Question Bank

Engineering Chemistry I

Module 2: Phase Rule Introduction:

1. Explain any two of the following terms- 1) Phases 2) Components 3) Degree of freedom.
2. Define 1) phases 2) components 3) Degrees of freedom
3. State Gibb's phase rule and the terms involved in it. Explain meaning of each term.

One component system:

4. State Gibb's phase rule. Explain its application to one component system. **OR** Write short note on one component system- water
5. Draw the phase diagram of one component system and explain 1. Curves 2. triple point
6. What is triple point? Explain it with reference to one component system. **OR** Explain application of phase rule to one component system with the help of diagram and triple point.

Two component system:

7. What is condensed system? State and explain condensed phase rule. **OR** Reduced phase rule.
8. What is condensed phase rule? Explain its application with the help of phase diagram of two component lead-silver system.
9. What is phase rule? Explain its application with the help of phase diagram of lead-silver system.
10. What is reduced phase rule? Diagram of lead silver system.

Advantages and Limitations:

11. Give the demerits/ limitations of Gibb's phase rule.
12. State phase rule with equation and give any three advantages/merits/applications of phase rule.

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Numericals

13. Using Phase rule find the no. of degrees of freedom in following systems at equilibrium.
    A. In water system when,ice ↔ Water ↔ Water vapour
    B. A gaseous mixture of nitrogen and hydrogen.
    C. Decomposition of CaCO3.
14. Find number of phases : 1. Saturated solution of NaCl, 2. Mixture of Rhombic and Monoclinic sulphur, 3. Mixture of O_2 and N_2, 4. Ice ↔ water.
15. Find number of phases and components in

A. ice ↔ Water ↔ Water vapour

B. Mixture of rhombic and monoclinic sulphur

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Chapter 2:Phase Rule

Gibb's Phase Rule:

Gibb’s phase rule states that, **If equilibrium in a heterogeneous system is affected only by external factors like temperature, pressure and concentration and not by electric or magnetic forces or by gravity or surface tension, then, the number of degrees of freedom (F) is related to the number of components (C) and number of phases (P) by the equation**,

$$\boxed{F = C - P + 2}$$

Explanation of terms:

Phase

A phase is defined as “any homogenous, physically distinct, mechanically separable portion of the system, which is separated from other such part of the system by definite boundary surfaces.”

For example:

- Gaseous phase: Since gases are completely invisible, a gaseous mixture containing a number of gases or vapours constitutes a single phase. Air is a mixture of N_2, O_2, CO_2, water vapour etc., which constitutes a single phase.

- Liquid phase: The number of liquid phases depends on the number of liquids present and their mutual solubility. Two or more liquids completely miscible with one another give rise to only one liquid phase, for example, water and ethanol are miscible and the phase is one. A mixture of two immiscible liquid that is water and benzene or chloroform exist in two distinct liquid phases. Since solubility depend on temperature number of phases are also depends on temperature.

- Solid Phase: Every solid in a system constitutes a separate phase and each phase is separated from others by a definite bounding surface. Hence, a heterogeneous mixture of solids consists of as many phases as the number of solid substances present in the mixture. e.g. mixture of sugar and salt.
- In the decomposition of calcium carbonate

$$CaCO_{3(s)} \leftrightarrow CaO_{(S)} + CO_{2(g)}$$

The system consists of three phases namely: solid $CaCO_3$, solid CaO and gaseousCO2

Solution of a solute in a solvent constitutes a single phase e. g. solution of salt in water.
At triple point, water exists in three phases viz.

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Ice $_{(s)}$ ↔Water $_{(l)}$ ↔ Water Vapour $_{(g)}$

Component:

It is defined as, "The smallest number of independent variable constituents which are required to express the composition of each phase in the system either directly or by means of a chemical equation".

The number of components of a system may or may not be the same as the actual number of substances present in the system.

For example

- Sulphur system consist of four phases

  Monoclinic sulphur, rhombic sulphur, liquid sulphur and sulphur vapour. The composition of each phase of the system can be expressed in terms of one constituent sulphur (S). Hence, it is one component system.
- Water system: At the triple point all the three phases co-exists.

  Ice (solid) ↔ Water (liquid) ↔ Vapour (gas)

  It is one component system because the composition of each of the three phases present can be directly expressed as H_2O.
- Decomposition of $CaCO_3$.

$CaCO_3$ (s) ↔ CaO (s) + CO_2 (g)

There are three different phase i.e. solid calcium carbonate, solid calcium oxide and CO_2 gas.

At first sight, it seems that it is a three component system. But it is considered as two component system because the composition of each of the above phase can be expressed in terms of any two of the three constituents present.

For example , if only $CaCO_3$& CaO are considered as components, then composition of each phase can be given as,

$CaCO_3 = CaCO_3 + 0CaO$

$CaO = 0CaCO_3 + CaO$

$CO_2 = CaCO_3 – CaO$

Thus composition of all three the three phases can be expressed by taking two of the constituents only. Hence it forms a two component system.

Degrees of freedom

The number of degree of freedom is defined as "the minimum number of variable factors such as temperature, pressure and concentration which should be arbitrarily fixed in order to define the system completely."

