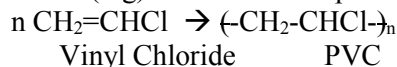


## UNIT – I POLYMER CHEMISTRY PART – A

### 1. What is polymerization?

**Ans:** Under the proper conditions of temperature, pressure and catalyst, the micro (smaller) molecules are combining together to form a macro (big) molecule. This process is called polymerization.



### 2. What are monomers and polymers?

**Ans:** In the process of polymerization, Micro molecules are called ‘Monomer’. (Eg. Vinyl chloride)

Polymer is a macro molecule formed by joining two or more micromolecules. (Eg. PVC)

Requirements of a monomer: a) multiple bonds or b) reactive functional groups.

### 3. What is degree of polymerization? (Jan 2014)

**Ans:** The number of monomers present in a polymer is ‘Degree of polymerisation’ (n)

Degree of Polymerisation = Mol. wt of polymer / Mol. wt of monomer

If n = low, Mol.wt = 500 – 5000 Dalton units, it is Oligo polymer.

If n = High, Mol.wt = 10,000 – 2, 00,000 Dalton units, it is High polymer.

### 4. What are the different methods to classify polymers?

**Ans:** a) Based on origin:

Natural – Cotton, silk, wool, rubber

Synthetic – PVC, Nylon, Epoxy resin

b) Based on chemicals:

Organic polymers – PVC, Nylon

Inorganic polymers – Glass, silicone rubbers

c) Based on thermal nature:

Thermoplastics – Polyethylene, polyvinyl chloride

Thermosetting plastics - Bakelite, Urea formaldehyde

### 5. What are homo polymer and hetero polymer?

**Ans:** If the polymer consists of identical monomers, it is homo polymer. (eg)PVC

If the polymer consists of different monomers, it is hetero (or) copolymer. (eg) SBR

### 6. What are homo chain and hetero chain polymers?

**Ans:** If the main chain of a polymer is made up of same species of atoms, the polymer is known as homochain polymer. -C-C-C-C-                      Eg: Polyethylene, polyvinyl chloride.

If the main chain of a polymer is made up of different species of atoms, the polymer is known as heterochain polymer. -C-O-C-O-                      Eg: Terylene, Nylon 6,6.

### 7. What is functionality of monomers? (June 2014)

**Ans:** Number of reactive sites present in a monomer is called ‘Functionality’ (F)

Example:  $\text{CH}_2 = \text{CH}_2$  (Ethylene) The double bond is acting as two reactive sites. Therefore its functionality is 2.

If F = 2, they form linear chain structure.

If F = 3, they form branched structure.

If F ≥ 4, they form complex 3D structure.

### 8. What is tacticity? Mention its types.

**Ans:** Orientation of monomers in a polymer chain is called “Tacticity”.

If the groups are in same orientation, it is “isotactic polymer”.

If the groups are in random orientation, it is “atactic polymer”.

If they are arranged in alternative fashion, it is “syndiotactic polyme”.

### 9. Differentiate thermoplastics and thermosetting plastics with an example for each.

**Ans:**

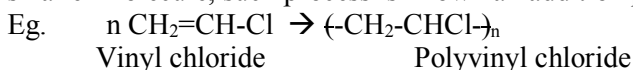
S.No	THERMOPLASTICS	THERMOSETTING PLASTIC
1	Eg. PVC , Polyethylene	Eg. Polyester, Bakelite
2	They can be remelted and remoulded into any desired shape for any number of times.	They cannot be remoulded after their first usage.
3	Their scrap can be used again.	Their scrap cannot be used again.
4	They are formed by addition polymerisation	They are formed by condensation polymerisation

### 10. Why thermosetting plastics cannot be remoulded?

**Ans:** Thermosetting polymers consist of strong network of covalent bonds. So, they do not soften on heating and cannot be remoulded and reused.

### 11. What is addition polymerization?

**Ans:** When two or more monomers are added together to form a polymer without any elimination of smaller molecule, such process is known as addition polymerization.



### 12. Explain condensation polymerization with an example.

**Ans:** It is otherwise known as “Step wise Polymerization”. Here, monomers are condensed to form polymer with elimination of smaller molecules. Here, Monomers must have two or more functional groups.

(eg) Condensation polymerisation of Hexa methylene diamine and Adipic acid gives Nylon 6,6.



### 13. What are the different types of addition polymerization mechanism?

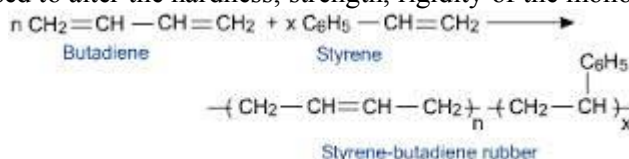
- Ans:** a) Free radical mechanism  
 b) Cationic polymerization mechanism  
 c) Anionic polymerization mechanism  
 d) Coordination mechanism (or) Ziegler-Natta polymerisation

### 14. What are the steps involved in Free radical mechanism?

**Ans:** 1. Initiation    2. Propagation    3. Termination

### 15. What is co polymerization?

**Ans:** It is a special kind of polymerisation, also known as “Joint polymerisation”. The product is known as ‘Co-polymer’. It is used to alter the hardness, strength, rigidity of the monomers.



### 16. What is Tg?

**Ans:** Tg is known as glass transition temperature. At this temperature, the chain segment of the polymer molecule starts leaving their lattice sites. Below this Tg, the polymer becomes brittle and above Tg, it becomes soft elastomer.

### 17. The Tg of Perspex, polystyrene and nylon 6,6 are 105°C, 100°C and 45°C respectively.

What is likely to happen to a sample of each of them, if it were hit by hammer at

i) 0°C ii) 20°C iii) 80°C iv) 120°C? Give reason.

**Ans:** i) & ii) All would shatter    iii) Only nylon 6,6 will be broken    iv) None would be broken

Reason: Below Tg, samples are brittle. Above Tg, they undergo deformation but will not be broken.

### 18. Define Number average molecular weight.

**Ans:** It is defined as the total mass of (w) of all the molecules in a polymer sample divided by the total number of molecules present. It is denoted as (M<sub>n</sub>).

### 19. What is polydispersity index?

**Ans:** The ratio between weight average molecular mass (M<sub>w</sub>) and number average molecular mass (M<sub>n</sub>) is known as polydispersity index (PDI).

$$\text{PDI} = M_w/M_n$$

### 20. Name any four polymerization techniques.

- Ans:** a) Bulk polymerization                      b) Solution polymerization  
 c) Emulsion polymerization                      d) Suspension polymerization

### 21. What is bulk polymerization?

**Ans:** It is the simplest method involving the use of monomers and initiator only. It involves two steps namely pre-polymerisation and post-polymerisation. (eg) PVC, PMA, Polystyrene are prepared by this method.

### 22. Write the process of emulsion polymerization?

**Ans:** In this method, the monomers are dispersed as fine droplets in large amount of water and emulsified using soap. Then initiators are added to cause polymerization. If needed, some electrolytes are also added to break the polymer to get the required products.

Advantages: Rapid production, Easy control of temperature and high average molecular weight.

Eg. PVC, PVA are prepared by this method.

### 23. Compare solution polymerization and suspension polymerization.

**Ans:**

S.no	Solution polymerization	Suspension polymerisation
1	The monomer is dissolved in a suitable solvent .	The monomer is dispersed as large droplets in water.
2	It is kept as solution .	It is kept as suspension.
3	The polymer is precipitated by adding a suitable non-solvent to the mix, filtered and dried.	The suspension is stabilized by Aluminium hydroxide stabilizer, washed, filtered and dried.
4	Used to prepare Acrolonitrile, N-Vinyl Pyrrolidone	Used to prepare PVC, Polystyrene

### 24. Write the properties and uses of Epoxy resin. (Jan 2014)

**Ans:** Properties: a) It is not affected by water, acids and alkalis.

b) It is not affected by heat.

c) It has good adhesive nature.

Uses: a) It is used as adhesives for glass and metals (as araldite)

b) It is used in aircraft and automobile components

c) It is used to give crease resistance and shrinkage control coating

d) It is used as laminating materials in electrical equipments.

### 25. Mention two properties and uses of Nylon 6,6. ( June 2014)

**Ans:** Properties: 1.Flexibility 2.Elasticity 3 Absorbs only little moisture

Uses: Tooth brush bristles, Automobile gears, Textile industry, ropes, Socks, Carpets.

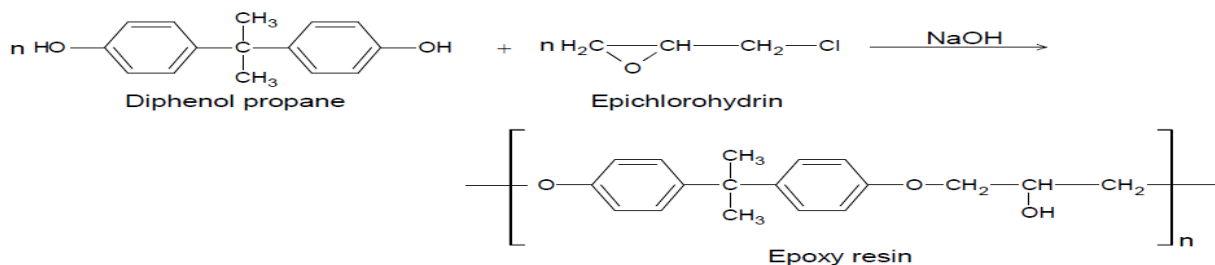
### 26. How will you prepare Nylon 6,6?

**Ans:** Condensation polymerisation of Hexa methylene diamine and Adipic acid gives Nylon 6,6.



### 27. Explain the synthesis of Epoxy resin.

**Ans:** When Bisphenol- A (Diphenol propane) is condensed with epichlorohydrin, in presence of alkaline catalyst at 60°C, HCl molecule is eliminated, we get Epoxy resin.



### 28. All the polymers are macromolecules but all macromolecules are not polymers. Justify the statement.

**Ans:** Polymers are high molecular weight substances, which consist of large number of repeating units known as monomers. Examples: Polyethylene, Polyvinylchloride

Macromolecules are not polymers because they do not contain the repeating units of monomers.

Examples: Cholesterol, Chlorophyll

### 29. How copolymerization is superior to homo Polymerization?

**Ans:** Copolymerization is the joint polymerization of two or more different type of monomeric units. It controls various polymer properties such as hardness, rigidity, heat resistance and crystallinity. So it is superior to homo polymerization.

### 30. What is meant by thermal initiator? Give two examples?

**Ans:** Thermal initiator is a substance used to produce free radicals by homolytic dissociation at high temperature. Free radicals are used to initiate the addition polymerization reaction.

Eg.: Acetyl peroxide, Benzoyl peroxide.

**31. What are living and dead polymers?**

**Ans:** The growing chain of addition polymerization is known as living polymer. The product of addition polymerization is known as dead polymer.

**32. What are plastics? Differentiate it from resins?**

**Ans:** Plastics are high molecular weight organic materials which can be moulded into any desired shape by the application of heat and pressure, or in presence of a catalyst.

Resins are the basic binding materials. They are the major part of the plastics, which actually undergo polymerization reactions during their moulding operations.

**33. Thermoplastic materials are more soluble in organic solvents when compared to thermosetting polymers. Why?**

**Ans:** Thermoplastic materials are more soluble in organic solvents when compared to thermosetting polymers because of their weak intermolecular forces of attraction.

**34. What type of monomers follow anionic mechanism in addition polymerisation?**

**Ans:** Monomers containing electronegative groups like  $\text{Cl}^-$ ,  $\text{CN}^-$  at one of the carbon atoms connected by the double bond follow this mechanism.(eg) Vinyl chloride, Acrylonitrile.

**35. What are the catalysts used in the initiation of anionic polymerisation reaction?**

**Ans:** The catalysts used to initiate the reaction are  $\text{KNH}_2$ ,  $\text{NaNH}_2$  (Lewis bases).

**36. What type of monomers follow cationic mechanism in addition polymerisation?**

**Ans:** Monomers containing electropositive groups like  $\text{CH}_3$ ,  $\text{C}_6\text{H}_5$  at one of the carbon atoms connected by the double bond follow this mechanism.

Examples: Isoprene, Styrene.

**37. What are the catalysts used in the initiation of cationic polymerisation reaction?**

**Ans:** The catalysts used to initiate the reaction are  $\text{AlCl}_3$ ,  $\text{BF}_3$  (Lewis acids).

**38. Distinguish between number average and weight average molecular weights of polymers.**

**Ans:** Number average molecular weight ( $M_n$ ): It is defined as the ratio of sum of molecular weights of individual molecules to the total number of molecules in the mixture.

Weight average molecular weight ( $M_w$ ): It is defined as the ratio of sum of weights of individual polymer molecules to the total weight of polymer molecules in the mixture.

**39. Differentiate homogeneous polymerisation and heterogeneous polymerisation.**

**Ans:** Homogeneous polymerisation: In this technique the reaction takes place in one phase. This may occur in solvent or in a reaction vessel containing only a monomer.

Examples: Bulk polymerisation, Solution polymerisation

Heterogeneous polymerisation: In this technique more than one phase is involved.

Examples: Emulsion polymerisation, Suspension polymerisation.

**PART-B**

**1. Distinguish between thermoplastics and thermosetting plastics with examples.(Jan 2014, June 2014)**

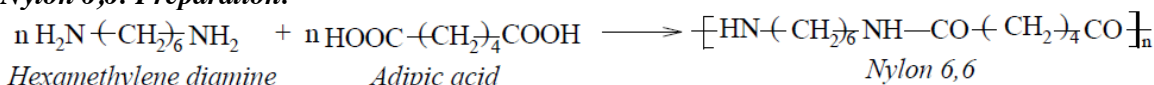
No	THERMOPLASTICS	THERMOSETTING PLASTIC
1	Eg. PVC , Polyethylene	Polyester, Bakelite
2	Can be remoulded.	Cannot be remoulded .
3	Scrap can be reused.	Scrap cannot be reused.
4	Formed by addition polymerisation	Formed by condensation polymerisation
5	Linear structure	3D complex structure.
6	Bond strength is low	Bond strength is high
7	Molecular weight is low	Molecular weight is high
8	Soluble in organic solvents.	Insoluble in organic solvents.
9	Prepared by injection moulding	Prepared by compression moulding.

## 2. Discuss briefly on the preparation, properties and uses of

a) Nylon 6, 6 (Jan 2014)

b) Epoxy resin. (June 2014)

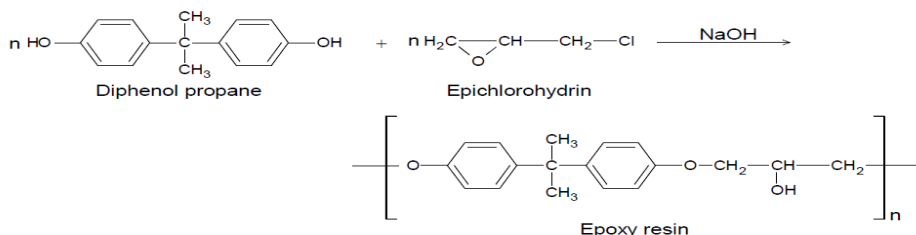
### Nylon 6,6: Preparation:



**Properties:** Flexibility -. Elasticity - Absorbs only little moisture- Translucent nature

**Uses:** Tooth brush bristles - Automobile gears- Textile industry- Nylon ropes- Socks - Carpets

### Epoxy resins: Preparation:



### Properties:

Adhesiveness - stable ether linkage- resistance to chemical attack, water, acids, alkalis - electrical insulation.

**Uses:** Bonding glasses, metallic ceramic article - “Prepeg” - “Araldite” - aircraft industry -Fibre reinforced plastics - coatings and linings - crease resistance and shrinkage control in textile industry – Insulators.

## 3. Write the mechanism of free radical polymerization. (June 2014)

(eg) PVC polymerisation

### 1. Initiation

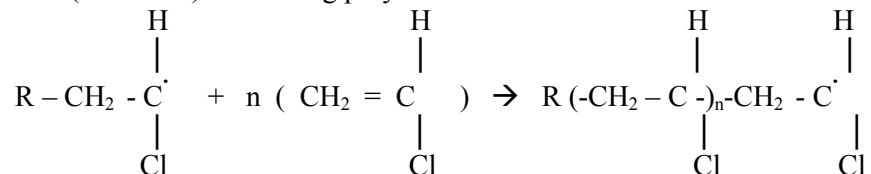
a) Initiator  $\rightarrow$  Radical



b) Radical + Monomer  $\rightarrow$  Chain Initiating Species (CIS)

### 2. Propagation:

CIS + n (monomer)  $\rightarrow$  Living polymer



### 3. Termination

a) Coupling: CIS /Radical + CIS / Radical  $\rightarrow$  Macromolecule (Dead polymer)

b) Disproportionation (by Hydrogen transformation)

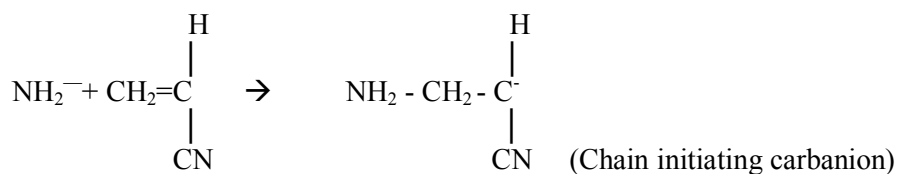
Cis / Radical + CIS / Radical  $\rightarrow$  Unsaturated polymer + Saturated polymer

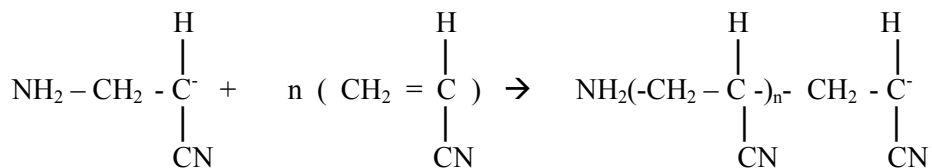
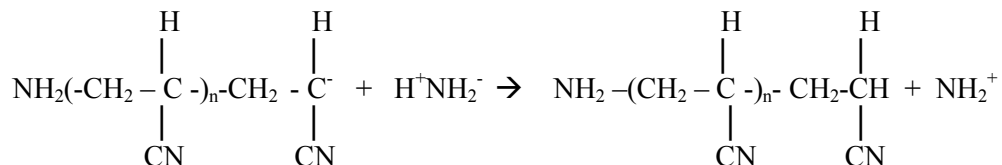
The products are known as dead polymers.

## 4. Explain cationic and anionic polymerization mechanism. (Jan 2014)

(eg) Acrylonitrile

1.Initiation:  $\text{KNH}_2 \rightarrow \text{K}^+ + \text{NH}_2^-$

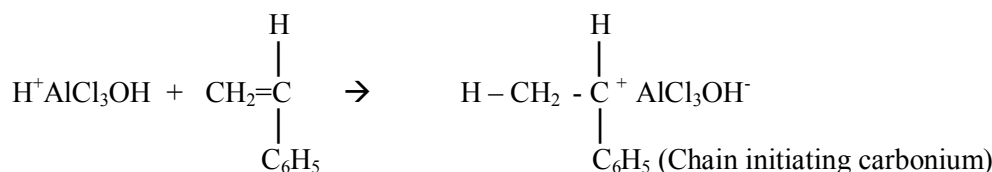
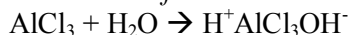
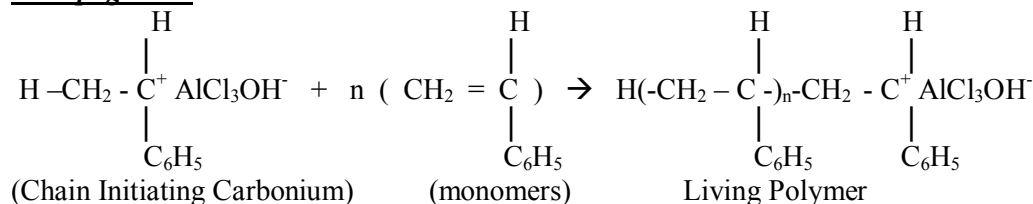
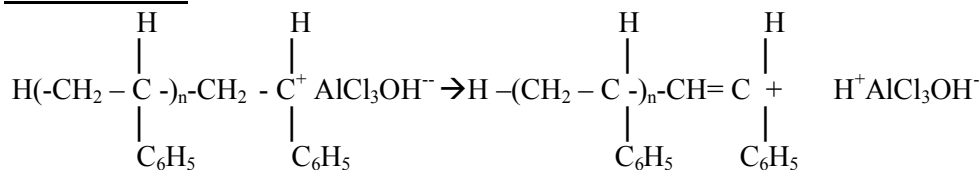


**2. Propagation:****3. Termination:****MECHANISM OF CATIONIC ADDITION POLYMERISATION:**

(eg) Polystyrene

**1. Initiation:**

Here, Chain Initiating carbonium ion formation is taking place.

**2. Propagation:****3. Termination:**

Living Polymer

Product + Lewis acid catalyst

**5. Write a note on the following polymer properties: (Jan 2014)****(i) WEIGHT AVERAGE MOLECULAR WEIGHT ( $\bar{M}_w$ )**

It is the ratio of sum of molecular weights of individual molecules to the total weight of molecules in the mixture.

