5 \text{ ml of } 0.1 \text{ N H}_2\text{SO}_4$$

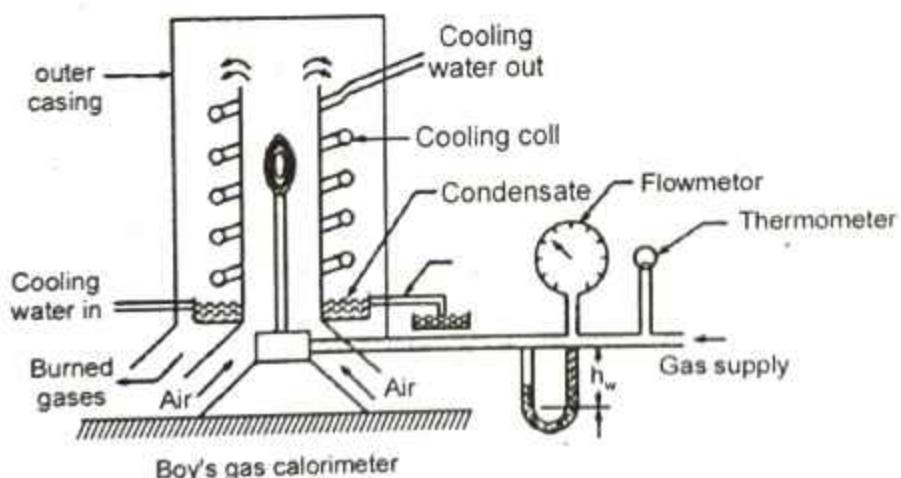
$$\% \text{N} = \frac{\text{Volume of H}_2\text{SO}_4 \times N \times 1.4}{\text{weight of coal sample}}$$

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

**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 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

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

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

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

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

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

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

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

**Q.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  $\text{m}^3$  of the gas.** (6)

**Ans.**

Constituent	Amount	Reaction	Vol. of $\text{O}_2$ required
$\text{H}_2$	18.3	$\text{H}_2 + \frac{1}{2}\text{O}_2 \rightarrow \text{H}_2\text{O}$ mole $y_2$ mole	$0.183 \times \frac{1}{2} = 0.0915$
$\text{CH}_4$	0.034	$\text{CH}_4 + \text{O}_2 \rightarrow 2\text{H}_2\text{O}$ 1 mole 1 mole	$0.034 \times 1 = 0.034$
CO	0.254	$\text{CO} + \frac{1}{2}\text{O}_2 \rightarrow \text{CO}_2$ 1 mole $y_2$ mole	$0.254 \times \frac{1}{2} = 0.127$
$\text{CO}_2$	0.051	-	
$\text{N}_2$	0.478		

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

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

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

Ans. 4(a) Refer Q.No.3(a) of First Term Exam 2016 (Pg. No. 4-2916)

**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  $42^\circ\text{C}$

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

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

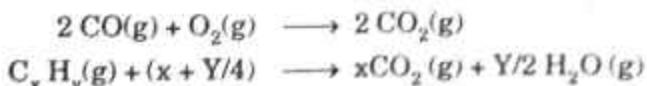
$$\begin{aligned}P &= 1 \quad (\text{crystal}) \\ C &= 1 \quad (\text{CuSO}_4 \cdot 5\text{H}_2\text{O}) \\ F &= C - P + 2 \\ &= 1 - 1 + 2 = 2 \text{ (bivariant)}\end{aligned}$$

(3) An aqueous solution of glucose

$$\begin{aligned}P &= 1 \quad (\text{solution}) \\ C &= 2 \quad (\text{water} + \text{glucose}) \\ F &= C - P + 2 \\ &= 2 - 1 + 2 = 3 \text{ Invariant.}\end{aligned}$$

**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 if 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.**

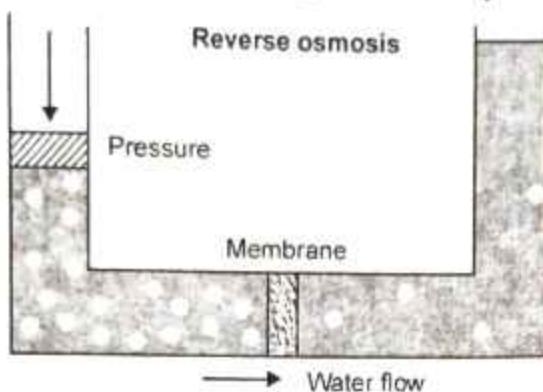
**Ans. (i) Reverse Osmosis**

**Ans. Reverse osmosis:** Spontaneous process, "the flow of solvent from the conc. 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.

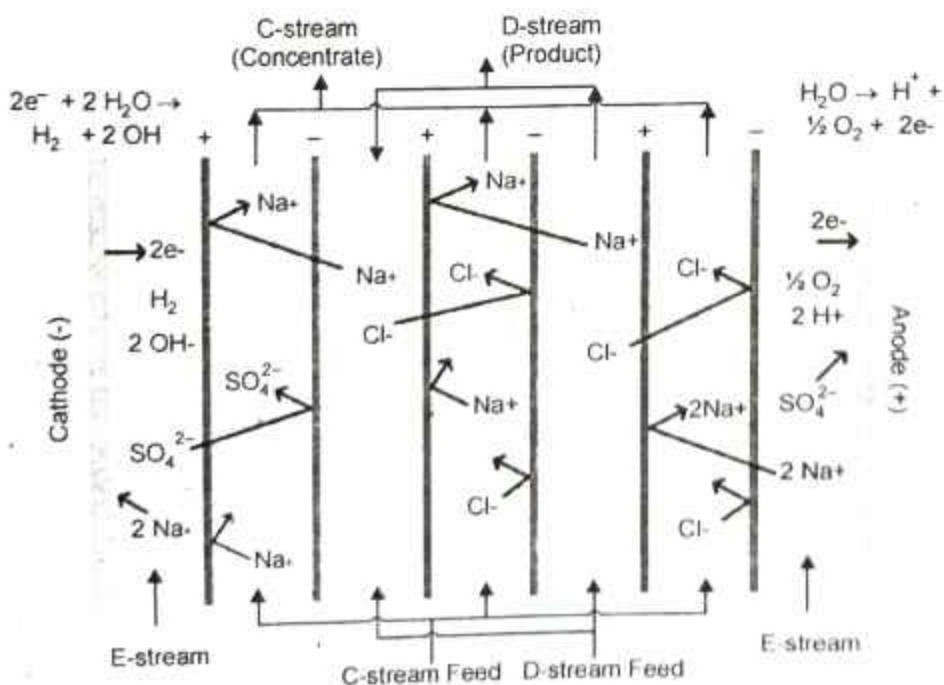
**Process:** Desalination of sea water/ brackish water is carried out in a reverse osmosis cell. In this cell saline water is separated from the fresh water through semi permeable membrane made of very thin films of cellulose acetate affixed to side of a perforated plate or tube, pressure of the order 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

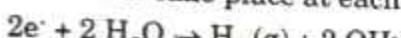
**Ans. Electro dialysis (ED)** is used to transport salt ions from one solution through ion-exchange membranes to another solution under the influence of an applied electric potential difference. This is done in a configuration called an electrodialysis cell. The cell consists of a feed (dilute) compartment 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 an electrical potential difference, the negatively charged ions (e.g., chloride) in the diluate 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 of 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 solids 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 decreases 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 soln.

$M_1 V_1 M^{32}$ 

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

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

$$\begin{aligned}\text{Total hardness} &= M \times \text{Mo 1. mass of } CaCO_3 \\ &= 3 \times 10^{-3} \times 100 g/L \\ &= 3 \times 10^{-3} \times 100 \times 1000 = 300 mg/L \\ &= 300 PPM\end{aligned}$$

Titration of EDTA with boiled water

$$\begin{aligned}M_1 V_2 &= M_2 V_2 \\ M_1 \times 50 &= 0.01 \times 5\end{aligned}$$

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

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

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

#### **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 ( $Na_2CO_3$ ) is usually present in small proportion in the softened water. In high-pressure boilers,  $Na_2CO_3$  decomposes to give sodium hydroxide and  $CO_2$ .



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 ( $Fe_3O_4$ ).



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 joint etc. (anode)	Concentrated NaOH solution	Dilute NaOH Solution	Iron at plane surface (cathode)
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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 the 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 of by external treatment?**

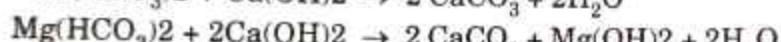
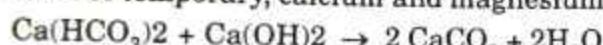
**Ans.** Softening of water (Removing of the dissolved salt) –The process of removing the hardness causing salts from the water called softening of water.

**Lime-soda process:**

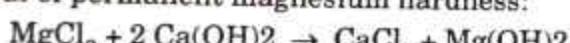
**1. Lime- soda process:** Principle : Conversion of all the soluble hardness causing salts into insoluble precipitate by the addition of soda and lime which can be easily removed by settling and filtration In this method, the soluble calcium and magnesium salts in water are converted chemically into 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, 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.

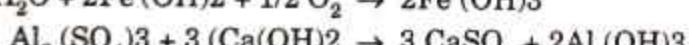
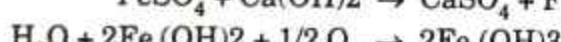
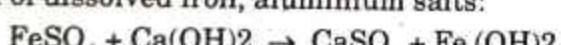
(a) Removal of temporary, calcium and magnesium hardness:



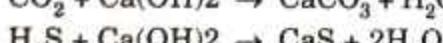
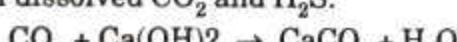
(b) Removal of permanent magnesium hardness:



(c) Removal of dissolved iron, aluminium salts:



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



**Function of soda:**



## 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) Zinx 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 sorrosion 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 9(i) . Refer Q.No.1(e)(iii) of End Term Exam 2017 (Pg No. 11-2017)**

**(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 noble 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 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 which 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.

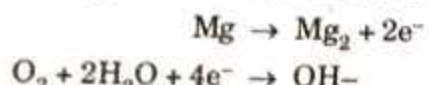
**(iii) Corrosion inhibitors.**

**Ans.** Refer Q.No.9(a)(iii) of End Term Exam 2015 (Page No.: 26-2015)

**(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 DC 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 Q.No.9(a)(iv) of End Term Exam 2015 (Page No.: 27-2015)

anode and cathode. In the presence of galvanic cell, metal which is more active than iron will form an electrode pair with iron. The more noble metal will form a cathode and the anode. The more noble metal corrodes more quickly and vice versa. Metal corrosion occurs slowly.

Galvanic series based on differential aeration cell potential, soil ion migration passes through clay then through aqueous phase. Metal corrosion in soil pipelines takes place

#### Electrolytic Corrosion

This type of corrosion occurs when DC plate is fixed below the shop. Zn or Al plate is recommended as this more active Zn metal corrodes faster. Hence they must be replaced by fresh one. There are two types of electrolytic corrosion.

Ways to prevent and overcome and its control:  
Ways to prevent corrosion that affects buried metals and concrete that come in contact with soil. Soil corrosion is a complex phenomenon, with a number of factors. Among corrosion and stress-corrosion cracking (SCC) are major causes of underground oil and gas transmission pipelines.

Soil corrosion mainly resembles atmospheric corrosion. Corrosive soils contain elements that can react with construction materials, such as sulfur, which may damage foundations and buried pipelines. Both factors influence the groundwater composition.

Control of corrosion are:

#### Electrolytic Corrosion

Adding inhibitors or inhibitors

Inhibitors may affect the anodic and cathodic polarization minimally.

Based on the resistivity scale and therefore considered the least resistive soils contaminated with saline water are on the opposite side.

Some controlled by:

Electrostatic coatings

Painting

Cladding

Some of the following:

Coatings

Electroplating

Electrolytic protection

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

Time: 1½ Hours

M.M. : 30

*Note: Q. No. 1 is compulsory. Attempt any two more Question from the rest.*

**Q. 1. (a) Differentiate between Proximate and Ultimate analysis of coal.**  
(2 × 5 = 10)

**Ans.** In ultimate analysis chemical determination of following elements is made by weight: Fixed and combined carbon, H<sub>2</sub>O<sub>2</sub>, N<sub>2</sub>, S, water and ash. Heating value is due to C, H<sub>2</sub> and S.

In proximate analysis following constituents are mechanically by weight. Moisture volatile matter, fixed carbon and ash. Heating value is due to fixed carbon and volatile matter.

Ultimate analysis tests produce more comprehensive results than the proximate analyses.

**Q.1. (b) What is sweetening of petrol? Give reaction also.**

**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 odour and increase toxic sulfur dioxide engine emissions. However, this process only reduces the odour.

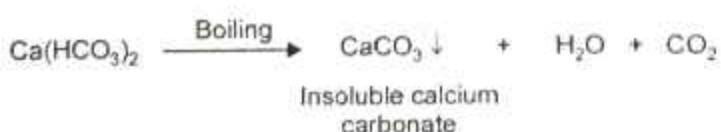
These sulfur compounds can be removed with the following chemical reactions (sour gasoline) 2RSH + Na<sub>2</sub>PbO<sub>2</sub> + S <sup>in the presence of NaOH</sup> ---- R-S-S-R + PbS + 2NaOH (alkyl disulfide)

**Q.1. (c) Explain Temporary and Permanent Hardness of water. How Temporary Hardness is removed by boiling?**

**Ans.** Temporary hardness is due to the presence of bicarbonate ions of calcium and magnesium. It is also called carbonate hardness or alkaline hardness. It can be removed by mere boiling of water.

Permanent hardness is due to the presence of sulphates and chlorides of calcium and magnesium. It is also called non-carbonate hardness and cannot be removed by boiling.

We can boil water to remove temporary hardness. Temporary hardness in water can be easily removed by boiling. On boiling, calcium/magnesium bicarbonate decomposes to give calcium/magnesium carbonate, which is insoluble in water. Therefore, it precipitates out.



**Q.1. (d) State phase rule and mention its advantages and limitations.**

**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 the formulation assumes that both  $T$  and  $P$  can be varied.

#### **Advantages of phase rule:**

- (a) It gives a simple method of classifying equilibrium states of systems.
- (b) It confirms that the different systems having the same number of degrees of freedom behave in like manner.
- (c) It predicts the behaviour of systems when subjected to changes in the variables such as pressure, temperature and volume.
- (d) The phase rule is applicable to macroscopic systems. Therefore, it is not necessary to take into account about their molecular structures.
- (e) It is applicable to physical as well as chemical reactions.
- (f) Phase rule takes no account of nature of the reactants or the products in phase reactions.
- (g) Phase rule predicts that a number of substances would remain in equilibrium if some of the substances have been transformed into the new substances.

#### **Limitations of Phase Rule**

- (a) As the phase rule is applicable to heterogeneous systems in equilibrium, it is therefore of no use for such systems which are slow in reaching the equilibrium state.
- (b) As the phase rule is applicable to a single equilibrium state, it never tells about the number of other equilibrium possible in the system.
- (c) In phase rule, various variables are temperature, pressure and composition. This phase rule does not consider the electric or magnetic influences. If such variables are considered, the factor 2 of the phase rule has to be adjusted accordingly.
- (d) All the phases in the system must be present under the same pressure, temperature and gravitational force.
- (e) No liquid or solid phases should be finely divided otherwise their vapour pressures will differ from their normal values.

**Q.1. (e) A eutectic mixture has a definite composition and a sharp melting point yet it is not compound.**

**Ans.** The elements or compounds that make up a eutectic mixture keep their identities—they are merely mixed together, not combined chemically. They are completely miscible with one another as liquids, but completely immiscible with one another as solids.

When a eutectic is solid (below its melting point) it consists of separate crystals or solidified droplets of the pure constituents. In the liquid state, they are merely dissolved in each other, but do not react chemically to form new compounds.

It's worth mentioning that in some respects the eutectic (lowest melting) composition does indeed behave much like it's a compound unto its own right, but it's NOT. Again, no chemical reaction involved.

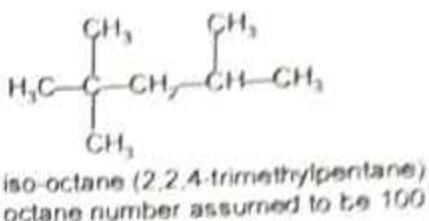
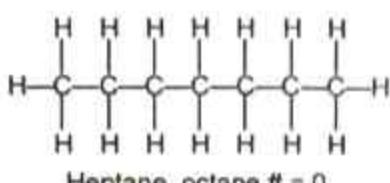
**Q. 2. (a) Explain octane and cetane number with their significance.**

(4+3+3)

**Ans.** The Octane Number of a gasoline is defined as the volume percent of iso-octane (2,2,4-trimethylpentane, an isomer of octane) in a blend of iso-octane and

n-heptane. An 87-octane gasoline, for example, has the same octane rating as a mixture of 87 vol-% iso-octane and 13 vol-% n-heptane. Isooctane is given a maximum octanenumber, i.e. 100.

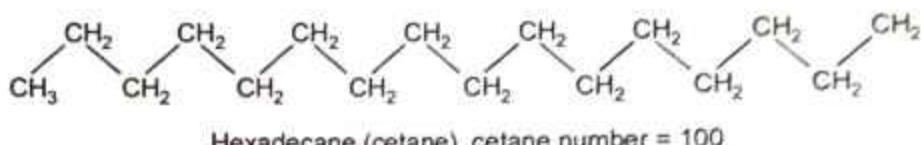
- N-heptane is given a minimum octanenumber, i.e. 0.



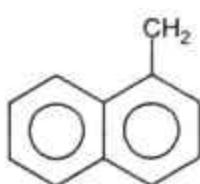
It's important that the fuel catch fire safely, and not explode. If the fuel drops exploded when catching fire, that would cause 'knocking' in the engine. This is dangerous, for it can damage the piston and cause leakage of hot fuel into other parts of the engine. That's why the octane rating (also called octane number) is important.

The cetane number of a fuel is defined as the volume percent of n-hexadecane in a blend of n-hexadecane and 1-methylnaphthalene that gives the same ignition delay period as the test sample. For example, a fuel with a cetane number of 40 will perform the same in the engine as a blend of 40% n-hexadecane and 60% 1-methylnaphthalene. N-hexadecane is given a maximum octanenumber, i.e. 100. 1-methylnaphthalene is given a minimum octane number, i.e. 0.

### **n-Hexadecane**



### **1-Methylnaphthalene**



J-Methylnaphthalene, cetane number = 0

CETANE number, a measure of the ignition quality of a fuel, is of importance in the satisfactory operation of a diesel engine; however, there is considerable evidence that cetane number is not the only criterion of a good diesel fuel and that other characteristics indicative of its burning properties must be considered.

### **Q.2. (b) Discuss advantages of catalytic cracking over thermal cracking..**

#### **Ans. Advantages of Catalytic Cracking over Thermal Cracking**

1. In catalytic cracking temperature and pressure is low as compare to thermal cracking.
2. Yield and octane number of petrol produced is higher.
3. Petrol produce has less quantity of gum and gum forming material.
4. Sulphur content of the product is low.

**Q.2. (c)** 1.26g of the coal was kjeldahlized and  $\text{NH}_3$  gas thus evolved was absorbed in 15ml of 0.1N  $\text{H}_2\text{SO}_4$ . After absorption the excess acid required 6.75ml of 0.1N NaOH for exact neutralization. Determine the percentage of nitrogen in the given sample.

**Ans.**

$$6.75 \text{ ml of } 0.1\text{N NaOH} = 6.75 \text{ ml of } 0.1\text{N H}_2\text{SO}_4$$

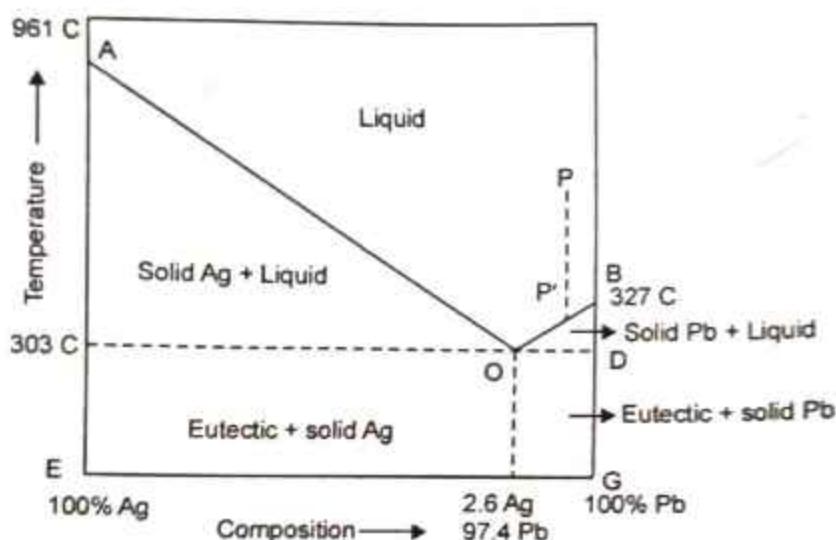
Vol. of  $\text{H}_2\text{SO}_4$  used to neutralize  $\text{NH}_3$

$$\begin{aligned}\text{Evolved} &= 15 \text{ ml of } 0.1\text{N} - 6.75 \text{ ml of } 0.1\text{N H}_2\text{SO}_4 \\ &= 8.25 \text{ ml of } 0.1\text{N H}_2\text{O}_4\end{aligned}$$

$$\% \text{ of N} = \frac{8.25 \times 0.1 \times 1.4}{1.86}$$

**Q.3. (a)** What is pattinson's process for desilverization of lead. Draw its phase diagram. [4+3+3]

**Ans. Pb-Ag system:** It is a two component system. The phase diagram of the Pb-Ag system is shown in the fig.



**Curve AO:** Point A is the melting point of pure Silver. Curve AO shows melting point depression of silver by the addition of lead. At any point in this curve there is equilibrium between solid Ag and liquids part. According to reduced phase rule equation The system is univariant.

$$F = C - P + 1; \quad F' = 2 - 2 + 1; \quad F = 1$$

**Curve BO:** Point B is the melting point of pure lead. ( $327^\circ\text{C}$ ). curve BO shows the melting point depression of lead on gradual addition of silver to it. Along this curve solid lead and solution co-exist and hence the system is univariant.

**Point O:** The two curves AO and BO meet at point O. Where three phase solid pb, solid Ag and their solution co-exist according to condensed phase rule the system is invariant.

$$F = C - P + 1; \quad F = 2 - 1 + 1; \quad F = 2$$

The point 'O' is known as eutectic point, its composition ( $\text{Ag} = 2.6\%$ ;  $\text{Pb} = 97.4\%$ ) and temperature ( $303^\circ\text{C}$ ) is known as eutectic composition and eutectic temperature respectively. Further cooling below UK eutectic temperature respectively. Further cooling below the eutectic temperature will cause simultaneous crystallization of a mixture of lead and silver.

**Area AOB:** Consists of only one phases namely pb-Ag solution. According to reduced phase rule equation.

$$F = C - P + 1; \quad F = 2 - 1 + 1; \quad F = 2$$

The system is bivariant i.e., both T and composition has to be specified to define the system.

Let us consider a point p, which represents a sample of lead containing less than 2.6% silver. On cooling the temperature falls gradually till point p. On further cooling lead begins to separate and the concentration of Ag increase in the solution till the point O is reached, after that whole mass solidifies (2.6% Ag: 97.4% pb). This process is utilized in the pattinson's process of desilverization of lead.

Below the eutecuc point (O), area COEF consists of solid and eutectic compound, where crystalline silver and eutectic compounds are stable. Similarly the area ODFG consists of solid Pb and eutectic compound, where crystalline lead eutectic compounds are stable.

**Applications to Pattinson's process:** If a sample of argent ferrous lead, containing less than 2.6% Ag is allowed to cool gradually, lead will separate out and the solution will become progressively richer in Ag, till the percentage 2.6 of Ag is reached: and on further cooling, the whole mass will solidify as such. On the other hand, if lead-silver alloy containing Ag greater than 2.6% is allowed to cool and then pure silver separates along the curve AO, till the eutectic composition at O is reached.

**Q. 3. (b) How is alkalinity caused in natural water. Explain Phenolphthalein alkalinity of water.**

**Ans.** Alkalinity of water may be due to the presence of one or more of a number of ions. These include hydroxides, carbonates and bicarbonates. Hydroxide ions are always present in water, even if the concentration is extremely low. However, significant concentrations of hydroxides are unusual in natural water supplies, but may be present after certain types of treatment. Small amounts of carbonates are found in natural water supplies in certain sections of the country, rarely exceeding 3 or 4 gpg. They may also be found in the water after lime soda has been used to soften the water. Bicarbonates are the most common sources of alkalinity. Almost all natural supplies have a measurable amount of this ion, ranging from 0 to about 50 gpg

**Q.3. (c) 50 ml of a sample of hard water was titrated against 0.01M EDTA, it required 15ml of EDTA for titration. 50ml of the same hard water after boiling and filtration required 5ml of the EDTA for titration. Calculate total and temporary hardness.**

**Ans.** Total hardness

$$1\text{ml fo } 0.01\text{M EDTA} = 1\text{mg of CaCO}_3$$

$$\begin{aligned} 15 \text{ ml of } 0.01 \text{ M EDTA} &= \frac{1 \times 18}{0.01} \times 0.01 = 18 \text{ mg.} \\ &= 18 \text{ mg of CaCO}_3 \end{aligned}$$

50 ml of water contain 18mg of  $\text{CaCO}_3$ . So

$$\begin{aligned} \text{Hardness present is } 1\text{L} &= \frac{18}{50} \times 1000 = 360 \text{ mg/l. of CaCO}_3 \end{aligned}$$

## Temporary hardness

$$5 \text{ ml of EDTA} = 5 \text{ mg of } \text{CaCO}_3$$

$$50 \text{ ml of EDTA} = 50 \text{ mg of EDTA}$$

$$100 \text{ ml of EDTA} = \frac{5}{50} \times 1000 = 100 \text{ mg of } \text{CaCO}_3$$

**Q.4. (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.** Refer Q 1. (b) of End Term 2015.

**Q.4. (b) The % analysis by volume of a 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  $\text{m}^3$  of the gas if 20% excess air is used. Also calculate the percentage composition of dry products of combustion.**

**Ans.**

Constituents	Amount of fuel	Reaction	Volume of oxygen ( $\text{m}^3$ )	Volume of dry product ( $\text{m}^3$ )
$\text{H}_2$	0.183	$\text{H}_2 + \frac{1}{2} \text{O}_2 \rightarrow \text{H}_2\text{O}$	$0.183 \times 0.5$ = 0.0915	$0.034 \times 1$ = 0.034
$\text{CH}_4$	0.034	$\text{CH}_4 + 2\text{O}_2 \rightarrow \text{CO}_2 + 2\text{H}_2\text{O}$	$0.034 \times 2$ = 0.068	
CO	0.254	$\text{CO} + \frac{1}{2} \text{O}_2 \rightarrow \text{CO}_2$	$0.254 \times 0.5$ = 0.127	$0.254 \times 1$ = 0.254
$\text{CO}_2$	0.051			
$\text{N}_2$	0.478			

$$\text{Vol. of Oxygen required} = 0.0915 + 0.068 + 0.127 \\ - 0.2865 \text{ m}^3$$

$$\text{Vol. of air required} = 0.2865 \times \frac{100}{21} \\ = 1.364 \text{ m}^3$$

$$\text{Vol. of air actually supplied} = 1.364 \times \frac{120}{100} \\ = 1.63 \text{ m}^3$$

$$\text{Excess air} = 1.63 - 1.364 = 0.2728 \text{ m}^3$$

Vol. of dry product of combustion

$$\text{Vol. of } \text{CO}_2 \text{ Calculated from product of combustion} \\ = 0.034 + 0.254 = 0.288 \text{ m}^3$$

$$\text{Total Vol. of } \text{CO}_2 = 0.288 + 0.051 = 0.339 \text{ m}^3$$

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

$$\approx \left[ \frac{1.63 \times 70}{100} \right] = 0.418$$

$$\approx 1.76 \text{ m}^3$$

$$\text{Vol. of } O_2 = \left[ \text{Excess air} \times \frac{21}{100} \right]$$

$$\approx 0.2728 \times \frac{21}{100}$$

$$\approx 0.0572 \text{ m}^3$$

$$\text{Total vol of dry product} \approx 0.339 + 1.76 + 0.0572 \\ \approx 2.156 \text{ m}^3$$

$$\% \text{ of CO}_2 = \frac{0.339}{2.156} \times 100 = 15.7\%$$

$$\% \text{ of N}_2 = \frac{1.76}{2.156} \times 100 = 12.83\%$$

$$\% \text{ of O}_2 = \frac{0.0572}{2.156} \times 100 = 2.65\%$$

**PRE-UNIVERSITY EXAMINATION [NOV. 2015]**  
**FIRST SEMESTER [B.TECH]**  
**APPLIED CHEMISTRY [ETCH-113]**

Time: 3 Hours

M.M.: 75

*Note: Q. No. 1 is compulsory. Attempt any one Question from each unit.*

**Q. 1. (a) Differentiate between caking coal and coking coal. ( $2.5 \times 10 = 25$ )**

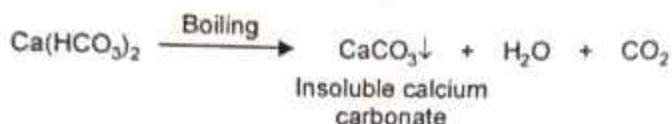
**Ans.** When many bituminous coals are heated, they soften and form a plastic mass that swells and resolidifies into a porous solid. Coals that exhibit such behaviour are called **caking coals**. Strongly **caking coals**, which yield a solid product (coke) with properties suitable for use in a blast furnace, are called **coking coals**. All coking coals are caking, but not all **caking coals** are suitable for coke...

**Q. 1. (b) What is sweetening of petrol?**

**Ans.** Sweetening process means removing of sulphur and its compounds like hydrogen sulphide, mercaptans etc from petroleum products. If these impurities are present in petroleum products it means petroleum products are not completely purified.

**Q. 1. (c) What happens when temporary hard water is boiled (give equations).**

**Ans.** Temporary hardness in water can be easily removed by boiling. On boiling, calcium/magnesium bicarbonate decomposes to give calcium/magnesium carbonate, which is insoluble in water. Therefore, it precipitates out.