It is obtained by light scattering and ultra centrifugation techniques.

$$\bar{M}_w = \frac{w_1 M_1 + w_2 M_2 + \dots + w_i M_i}{w_1 + w_2 + \dots + w_i}$$

$$\bar{M}_w = \frac{\sum w_i M_i}{\sum w_i}$$

$$\bar{M}_w = \frac{n_1 M_1 \cdot M_1 + n_2 M_2 \cdot M_2 + \dots + n_i M_i \cdot M_i}{n_1 M_1 + n_2 M_2 + \dots + n_i M_i}$$

$$\bar{M}_n = \frac{\sum n_i M_i^2}{\sum n_i M_i}$$

(ii) NUMBER AVERAGE MOLECULAR WEIGHT ( $\bar{M}_n$ )

It is the ratio of sum of molecular weights of individual molecules to the total number of molecules in the mixture.

$$\bar{M}_n = \frac{n_1 M_1 + n_2 M_2 + \dots + n_i M_i}{n_1 + n_2 + \dots + n_i}$$

$$\bar{M}_n = \frac{\sum n_i M_i}{\sum n_i}$$

(iii) POLYDISPERSITY INDEX (PDI)

The ratio of weight average molecular weight  $\bar{M}_w$  to number average molecular weight  $\bar{M}_n$  is known as polydispersity index or distribution ratio.

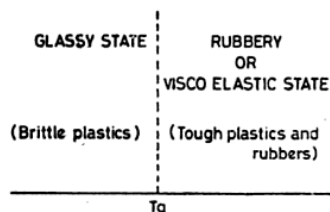
$$\text{Polydispersity index} = \bar{M}_w / \bar{M}_n$$

For polydispersed system,  $\bar{M}_w > \bar{M}_n$

For monodispersed system,  $\bar{M}_w = \bar{M}_n$

(iv) GLASS TRANSITION TEMPERATURE ( $T_g$ )

It is the temperature at which a polymer abruptly transforms from glassy (hard) to rubbery state (soft).  $T_g$  curve for a linear polymer is sharp. A cross-linked polymer does not possess any  $T_g$ .



Factors influencing  $T_g$  Value: Cross linkage - Crystallinity - Molecular mass – Tacticity - Presence of plasticizers

Significance of glass transition temperature: (i) To evaluate the flexibility of a polymer (ii) To determine Coefficient of thermal expansion, heat capacity, refractive index, modulus of elasticity

(v) TACTICITY:

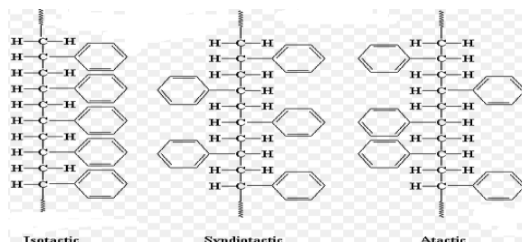
Orientation of monomers in a polymer chain is called “Tacticity”.

i) Isotactic : If the functional groups are in same orientation, it is isotactic. (eg) Cis-isoprene

ii) Atactic: If the functional groups are arranged randomly it is “atactic”. (eg) Polypropylene

iii) Syndiotactic: If the functional groups are arranged in alternative fashion, it is syndiotactic. (eg) Trans-isoprene

Representation of Tacticity:



**6. Discuss Bulk polymerization technique. Mention any two polymers synthesized by this technique.**  
(June 2014)

i) Process: Homogeneous polymerization method.

Pre polymerization stage - Post polymerization stage

ii) Reaction: Monomer (Liquid) + Initiator  $\rightarrow$  Polymer

iii) Advantages: Free from impurities - The amount of initiator left behind in the reactor is very small.

iv) Disadvantages: temperature control is difficult - Difficult to remove the traces of monomer and initiator.

v) Examples: PVC, Polystyrene, PMMA

**7. Write a note on the following polymerization techniques.**

(i) **SOLUTION POLYMERISATION**

i) Process: The monomer and initiator is dissolved in a solvent to form a homogenous mixture and heated with constant stirring. After the reaction, solvent is evaporated and polymer is isolated.

ii) Reaction: Monomer (In solvent) + Initiator  $\rightarrow$  Polymer

iii) Advantages: Stirring and heat control is easy.

iv) Disadvantage: Costly - High molecular mass polymers cannot be prepared by this method.

v) Examples: PVC, polyethylene, N- vinylpyrrolidine, acrylic acid

(ii) **SUSPENSION POLYMERISATION: (PEARL POLYMERISATION)**

i) Process: Polymerisation takes place inside the tiny droplets and the product is obtained as spherical beads/ pearls. So, it is also known as pearl polymerization. The unreacted monomer is recycled.

ii) Reaction:

Monomer (Suspended in water) + Initiator (Soluble only in monomer)  $\rightarrow$  Polymer

iii) Polystyrene production set up needs the following:

S.No	Content	Example
1	Monomer	Styrene
2	Solvent	Water
3	Initiator	Peroxide
4	Stabiliser	gelatin, aluminium hydroxide
5	Buffer ( Optional)	Phosphate

iv) Advantages: Cheap - Product isolation is easy.

v) Disadvantages: Sensitive to agitation - difficult to control.

vi) Examples: Polystyrene beads and styrene-divinyl benzene copolymer beads

(iii) **EMULSION POLYMERISATION**

i) Process: A water insoluble monomer is dispersed in the water to form an emulsion of the size  $10^{-5}$  to  $10^{-6}$  mm. The emulsion is stabilized by surfactants. It forms micelle and lowers the surface tension at monomer – Water interface and facilitates the emulsification.

ii) Rxn: Monomer (Water insoluble) + Water + Emulsifier + Initiator  $\rightarrow$  Polymer

iii)

S.No	Content	Example
1	Monomer	Styrene
2	Solvent	Water
3	Initiator	K <sub>2</sub> S <sub>2</sub> O <sub>8</sub> Persulphate
4	emulsifier	Sodium lauryl sulphate
5	buffer	Phosphate

iv) Advantages: agitation is easy b) High molecular weight polymers can be produced.

v) Disadvantages: Needs further purification.

vi) Example: Polystyrene, PVC, PVA, Poly methyl meth acrylate (PMMA).



**8. Distinguish between addition and condensation polymerization.**

No	Addition Polymerisation	Condensation Polymerisation
1	Longer processing time is needed to increase yield.	Longer time is essential for increasing molecular weight.
2	Chain growth polymerisation	Step wise polymerisation
3	Monomers are adding together to form polymers.	Monomers are condensed to form polymer.
4	No elimination of other molecules.	Elimination of smaller molecules occurs.
5	At least one multiple bond presence is essential condition.	Monomers must have two or more functional groups.
6	Homo polymers are formed.	Hetero polymers are formed.
7	Thermoplastics are formed.	Thermo set plastics are formed.
8	Molecular weight of the polymer is the integral multiple of monomers.	Need not be so.
9	Monomers disappear slow and steadily.	Monomers disappear at the initial stage of the reaction.
10	Eg. PVC	Eg. Nylon 6,6

**9. Explain the different types of classification of plastics with suitable examples.**

Plastics are high molecular weight organic materials that can be moulded into any desired shape by the application of heat and pressure in the presence of a catalyst.

The classification of plastics can be done in two ways.

(i) Based on applications:

a) Commodity plastics – They are used in domestic and household applications. They have low strength and applicability. (eg) Low grade PVC

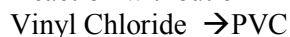
b) Engineering plastics – They are used mainly in industrial applications. They have high strength and toughness. (eg) Bakelite

(ii) Based on thermal properties:

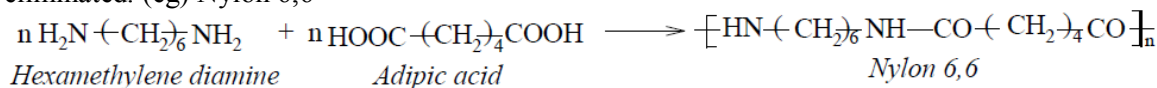
a) Thermoplastics b) Thermosetting plastics – their differences.

**10. How is polymerization classified? Give one example for each class.****Addition Polymerisation:**

Monomers having multiple bonds (double or triple bond) undergo addition polymerization. Monomers combine to give polymer through addition reaction without elimination of any smaller molecules.

**Condensation Polymerisation:**

Monomers having same or different types of functional groups undergo condensation polymerization. The polymerization proceeds by step wise reaction between reactive functional groups and small molecules are eliminated. (eg) Nylon 6,6

**Co-Polymerisation:**

1. It is a special kind of polymerisation, otherwise known as “Joint polymerisation”.

The product is known as ‘Co-polymers’. This is superior to other polymerization because it is used to alter the hardness, strength, rigidity and crystallinity of the monomers.

e.g SBR synthesis

**UNIT– 2- CHEMICAL THERMODYNAMICS****PART - A****1. What are extensive and intensive properties of a system?**

**Ans:** *Extensive properties:* Extensive properties are those which depend on the amount of the substance present in the system. Eg: Mass, Volume, Internal energy, Enthalpy and Entropy.

*Intensive properties:* Intensive properties are those which are independent of the amount of the substance present in the system. Eg: Temperature, Pressure, Density, Concentration etc.

**2. Distinguish between an adiabatic process and an isothermal process.****Ans:**

S.No	Isothermal Process	Adiabatic Process
(i)	Exchange of heat takes place between the system and its surroundings.	No exchange of heat takes place between the system and its surroundings.
(ii)	It involves no change in temperature [ $dT = 0$ ]	It involves no change in heat [ $dq = 0$ ].

**3. Distinguish between a reversible process and an irreversible process****Ans:**

S.No	Reversible Process	Irreversible Process
(i)	It is a slow process and takes infinite time to complete.	It proceeds fast and completes soon.
(ii)	It is an equilibrium state at all the stages of the operation.	It is in equilibrium only at the initial and final stages of the operation.
(iii)	It can be reversed by any of the thermodynamic variables.	It cannot be reversed.
(iv)	It is unreal process.	It is real process

**4. State the first law of thermodynamics. (or) What is the law of conservation of energy?**

**Ans:** *Law of conservation of energy:* "Energy can neither be created nor be destroyed although it can be converted from one form to another".

*Mathematical statement:*  $\Delta E = q - P\Delta V$ . The net energy change ( $\Delta E$ ) of a closed system is equal to heat transferred to the system minus the work done by the system.

**5. What are the limitations of first law of thermodynamics?**

**Ans:** The first law of thermodynamics does not provide the details about feasibility of a reaction, extent of feasibility and possibility of converting internal energy into work.

**6. State second law of thermodynamics? (June 2014)**

**Ans:** *Kelvin-Planck statement:* It is impossible to take heat from a hot reservoir and convert into work by a cyclic process without transferring a part of heat to a cold reservoir.

**7. Define the terms (a) Spontaneous process (b) Spontaneity.**

**Ans:** A process which proceeds on its own under a given set of conditions is called as *spontaneous process*. It is also called as natural process. It occurs in one direction only.

The tendency of a process to occur spontaneously is called spontaneity. *Examples:* Flow of water from hills; Flow of heat from a hot body into a cold body; Melting of ice.

**8. Define entropy. (Jan 2014, June 2014)**

**Ans:** Entropy is a measure of degree of disorder or randomness in the system. It is also considered as a measure of unavailable form of energy.

**9. How does the entropy of the system change when a gas is liquefied?**

**Ans:** The entropy of the system decreases. This is because, on cooling, the gaseous molecules come closer together and the orderliness of gaseous molecules (Example: water molecules) increases because of intermolecular forces of attraction.

**10. Give the mathematical expression for entropy. What is its unit?**

**Ans:** The change in entropy is equal to the ratio of heat change to the temperature at which heat change occurs in a reversible cyclic process.

$$\Delta S = q_{\text{rev}} / T$$

$q$  = the heat absorbed or evolved in calories &  $T$  = is the temperature in degrees.

The unit of entropy in S.I. unit is joules per kelvin ( $\text{JK}^{-1}$ ).

**11. Give the criteria for a reversible process and a spontaneous process in terms of entropy.**

**Ans:** The entropy change in a reversible isothermal process is zero. In other words, the entropy remains constant during a reversible process.

The total change in entropy of the system and its surroundings is called as entropy change of the universe. Since all natural processes that take place spontaneously are irreversible processes, the entropy of the universe always increases.

**12. Write briefly on the physical significance of entropy.**

**Ans:** When heat is supplied to the system, some portion of the heat is used up in doing work. This portion of heat is called workable or available energy. The remaining portion of heat which remains uncovered called unavailable energy.

The second law of thermodynamics says that entropy is a measure of unavailable energy. Hence entropy can be defined as unavailable energy per unit temperature.

**13. Why does entropy of a solid increase on fusion?**

**Ans:** On fusion (melting), the highly ordered solid molecules is changed into less ordered liquid form and hence the entropy of a solid increases.

**14. At absolute zero (0 K), the entropy of a pure crystal is zero. Comment this statement (or)**

**Under what condition the entropy of a substance does becomes zero?**

**Ans:** The water molecules in the ice crystals are highly ordered and hence the entropy of the system is very low. The only freedom that the water molecules have in ice crystals is vibration or rotation. On further cooling, even these movements get slowed down and at absolute zero, all molecular vibration ceases and water molecules are in perfect order. Hence at absolute 0 K, the entropy of a pure crystal is zero.

**15. Define entropy of vapourisation.**

**Ans: Entropy of vapourisation:** It is defined as the change in entropy when one mole of a liquid substance change into vapours at its boiling point.

$\Delta S_{\text{vapour}} = \Delta H_{\text{vapour}} / T$  ;  $\Delta H_{\text{vapour}}$  - latent heat of vapourisation, For water it is 540 cal/gm

**16. Define entropy of fusion.**

**Ans: Entropy of fusion:** It is defined as the change in entropy when one mole of a solid substance changes into liquid form at its melting point.

$\Delta S_{\text{fusion}} = \Delta H_{\text{fusion}} / T$

$\Delta H_{\text{fusion}}$  is the latent heat of fusion. Latent heat of fusion of ice at 0 °C is 80 cal/gm.

**17. Define the terms (a) free energy (b) work function.**

**Ans: (a)Free energy:** The isothermally available energy present in a system is called free energy. It is mathematically defined as:  $G = H - TS$ .

**(b)Work function:** The internal energy which is isothermally available to do useful work is called work function. It is mathematically defined as  $A = E - TS$ .

**18. Discuss the criteria for a chemical reaction to be spontaneous.**

**Ans:** For a process to be spontaneous,  $\Delta S_{\text{total}}$  should be positive.

For a process to be spontaneous  $\Delta G_{\text{sys}}$  should be negative

**19. Define an isolated system.**

**Ans:** It is the system which can exchange neither matter nor energy with the surroundings. For such a system matter and energy remain constant. E.g., a system consists of 100 ml water in an insulated container.

**20. What is an open system?**

**Ans:** It is the system which is capable of exchanging both matter and energy with the surroundings. E.g., a system consists of 100ml water in an open container. It can exchange energy with the surroundings. Since the vessel is opened, the water vapour (matter) can escape to the surroundings also.

**21. Write Gibb's – Helmholtz equation? What is its application?**

**Ans:**  $\Delta G = \Delta H - T \left( \frac{\partial \Delta G}{\partial T} \right)_P$ , where,  $\Delta G$  = free energy change of a system,  $\Delta H$  = enthalpy change of a system and  $T$  = temperature in kelvin.

Applications:

(i) Enthalpy change ( $\Delta H$ ) for the cell reaction can be calculated.

(ii) Entropy change ( $\Delta S$ ) can be calculated.

(iii) It is used to calculate  $\Delta H$  from values from free energy change at two different temperatures.

**22. What is the significance of free energy?**

**Ans:** Decrease in free energy ( $-\Delta G$ ) of a process at constant temperature and pressure is equal to useful work done by the system.

**23. What is a state function?**

**Ans:** State function is the thermodynamic property which depends only on the state of the system and is independent of the path followed to bring about the change. E.g., internal energy, enthalpy, entropy etc.

**24. What is the entropy change in reversible and irreversible processes?**

**Ans:** Entropy change in a reversible process is zero.  $\Delta S_{Total} = 0$

Entropy of the system increases in an irreversible process.  $\Delta S_{Total} > 0$

**25. What is standard free energy change?**

**Ans:** Standard free energy change ( $\Delta G^0$ ) is defined as the free energy change for a process at 298 K in which the reactants in their standard states are converted into products in their standard states. Thus,

$$\Delta G^0 = \sum G_{products}^0 - \sum G_{reactants}^0$$

**26. Write any two Maxwell's thermodynamic relations.**

**Ans:** 1.  $[\partial T / \partial V]_S = [-\partial P / \partial S]_V$

2.  $[\partial S / \partial V]_T = [\partial P / \partial T]_V$

where  $\partial T$  = change in temperature

$\partial V$  = change in volume

$\partial P$  = change in pressure

$\partial S$  = change in entropy

**27. The value of equilibrium constant for a reaction is found to be 10,000 at 25 °C. Calculate  $\Delta G^0$  for the reaction.**

**Ans:** We know that  $\Delta G^0 = -RT \ln K$ .

Given  $K = 10,000$ ;  $T = 25 + 273 = 298$  K;  $R = 8.314$  J/K/mol

On substituting,  $\Delta G^0 = -8.314 \times 298 \times 2.303 \log 10000$

$$= -22823.2 \text{ J/mol} = -22823.2 \times \frac{1.9877}{80314} = -5456.6 \text{ cal.}$$

**28. Calculate the change in entropy accompanying the isothermal expansion of 4 moles of an ideal gas at 300 K until its volume has increased three times.**

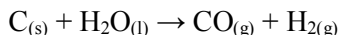
**Ans:** Entropy change in an isothermal expansion of an ideal gas

$$\Delta S = 2.303 nR \log \frac{V_2}{V_1}$$

Given  $V_1 = 1$ ,  $V_2 = 3$ ;  $n = 4$ ;  $R = 1.987$  cal/K/mol

$$\Delta S = 2.303 \times 4 \times 1.987 \times \log (3/1) = 8.733 \text{ cal}$$

**29. Predict whether the following reaction is spontaneous or not at 25 °C.**



$\Delta H = 31.4$  kcal/mol and  $\Delta S = 32$  cal/deg at 25 °C.

**Ans:** We know that  $\Delta G = \Delta H - T\Delta S$

Given  $\Delta H = 31.4$  kcal;  $\Delta S = 32$  cal or 0.032 kJ;  $T = 298$  K

On substituting these values in the above equation

$\Delta G = 31.4 - 298 \times 0.032 = 21.9$  kJ. Since  $\Delta G$  is positive the reaction is non spontaneous.

**30. What do you mean by a thermodynamic system?**

**Ans:** A thermodynamic system is defined as any portion of matter under consideration, which is separated from the surroundings by real or imaginary boundaries. A system usually has a definite amount of a specific substance.

**31. What is an isothermal process?**

**Ans:** Those processes in which the temperature remains fixed are termed isothermal processes. This is achieved by placing the system in a thermostat. i.e.  $dT = 0$ .

**32. What do you mean by an adiabatic process?**

**Ans:** Adiabatic process is the one in which no heat can leave or enter the system. This is achieved by carrying out the process in an insulated container. i.e.  $dq = 0$ .

**33. What is an isobaric process?**

**Ans:** An isobaric process is carried out at constant pressure. i.e.,  $dP = 0$ .

**34. What do you mean by isochoric process?**

**Ans:** Those processes in which the volume is kept constant. i.e.,  $dV = 0$ .

**35. Calculate the entropy change for the reversible isothermal expansion of 10 moles of an ideal gas to 50 times its original volume at 298 K. (Jan 2014)**

**Ans:**

$$\Delta S = 2.303 nR \log \frac{V_2}{V_1}$$

Given  $V_1 = 1$ ,  $V_2 = 50$ ;  $n = 10$ ;  $R = 1.987 \text{ cal/K/mol}$

$$\Delta S = 2.303 \times 10 \times 1.987 \times \log (50/1) = 77.7 \text{ cal}$$

**PART B**

**1. Distinguish between the followings:**

a) Open system and closed system.

**Closed System:** - can exchange energy but not matter with its surroundings.

**Open System:** - can exchange energy as well as matter with its surroundings.

b) Reversible process and Irreversible process. **(June 2014)**

**Irreversible Process:** - If the driving force and the opposing force differ by a large amount.

**Reversible Process:** - If the driving force and opposing force differ by an infinitesimally small amount.

c) Closed system and isolated system.

**Isolated System:** - cannot exchange both energy and matter with its surroundings

**Closed System:** - can exchange energy but not matter with its surroundings.

d) Intensive and extensive properties.

**Intensive properties:** - Properties which depend only on nature of the substance present in the system.

**Examples:** Temperature, pressure, concentration and density.

**Extensive properties:** - Properties which depend on the amount of substance present in the system.

**Examples:** Mass, volume, internal energy (E), enthalpy (H), entropy (S), Free Energy (G).

e) Adiabatic process and an isothermal process.

**Isothermal Processes:** - processes in which the temperature remains fixed i.e.  $dT=0$

**Adiabatic processes:** - processes in which no heat can flow into or out of the system i.e.  $dq=0$

**2. What are the limitations of first law of thermodynamics? Explain how second law of thermodynamics overcomes these limitations.**

1. Second law predicts the feasibility of a process and also it explains why it is not possible to convert heat into an equivalent amount of work.

2. The second law is able to predict the direction of energy transformed and spontaneous process.

**3. Explain with at least two examples that a spontaneous process is always followed by an increase in the randomness of the system.**

$$\Delta S_{\text{Total}} = \Delta S_{\text{System}} + \Delta S_{\text{Surroundings}}$$

$$\Delta S_{\text{Total}} = \text{Positive}$$

$$\Delta S_{\text{Total}} > 0$$

i.e., In an irreversible process, the entropy of the system increases.

**4. Derive the expression of entropy change in (i) a reversible process and (ii) an irreversible process.**

Entropy change in a reversible (non-spontaneous) process

$$\Delta S_{\text{Total}} = 0$$

i.e., In a reversible isothermal process, there is no net change in entropy.

Entropy change in an irreversible (spontaneous) process

$$\Delta S_{\text{Total}} = \text{Positive}$$

$$\Delta S_{\text{Total}} > 0$$

**i.e., In an irreversible process, the entropy of the system increases.**

Since all spontaneous process is natural and irreversible process, the entropy of the system always increases.

- 5. Derive the expression of entropy change for an ideal gas (i) as a function of temperature and pressure and (ii) as a function of temperature and volume.**

(or)

- 6. Derive the expression of the entropy change for an isothermal process.**

**Entropy Change in an Isothermal Expansion of an Ideal Gas**

$$\Delta S = nR \ln \frac{V_2}{V_1} \quad \text{Or}$$

$$\Delta S = 2.303nR \log \frac{V_2}{V_1} \quad \text{Or}$$

$$\Delta S = 2.303nR \log \frac{P_1}{P_2}$$

- 7. Write down Gibbs free energy equation. Under what conditions a reaction is spontaneous at all temperatures. (or) Explain the significance of free energy. (June 2014)**

Available energy (G) = Total energy (H) – Unavailable energy (TS)

$$G = H - TS$$

$$\Delta G = \Delta H - T\Delta S$$

$$-\Delta G = w_{\text{useful}}$$

Thus, the decrease of free energy(-ΔG) of a process at constant temperature and pressure is equal to the useful work obtainable from the system.

ΔH = -ve, ΔS = +ve, ΔG will be negative

∴ the reaction will be spontaneous at all temperatures.

- 8. Derive Gibbs-Helmholtz equation and mention its applications. (Jan 2014, June 2014)**

**GIBBS'S HELMHOLTZ EQUATION (OR) RELATION BETWEEN ΔG and ΔH**

$$\Delta G = \Delta H + T \left[ \frac{\partial(\Delta G)}{\partial T} \right]_p \quad \text{Or}$$

$$\Delta A = \Delta E + T \left[ \frac{\partial(\Delta G)}{\partial T} \right]_p$$

**Significance of Gibbs – Helmholtz equation**

1. - relates (ΔG) to (ΔH) and the rate of change of free energy with temperature at constant pressure.
2. - helps in understanding the nature of the chemical reaction

**Application of Gibb's – Helmholtz Equation**

Calculation of Enthalpy Change (ΔH) for the cell Reaction (Galvanic Cell)

1. Calculation of EMF of the cell
2. Calculation of Entropy Change (ΔS)
3. Calculation of ΔH from the values of free energy change at two different temperature

- 9. Derive any two forms Maxwell relations. (June 2014)**

$$\left( \frac{\partial T}{\partial V} \right)_S = - \left( \frac{\partial P}{\partial S} \right)_V$$

$$\left(\frac{\partial T}{\partial P}\right)_S = \left(\frac{\partial V}{\partial S}\right)_P$$

$$\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V$$

$$\left(\frac{\partial S}{\partial P}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_P$$

### Significance of Maxwell Relations

- Using these relations tedious experimental work can be reduced
- To deduce many other thermodynamic relations viz., Clapeyron equation, thermodynamic equation of state, etc.

**10. Give the mathematical statement of Clausius-Clapeyron equation for liquid- vapour equilibria.**

(or)

**11. Derive the Clausius - Clapeyron equation both in the differential as well as integrated forms.**

$$\frac{dP}{dT} = \frac{q}{T(V_B - V_A)} \quad \dots\dots\dots (18)$$

### Applications of clausius – clapeyron equation

- Calculation of latent heat of vapourization
- Calculation of boiling point (or) freezing point
- Calculation of Vapour pressure at another temperature
- Calculation of a molar elevation constant

**12. Derive Vant Hoff's isotherm equation. (Jan 2014)**

$$\Delta G^\circ = -RT \ln K_{eq} + RT \ln \left[ \frac{(P_C)^c (P_D)^d}{(P_A)^a (P_B)^b} \right]_{eq}$$

(Or)

$$-\Delta G^\circ = RT \ln K_{eq} - RT \ln \left[ \frac{(P_C)^c (P_D)^d}{(P_A)^a (P_B)^b} \right]_{eq}$$

**13. Derive Vant Hoff's isochore**

$$-\Delta H^\circ = -RT^2 \frac{d(\ln Kp)}{dT} \quad (\text{Or})$$

$$\Delta H^\circ = RT^2 \frac{d(\ln Kp)}{dT} \quad (\text{Or})$$

$$\frac{d(\ln Kp)}{dT} = \frac{\Delta H^\circ}{RT^2}$$

$$\ln K_p^2 - \ln K_p^1 = \frac{\Delta H}{2.303R} \left[ \frac{T_2 - T_1}{T_2 T_1} \right]$$

**14. Discuss the criteria for chemical reaction to be spontaneous (Jan 2014).**

**Criteria for the Spontaneous Process (or) Gibbs Free Energy and Spontaneity**

$$-T\Delta S_{total} = \Delta G \quad (\text{or}) \quad T\Delta S_{total} = -\Delta G$$

When  $\Delta G = -ve$  ( $\Delta G < 0$ ), the process is spontaneous.

When  $\Delta G = 0$ , the process is in equilibrium.

When  $\Delta G = +ve$  ( $\Delta G > 0$ ), the process is non-spontaneous.

Conditions of Spontaneity Enthalpy, Entropy and Free energy changes and the Nature of Reaction

$\Delta H$	$\Delta S$	$\Delta G = \Delta H - T \Delta S$	conclusion
- (exothermic)	+	-	Spontaneous change
- (exothermic)	-	-(at low T)	Spontaneous change
		+(at high T)	Non-Spontaneous
+ (endothermic)	+	+(at low T)	Non-Spontaneous
		-(at high T)	Spontaneous
+ (endothermic)	-	+	Forbidden in the forward direction

**15. Compute free energy change when 5 moles of an ideal gas expands reversibly and isothermally at 300 K from an initial volume of 50 L to 1000 L. ( Jan 2014)**

$$\Delta H = 20,000 \text{ cal mole}^{-1}, n = 5, T = 300\text{K}, V_1 = 50 \text{ L}, V_2 = 1000 \text{ L}$$

$$\Delta S = 2.303nR \log \frac{V_2}{V_1}$$

$$\Delta S = 59.147 \text{ cal K}^{-1}$$

$$\Delta G = \Delta H - T \Delta S$$

$$\Delta G = 2,255.9 \text{ cal}$$

### UNIT-III PHOTOCHEMISTRY AND SPECTROSCOPY

#### PART – A

**1. Differentiate photochemical reactions and thermal reaction.**

**Ans:**

S.No	Photochemical Reactions	Dark or Thermal Reactions
1.	The activation energy is provided by light radiations of visible or ultraviolet of electromagnetic spectrum.	The activation energy is provided by the collision of reactant molecules.
2.	Examples: Ozonisation of oxygen; Photosynthesis occurring in plants	Examples: Formation of ammonia; Dissociation of $\text{PCl}_5$ .

**2. State Lambert's law.**

**Ans:** Lambert's law states that "When a beam of monochromatic radiation passes through a transparent absorbing medium, the rate of decrease of intensity of radiation with the thickness of the absorbing medium is proportional to the intensity of incident radiation".

**3. State Beer's law.**

**Ans:** Beer's law states that, "When a beam of monochromatic radiation passes through a solution containing an absorbing substance, the rate of decrease of intensity of radiation with the thickness of the absorbing solution is proportional to the intensity of incident radiation as well as the concentration of solution".

**4. What are the limitations of Beer-Lambert's law?**

**Ans:** a) When the absorbing solute dissociates or associates in solution.

b) At higher concentrations on an absorbance versus concentration plot, where the curve bends towards the concentration axis.

c) In scattering of light due to particulates in the sample.

d) In changes of refractive index of the medium with concentration.

**5. What is photochemistry?**

**Ans:** The study of chemical reactions, isomerization and physical behavior that may occur under the influence of visible or ultraviolet light is called photochemistry.

i.e. the study of physical and chemical changes in the molecules by the interaction of light is known as photochemistry.



**6. What are the laws of photochemistry?**

- Ans:** 1. Grotthus-Draper law  
2. Stark-Einstein law of photochemical equivalence  
3. Lambert's law  
4. Beer Lambert's law

**7. State Grotthus-Draper law**

**Ans:** Grotthus – Draper law states that “When the light falls on any substance, only the fraction of light that is absorbed by a substance can bring a chemical change; the reflected or transmitted light does not produce any such effect”.

**8. State Stark-Einstein law.**

**Ans:** Stark–Einstein law states that “When an atom or molecule absorbs light of a given frequency, it absorbs photon of one quantum only”.

**9. Mention the causes for high quantum yield.**

- Ans:** 1. Absorption of radiations in the primary step involves production of atoms or free radicals, which initiate a series of chain reactions  
2. Formation of intermediate products will acts as a catalyst.  
3. The active molecules, produced after absorption of radiation, may collide with other molecules and activate them which in turn activate other reacting molecules.

**10. Mention any two reasons for low quantum yield.**

- Ans:** 1. Excited molecules may lose their energy by collision with non-excited molecules. In such cases, the value of  $\phi$  will be less than one  
2. The excited molecules produced in the primary reaction may recombine to form the reactants so as to give low quantum yield.

**11. Distinguish between resonance fluorescence and sensitized fluorescence.**

**Ans: Resonance fluorescence:** When an incident light falls on a substance and it emits light of same frequency as that of incident light, the phenomenon is known as *resonance fluorescence*.

**Sensitized fluorescence:** A substance which is normally non-fluorescent, may be made fluorescent in the presence of other fluorescent substances. This phenomenon is known as *sensitized fluorescence*.

**12. Differentiate inter conversion and inter-system crossing.**

**Ans: Inter conversion:** If the transitions occur between states of the same multiplicity without emitting heat, it is called internal conversion.

**Inter-system crossing:** If the transitions occur between states of the different multiplicity without emitting heat, it is called intersystem crossing.

**13. What is meant by quenching of fluorescence?**

**Ans:** When an excited state of molecule undergoes collision with another molecule before it has a chance to radiate as fluorescence, the process may be stopped. This phenomenon is known as *quenching*.

**14. What are photosensitized reactions?**

**Ans:** Reactions in which the molecules absorbing light do not react themselves but can induce other molecules to react are called *photosensitized reactions*

**15. What are photosensitizers? Give two examples.**

**Ans:** Substances which when added to a reaction mixture helps to induce the photochemical reaction but do not react themselves are called *photosensitizers* and the process is called *photosensitization*.

**Examples**

- (i) Chlorophyll acts as photosensitizer for the reaction between  $\text{CO}_2$  and  $\text{H}_2\text{O}$  to form carbohydrate (photosynthesis).  
(ii) Mercury vapours acts as photosensitizer for the decomposition of ammonia.

**16. State Beer Lambert law**

**Ans:** When a beam of monochromatic radiation passes through a transparent absorbing medium, the amount of light absorbed is proportional to the concentration of the absorbing substance and the thickness of the absorbing material.

$$A = \epsilon Cl$$

A = absorbance ( $\log I_0/I$ );  $\epsilon$  = molar absorptivity

C = molar concentration of the solution; l = thickness or path length of the cell.

**17. What is quantum yield?**

**Ans:** Quantum yield is defined as the number of molecules of reactants reacted or products formed per quantum of light absorbed. It is denoted by  $\phi$  and is also known as quantum efficiency.

$\Phi$  = Number of molecules formed or reacted in a given time / Number of quanta (photons) absorbed in the same time

**18. Give the formula for energy contained in one Einstein**

**Ans:**  $E = Nh\nu = Nhc/\lambda$

**19. Give the formula for energy contained in one photon**

**Ans:**  $E = h\nu = hc/\lambda$

**20. Compare the free energy change in photochemical and thermo chemical reactions.**

**Ans:** In photochemical reactions the free energy change may be positive or negative, while in thermo chemical reactions it is always negative.

**21. Calculate the energy associated with (a) One photon or quantum**

**(b) One Einstein of radiation of wavelength 530 nm.**

**Ans:** (a) Energy of photon =  $hc/\lambda$

$$= 6.625 \times 10^{-34} \text{ Js} \times 3 \times 10^8 \text{ ms}^{-1} / 530 \times 10^{-9} \text{ m} = 3.76 \times 10^{-19} \text{ J}$$

(b) Energy per Einstein,  $E = Nh\nu$

$$= 6.023 \times 10^{23} \times 3.76 \times 10^{-19} \text{ J} = 2.26 \times 10^5 \text{ J}$$

**22. A solution of thickness 2 cm transmits 40% incident light. Calculate the concentration of the solution given  $\epsilon = 6000 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$**

**Ans:** Given: Transmittance  $I/I_0 = 0.4$ ;  $I_0/I = 2.5$ ;  $\log I_0/I = 0.3980$ ;

$$\epsilon = 6000 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$$

$$l = 2 \text{ cm}$$

$$\log I_0/I = \epsilon Cl$$

$$C = (0.3980) / (6000 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1} \times 2 \text{ cm}) = 3.316 \times 10^{-5} \text{ mol dm}^{-3}$$

**23. If the transmittance of a solution is 19.4% what is its absorbance or optical density?**

**Ans:** Given:  $T = 0.194$ ;

$$\text{Absorbance} = -\log T = 1/\log T = 0.712$$

**24. A solution of transmission of 20% when taken in a cell of 2.5 cm thickness. Calculate its concentration if the molar absorption coefficient is  $12000 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$**

**Ans:** Given:  $T = 0.2$ ;  $l = 2.5 \text{ cm}$ ;  $\epsilon = 12000 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$

$$\log 1/T = \epsilon Cl; \log 1/0.2 = 12000 \times 2.5 \times c$$

$$c = 0.699/(12000 \times 2.5); c = 2.33 \times 10^{-5} \text{ mol/dm}^3$$

**25. What is fluorescence?**

**Ans:** When a beam of light is incident on certain substances, they emit visible light and they stop emitting light as soon as the incident light is cut off, this phenomenon is called **fluorescence**. Substances that exhibit **fluorescence** are called **fluorescent** substances.

Example: Calcium fluoride, Uranium, Chlorophyll, Vapours of Sodium, Iodine, Mercury.

**26. What is phosphorescence? (June 2014)**

**Ans:** When light radiation is incident on certain substances, they emit light continuously even after the incident light is cut off. This type of delayed **fluorescence** is called phosphorescence. The substances which exhibit phosphorescence are called phosphorescent substances.

Example: Zinc sulphide, Alkaline- earth sulphide.

**27. What is chemiluminescence? (Jan 2014)**

**Ans:** If light is emitted at ordinary temperature, as a result of chemical reactions, then the phenomenon is known as chemiluminescence.

Eg: Grignard reagent produces greenish blue light, on oxidation by air.

**28. What are the infrared active molecules? Give examples.**

**Ans:** Those molecules which possess either a permanent dipole moment or the dipole moment arise due to vibration of atoms in molecules are *infrared active*. Eg: CO, NO, CN, HCl.

**29. What are the limitations of IR spectroscopy?**

**Ans:** (i) The aqueous solutions cannot be used for infrared spectra. (ii) Samples containing mixture of substances cannot be analyzed. (iii) Background solvent or solid must be relatively transparent in the spectral region of interest

**30. What happens to a molecule when it is irradiated with (i) IR light (b) Microwave radiation?**

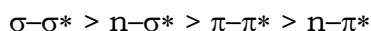
**Ans:** (i) IR light causes to undergo vibrational and rotational transitions.  
(ii) Microwave radiation causes to rotation transition.

**31. Give the regions of UV-visible spectrum.**

**Ans:** (i) The near ultraviolet region: It ranges from 200 to 380 nm.  
(ii) The visible region: It ranges from 380 to 780 nm.

**32. Give the order of energy required for electronic transitions in organic molecules.**

**Ans:** The order of required energy of various electronic transitions in organic molecules is:



**33. Describe the terms bathochromic shift and hypsochromic shift.**

**Ans:** *Bathochromic Shift (Red Shift):* Shift of an absorption maximum towards longer wavelength is known as bathochromic shift. It may be caused by: (a) when an auxochrome is attached to a carbon- carbon double bond (b) changing a solvent.

*Hypsochromic Shift (Blue Shift):* Shift of an absorption maximum towards shorter wavelength is known as hypsochromic shift. It may be caused by a change of solvent or by removing conjugation.

**34. What is spectrophotometer?**

**Ans:** Spectrophotometer is composed of two devices namely a spectrometer (capable of producing a light of particular wavelength) and a photometer (capable of measuring the intensity of transmitted light). It can scan an entire wavelength range of near UV and visible regions (200-800nm) in order to measure the absorption of light by a sample as a function of wavelength. The corresponding plot of absorbance versus wavelength is known as UV- visible spectrum.

**35. Write the principle of UV spectroscopy.**

**Ans:** When a light of specific wavelength is absorbed by a substance, the valence (outer) electrons are promoted from their normal ground state (either  $\sigma$ - bonding orbitals or  $\pi$ - bonding orbitals or non-bonding orbitals lone pair electrons) to higher energy excited states. That is, a transition occurs from one of these orbital's to an empty orbital, usually an anti-bonding orbital,  $\sigma^*$  or  $\pi^*$ . The energy ( $E=h\nu=hc/\lambda$ ) required for this transition corresponds to the absorption of light by the sample.

**36. What are the common sources used in uv-visible spectrophotometer?**

**Ans:** Most commonly used sources of uv radiation are the hydrogen lamp and the deuterium lamp. Tungsten filament lamp is the most commonly used source for visible radiation.

**37. Give any two detectors used in uv-visible spectrophotometer.**

**Ans:** There are three basic kinds of detectors used in ultraviolet and visible region.  
They are (i) Photocells (ii) Phototubes and (iii) Photomultiplier tubes.

**38. What are the wavelength ranges for UV, IR and Visible regions?**

**Ans:**

S.No	Name of the Region	Wavelength Range
1.	Infrared Region	0.8 – 200 $\mu$ m
2.	Ultraviolet Region	200 – 380 nm
3.	Visible Region	380 – 780 nm

**39. What is an Electromagnetic spectrum?**

**Ans:** The arrangement obtained by arranging various types of electromagnetic waves in order of their increasing wavelengths or decreasing frequencies is called an electromagnetic spectrum.

**40. Define absorbance (A).**

**Ans:** Absorption of a solution is defined as the negative logarithm to the base 10 of the transmittance T of the solution i.e.,  $A = \log 1/T = \epsilon c l$ . where  $\epsilon$ = molar absorptivity, c= molar concentration of solution, l= thickness or path length of the cell.

**41. Define transmittance.**

**Ans:** It is defined as the fraction of the incident light that is transmitted by a given species is called transmittance  $T = I/I_0$

I is the intensity of transmitted light,  $I_0$  is the intensity of incident light.

**42. What is monochromator?**

**Ans:** A monochromator is a device which resolves polychromatic radiation into its individual wavelengths and isolates these wavelengths into very narrow bands.

### 43. How does molecular spectrum arise?

**Ans:** It arises due to the interaction of electromagnetic radiation with molecules. This results in transition between rotational, vibrational and electronic energy levels.

### 44. What are chromophores and auxochromes? Give some examples.

**Ans:** Groups with multiple bonds are called chromophores. Ex.  $-N=N-$  ;  $-N=O$ ;

Auxochromes are the groups which could not cause any colour effects by themselves but will deepen the colour of the chromophores. Ex.  $-OH$ ,  $-OR$ ,  $-NH_2$

### 45. What is meant by wave number? (Jun 2014)

**Ans:** The wave number is defined as the number of waves per centimeter. It is denoted as  $\tilde{\nu}$ .

$$\tilde{\nu} = 1 / \lambda$$

### 46. What is finger print region? Mention its importance.

**Ans:** The IR region  $1400-700 \text{ cm}^{-1}$  gives very rich and intense absorption bands. This region is called finger print region. Using this finger print region, it is possible to identify the organic compounds.

### 47. What are the sources of UV light in UV- visible spectrophotometer?

**Ans:** Hydrogen discharge or deuterium lamp, mercury lamp, quartz capillary is the sources of UV light in UV- visible spectrophotometer.