**Q. 1. (d) Derive 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.

$$\begin{array}{ll} T, & P, \\ X_{1\alpha} & X_{1\beta}, X_{1\gamma}, \dots \\ X_{2\alpha} & X_{2\beta}, X_{2\gamma}, \dots \\ \vdots & \vdots \end{array}$$

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

$$X_{1\alpha} + X_{2\alpha} + X_{3\alpha} + \dots = 1$$

$$X_{1\beta} + X_{2\beta} + X_{3\beta} + \dots = 1$$

⋮

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  $\alpha, \beta, \gamma, \dots, \zeta$ .)

$$\mu_{1\alpha} = \mu_{1\beta} \quad \mu_{2\alpha} = \mu_{2\beta} \quad \dots \quad \mu_{c\alpha} = \mu_{c\beta}$$

$$\mu_{1\beta} = \mu_{1\gamma} \quad \mu_{2\beta} = \mu_{2\gamma} \quad \dots \quad \mu_{c\beta} = \mu_{c\gamma}$$

⋮      ⋮      ⋮      ⋮

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

(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. (e) Hydrocarbons that are poor gasoline fuels are quite good diesel fuels. Explain.**

**Ans.** Straight chain hydrocarbons have low cetane number but they have high octane number. Thus in petrol engines they knock badly. However they don't knock at all in diesel engines. Thus hydrocarbons that are poor gasoline fuel are quite good diesel fuel.

**Q.1. (f) In a phase diagram of water the fusion curve of ice has a negative slope. Explain.**

**Ans.** This is because the freezing point of water is depressed by the increase of pressure. Therefore, the fusion curve is inclined towards the pressure axis i.e., it has a negative pole.

But the sublimation curve has a positive slope i.e., it is inclined away from the pressure axis. This is because the vapour pressure of water increases with the rise of temperature.

**Q.1. (h) Phosphate conditioning is better than carbonate conditioning explain.**

**Ans.** This is so because carbonate conditioning forms soft scale, but phosphate conditioning forms soft sludge, which can be removed by blow down operation, so its better than carbonate conditioning. Phosphate can be chosen according to quality of boiler feed water i.e. alkaline, weakly alkaline, acidic.

**Q.1. (g) Differentiate between physical adsorption and chemical adsorption.**

**Ans. DIFFERENCE BETWEEN Physical Adsorption and Chemical Adsorption**

S.No.	Physical adsorption	S.No.	Chemical adsorption
1.	Molecules are held due to vanderwaal's forces.	1.	Molecules are held due to chemically bound forces.
2.	Heat of adsorption are in the range of 20 – 40 KJ/Mol.	2.	Heat of adsorption are in the range of 40 – 400 KJ/Mol.
3.	Activation energy are small.	3.	Activation energy are appreciable.
4.	Usually occurs rapidly at low temperatures and decreases with increase in temperature.	4.	Can occur at high temperatures.
5.	Usually completely reversible.	5.	Often irreversible.
6.	The extent of adsorption is approximately related to the ease of liquification of gas.	6.	No such correlation is there.
7.	Not very specific.	7.	Often highly specific.
8.	Form multilayer on the surface of adsorbent.	8.	Forms unimolecular layer.
9.	No surface compound is formed.	9.	Surface compounds are formed.

**Q.1. (i) 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.

Specific Volume Ratio =  $MO/M$

$MO$  = Volume of Metal Oxide,  $M$  = Volume of Metal

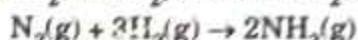
Smaller the specific volume ratio greater is the oxidation corrosion. Alkali and alkaline earth metals form oxide of volume less than the volume of metal, thus the oxide layer faces stress and strain, developing cracks and pores. Porous oxide scale permits free access of oxygen to the underlying metal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

Metal like Aluminium 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. (j) Explain the role of Catalytic Promoters and Poisons.**

**Ans. Catalytic promoters:** Certain substances were found to increase the activity of catalyst, although they are not considered as catalyst. These substances are called **promoters or activators**. e.g. 1. In the Haber's process for the manufacture of  $N_2$  from  $H_2$  and  $N_2$ , Mo and  $(Al_2O_3 + K_2O)$  is used as a promoter.



Fe and  $Mo/Al_2O_3, K_2O$  act as catalyst.

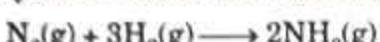
2. In the Bosch's process, for the manufacture of hydrogen from the water gas, finely divided iron is used as catalyst and metallic copper is used as a promoter.

#### Mechanism of Action of catalytic promoters:

**Active Centers:** Surface of the catalyst is not uniform, there are a number of edges, peaks and cracks. The catalytic activity at these sites is relatively high due to the presence of more residual forces at these spots.

**Catalytic Poisons:** Any substance which inhibit or destroy the catalytic activity to accelerate the reaction is called **catalytic poison**. **Example:** 1. In contact process for the manufacture of  $H_2SO_4$ , catalytic poison  $AS_2O_3$  absorbs on the active site of Pt forming  $PtS$  on the surface of the Pt reducing the catalytic activity of Pt.

2. In Haber's process for the manufacture of ammonia, the iron catalyst used to catalyse the reaction between  $H_2$  and  $N_2$  is poisoned by the presence of  $H_2S$ .



Fe, poisoned by  $H_2S$

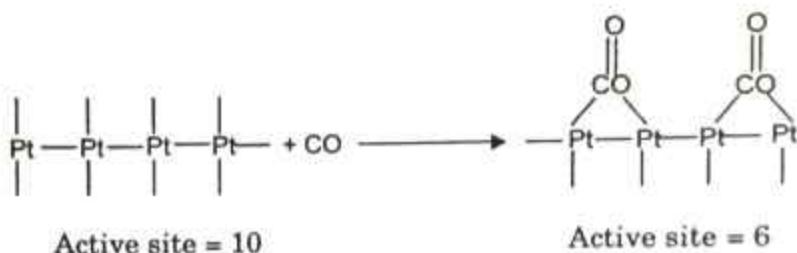
#### TYPE OF CATALYTIC POISON:

**1. Temporary poisoning:** In which the catalyst regains its activity when the poison is removed from the reactants. e.g. In the reaction between  $H_2$  and  $N_2$  catalysed by Fe catalyst in Haber's process, water vapour and  $O_2$  acts as temporary poison.

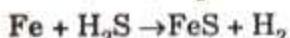
**2. Permanent poisoning:** In which the catalyst cannot regain its activity even by removing the poison. e.g.  $AS_2O_3$  poison permanently the Pt powder catalyst in contact process for the manufacture of  $SO_3$  from  $SO_2$  and  $O_2$ .

#### Mechanism of Catalytic Poisoning:

1. By preferential adsorption of catalytic poison on the surface of solid catalyst. e.g. A monolayer of CO on the Pt surface makes the surface unavailable for further adsorption of reactants. Thus the rate of reaction decreases.



2. The catalyst combine with chemically with the catalytic poison e.g. Poisoning of iron catalyst by  $H_2S$



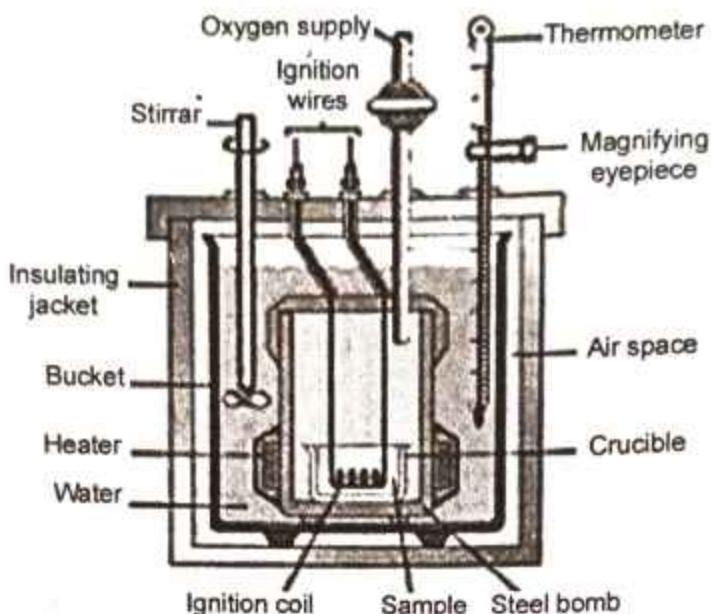
#### UNIT-I

#### Q.2. (a) How the Calorific Value of fuel can be determined by Bombs Calorimeter, explain with diagram.

**Ans.** The calorific value of solid or liquid fuels can be determined with the help of bomb calorimeter.

**Description:** Bomb Calorimeter consists of a strong stainless steel bomb where the fuel sample is burnt. The bomb has oxygen inlet valve and two stainless steel electrodes. A small ring is attached to one of the electrodes. In this ring, a nickel or stainless steel crucible is placed.

The bomb is placed in a copper calorimeter containing a known weight of sample. The copper calorimeter is provided with a Beckmann's thermometer, stirrer for stirring water. The copper calorimeter is covered by an air jacket and jacket.



**Functioning:** A known weight of the fuel sample is taken into the crucible. The fine magnesium wire is touching the fuel sample and then stretched across the electrodes. The bomb lid is tightly closed with the help of screw. The bomb is filled with oxygen at 25 atmospheric pressure. The bomb is now placed in a copper calorimeter which containing known weight of water. Initial temperature of the water in the calorimeter is noted ( $t_1$  °C) after stirring. The electrodes are connected to a battery (6 V). The current is now supplied to the fuel sample which undergoes burning with the evolution of heat. The liberated heat increases the temperature of water in the calorimeter. The maximum temperature of the water during experiment is finally noted ( $t_2$  °C). From the temperature difference, calorific value of the fuel can be calculated as follows:

#### Calculation:

Weight of the fuel sample taken in the crucible =  $x$  g

Weight of water taken in the calorimeter =  $W$  g

Weight of calorimeter and stirrer in terms of water Equivalent =  $A$  g

Initial temperature of water in the calorimeter =  $t_1$  °C

Final temperature of water in the calorimeter =  $t_2$  °C

Heat absorbed by the water =  $W(t_2 - t_1)$  cal ----- (1)

Heat absorbed the calorimeter =  $A(t_2 - t_1)$  cal ----- (2)

Total heat absorbed by the water =  $W(t_2 - t_1) + A(t_2 - t_1)$  cal =  $(W+A)(t_2 - t_1)$  cal ----- (3)

The relationship between heat liberated by the fuel and HCV is as follows:

Heat liberated by the fuel =  $x \times (HCV)$  ----- (4)

Therefore, heat liberated by the fuel = Heat absorbed by the water and calorimeter

X Weight of fuel

Compare equation (3) and (4), we get

$$\text{g g (HCV)} = (W + A)(t_2 - t_1)$$

$$\text{HCV} = (W + A)(t_2 - t_1) / \text{ kcal/g}$$

Calculation of Lower Calorific Value (LCV),

The percentage of hydrogen in the fuel = H

Weight of water produced 1 g of the fuel =  $\frac{1}{2} H / 1.176 \text{ g} = 0.587 \text{ g}$

Therefore, heat liberated during the Combustion of excess =  $0.587 H \times 587 \text{ cal/g}$

Lower calorific value of the fuel = HCV - Latent heat of water liberated by the fuel

$$\text{LCV} = \text{HCV} - (0.09 H \times 587) \text{ cal/g}$$

**Q.2. (b)** 2g of the coal was Kjeldahlized and  $\text{NH}_3$  gas thus evolved was absorbed in 24 ml of 0.1N  $\text{H}_2\text{SO}_4$ . After absorption the excess acid required 12 ml of 0.1N NaOH for exact neutralization. Determine the percentage of nitrogen in the given sample.

**Ans.** 12 ml of 0.1N NaOH = 12 ml of 0.1N  $\text{H}_2\text{SO}_4$

vol. of  $\text{H}_2\text{SO}_4$  used to neutralise  $\text{NH}_3$ ,

$$\text{Evolved} = 24 \text{ ml of } 0.1\text{N} - 12 \text{ ml of } 0.1\text{N } \text{H}_2\text{SO}_4$$

$$= 12 \text{ ml of } 0.1\text{N } \text{H}_2\text{SO}_4$$

$$\% \text{ of N} = \frac{\text{Vol. of } \text{H}_2\text{SO}_4 \times \text{N} \times 1.4}{\text{Weight of coal sample}}$$

$$= \frac{12 \times 0.1 \times 1.4}{2} = .54$$

**Q.2. (c) Differentiate between Fixed bed and Moving bed Catalytic Cracking.** (5.5+7)

**Ans.**

S.N.	Fixed bed CC	S.N.	Moving bed CC
1.	Catalyst is in the form of generates	1.	Catalyst is in fine powder form.
2.	Catalyst is in the form of fixed bed in catalytic towers.	2.	Catalyst keeps on circulating in gas stream.
3.	No regenerating chamber is there.	3.	Catalytic of regenerating chamber are placed side by side.
4.	Catalyst stopped working after 10-11 hrs.	4.	This process does not stop.
5.	Catalyst is regenerated outside apparatus.	5.	Catalyst is regenerated side by side inside the apparatus.

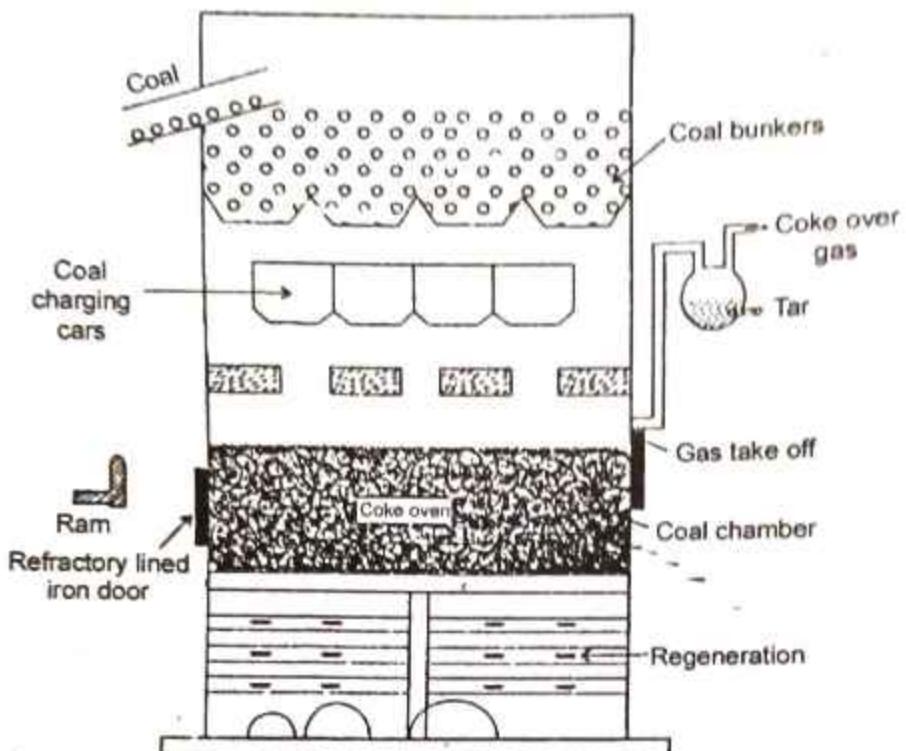
**Q.3. (a) Explain the Otto-Hoffmann's byproduct oven method for the manufacturing of metallurgical coke.**

**Ans.** The Otto Hoffmann's Oven consists of number of narrow silica chambers. Each chamber is nearly 10-12 meter long, 3-4 m 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 lime 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  $1200^{\circ}\text{C}$  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 into a 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 benzole, 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  $H_2SO_4$  to form  $(NH_4)_2SO_4$ , 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  $(NH_4)_2CO_3$ .

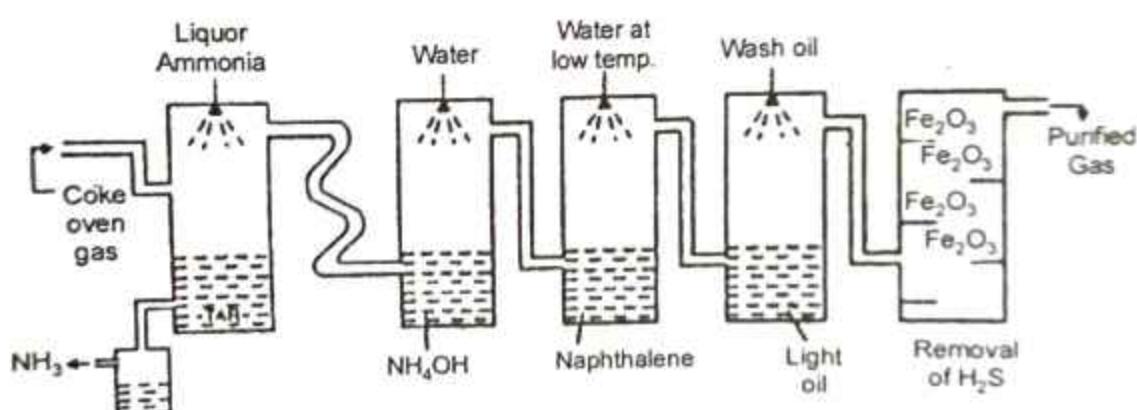
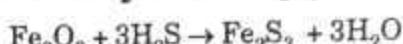
(iii) **Recovery of Naphthalene:** The gases are passed through a cooling tower, where water at a low temperature is sprayed. The gas is scrubbed with water until its temperature reduces. The naphthalene gets condensed here which is collected along with water and recovered.

(iv) **Recovery of Benzol:** The gases are then introduced into a light oil or benzol 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  $H_2S$ :**  $H_2S$  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,  $SO_2$  and  $SO_3$  aid corrosion. Moreover  $H_2S$  has offensive odour.

For the removal of sulphur and  $H_2S$  gas, the gas is passed through a chamber, packed with moist  $Fe_2O_3$ , which reacts with  $H_2S$  to give  $Fe_2S_3$ .



Schematic Diagram of Coke-Oven Gas Treatment Plant

After some time when all the  $Fe_2O_3$  is converted into  $Fe_2S_3$ , the purifier is exposed to the atmosphere when  $Fe_2S_3$  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.3. (b)** The composition by weight of a coal sample is: C = 82%, H = 4%, O = 8%, S = 1%, N = 2% Ash = 3%. Calculate (i) minimum air required for complete combustion of 1Kg. of coal (ii) the % composition of dry products of combustion if 20% excess air supplied.

**Ans.** 1 kg of coal contain = C = 0.82 kg, H = 0.04 kg, O = 0.08 kg, S = 0.01 kg, N = 0.02 kg.

Constituent	Combustion reaction	Amount of $\text{O}_2$	Amount of dry products
C	$\text{C} + \text{O}_2 \rightarrow \text{CO}_2$ 12 32 44	$\frac{32}{12} \times 0.82 = 2.18$	$\frac{44}{12} \times 0.82 = 3.00$
H	$\text{H}_2 + \frac{1}{2}\text{O}_2 \rightarrow \text{H}_2\text{O}$ 2 16 18	$\frac{16}{2} \times 0.04 = 0.32$	—
O	—	—	—
S	$\text{S} + \text{O}_2 \rightarrow \text{SO}_2$ 32 32 64	$\frac{32}{32} \times 0.01 = 0.01$	$\frac{64}{32} \times 0.01 = 0.02$
N	—	—	—

$$\text{O}_2 \text{ required} = [2.18 + 0.32 + 0.01] - 0.08 = 2.43 \text{ kg}$$

$$\text{Air required} = 2.43 \times \frac{100}{23} = 10.56 \text{ kg}$$

$$\text{Amount of air actually supplied} = 10.56 \times \frac{120}{100} = 12.67 \text{ kg}$$

$$\text{Excess air} = 12.67 - 10.56 = 2.11 \text{ kg}$$

#### Amount of dry products

$$\text{Amount of } \text{CO}_2 = 3.00 \text{ kg}$$

$$\text{Amount of } \text{SO}_2 = 0.02 \text{ kg}$$

#### Amount of

$$\text{N}_2 = 77\% \text{ of air used} + \text{N}_2 \text{ present in fuel.}$$

$$= \left[ \left( \frac{77}{100} \times 12.67 \right) + 0.02 \right] = 9.77$$

$$\text{Total amount of dry product} = 3 + 0.02 + 9.77 = 12.79 \text{ kg}$$

$$\% \text{ of } \text{CO}_2 = \frac{3}{12.79} \times 100 = 23.4\%$$

$$\% \text{ of SO}_2 = \frac{0.02}{12.79} \times 100 = 0.15\%$$

$$\% \text{ of N}_2 = \frac{9.77}{12.79} \times 100 = 76\%$$

## UNIT-II

**Q.4. (a) Draw and explain the phase diagram of water system in detail.**

(6.5)

**Ans. Water System:** The water system consists of three phases (ice, water and water vapour) and is the simplest and typical example of one component system.

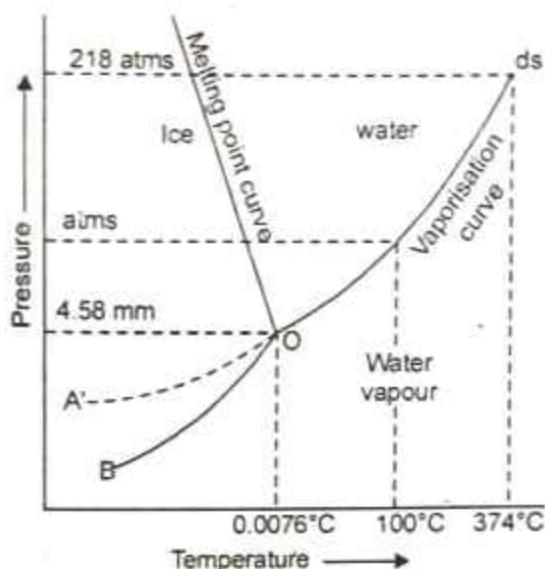
In this case,

$$C = 1$$

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

or

$$F + P = 3$$



**1. Areas:** AOB, AO<sub>C</sub> and BO<sub>C</sub> are the fields of existence of vapour, liquid and ice phase respectively. Within these single phase areas, it is necessary to state both temperature and pressure of the phase because to locate any point in an area, both the temperature and pressure coordinates are required. So the system is bivariant. This also follows from phase rule equation.

$$F = 3 - P = 2.$$

**2. Boundary lines:** Separating the areas are lines OA, OB and OC which shows two phases are in equilibrium. When two phases are in equilibrium it is sufficient to state either the temperature or the pressure. Hence any point or boundary lines has one degree of freedom or is univariant. This also follows from phase rule equation.

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

(i) The curve OA, that separates the liquid from vapour region is called vapour pressure curve for water, the vapour pressure increasing with rise in temperature. There is an upper limit for OA terminating at A, its critical state (374°C) above which temperature the distinction between the liquid and vapour vanishes.

(ii) The curve OB is the sublimation curve of ice. It registers the vapour pressure under which ice is in equilibrium with its vapour at different temperatures. This is the line of demarcation between ice and vapour. The point B has a natural limit at  $-273^{\circ}\text{C}$ , beyond which the two phases merge into each other.

(iii) The curve OC is the freezing point curve indicating the equilibria at different temperatures between ice and water. The line has a negative slope i.e., melting point is lowered with increase in pressure.

**3. Triple point :** The point 'O' where the three lines meet, all the three phases i.e., ice, water and vapour should coexist. This is called a triple point. Triple point has  $P = 4.58 \text{ mm}$ ,  $t = 0.0099^{\circ}\text{C}$ . Since there are three phases,

$$F = 3 - P = 0$$

i.e., the system is non-variant at triple point. If either the temperature or the pressure is changed, the three phases would not co-exist.

4. It is however possible to cool water below the freezing point without solidification. The liquid below its freezing point is said to remain in supercooled state. This supercooled state is not stable and is called a metastable state. The dotted curve OA' is the vapour pressure curve of super cooled water which is a continuation of AO. The line OA' is above OB, the vapour pressure curve of ice indicating that the metastable super cooled water has a higher vapour pressure than ice. As a principle, the vapour pressure of metastable phase is greater than that of stable phase.

**Q.4. (b) Find the no. of phases, components and Degree of freedom in the following:** (6)

(i) An aqueous solution of glucose

(ii) Solid Iodine in equilibrium with its vapours.

**Ans.** (i) The number of components ( $C$ ) = 2 (Glucose and water)

$$F = C - P + 2$$

$$= 2 - 1 + 2$$

= 3 (temperature, pressure, and concentration of solution)

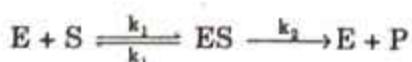
(ii) Iodine in equilibrium with its vapour forms a single component system having two phases. Hence,

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

**Q.5. (a) Derive Michaelis-Menten's equation for enzyme catalysis.**

(6.5)

**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:

$$V = k_2[\text{ES}]$$

(Equation 1)

At this point it is 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 rearrangements of this equation they are both multiplied by  $[ES]$ , this gives 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 gives us:

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

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:

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

This can now be rearranged in several steps

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

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

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

Then 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 gives us:

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

Substituting this 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.

**Q.5. (b) Differentiate between homogeneous and heterogeneous catalysis with suitable example.** (3)

#### Ans. HOMOGENEOUS 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.

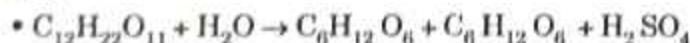
##### • Example

##### • (A) In Gas Phase :

- Oxidation of sulphur ( $SO_2$ ) to sulphur trioxide ( $SO_3$ ) with nitric oxide (NO) as catalyst.

##### • (B) In Solution Phase:

- I. Hydrolysis of cane sugar in aqueous solution in the presence of mineral acid as catalyst.



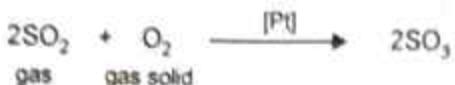
Glucose Fructose

#### HETEROGENEOUS CATALYSIS:

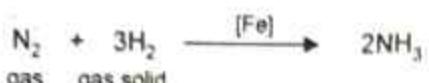
- The catalysis in which the catalyst is in a different physical phase from the reactants is termed heterogeneous catalysis, most important of such reaction are those in which the reactants are in the gas phase while the catalyst is a solid the process is called Contact Catalysis.

**Examples of Heterogeneous Catalysis:**

- (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)



- (B) Combination of nitrogen and hydrogen to form ammonia in the presence of finely divided iron (Haber process for ammonia).

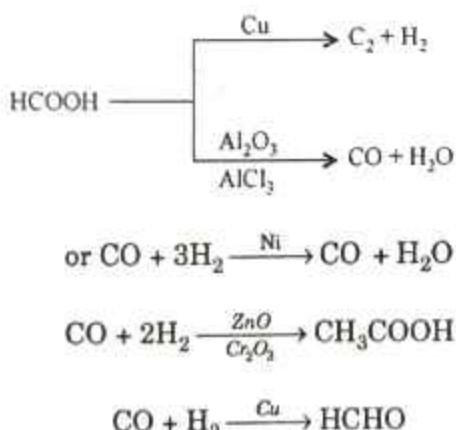


**Q.5. (c) What is the criteria for choosing the catalyst for industrial purpose.**

(3)

**Ans.**

1. The catalyst remains unchanged (in mass and chemical composition) in the reaction (Activity of catalyst.)
2. A small quantity of the catalyst is required. e.g. One mole of colloid Pt catalyses  $10^6 \text{ L H}_2\text{O}_2$
3. The catalyst does not change the equilibrium constant. But the equilibrium approaches earlier.
4. **Specificity of Catalyst:** The catalyst is specific in nature. It means by the change of catalyst, nature of the products changes or specific catalyst for a specific reaction.



5. The catalyst can not make impossible reaction to occur and does not initiate a reaction.
6. The catalyst exhibits maximum activity at a particular temperature which is known as **optimum temperature**.

### UNIT-III

**Q.6. (a) What is Caustic Embrittlement? Explain its causes and prevention.**

(5)

**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

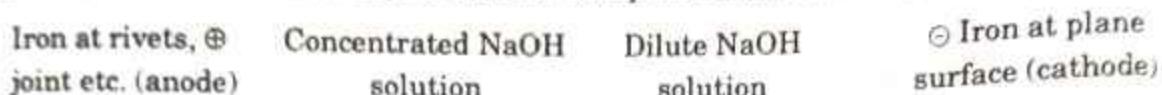
sodium carbonate ( $\text{Na}_2\text{CO}_3$ ) is usually present in small proportion in the softened water. In high-pressure boilers,  $\text{Na}_2\text{CO}_3$  decomposes to give sodium hydroxide and  $\text{CO}_2$



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 evaporate and the concentration of NaOH increases slightly. This caustic soda attack 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:



By the electrochemical action the point of high local stress gets corroded. Here the iron surface surrounded by dilute NaOH area 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 the boiler. It has been observed that in boiler if the ratio of  $\text{Na}_2\text{SO}_4$ : 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.6.(b) What are the methods of water softening by external treatment of water? Discuss any one in detail.** (7.5)

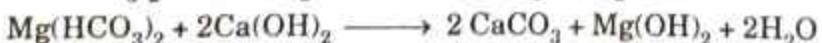
**Ans.** Softening of water (Removing of the dissolved salt)—The process of removing the hardness causing salts from the water called softening of water.

### 1. Lime-soda process :

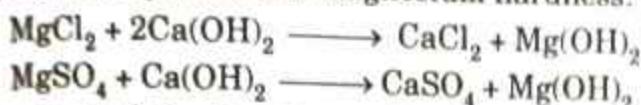
**Principle :** Conversion of all the soluble hardness causing salts into insoluble precipitate by the addition of soda and lime which can be easily removed by settling and filtration. In this method, the soluble calcium and magnesium salts in water are converted chemically into insoluble compounds by 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, 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.

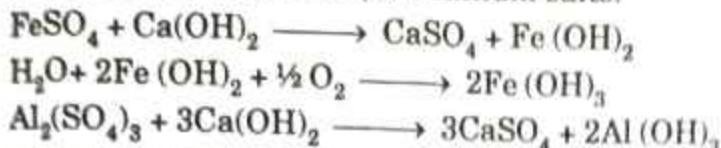
#### (a) Removal of temporary, calcium and magnesium hardness:



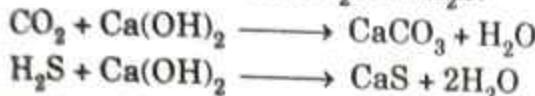
(b) Removal of permanent magnesium hardness:



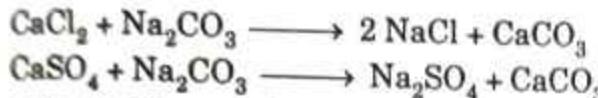
(c) Removal of dissolved iron, aluminium salts:



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



#### Function of soda:



(a) **Cold lime soda process:** It 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 50-60 ppm.



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 94-106. 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 15-30 ppm.

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.

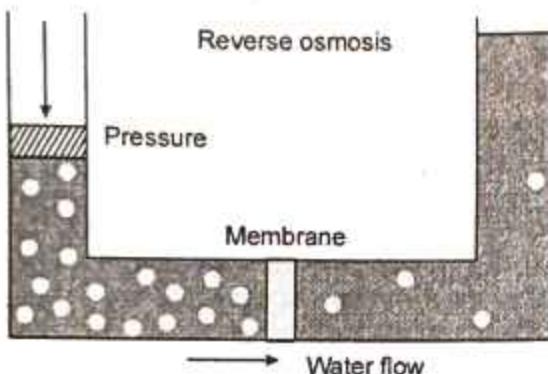
**Q.7. (a) Explain the following:**

**Q.7. (i) R.O.**

**Ans. Reverse osmosis:** Spontaneous process, the flow of solvent from the conc. solution to dilute solution 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 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 conc as compared to fresh water. If sea water kept in contact with fresh water through semi permeable and pressure of order  $15\text{-}40 \text{ kg/cm}^2$  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  $15\text{-}40 \text{ kg/cm}^2$  is applied to sea water. Reverse osmosis take place.



**Advantage:** 1. The process removes ionic as well as non ionic dissolved salt. It is also effective in removing colloidal impurities.

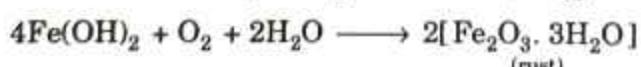
2. The process involves a very low capital and operating cost. It is suitable for converting sea water into drinking water.

3. The water obtained by this process may be used in high pressure boilers.

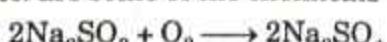
4. It removes colloidal silica which is not removed by demineralization.

**Q.7. (a) (ii) Boiler corrosion due to dissolved oxygen.**

**Ans.** Dissolved oxygen in water is mainly responsible for the corrosion of boiler. The dissolved oxygen in water attacks the boiler material at high temperatures.



Dissolved oxygen can be removed from water by chemical and mechanical means. Sodium sulphite, hydrazine, etc. are some of the chemicals used for removing oxygen.



Hydrazine is found to be an ideal compound for removing dissolved oxygen since the products are water and inert  $\text{N}_2$  gas. It removes oxygen without increasing the

concentration of dissolved salts. Dissolved oxygen can also be removed by mechanical deaeration.

**Q.7. (b) Calculate the quantity of lime and soda required for softening 24,000 liters, of water with the following analysis using 10 ppm of sodium aluminate as coagulant.** (6.5)

$$\text{Ca}^{+2} = 95 \text{ ppm}; \text{Mg}^{+2} = 36 \text{ ppm}; \text{CO}_2 = 66 \text{ ppm}; \text{HCO}_3^- = 264 \text{ ppm}; \text{H}^+ = 2 \text{ ppm}.$$

**Ans.**

Constituent	Amount	CaCO <sub>3</sub> equivalence
Ca <sup>2+</sup>	95	$\frac{100}{40} \times 95 = 237$
Mg <sup>2+</sup>	36	$\frac{100}{24} \times 36 = 150$
CO <sub>2</sub>	66	$\frac{100}{44} \times 66 = 150$
HCO <sub>3</sub> <sup>-</sup>	264	$\frac{100}{122} \times 264 = 216$
H <sup>+</sup>	2	$\frac{100}{2} \times 2 = 100$
NaAlO <sub>2</sub>	10	$\frac{100}{54.6} \times 54.6 = 546$

$$\begin{aligned}\text{Lime required} &= \frac{74}{100} [150 + 150 + 100 + 216 - 546] \times 24000 \\ &= \frac{74}{100} \times 70 \times 24000 = 1.176 \text{ kg} \\ &= 1.176 \text{ kg}\end{aligned}$$

$$\begin{aligned}\text{Soda required} &= \frac{106}{100} [237 + 150 + 100 - 216] \times 24000 \\ &= 6.894 \text{ kg.}\end{aligned}$$

#### UNIT-IV

**Q.8. What happens when (any 2).**

(6)

**Q.8. (a) (i) An iron pole is partly buried under earth.**

**Ans.** 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.

**Q.8 (a) (ii) Zinc plate fixed below ship.**

**Ans. 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. (a) (iii) Why noble metals are resistant towards corrosion.**

**Ans.** In the galvanic chart or galvanic series of metals, noble metals have a potential that is higher than the potential of all metals and this means that they will not corrode when placed in contact with other metals.

**Q.8. (b) Write the mechanism of wet or electrochemical corrosion. (6.5)**

**Ans.** Refer Q.5. (a) End Term Examination 2015.

**Q. 9. (a) Write the short note on the following. (12.5)****Q.9. (a) (i) Electroplating**

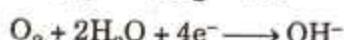
**Ans.** Electroplating is a process that uses electrical current to reduce dissolved metal cations so that they form a coherent metal coating on an electrode. The process used in electroplating is called electrodeposition. It is analogous to a galvanic cell acting in reverse. The part to be plated is 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). (ii) Cathodic protection.**

**Ans. 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 and connected by a wire. Mg- anode (oxi), Fe cathode(red) reduce O<sub>2</sub> to OH<sup>-</sup>.

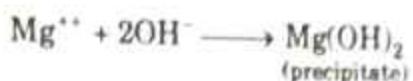
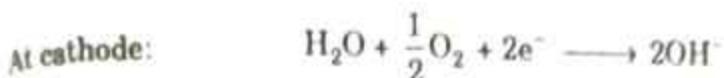
**2. Impressed current cathodic protection:**

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

**Q.9. (a) (iii) Corrosion inhibitors.**

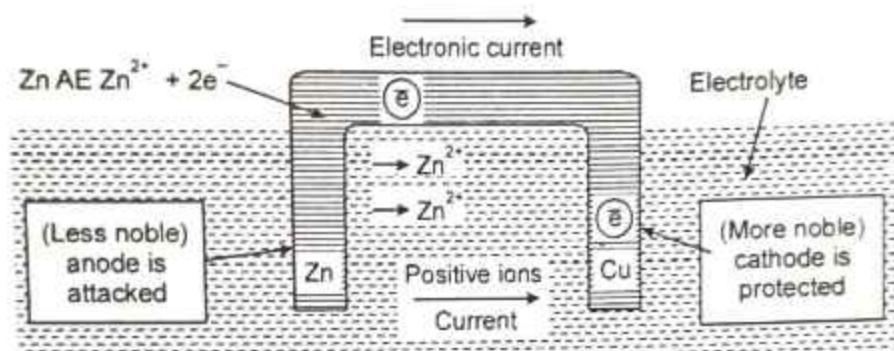
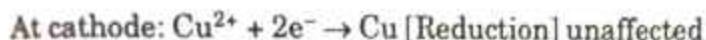
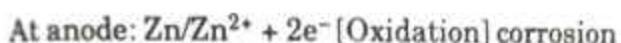
**Ans.** There are some chemicals which reduce the rate of corrosion. These chemicals are called corrosion inhibitors. They are of two types, anodic and cathodic. Phosphate, chromate, tungstate protect anode.

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.



**Q.9. (a) (iv) Galvanic corrosion.**

**Ans. 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



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.

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

**Time: 3 Hours**

**M.M. : 75**

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

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

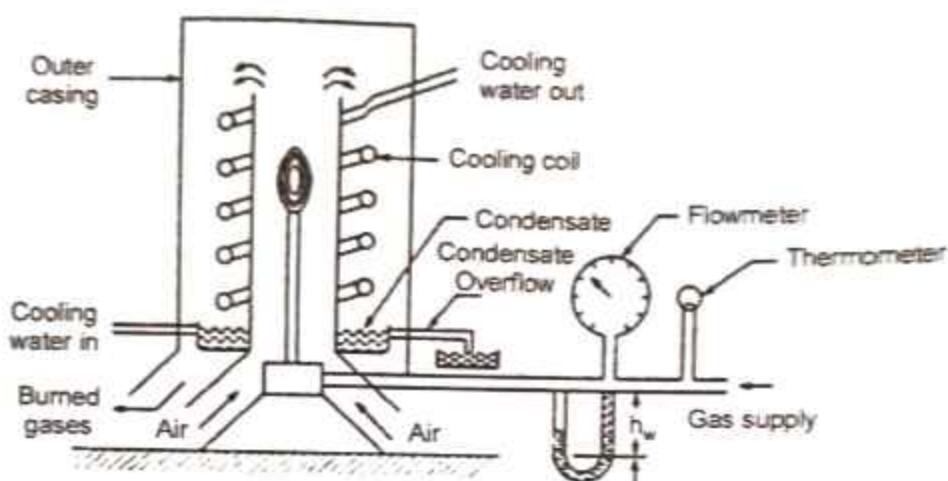
**(3x5=15)**

**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'.

$m$  = 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)

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

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

(ii) 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

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

Gross calorific value ( $L$ ) =  $W(T_2 - T_1)/V$

LCV = HCV - Latent heat of water produced

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

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

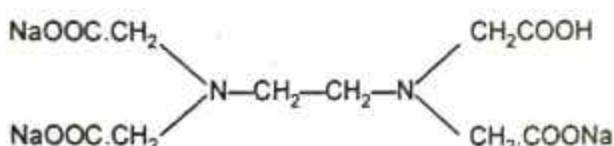
Net calorific value = GCV -  $(m \times 587)/V$

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

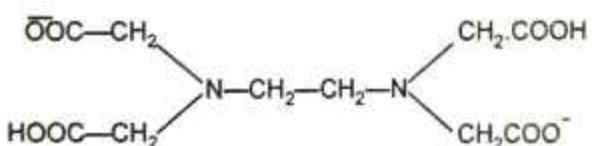
**Ans.** This is a complexometric method. Ethylene diamine tetraacetic acid (EDTA) in the form of its sodium yields the anion.

### 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:



$V$  = 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

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

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

LCV = HCV – Latent heat of water produced

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

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

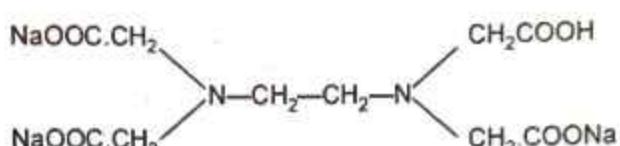
Net calorific value = GCV –  $(m \times 587)/V$

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

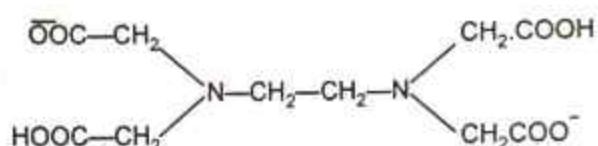
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### Theory

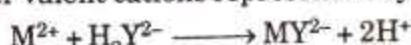
The disodium salt of ethylenediamine tetra acetic acid (EDTA).



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



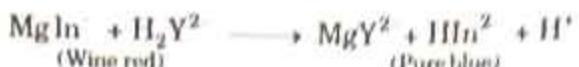
Wine red colour. As EDTA ( $\text{H}_2\text{Y}^{4-}$ ) is added, free  $\text{Ca}^{2+}$  ions are first complexed to  $\text{CaY}^{2-}$ , this being the most stable complex:



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, 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.

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

**Ans.** But it can never be due to the presence of OH<sup>-</sup> and HCO<sub>3</sub><sup>-</sup> together because they combine to form CO<sub>3</sub><sup>-2</sup> and H<sub>2</sub>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 H<sub>2</sub>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 H<sub>2</sub>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 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.** (6)

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

**Q.2. (b) What is the significance of Ash, Moisture and Volatile matter present in a coal sample?** (4)

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

(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	$C + O_2 \longrightarrow O_2$ 12 32	$\frac{32}{12} \times 84 = 224$
H	$H_2 + \frac{1}{2}O_2 \longrightarrow H_2O$ 2 16	$\frac{16}{2} \times 9 = 72$
S	$S + O_2 \longrightarrow SO_2$ 32 32	$\frac{32}{32} \times 1.5 = 1.5$
N	—	—
O	—	—

Theoretical  $O_2$  required for 100 kg of fuel

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

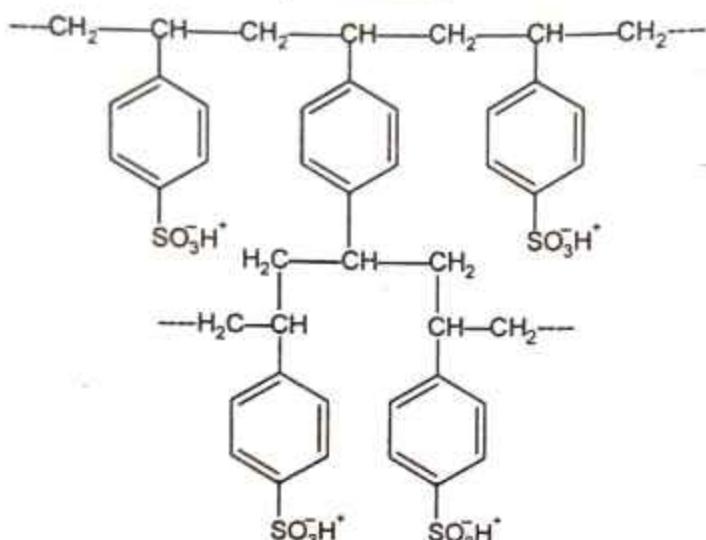
$$\begin{aligned}\text{Net amount required} &= \text{O}_2 \text{ required} - \text{O}_2 \text{ present in fuel} \\ &= 297.5 - 3.5 = 294.0 \text{ kg}\end{aligned}$$

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

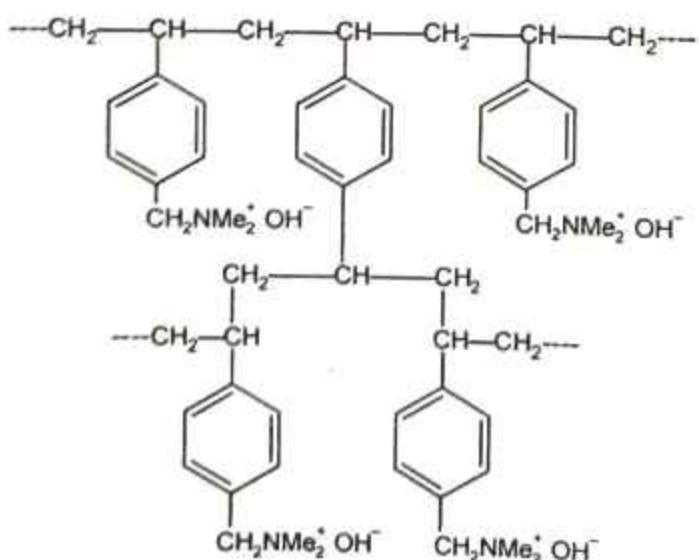
**Q.3. (a)** What are ion-exchange resins? How are they used for softening of water, explain with reactions and diagram? How can they be regenerated after getting exhausted? (7)

**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  $\text{H}^+$  ions with the cations. They are denoted as  $\text{RH}$ . 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  $\text{ROH}$ . They are mainly styrene divinyl benzene or amine-formaldehyde copolymers. e.g. Amberlite-400, Dowex-3.



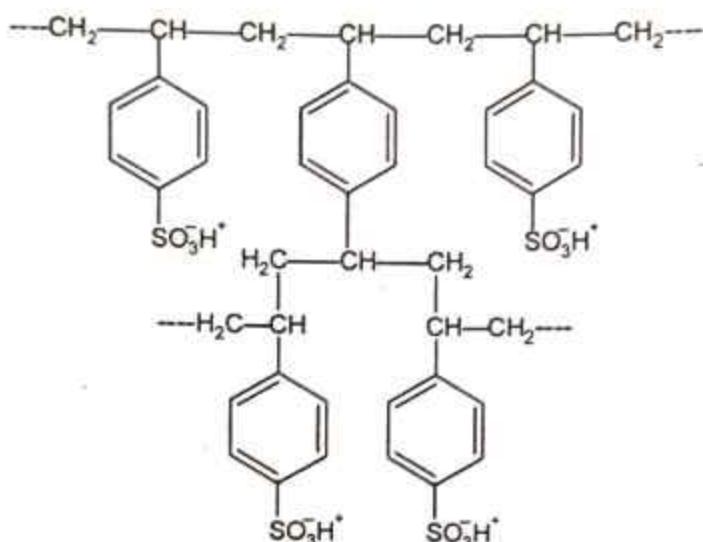
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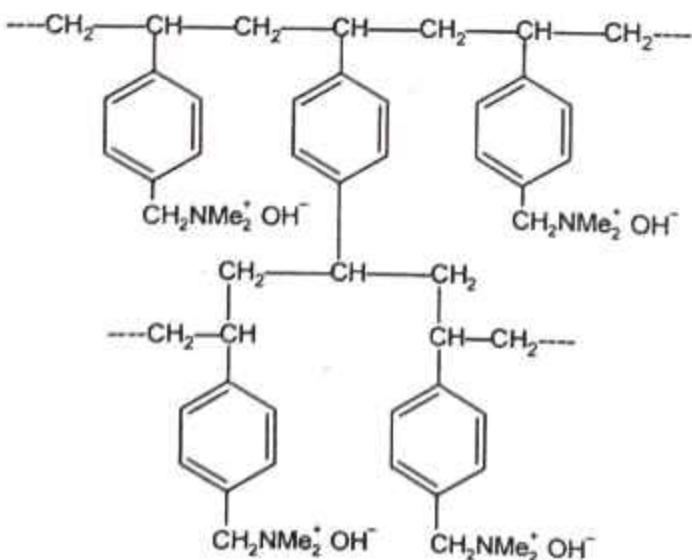
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**Principle:** When hard water is passed through cation exchange column  $H^+$  ion are replaced by cations present in hard water.

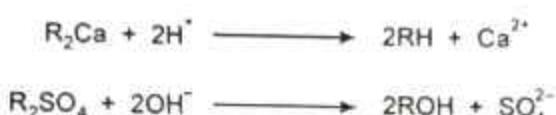


Then water is passed through anion exchange column, where anions are removed from water.

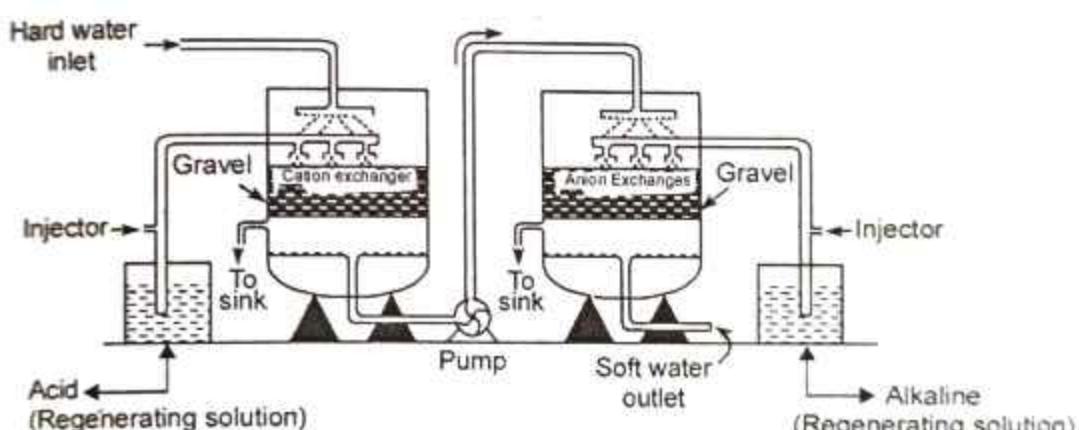


The  $H^+$  and  $OH^-$  ions released will combine to form water.

**Regeneration:** As the cation and anion exchangers are used continuously they lose their ion exchanging capacity and become exhausted. They are treated with dil. HCl/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 <sub>3</sub> equivalence
Ca(HCO <sub>3</sub> ) <sub>2</sub>	40.5	100 162	25
Mg(HCO <sub>3</sub> ) <sub>2</sub>	36.5	100 146	25

MgSO <sub>4</sub>	30.0	$\frac{100}{120}$	25
CaSO <sub>4</sub>	34.0	$\frac{100}{136}$	25
CaCl <sub>2</sub>	27.75	$\frac{100}{111}$	25
NaCl	—		

Lime requirement

$$\begin{aligned}
 &= \frac{74}{100} [\text{Ca}(\text{HCO}_3)_2 + 2 \times \text{Mg}(\text{HCO}_3)_2 + \text{MgSO}_4] \\
 &= \frac{74}{100} [25 + 2 \times 25 + 25] \times 50,000 \times \frac{100}{84} \\
 &= 4.404 \text{ kg.}
 \end{aligned}$$

Soda requirements

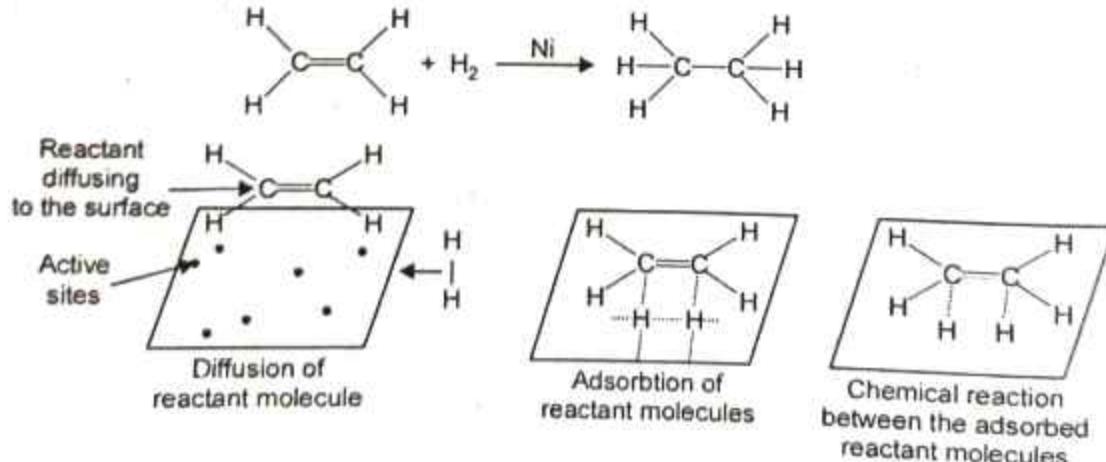
$$\begin{aligned}
 &= \frac{106}{100} [\text{MgSO}_4 + \text{CaSO}_4 + \text{CaCl}_2] \\
 &= \frac{106}{100} [25 + 25 + 25] \times 50,000 \times \frac{100}{92} \\
 &= 4.320 \text{ kg}
 \end{aligned}$$

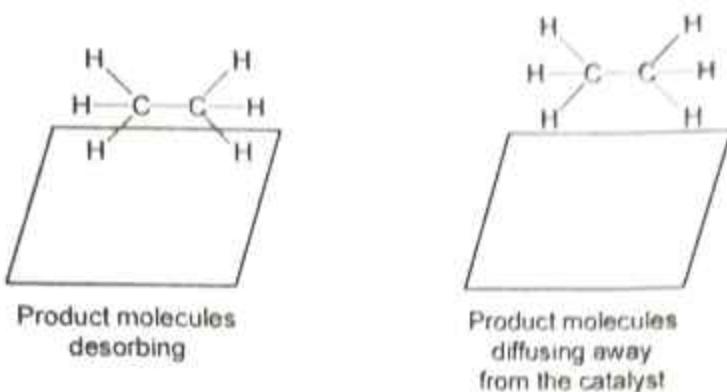
**Q.4. (a) Explain Adsorption theory of catalysis. Which step is the rate determining step?** (5)

**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.

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

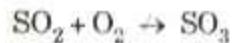
The above sequence is illustrated by hydrogenation of ethylene in the presence of hydrogen.





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.

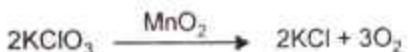


Catalyst = Pt

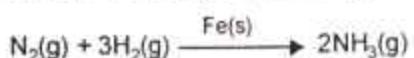
Poison =  $\text{As}_2\text{O}_3$

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

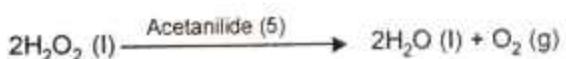
**Ans. Positive Catalyst:** The catalyst which increases the rate of reaction is called positive catalyst. e.g. 1. Decomposition of potassium chlorate in the presence of small amount of



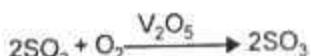
2. Manufacture of ammonia by Haber's process using finely divided iron as a catalyst



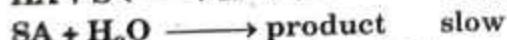
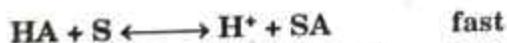
**Negative Catalyst:** The catalyst which decreases the rate of reaction is called negative catalyst. e.g. 1. Decomposition of  $\text{H}_2\text{O}_2$  is retarded in the presence of acetanilide



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

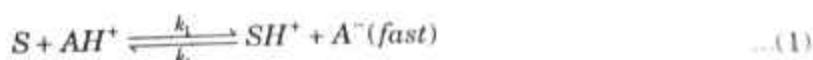


**Q.4. (c) Derive the rate expression for the following acid catalyst reaction. (4)**



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.

$$\frac{d[SH^+]}{dt} = 0 = k_1[S][AH^+] - k_2[SH^+][A^-] - k_3[SH^+] \quad \dots(3)$$

$$k_1[S][AH^+] = k_2[SH^+][A^-] + k_3[SH^+] \quad \dots(3)$$

$$[SH^+] = [k_2[A^-] + k_3][SH^+] \quad \dots(3)$$

$$[SH^+] = \frac{k_3[S][AH^+]}{k_2[A^-] + k_3} \quad \dots(3)$$

Substitute in equation (3)

$$r = k_3[SH^+] = \frac{k_3k_1[S][AH^+]}{k_2[A^-] + k_3} \quad \dots(3)$$

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

$$r = k_1[S][AH^+] \quad \dots(3)$$

This is general acid catalysis.

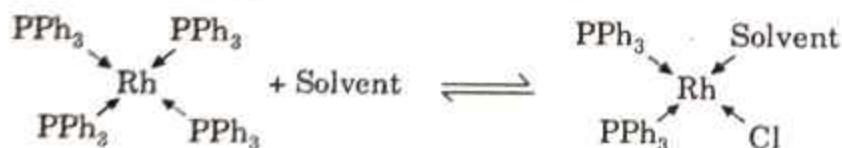
If  $k_2(A^-) \gg k_3$ , ignore  $k_3$

$$r = \frac{k_1k_2[S][AH^+]}{k_2[A^-]} \quad \dots(3)$$

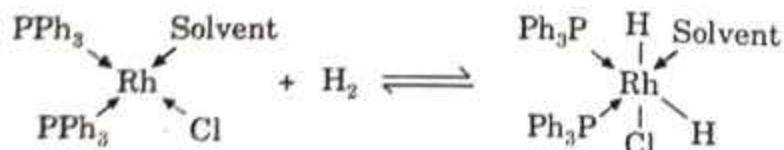
**Q.4. (d) Explain the mechanism of hydrogenation of alkenes by using Wilkinson catalyst.**

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

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

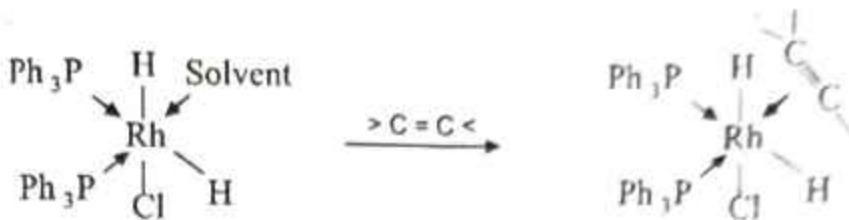


2. The reactant, alkene and molecular  $H_2$  are brought close to catalysis. The H-H bond breaks and each  $H_2$  attack separately to Rh.

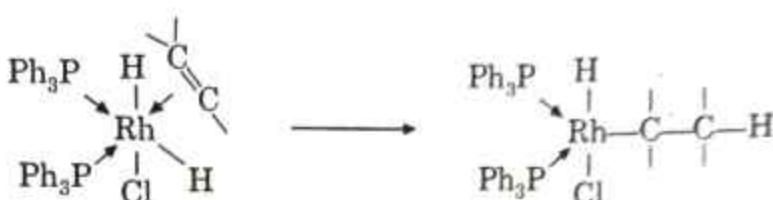


Platinum changes from oxidation state (I) to (III)

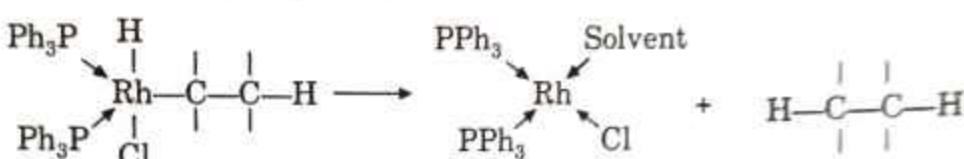
3. Alkene react with catalyst replacing a solvent molecule. The bonding occur by overlapping of an empty orbital of metal with  $\pi$ -cloud of alkene.



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.

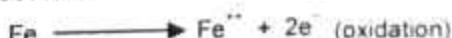
It is a common type of corrosion of metal in aqueous corrosive environment. This type of corrosion occurs when the metal comes in contact with a conducting liquid or when two dissimilar metals are immersed or dipped partly in a solution. According to this theory, there is the formation of a galvanic 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  $\text{H}_2$

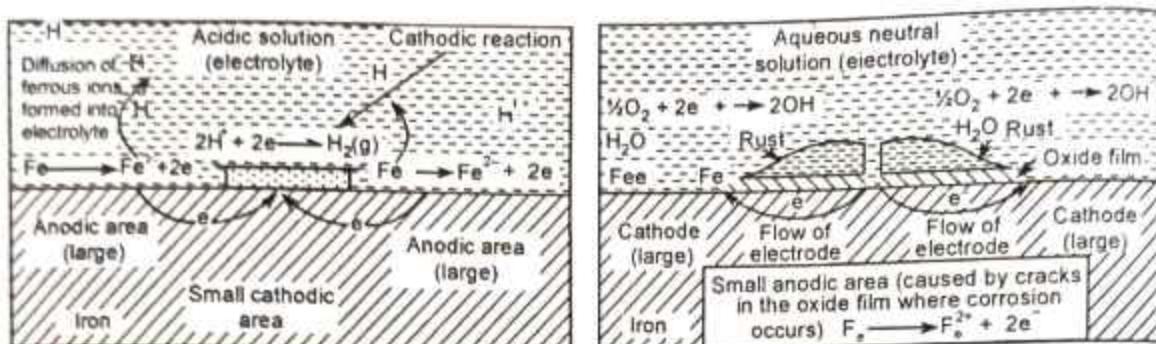
The hydrogen ions ( $\text{H}^+$ ) are formed due to the acidic environment and the following reaction occurs in the absence of oxygen



The overall reaction is

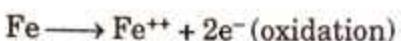


In this case, metals react in the acidic environment and are dissolved (undergo corrosion) to release  $\text{H}_2$  gas. All metals above hydrogen in electrochemical series can show this type of corrosion. In hydrogen evolution type of corrosion, anodic area is large as compared to its cathodic area

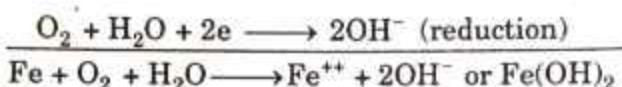


**Case II: Absorption of  $\text{O}_2$ .** This type of corrosion takes place in neutral or basic medium in the presence of oxygen. The small scratch on the surface creates small anodic area and rest of the surface acts as cathodic area. The following chemical reactions occur at anode and cathode.