### 48. Convert the % T values to A.(i) 32%

**Ans:** % T=32 or T= 0.32,  $A = \log 1/T$

$$A = \log 1/0.32 = 0.49$$

### 49. Calculate the absorbance of $1.03 \times 10^{-3} \text{ M}$ solution if $\epsilon = 720$ and path length is 1cm.

**Ans:**  $A = \epsilon l c$ ,  $= 720 \times 1 \times 1.03 \times 10^{-3}$ ,  $= 0.74$ .

### 50. What are the sources of IR radiation in IR spectrophotometer?

**Ans:** Nernst Glower and Nichrome wire are the sources of IR radiation in IR spectrophotometer.

### 51. Mention the various types of electronic transitions taking place in UV spectroscopy.

**Ans:**  $n \rightarrow \sigma^*$ ,  $n \rightarrow \pi^*$ ,  $\sigma \rightarrow \sigma^*$ ,  $\pi \rightarrow \pi^*$  are the various electronic transitions in UV spectroscopy.

### 52. Mention few applications of IR spectroscopy.

**Ans:** a) Identification of Hydrogen bonding. b) Identification of the compounds.  
c) Identification of functional groups. d) Determination of molecular weight.

### 53. Calculate the number of modes of vibrations for the following molecules.i. $\text{CH}_4$ ii. $\text{CO}_2$

**Ans:**  $\text{CH}_4$  is a non linear molecule. So the fundamental modes of vibration are equal to  $3N-6$ .

For  $\text{CH}_4$   $N=5$ ,  $3 \times 5 - 6 = 9$ .

$\text{CO}_2$  is a linear molecule. Hence the fundamental modes of vibration are equal to  $3N- 5$ .

Here,  $N= 3$ ,  $3 \times 3 - 5 = 4$ .

### 54. Mention the applications of UV spectroscopy.

**Ans:** 1. Electronic spectra are useful in the determination of atomic groups present in organic compounds.

2. The percentage of various keto-enol forms present can be studied using electronic spectra.

3. The impurities in organic compounds can be detected using electronic spectra since the bands due to impurities are very intense.

4. Molecular weight of a compound may be determined..

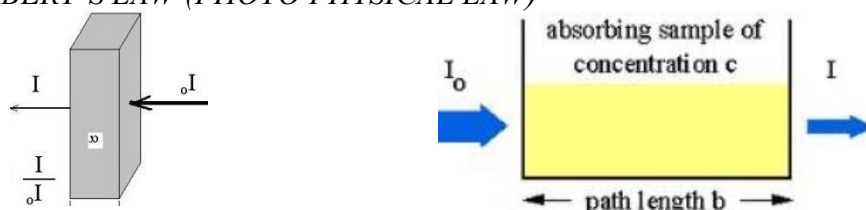
### 55. What is meant by absorption of radiation? (Jan 2014)

**Ans:** When a beam of light radiation falls on a substance (atom or molecule) it absorbs a photon of light and moves from ground state to excited state causing electronic, vibrational, rotational or combination of these transitions.

## PART - B

### 1. Derive the mathematical expression for Beer - Lamberts law.

BEER LAMBERT'S LAW (PHOTO PHYSICAL LAW)



**Lambert's law:** Lambert's law states that "When a beam of monochromatic radiation is passed through a homogeneous absorbing medium, the rate of decrease of intensity of the radiation (-dI) with thickness of absorbing medium (dx) is proportional to the intensity of incident radiation (I).

i.e.,  $\frac{-dI}{dx} \propto I$

$$\frac{-dI}{dx}$$

$$= K I$$

(Where K = absorption coefficient.)

Integrating on both sides,  $\frac{-dI}{I} = K dx$

$$-\ln I / I_0 = K x$$

$$2.303 \log I_0 / I = K \cdot x$$

$$\log \frac{I_0}{I} = \frac{K}{2.303} \cdot x$$

$$A = \epsilon x \quad \text{Lambert's law.}$$

**Beer's law:** This is used for dilute solution. When a beam of monochromatic radiation is passed through a solution of an absorbing substance, the rate of decrease of intensity of radiation (-dI) with thickness of the absorbing solution (dx) is proportional to the intensity of incident radiation (I) as well as the concentration of the solution (C).

i.e.,  $\frac{-dI}{dx} \propto IC$

$$\frac{-dI}{dx}$$

$$= K IC$$

(Where K = absorption coefficient).

Integrating

$$-dI/I = KCdx$$

$$-\ln I / I_0 = KCx$$

$$\ln I_0 / I = KCx$$

$$2.303 \log I_0 / I = KCx$$

$$\log I_0 / I = \frac{KCx}{2.303}$$

$$A = \epsilon C x \quad \text{Beer-Lambert's law.}$$

$\log (I_0 / I) = A$ , Absorbance (or) Optical activity

$K/2.303 = \epsilon$ , molar absorptivity constant.

**Application of Beer-Lambert's law:** Concentration of unknown solution- determination.

**Step 1:**  $C_s$  = Solution of standard concentration,  $A_s$  = Absorbance

Beer- Lambert's law,  $A_s = \epsilon C_s x$ ,  $A_s / C_s = \epsilon x$  ----- (1)

**Step 2:**  $C_u$  = Sample solution of unknown concentration,  $A_u$  = Absorbance

Beer- Lambert's law,  $A_u = \epsilon C_u x$ ,  $A_u / C_u = \epsilon x$  ----- (2)

Comparing (1) and (2)  $\frac{A_u}{C_u} = \frac{A_s}{C_s}$ ;  $C_u = A_u \cdot \frac{C_s}{A_s}$

**2. Give a detailed account on the photophysical processes which deactivate the excited state molecule.**

### PHOTOPHYSICAL PROCESS:

Molecules go to excited state by absorption of radiation. If the absorbed radiation is not used to produce the reaction, it will be re-emitted as light of longer wavelength.

Types: a) Fluorescence b) Phosphorescence

### FLUORESCENCE:

**1. Definition:** When radiation is passed through substances it get excited and come back to ground state and reemits excess energy. The emission is stopped when incident radiation is cut off.

Substances -fluorescent substances.(eg) Fluorite, Eosin dye, Fluorescein dye, chlorophyll, riboflavin

**3. Applications of fluorescence:**

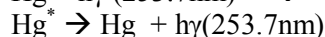
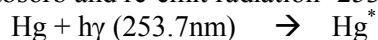
Fluorescent lamps, reflectors -High ways, forged documents, decayed eggs – detection.

**4) Types of Fluorescence:**

a) Resonance fluorescence b) Sensitised fluorescence

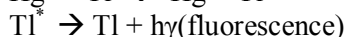
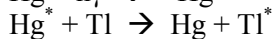
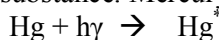
a) Resonance fluorescence: Incident and re-emitted radiations – same wavelength.

Eg. Mercury vapours- absorb and re-emit radiation -253.7nm



b) Sensitized fluorescence: Non-fluorescent substance can be made as fluorescent substance by using foreign fluorescent substances such as Fluorescent Sensitizer.

Eg. Thallium- non- fluorescent substance. Mercury – Fluorescent Sensitizer



### PHOSPHORESCENCE:

When radiation is passed through a substance it is excited and comes to ground state and emits visible light continuously for some time even after the incident light is cut off. The delayed fluorescence is Phosphorescence. Eg. Ruby, emerald, Cadmium sulphide, Barium sulphide

Uses: In dials of clocks and watches, Luminous paints -painting watches, electric switches and advertisement boards.

### 3. Distinguish between fluorescence and phosphorescence. (Jan 2014)

No	FLUORESCENCE	PHOSPHORESCENCE
1	Stops emitting radiation as incident radiation is cut off.	Continues emission of radiation for sometime even after the incident radiation is cut off.
2	Fast process. Occurs in $10^{-8}$ sec.	Slow process. Takes time of $10^{-3}$ to 10s.
3	Allowed transition.	Forbidden transition.
4	It is transition due to of $S_1 \rightarrow S_0$	It is due to transition of $T_1 \rightarrow S_0$
5	Eg. Fluorite, Eosin dye, Fluorescein dye, chlorophyll, riboflavin	Eg. Ruby, emerald, Cadmium sulphide, Barium sulphide
6	Fluorescent lamps, detection-forged documents, of decayed eggs.	Dials of clocks and watches, painting watches, electric switches and advertisement boards.

### 4. Explain the various components and working of UV – Visible spectrophotometer. Write the principle of UV spectroscopy. (Jan 2014, June 2014)

#### Principle

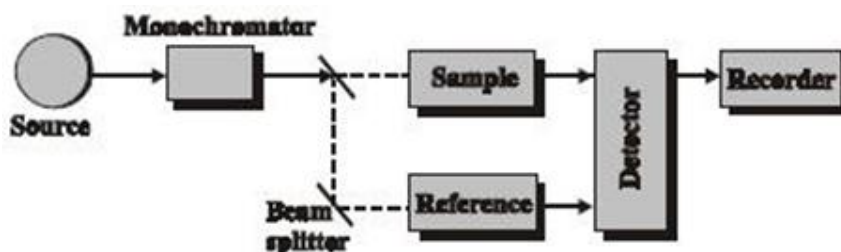
Visible and Ultraviolet (UV) spectra arise from the transition of valency electrons within a molecule or ion from a lower electronic energy level (ground state  $E_0$ ) to higher electronic energy level (excited state  $E_1$ ).

UV transition – 100 to 400 nm, visible – 400 to 750 nm. Amount of energy depends on the difference in energy between ground state and excited state of the electrons.

$$E_1 - E_0 = h\nu$$

#### Instrumentation

1. *Radiations source*: Hydrogen (or) Deuterium lamps.
2. *Monochromators*: Disperse the radiation according to the wavelength. Eg: prism or grating (or) a filter.
3. *Cells (sample cell and reference cell)*: It should be uniform in construction, inert to solvents, must transmit the light of required wavelength used.
4. *Detectors*: It converts the radiation into current. Eg: Photomultiplier tube, Photocell
4. *Recording system*: The signal is recorded by recorder pen.



Block diagram of visible uv spectrophotometer

### **Working of UV- visible spectrophotometer**

The radiation from the source is pass to through the monochromator unit.

It allows a narrow range of wavelength to pass through an exit slit and it is split into two equal beams One-half passed through a transparent cell containing a solution of the compound to be analyzed and the half is passed through an identical cell that contains only the solvent. The instrument can compare the intensities of the two beams.

If the compound absorbs light at a particular wavelength, then intensity of the sample beam (I) will be less than that of the reference beam ( $I_0$ ). The instrument gives output graph, which is a plot of wave length Vs absorbance of the light. This graph is known as an absorption spectrum.

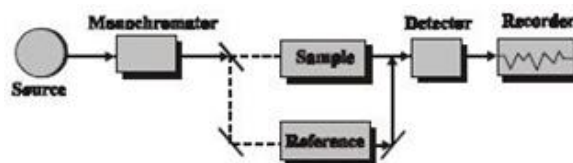
### **5. Discuss the principle and instrumentation of IR spectrometer. (Jan 2014)**

#### **Principle**

An IR spectrum is produced by the absorption of energy by a molecule in the infrared region and the transitions occur between vibrational levels.

#### **Instrumentation**

1. **Radiation source:** i) Nichrome wire, ii) Nernst glower
2. **Monochromator:** It allows only the light of the required wave length to pass through it.
3. **Sample Cell:** It must be transparent to IR radiation.
4. **Detector:** It converts thermal radiant energy into electrical energy.  
Eg: Photoconductivity cell, Thermocouple, Pyroelectric detectors
5. **Recorder:** The recorder records the signal coming out from the detector.



Block diagram of double beam  
IR spectrophotometer.

### **II. Working of IR Spectrophotometer**

The radiation emitted by the source is split into two identical beams having equal intensity. One of the beams passes through the sample and the other through the reference sample. When the sample cell contains the sample, the half-beam travelling through it becomes less intense. When the two half beams (one coming from the reference and the other from the sample) recombine, they produce an oscillating signal, which is measured by the detector. The signal from the detector is passed to the recording unit and recorded.

### **6. State and explain the following laws of photochemistry in detail. (Jan 2014, June 2014)**

#### **(i) GROTTHUS - DRAPER LAW** (Principle of Photochemical activation)

**Statement:** When light radiation falls on any substance, only a fraction of absorbed light can cause a photochemical change.

#### **Limitations of Grotthus - Draper Law:**

1. It is purely qualitative
2. It mainly concerns about the primary process of a photochemical reaction. In secondary process it may fail.

#### **ii) STARK- EINSTEIN LAW**

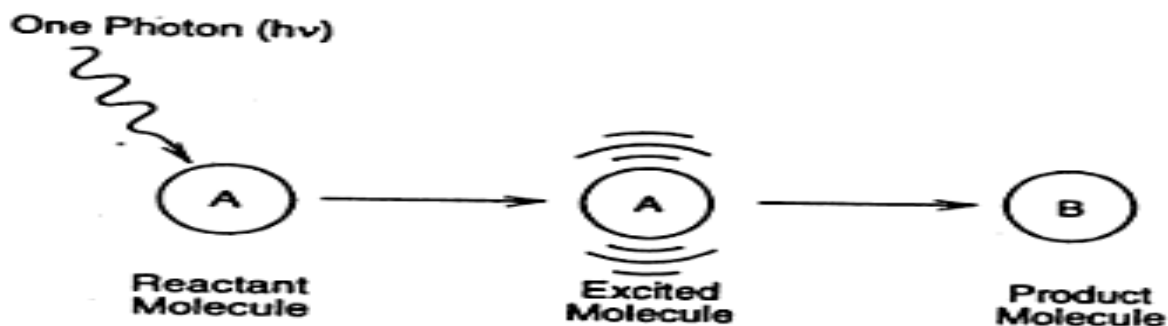
**Statement:** In a primary photochemical process (I step) each molecule is activated by absorption of one quantum of radiation.

#### **Steps Involved:**

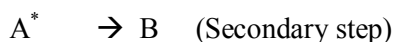
**a) Primary process:** Molecule absorbs photon and forms activated molecule.

**b) Secondary process:** Activated molecule may or may not react. If it reacts it may cause chain of reactions also. This is known as of photochemical reaction.

#### **Illustration:**



From the diagram, it is evident A absorbs a photon of light and gets activated. This is primary step. The activated molecule A\* then decomposes to yield B.



### (iii) BEER –LAMBERT’S LAW

When a beam of monochromatic radiation is passed through a solution of an absorbing substance, the rate of decrease of intensity of radiation ( $-dI$ ) with thickness of the absorbing solution ( $dx$ ) is proportional to the intensity of incident radiation ( $I$ ) as well as the concentration of the solution ( $C$ ).

i.e.,  $\frac{-dI}{dx} \propto I.C$

$$\frac{-dI}{dx} = K I.C \quad (\text{Where } K = \text{absorption coefficient}).$$

Integrating on both sides,

$$\frac{-dI}{I} = K.C dx$$

$$-\ln I / I_0 = K.C x$$

$$\ln I_0 / I = K C x$$

$$2.303 \log I_0 / I = K.C.x$$

$$\log \frac{I_0}{I} = \frac{K}{2.303} \cdot C \cdot x$$

$$\boxed{A = \epsilon C x} \quad \text{Beer Lambert's law.}$$

### 7. What do you understand by the term quantum yield of a photochemical reaction? How is it determined experimentally?

$$\text{Quantum yield } (\Phi) = \frac{\text{Number of molecules reacted (or) formed}}{\text{Number of Photons absorbed}}$$

$\Phi$  value varies from 0 to  $10^6$ .

If a reaction obeys Einstein's law, then one molecule is decomposed per photon.

$$\text{Quantum yield } (\Phi) = \frac{\text{Number of molecules reacted (or) formed}}{\text{Number of Photons absorbed}} = \frac{1}{1} = 1$$

$\Phi > 1$  - high quantum yield.  $\Phi < 1$  - low quantum yield

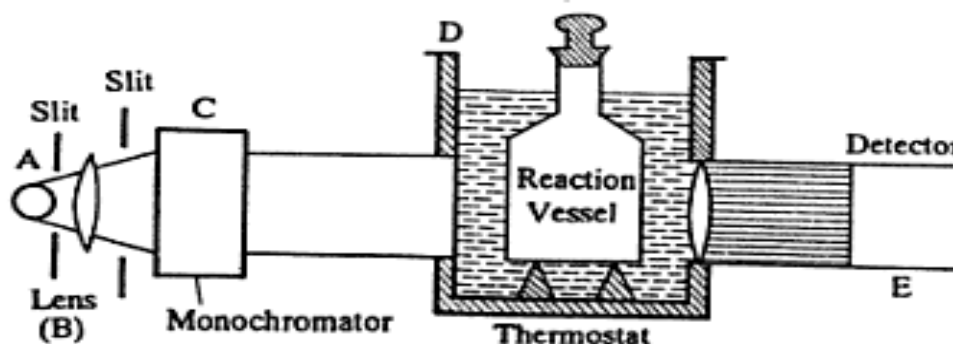
#### **DETERMINATION OF QUANTUM YIELD:**

Determination can be done in two steps.

a) Measuring the number of molecules decomposed or formed.



b) Measuring the amount of quanta absorbed using chemical actinometers:(eg) **Uranyl oxalate actinometer, Ferrioxalate actinometer**



**8. Define quantum efficiency. How would you explain high and low quantum efficiency of photochemical reactions?**

**QUANTUM EFFICIENCY (OR) QUANTUM YIELD( $\Phi$ )**

$$\text{Quantum yield } (\Phi) = \frac{\text{Number of molecules reacted (or) formed}}{\text{Number of Photons absorbed}}$$

$\Phi$  value varies from 0 to  $10^6$ .

$$\text{Quantum yield } (\Phi) = \frac{\text{Number of molecules reacted (or) formed}}{\text{Number of Photons absorbed}} = \frac{1}{1} = 1$$

$\Phi > 1$  - high quantum yield.  $\Phi < 1$  - low quantum yield

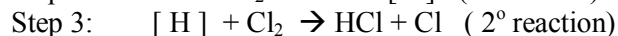
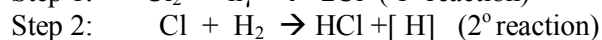
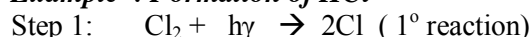
**A) HIGH QUANTUM YIELD AND LOW QUANTUM YIELD: Conditions to get proper quantum yield:**

- All the molecules should have equal reactivity.
- Reactivity of the molecule is temperature independent.
- The activated molecules should decompose to form product.

**Reasons for high yield:**

- In primary step absorption, Free radicals are produced to cause chain reaction.
- Collision of active molecules with other molecules also cause chain reaction
- Intermediate products formed may act as catalysts.
- The exothermic reaction evolving heat may activate further molecules.

**Example : Formation of HCl**

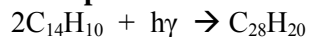


The Cl consumed in step (2) is regenerated in step (3) and the reaction is becoming a chain reaction with  $\Phi = 10^4$  to  $10^6$ .

**Reasons for Low yield:**

- Excited molecules may lose energy by collision with non-excited molecules.
- Molecules may not receive sufficient energy to react.
- Primary step may be reversible.
- Recombination of dissociated fragments to form reactants.

**Example: - Dimerisation of anthracene.**



As per theory, it should have  $\phi = 2$ . But practically found to be  $\phi = 0.5$ .

This is because the reaction is reversible.

**Classification of Photochemical reactions based on quantum yield**

No	Condition	Type	Examples
1	$\Phi$ = small integers like 1,2	Normal quantum yield reactions	1)Dissociation of HI, 2) Dissociation of HBr

2	$\Phi < 1$	Low quantum yield reactions	1) Anthracene dimerisation (0.5) 2) Dissociation of $\text{NH}_3$ (0.2)
3	$\Phi$ is very high ( $10^2$ to $10^6$ )	High quantum yield reactions	1) Combination of $\text{H}_2 + \text{Cl}_2$ ( $10^6$ ) Combination of $\text{CO} + \text{Cl}_2$ ( $10^3$ )

**9. Sketch a Jablonski diagram and show the terms absorption, fluorescence, phosphorescence, internal conversion and inter-system crossing with it.**

#### MECHANISM OF PHOTO PHYSICAL PROCESS BY JABLONSKI DIAGRAM

Jablonski diagram is used to explain mechanism of photo physical process. It involves Non radiative transitions (Internal conversion, Inter System Crossing) and radiative transitions (Fluorescence, Phosphorescence).

#### Singlet and Triplet States:

$(2S + 1)$  is known as spin multiplicity.

If  $(2S + 1) = 1$ , it is singlet state.

If  $(2S + 1) = 3$ , it is triplet state.

#### Ground state:

Before absorbing energy, molecules have paired electrons in ground state. ( $\uparrow\downarrow$ ). The Upward orientation spin gets cancelled by downward orientation spin.

$$\text{i.e., } S_1 = +\frac{1}{2} \quad S_2 = -\frac{1}{2}$$

$$S = S_1 + S_2 = 0$$

Hence,  $2S + 1 = 2(0) + 1 = 1$ , This is singlet ground state

#### Excited state:

On absorbing energy, one of the paired electrons goes to excited state with Parallel orientation ( $\uparrow\uparrow$ ) or Anti-parallel orientation ( $\uparrow\downarrow$ ).

For parallel Orientation,  $S_1 = +\frac{1}{2} \quad S_2 = +\frac{1}{2}$

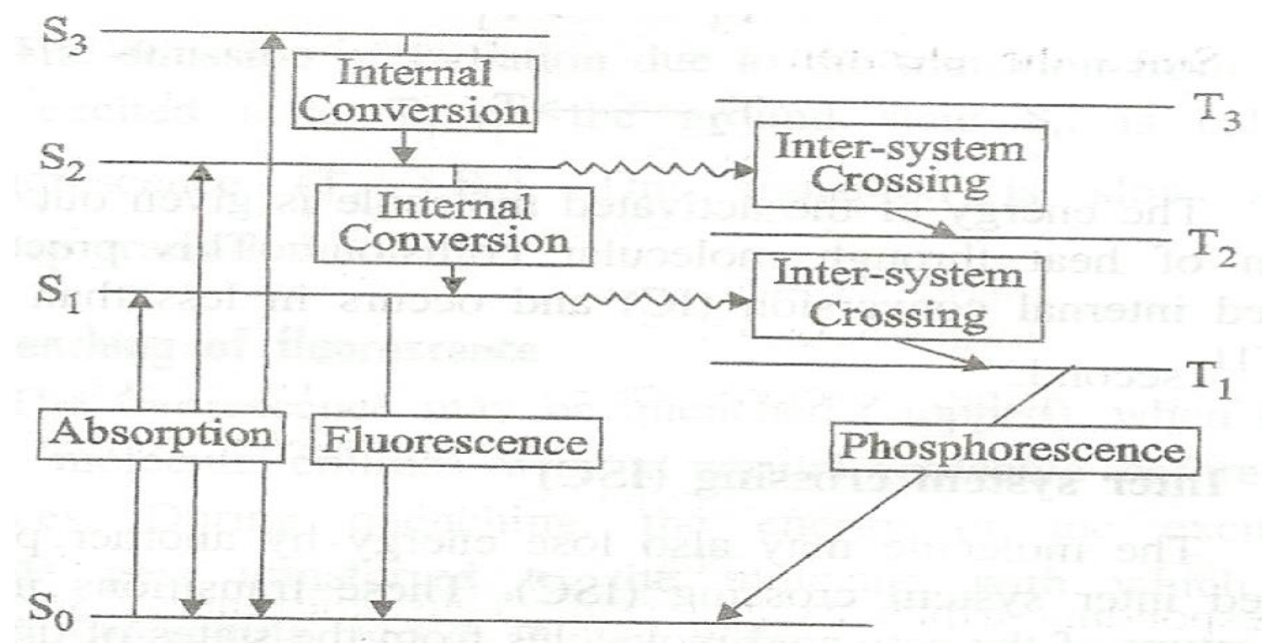
$$S = S_1 + S_2 = 1$$

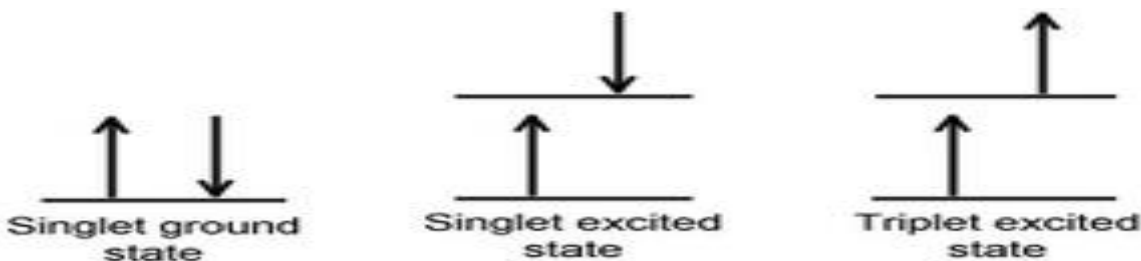
Hence,  $2S + 1 = 2(1) + 1 = 3$ , This is Triplet excited state.

For Anti - parallel Orientation,  $S_1 = +\frac{1}{2} \quad S_2 = -\frac{1}{2}$

$$S = S_1 + S_2 = 0$$

Hence,  $2S + 1 = 2(0) + 1 = 1$ , This is Singlet excited state.



**Non- Radiative transitions:**

If the excited molecules come to lower state without emitting radiation, it is known as non- radiative transition. Here, the energy is lost as heat. This occur within excited states only.

- Internal Conversion:** If the transition is between higher excited state to first excited state of same spins, it is known as Internal Conversion. ( $T_3 \rightarrow T_1$ ,  $T_2 \rightarrow T_1$ ,  $S_3 \rightarrow S_1$ ,  $S_2 \rightarrow S_1$ ). It occurs in less than  $10^{-11}$  seconds.
- Inter - System Crossing:** If the transition takes place between excited states of different spins, it is known as Inter System Crossing. (ISC). ( $S_1 \rightarrow T_1$ ,  $S_2 \rightarrow T_2$ ,  $S_3 \rightarrow T_3$ ). It is forbidden process. It occurs very slowly.
- Non- Radiative transitions:** If the excited molecules come to ground state by emitting radiation, it is known as radiative transition. Here, the energy is emitted as light.

a) **Fluorescence** : If the transition is between excited state to ground state of same spins, it is known as Fluorescence. It is allowed transition and occurs fast i.e., in ( $10^{-8}$ ) seconds. ( $S_1 \rightarrow S_0$ ).

b) **Phosphorescence**: If the transition is between excited state to ground state of different spins, it is known as Phosphorescence. It is forbidden transition and occurs very slowly i.e., in ( $10^{-3}$  to  $10$ ) seconds. ( $T_1 \rightarrow S_0$ ).

**Quenching of Fluorescence:** Stopping the process of fluorescence is known as “quenching”.

- Internal quenching:** If molecule is changed its spin state from  $S_1$  to  $T_1$ , then fluorescence will be stopped. This is known as ‘internal quenching of fluorescence’.
- External quenching:** If quenching is stopped by adding external substance which absorbs energy from excited molecule, then it is known as ‘External quenching of fluorescence’.

The transitions can be tabulated as follows:

No	Type of Transition	Name	Transition involved	Nature of Transition
1	Non- Radiative	Internal Conversion	$T_3 \rightarrow T_1$ , $T_2 \rightarrow T_1$ , $S_3 \rightarrow S_1$ , $S_2 \rightarrow S_1$	Allowed
2		Inter System Crossing	$S_1 \rightarrow T_1$ , $S_2 \rightarrow T_2$ , $S_3 \rightarrow T_3$	Forbidden
3	Radiative	Fluorescence	$S_1 \rightarrow S_0$	Allowed
4		Phosphorescence	$T_1 \rightarrow S_0$	Forbidden

### 10. Explain fluorescence and photosensitization with mechanism. (June 2014)

#### FLUORESCENCE:

1. *Definition:* When a radiation is passed on certain substances, they get excited. On coming back to ground state, it re-emits excess energy. If the emission is stopped as soon as the incident radiation is cut off, such phenomenon is known as Fluorescence.

2. The substances showing this property are 'fluorescent substances'. (eg) Fluorite, Eosin dye, Fluorescein dye, chlorophyll, riboflavin

3. *Applications of fluorescence:*

- Used in fluorescent lamps
- Different inks show different types of fluorescence. So, forged documents are found out.
- When UV light is sent through newly laid eggs, they fluoresce with rose colour while decayed eggs appear in blue colour.
- To prevent accidents, reflectors are used in High ways. They use the principle of fluorescence.

4) *Types of Fluorescence:*

- Resonance fluorescence
- Sensitized fluorescence

#### PHOTO SENSITIZATION:

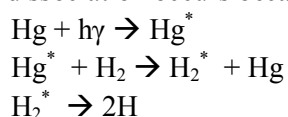
Photo sensitization: The foreign substance which absorbs the radiation and transfers the energy to the reactant is called photo sensitizer. The process is known as photo sensitization.

(eg) Mercury, Cadmium, Zinc, Benzophenone, Sulphur dioxide

When the excited sensitizer loses its energy by collision with other molecules, it is called quenching of photo sensitization.

*Examples of Photo sensitization:*

a) *Dissociation of Hydrogen:* At 253.7 nm, H<sub>2</sub> does not absorb any radiation. But, on adding mercury vapour, the dissociation occurs because of photo sensitization.



b) *Photo synthesis in plants:* CO<sub>2</sub> and H<sub>2</sub>O do not absorb sun light directly in the range of 600 – 700 nm. But in presence of chlorophyll, sun light is absorbed and photosynthesis is taking place.

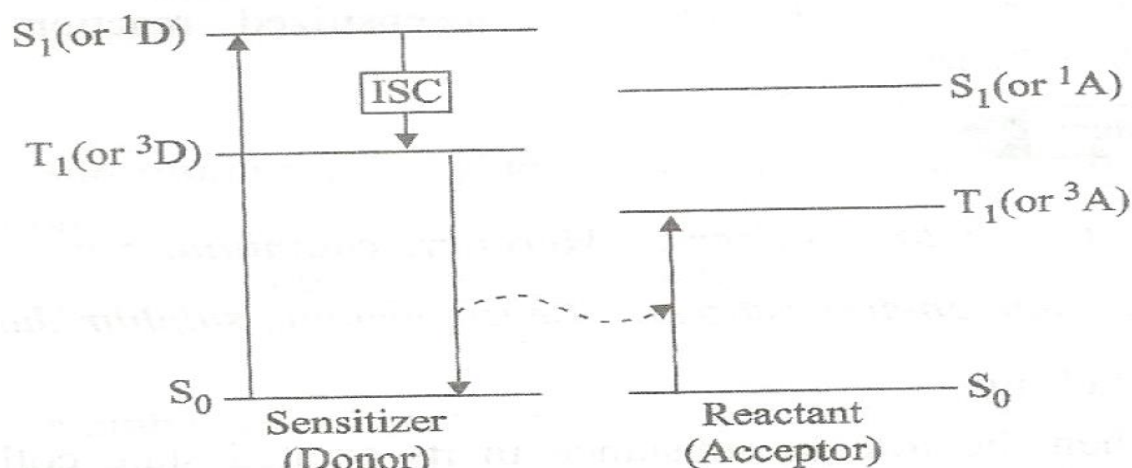


Chlorophyll

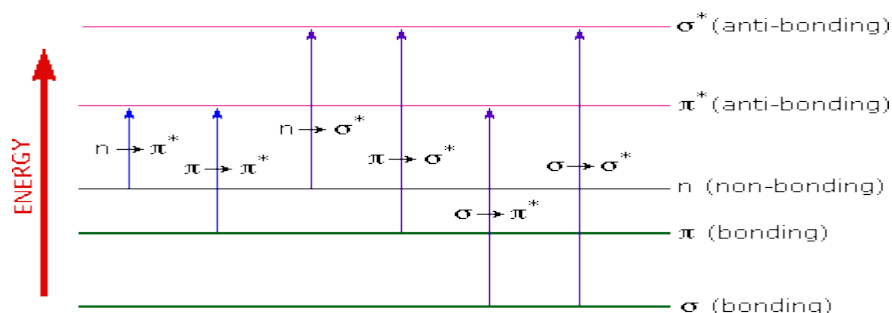
*Mechanism:*

Let us consider a Donor – Acceptor system. Sensitizer is acting as Donor (D) and the reactant is acting as acceptor (A). The process involves some of the following steps:

Step	Reaction	Explanation
I	$\text{D} + h\nu \rightarrow {}^1\text{D}$	Donor absorbs energy and excites to singlet state ${}^1\text{D}$
II	${}^1\text{D} \rightarrow {}^3\text{D}$ (By ISC)	By Inter system crossing, it crosses from singlet ( ${}^1\text{D}$ ) to triplet state ( ${}^3\text{D}$ )
III	${}^3\text{D} + \text{A} \rightarrow {}^3\text{A} + \text{D}$	Triplet state donor ${}^3\text{D}$ collides with acceptor A and A goes to triplet excited state.
IV	${}^3\text{A} \rightarrow \text{Product}$	Triplet excited state acceptor gives the product. These entire process is known as Photo sensitization.
V	${}^3\text{D} \rightarrow \text{Product}$	Instead of sensitization, sometimes the sensitizer itself forms the product or it may lose its energy by colliding with another molecule. This is known as quenching.



**11. Explain various electronic transitions occur in the spectroscopy. (June 2014)**



**(i)  $n - \pi^*$  Transitions:**

- Occurs in unsaturated molecules containing hetero atoms like N, O and S
- Transition of non bonding lone pair of electrons to the antibonding orbitals.
- Transition shows a weak band at longer wavelength with low intensity.
- Eg : Aldehyde & Ketone : Acetone

**(ii)  $\pi - \pi^*$  Transitions:**

- Occurs in unsaturated molecules
- Transition of an electron from bonding  $\pi$  orbital to an antibonding  $\pi^*$  orbital
- Eg : UV spectrum of  $\text{CH}_2 = \text{CH}_2$  shows intense band at 174 nm and weak band at 200 nm due to  $\pi - \pi^*$  Transitions.

**(iii)  $\sigma - \sigma^*$  Transitions:**

- Occurs in compounds with single bonds without lone pair of electrons
- Energy required is large
- Absorption band occurs in the far UV region (120 – 136 nm)
- Eg :  $\text{CH}_4$  shows  $\sigma - \sigma^*$  transitions at 121.9 nm

**(iv)  $n - \sigma^*$  Transitions:**

- Occurs in saturated compounds having lone pair of electrons in addition to  $\sigma - \sigma^*$  transitions
- Energy required is less than  $\sigma - \sigma^*$  transitions
- Absorption band occurs in the near UV region (180 – 200 nm) at longer wavelength
- Eg  $(\text{CH}_3)_3\text{N}$  shows  $n - \sigma^*$  transitions at 227 nm and  $\sigma - \sigma^*$  transitions at 99 nm,

## UNIT– IV PHASE RULE AND ALLOYS

### PART – A

#### 1. State phase rule and explain the terms involved.

**Ans:** If the equilibrium between any number of phases is not influenced by gravity, or electrical, or magnetic forces but are influenced only by pressure, temperature and concentration, then the number of degrees of freedom (F) of the system is related to number of components (C) and the number of phases (P) by the following phase rule relation  $F = C - P + 2$

#### 2. What are degrees of freedom (F)?

**Ans:** Degrees of freedom (F) is defined as, “the minimum number of independent variable factors such as temperature, pressure and concentration, which must be fixed in order to define the system completely”.

#### 3. Define a) Phase b) Component

**Ans:** (a)Phase is defined as, “any homogeneous physically distinct and mechanically separable portion of a system which is separated from other parts of the system by definite boundaries”.

(b)Component is defined as, “the smallest number of independent variable constituents, by means of which the composition of each phase can be expressed in the form of a chemical equation”.

#### 4. Mention the merits of phase rule.

**Ans:** (i) It is applicable to both physical and chemical equilibrium

(ii) It is a convenient method of classifying the equilibrium states in terms of phases, components, and degree of freedom.

(iii) It helps in deciding whether the given numbers of substances remain in equilibrium or not.

#### 5. What are the limitations of phase rule?

**Ans:** (i) Phase rule can be applied only for the systems in equilibria.

(ii) Only three variables like P, T & C are considered, but not electrical, magnetic and gravitational forces.

(iii) All the phases of the system must be present under the same conditions of T and P.

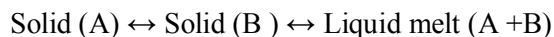
(iv) Solid and liquid phases must not be in finely divided state, otherwise deviations occur.

#### 6. What is eutectic mixture?

**Ans:** Eutectic mixture is an unique mixture of two solids which has the lowest melting point. Since it is completely immiscible in the solid state, it is a mixture not a compound

#### 7. What is an Eutectic point in a binary alloy system?

**Ans:** It is the point at which two solids and one liquid phase are in equilibrium in a binary alloy system.

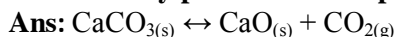


#### 8. State the conditions under which two substances can form a simple eutectic.

**Ans:** (i) They must be completely miscible in the liquid state but completely immiscible in the solid state.

(ii) They should not chemically react with each other

#### 9. How many phases and components are present in the following system?



It consists of two solid phases and one gaseous phase.  $P = 2$ ;  $C = 2$

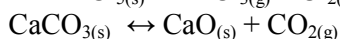
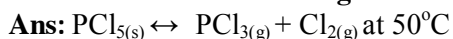
$$F = C - P + 2 = 2 - 2 + 2 = 2$$

#### 10. Give the percentage composition of Bronze.

**Ans:** Bronze is also a copper alloy containing copper and tin in the following composition:

$\text{Cu} = 80 - 95 \%$ ,  $\text{Sn} = 20 - 5\%$

#### 11. State the number of degrees of freedom for the following system:



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

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

#### 12. State condensed phase rule. (Jan 2014)

**Ans:** A solid – liquid equilibrium of an alloy has practically no gaseous phase and the effect of pressure is negligible. Therefore, experiments are conducted under atmospheric pressure. Thus the system in which only the solid and liquid phases are considered and the gas phase is ignored is called a condensed system. Since the pressure is kept constant, the phase rule becomes  $F' = C - P + 1$ . This equation is called reduced phase rule or condensed phase rule.

**13. What is meant by phase diagram?**

**Ans:** Phase diagram is a graph obtained by plotting one degree of freedom against the other.

It is possible to predict from the phase diagrams whether an eutectic alloy or a solid solution is formed on cooling a homogeneous liquid containing mixture of two metals.

**14. What is meant by annealing of steel?**

**Ans:** Annealing means softening. This is done by heating the metal to high temperature, followed by slow cooling in a furnace.

Annealing can be done in two ways

- (i) Low temperature annealing (or) process annealing
- (ii) High temperature annealing (or) full annealing.

**15. What are the non-ferrous alloys? Give their properties.**

**Ans:** These are alloys do not contain iron as one of the main constituent. The main constituents of non – ferrous alloys are copper, aluminium, lead, tin, etc.

They are widely used because of their

- Softness and good formability.
- Attractive (or) very good colours
- Good electrical and magnetic properties.
- Low density and co – efficient of friction.
- Corrosion resistance.

**16. What are the main purposes of alloying steel or advantages of alloy making?**

**Ans:** (i) To increase the hardness of the metal

(ii) To resist the corrosion of the metal

(iii) To lower the melting point of the metal

(iv) To modify chemical activity of the metal

(v) To get good casting of metal

**17. Mention two non-ferrous alloys.**

**Ans:** Brass and bronze are two non ferrous alloys.

**18. Write the number of phases and components in the following heterogeneous system.**

**Ans:**  $\text{CuSO}_{4(s)} + 5\text{H}_2\text{O}_{(l)} \leftrightarrow \text{CuSO}_4 \cdot 5\text{H}_2\text{O}_{(s)}$

Number of phases = 3

Number of components = 2

**19. Give any two uses each of brass and bronze.**

**Ans:** Uses of brass

a) Guilding metal: It is used in forgings, rivets, hardwares and jewellery.

b) Dutch metal: It is also used in the manufacture of cheap jewellery, battery caps and flexible hoses.

Uses of bronze

a) Coinage bronze: It is used in the manufacture of pumps, valves, coins and statues.

b) Gun metal: It is also used in foundry works, steam plants and water fittings.

**20. What are alloys? (Jan 2014)**

**Ans:** An alloy is defined as “homogeneous solid solution of two or more different elements, one of which atleast is essentially a metal”.

**21. What are the objectives of heat treatment?**

**Ans:** Heat treatment causes,

- (i) Improvement in magnetic and electrical properties.
- (ii) Refinement of grain structure.
- (iii) Removal of the imprisoned trapped gases.
- (iv) Removal of internal stresses.
- (v) Improves fatigue and corrosion resistance.

**22. Calculate the number of components and degree of freedom for the following equilibrium.**



**Ans:** This system consists of two phases and one component.

$$P = 2; C = 1;$$

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

**23. What are the constituents of German silver and nickel bronze? What are their uses?**

**Ans:** German silver:

Constituents : Cu = 25 – 50%, Zn = 10 – 35% ,Sn = 5 – 35%

Uses: Utensils, bolts, screws, ornaments, coinage and decorative articles.

Nickel bronze: Constituents : Cu = 90% Ni = 9% Fe = 1%

Uses: For rolling purposes, valves and general purpose semi-hard bearings.

**24. Write the significance of eutectic mixture.**

**Ans:** (i) Suitable alloy composition can be predicted with the help of eutectic systems

(ii) Eutectic systems are used in preparing solders, used for joining two metal pieces together.

**25. A system consists of benzene and water. Give the number of phases?**

**Ans:** Two liquid phases and one vapour phase.

**26. What is metastable equilibrium?**

**Ans:** Sometimes water can be cooled below 0°C without the formation of ice, this water is known as super-cooled water. The equilibrium between super-cool water and the vapour is known as metastable equilibrium

**27. Give the composition of a) Brass b) Bronze.**

**Ans:**

a) Brass : Cu = 60 – 90% Zn = 40 – 10%

b) Bronze: Cu = 80 – 95% Sn = 20 – 5%

**28. Predict the number of degrees of freedom required to define the state of the following systems with out using the phase rule.**

a) One mole of a pure gas enclosed in a cylinder. **Ans:** F = 2

b) A liquid in a equilibrium with its vapour at its boiling point. **Ans:** F = 1

c) All the three forms of water in equilibrium. **Ans:** F = 0

**29. Calculate the number of phases present in the following systems.**

$\text{MgCO}_{3(s)} \leftrightarrow \text{MgO}_{(s)} + \text{CO}_{2(g)}$  **Ans:** = 3 phases

$\text{Rhombic sulphur}_{(s)} \leftrightarrow \text{Monocline sulphur}_{(s)}$  **Ans:** = 2 phases

$\text{Ice}_{(s)} \leftrightarrow \text{Water}_{(l)} \leftrightarrow \text{water vapour}_{(g)}$  **Ans:** = 3 phases

**An emulsion of oil in water** **Ans:** = 2 phases

**30. What is stainless steel?**

**Ans:** Stainless steel is an alloy of iron and chromium along with other elements such as molybdenum, nickel etc. It is very effective against corrosion if it contains more than 16% chromium.