At anode



At cathode



Ferric hydroxide is actually hydrated ferric oxide,  $\text{Fe}_2\text{O}_3 \cdot \text{H}_2\text{O}$ , 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 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  $\text{O}_2$  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

In the electrolyte solution are reduced at the interface between the solution and anode.

These coatings are used in particular for tribological applications, for example wear reduction and improved wear resistance. To refine metallic surfaces, various electrochemical processes are regularly used, in which for example the surfaces are plated 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 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.S. (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  $P = 2 - P + 2 = 4 - P$

The minimum number of phase at equilibrium is one.

Then  $P = 4 - 1 = 3$ .

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

**Ans.** Applications of Eutectic system.

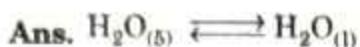
1. The Eutectic is used in preparation of alloy such as various type of solders in electric fuses.

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 desilverisation of an gentiferrous lead.

**Q.6. (c) Determine the number of components and number of phases for the following:** (i)  $\text{H}_2\text{O}_{(l)} \rightleftharpoons \text{H}_2\text{O}_{(l)}$  (ii)  $\text{NH}_4\text{Cl}_{(s)} \rightleftharpoons \text{NH}_3_{(g)}$ , 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  $\text{CaCO}_3$

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

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

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

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

Time : 1½ hrs.

M.M. : 30

Note: Q. No. 1. is compulsory. Attempt any two questions from the rest.

**Q.1. (a) Define the terms GCV and NCV of fuels.** (2×5=10)

**Ans. Higher or Gross Calorific Value (HCV)**

It is concerned with the hydrogen containing fuels which on burning get converted into steam. The products of combustion get cooled down to room temperature and the latent heat of condensation is also included in calculation but in true sense HCV is the total amount of heat produced when unit mass (or volume) of the fuel is burnt completely and the products of combustion were cooled to temperature 15°C or 60°F.

**Lower or Net Calorific Value (LCV):** When any fuel is burnt, water or moisture is not condensed and it escapes along with hot combustion which means that a lesser amount of heat is available. LCV can be understood as the net amount of heat obtained on burning completely one unit mass (or volume) of fuel when the products are permitted to escape. Hence

$$LCV = HCV - \text{Latent Heat of water/moisture vapour formed}$$

**Q.1. (b) Discuss advantages of catalytic cracking over thermal cracking.**

**Ans.** Advantage of catalytic cracking over thermal cracking are as follows:

1. The yield of petrol is high because catalyst are selective in nature
2. The quality of petrol is better
3. No external fuel is required for cracking
4. A much lower pressure is needed in catalytic cracking
5. The cracking process can b easily controlled ,so the desired product can be obtained
6. The percaentage of gum froming compound is very low.

**Q.1. (c) State Gibb's Phase Rule. Mention its advantages and limitations.**

**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

**Advantages of Gibbs Phase Rule**

This equation gives the phase rule given by Willard Gibb's, the fundamental relation controlling the equilibria in heterogeneous systems. Advantages of phase rule:

- (a) It gives a simple method of classifying equilibrium states of systems.
- (b) It confirms that the different systems having the same number of degrees of freedom behave in like manner.

- (c) It predicts the behavior of systems when subjected to changes in the variables such as pressure, temperature and volume.
- (d) The phase rule is applicable to macroscopic systems. Therefore, it is not necessary to take into account about their molecular structures.
- (e) It is applicable to physical as well as chemical reactions.

### **Limitations of Phase Rule**

- (a) As the phase rule is applicable to heterogeneous systems in equilibrium, it is therefore of no use for such systems which are slow in reaching the equilibrium state.
- (b) As the phase rule is applicable to a single equilibrium state, it never tells about the number of other equilibrium possible in the system.
- (c) In phase rule, various variables are temperature, pressure and composition. This phase rule does not consider the electric or magnetic influences. If such variables are considered, the factor 2 of the phase rule has to be adjusted accordingly.
- (d) All the phases in the system must be present under the same pressure, temperature and gravitational force.
- (e) No liquid or solid phases should be finely divided otherwise their vapour pressures will differ from their normal values.

**Q.1. (d) Hydrocarbons that are poor gasoline fuels are good diesel fuels. Explain.**

**Ans.** Gasoline is of good quality if its octane no is high i.e. hydrocarbon should be branched. If straight chain hydrocarbon are used in gasoline engine it will produce knocking. Similarly branched hydrocarbons cannot be used in diesel engines as they have poor cetane no and will produce knocking diesel engine. That's why poor gasoline fuel is good diesel fuel.

**Q.1. (e) A eutectic mixture has a definite composition and a sharp melting point yet it is not a compound. Explain.**

**Ans.** The elements or compounds that make up a eutectic mixture keep their identities - they are merely mixed together, not combined chemically. They are completely miscible with one another as liquids, but completely immiscible with one another as solids.

When a eutectic is solid (below its melting point) it consists of separate crystals or solidified droplets of the pure constituents. In the liquid state, they are merely dissolved in each other, but do not react chemically to form new compounds.

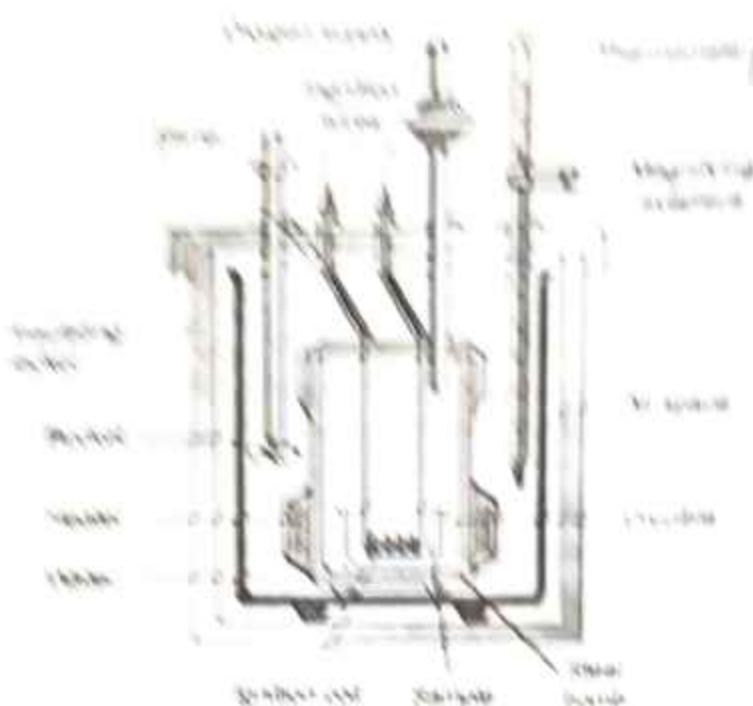
It's worth mentioning that in some respects the eutectic (lowest melting) composition does indeed behave much like it's a compound unto its own right, but it's NOT. Again, no chemical reaction involved.

**Q.2. (a) How the calorific value of a fuel can be determined by Bomb's calorimeter? Explain with the help of neat diagram. (6)**

**Ans.** The calorific value of solid or liquid fuels can be determined with the help of Bomb's calorimeter.

**Description:** Bomb Calorimeter consists of a strong stainless steel bomb where the fuel sample is burnt. The bomb has oxygen inlet valve and two stainless steel electrodes. A small ring is attached to one of the electrodes. In this ring, a nickel or stainless steel crucible is placed.

The bomb is placed in a copper calorimeter containing a known weight of water sample. The copper calorimeter is provided with a Beckmann's thermometer and stirrer for stirring water. The copper calorimeter is covered by an air jacket and water jacket.



**Procedure:** A known weight of the fuel sample is taken into the crucible. The two electrodes wire is inserted the fuel sample and then stretched across the electrodes. A small stirrer agency fitted with the help of screw. The bomb is filled with oxygen at all required pressure. The bomb is now placed in a copper calorimeter which containing some weight of water. Initial temperature of the water in the calorimeter is noted ( $t_1$ ) in degrees. The electrodes are connected to a battery (DC). The current is now supplied to the sample which undergoes burning with the evolution of heat. The liberated heat raises the temperature of water in the calorimeter. The maximum temperature of the surrounding apparatus is finally noted ( $t_2$ ).

From the temperature difference, calorific value of the fuel can be calculated as given.

#### Calculation:

Weight of the fuel sample taken in the crucible =  $x$  g

Weight of water taken in the calorimeter =  $W$  g

Weight of calorimeter and stirrer in terms of water Equivalent =  $A$  g

Initial temperature of water in the calorimeter =  $t_1$  °C

Final temperature of water in the calorimeter =  $t_2$  °C

$$\text{Heat absorbed by the water} = W(t_2 - t_1) \text{ cal} \quad (1)$$

$$\text{Heat absorbed the calorimeter} = A(t_2 - t_1) \text{ cal} \quad (2)$$

$$\text{Heat heat absorbed by the water} = W(t_2 - t_1) + A(t_2 - t_1) \\ \text{cal} = (W + A)(t_2 - t_1) \text{ cal} \quad (3)$$

The relationship between heat liberated by the fuel and HCV is as follows:

$$\text{Heat liberated by the fuel} = X \times (\text{HCV}) \quad (4)$$

Therefore, heat liberated by the fuel = Heat absorbed by the water and calorimeter

$\therefore$  Weight of fuel

Compare equation (3) and (4), we get

$$X \text{ (HCV)} = (W + A)(t_2 - t_1)$$

$$\text{HCV} = (W + A)(t_2 - t_1) / \times \text{cal/g}$$

Calculation of Lower Calorific Value (LCV):

The percentage of hydrogen in the fuel = H

Weight of water produced 1 g of the fuel = 9 H/100 g = 0.09 g

Therefore, heat liberated during the Condensation of steam = 0.09 H × 587 cal/g

Lower calorific value of the fuel = HCV – Latent heat of water liberated by the fuel

$$\text{LCV} = \text{HCV} - (0.09 H \times 587) \text{ cal/g.}$$

**Q.2. (b)** 2.16g of coal was kjeldahlized and  $\text{NH}_3$  gas thus evolved was absorbed in 25ml of 0.1N  $\text{H}_2\text{SO}_4$ . After absorption, the excess acid required 12.5ml of 0.1N  $\text{H}_2\text{SO}_4$  for exact neutralization. Determine the % of nitrogen in sample of coal. (4)

**Ans.** 12.5ml of 0.1 N NaOH = 12.5 ml of 0.1N  $\text{H}_2\text{SO}_4$

vol. of  $\text{H}_2\text{SO}_4$  used to neutralise

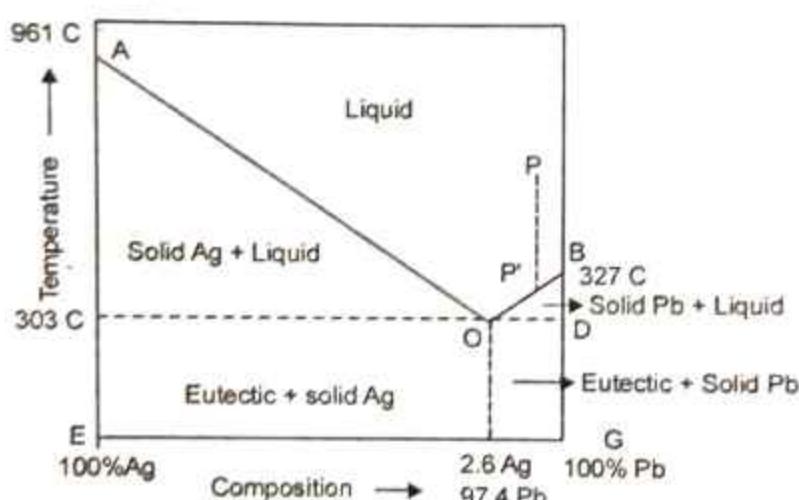
$$\begin{aligned}\text{NH}_3 \text{ evolved} &= 25 \text{ ml of } 0.1 \text{ N} - 12.5 \text{ ml } 0.1 \text{ N } \text{H}_2\text{SO}_4 \\ &= 12.5 \text{ ml}\end{aligned}$$

$$\% \text{ of N} = \frac{\text{Vol. of } \text{H}_2\text{SO}_4 \times \text{N} \times 1.4}{W}$$

$$= \frac{12.5 \times 0.1 \times 1.4}{2.16} = 0.82$$

**Q.3. (a)** Draw and explain the phase diagram of Pb-Ag system. (5)

**Ans.** Pb-Ag System: It is a two-component system. The phase diagram of the Pb-Ag system is shown in the fig.



**Curve AO:** Point A is the melting point of pure Silver. Curve AO shows melting point depression of silver by the addition of lead. At any point in this curve there is equilibrium between solid Ag and liquids parts. According to reduced phase rule equation. The system is univariant.

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

$$F = 2 - 2 + 1;$$

$$F' = 1$$

**Curve BO:** Point B is the melting point of pure lead. ( $327^\circ\text{C}$ ). Curve BO shows the melting point depression of lead on gradual addition of silver to it. Along this curve solid lead and solution co-exist and hence the system is univariant.

**Point O:** The two curves AO and BO meet at point O. Where three phases solid Pb, solid Ag and their solution co-exist, according to condensed phase rule the system is invariant.

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

$$F = 2 - 1 + 1;$$

$$F=2$$

The point 'O' is known as eutectic point, its composition (Ag=2.6%; Pb=97.4%) and temperature (303°C) is known as eutectic composition and eutectic temperature respectively. Further cooling below the eutectic temperature will cause simultaneous crystallization of a mixture of lead and silver.

**Area A OB:** Consists of only one phases namely Pb-Ag solution. According to reduced phase rule equation.

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

$$F = 2 - 1 + 1;$$

$$F=2$$

The system is bivariant i.e. both T and composition has to be specified to define the system.

Let us consider a point p. which represents a sample of lead containing less than 2.6% silver. On cooling the temperature falls gradually till point p. On further cooling lead begins to separate and the concentration of Ag increase in the solution till the point is reached, after that whole mass solidifies (2.6% Ag; 97.4% Pb.) This process is utilized. the pattinson's process of de-desilverization of lead.

Below the eutectic point (O), area COEF consists of solid and eutectic compound, where crystalline silver and eutectic compounds are stable. Similarly the area ODFG consists of solid Pb and eutectic compound, where crystalline lead eutectic compounds stable.

**Applications to pattinson's process:** If a sample of argent ferrous lead, containing less than 2.6% Ag is allowed to cool gradually, lead will separate out and the solution will become progressively richer in Ag. till the percentage 2.6 of Ag is reached; and on further cooling, the whole mass will solidify as such. On the other hand, if lead-silver alloy containing Ag greater than 2.6% is allowed to cool, and then pure silver separates along the curve AO, till the eutectic composition at O is reached.

**Q.3. (b) Write three applications of eutectic mixture.**

(3)

**Ans. Applications of eutectic system are:**

- Sodium chloride and water form a eutectoid when the mixture is 23.3% salt by mass with a eutectic point at -21.2 °C. The system is used to make ice cream and to melt ice and snow.
- The eutectic point of the mixture of ethanol and water is nearly pure ethanol. The value means there is a maximum proof or purity of alcohol that can be obtained using distillation.
- Eutectic alloys are used for soldering. A typical composition is 63% tin and 37% lead, by mass.
- Eutectoid glassy metals exhibit extreme corrosion resistance and strength.
- Inkjet printer ink is a eutectic mixture, permitting printing at a relatively low temperature.

**Q.3. (c) In phase diagram of water, the fusion curve of ice has a negative slope. Explain.**

(2)

The melting curve or fusion curve of ice/water is very special. It 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.

**Q.4. (a) Find the number of phases, components and degree of freedom in the following: (Any two)** (2)

(i) An aqueous solution of glucose

**Ans.** (i) The number of components ( $C$ ) = 2 (glucose and water)

$$F = C - P + 2$$

$$= 2 - 1 + 2$$

= 3 (temperature, pressure and concentration of solution)

**Q.4. (ii)  $\text{NH}_3$  (g) at  $42^\circ\text{C}$  and.**

**Ans.**  $\text{NH}_3$  (g) at  $45^\circ\text{C}$

No of phase = 1

Component = 1

$$F = C - P + 2$$

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

**Q.4. (iii) Water system at 4.58mm of Hg and at  $0.0098^\circ\text{C}$ .**

**Ans.** Water system at 4.58mm of Hg and at  $0.0098^\circ\text{C}$

No. of phases = 3

No. of component = 1

$$F = C - P + 2$$

$$1 - 3 + 2 = 0 \text{ (INVARIANT)}$$

**Q.4. (b) What is Pattinson's process?** (2)

**Ans.** Refer Q. 3. (a) of First Term Examination 2016.

**Q.4. (c) The composition by weight of a coal sample is C = 80%, H = 6%, O = 8%, S = 2%, N = 1% and ash = 3%. Calculate: (i) the minimum air required for complete combustion of 1 Kg of coal (ii) the % composition of dry products of combustion if 20% excess air is supplied.** (6)

**Ans.**

$$C = \frac{80}{100} \times 1000 = 800 \text{ g}$$

$$H = \frac{6}{100} \times 1000 = 60 \text{ g}$$

$$O = \frac{8}{100} \times 1000 = 80 \text{ g}$$

$$S = \frac{2}{100} \times 1000 = 20 \text{ g}$$

$$N = \frac{1}{100} \times 1000 = 10 \text{ g}$$

as

$$\text{Ash} = \frac{3}{100} \times 1000 = 30 \text{ g}$$

	Weight of O <sub>2</sub> required	Weight of dry product
$\text{S} + \frac{3}{2}\text{O}_2 \rightarrow \text{SO}_2$	$\frac{32}{12} \times 800 = 2133\text{g}$	$\frac{44}{12} \times 800 = 2933.3\text{g}$
$\text{H}_2 + \frac{1}{2}\text{O}_2 \rightarrow \text{H}_2\text{O}$	$\frac{16}{2} \times 60 = 480\text{ g}$	
$\text{S} + \frac{3}{2}\text{O}_2 \rightarrow \text{SO}_2$	$\frac{32}{32} \times 20 = 20\text{g}$	$\frac{64}{32} \times 20 = 40\text{g}$

Theoretically

$$\text{O}_2 \text{ required in combustion} = 2133 + 480 + 20 = 2633\text{ g}$$

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

$$2633 - 80 = 2553\text{g}$$

$$\text{Air required} = 2553 \times \frac{100}{23} = 11100\text{g} = 11.1\text{kg}$$

Weight of dry products

$$\text{N}_2 = 77\% \text{ of wt. of air} + \text{N}_2 \text{ in fuel}$$

$$\frac{77}{100} \times 11100\text{g} + 10 = 8557\text{g}$$

$$\text{wt. of CO}_2 = 2933.3\text{g}$$

$$\text{wt. of SO}_2 = 40\text{g}$$

$$\text{Total wt. of dry products} = 2933.3 + 40 + 8557\text{g}$$

$$= 11530.3\text{g}$$

$$\% \text{ of CO}_2 = \frac{2933.3}{11530.3} \times 100 = 25.4\%$$

$$\% \text{ of N}_2 = \frac{8557}{11530.3} \times 100 = 74\%$$

$$\% \text{ of SO}_2 = \frac{40}{11530.3} \times 100 = 0.34\%$$

# END TERM EXAMINATION

## FIRST SEMESTER B.TECH. [DEC. 2016]

### APPLIED CHEMISTRY (ETCH-113)

Time : 3 hrs.

M.M. : 75

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

**Q.1. (a) Define HCV and GCV.** (2.5)

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

**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.**

**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?**

**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.

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

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

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.

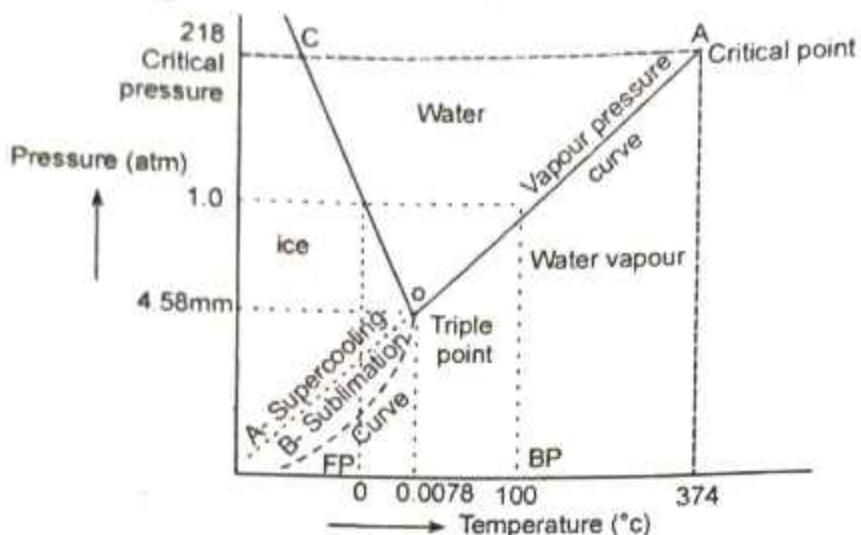
**Q.1. (f) What is an eutectic mixture?**

**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?**

**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

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:**

(2.5x4=10)

**(i) Chemical fuel and nuclear fuel**

**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		
(a) Aromatic hydrocarbons	Lower	Higher
(b) Aliphatic hydrocarbons	Higher	Lower
10. Uses	Domestic	Metallurgy

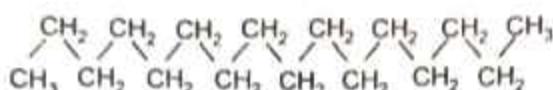
**Q.2. (a)(iii) Fixed and Fluidized bed catalytic cracking.**

**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 .

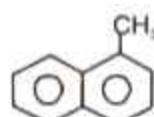
In this reactor catalyst remains in fluidized form and it cracks the gas oil molecules into lighters like naphtha and LPG. In this process regeneration occur within reactor so process does not stop

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

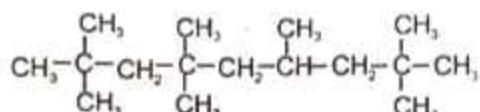
**Ans.** Octane number of a gasoline fuel is given by the percentage of iso-octane in a mixture of iso-octane (octane number 100) and *n*-heptane (octane number 0) that would yield the same anti-knock properties as the given fuel. Octane number is a fuel rating valid for gasoline (or petrol). Octane 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.

**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?**

(2.5)

**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)  $2\text{RSH} + \text{Na}_2\text{PbO}_2 + \text{S} \xrightarrow{\text{NaOH}} \text{R-S-S-R} + \text{PbS} + 2\text{NaOH}$  (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.**

(6.5)

**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 =  $0.01\text{ kg}$ .  
 Latent heat of steam =  $587\text{ Kcal/kg}$

(6)

**Ans.**

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

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

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

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

$$\text{NCV} = \text{GCV} - \frac{m}{V} \times \text{latent heat of condensation}$$

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

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

## 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

$$F = C - P + 2$$

$$2 - 1 + 2 = 3$$

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

Ans. No. of component : 1

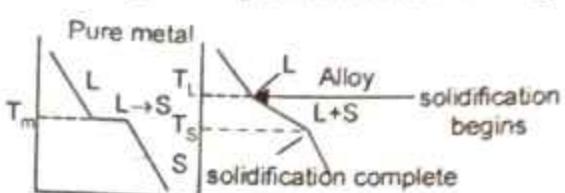
No. of phases : 1

$$F = C - P + 2$$

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

Q.4. (b) What are cooling curves? (2.5)

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.

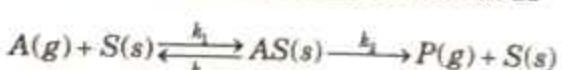
Step 1 and 5 are generally very fast and step 2 and 4 are generally faster than 3. Thus step 3 is the rate determining step in the surface reaction, i.e., chemisorption of the reactants on the surface of the solid adsorbent.

**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/ Heterogenensis 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  $[S]_0$ , concentration of adsorbed species on the catalyst surface,  $[AS]$  can be written as

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

and  $[S]$  can be written as

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

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

We can now write Equation (1) as

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

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

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

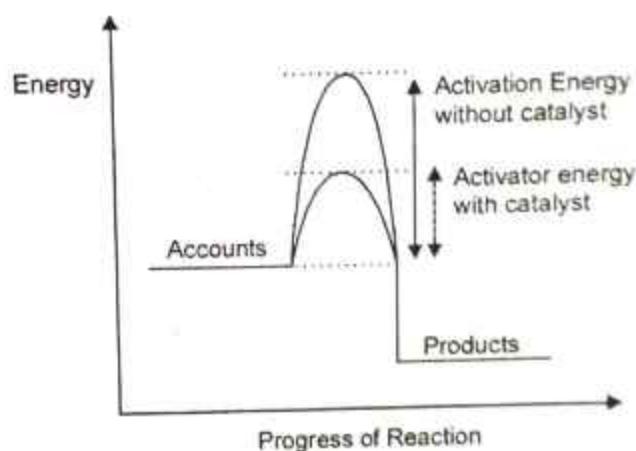
The rate of production of P can be written as

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

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:

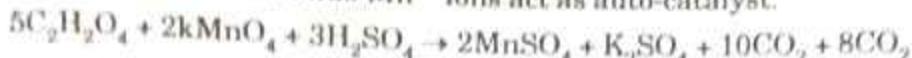


A catalyst speeds up both forward/backward reactions of a reversible reaction. The idea is that the activation energies are lowered for both the forward and backward reactions. The activation energy is lowered by exactly the same amount in each direction.

### 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,

(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.



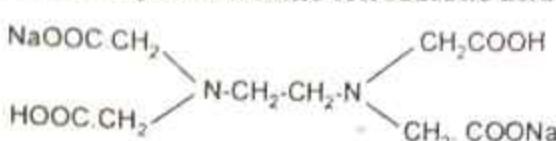
### UNIT-III

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

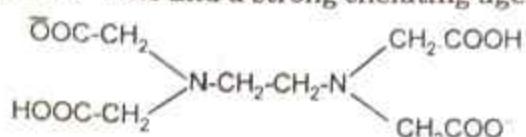
**Ans.** This is a complexometric method. Ethylene diamine tetraacetic acid (EDTA) in the form of its sodium yields the anion.

Theory

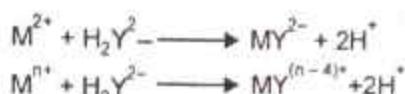
The disodium salt of the ethylenediamine tetraacetic acid (EDTA)



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.

**Q.R. (d)** 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 reacted 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

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

$$\begin{aligned} 1000 \text{ ml/1L sample required} &= 15 \times \frac{50}{42} \times \frac{1000}{50} \\ &= 357.14 \text{ PPM} \end{aligned}$$

#### Temp. hardness

50 ml of boiled water required = 9 ml of EDTA

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

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

$$\begin{aligned} \text{Permanent hardness} &= \text{Total hardness} - \text{Temp. hardness} \\ &= 357.14 - 214.28 \\ &= 142.86 \text{ PPM.} \end{aligned}$$

#### 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	$Na_3PO_4$	(Tri sodium Phosphate)	highly acidic water
2	$Na_2HPO_4$	(Di sodium hydrogen Phosphate)	slightly acidic water
3	$NaH_2PO_4$	(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 [ $Ca(OH)_2$ ] and soda [ $Na_2CO_3$ ]. Precipitates of calcium carbonate [ $CaCO_3$ ] and magnesium hydroxide [ $Mg(OH)_2$ ] formed are filtered off.

**Function of lime:** Lime removes temporary Ca and Mg hardness, permanent Mg, Al, Fe hardness and dissolved  $CO_2$  and  $H_2S$  gases and free mineral acid present in water. Lime does not react with  $CaCl_2$  and  $CaSO_4$  so it cannot remove calcium permanent hardness.

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



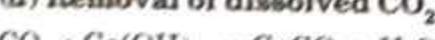
#### (b) Removal of permanent magnesium hardness:



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



#### (d) Removal of dissolved $CO_2$ and $H_2S$ :



#### 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,

precipitate aluminium hydroxide and entraps the fine precipitates. Chloride as a coagulant helps the removal of silica as well as oil. Cold Lime process removes water having a residual hardness of 50-60 ppm.



Aluminate



Sodium aluminate bicarbonate

removes it water

#### (c) Hot lime-soda process:

This process involves in treating water with softening chemicals at a temperature of 60-70 °C. This process is operated at a temperature close to the boiling point of the water.

- The reaction proceeds faster.
- The softening capacity of hot process is increased to many fold.
- No flocculants are needed as the precipitate and sludge formed settle down rapidly.
- Also, all the dissolved gases are driven out of the water.
- Filtration of water becomes much easier as the viscosity of softened water is lower.
- In turn, increases the filtering capacity of filters. Hot lime-soda process produces relatively lower residual hardness of 15-30 ppm.

The lime-soda plant consists of mainly 3 parts.

- "Reactant tank" in which raw water, chemicals and steam are thoroughly mixed.
- "Chemical sedimentation vessel" in which the sludge settles down.
- "Sand filter" that ensures complete removal of sludge from the softened water.

## UNIT-IV

**Q.S. or 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 is its tendency to undergo corrosion." More active metal - anode and less the difference in position of two metals in galvanic series- higher is rate of corrosion of more active metal.

2. **Oversvoltage:** "The difference between the voltage required for an electrode reaction and the 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  $\text{H}_2\text{SO}_4$ , the rate of rust is slow due to low overvoltage (0.70 V) inspite of high activity of Zn. On addition of  $\text{CuSO}_4$ , the rate of corrosion becomes fast due to small overvoltage (0.33 V) forming mixture cathode.

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 rapid and severe corrosion.