**31. What is the role of chromium in stainless steel?**

**Ans:** Presence of chromium in stainless steel produces an exceptionally tough and coherent dense film of chromium oxide at the surface of alloy which gives complete protection against atmospheric corrosion.

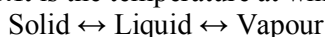
**32. Mention the composition and applications of nichrome. (June 2014)**

**Ans:** Nichrome is a type of steel, which contains 60% nickel, 12% chromium, 26% Iron and 2% Manganese.

**Applications:** It finds applications in boiler parts, gas turbines, steam lines, annealing boxes and other equipments exposed to high temperatures.

**33. What is triple point? (June 2014)**

**Ans:** It is the temperature at which three phases (solid, liquid, vapour) are in equilibrium.





**PART B****1. State Gibb's phase rule. Explain the terms involved in it with suitable examples. (June 2014)**

**PHASE RULE:** If equilibrium between phases is not influenced by gravitational/electrical/magnetic forces but is influenced by pressure, temperature and concentration, then phase rule is:  $F = C - P + 2$

**EXPLANATION OF TERMS WITH EXAMPLES**

**(1) PHASE (P):** "Any homogeneous physically distinct and mechanically separable portions of a system separated from other parts of the system by definite boundaries".

**a) Gaseous phase (g):** All gases are completely miscible and have no boundaries between them constituting a single phase.

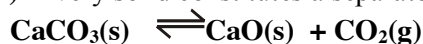
Eg: Air, a mixture of  $O_2$ ,  $H_2$ ,  $N_2$ ,  $CO_2$  and water vapor, etc., constitutes a single phase.

**(b) Liquid Phase (l):** The number of liquid phases depends on the number of liquids present and their miscibilities.

(i) If two liquids are immiscible form two separate liquid phases. (e.g.) Benzene – Water system.

(ii) If two liquids are completely miscible form only one liquid phase. (e.g.) Alcohol - Water system.

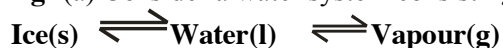
**(c) Solid Phase (s):** Every solid constitutes a separate single phase. (e.g.) Decomposition of  $CaCO_3$



It involves 3 phases namely solid  $CaCO_3$ , solid  $CaO$  and gaseous  $CO_2$ .

**2. COMPONENT (C):** "The minimum number of independent variable constituents, by which the composition of each phase can be expressed in the form of a chemical equation".

Eg: (a) Consider a water system consisting of three phases.



The chemical composition of all the three phases is  $H_2O$ . Hence the number of component is one.

(b) Thermal decomposition of  $CaCO_3$



The system has 3 phases (solid  $CaCO_3$ , solid  $CaO$  and gaseous  $CO_2$ ) and 2 components. When  $CaCO_3$  and  $CaO$  are considered as components, the chemical equations are:

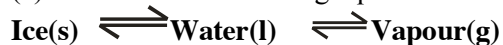
Phase	Components
$CaCO_3$	$CaCO_3 + 0CaO$
$CaO$	$0CaCO_3 + CaO$
$CO_2$	$CaCO_3 - CaO$

**3. DEGREES OF FREEDOM (F):** "The minimum number of independent variable factors like temperature, pressure and concentration, which must be fixed to define the system completely".

A system having 1, 2, 3 or 0 degrees of freedom are called as univariant, bivariant, trivariant and non-variant systems respectively.

**Examples:**

(a) Consider the following equilibrium



These 3 phases will be in equilibrium only at a particular temperature and pressure. Hence, this system does not have any degree of freedom, so it is non-variant (or) zero-variant (or) in-variant system.

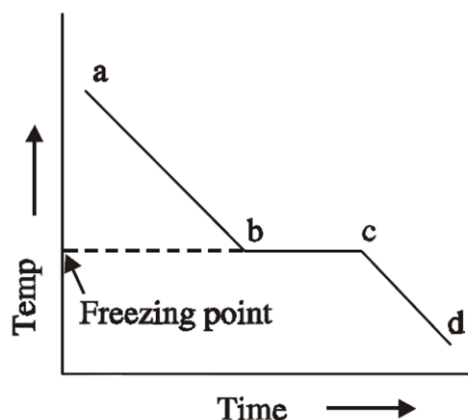
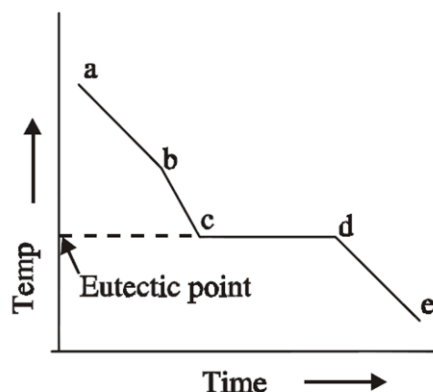
**2. What is thermal analysis? Explain how it is used for constructing a simple eutectic system.****Thermal Analysis (or) Cooling Curves**

- A method to study the cooling curves of various compositions of a system during solidification.
- The shapes of the freezing point curves for any system (involving metals) can be determined.

- The form of cooling curves indicates the composition of the solid.

**Example 1:**

A pure solid substance in the fused state is allowed to cool slowly and the temperature is noted at different time intervals. Then a graph is plotted between temperature and time and it is the cooling curve for the pure solid substance.

**Cooling curve of pure solid****Cooling curve of a mixture A+B**

Initially the rate of cooling of liquid melt is continuous from 'a' till the point 'b', where solid begins to appear. Then the temperature remains constant until the liquid melt is completely solidified and solidification completes at the point 'c'.

The horizontal line 'bc' represents the equilibrium between the solid and liquid melt. After the point 'c', along the curve 'cd' cooling of solid mass begins and the temperature begins to decrease.

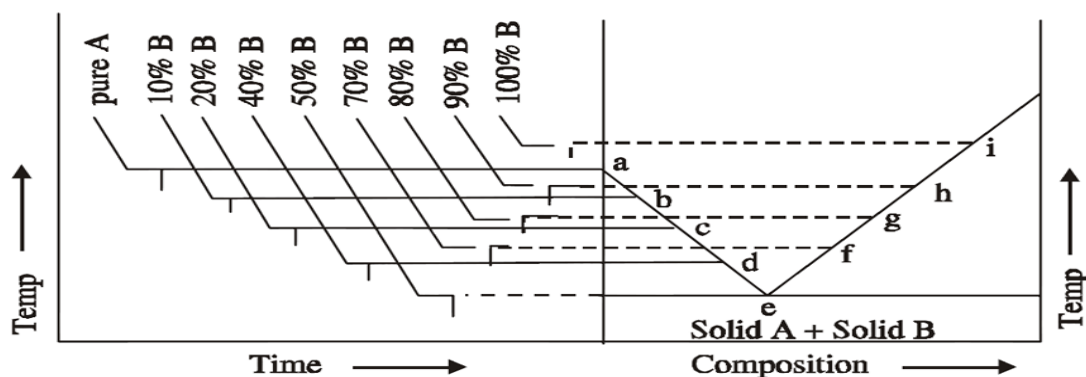
**Example 2:**

If a mixture of two substances (say A and B) in the fused state are allowed to cool slowly, the cooling curve is obtained as above:

Initially the rate of cooling of liquid melt is continuous from 'a' till the point 'b'. When it reaches the point 'b' one substance (either A or B) begins to solidify out of the melt. This is indicated by a break where the rate of cooling is different. On further cooling at the breakpoint 'c' the second substance also begins to solidify. Now the temperature remains constant until the liquid melt is completely solidified, which forms the eutectic mixture along the line 'cd'. After the breakpoint 'd' cooling of solid mass begins. The temperature of horizontal line 'cd' gives the eutectic temperature.

The experiment is repeated for different compositions of A and B and the various cooling curves are recorded.

From the cooling curves of various compositions, the main phase diagram can be drawn by taking composition in X-axis and the temperature in Y-axis.

**Cooling curve of various compositions of two solids**

### Uses of Cooling Curves:

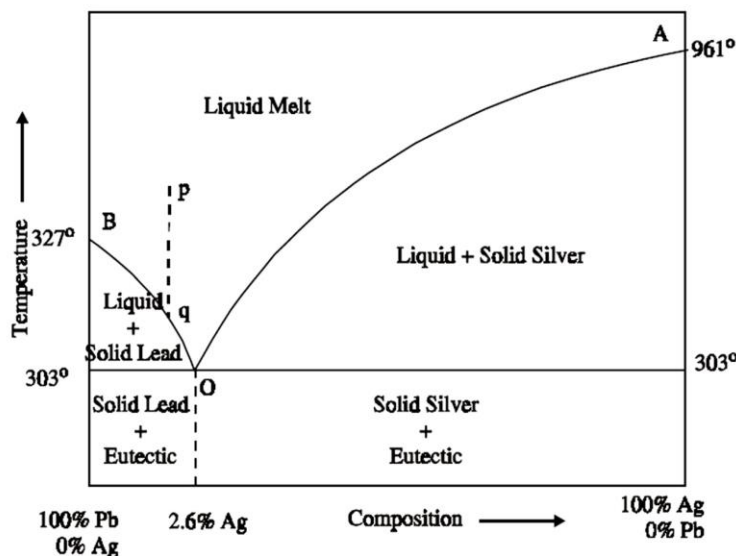
1. Melting point and eutectic temperature can be noted.
2. Percentage purity of the compounds can be noted.
3. The behavior of the compounds can be clearly understood.
4. The composition corresponding to its freezing point yields the composition of the alloy.
5. The phase diagram for any two component system can be obtained.

### 3. Draw the phase diagram for Pb-Ag system and explain the application of this system to de-silverisation of lead. (June 2014)

#### The Lead-Silver System

The Lead-Silver system is studied at constant pressure and the vapour phase is ignored. The condensed phase rule is:  $F' = C - P + 1$

The phase diagram of lead-silver system is shown as follows. It contains curves, areas and eutectic point.



Phase diagram of Lead - Silver system

#### (i) Curve AO

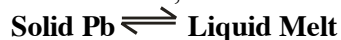
The curve AO is known as freezing point curve of silver. Point A is the melting point of pure Ag (961°C). The curve AO shows the melting point depression of Ag by the successive addition of Pb. Along this curve AO, solid Ag and the melt are in equilibrium.



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

#### (ii) Curve BO

The curve BO is known as freezing point curve of lead. Point B is the melting point of pure lead (327°C). The curve BO shows the melting point depression of Pb by the successive addition of Ag. Along this curve BO, solid Pb and the melt are in equilibrium.



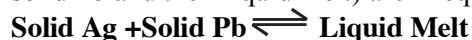
$$F' = C - P + 1; F' = 2 - 2 + 1; F' = 1$$

#### Along the curves AO and BO

The system is univariant which means either temperature (or) composition must be fixed to define the system.

#### (iii) Point 'O' (Eutectic point)

The curves AO and BO meet at point 'O' at a temperature of 303°C, where three phases (solid Ag, solid Pb and their liquid melt) are in equilibrium.



According to reduced phase rule equation.

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

The system is non-variant.

The point 'O' is called eutectic point or eutectic temperature and its corresponding composition, 97.4%Pb + 2.6%Ag, is called eutectic composition.

Below this point the eutectic compound and the metal solidify.

#### (iv) Area

The area above the line AOB has a single phase (molten Pb+Ag) or liquid melt. According to reduced phase rule the degree of freedom.

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

The system is bivariant which means both the temperature and composition have to be fixed to define the system completely.

The area below the line AO (solid Ag + liquid melt), below the line BO (solid Pb + liquid melt) and below the point 'O' (Eutectic compound + solid Ag or solid Pb) have two phases and hence the system is univariant

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

#### Application of Pattinson's process for the desilverisation of Argentiferous lead

The argentiferous lead, having a very small amount of silver (say 0.1%), is heated to a temperature above its melting point, so that the system has only the liquid phase represented by the point 'p' in the phase diagram.

It is then allowed to cool where the temperature decreases along the line 'pq'. As soon as the point 'q' is reached, Pb is crystallized out and the solution will contain relatively increasing amounts of 'Ag'. On further cooling, more and more of 'Pb' is separated along the line 'BO'. The melt continues to be richer and richer in Ag until the point 'O' is reached, where the percentage of Ag rises to 2.6%.

Thus, the process of raising the relative proportions of Ag in the alloy is known as Pattinson's process.

#### Uses of Eutectic system

1. Suitable alloy composition can be predicted.
2. Making solders, used for joining two metal pieces together.

#### 4. Draw and explain the phase diagram for water system and calculate the degrees of freedom along the curves, in areas and at triple point. .(Jan 2014)

##### The Water System

Water exists in 3 possible phases, namely solid ice, liquid water and water-vapour. Hence, there can be three forms of equilibria, each involving two phases such as.

Solid Ice  $\rightleftharpoons$  Liquid Water

Liquid Water  $\rightleftharpoons$  Water- vapour

Solid Ice  $\rightleftharpoons$  Water- vapour

The phase diagram for the water system is as follows and it contains curves, areas, and triple point.

##### 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.

**Liquid Water  $\rightleftharpoons$  Water-vapour**

- ❖ This equilibrium (i.e. line OA) will extend upto the critical temperature (374°C).
- ❖ Beyond the critical temperature the equilibrium will disappear and only water vapour will exist

##### Curve OB

- ❖ The curve OB is called sublimation curve of ice, it represents the equilibrium between solid ice and water-vapour.
- ❖ At any point on the curve the following equilibrium will exist.

**Solid Ice  $\rightleftharpoons$  Water- vapour**

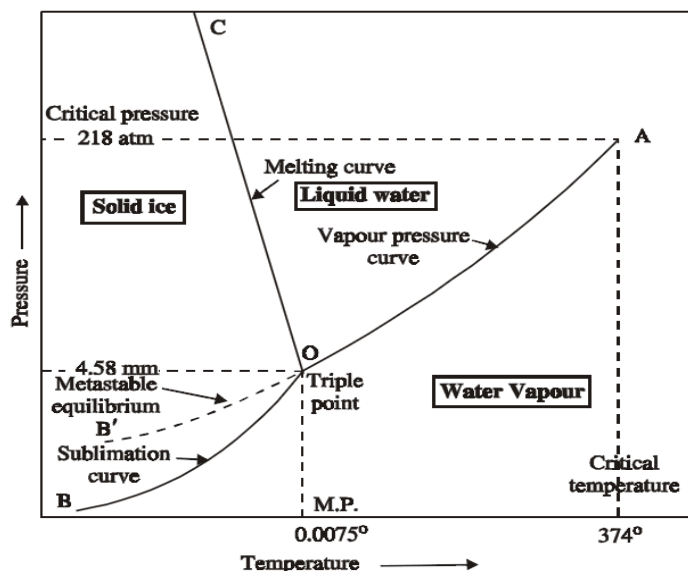
- ❖ This equilibrium (i.e. line OB) will extend up to the absolute zero (- 273°C)
- ❖ Beyond absolute zero only solid ice will exist and no water-vapour.

##### 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.

## Solid Ice $\rightleftharpoons$ Liquid Water

❖ The curve OC is slightly inclined towards pressure axis. This shows that melting point of ice decreases with increase of pressure.



### Curve OB'(Metastable Equilibrium)

❖ The curve OB' is called vapour pressure curve of the super-cooled water (or) metastable equilibrium where the following equilibrium will exist.

### Super- cooled water $\rightleftharpoons$ Water- vapour

- ❖ Sometimes water can be cooled below its freezing point (0°C) without the formation of ice, this water is called super-cooled water.
- ❖ Super cooled water is unstable and it can be converted into solid ice by “seeding” (or) by slight disturbance.

### Along the curves OA, OB, OC and OB'

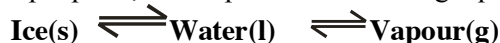
The no. of phases(P) is 2, component(C) is 1 and the degree of freedom of the system is one i.e., univariant. This is predicted by the phase rule:

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

Therefore, either temperature (or) pressure must be fixed to define the system.

### Point 'O' (Triple point)

- ❖ The three curves OA, OB and OC meet at a point 'O', where three phases namely solid ice, liquid water and water-vapour are simultaneously at equilibrium.
- ❖ This point is called triple point, at this point the following equilibrium will exist



At this point the no. of phases(P) is 3, component(C) is 1 and the degree of freedom of the system is zero i.e., non - variant. This is predicted by the phase rule:

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

This takes place only at a constant temperature (0.0075°C) and pressure (4.58 mm of Hg).

### Areas

Areas AOC, BOC, AOB represents liquid water, solid ice and water-vapour respectively where the no. of phases(P) and component(C) are one. Hence the degree of freedom of the system is two i.e., bivariant. This is predicted by the phase rule:

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

Therefore, both temperature and pressure must be fixed to define the system at any point in the areas.

### 5. What do you understand by reduced phase rule?

The maximum number of degrees of freedom for a two component system will be three, when the system exists as a single phase.

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

In order to represent the conditions of equilibrium graphically, it requires three coordinates, namely P, T and C. This requires three dimensional graph, which cannot be conveniently represented on paper. Therefore, any two of the three variables must be chosen for graphical representation.

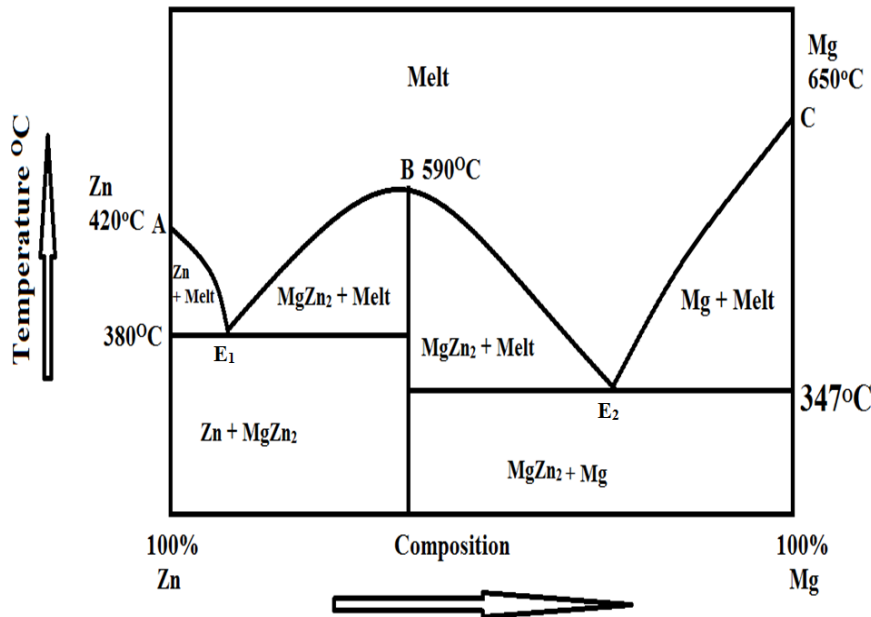
A solid-liquid equilibrium of an alloy has practically no gaseous phase and the effect of pressure is negligible. Therefore, experiments are conducted under atmospheric pressure.

Thus, the system in which only the solid and liquid phases are considered and the gas phase is ignored is called a condensed system.

Since, pressure is kept constant, the phase rule is  $F' = C - P + 1$

### 6. Draw and explain the phase diagram of Zn- Mg alloy system.(Jan 2014)

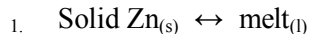
**Two components system – Compounds with congruent melting point**  
**Zinc-Magnesium alloy system**



Zn-Mg binary alloy system is a very good example for the formation of compounds with congruent melting point. A compound is said to possess congruent melting point, if it melts exactly at a constant temperature into liquid having the same composition as that of solid.

#### 1. Curve AE<sub>1</sub>

The curve AE<sub>1</sub> is freezing point curve of Zn. Point A is the melting point of pure zinc (420°C). The curve AE<sub>1</sub> shows the melting point depression of Zn by the successive addition of Mg. Along the curve AE<sub>1</sub>, solid Zn and melt are in equilibrium.



By applying reduced phase rule

$$F' = C - P + 1; F' = 2 - 2 + 1; F' = 1 (\text{Univariant system})$$

#### 2. Point E<sub>1</sub> (Eutectic point)

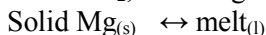
The point E<sub>1</sub> is the eutectic point where three phases (solid Zn, solid MgZn<sub>2</sub> and melt) are in equilibrium. The temperature at this point is 380°C

By applying reduced phase rule

$$F' = C - P + 1; F' = 2 - 3 + 1; F' = 0 (\text{In-variant system})$$

### 3. Curve CE<sub>2</sub>

The curve CE<sub>2</sub> is freezing point curve of Mg. Point C is the melting point of pure Mg(650°C). The curve CE<sub>2</sub> shows the melting point depression of Mg by the successive addition of Zn. Along this curve CE<sub>2</sub>, solid Mg and the melt are in equilibrium.