4. **Purity of the metal:** Presence of impurities in metal accelerate its corrosion. E.g. presence of  $\text{P}, \text{Fe}, \text{Si}$  or  $\text{C}$  is present in Zn, tiny electrochemical cells are set up and Zn corrodes.

**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.  $PbSO_4$  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. 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  $\text{H}_2$

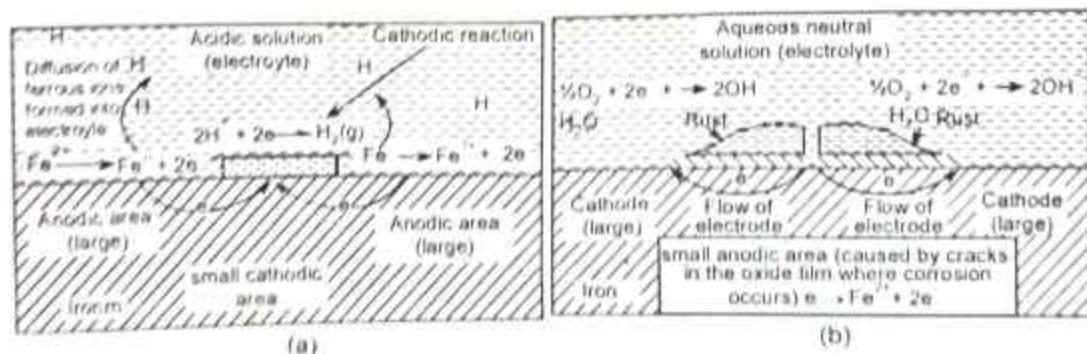
The hydrogen ions ( $\text{H}^+$ ) are formed due to the acidic environment and the following reaction occurs in the absence of oxygen



The overall reaction is



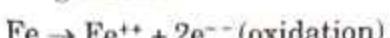
In this case, metals react in the acidic environment and are dissolved (undergo corrosion) to release  $\text{H}_2$  gas. All metals above hydrogen in electrochemical series can show this type of corrosion. In hydrogen evolution type of corrosion, anodic area is large as compared to its cathodic area.



**Case II: Absorption of O<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

**FIR<sub>S</sub> TERM EXAMINATION [SEPT. 2017]**  
**FIRST SEMESTER [B.TECH]**  
**APPLIED CHEMISTRY [ETCH-113]**

Time : 1.30 Hrs.

M.M. : 30

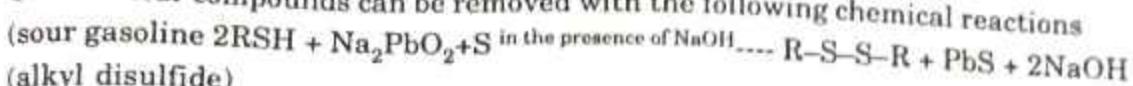
Note: Q. I is compulsory. Attempt any two more Questions from the rest.

**Q.1. Attempt any five**

**Q.1. (a) What is sweetening of petrol? Give reactions also.**

**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



**Q.1. (b) Discuss the advantages of catalytic cracking over thermal cracking.**

**Ans.** Advantage of catalytic cracking over thermal cracking

- (1) The yield of petrol is high because catalyst are selective in nature
- (2) The quality of petrol is better
- (3) No external fuel is required for cracking
- (4) A much lower pressure is needed in catalytic cracking
- (5) The cracking process can be easily controlled ,so the desired product can be obtained
- (6) The percentage of gum forming compound is very low.

**Q.1. (c) Hydrocarbons that are poor gasoline fuels are good diesel fuel. Explain.**

**Ans.** Diesel fuel is considered good if it contains large amount of straight chain compounds and its cetane number decreases by presence of branched hydrocarbons. In case of gasoline octane number is high due to branched hydrocarbons .thus if a fuel has higher amount of straight chain hydrocarbons it is good for diesel engine but bad for gasoline engines.

**Q.1. (d) Differentiate the high temperature and low temperature carbonization.**

(2)

**Ans.**

Characteristics	Low temperature carbonization	High temperature carbonization
I Heating temperature	500-700°C	900-1200°C
II Yield of coke	75-80%	65-75%
III Volatile matter content	5-15%	1-3%
IV Mechanical strength	Poor	Good
V 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> /tone	300-390 m <sup>3</sup> /tone
7. Coke produced	Soft	Hard
8. Smoke produced	Smokeless	Smoky
9. In gas, percentage of (a) Aromatic hydrocarbons (b) Aliphatic hydrocarbons	Lower Higher	Higher Lower
10. Uses	Domestic	Metallurgy

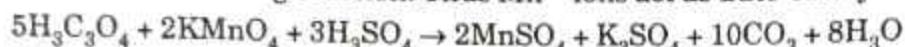
**Q.1 (e) Explain autocatalysis with suitable examples.**

(2)

**Ans. Autocatalysis**

In certain reactions, one of the product 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:

(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<sup>3+</sup> ions which are formed during reaction. Thus Mn<sup>3+</sup> ions act as auto-catalyst.

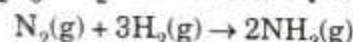


**Q.1. (f) Explain the action of catalytic promoter and poisons with suitable example.**

(2)

**Ans. Catalytic promoters:** Certain substances were found to increase the activity of catalyst, although they are not considered as catalyst. These substances are called promoters or activators.

e.g. 1. In the Haber's process for the manufacture of NH<sub>3</sub> from H<sub>2</sub> and N<sub>2</sub>, Mo and (Al<sub>2</sub>O<sub>3</sub> + K<sub>2</sub>O) is used as a promoter.



Fe and Mo/Al<sub>2</sub>O<sub>3</sub>, K<sub>2</sub>O act as catalyst.

**Catalytic Poisons:** Any substance which inhibits or destroys the catalytic activity to accelerate the reaction is called catalytic poison.

e.g. 1. In contact process for the manufacture of H<sub>2</sub>SO<sub>4</sub>, catalytic poison AS<sub>2</sub>O<sub>3</sub> absorbs on the active site of Pt forming PtS on the surface of the Pt reducing the catalytic activity of Pt.

#### TYPE OF CATALYTIC POISON:

1. Temporary poisoning: In which the catalyst regains its activity when the poison is removed from the reactants.

e.g. In the reaction between H<sub>2</sub> and N<sub>2</sub> catalysed by Fe catalyst in Haber's process, water vapour and O<sub>2</sub> acts as temporary poison.

2. Permanent poisoning: In which the catalyst cannot regain its activity even by removing the poison.

e.g. AS<sub>2</sub>O<sub>3</sub> poison permanently poisons the Pt powder catalyst in contact process for the manufacture of SO<sub>3</sub> from SO<sub>2</sub> and O<sub>2</sub>.

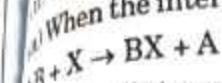
**Q.1. (g) Discuss intermediate complex formation theory of catalysis.** (2)

**Ans. Intermediate compound theory**

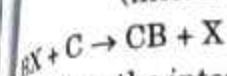
(i) This theory was proposed by Clement and Desorme in 1806. According to this theory, the desired reaction is brought about by a path involving the formation of an

(i) The intermediate compound, followed by its decomposition into the desired end products with the regeneration of the catalyst.

(ii) When the intermediate compound may be formed in either of two ways

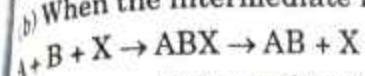


(intermediate)



...(i)

(b) When the intermediate compound is reactive and reacts with the other reactants.



...(ii)

(intermediate)

Where, A, B and C are the reactant molecules and X is the molecule of the catalyst.

The first type of reaction sums up to,  $AB + C \rightarrow CB + A$

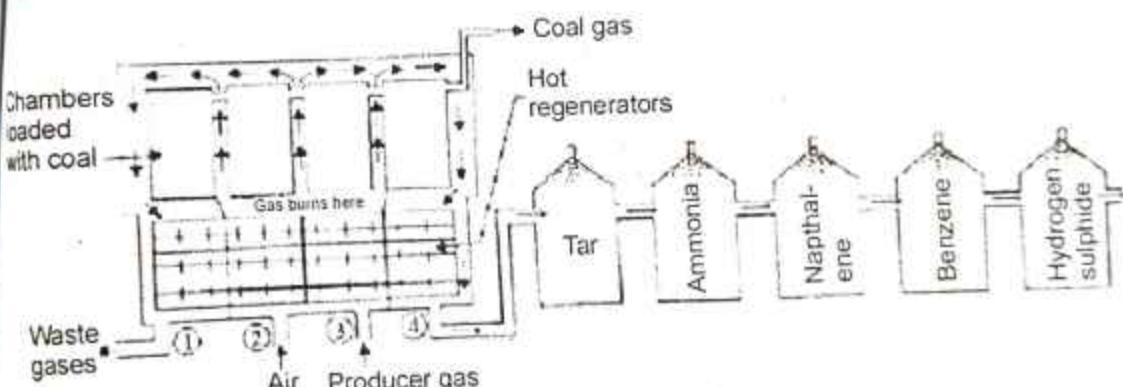
While the second to,  $A + B \rightarrow AB$  in many cases, the intermediate compounds postulated to be formed are known compounds and often their presence is detected.

**Q.2. (a) Describe the manufacturing of metallurgical coke by Otto-Hoffmann methods.** (6)

#### Ans. Manufacture of Metallurgical coke by Otto Hoffmann's method:

In order to (i) save the fuel for heating purpose and (ii) recover valuable by-products like coal gas, ammonia, benzol oil, tar etc.

2) Otto Hoffmann developed a modern by-product coke oven. Here, the heating is done internally by a portion of coal gas produced during the process itself. It also utilizes the waste flue gases for heating the checker work bricks. The oven consists of a number of narrow silica chambers, each about 10-12 m long, 3-4 m tall and 0.4-0.45 m wide, erected side by side with vertical flues between them to form a sort of battery. Each chamber has a hole at the top to introduce the charge, a gas off take and a refractory lined cast iron door at each end for coke discharge.



Finely powdered, crushed coal is introduced through the charging hole at the top of the chambers which are then tightly closed at both ends to cut off the supply of air. The ovens are heated to  $1200^{\circ}$  deg C by burning producer gas. The air required for the combustion of the fuel is preheated in regenerators flanking the retorts, while the flue gases leave their acquired heat to one generator; the other generator is used for preheating the air alone. The cycle goes on and the heating is continued until all the volatile matter has escaped. It takes nearly 18 hours for carbonization of a charge. The heating of air alone is required if the fuel gas is coal gas which has a high calorific. When the carbonization is over, the red hot coke is pushed out into truck by a massive ram. It is

then quenched by spraying water (wet quenching). Alternatively, the red hot coke may be placed in a chamber and cooled by sending in inert gases from boilers. The inert gases are then circulated to boilers where they generate steam. This method is known as dry quenching. The dry quenched coke is cleaner, drier and stronger and contains lesser dust than the wet quenched. The yield is about 70 %.

**Recovery of by-products:** The gas coming out of the retort is known as coke oven gas. This consists of tar, ammonia, moisture, aromatic hydrocarbons (naphthalene, benzene),  $H_2S$  etc. It can be used as a fuel after removing coal tar and ammonia.

(i) **Recovery of tar:** The coke oven gas is first passed through a tower in which liquid ammonia is sprayed. Tar and dust get collected in a tank below, which is heated by a steam coil to recover back the ammonia sprayed.

(ii) **Recovery of ammonia:** The coke oven gas is passed through another tower in which water is sprayed. Gaseous ammonia goes into solution as  $NH_4OH$ .

(iii) **Recovery of naphthalene:** After recovering ammonia, the remaining gases are led through another tower where water is sprayed at low temperature where naphthalene gets condensed.

(iv) **Recovery of benzene:** The resultant gas from the previous step is sprayed with petroleum whereby benzene and its homologues can be recovered.

(v) **Recovery of  $H_2S$ :** The gases are then passed through a purifier, packed with moist  $Fe_2O_3$ . Hydrogen sulphide is retained here.  $Fe_2O_3 + 3 H_2S \rightarrow Fe_2S_3 + 3 H_2O$  When all the  $Fe_2O_3$  is converted into  $Fe_2S_3$ , the purifier on exposure to the atmosphere, regenerates  $Fe_2O_3$  in the following manner.  $Fe_2S_3 + 4 O_2 \rightarrow 2 FeO + 3 SO_2$   $2 FeO + O_2 \rightarrow 2 Fe_2O_3$

**Q.2. (b)** 1.26 g of the coal sample was kjeldahlized and  $NH_3$  gas thus evolved was absorbed in 15 ml of 0.1 N  $H_2SO_4$ . After absorption, the excess acid required 6.75 ml of 0.1 N NaOH for exact neutralization. 2.0 g of coal sample in a quantitative analysis gave 0.233 g of  $BaSO_4$ . Calculate the percentage of Nitrogen and Sulphur.

(4)

$$\text{Ans. } 6.75 \text{ ml of } 0.1 \text{ N NaOH} = 6.75 \text{ ml of } 0.1 \text{ N } H_2SO_4$$

$$\begin{aligned} &\text{Vol. of } H_2SO_4 \text{ used to neutralise } NH_3 \text{ evolved} \\ &= 15 \text{ ml of } 0.1 \text{ N} - 6.75 \text{ ml of } 0.1 \text{ N } H_2SO_4 \\ &= 8.25 \text{ ml of } 0.1 \text{ N } H_2SO_4 \end{aligned}$$

$$\% \text{ of } N = \frac{8.25 \times 0.1 \times 1.4}{1.26} = 0.91\%$$

$$\% \text{ of sulphur} = \frac{\text{wt of Base } BaSO_4 \text{ obtained} \times 332 \times 100}{233 \times \text{wt of sample taken}}$$

$$\frac{0.233 \times 32 \times 100}{233 \times 2} = 16.02\%$$

**Q.3. (a) Derive the Michaelis-Menten equation for enzyme catalysis.** (6)

**Ans.** Refer Q. 4. (b) of End Term 2017

**Q.3. (b) 0.72 g of a fuel on burning in a bomb calorimeter increased the temperature of water from 27.3°C to 29.1°C. If the calorimeter contains 250 g of water and its water equivalent is 150 g, calculate the GCV and NCV of the fuel, if the fuel contains 5% of Hydrogen. (Latent heat of vaporization = 580 cal/g)**

Mass of fuel taken (X) = 0.72 g

Mass of water = (W) = 250 g

Water equivalent (w) = 150 g

$$t_1 = 27.3^\circ\text{C} = 27.3 + 273 = 300.3 \text{ K}$$

$$t_2 = 29.1^\circ\text{C} = 29.1 + 273 = 302.1 \text{ K}$$

Heat liberated = heat absorbed

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

$$HCV = L = \frac{(W+w)(t_2 - t_1)}{X}$$

$$L = \frac{(250 + 150)(302.1 - 300.3)}{0.72} = \frac{400 \times 1.8}{0.72}$$

$$= 1000 \text{ kcal/g}$$

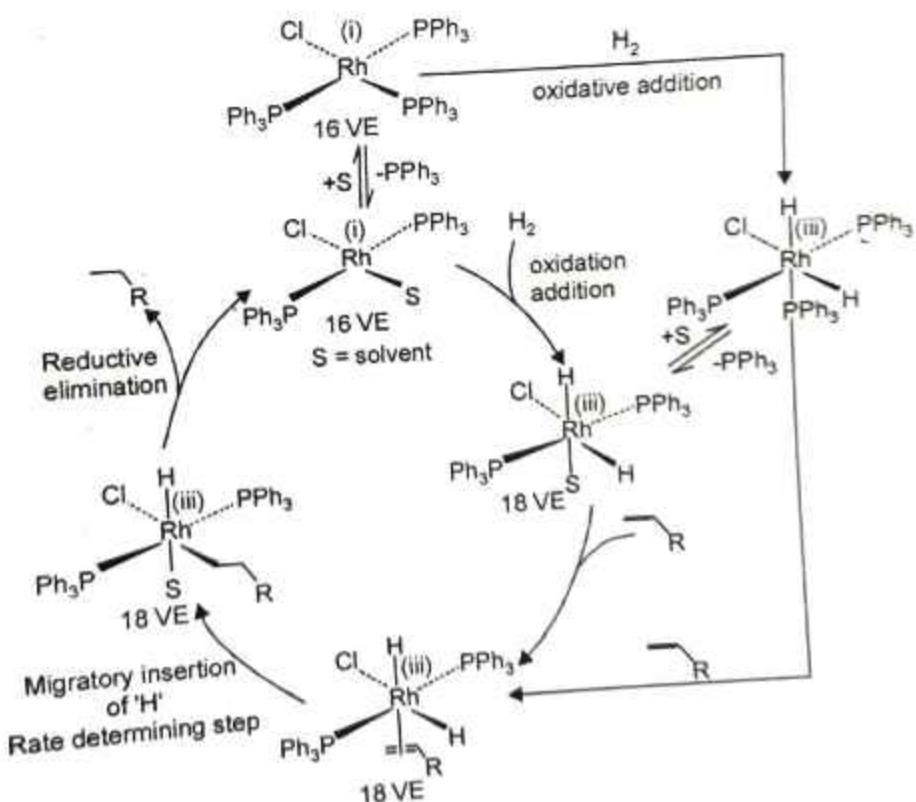
LCV = HCV – Latest heat of water formed

$$= HCV - 0.09 \times 4 \times 587$$

$$= 1000 - 0.09 \times 5 \times 587 = 735.85 \text{ kcal/g.}$$

**Q.4. (a) Explain the mechanism of hydrogenation of alkenes using Wilkinson catalyst.** (3)

**Ans.** Wilkinson's catalyst is a pre-catalyst that is converted to an active form by losing one triphenylphosphine ligand before entering the catalytic cycle. Usually, the solvent molecule fills the vacant site.



Initially, the catalyst activates the molecular dihydrogen by oxidative addition mechanism to give a 18 valence electron dihydrido complex. The oxidation state of Rh is increased to +3. Thus formed dihydrido complex binds to the olefin in the next step with the concomitant loss of solvent or  $\text{PPh}_3$  ligand. Since the activation of dihydrogen occurs before addition of olefin, this path is referred to as dihydridepath.

Now one of the hydrogen undergoes migratory insertion at the double bond. This is a slow step i.e., Rate Determining Step (RDS).

Immediately and finally, the alkane is released rapidly by an irreversible reductive elimination step that completes the catalytic cycle. The oxidation state of Rh is decreased to +1 and the catalyst is regenerated.

However, other paths and intermediates are also possible under the given reaction conditions (see below).

**Q.4. (b) Explain the Heterogeneous and Homogeneous catalysis with suitable examples.**

**Ans. HOMOGENOUS CATALYSIS:**

- In homogenous catalysis, the catalyst is in the same phase as reactants and it is evenly distributed throughout this type of catalysis can occur in gas & liquid(solution)phase.

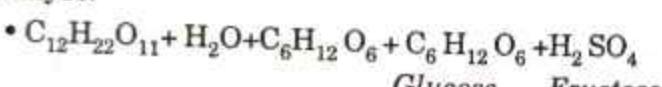
**Example**

**(A) In Gas Phase :**

- Oxidation of sulphur ( $\text{SO}_2$ ) to sulphur trioxide( $\text{SO}_3$ ) with nitric oxide (NO) as catalyst.

**(B) In Solution Phase:**

- I. Hydrolysis of cane sugar in aqueous solution in the presence of mineral acid as catalyst.



**HETEROGENOUS CATALYSIS:**

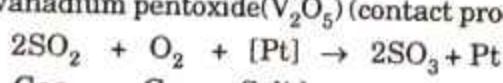
- The catalysis in which the catalyst is in a different physical phase from the reactants is termed heterogeneous catalysis, most important of such reaction are those in which the reactants are in the gas phase while the catalyst is a solid the process is called Contact Catalysis.

**Examples of Heterogeneous Catalysis:**

**(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).



**Q.4. (c) A fuel is found to contain: C = 90%, H = 6.0%, S = 2.5%, O = 1.0% and ash = 0.5%. Calculate: (i) the minimum air required for complete combustion of 1kg of the fuel; (ii) the composition of dry products of combustion if 25% of excess air is used.**

(5)

**Ans.** 1kg of coal contain : C = 90 kg, H = 0.06 kg,

S = 0.025 kg, O = 0.01 kg + ash = 0.5%

Constituents	Combustion $R \times n$	Amount of $O_2$	Amt. of dry products
C	$C + O_2 \rightarrow CO_2$ 12 32 44	$\frac{32}{12} \times 0.9 = 2.4$	$\frac{44}{12} \times 0.9 = 3.3$
H	$H_2 + \frac{1}{2} O_2 \rightarrow H_2O$ 2 16 18	$\frac{16}{2} \times 0.06 = 0.48$	-
S	$S + O_2 \rightarrow SO_2$ 32 32 64	$\frac{32}{32} \times 0.025$ = 0.025	$\frac{64}{32} \times 0.02$ $= \frac{64}{32} \times 0.02 = 0.05$
O	-	-	-
N	-	-	-

$$O_2 \text{ required} = [2.4 + 0.48 + 0.025] - 0.01 = 2.895 \text{ kg}$$

$$\text{air required} = 2.895 \times \frac{100}{23} = 12.58 \text{ kg}$$

$$\text{amount of air actually supplied} = \frac{125}{100} \times 12.58 = 15.72 \text{ kg}$$

$$\text{Excess air} = 15.72 - 12.58 = 3.145 \text{ kg}$$

Amount of dry product

$$\text{Amt of } CO_2 = 3.3 \text{ kg}$$

$$\text{Amount of } SO_2 = 0.05 \text{ kg}$$

$$\text{Amount of dry product} = 3.3 + 0.05 = 3.35 \text{ kg}$$

$$\% \text{ of } CO_2 = \frac{3.3}{3.35} \times 100 = 98.5\%$$

$$\% \text{ of } SO_2 = \frac{0.05}{3.35} \times 100 = 1.492\%$$

**END TERM EXAMINATION [DEC. 2017]**  
**FIRST SEMESTER [B.TECH]**  
**APPLIED CHEMISTRY [ETCH-113]**

Time : 3 Hrs.

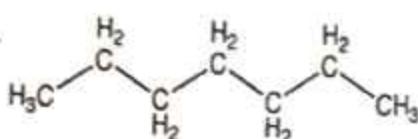
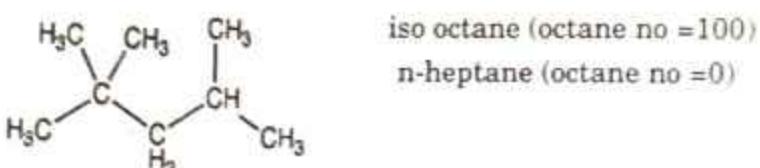
M.M. : 75

**Note:** Attempt any five questions including Q.No. 1 which is compulsory. Select one question from each unit. Assume suitable missing data, if any.

**Q.1. (a) Define: (i) Octane and Cetane number**

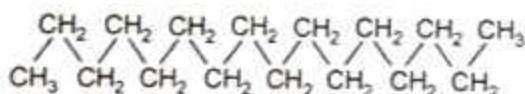
(1.5)

**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.

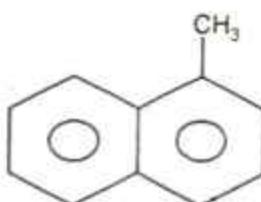


Cetane number, on the other hand, is given for a diesel fuel by the percentage of cetane in a mixture of cetane (cetane number 100) and isocetane (cetane number 15) that would give the same ignition characteristics as the given fuel. Cetane number is a rating for diesel fuel. Cetane number describes 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.

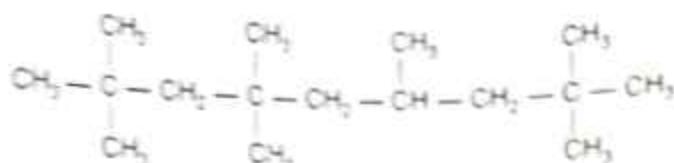
***n*-Hexadecane**



**1-Methylnaphthalene**



**1-Methylnaphthalene, cetane number = 0**

**Heptamethylnonane**

2, 2, 4, 4, 6, 8, 8, Heptamethylnonane (Isocetane).

cetane number = 15

**Q.1. (a)(ii) Synthetic Petrol and Power alcohol**

(1.5)

**Ans.** In general, synthetic petroleum refers to a laboratory manufactured, custom-designed petroleum substitute. Synthetic petroleum could be better than the naturally occurring product because it is pure from any of the non-beneficial properties found in conventional petroleum. It is obtained from coal, natural gas, oil shale, or biomass. Methods of producing synthetic petrol:

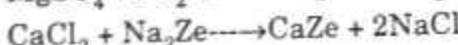
- Polymerisation
- Fischer-Tropsch method
- Bergius process

Power alcohol is mixture liquid. The major use of power alcohol is found in the automobiles as they generate energy from it for their operation. It act as a good fuel for the automobiles and is formed by mixing the petrol and ethyl alcohol in the fixed ratio. The ratio to make power alcohol is 75% petrol and 25% ethyl alcohol. Ethyl alcohol has good antiknocking property so addition of ethyl alcohol increases the octane number of petrol. Power alcohol is cheaper than petrol.

**Q.1. (b) Distinguish between softening and demineralization of water with chemical equations.**

(3)

**Ans.** The water that lathers with soap easily is called or known as soft water. It describes type of water that contain few or no minerals like calcium (Ca) or magnesium (Mg) ions. One of the method to make hard water soft is zeolite method or permute method. Zeolite have the property of exchanging their Na ions for hardness causing ions like Ca++ and Mg++. Calcium and magnesium zeolite on treatment with a solution of NaCl can replace Ca++ and Mg++ ion with Na+ ions, thereby regenerating the zeolite. The reactions taking place during the process of softening are presented below:



where Ze represents zeolite

Zeolite can be regenerated by passing NaCl solution.



Demineralised water is specially purified water that has had most or all of its mineral and salt ions removed, such as Calcium, Magnesium, Sodium, Chloride, Sulphate, Nitrate and Bicarbonate. It is also known as Deionised water, DI or Demineralised water.

As the raw water passes through the cation exchange resin, Ca++, Mg++ and other ions are exchanged with H+ ions of the resin.



Thus, sulphates, chlorides, bicarbonates, get converted into sulphuric, hydrochloric and carbonic acids. The acidic water emerging from the cation exchange bed is passed through the anion exchange bed where the anions are exchanged for the OH ions of resin.



The water emerging from the anion exchange bed is free from both cations and anions and hence completely demineralized.

**Q.1. (c) Name the disinfecting agents of water.** (3)

**Chemical disinfectants** are chemical substances which are used to kill or deactivate pathogenic microorganisms.

**Examples are:** Chlorine, Sodium hypochlorite, Chlorine dioxide, Chloramines, Hydrogen peroxide, Copper/ silver ionisation, Bromine ozone, UV, Potassium permanganate

**Q.1. (d) What is corrosion? How is it different from erosion?** (3)

**Ans.** Corrosion is the deterioration of a metal as a result of chemical reactions between it and the surrounding environment. Both the type of metal and the environmental conditions, particularly gasses that are in contact with the metal, determine the form and rate of deterioration. Corrosion is an electrochemical reaction that appears in several forms, such as chemical corrosion and atmospheric corrosion, the latter of which is the most common form. When acidic substances (including water) come in contact with metals, such as iron and/or steel, rust begins to form. Rust is the result of corroding steel after the iron (Fe) particles have been exposed to oxygen and moisture (e.g., humidity, vapor, immersion).

**Difference Between Erosion and Corrosion**

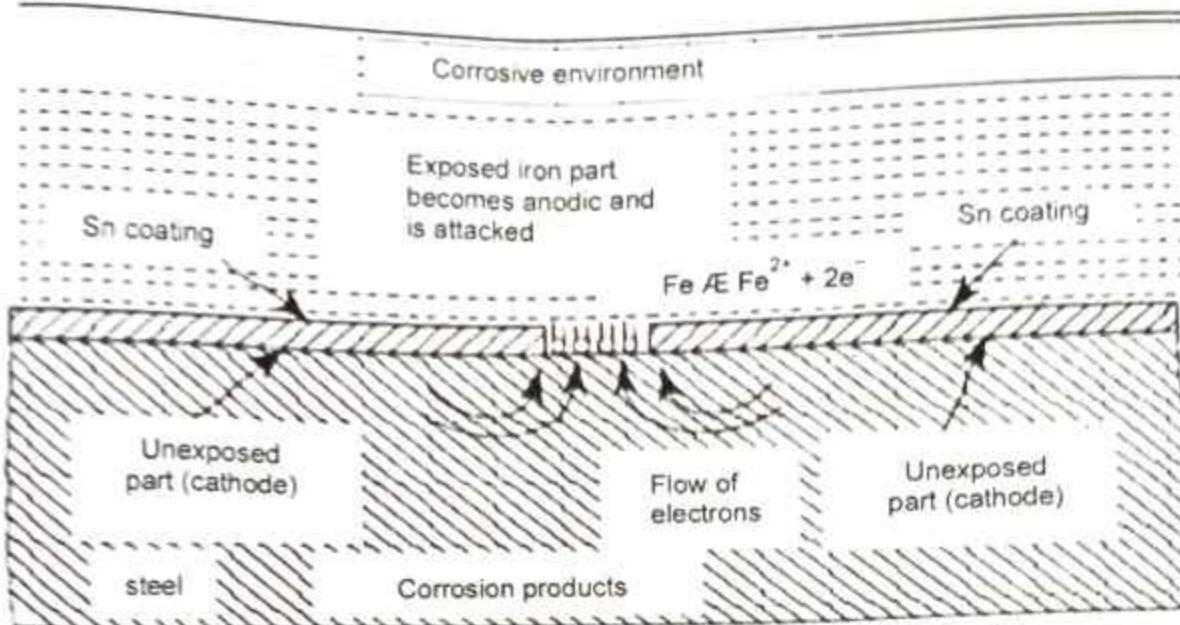
- Erosion refers to movement of small fragments of rocks under the influence of gravity and a natural agent such as water, winds or melting ice.
- Corrosion refers to change in the chemical composition of some surface (mostly metals) because of the action of oxygen in the presence of moisture
- Erosion can be prevented to an extent by afforestation and planting more trees on terraces whereas corrosion can be prevented by putting on a protective layer on the surface of metals such as paint.
- Erosion does not change the chemical composition of the fragments that are carried away while corrosion leads to the formation of a totally new substance (such as rust in the case of corrosion of iron)

One example is the corrosion and the subsequent erosion happening to ships and other marine vessels fabricated in steel. The salt water flowing against the bottom and the sides of the ships removes the corrosion and the next layer of metal starting to corrode. Repeated cycles of corrosion and its removal by erosion leading to the thinning of the steel plates is one such form of corrosion.