By applying reduced phase rule

$$F' = C - P + 1; F' = 2 - 2 + 1; F' = 1(\text{Univariant system})$$

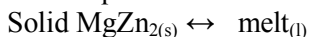
### 4. Point E<sub>2</sub> (Eutectic point)

The point E<sub>2</sub> is the eutectic point, where three phases ( solid Mg, solid MgZn<sub>2</sub> and melt) are in equilibrium. The temperature at this point is 347°C

$$F' = C - P + 1; F' = 2 - 3 + 1; F' = 0(\text{In-variant system})$$

### 5. Curve E<sub>1</sub>BE<sub>2</sub>

The curve E<sub>1</sub>BE<sub>2</sub> is the freezing point curve of MgZn<sub>2</sub>. Along the curve, solid MgZn<sub>2</sub> and the melt are in equilibrium.



By applying reduced phase rule

$$F' = C - P + 1; F' = 2 - 2 + 1; F' = 1(\text{Univariant system})$$

### 6. Point B (Congruent melting point)

The Point B is the melting point of the compound MgZn<sub>2</sub>. The temperature at this point is 590°C. Here the solid has the same composition as that of liquid. So MgZn<sub>2</sub> is said to possess congruent melting point. At this point two component becomes one component as the composition in both solid and liquid phase is only MgZn<sub>2</sub>.

By applying reduced phase rule

$$F' = C - P + 1; F' = 1 - 2 + 1; F' = 0(\text{In-variant system})$$

## 7. Areas

#### a. Below the line AE<sub>1</sub>

The area below the line AE<sub>1</sub> consists of solid Zn and the solution.

By applying reduced phase rule

$$F' = C - P + 1; F' = 2 - 1 + 1; F' = 2(\text{Bivariant system})$$

#### b. Below the line CE<sub>2</sub>

The area below the line CE<sub>2</sub> consists of solid Mg and the solution.

By applying reduced phase rule

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

#### c. Below the line E<sub>1</sub>BE<sub>2</sub>

The area below the line E<sub>1</sub>BE<sub>2</sub> consists of solid MgZn<sub>2</sub> and the solution.

applying reduced phase rule

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

#### d. Below the point E<sub>1</sub> and E<sub>2</sub>

The area below the point E<sub>1</sub> and E<sub>2</sub> consists of solid Zn + solid MgZn<sub>2</sub> and Solid MgZn<sub>2</sub> + Solid Mg respectively.

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

#### e. Above the line AE<sub>1</sub>BE<sub>2</sub>

The area above the line AE<sub>1</sub>BE<sub>2</sub> consists of only liquid phase.

By applying reduced phase rule

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

### Uses (or) merits of phase rule

1. Applicable to both physical and chemical equilibria.
2. A convenient method to classify the equilibrium systems in terms of phases, components and degree of freedom.
3. Indicates that different systems having the same degrees of freedom behave similarly.
4. Decides whether the given number of substances remains in equilibrium or not.
5. Applicable to macroscopic systems without considering their molecular structures.
6. Does not consider the nature (or) amount of substances in the system.



**7.What are non-ferrous alloys? Write the composition, properties and uses of varieties of brass.****(Jan 2014)**

Non - Ferrous alloys do not contain iron as one of the main constituent. The main constituents of non-ferrous alloys are copper, aluminium, lead, tin, etc. Generally, the melting points of non-ferrous alloys are lower than those of ferrous alloys.

**Properties of Non-ferrous alloys**

- (i) Softness and good formability
- (ii) Attractive (or) very good colors
- (iii) Good electrical and magnetic properties
- (iv) Low density and co-efficient of friction
- (v) Corrosion-resistance.

**Copper Alloy (BRASS)**

Brass is an important copper alloy, containing mainly copper and zinc. They possess,

- (i) Greater strength, durability and machinability than Cu
- (ii) Lower melting points than Cu and Zn
- (iii) Good corrosion resistance and water resistance property

**Important Brasses their properties and uses:**

Some important brasses and their composition, properties and uses are given in the following table.

Type of Brasses	Composition	Properties	Uses
Brass	Cu = 60-90% Zn = 40-10%	(i) They possess greater strength, durability and low m.pt than Cu. (ii) They are good corrosion resistant.	
<b>Main Brasses</b>			
(i) Commercial Brass (or) Guilding Metal (or) French Gold	Cu = 90% Zn = 10%	(i) It is golden in colour. (ii) It is stronger and harder than pure Cu.	Forgings, rivets, hardwares, jewellery, etc.
(ii) Dutch - Metal (or) Low Brass	Cu = 80% Zn = 20%	(i) It is golden in colour. (ii) It is suitable for all drawing and forming operations.	Cheap jewellery, battery caps, flexible hoses, tubes, etc.
(iii) Cartridge Brass (or) Spinning Brass	Cu = 70% Zn = 30%	(i) It is soft ductile, harder and stronger than Cu. (ii) It can be cold deformed like extraction.	Condenser tubes, sheet fabrication and house hold articles.
<b>Special Brasses</b>	It contains metals other than Cu and Zn		
(i) German Silver	Cu = 25-50% Zn = 10-35% Sn = 05-35%	(i) It is ductile malleable and looks like silver. (ii) It possesses good strength and corrosion resistance to salt water.	Utensils, bolts, screws, jewellery, coins, decorative articles.



(ii) Admirably Brass (or)Jobin Brass	Cu = 59-62% Sn = 0.5-1.5% Zn = rest	It possesses high corrosion and abrasion resistances.	It is used in propellers and marine works
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## 8.What is heat treatment of steel? Discuss the different methods of heat treatment of steel.

(Jan 2014, June 2014)

Heat treatment is defined as, “the process of heating and cooling of solid steel article under carefully controlled conditions,” During heat treatment certain physical properties are altered without altering its chemical composition.

### Purpose of Heat treatment:

- (i) Improvement in magnetic and electrical properties.
- (ii) Refinement of grain structure.
- (iii)Removal of imprisoned gases.
- (iv)Removal of internal stress and strain.
- (v)Improves fatigue and corrosion resistance.

### Types of Heat Treatment of Alloys (Steel)

The different heat-treatment processes are as follows:

1. Annealing
2. Hardening
3. Tempering
4. Normalizing
5. Case-Hardening
- a) Carburizing b) Nitriding c) Cyaniding

#### 1. Annealing

Annealing means softening done by heating the metal to high temperature, followed by slow cooling in a furnace.

#### Purpose

- (i) It increases the machinability.
- (ii) It also removes the imprisoned gases.

#### Annealing can be done in two ways

- (i) Low temperature annealing (or) process annealing.
- (ii)High temperature annealing (or) full annealing.

#### 2.Hardening (or) Quenching:

It is the process of heating steel above critical temperature followed by sudden cooling in oil /brine-water. Hardening increases the hardness of steel.

#### Purpose

1. High resistance to wear, ability to cut other metals and strength, but steel becomes extra brittle.
2. High abrasion-resistance.

#### 3.Tempering

It is the process of heating the already hardened steel to a temperature lower than its own hardening temperature with slow cooling in air.

#### Purpose

1. Removes any stress and strains
2. Reduces the brittleness and also some hardness.
3. Increases toughness and ductility.
4. Cutting-tools like blades, cutters, tool-bites always require tempering.

#### 4. Normalizing

It is the process of heating steel to a definite temperature (above its higher critical temperature) and allowing it to cool gradually in air.Normalized steel will not be as soft as an annealed steel.

#### Purpose

- 1 Recovers the homogeneity of the steel structure.
2. Refines grain structure.
3. Removes the internal stress and strain.
4. Increases the toughness.
5. Normalized steel is suitable for use in engineering works.

### 5. Case- Hardening (or) Surface hardening

The process of getting a hard and wear resistant surface over a strong, tough and ductile core are known as case-hardening. The steel best suited for this are low-carbon and low-alloy steel.

The different case-hardening processes are as follows:

#### 5. a) Carburizing

The mild steel article is taken in a cast iron box containing small pieces of charcoal (carbon material). It is then heated to about 900 to 950°C and allowed to keep it as such for sufficient time, so that the carbon is absorbed to required depth.

The article is then allowed to cool slowly within the iron box itself. The outer surface of the article is converted into high-carbon steel containing about 0.8 to 1.2% carbon.

**Purpose:** To produce hard-wearing surface on steel article.

#### 5. b) Nitriding

It is the process of heating the metal alloy in presence of ammonia at a temperature of about 550°C. The nitrogen (obtained by the dissociation of ammonia) combines with the surface of the alloy to form hard nitride.

**Purpose:** To get super-hard surface

#### 5.c) Cyaniding

Cyaniding is the process in which pre-heated steel are dipped in a cyanide bath having sodium cyanide, sodium carbonate and sodium chloride. During this process, carbon and nitrogen gets diffused into the surface of steel making it hard.

### 9. What is an alloy? Explain the significance of alloying.

#### DEFINITION

An alloy is defined as *“homogeneous solid solution of two or more different elements, one of which at least is essentially a metal”*. Alloys containing Hg as a constituent element are called amalgams. The metals in excess amount are known as base metal and other elements in lesser amounts are known as alloying elements.

#### PROPERTIES OF ALLOY

- Alloys are harder, good strength less malleable and ductile.
- Alloys have low electrical conductivity and low melting point than pure metals.
- Alloys resist corrosion and the action of acids.

#### IMPORTANCE (OR) NEED (OR) PURPOSE OF MAKING ALLOYS

- Generally pure metals possess some useful properties like high melting point, high densities, malleability, ductility, good thermal and electrical conductivity.
- As said above, the properties of a given metal can be improved by alloying it with some other metal (or) non-metal. The purpose of making alloys are as follows:

1. To increase the hardness of metal
2. To increase the strength of metals
3. To lower the melting points of metals.
4. To resist the corrosion of metals
5. To modify chemical activity of metals
6. To modify the colour of metals
7. To Get Good Casting of metals

#### Functions (or) Effect of alloying elements

*Addition of small amounts of certain metals, such as Ni, Cr, Mo, Mn, Si, V and Al imparts some special properties like hardness, tensile strength, resistance to corrosion and coefficient of expansion, on steel.*

Such products are known as special steels (or) alloying steels.

### 10. What is stainless steel? Discuss the composition, properties and uses of heat treatable and non-heat treatable stainless steel.

#### Stainless Steels (or) Corrosion Resistant Steels

These are alloy steels containing chromium together with other elements such as nickel, molybdenum, etc., Chromium is effective if its content is 16% (or) more. The carbon content in stainless

steel ranges from 0.3 to 1.5%.Stainless steel resists corrosion by atmospheric gases and also by other chemicals. Protection against corrosion is mainly due to the formation of dense, non - porous, tough film of chromium oxide at the surface of metal. If this film cracks, it gets automatically healed-up by atmospheric oxygen.

### **Types of Stainless Steels**

There are two main types of stainless steels.

1. Heat treatable stainless steels.
2. Non-heat treatable stainless steels.

### **Heat Treatable Stainless Steels**

#### **Composition**

Heat - treatable stainless steels mainly contain up to 1.2% of carbon and less than 12-16% of chromium.

#### **Properties**

1. Heat - treatable stainless steels are magnetic, tough and can be worked in cold condition.
2. They can be used up to 800°C.
3. They have good resistant towards weather and water.

#### **Uses**

They are used in making surgical instruments, scissors, blades, etc.,

### **Non - Heat Treatable Stainless Steels**

These steels possess less strength at high temperature. They are more resistant to corrosion. There are of two types of Non-Heat Treatable Stainless Steel according to their composition:

#### **(i) Magnetic type**

##### **Composition**

It contains 12 - 22% of chromium and 0.35% of carbon.

##### **Properties**

1. It can be forged, rolled and machined by the use of specially designed tools.
2. It has better corrosion resistance than heat-treatable stainless steel.

##### **Uses**

It is used in making chemical equipments and automobile parts.

#### **(i) Non-Magnetic type**

##### **Composition**

It contains 18 - 26% of chromium, 8 - 21% of nickel and 0.15% of carbon. The total percentage of Cr and Ni in such steel should be more than 23%.

##### **18/8 Stainless Steel**

The steel having 18% Cr and 8% Ni are known as 18/8 stainless steel. It is the most widely used stainless steel.

##### **Properties**

1. It shows maximum corrosion resistance
2. Corrosion resistance can be further increased by adding small amounts of molybdenum.

##### **Uses**

It is used in making household utensils, sinks, dental and surgical instruments.

**11. What are bronzes? Explain its types, with their percentage composition and applications.**

##### **Copper Alloys (BRONZE)**

Bronze is also a copper alloy having copper and tin.

They possess,

- (i) Lower melting point than steel
- (ii) Better heat and electrical conducting property than most of the steels,
- (iii) Corrosion resistance and water resistance property.

**Important Bronzes, their properties and uses:**

Some important bronzes and their compositions, properties and uses are given in the following table.

Type of Bronzes	Composition	Properties	Uses
Bronze	Cu = 80-95% Sn = 20-05%	They are tough, strong and corrosion resistant.	
<b>Main Bronze</b>			
(i) Coinage Bronze (or) Common Bronze	Cu = 89-92% Sn = 11-08%	It is soft, ductile and durable	Pumps, valves, wires, utensils, coins, statues, etc.
<b>Special Bronzes</b>			
It contains metals other than Cu and Sn			
(i) Gun Metal	Cu = 85% Zn = 04% Sn = 08% Pb = 03%	It is hard, tough, strong to resist the force of explosion.	Foundry works, heavy-load bearings, steam plants, water fittings, etc.
(ii) Aluminium Bronze	Cu = 90-93% Al = 10-07%	(i) It is golden yellow colour. (ii) It is quite strong, fusible, abrasion resistant and corrosion resistant.	Bushes, jewellery, utensils, coins, photoframes, etc.
(iii) High Phosphorous Bronze	Sn = 10-13% P = 0.4-1% Cu = rest	(i) It is hard, brittle and abrasion resistant. (ii) It possess low co-efficient of friction	Bearings, gears, taps, bushes, springs, turbine blades, fuses, etc.
(iv) Nickel Bronze	Cu = 90% Ni = 09% Fe = 01%	It is hard, good tensile strength and corrosion resistant than Cu.	For rolling purposes, valves and general purpose semi-hard bearings.

**12. Explain the effect of alloying elements on the properties of steel.**

Element	Effect on properties	Uses of alloys
1. Nickel	(i) Fine grains are produced. (ii) Co-efficient of expansion decreases and corrosion resistance increases.	For making balance wheels.
2. Chromium	Tensile strength, depth hardening and resistance to corrosion are increased.	For making surgical instruments, cutlery, connecting rods, etc.

3. Manganese	(i) Hot shortness is removed.  (ii) Resistance to abrasion is increased.	For making grinding wheels, steering spindles and rails.
4. Vanadium	(i) Reversible stresses are produced. (ii) Tensile strength and resistance to abrasion are increased.	For making axles, crank pins, heavy locomotive forgings, piston rods., etc.

### **13.Discuss the composition, properties and uses of ferrous alloys. (June 2014)**

#### **FERROUS ALLOYS (OR) ALLOY STEELS**

Ferrous alloys are type of steels with elements like Al, B, Cr, Co, Cu, Mn in sufficient quantities, addition to carbon and iron, to improve their properties

##### **Properties of Ferrous alloys**

1. High yield point and high strength.
2. Sufficient formability, ductility and weldability.
3. Good corrosion and abrasion resistance.
4. Less distortion and cracking.
5. High temperature strength.

#### **IMPORTANT FERROUS ALLOYS**

##### **Nichrome**

Nichrome is an alloy of nickel and chromium.

##### **Properties**

1. Good resistance to oxidation and heat.
2. High melting point.
3. Withstand heat upto 1000 to 1100°C.
4. High electrical resistance.

##### **Uses**

It is widely used for making,

1. Resistance coils and heating elements in stoves.
2. Electric iron box and other household electrical appliances.
3. Boiler parts, steam-lines stills, gas-turbines, aero-engine valves, retorts, annealing boxes.
4. Machineries (or) equipments exposed to very high temperatures.

##### **Stainless Steels (or) Corrosion Resistant Steels**

These are alloy steels containing chromium together with other elements such as nickel, molybdenum, etc., Chromium is effective if its content is 16% (or) more. The carbon content in stainless steel ranges from 0.3 to 1.5%. Stainless steel resists corrosion by atmospheric gases and also by other chemicals. Protection against corrosion is mainly due to the formation of dense, non - porous, tough film of chromium oxide at the surface of metal. If this film cracks, it gets automatically healed-up by atmospheric oxygen.

### **Types of Stainless Steels**

There are two main types of stainless steels.

1. Heat treatable stainless steels.
2. Non-heat treatable stainless steels.

### **Heat Treatable Stainless Steels**

#### **Composition**

Heat - treatable stainless steels mainly contain upto 1.2% of carbon and less than 12-16% of chromium.

#### **Properties**

1. Heat - treatable stainless steels are magnetic, tough and can be worked in cold condition.
2. They can be used upto 800°C.
3. They have good resistant towards weather and water.

#### **Uses**

They are used in making surgical instruments, scissors, blades, etc.,

#### **(b) Non - Heat Treatable Stainless Steels**

These steels possess less strength at high temperature. They are more resistant to corrosion. There are of two types of Non-Heat Treatable Stainless Steel according to their composition:

##### **(i) Magnetic type**

#### **Composition**

It contains 12 - 22% of chromium and 0.35% of carbon.

#### **Properties**

1. Forged, rolled and machined using specially designed tools.
2. Better corrosion resistance than heat-treatable stainless steel.

**Uses:** Chemical equipments and automobile parts.

##### **(ii) Non-Magnetic type**

#### **Composition**

It contains 18 - 26% of chromium, 8 - 21% of nickel and 0.15% of carbon. The total percentage of Cr and Ni in such steel should be more than 23%.

#### **18/8 Stainless Steel**

The steel having 18% Cr and 8% Ni are known as 18/8 stainless steel which most widely used stainless steel.

#### **Properties**

1. High corrosion resistance
2. Corrosion resistance can be increased by adding little of molybdenum.

**Uses:** Household utensils, sinks, dental and surgical instruments.

## **UNIT - V NANOCHEMISTRY**

### **PART - A**

#### **1. Define nanochemistry.**

**Ans:** Nanochemistry is a branch of nanoscience which deals with synthesis and characterization of materials at nanoscale. They find applications from nanoelectronics to nanomedicine.

#### **2. Define nanotechnology.**

**Ans:** Nanotechnology refers to the manipulation or self assembly of atoms or molecules to create nanodevices with new and different properties.

#### **3. What are nanomaterials?**

**Ans:** Materials, which possess grain size less than 100 nm in at least one coordinate (dimension), are known as nanomaterials or nanostructure material

#### **4. How are nanomaterials classified on the basis of dimensions?**

**Ans:**

S.No.	Dimensionality	Examples
1.	0-D. All dimensions $x$ , $y$ , $z$ at nanoscale	nanoparticles.

2.	1-D.Two dimensions x,y are at nano scale and other dimension, length (L) is not at nanoscale.	Nanotubes, nanowires,nanorods
3.	2-D One dimension(thickness t) at nano scale and other two dimensions (length lx and ly) are not at nanoscale	Nanofilms, nanocoatings

**5. Define the terms: top-down nanofabrication and bottom-up nanofabrication.**

**Ans:** Bottom-up nanofabrication: The building of nanostructures starting with small components such as atoms or molecules is called bottom-up approach.

Examples: Chemical vapour deposition; Sol-gel process; Chemical reduction

Top-down nanofabrication: The process of conversion of bulk materials into smaller particles of nano scales structure is called top-down approach.

Examples: Lithography; Ball milling

**6. Mention any four methods for the synthesis of nanomaterials.**

**Ans:** (i) Chemical vapour deposition (CVD) (ii) Sol-gel process  
(iii) Chemical reduction (iv) Plasma arcing (v) Thermolysis  
(vi) Precipitation (vii) Hydrothermal/Solvothermal synthesis etc.

**7. Name the various tools used for characterizing nanomaterials.**

**Ans:** (i) Scanning electron microscope (ii) Transmission electron microscope (iii) Scanning tunneling microscope (iv) Atomic force microscope (v) Magnetic force microscope  
(vi) Scanning near field optical microscope

**8. What is Bucky ball?**

**Ans:** The Bucky ball (or) Fullerene,  $C_{60}$  (short term of buck Minster Fullerene) is a single, stable molecule containing 60 carbon atoms arranged in a soccer ball. It is of about 1nm in diameter.

**9. Mention the various properties which get altered by size reduction.**

**Ans:** The various properties, which get tremendously altered due to the size reduction are:

- (i) Chemical properties: Reactivity; Catalysis.
- (ii) Thermal property: Melting point temperature.
- (iii) Electronic properties: Electrical conduction.
- (iv) Optical properties: Absorption and scattering of light.
- (v) Magnetic properties: Magnetization.

**10. Name any four methods of gas phase synthesis of nanomaterials.**

**Ans:** (i) Laser ablation (ii) Sputtering (iii) Chemical vapour deposition (iv) Plasma arcing.

**11. Name any four methods of liquid phase synthesis of nanomaterials.**

**Ans:** (i) Electrodeposition (ii) Hydrothermal/ Solvothermal synthesis (iii) Chemical reduction (iv) Precipitation.

**12. What are nanoparticles?**

**Ans:** Particles (or) powders with grain size (diameter) less than 100 nm are called nanoparticles.

**13. Mention some of the applications of nanoparticles.**

**Ans:** Since Ag nanoparticles have good antibacterial properties, it is used in refrigerators, air-conditioners, water purifiers etc.