**Q.1. (e) Explain the following terms: (i) Tinning (ii) Metal cladding (iii) Electroplating.** (3)

**Ans. (i) Tining:** 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.



#### **Q.1. (e)(ii) Metal cladding**

**Ans.** **Metal Cladding** is the process of bringing 2 types of metal together in order to create a new sheet of metal that is extra strong and extra durable for the exterior of a building. Cladding is popular both because it protects the outside structure of a building and improves the aesthetic, and unlike other forms of cladding metal can also be used for roofing.

Metal cladding is a type of protective coating, where the protective material such as metal powder or foil is bonded to a substrate by applying heat and/or pressure. The study of metal cladding is significant because this method of corrosion protection and wear protection is generally very reliable and cost-effective. Metal cladding is a method of protecting one metal (or composite) by forming a layer of a second metal to its surface by using techniques such as diffusion, deformation and lasers.

The advantage of cladding is that the process as well as the material can be chosen as per the needs of the application and the bond strength required. The laser beam method of cladding can be used for ceramic coating as well as metallic coating.

#### **(iii) Electroplating.**

**Ans. (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 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 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.1. (f) Define: (i) Gibb's Phase rule (ii) Degree of freedom**

(3)

**Ans. (i) Gibbs phase rule**

If the equilibrium of a heterogeneous system is not influenced by gravitational, electrical or magnetic forces or by surface action but only by temperature, pressure and concentration, then the number of degrees of freedom of the system is related to the number of components and phases by the phase rule equation-

$$F = C - P + 2$$

For any system at equilibrium at definite temperature and pressure.

**(ii) Degree of freedom**

**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. 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

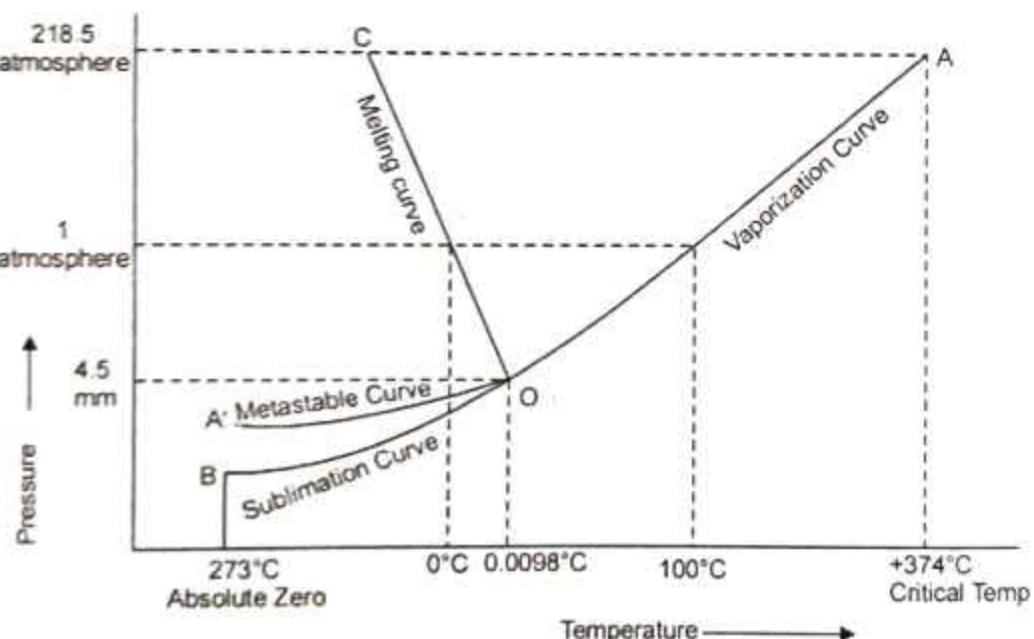
For considering a system consisting of water vapour phase only both temperature and pressure should be stated in order to define the system. Then the system is bivariant

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

(3)

**Ans. Phase diagram of water**

In water there is only one component i.e. water and its three phases: ice, water, steam which are solid, liquid, and gaseous respectively. Figure below represents phase diagram or pressure v/s temp diagram for the water system.



The three curves OA, OB and OC represent the equilibrium conditions between two phases solid with vapour, vapour with liquid and liquid with solid phase of water.

#### Significance of triple point

The triple point temperature of a pure substance is the unique temperature at which the solid, liquid and vapour phases of the substance co-exist in thermal equilibrium. Such triple points make ideal reference points for the calibration of thermometers. They can be realised by using a sealed, evacuated, cylindrical glass cell filled with the pure substance, with an axial re-entrant well for the insertion of the thermometer.

Triple point of water is at a pressure of 4.5 mm and temperature 0.00°C which means that ice water and water vapours will coexist only at above condition.

**Q.1. (h) Name of catalyst of the following reactions:**

- (i) Hydrogenation of vegetable oils
- (ii) Homogeneous catalysis of alkenes
- (iii) Zeigler - Natta Polymerisation
- (iv) Haber's Process

**Ans.** 1. Hydrogenation of oil : Ni

2. Homogenous hydrogenation reaction : Ni or Pt

3. Zeigler Natta polymerization :  $TiCl_3 + (C_2H_5)_2Al$

4. Haber's process : Fe

(4)

#### UNIT-I

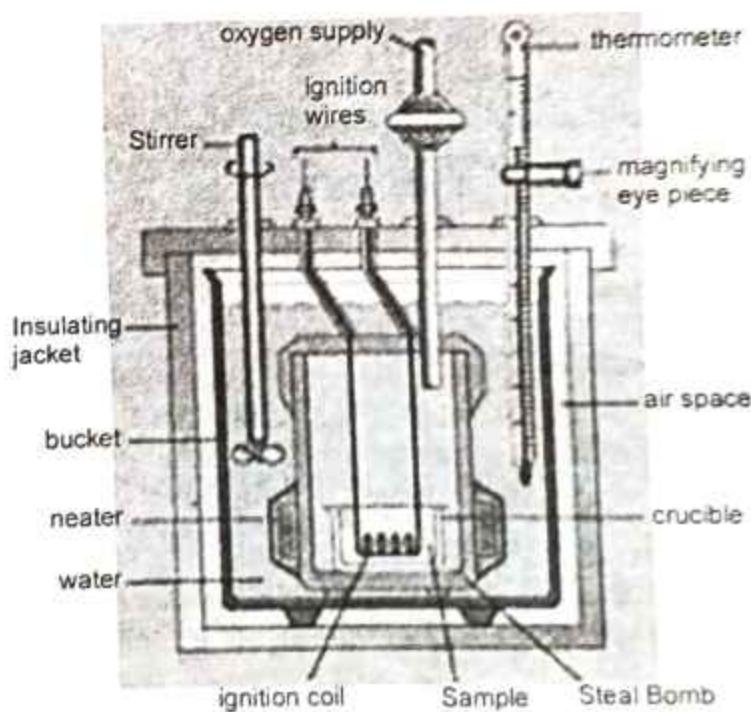
**Q.2. (a) Explain the working of Bomb Calorimeter in detail with neat diagram.**

(6)

**Ans.** The calorific value of solid or liquid fuels can be determined with the help of bomb calorimeter.

**Description:** Bomb Calorimeter consists of a strong stainless steel bomb where the fuel sample is burnt. The bomb has oxygen inlet valve and two stainless steel electrodes. A small ring is attached to one of the electrodes. In this ring, a nickel or stainless steel crucible is placed.

The bomb is placed in a copper calorimeter containing a known weight of water sample. The copper calorimeter is provided with a Beckmann's thermometer and stirrer for stirring water. The copper calorimeter is covered by an air jacket and water jacket.



then quenched by spraying water (wet quenching). Alternatively, the red hot coke may be placed in a chamber and cooled by sending in inert gases from boilers. The inert gases are then circulated to boilers where they generate steam. This method is known as dry quenching. The dry quenched coke is cleaner, drier and stronger and contains lesser dust than the wet quenched. The yield is about 70 %.

**Q.3. (b) Distinguish between proximate and ultimate analysis. Calculate the weight and volume of air required for condensation of 1 kg of carbon. (6.5)**

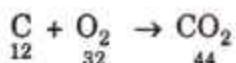
**Ans.** Proximate analysis of coal examines the chemical composition of a coal sample. The proximity analysis parameters are

- (1) Moisture,
- (2) Volatile compounds,
- (3) Ash content
- (4) Fixed carbon.

Proximate analysis used to ascertain "Rank" of coals as the above parameters will indicate the Heating value of the coal. Proximate analysis is used to establish the rank/category/type of coals and provide the ratio of combustible to non-combustible constituents.

**Ultimate analysis**, which is more comprehensive, is dependent on quantitative analysis of various elements present in the coal sample such as carbon, hydrogen, sulfur, oxygen, and nitrogen. Ultimate analysis tests produce more comprehensive results than the proximate analyses. An ultimate (chemical) analyses determines the elemental components in coal.

$$\text{Weight of C} = 1 \text{ kg}$$



$$\text{Weight of O}_2 \text{ required} = \frac{32}{12} = 2.67 \text{ kg}$$

$$\text{Weight of air required} = 2.67 \times \frac{100}{23} = 11.60 \text{ kg} = 11600 \text{ g}$$

$$\text{Volume of air required for combustion of 1 kg of C} = \frac{11600}{\text{molar mass of air}} \times 22.44$$

$$= \frac{11600}{28.94} \times 22.42 \text{ L} = 8978.6 \text{ L} = 8.97 \text{ m}^3$$

**Q.4. (a) Explain Heterogeneous catalysis with examples. Discuss the elementary steps of heterogeneous catalysis according to Langmuir - Hinshelwood mechanism. (6)**

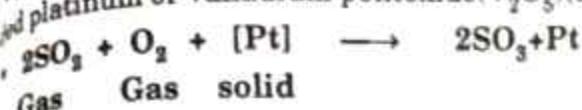
**Ans. HETEROGENOUS CATALYSIS:**

- The catalysis in which the catalyst is in a different physical phase from the reactants is termed heterogeneous catalysis, most important of such 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:

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).



Langmuir-Hinshelwood has proposed a mechanism for adsorption of gases on 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.

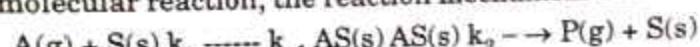
Step 1 and 5 are generally very fast and step 2 and 4 are generally faster than 3. Thus step 3 is the rate determining step in the surface reaction, i.e., chemisorption of the reactants on the surface of the solid adsorbent.

Two features 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



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

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

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

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

and  $[\text{S}]$  can be written as

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

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

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

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

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

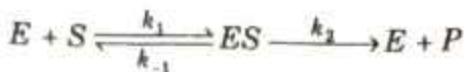
The rate of production of P can be written as

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

**Q.4. (b) Derive the Michaelis-Menten equation for an enzyme catalysed reaction. Discuss the role of inhibitors in catalysis.** (6.5)

**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 Term  $k_1$ ,  $k_{-1}$  and  $k_2$  are rate constants.

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

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. Thus, at steady state we can write:

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

The next couple of steps

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

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

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  $K_M$ .

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

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

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:

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

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

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

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

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

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

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

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

Substituting this 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.

An enzyme inhibitor is a molecule that binds to an enzyme and decreases its activity. Since blocking an enzyme's activity can kill a pathogen or correct a metabolic imbalance, many drugs are enzyme inhibitors. They are also used as pesticides. Not all molecules that bind to enzymes are inhibitors. Inhibitors, increase energy of activation of reaction. In the food-processing industry inhibitors which prevent hydrolysis of fats, reactions of oxidation and fermentation are widely used.

### Types of Inhibition

Reversible and irreversible inhibitors are chemicals which bind to an enzyme to suppress its activity.

One method to accomplish this is to almost permanently bind to an enzyme. These types of inhibitors are called irreversible.

However, other chemicals can transiently bind to an enzyme. These are called reversible. Reversible inhibitors either bind to an active site (competitive inhibitors), or to another site on the enzyme (non-competitive inhibitors).

**Q.5. (a) What are phase diagrams? Draw the cooling curves for the following:**

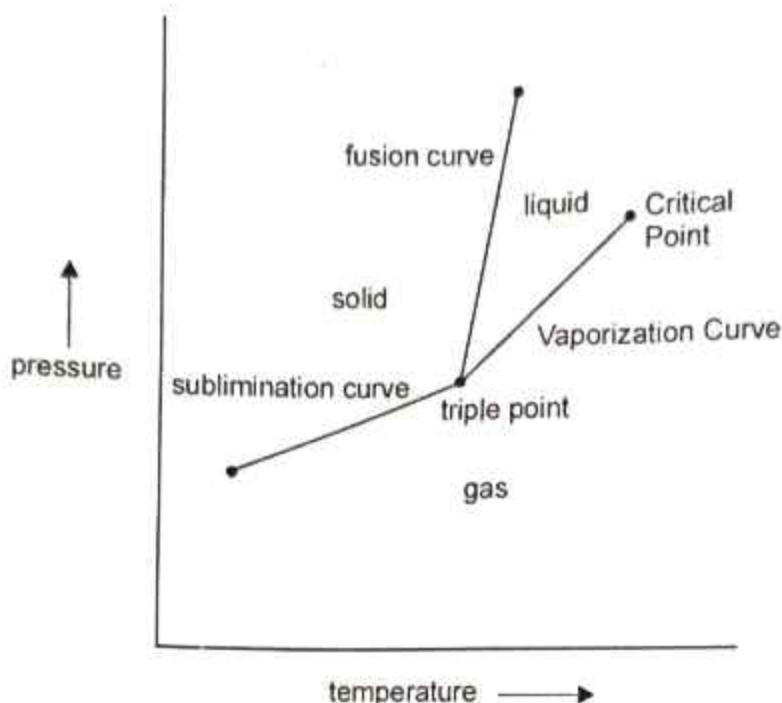
(i) Pure substance in molten state.

(ii) Molten mixture of two solids.

Also, define the eutectic point.

(6.5)

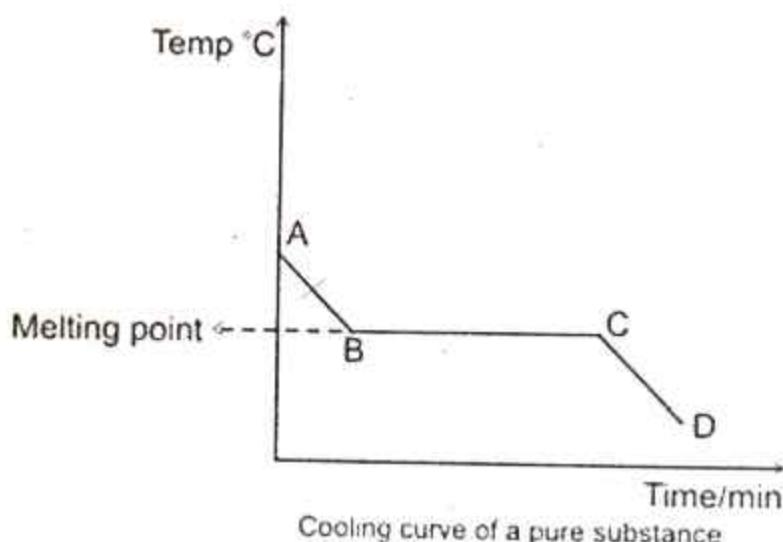
**Ans.** Phase diagram is a graphical representation of the physical states of a substance under different conditions of temperature and pressure. A typical phase diagram has pressure on the y-axis and temperature on the x-axis. In addition, two states of the substance coexist in equilibrium on the lines or curves. The figure shown below displays a typical phase diagram for a one-component system



Phase diagrams are specific for each substance and mixture.

#### **The Cooling Curve of a pure substance**

When a solid substance is heated until it is completely melted, and then heated further and allowed to cool slowly, the curve obtained by plotting temperature against time is known as the cooling curve.



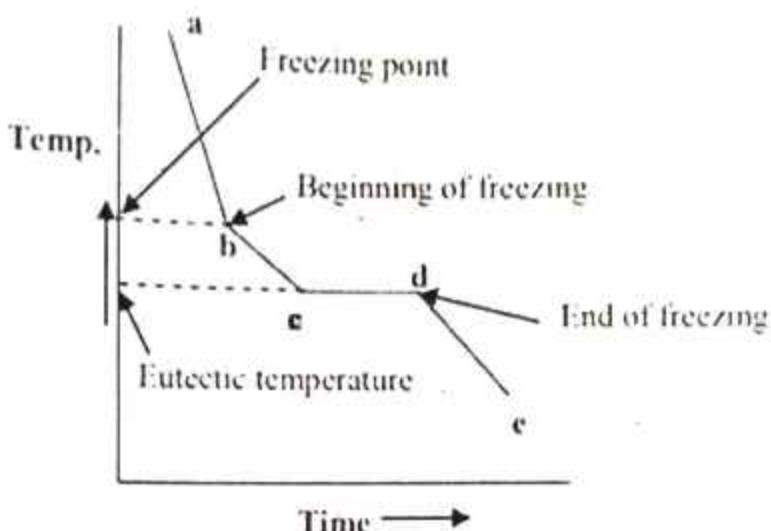
Between A and B, the temperature falls with time - there is no change of state, hence the substance is still in the liquid state.

Between B and C, there is a constant temperature over time. This suggests that there is a change of state going on from liquid to solid. The heat lost between these points is that gained in liquefying the solid substance (latent heat of fusion).

Between C and D, the temperature falls again with time. Here, the substance is totally in the solid state.

**Cooling curve of mixture**

Considering a mixture of two solids A and B is in fused state. Allow to cool slowly. Initially the rate of cooling curve will be continuous (ab), when the crystals of either A or B formed from the liquid melt, which is indicated by break in continuity of the cooling curve. Now the temperature again decreases with time but at a different rate, because solid crystal and liquid melt are not of the same composition. The slope 'bc' of the curve represents a continuous and progressive change in composition of liquid melt.



Finally the liquid melt reaches the point 'c' at which it separates as solid A and solid B. Now the temperature will remain constant until the liquid melt is completely solidified. Point 'c' called eutectic point a minimum freezing point corresponding to eutectic mixture. Thereafter temperature remain constant till solidification up to 'd'.

The minimum freezing point attainable corresponding to the eutectic mixture is known as "**Eutectic Point**" (which means lowest melting point).

This is the point where all the three phases of the solid-liquid system namely, liquid melt of the two metals and the solid phases of each of the components respectively co-exist at equilibrium.

The composition of the components corresponding to the eutectic point has the *lowest melting point*.

The system is *invariant* at this point ( i.e. the degrees of freedom or variance is zero) and also has a definite *temperature* and *composition*.

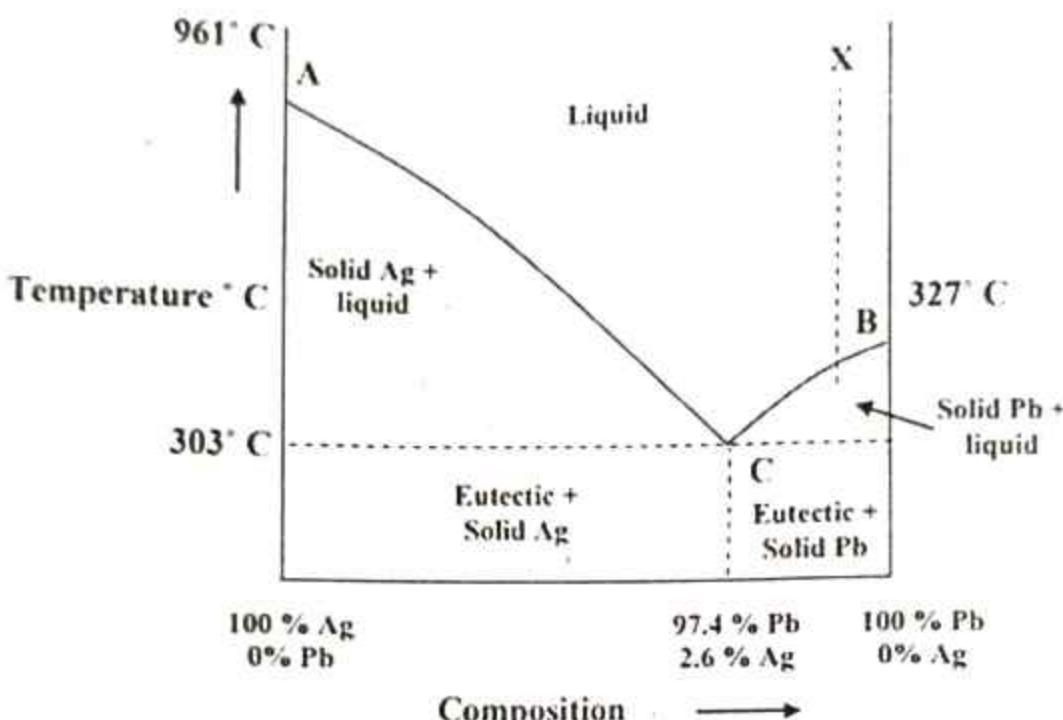
**Q.5. (b) Draw and explain the phase diagram of Pb-Ag system.** (6)

**Ans.** Simple eutectic systems (Pb-Ag system) .

The salient features of the diagram are: (a) Two curves, AC and BC (b) Eutectic point C (c) Three areas (i) above ACB (ii) below AC (iii) below BC

Curve AC (the freezing point curve of Ag.) shows the effect on freezing point of Ag on addition of lead in small quantities. The curve starts A ( $961^{\circ}\text{C}$ ), the melting point of Ag, where pure Ag co-exists as solid and liquid (vapour being neglected). This curve indicates that the melting point of Ag falls gradually on adding Pb, along AC, till the lowest point C ( $303^{\circ}\text{C}$ ) is reached, where the solution gets saturated with respect to lead. At C, no more lead can go in solution and consequently, melting point of Ag does not fall any further; and if any lead is added, it separates as the solid phase. Along this curve, solid

Ag and solution co-exist and hence, according to reduced phase rule equation:  $F = C - P + 1 = 3 - 2 + 1 = 2$ , i.e., the system is univariant. The point C ( $303^{\circ}\text{C}$ ) corresponds to a fixed composition of 2.6% Ag and 97.4% Pb and is known as eutectic composition. On cooling, the whole mass crystallizes out as such. C Composition Temperature  $^{\circ}\text{C}$  Solid Ag + liquid Eutectic + S



Curve BC (freezing point curve of Pb) represents the effect on freezing point of Pb by gradual addition of small amounts of Ag to it. Point B is the melting point of pure lead ( $327^{\circ}\text{C}$ ). Along BC, the melting point gradually falls on the addition of Ag, till lowest point O is reached, where the solution gets saturated with respect to Ag and the melting point of lead does not fall any more. On cooling, the whole mass (having eutectic composition) crystallizes out. The system is monovariant.

**Eutectic point C:** The curve AC and BC intersect at C, which is called the eutectic point. Here three phases solid Ag, solid Pb, and solution are in equilibrium. Applying the reduced phase rule;

$$F = C - P + 1 = 2 - 3 + 1 = 0 \text{ (nonvariant)}$$

Both variables temperature ( $303^{\circ}\text{C}$ ) and composition (97.4 % Pb, 2.6% Ag; eutectic composition) are fixed. If the temperature is raised above the eutectic temperature, the solid phases Ag and Pb disappear. No mixture of lead and silver has a melting point lower than the eutectic temperature. Below the temperature line of eutectic, there are two regions viz., (i) the region marked eutectic + solid Ag, in which crystalline silver and solid eutectic are stable, and (ii) the region marked eutectic + solid Pb, in which crystalline lead and solid eutectic are stable.

**Area ACB:** This region represents the single phase system, the solution of molten Ag and Pb. Applying the reduced phase rule;

$$F = C - P + 1 = 2 - 1 + 1 = 2 \text{ (Bivariant)}$$

Application of reduced phase rule to the above systems: Pattinson's Process for the Desilverisation of Argentiferrous lead:

The argentiferous lead containing small amount of silver is melted well above the melting temperature of pure lead (327°C). Let the point X represent the system 'molten lead' on the diagram. It is then allowed to cool corresponding to Y on the curve BC. As the temperature solution would contain relatively larger amount of silver. On further cooling, more of lead separates along the curve BC until the eutectic point C is reached. Lead is continuously removed by means of ladles and the percentage of silver in the melt goes on increasing. At C, an alloy containing 2.6% Ag and 97.4% Pb is obtained.

### UNIT-III

**Q.6. (a) Discuss the lime-soda process used for removal of calcium and magnesium hardness.** (6.5)

**Ans. 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  $[Ca(OH)_2]$  and soda  $[Na_2CO_3]$ . Precipitates of calcium carbonate  $[CaCO_3]$  and magnesium hydroxide  $[Mg(OH)_2]$  formed are filtered off.

**Function of lime:** lime removes temporary Ca and Mg hardness, permanent Mg, Al, Fe hardness and dissolved  $CO_2$  and  $H_2S$  gases and free mineral acid present in water. Lime does not react with  $CaCl_2$  and  $CaSO_4$ , so it cannot remove calcium permanent hardness.

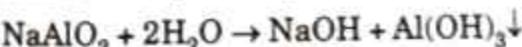
(a) Cold lime soda process: can be carried at room temperature

water + soda + lime + coagulant  $\rightarrow$  insoluble ppt (in the form of sludge settle down & taken out through outlet at the bottom)  $\rightarrow$  softened water and taken out from an outlet provided at the top.

The softened water contains 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, aluminum sulphate, sodium aluminate etc., that hydrolyze to flocculent, gelatinous precipitate of aluminum 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 50-60 ppm.



Sodium aluminate



Coagulant  
(hardness in water)

calcium bicarbonate

**(ii) Hot Lime-soda process:**

The process involves in treating water with softening chemicals at a temperature of 94-100°, 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 15-30 ppm.

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) "Sand filter" that ensures complete removal of sludge from the softened water.

**Q.6. (b) Calculate the amount of lime required for softening of 6000 L of hard water containing 90 ppm of  $MgSO_4$ .** (6)

$$\begin{aligned} \text{Ans. CaCO}_3 \text{ equivalent of } MgSO_4 &= \frac{100}{120} \times 90 \\ &= 75 \text{ PPM} \end{aligned}$$

Lime required

$$\begin{aligned} &= \frac{74}{100} \times 75 \times 600 = 7830 \text{ g} \\ &= 7.83 \text{ kg.} \end{aligned}$$

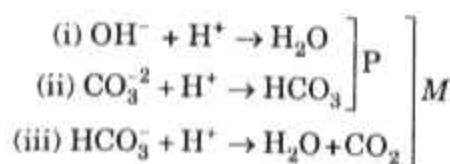
**Q.7. (a) What is alkalinity of water and explain a method for its determination using methyl orange and phenolphthalein indicators.** (6.5)

**Ans.** Alkalinity of water may be defined as its capacity to neutralise acids.

The alkalinity of water may be due to the presence of:

- (i)  $OH^-$  ions
- (ii)  $CO_3^{2-}$  ions
- (iii)  $HCO_3^-$  ions

When these ions react with acids following reactions occur:



The alkalinity of water sample with phenolphthalein and potentiometer and potentiometer with methyl orange and methyl orange and potentiometer. While the titration of water sample (i), (ii) and (iii).

So,

$$P = \text{N}_1 V_1 + \text{N}_2 V_2$$

$$M = \text{N}_1 V_1 + \text{N}_2 V_2 + \text{HCO}_3^-$$

The alkalinity of water may be due to the presence of

(i)  $\text{OH}^-$  only

(ii)  $\text{CO}_3^{2-}$  only

(iii)  $\text{HCO}_3^-$  only

In the same solution add 2 drops of Methyl orange. The colour becomes yellow. Increase it with N/50  $\text{H}_2\text{SO}_4$ , till it becomes pink in colour. Let the total volume is 2 ml.

Phenolphthalein Alkalinity is P

Water vs Acid

$$\text{N}_1 V_1 = \text{N}_2 V_2$$

$$\text{N}_1 \times 10 = \text{N}/50 \times A$$

$$\text{N}_1 = \text{N}/50 \times A/10$$

Phenolphthalein alkalinity (P) =  $A/500 \times 50 \times 1000$  ppm

Methyl Orange Alkalinity (M)

Water vs Acid

$$\text{N}_1 V_1 = \text{N}_2 V_2$$

$$\text{N}_1 \times 10 = \text{N}/50 \times B$$

$$\text{N}_1 = \text{N}/50 \times B/10$$

Methyl Orange alkalinity (M) =  $B/500 \times 50 \times 1000$  ppm

#### Nature of alkalinity

Alkalinity	$\text{OH}^-$ group	$\text{CO}_3^{2-}$ group	$\text{HCO}_3^-$
P = 0	0	0	M
P = M	P	0	0
P = $\frac{1}{2} M$	0	2P	0
P > $\frac{1}{2} M$	$2P - M$	$2(M - P)$	0
P < $\frac{1}{2} M$	0	2P	$M - 2P$

**Q.7. (b) 100 ml of a sample required 10 ml of  $\frac{N}{50}$  HCl using methyl orange as indicator. Another 100 ml of sample required 4 ml of  $\frac{N}{50}$  HCl using phenolphthalein as indicator. Express the alkalinites in terms of mg of  $\text{CaCO}_3$  per litre.** (6)

**Ans.** Phenolphthalein alkalinity

100 ml of sample water required 10 ml of  $\frac{N}{50}$  HCL

$$N_1 V_1 = N_2 V_2$$

$$N_1 \times 100 = \frac{1}{50} \times 10$$

$$N_1 = \frac{1}{50} \times \frac{10}{100} = \frac{1}{500}$$

$$\text{Strength (P)} = N_1 \times 50 \times 1000$$

$$= \frac{1}{500} \times 50 \times 1000 = 100 \text{ mg/L}$$

### Methyl Orange alkalinity

100 ml of sample require 4 ml of  $\frac{N}{50}$  HCL using methyl orange indicator.

$$N_1 V_1 = N_2 V_2$$

$$N_1 \times 100 = \frac{1}{50} \times 4$$

$$N_1 = \frac{1}{50} \times \frac{4}{100}$$

$$\text{Strength (M)} = N_1 \times 50 \times 1000$$

$$= \frac{1}{50} \times \frac{4}{100} \times 50 \times 1000 = 400 \text{ mg/L}$$

$$\text{Since } P < \frac{1}{2} M \quad 100 < \frac{1}{2} \times 400$$

$$100 < 200$$

Alkalinity is due to presence of  $\text{CO}_3^{2-} + \text{HCO}_3^-$

Alkalinity due to  $\text{CO}_3^{2-} = 2P = 2 \times 100 = 200 \text{ PPM}$

Alkalinity due to  $\text{HCO}_3^- = (M - 2P) = (400 - 2 \times 100) = 200 \text{ PPM}$

## UNIT-IV

**Q.8. (a) What are factors influencing corrosion?** (6.5)

**Ans.** 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 diff in position of two metals in galvanic series- higher is rate of corrosion of more active metal.

**2. Overvoltage :** "The diff 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  $\text{H}_2\text{SO}_4$ , the rate of rxn is slow due to high overvoltage.

**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.

**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.

**(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  $\text{CO}_2$ ,  $\text{H}_2\text{S}$ , fumes of  $\text{HCl}$ ,  $\text{H}_2\text{SO}_4$  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  $\text{H}_2\text{S}$ ,  $\text{SO}_2$  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) Define the following terms:

(6)

#### (i) Cathodic Protection

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  $\text{O}_2$  to  $\text{OH}^-$



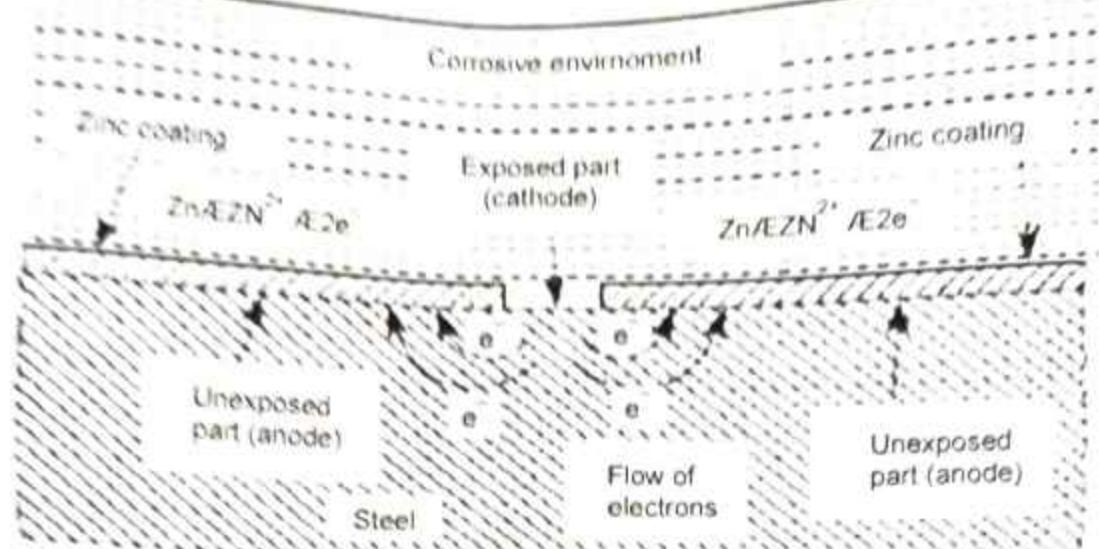
#### 2. Impressed current cathodic protection:

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

### Q.8. (b) (ii) Galvanization

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 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.



**Q.8. (iii) Sherardizing:** Sherardizing is a process of galvanization of ferrous metal surfaces, also called vapor galvanizing and dry galvanizing. Sherardizing is the formation of a corrosion-resistant, zinc-iron alloy coating, on the surface of steel or iron. The method involves the heating of the object in an airtight container that has zinc powder. A thermal diffusion process occurs and the zinc diffuses into the object's metal surface, forming the zinc-iron alloy. The external layer of the zinc-iron alloy formed is a pure zinc adherent coating with a smooth surface and uniform thickness. It provides a very strong and long-term protection against corrosion and abrasion.

The Sherardizing process involves diffusing of the zinc into the base metal of the object, which is mainly iron. The temperature of the container is controlled such that the melting point of zinc is not reached and this ranges between 608-932°F (320-500°C).

#### Other advantages include:

- Use of low temperatures for the process
- Suitable for irregularly shaped objects
- Suitable for recessed objects
- No hydrogen embrittlement
- Suitable for sintered material since it is a dry process

**Q. 9. (a) Discuss the mechanism of the following:** (6)

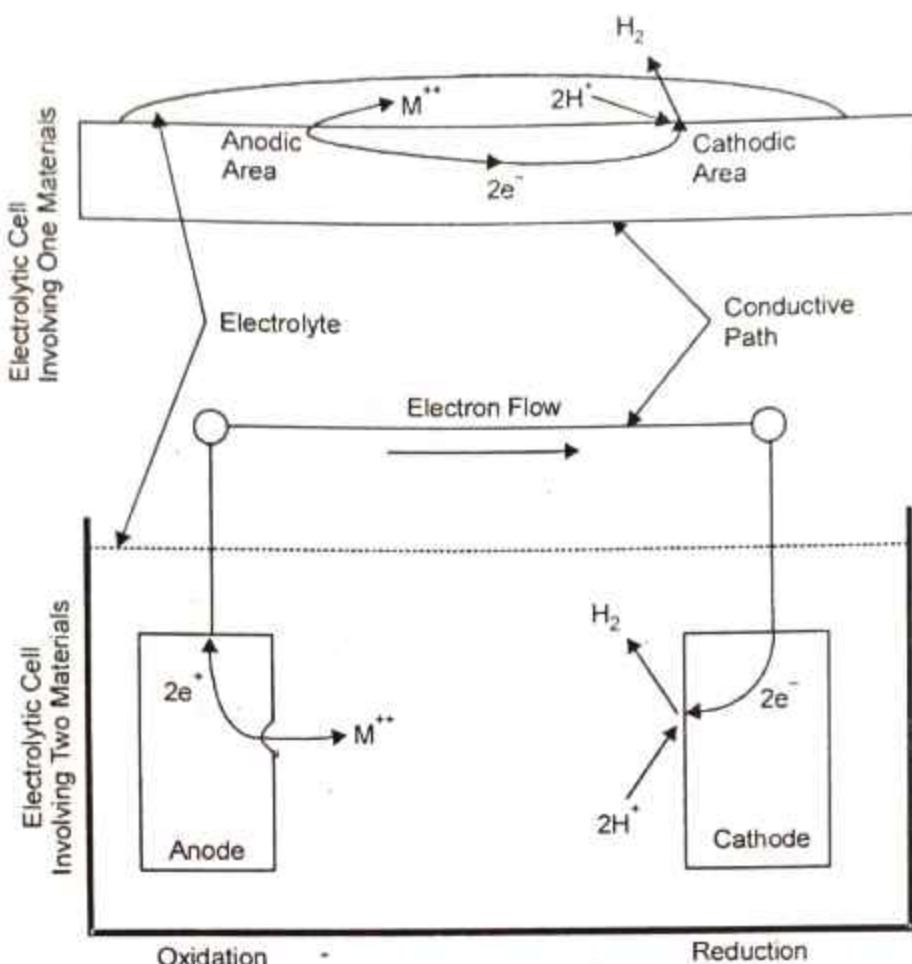
#### Q.9. (a) (i) Oxidation Corrosion

#### CORROSION BY OXYGEN or OXIDATION CORROSION:

Oxidation Corrosion is brought about by the direct attack of oxygen at low or high temperature on metal surfaces in the absence of moisture. Alkali metals (Li, Na, K etc.) and alkaline earth metals (Mg, Ca, Sn, etc.,) are rapidly oxidized at low temperature. At high temperature, almost all metals (except Ag, Au and Pt) are oxidized.

**The reactions of oxidation corrosion are as follows:** Mechanism: 1) Oxidation takes place at the surface of the metal forming metal ions  $M_{2+} + M \rightarrow M_{2+} + 2e_2$  Oxygen is converted to oxide ion ( $O_2^-$ ) due to the transfer of electrons from metal.  $n/2 O_2 + 2n e^- \rightarrow n O_2^-$  3) The overall reaction is of oxide ion reacts with the metal ions to form metal

oxide film.  $2M + n/2 O_2 \rightarrow 2Mn^+ + nO_2^-$ . The Nature of the Oxide formed plays an important part in oxidation corrosion process. Metal + Oxygen  $\rightarrow$  Metal oxide (corrosion product). When oxidation starts, a thin layer of oxide is formed on the metal surface and the nature of this film decides the further action. If the film is



**(i) Stable layer:** A Stable layer is fine grained in structure and can get adhered tightly to the parent metal surface. Hence, such layer can be of impervious nature (i.e., which cuts-off penetration of attaching oxygen to the underlying metal). Such a film behaves as protective coating in nature, thereby shielding the metal surface. The oxide films on Al, Sn, Pb, Cu, Pt, etc., are stable, tightly adhering and impervious in nature.

**(ii) Unstable oxide layer:** This is formed on the surface of noble metals such as Ag, Au, Pt. As the metallic state is more stable than oxide, it decomposes back into the metal and oxygen. Hence, oxidation corrosion is not possible with noble metals.

**(iii) Volatile oxide layer:** The oxide layer film volatilizes as soon as it is formed. Hence, always a fresh metal surface is available for further attack. This causes continuous corrosion.  $M_2O_3$  is volatile in nature.

**(iv) Porous layer:** The layer having pores or cracks. In such a case, the atmospheric oxygen have access to the underlying surface of metal, through the pores or cracks of the layer, thereby the corrosion continues unobstructed, till the entire metal is completely converted into its oxide.

**Q.9. (a) (ii) Electrochemical or wet corrosion**

**Ans.** Refer Q. 9. (a) of End Term 2016.

**Q.9. (b) Discuss in detail the protective measures used against corrosion.** (6.5)

**Ans. CORROSION CONTROL (PROTECTION AGAINST CORROSION)**

**1. Choice of metals and alloys:**

- The first choice is to use noble metals such as gold and platinum.

- The next choice is to use purest possible metal.

**2. Proper Designing:**

- (a) Use always simple design and structure

(b) The design must avoid more complicated shapes having more angles, edges, corners etc.

- (c) Avoid the contact of dissimilar metals as they may lead to galvanic type corrosion.

**3. CATHODIC PROTECTION:** The reduction or prevention of corrosion by making metallic structure as cathode in the electrolytic cell is called cathodic protection. There are two methods of applying cathodic protection to metallic structures.

- (a) Sacrificial anodic protection (galvanic protection)

- (b) Impressed current cathodic protection

**4. IMPRESSED CURRENT CATHODIC PROTECTION METHOD:** In this method, an impressed current is applied in opposite direction to nullify the corrosion current and convert the corroding metal from anode to cathode.

**5. MODIFYING THE ENVIRONMENT-CORROSION CONTROL:**

Environment plays a major role in the corrosion of metals. Some of the methods are

- Deaeration

- By using inhibitors

**6. ANODIC PROTECTION** This is an electrochemical method of corrosion control in which an external potential control system, called potentiostat, is used to produce and maintain a thin non corroding, passive film on a metal or an alloy. The use of potentiostat is to shift corrosion potential into passive potential so that the corrosion of the metal is stopped.

**7. PROTECTIVE COATINGS**

In order to protect metals from corrosion, it is necessary to cover the surface by means of protective coatings. These coatings act as a physical barrier between the coated metal surface and the environment.

**Classification:** Protective coatings can be broadly classified into two types.

They are 1. Inorganic coatings 2) Organic coatings Inorganic coatings are further classified into two types. They are

**(i) Metallic coating:**

1. Hot dipping- Galvanising, Tinning

2. Metal cladding

3. Cementation-Sherardising, Chromising, Calorising
4. Electroplating

**31 (ii) Non-metallic coating:**

1. Surface coating or chemical conversion coating – Chromate coating, Phosphate coating and Oxide coating.
2. Anodising
3. Enamel coating or Vitreous or Porcelain coating.

Organic coatings consists of Paints, Varnishes, Lacquers and Enamels.

**FIRST TERM EXAMINATION [SEP. 2018]**  
**FIRST SEMESTER [B.TECH]**  
**APPLIED CHEMISTRY [ETCH-113]**

Time : 1½ hrs.

M.M. : 30

Note: Q. 1. is compulsory. Attempt any two questions from the rest.

**Q.1. (a) Define calorific value of a fuel and explain the condition when GCV = NCV.** (2)

**Ans.** It is a amount of energy released when unit amount of fuel burnt in presence of oxygen and product of combustion released to atmosphere.

The device used to measure the measure calorific value is called calorimeter.

There are two calorimeter to measure calorific value depending upon type of fuel.

If fuel is solid or liquid then bomb calorimeter is used

and if fuel is gaseous then use boy's gas calorimeter

If the fuel does not contain hydrogen (e.g. pure carbon, sulphur etc.), then  $GCV = NCV$  (2)

**Q.1. (b) Explain Dulong's Formula.**

**Ans.** The right formula is as following:

$$H.C.V = \frac{1}{100}[8080 \times C + 34500(\text{H-O}/8) + 2240 * S]$$

If the fuel contains oxygen, then it is assumed that the whole amount is combined with hydrogen having mass equal to 1/8th of that of oxygen. Therefore, while finding the Calorific value of the fuel, this amount of hydrogen should be subtracted.

$$LCV = [HCV - 0.09H^*587]$$

(2)

**Q.1. (c) Why catalytic cracking is better than thermal cracking?** (2)

**Ans.** Advantage of catalytic cracking over thermal cracking

(1) The yield of petrol is high because catalyst are selective in nature

(2) The quality of petrol is better

(3) No external fuel is required for cracking

(4) A much lower pressure is needed in catalytic cracking

(5) The cracking process can be easily controlled, so the desired product can be obtained

(6) The percentage of gum forming compound is very low.

**Q.1. (d) Explain the various terms in Gibb's Phase Rule with suitable examples.** (2)

**Ans. PHASE** may be defined as any particular 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  $H_2O$  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  $H_2O$  and only one chemical parameter or component is required to describe the composition of each phase.

**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. 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.

$$F = C - P + 2$$

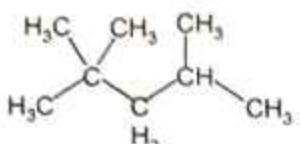
Where  $F$  is the number of degrees of freedom,  $C$  is the number of chemical components and  $P$  is the number of phases in the system. The number two is specified because this formulation assumes that both  $T$  and  $P$  can be varied.

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

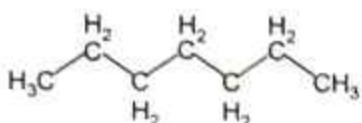
**Q.1. (e) What do you mean by Octane Number? Explain its significance.**

(2)

**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.



iso octane (octane no =100)



n-heptane (octane no =0) significance

Higher the octane number, better the quality of petrol, and hence the vehicle gives higher efficiency.

**Q.2. (a) How calorific value of a solid fuel can be determined by Bomb's calorimeter? Explain with the help of neat and labeled diagram.**

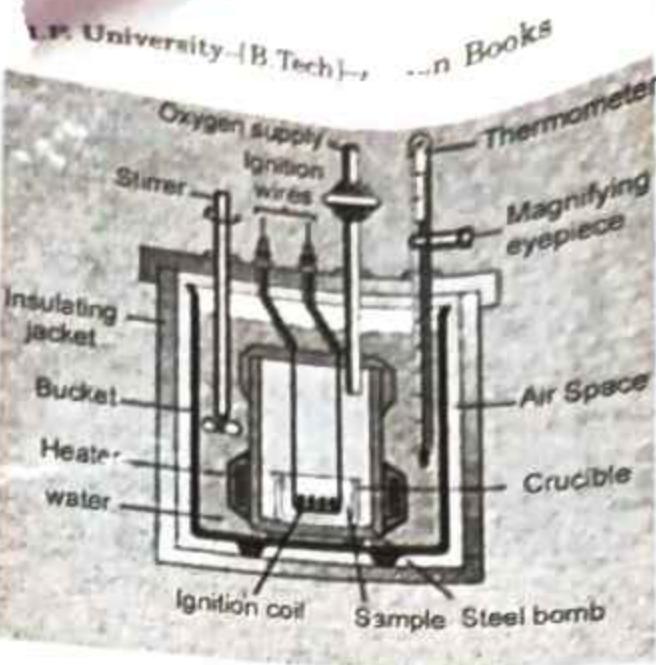
(6)

**Ans.** The calorific value of solid or liquid fuels can be determined with the help of bomb calorimeter.

**Description:**

Bomb Calorimeter consists of a strong stainless steel bomb where the fuel sample is burnt. The bomb has oxygen inlet valve and two stainless steel electrodes. A small ring is attached to one of the electrodes. In this ring, a nickel or stainless steel crucible is placed.

The bomb is placed in a copper calorimeter containing a known weight of water sample. The copper calorimeter is provided with a Beckmann's thermometer and stirrer for stirring water. The copper calorimeter is covered by an air jacket and water jacket.



### Functioning:

A known weight of the fuel sample is taken into the crucible. The fine magnesium wire is touching the fuel sample and then stretched across the electrodes. The bomb lid is tightly closed with the help of screw. The bomb is filled with oxygen at 25 atmospheric pressure. The bomb is now placed in a copper calorimeter which containing known weight of water. Initial temperature of the water in the calorimeter is noted ( $t_1$  °C) after stirring. The electrodes are connected to a battery (6 v). The current is now supplied to the fuel sample which undergoes burning with the evolution of heat. The liberated heat increases the temperature of water in the calorimeter. The maximum temperature of the water during experiment is finally noted ( $t_2$  °C). From the temperature difference, calorific value of the fuel can be calculated as follows:

### Calculation:

Weight of the fuel sample taken in the crucible =  $x$  g

Weight of water taken in the calorimeter =  $W$  g

Weight of calorimeter and stirrer in terms of water Equivalent =  $A$  g

Initial temperature of water in the calorimeter =  $t_1$  °C

Final temperature of water in the calorimeter =  $t_2$  °C

Heat absorbed by the water =  $W(t_2 - t_1)$  cal ... (1)

Heat absorbed by the calorimeter =  $A(t_2 - t_1)$  cal ... (2)

Total heat absorbed by the water =  $W(t_2 - t_1) + A(t_2 - t_1)$  cal =  $(W+A)(t_2 - t_1)$  cal ... (3)

The relationship between heat liberated by the fuel and HCV is as follows:

Heat liberated by the fuel =  $x \times (\text{HCV})$  ... (4)

Therefore, heat liberated by the fuel = Heat absorbed by the water and calorimeter

Weight of fuel =  $X$

Compare equation (3) and (4), we get

$$x \times (\text{HCV}) = (W+A)(t_2 - t_1)$$

$$\text{HCV} = (W+A)(t_2 - t_1) / x \text{ cal/g}$$

**Calculation of Lower Calorific Value (LCV):**

The percentage of hydrogen in the fuel = H

Weight of water produced 1 g of the fuel =  $9 \text{ H}/100 \text{ g} = 0.09 \text{ g}$

Therefore, heat liberated during the Condensation of steam =  $0.09 \text{ H} \times 587 \text{ cal/g}$

Lower calorific value of the fuel = HCV – Latent heat of water liberated by the fuel.

LCV = HCV – ( $0.09 \text{ H} \times 587$ ) cal/g.

**Q.2. (b) 1.0 g of a sample of coal was used for nitrogen estimation by Kjeldahl's method. The evolved ammonia was collected in 25 ml (N/10)  $\text{H}_2\text{SO}_4$ . To neutralize excess acid 15 ml of 0.1 N NaOH was required. Determine the percentage of nitrogen in the given sample. (4)**

**Ans.** 15 ml of 0.1 N NaOH = 15 ml of 0.1 N  $\text{H}_2\text{SO}_4$

Vol. of  $\text{H}_2\text{SO}_4$  used to neutralize  $\text{NH}_3$  evolved = 25 ml of 0.1  $\text{H}_2\text{SO}_4$  – 15 ml of 0.1  $\text{H}_2\text{SO}_4$

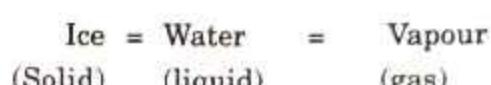
$$= 10 \text{ ml of } 0.1 \text{ N } \text{H}_2\text{SO}_4$$

$$\% \text{ of N} = \frac{\text{Volume of } \text{H}_2\text{SO}_4 \times \text{N} \times 1.4}{\text{Weight of coal sample}}$$

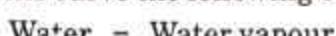
$$= \frac{10 \times 0.1 \times 1.4}{1.0} = 1.4\%$$

**Q.3. (a) Draw and discuss the phase diagram of water system in detail. (6)**

**Ans.** The water system is a one component system

**(1) Curve OA**

The curve OA is called vapourisation curve, it represents the equilibrium between water and vapour. At any point on the curve the following equilibrium will exist.



The degree of freedom of the system is one, i.e., univariant. Thus applying phase rule equation,

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

**(2) Curve OB**

The curve OB is called sublimation curve of ice, it represents the equilibrium between ice and vapour. At any point on the curve the following equilibrium will exist.

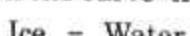


The degree of freedom of the system is one, i.e., univariant. This is predicted by the phase rule.

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

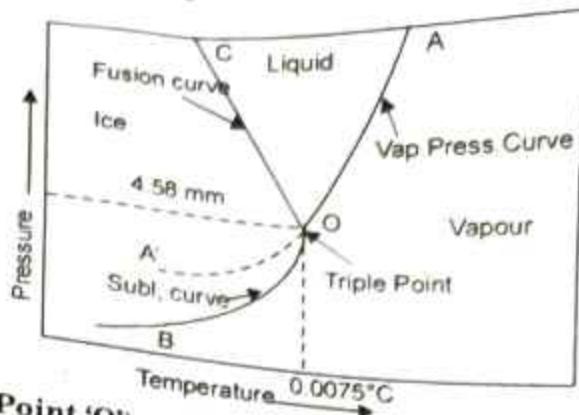
**(3) Curve OC**

The curve OC is called melting point curve of ice, it represents the equilibrium between ice and water. At any point on the curve the following equilibrium will exist.



The curve OC is slightly inclined towards pressure axis. This shows that melting point of ice decreases with increase of pressure.

The degree of freedom of the system is one, i.e., univariant.



#### (4) Triple point (Point 'O')

At triple point all the three phases namely ice, water and vapour coexist. Thus the value of  $P$  is 3. Applying phase rule equation, the degree of freedom at this point is zero. It means that three phases can coexist in equilibrium only at a definite temperature and pressure. The values are  $0.0075^{\circ}\text{C}$  and  $4.58 \text{ mm}$  respectively.

#### (5) Curve OA' (Metastable equilibrium)

The curve OA' is called vapour pressure curve of the super-cool water or metastable equilibrium.

Where the following equilibrium will exist.

Super-cool water = Vapour

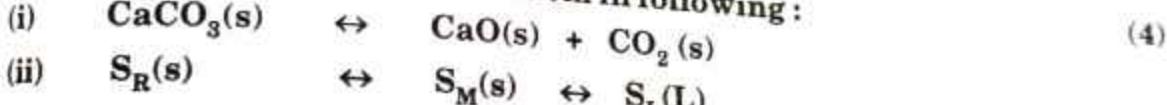
Sometimes water can be cooled below  $0^{\circ}\text{C}$  without the formation of ice, this water is called super-cooled water.

#### (6) Areas

Area AOC, BOC, AOB represents water ice and vapour respectively. In order to define the system at any point in the areas, it is essential to specify both temperature and pressure. The degree of freedom of the system is two. i.e., Bivariant. This is predicted by the phase rule

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

#### Q.3. (b) Calculate degree of freedom in following :



Ans. (i)  $\text{CaCO}_3(\text{s}) \leftrightarrow \text{CaO}(\text{s}) + \text{CO}_2(\text{s})$

Phase-P = 3

Component C = 2

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

univariant



Phase (P) = 3

Component (C) = 1

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

**Q. 4. (a) What are the requisites of Metallurgical Coke?**

(2)

**Ans. Requisite of metallurgical coke**

1. It should have low moisture, ash, sulphur and phosphorus content.
2. The coke should be porous to provide contact between carbon and oxygen.
3. The coke used should have high strength so as to withstand the weight of the ore.
4. Metallurgical coke should be of medium size — neither too big nor too small.
5. The calorific value should be high.
6. The reactivity should not be very high.
7. Coke should be cheap and easily available.

**Q. 4. (b) A coal sample contains C = 80%, H<sub>2</sub> = 4%, O<sub>2</sub> = 6%, N<sub>2</sub> = 2% and ash = 28%. Calculate the minimum weight of air required for the complete combustion of 1 kg of coal.**

(5)

**Ans.** 1 kg of coal contain

$$C = \frac{80}{100} \times 1000 = 800 \text{ g}$$

$$H_2 = \frac{4}{100} \times 1000 = 40 \text{ g}$$

$$O_2 = \frac{6}{100} \times 1000 = 60 \text{ g}$$

Minimum weight of air required for complete combustion of 1 kg of coal = Weight of

$$\left[ C \times \frac{32}{12} + \left( H_2 \times \frac{16}{2} \right) - O_2 \right] \times \frac{100}{23}$$

$$= \left[ \left( 800 \times \frac{32}{12} \right) + \left( 40 \times \frac{16}{2} \right) - 60 \right] \times \frac{100}{23}$$

$$= [1600 - 32 - 60] \times \frac{100}{23}$$

$$= 6834.75 \text{ g} = 6.834 \text{ kg}$$

**Q. 4. (c) What are the applications of phase rule?**

(2)

**Ans. APPLICATIONS OF GIBBS PHASE RULE:**

This equation gives the phase rule given by Willard Gibbs, the fundamental relation controlling the equilibria in heterogeneous systems.

**Advantages of phase rule:**

- (a) It gives a simple method of classifying equilibrium states of systems.
- (b) It confirms that the different systems having the same number of degrees of freedom behave in like manner.
- (c) It predicts the behavior of systems when subjected to changes in the variables such as pressure, temperature and volume.
- (d) The phase rule is applicable to macroscopic systems. Therefore, it is not necessary to take into account about their molecular structures.
- (e) It is applicable to physical as well as chemical reactions.

# **END TERM EXAMINATION [NOV. DEC. 2018]**

## **FIRST SEMESTER [B.TECH]**

### **APPLIED CHEMISTRY [ETCH-113]**

**Time : 3 hrs.**

**M.M. : 75**

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

**Q.1. (a) What is a fuel? State the features of a good fuel. (5)**

**Ans.** A fuel is a substance which gives heat energy on combustion. A fuel contains carbon and hydrogen as main combustible elements. This energy that releases is generally in the form of chemical energy or heat energy.

#### **Types of Fuel**

- Solid Fuel
- Liquid Fuel
- Fuel Gas
- Biofuel
- Fossil Fuel

#### **Characteristics Of A Good Fuel**

1. The fuel selected must be suitable for the purpose.
2. The fuel should have high calorific value.
3. The fuel should be cheap and readily available.
4. It should possess a moderate ignition temperature. Too high temperature causes difficulty in kindling while too low ignition temperatures may cause safety problems during storage, transport and usage.
5. The supply position of the fuel must be reliable.
6. The velocity of combustion should be moderate.
7. The fuel should have reasonable flexibility and control.
8. The fuel should be such that safe and clean operation is ensured. Too much smoke and obnoxious odors are not desirable.
9. It should be safe, convenient and economical for storage and transport.
10. It should have low moisture content.
11. In case of solid fuel, the ash content should be less and the size should be uniform.

**Q.1. (b) Draw the phase diagram of water. Explain the terms-critical point and triple point. (5)**

**Ans.** Refer Q. 3. (a) of First Term Examination 2018.

**Q.1.(c) What is a catalyst? Describe its characteristics features. (5)**

**Ans.** Catalyst, in chemistry, any substance that increases the rate of a reaction without itself being consumed. Enzymes are naturally occurring catalysts responsible for many essential biochemical reactions. Most solid catalysts are metals or the oxides, sulfides, and halides of metallic elements and of the semimetallic elements boron, aluminum, and silicon. Gaseous and liquid catalysts are commonly used in their pure form or in combination with suitable carriers or solvents; solid catalysts are commonly

dispersed in other substances known as catalyst supports. In general, chemical reactions occur faster in the presence of a catalyst because the catalyst provides an alternative reaction pathway with a lower activation energy than the non-catalyzed mechanism.

### **Characteristics of Catalysis**

The following are the characteristics which are common to most of catalytic reactions.

(1) A catalyst remains unchanged in mass and chemical composition at the end of the reaction.

(2) A small quantity of the catalyst is generally sufficient to catalyse almost unlimited reactions.

In Friedel craft's reaction, anhydrous aluminium chloride is required in relatively large amount to the extent of 30% of the mass of benzene,



(3) **The catalyst can not initiate the reaction:** The function of the catalyst is to alter the speed of the reaction rather than to start it.

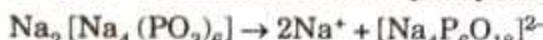
(4) **The catalyst is generally specific in nature:** A substance, which acts as a catalyst for a particular reaction, fails to catalyse the other reaction, different catalysts for the same reactant may form different products.

**Q.1. (d) Describe what is water softening by internal treatment. (5)**

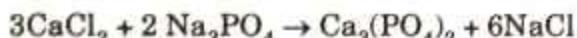
**Ans.** Suitable chemicals are added to the boiler water either to precipitate or to convert the scale into compounds is called internal treatment of the boiler feed water. Internal treatment can be done following types.

**1. Calgon conditioning:** Involves in adding calgon to boiler water. It prevents the scale and sludge formation by forming soluble complex compound with  $\text{CaSO}_4$ .

Calgon = Sodium hexa meta phosphate =  $\text{Na}_2[\text{Na}_4(\text{PO}_3)_6]$



**2. Phosphate conditioning:** The addition of sodium phosphate in hard water reacts with the hardness causing agents and gives calcium and magnesium phosphates which are soft and non-adhere and can be removed easily by blow-down operation.



Generally three types of Phosphates are employed.

(i) Tri sodium Phosphate ( $\text{Na}_3\text{PO}_4$ ): is too alkaline used for treat to too acidic water.

(ii) Di sodium Phosphate ( $\text{Na}_2\text{HPO}_4$ ): is weakly alkaline used for treat to weakly acidic water.

(iii) Sodium dihydrogen Phosphate ( $\text{Na H}_2\text{PO}_4$ ): is too acidic used for treat to too alkaline water.

**3. Colloidal conditioning:** The addition of organic substances such as Kerosene, tannin, Gel. These substances gets coated over the scale forming precipitates and gives a loose and non-sticky precipitates which can be removed by using blow-down operation.

**Q.1.(e) Discuss in detail the factors influencing corrosion. (5)**

**Ans.** 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 diff in position of two metals in galvanic series- higher is rate of corrosion of more active metal.

2. Overtension : 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 reaction is slow due to high overvoltage( 0.70 V) inspite of high activity of Zn. On addition of  $CuSO_4$ , 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 & 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, & Zn corroded.

5. Physical state of the metal : Grain size-The rate of corrosion increases with a decreases in grain size.. 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 then 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. 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.

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.