Au – nanoparticles are used to produce silicon nanowire and in medicine

$ZnO$ ,  $TiO_2$  nanoparticles are used as sunscreen cosmetics because they absorb  $uv$  and give protection to skin

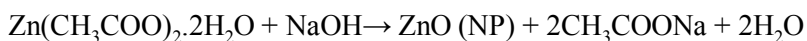
**14. What are the characteristic properties of nanoparticles?**

**Ans:** As the particle size decreases, surface to volume ratio increases. This enhances catalytic activity of nanoparticles. Size reduction also influences thermal properties like melting point.

Melting point decreases with the particle size reduction.

**15. How are nanoparticles synthesized by precipitation method?**

**Ans:** In precipitation techniques, the metal precursors are dissolved in a common solvent such as water and a suitable precipitating agent is added to form an insoluble product of nanoparticles. For the production of metallic oxide nanoparticles, precipitating agents like  $NaOH$ ,  $NH_4OH$  is added to the aqueous metal salt precursor solution.



**16. What is hydrothermal synthesis for nanomaterials?**

**Ans:** Hydrothermal synthesis (also called thermal hydrolysis or hydrothermal hydrolysis) generally refers to processing aqueous solution of metal salts on autoclaving of precursor material at elevated temperatures (typically 100–300°C) and pressures above 1 atm.

In hydrothermal process, water is mixed with metal precursors and the solution mixture is placed in an autoclave and maintained at relatively high temperatures and pressures to carry out the growth of nanoparticles.

**17. Mention any advantages and limitations of hydrothermal synthesis of nanomaterials.**

**Ans:** Advantages: Most materials can be made soluble in proper solvent by heating and pressuring the system close to its critical point. Easy and precise control of the size, shape distribution.

Disadvantages: Expensive autoclaves are required, Safety issues during the reaction.

**18. What are nanoclusters?**

**Ans:** Aggregate of atoms or molecules in nanoscale dimension (1–10 nm) is known as nanoclusters. Individual atoms/molecules can form clusters.

**19. What are nanorods? Give two examples of semiconducting nanorods.**

**Ans:** Nanorods are one dimensional cylindrical solid with an aspect ratio (length/diameter) of less than 20 with a diameter ranging from 10 – 100 nm.

*Examples of semiconducting nanorods:* Cadmium sulphide, Gallium nitride.

**20. What is hydrothermal synthesis for nanomaterials?**

**Ans:** In solvothermal synthesis, non-aqueous solvents such as benzene, xylene, dimethoxy ethane, ethylene diamine etc. are used in place of water used in hydrothermal synthesis. This is because the precursors used are sensitive to water. Solvothermal methods are successfully employed as solution routes to produce 1-D nanostructures such as CdS, GaN, InP nanorods etc.

**21. What are nanowires? Give two examples of semiconducting nanowires. (June 2014)**

**Ans:** Nanowires are one dimensional cylindrical solid with an aspect ratio (length/diameter) of greater than 20 with a diameter ranging from 10 – 100 nm.

Examples of semi conducting nanowires: Silicon, Gallium, Gallium arsenide.

**22. What is meant by VLS mechanism?**

**Ans:** A well accepted mechanism for the growth of nanowires through gas phase reaction is vapour-liquid-solid (VLS) process. To grow any nanowire, the material used must be soluble in the catalyst nanoparticles.

**23. What is electrodeposition method for the synthesis of nanostructures?**

**Ans:** Electrodeposition is a method by which ions from the solution are deposited at the surface of cathode. The deposited material can form a continuous layer, wires or tubes when prestructured (suitable template) matrixes are used.

**24. What are carbon nanotubes? (Jan 2014)**

**Ans:** Carbon nanotubes are cylindrical carbon molecules (graphite sheet is folded into a tube) with properties that make them potentially useful in extremely small scale electronic and mechanical applications. They exhibit unusual strength and unique electrical properties, and are efficient conductors of heat.

**25. What are single-walled carbon nanotube and multi-walled carbon nanotube?**

**Ans:** *Single-walled carbon nanotube (SWCNT):* If a nanotube has a single cylinder of graphene sheet, it is known as SWCNT.

*Multi-walled carbon nanotube (MWCNT):* If a nanotube has a number of concentric rings of graphene sheets, it is known as MWCNT.

**26. How are CNTs classified on the basis of chirality (or) helicity?**

**Ans:** Chirality (or) Helicity of carbon nanotubes refers to the rolling of hexagonal chains with respect to the tube axis. Helicity results in three different types of carbon nanotubes (i) Armchair tube (Metallic conducting) (ii) Zig-zag tube (Semiconducting) (iii) Chiral tube (Semiconducting)

**27. Mention some of the applications of CNTs.**

**Ans:** Catalyst supports: Since CNTs can provide large surface area and good chemical stability at elevated temperatures, they can be used as catalyst supports for various chemical reactions.



Hydrogen storage materials: Since CNTs can absorb and hold hydrogen (8% by weight) without leaking; they can be used as storage materials to store hydrogen gas in hydrogen – oxygen fuel cell.

**28. What are the unique properties of CNTs?**

**Ans:** (i)CNTs are 100 stronger and about six times lighter than steel

(ii)CNTs can conduct electricity like copper and acts as semiconductor like silicon (iii)CNTs can transport heat 10 times higher than silver

**29. Define CVD method?**

**Ans:** CVD is a chemical reaction which transforms gaseous molecules called precursors into a solid material in the form of tubes, wires, thin films or coatings on the surface of a substrate.

**30. What are the advantages of CVD process?**

**Ans:** a) Versatile – CVD can deposit any element or compound

b) High purity of 99.99% - 99.999% can be obtained

c) Economical in production since many products can be coated at a time.

**31. Distinguish between SWCNT and MWCNT.**

**Ans:**

S.no	SWCNT	MWCNT
1.	Single layer of graphene	Multi layer of graphene
2.	Diameter 1-2nm Length 1-100µm	Outer diameter 2-20nm Inner diameter 1-2nm Length 1-100µm Inter tubular distance 0.34nm

**32. Differentiate between molecules, nanomaterials and bulk materials. (Jan 2014, June 2014)**

**Ans:**

S.no	Property	Molecules	Nanomaterials	Bulk materials
1.	Size	Exhibits few angstroms(A)	Exhibit 1-100nm at least in one dimension	Exhibits more than one microns(µ)
2.	Number of constituents	Consist of more than one atom	Made up of one to several thousands depend upon their size	Consist of infinite number of atoms and or molecules

**33. What is laser ablation ? (Jan 2014 )**

**Ans:** It is a technique used to prepare high quality SWCNT using a pulsed or continuous laser beam of Nd : YAG or CO<sub>2</sub> through quartz tube on to the graphite target at the center of the furnace.

**PART B**

**1. Describe the size dependent properties of nanomaterials. (June 2014)**

- all the properties like hardness, strength, ductility, melting point and density change on reduction in grain size.

- large number of atoms reside at the grain boundaries. As the grain size decreases, there is a significant increase in the volume fraction of grain boundaries or interfaces.

**2. Explain the effect of size on the melting point and magnetization of Nanomaterials.**

**Melting points**

- Nano-materials have a significantly lower melting point and appreciable reduced lattice constants. This is due to huge fraction of surface atoms in the total amount of atoms.

### Magnetization

- Ferro-magnetic behavior of bulk materials disappear when the particle size is reduced. Ferromagnetism gets transformed to super-paramagnetism when particle size reduces. This is due to the huge surface area.

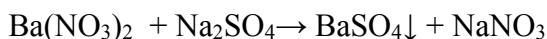
### 3. How is the synthesis routes classified for making nanostructures on the basis of media?

Explain any one method for the synthesis of nanostructures.

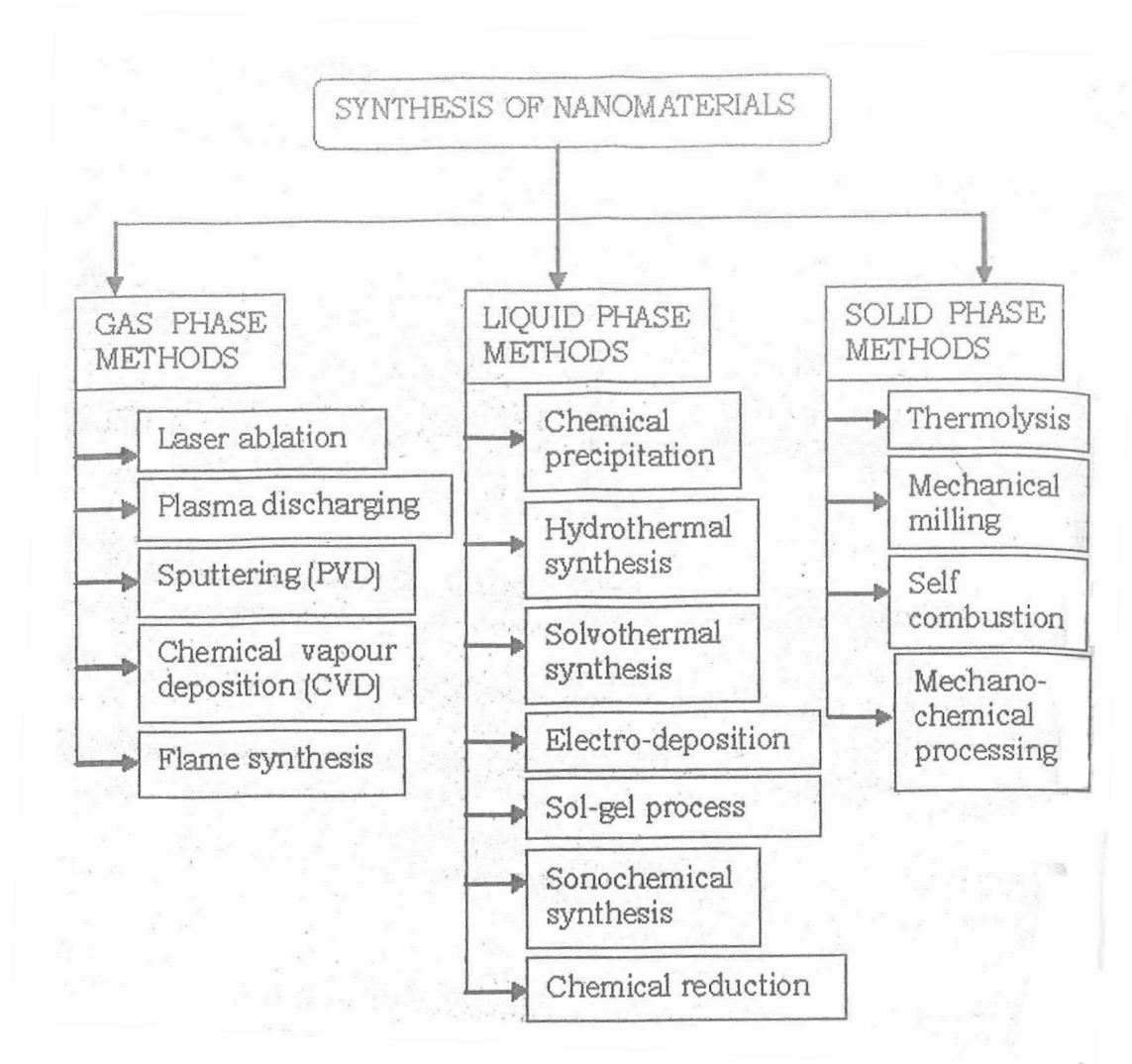
Any one of the below:

- Laser ablation
- CVD
- Electrodeposition
- Precipitation
- Hydrothermal method
- Solvothelmal method

For example **Precipitation**:



When the above reaction is carried out in the presence of a stabilizing agent,  $\text{BaSO}_4$  nanoparticles are formed.



#### 4. What are nanoparticles? Mention their properties and applications. (June 2014)

**Nanoparticles:** - Particles (or) powders with grain size (diameter) less than 100 nm are called nanoparticles.

#### PROPERTIES OF NANO-MATERIALS

##### 1. Melting points

Nano-materials have a significantly lower melting point and appreciable reduced lattice constants. This is due to huge fraction of surface atoms in the total amount of atoms.

##### 2. Optical properties

Reduction of material dimensions has pronounced effects on the optical properties of nano-materials are different from bulk forms.

The change in optical properties is caused by two factors.

1. The quantum confinement of electrons within the nano-particles increases the energy level spacing.

**Example:** The optical absorption peak of a semiconductor nano-particles shifts to a short wavelength, due to an increased band gap.

2. Surface plasma resonance, which is due to smaller size of nano -particles than the wavelength of incident radiation. **Example:** The colour of metallic nano-particles may change with their sizes due to plasma resonance.

##### 3. Magnetic properties

Magnetic properties of nano materials are different from that of bulk materials. Ferro-magnetic behavior of bulk materials disappear, when the particle size is reduced and transfers to super-paramagnetics. This is due to the huge surface area.

##### 4. Mechanical properties

The nano-materials have less defects compared to bulk materials, which increases the mechanical strength.

(i) Mechanical properties of polymeric materials can be increased by the addition of nano-fillers.

(ii) As nano-materials are stronger, harder and more wear resistant and corrosion resistant, they are used in spark plugs. **Example:** Nano-crystalline carbides are much stronger, harder and wear resistant and are used in micro drills.

##### 5. Electrical properties

(i) Electrical conductivity decreases with a reduced dimension due to increased surface scattering. However it can be increased, due to better ordering in micro-structure. **Example:** Polymeric fibres.

(ii) Nanocrystalline materials are used as very good separator plates in batteries, because they can hold more energy than the bulk materials.

**Example:** Nickel-metal hydride batteries made of nanocrystalline nickel and metal hydride, require far less frequent recharging and last much longer.

##### 6. Chemical properties

Any heat treatment increases the diffusion of impurities, structural defects and dislocations and can be easily push them to the nearby surface. Increased perfection will have increased chemical properties.

##### Applications of Nano Materials or Nanoparticles

They can be used for a wide variety of applications.

- Medicine
- Industries
- Electronics
- Bio materials (Biology)

#### 5. Discuss various types of synthesis involved in the preparation of Nanomaterials. (Jan 2014, June 2014)

Nanomaterials are prepared by the following methods.

1. Pyrolysis of hydrocarbons.
2. Laser evaporation
3. Carbon arc method
4. Chemical vapour deposition.

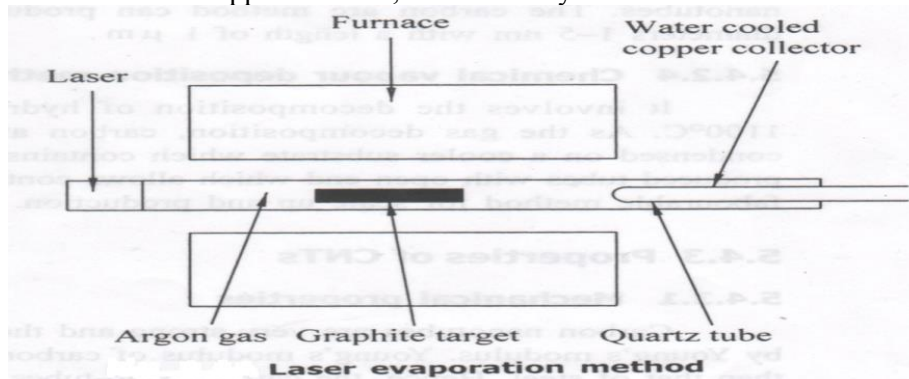
### 1. Pyrolysis of hydrocarbons:

Carbon nanotubes are synthesized by the Pyrolysis of hydrocarbons such as acetylene at about  $700^{\circ}\text{C}$  in the presence of Fe- Silica or Fe- graphite catalyst under inert conditions.

Acetylene  $700^{\circ}\text{C}$ , Fe/Silica CNT

### 2. Laser evaporation:

It involves the vaporization of graphite target containing small amount of cobalt and nickel which acts as catalyst. It is exposed to an intense pulsed laser beam at higher temperature ( $1200^{\circ}\text{C}$ ) in a quartz vessel. An inert gas such as argon is simultaneously allowed to pass through the reactor to drive away the evaporated carbon atoms from furnace to the colder copper collector, on which they condense as carbon nanotubes.



### 3. Carbon arc method:

Two graphite electrodes of 10 -20  $\mu\text{m}$  dia are taken, connected externally. At high pressure, when 20 -25V DC current is passed, CNT is produced.

### 4. Chemical vapour deposition:

It involves decomposition of vapour of hydrocarbons such as methane, acetylene at high temperatures ( $1100^{\circ}\text{C}$ ) in presence of metal nanoparticles catalysts like cobalt, nickel, iron supported on  $\text{MgO}$  or  $\text{Al}_2\text{O}_3$ . Carbon atoms produced by the decomposition condense on a cooler surface of the catalyst.

### 6. What are nanoclusters? Explain thermolysis method for the synthesis of nanoclusters.(Jan 2014)

**Definition:** Aggregate of atoms or molecules in nanoscale dimension (1–10 nm) is known as nanoclusters. Individual atoms/molecules can form clusters.

#### Thermolysis method:

- Thermolysis is characterized by subjecting the metal precursors (usually organometallic compounds in oxidation state zero) at high temperatures together with a stabilizing agent in a vacuum chamber. Inert gas is admitted inside chamber periodically.
- The organometallic compound vapourizes in the chamber at high temperature.
- Vapour cools and supersaturates to form nanocluster.

#### Synthesis of lithium metal nanoclusters:

- Lithium metal clusters can be made by decomposing lithium azide  $\text{LiN}_3$  in a quartz tube

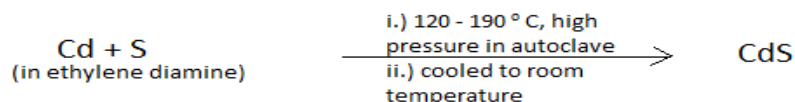
### 7. What are nanorods? Describe the synthesis of semiconducting nanorods by solvothermal techniques.

**Definition:** Nanorods are one dimensional cylindrical solid with an aspect ratio(length/diameter) of less than 20 with a diameter ranging from 10 – 100 nm.

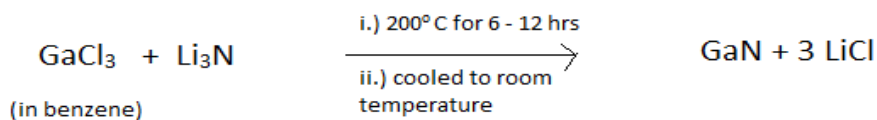
**Solvothermal synthesis:** Metal precursor + non aqueous solvents + templating agents  $\rightarrow$  solution mixture  $\rightarrow$  placed in autoclave at high temperature and pressure  $\rightarrow$  nanorods

**Semiconducting nanorods synthesis:**

i.



ii.



### 8. Discuss electrodeposition method for the synthesis of nanowires. (Jan 2014)

- Consists of an electrochemical cell: template cathode + reference electrode + aqueous solution containing metal cations to be deposited.
- When potential is applied, electrodeposition takes place followed by growth of nanowires.

### 9. What are CNTs? Explain their applications.

Applications:

- CNT in storage devices
- CNT as protective shields
- Sensors of gases
- Drug delivery vessels
- CNT in microscope
- Reinforcing elements in composites
- CNTs are used for making IMC (Integrated memory circuits)
- Quantum wire
- CNT in catalysis

### 10. What are single-walled carbon nanotubes (SWCNT) and multi-walled carbon nanotubes (MWCNT)? Compare the properties of CNTs with other conventional materials

1. Single walled carbon nanotubes (SWCNT) –diameter is 1 nm
2. Multi walled carbon nanotubes (MWCNT) –diameter is 10 nm
  - Mechanical properties: Tensile strength & Young's modulus
  - Electrical properties
  - Thermal conductivity
  - Vibrational property
  - Density

### 11. Explain CVD with basic principle, precursors used, chemical reactions involved, advantages and applications.

**Principle:** - chemically reacting a volatile compound of a material + other gases to produce a non-volatile solid that deposits automatically on a suitably placed substrate.

**The precursors :** acetylene, ethylene or methane.

**Steps:**

1. Transport of gaseous reactants on the surface.
2. Adsorption of gaseous reactant on the surface
3. Catalysed reaction occurs on the surface.
4. Product diffuses to the growth site.
5. Nucleation and growth occurs on the growth site.
6. Desorption of reaction product away from the surface.

**Advantages & Applications:**

- High purity, dense films & economical

**12. What are CNTs? Explain Laser ablation method for synthesis of CNTs.**

**CNT** - graphene sheet rolled up into a shape of the cylinder.

**Laser Ablation**

- In laser ablation high power laser pulse is used to evaporate the matter from the target. The total mass ablated from the target per laser pulse is referred to as the ablation rate.
- vaporization of graphite target containing small amount of cobalt and nickel which acts as catalyst using a laser beam.

**Reaction setup**

A typical laser ablation setup is shown in the figure.

When a beam of laser is allowed to irradiate the target, a supersonic jet of particles is evaporated from the target surface. Simultaneously an inert gas such as argon or helium is allowed into the reactor to sweep the evaporated particles from the furnace zone to the colder collector. The ablated species condense on the collector. The ablation takes place in a vacuum chamber either in vacuum or in the presence of some background gas.