## UNIT-II

**Q.2.(a) What's cracking? Differentiate between thermal and catalytic cracking.** (6.5)

**Ans. Cracking** is the process whereby complex organic molecules such as kerosens or long-chain hydrocarbons are broken down into simpler molecules such as light hydrocarbons. The rate of cracking and the end products are strongly dependent on the temperature and presence of catalysts. Cracking is the breakdown of a large alkane into smaller, more useful alkenes.



The process for cracking is again divided in to Thermal cracking and Catalytic cracking.

No	Thermal cracking	Catalytic cracking
1.	No catalyst is used	Zeolite bauxite or bentonite can be used as a catalyst
2.	Higher temperature and pressure is used Liquid phase, T = 420 – 5500 C, P = 15 – 100 kg / cm <sup>2</sup> , Vapour phase, T = 600 – 6500, P = 15 – 20 kg/cm <sup>2</sup>	Comparatively lower temperature and pressure is used Fixed bed, T = 425 – 5400 C, P = 1.5 kg/cm <sup>2</sup> , Moving bed, T = 550 – 5700 C, P = 1 kg/cm <sup>2</sup>
3.	Yield of gasoline is 50-60 %	Yield of gasoline is more than 70 %
4.	Octane rating is 70	Octane rating is 80-85
5.	Cracked vapours contains lesser percentage of aromatic iso paraffins and less of gum forming diolifines	Cracked vapours contains greater percentage of aromatic iso paraffins and less of gum forming diolifines
6.	Time required is comparatively more	Time required is comparatively less

**Q.2.(b) Explain knocking and anti knocking agents. What is cetane and octane number of a fuel?** (6)

**Ans. Knocking** is defined as ,A sharp metallic sound similar to rattling of hammer, which is produced in the internal combustion engine due to immature ignition of the air gasoline mixture. Knocking causes loss of energy & damage to piston & cylinder. The knocking tendency of fuel increases with the composition. It is observed that the straight chain saturated hydrocarbons have more knocking tendency than unsaturated hydrocarbons. The cyclic compounds have less tendency to knock than the straight chain compounds.

**Antiknock agents** are the chemical compounds added in small quantities to motor fuels to improve the antiknock ratings of the fuel.

Usually it is added to gasoline to raise its octane value. Higher octane value means gasoline will ignite at higher temperature and pressure. It helps the fuel to ignite at correct time reducing pre- detonation which can be harmful for the engines.

The octane number of gasoline increases in the order :-

Paraffin → Clefins → naphthene → Iso-paraffin → aromatics.

Some of the antiknock agents used are –

### 1. Tetraethyl Lead And Tetra methyl Lead (TEL/TML):

The addition of TEL/TML to gasoline is called doping. Since TEL is extremely poisonous, hence gasoline containing TEL is always coloured for identification and safety.

### 2. Benzole:

A typical composition of benzole is: Benzene = 75%, Toluene = 15% and Xylene = 10%

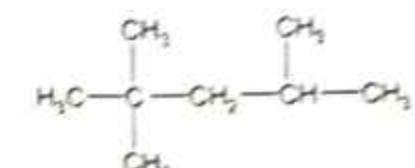
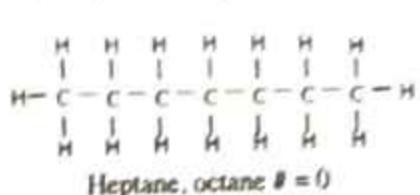
### 3. Methyl Tertiary Butyl Ether: (MTBE)

MTBE is the most adaptable octane enhancing oxygenate available for blending with unleaded gasoline. But is not widely accepted because of environmental concerns

#### Octane no.

The Octane Number of a gasoline is defined as the volume percent of iso-octane (2,2,4-trimethylpentane, an isomer of octane) in a blend of iso-octane and n-heptane. An 87-octane gasoline, for example, has the same octane rating as a mixture of 87 vol-% iso-octane and 13 vol-% n-heptane. Iso-octane is given a maximum octane number, i.e. 100

- N-heptane is given a minimum octane number, i.e. 0.

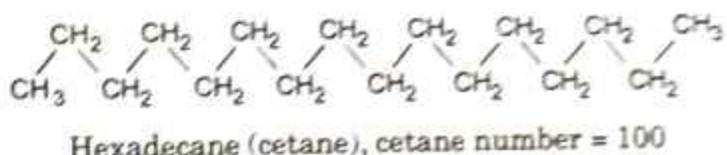


ISO-octane (2,2,4-trimethylpentane)  
octane number assumed to be 100

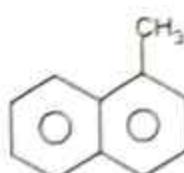
#### Cetane no.

The cetane number of a fuel is defined as the volume percent of n-hexadecane in a blend of n-hexadecane and 1-methylnaphthalene that gives the same ignition delay period as the test sample. For example, a fuel with a cetane number of 40 will perform the same in the engine as a blend of 40% n-hexadecane and 60% 1-methylnaphthalene. N-hexadecane is given a maximum octane number, i.e. 100. 1-methylnaphthalene is given a minimum octane number, i.e. 0.

#### n-Hexadecane



#### 1-Methylnaphthalene



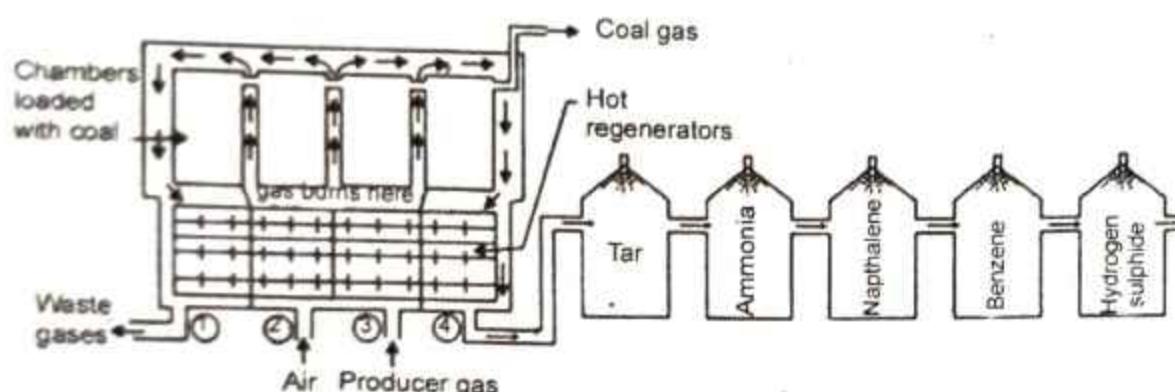
1-Methylnaphthalene, cetane number = 0

**Q. 3. (a) Draw a Labelled diagram and explain the working of Otto-Hoffmann's by-product oven for the manufacturing of metallurgical coke. (6.5)**

**Ans. Manufacture of Metallurgical coke by Otto Hoffmann's method:**

In order to (i) save the fuel for heating purpose and (ii) recover valuable by-products like coal gas, ammonia, benzol oil, tar etc.

Otto Hoffmann developed a modern by-product coke oven. Here, the heating is done externally by a portion of coal gas produced during the process itself. It also utilizes the waste flue gases for heating the checker work bricks. The oven consists of a number of narrow silica chambers, each about 10-12 m long, 3-4 m tall and 0.4-0.45 m wide, erected side by side with vertical flues between them to form a sort of battery. Each chamber has a hole at the top to introduce the charge, a gas off take and a refractory lined cast iron door at each end for coke discharge. The oven works on heat regenerative principle i.e. the waste gas produced during carbonization is utilized for heating. The ovens are charged from the top and closed to restrict the entry of air.



Finely powdered, crushed coal is introduced through the charging hole at the top of the chambers which are then tightly closed at both ends to cut off the supply of air. The ovens are heated to  $1200^{\circ}$  deg C by burning producer gas. The air required for the combustion of the fuel is preheated in regenerators flanking the retorts, while the flue gases leave their acquired heat to one generator; the other generator is used for preheating the 12 incoming air. The cycle goes on and the heating is continued until all the volatile matter has escaped. It takes nearly 18 hours for carbonization of a charge. The heating of air-alone is required if the fuel gas is coal gas which has a high calorific value. When the carbonization is over, the red hot coke is pushed out into truck by a massive ram. It is then quenched by spraying water (wet quenching). Alternatively, the red hot coke may be placed in a chamber and cooled by sending in inert gases from boilers. The inert gases are then circulated to boilers where they generate steam. This method is known as dry quenching. The dry quenched coke is cleaner, drier and stronger and contains lesser dust than the wet quenched. The yield is about 70 %.

**Recovery of by-products:** The gas coming out of the retort is known as coke oven gas. This consists of tar, ammonia, moisture, aromatic hydrocarbons (naphthalene, benzene),  $H_2S$  etc. It can be used as a fuel after removing coal tar and ammonia.

(i) **Recovery of tar:** The coke oven gas is first passed through a tower in which liquid ammonia is sprayed. Tar and dust get collected in a tank below, which is heated by a steam coil to recover back the ammonia sprayed.

(ii) **Recovery of ammonia:** The coke oven gas is passed through another tower in which water is sprayed. Gaseous ammonia goes into solution as  $NH_4OH$ .

(iii) **Recovery of naphthalene:** After recovering ammonia, the remaining gases are led through another tower where water is sprayed at low temperature when naphthalene gets condensed.

(iv) **Recovery of benzene:** The resultant gas from the previous step is sprayed with petroleum whereby benzene and its homologues can be recovered.

(v) **Recovery of H<sub>2</sub>S:** The gases are then passed through a purifier, packed with moist Fe<sub>2</sub>O<sub>3</sub>. Hydrogen sulphide is retained here.  $\text{Fe}_2\text{O}_3 + 3 \text{H}_2\text{S} \rightarrow \text{Fe}_2\text{S}_3 + 3 \text{H}_2\text{O}$  When all the Fe<sub>2</sub>O<sub>3</sub> is converted into Fe<sub>2</sub>S<sub>3</sub>, the purifier on exposure to the atmosphere, regenerates Fe<sub>2</sub>O<sub>3</sub> in the following manner.  $\text{Fe}_2\text{S}_3 + 4 \text{O}_2 \rightarrow 2 \text{FeO} + 3 \text{SO}_2$   $4 \text{FeO} + \text{O}_2 \rightarrow 2\text{Fe}_2\text{O}_3$

**Q. 3.(b)** The composition by weight of a coal sample is C=82%, H=6%, O=6%, S=1%, N=2% and ash = 3%.

Calculate the minimum air required for complete combustion of 1kg of coal. (6)

**Ans.**

Constituent	amount	Reaction	Weights of O <sub>2</sub> required
C	820g	C + O <sub>2</sub> → CO <sub>2</sub>	$\frac{32}{12} \times 820 = 2186$
H	60g	H <sub>2</sub> + $\frac{1}{2}$ O <sub>2</sub> → H <sub>2</sub> O	$\frac{16}{2} \times 60 = 480$
O	60g	-	-
S	10g	S + O <sub>2</sub> → SO <sub>2</sub>	$\frac{32}{32} \times 10 = 10$

N<sub>2</sub> does not burn, therefore does not consume O<sub>2</sub>

Theoretical O<sub>2</sub> required = 2186 + 480 + 10 = 2676 g of O<sub>2</sub>

Net amount of O<sub>2</sub> = O<sub>2</sub> required - O<sub>2</sub> present in fuel

$$= 2676 - 60 = 2616 \text{ g}$$

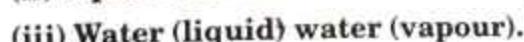
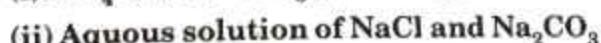
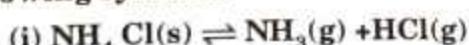
$$\text{Air required} = 2616 \times \frac{100}{23}$$

$$= 11373 \text{ g}$$

$$= 11.373 \text{ kg}$$

### UNIT-III

**Q. 4.(a)** State Gibb's Phase rule. Also, find the degree of freedom of the following systems:



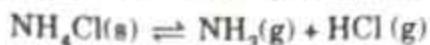
**Ans. Gibbs phase rule:** If the equilibrium of a heterogeneous system is not influenced by gravitational, electrical or magnetic forces or by surface action but only by temperature, pressure and concentration, then the number of degrees of freedom of

the system is related to the number of components and phases by the phase rule equation.

$$F = C - P + 2$$

For any system at equilibrium at definite temperature and pressure.

(i)



$$C = 1 [(\text{NH}_3) = (\text{HCl})]$$

$$P = 1$$

$$F = C - P + 2$$

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

(ii) aqueous solution of NaCl and  $\text{Na}_2\text{CO}_3$ 

$$C = 3 (\text{NaCl and } \text{Na}_2\text{CO}_3 \text{ and } \text{H}_2\text{O})$$

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

$$F = C - P + 2$$

$$= 3 - 1 + 2$$

$$= 4$$

(iii) Water (liquid)  $\rightleftharpoons$  water (vapour)

$$C = 1 \text{ (water)}$$

$$P = 2 \text{ (liquid + vapour)}$$

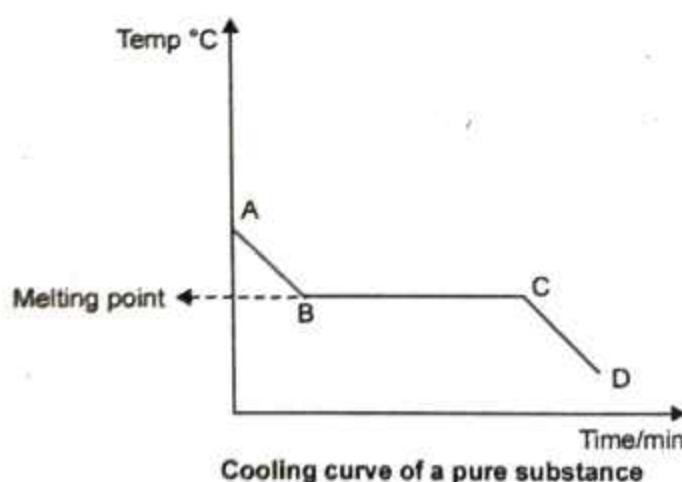
$$F = C - P + 2$$

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

**Q.4.(b) Draw the cooling curve of a pure substance and clearly identify the eutectic point in it.** (6.5)

**Ans. The Cooling Curve of a pure substance**

When a solid substance is heated until it is completely melted, and then heated further and allowed to cool slowly, the curve obtained by plotting temperature against time is known as the cooling curve.



Between A and B, the temperature falls with time - there is no change of state, hence the substance is still in the liquid state.

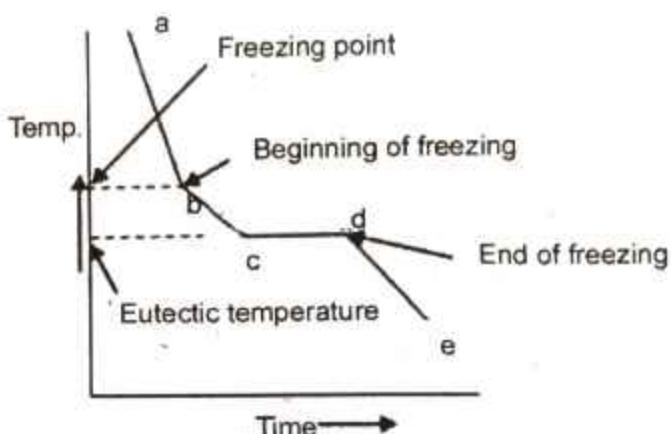
Between B and C, there is a constant temperature over time. This suggests that there is a change of state going on from liquid to solid. The heat lost between these

points is that gained in liquefying the solid substance (latent heat of fusion). Hence, there is a balance of heat, which explains why there is no reading of temperature change; this steady temperature is the melting point of the substance and the section, B and C represents liquid/solid state.

Between C and D, the temperature falls again with time. Here, the substance is totally in the solid state.

### Cooling curve of mixture

Considering a mixture of two solids A and B is in fused state. Allow to cool slowly. Initially the rate of cooling curve will be continuous (ab), when the crystals of either A or B is formed from the liquid melt, which is indicated by break in continuity of the cooling curve. Now the temperature again decreases with time but at a different rate, because the solid crystal and liquid melt are not of the same composition. The slope 'bc' of the curve represents a continuous and progressive change in composition of liquid melt.



Finally the liquid melt reaches the point 'c' at which it separates as solid A and solid B. Now the temperature will remain constant until the liquid melt is completely solidified. Point 'c' called eutectic point a minimum freezing point corresponding to eutectic mixture. There after temperature remain constant till solidification up to 'd'.

**Q.5.(a) Differentiate between congruent and Incongruent melting compound by giving suitable examples.** (6)

**Ans.** **Congruent melting** occurs during melting of a compound when the composition of the liquid that forms is the same as the composition of the solid. E.g. Mg-Zn system

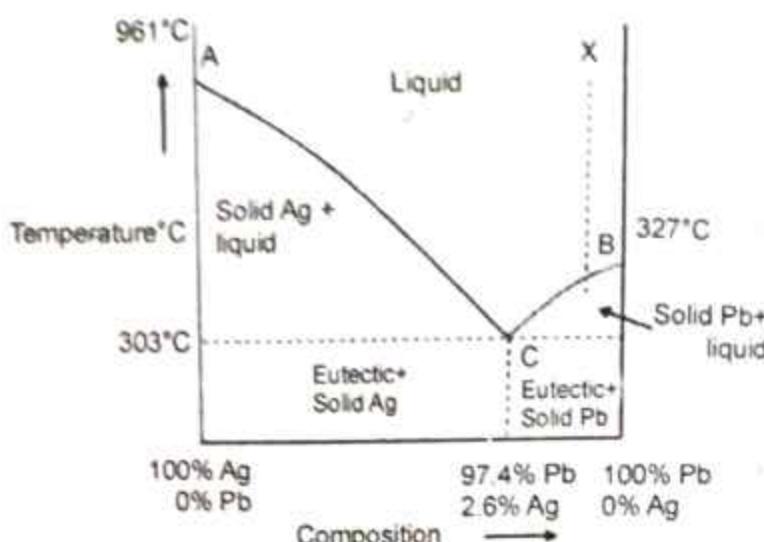
**Incongruent melting** occurs when a solid substance does not melt uniformly. During melting a new solid (of different composition) forms. E.g. Na-K system

$$\text{Original solid} = \text{new solid} + \text{melt (new solution)}$$

**Q.5.(b) Draw and explain the phase diagram of Lead-Silver System.** (6.5)

**Ans.** Simple eutectic systems (Pb-Ag system).

The salient features of the diagram are: (a) Two curves, AC and BC (b) Eutectic point C (c) Three areas (i) above ACB (ii) below AC (iii) below BC



**Curve AC** (the freezing point curve of Ag.) shows the effect on freezing point of Ag on addition of lead in small quantities. The curve starts A ( $961^{\circ}\text{C}$ ), the melting point of Ag, where pure Ag co-exists as solid and liquid (vapour being neglected). This curve indicates that the melting point of Ag falls gradually on adding Pb, along AC, till the lowest point C ( $303^{\circ}\text{C}$ ) is reached, where the solution gets saturated with respect to lead. At C, no more lead can go in solution and consequently, melting point of Ag does not fall any further; and if any lead is added, it separates as the solid phase. Along this curve, solid Ag and solution co-exist and hence, according to reduced phase rule equation:  $F = P - 3 + 2 = 1$ , i.e., the system is univariant. The point C ( $303^{\circ}\text{C}$ ) corresponds to a fixed composition of 2.6% Ag and 97.4% Pb and is known as eutectic composition. On cooling, the whole mass crystallizes out as such. Composition Temperature at eutectic is Solid Ag + liquid Eutectic + Solid(pb)

**Curve BC** (freezing point curve of Pb) represents the effect on freezing point of Pb on gradual addition of small amounts of Ag to it. Point B is the melting point of pure lead ( $327^{\circ}\text{C}$ ). Along BC, the melting point gradually falls on the addition of Ag, till lowest point O is reached, where the solution gets saturated with respect to Ag and the melting point of lead does not fall any more. On cooling, the whole mass (having eutectic composition) crystallizes out. The system is monovariant.

**Eutectic point C:** The curve AC and BC intersect at C, which is called the eutectic point. Here three phases solid Ag, solid Pb, and solution are in equilibrium. Applying the reduced phase rule;

$$F = C - P + 1 = 2 - 3 + 1 = 0 \text{ (nonvariant)}$$

Both variables temperature ( $303^{\circ}\text{C}$ ) and composition (97.4 % Pb, 2.6% Ag: eutectic composition) are fixed. If the temperature is raised above the eutectic temperature, the solid phases Ag and Pb disappear. No mixture of lead and silver has a melting point lower than the eutectic temperature. Below the temperature line of eutectic, there are two regions viz., (i) the region marked eutectic + solid Ag, in which crystalline silver and solid eutectic are stable, and (ii) the region marked eutectic + solid Pb, in which crystalline lead and solid eutectic are stable.

**Area ACB:** This region represents the single phase system, the solution of molten Ag and Pb. Applying the reduced phase rule;

$$F = C - P + 1 = 2 - 1 + 1 = 2 \text{ (Bivariant)}$$

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 a 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. 6. (b) Explain the use of catalyst in Industrially important processes. Give examples.** (6)

**Ans.**

Process	Catalyst	Equation
Making ammonia	Iron	$\text{N}_2(\text{g}) + 3\text{H}_2(\text{g}) \rightleftharpoons 2\text{NH}_3(\text{g})$
Making synthesis gas (carbon monoxide and hydrogen)	Nickel	$\text{CH}_4(\text{g}) + \text{H}_2\text{O}(\text{g}) \rightleftharpoons \text{CO}(\text{g}) + 3\text{H}_2(\text{g})$
Catalytic cracking of gas oil	Zeolite	Produces: a gas (e.g. ethene, propene) a liquid (e.g. petrol) a residue (e.g. fuel oil)
Reforming of naphtha	Platinum and rhenium on alumina	$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3(\text{g}) \rightarrow \text{C}_6\text{H}_6(\text{g}) + \text{H}_2(\text{g})$
Making epoxyethane	Silver on alumina	$\text{C}_2\text{H}_4(\text{g}) + \frac{1}{2}\text{O}_2(\text{g}) \rightarrow \text{H}_2\text{C}-\text{CH}_2\text{O}$
Making sulfuric acid	Vanadium(V) oxide on silica	$\text{SO}_2(\text{g}) + \frac{1}{2}\text{O}_2(\text{g}) \rightarrow \text{SO}_3(\text{g})$
Making nitric acid	Platinum and rhodium	$4\text{NH}_3(\text{g}) + 5\text{O}_2(\text{g}) \rightarrow 4\text{NO}(\text{g}) + 6\text{H}_2\text{O}(\text{g})$

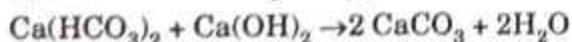
**Q.7.(a) Discuss the lime-soda process used for external treatment for water softening.** (6.5)

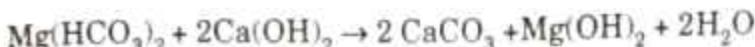
**Ans. Lime- soda process :**

**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.

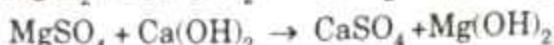
**Function of lime:** lime removes temporary Ca and Mg hardness, permanent Mg, Al, Fe hardness and dissolved  $\text{CO}_2$  and  $\text{H}_2\text{S}$  gases and free mineral acid present in water. Lime does not react with  $\text{CaCl}_2$  and  $\text{CaSO}_4$  so it cannot remove calcium permanent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



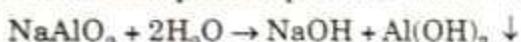
(a) Cold lime soda process: can be carried at room temperature

water + soda + lime + coagulant  $\rightarrow$  insoluble ppt (in the form of sludge settle down & taken out through outlet at the bottom)  $\rightarrow$  softened water & taken out from an outlet provided at the top.

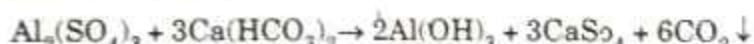
The softened water contain residual hardness of about 50-60 ppm.

**(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, aluminum sulphate, sodium aluminate etc., that hydrolyze to flocculent, gelatinous precipitate of aluminum 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 50-60 ppm.



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 94–100°C. 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 15-30 ppm.

Hot lime-soda plant consists of mainly 3 parts.

- A "reaction tank" in which raw water, chemicals and steam are thoroughly mixed.
- A "Conical sedimentation vessel" in which the sludge settles down.
- "Sand filter" that ensures complete removal of sludge from the softened water.

**Q.7.(b) A water sample has the following dissolved salts (mg/L). Calculate its temporary and permanent hardness in ppm of  $\text{CaCO}_3$ . (6)**

$$\text{Mg}(\text{HCO}_3)_2 = 80, \text{MgSO}_4 = 110, \text{CaSO}_4 = 85$$

$$\text{MgCl}_2 = 94, \text{CaCl}_2 = 84, \text{NaCl} = 50$$

**Ans.**

Salt	Amount	Multiplication factor	equivalent of $\text{CaCO}_3$
$\text{Mg}(\text{HCO}_3)_2$	80	$\frac{100}{146}$	$\frac{100}{146} \times 80 = 54.8$
$\text{MgSO}_4$	110	$\frac{100}{120}$	$\frac{100}{120} \times 110 = 91.6$
$\text{CaSO}_4$	85	$\frac{100}{136}$	$\frac{100}{136} \times 85 = 62.5$
$\text{MgCl}_2$	94	$\frac{100}{95}$	$\frac{100}{95} \times 94 = 98.9$
$\text{CaCl}_2$	84	$\frac{100}{111}$	$\frac{100}{111} \times 84 = 75.6$
NaCl	50	—	—

Temporary hardness is due to  $\text{Mg}(\text{HCO}_3)_2 = 54.8 \text{ PPM}$ .

$$\begin{aligned}\text{Permanent hardness} &= \text{MgSO}_4 + \text{CaSO}_4 + \text{MgCl}_2 + \text{CaCl}_2 \\ &= 91.6 + 62.5 + 98.9 + 75.6 \\ &= 328.6 \text{ PPM}\end{aligned}$$

#### UNIT-IV

**Q. 8. (a) Explain what is Soil Corrosion? How it is affecting the fertility of soil. How it can be prevented. (6.5)**

**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.

Corrosive soils contain chemical constituents, such as concrete and ferrous metals, which effects the fertility of soil.

#### **Soil corrosion can be prevented by:**

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

#### **Q. 8. (b) What is Cathodic protection and sacrificial Anodic protection. (6)**

##### **Ans. Sacrificial anode protection**

Sacrificial Anodes are highly active metals that are used to prevent a less active material surface from corroding. Sacrificial Anodes are created from a metal alloy with a more negative electrochemical potential than the other metal it will be used to protect. The sacrificial anode will be consumed in place of the metal it is protecting, which is why it is referred to as a "sacrificial" anode. Sacrificial anodes are among several forms of cathode protection.

The materials used for sacrificial anodes are either relatively pure active metals, such as zinc or magnesium, or are magnesium or aluminum alloys that have been specifically developed for use as sacrificial anodes. The current will flow from the newly introduced anode and the protected metal becomes cathodic creating a galvanic cell.

Sacrificial Anodes are used to protect the hulls of ships, water heaters, pipelines, distribution systems, above-ground tanks, underground tanks, and refineries.

##### **Cathodic protection**

cathodic protection connects the base metal at risk (steel) to a sacrificial metal that corrodes in lieu of the base metal. The technique of providing cathodic protection to steel preserves the metal by providing a highly active metal that can act as an anode and provide free electrons. By introducing these free electrons, the active metal sacrifices its ions and keeps the less active steel from corroding.

##### **Types of Cathodic Protection**

There are two basic types of cathodic protection: galvanic, and impressed current cathodic protection.

##### **Galvanic**

Galvanic protection consists of applying a protective zinc coating to the steel to prevent rusting. The zinc corrodes in place of the encapsulated steel. These systems

have limited life spans, as the sacrificial anode protecting the underlying metal will continue to degrade over time until the sacrificial anode is no longer capable of supplying protection.

### **Impressed Current Cathodic Protection**

Impressed current cathodic protection systems consist of anodes that are connected to a power source that provides a perpetual source of electrical flow. The sacrificial anode method of protection uses a metal more active than the base metal to "sacrifice" ions. These "sacrificial anodes" (usually alloys such as magnesium, aluminum, or zinc) have a stronger electrochemical potential. This method can often provide much longer protection than a sacrificial anode, as the anode is supplied by an unlimited power source.

#### **Q.9.What happens and why?**

##### **(a) A piece of iron is kept in Saline water.**

(3)

**Ans.** Rust (hydrous oxide) is an example of this change that results when iron is exposed to water or damp air. A thin film of oxide forms on the iron, which actually protects the metal from further corrosion by slowing the rate of oxidation. When salt is present, electrochemical corrosion occurs, and the protective oxide film does not form, thus the corrosion (buildup of rust) continues unchecked. Your iron nail will indeed rust more quickly and severely in salt water.

##### **Q.9.(b) A steel pipe is connected to copper plumbing.**

(3)

**Ans.** Whenever copper water lines is joined to galvanized steel pipe, corrosion caused by joining two dissimilar metals, called "galvanic corrosion." An electrochemical reaction occurs that causes the steel pipe (in this case) to rust and clog up. The steel acts as an anode in the galvanic reaction to the copper cathode. In the case of a pipe inside a copper tank, the steel pipe (anode) is smaller than the copper tank internal surface (cathode) and so the reaction is accelerated.

##### **Q.9.(c) A zinc plate is fixed below the ship.**

(3)

**Ans.** A ship is continuously in contact with water and moisture, laden winds which makes it highly susceptible to corrosion. It is for this reason sacrificial anodes are used to protect the parent material. In the case of a ship, seawater acts as an electrolyte and transfers the electrons from the anode by oxidizing it over the steel plate and making a protecting layer. If the metal is more active it will be easily oxidized and will protect the metallic compound by making it act as cathode. The anode will corrode first sacrificing itself for the other compound and it is thus called sacrificial anode. Zinc is the highest activity on the electrolysis chart, so the zinc will all be eaten away before the steel starts to go. Its is easier to replace one worn out block of zinc rather than the entire steel hull.

##### **Q.9. (d) Iron next/washers/values are cleaned and packed with zinc dust and rotated.**

(3.5)

**Ans.** When iron valves are washed with water ,moisture present in it can lead to rusting. the more active metal is attached it will be easily oxidized and will protect the metallic compound by making it act as cathode. The anode will corrode first sacrificing itself for the other compound and it is thus called sacrificial anode. Zinc is the highest activity on the electrolysis chart, so the zinc will be corroded away before the iron valve starts to go . So it is packed with Zn dust the zinc will act as a sacrificial anode which protect the valve from rusting.