Examples:

- A system consisting of a pure gas is a one component, one phase system. If the temperature and pressure are specified, the volume of the gas can be known (∵ **PV = nRT)**. That means in order to define the system completely, only two variables are necessary. Hence degree of freedom for this system is two i.e. the system is bivariant.

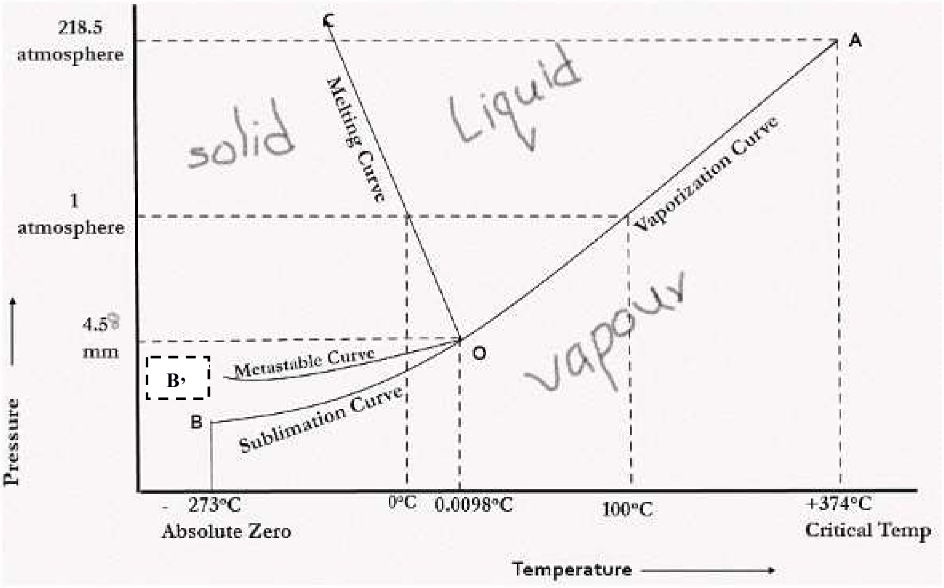
- A mixture of two gases (e.g. N_2& O_2) represents one phase and two component. For defining this system all the three variables i. e. temperature, pressure and composition are necessary. Therefore, F = 3, system is trivariant.
- In case of water system, Ice (solid) ↔ Water (liquid) ↔ Vapour (gas), if all these three phases are in equilibrium, then no condition needs to be specified, as these three phases can be in equilibrium only at a particular temperature and pressure. Therefore for this system degree of freedom is zero. And the system is invariant.
- For system, water ↔ water vapour, which has one component and two phases. It is necessary to specify only one variable i.e temperature or pressure. Hence, F = 1, system is univariant or monovariant.
- The system may be described as nonvariant, univariant, bivariant and trivarient according to the number of degrees of freedom, zero, one, two or three, respectively.

One Component system (The water system)

It is one component system as H_2O is the only chemical compound involved. Water exists in three possible phases, namely, solid, liquid and vapour.

The diagram consists of

1. **curve :** three curve are OA, OB and OC
2. **Areas:** three curves divide the diagram into three areas AOC, AOB and BOC.
3. **Triple point:** the above three curves meet at the point O which is known as triple point.



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Description of the phase Diagram:

Curve AO:

- This curve is known as **vapourization curve.**
- The curve starts from O which is the triple point of water and ends at A, the critical point (Temp. is 374^0C , press. 218 atm).[*critical point- temp. beyond which liquid phase merges with vapour phase and they are no longer distinguishable with each other*.]
- Along this curve there exists liquid water in equilibrium with water vapours. Water (liquid) ↔ Vapour (gas)

Curve OB:

- This curve is known as the **sublimation curve**.
- Along this curve solid ice is in equilibrium with its vapours.
- The curve starts at O and ends at B i.e. absolute zero (-273^0C) [*absolute zero-lowest temperature upto which one can remove heat from a system or a* system has the lowest energy]

Curve OC:

- It is known as **melting point or fusion curve**.
- The curve starts at O and ends at C. The inclination of the curve towards the pressure axis i.e. y axis indicates that the melting point of ice is lowered by increase of pressure.
- At any point on the curve two phases i.e. ice and liquid water is in equilibrium. **Along each curve** two phases are in equilibrium and as water is a one component system, applying phase rule,

$F = C - P + 2$

$F = 1 - 2 + 2$

$F = 1$

Each curve is univariant i. e. to locate any point on the curve either temperature or pressure should be known.

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Areas AOB, BOC and AOC:

- In the area AOB: only vapour phase exists.
- In the area AOC: only water phase exists.
- In the area BOC: only ice exists.

All these areas are bivariant, i.e. in order to locate any point in the area, the temperature and pressure must be defined. This also follows from the phase rule,

$F = C - P + 2$

$F = 1 - 1 + 2$

$F = 2$

Triple point:

- The three curves OA, OB and OC meet at a point which is known as **triple point**.

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- At this point all the three phases namely water, ice and vapour coexist. Thus the value of P is three.
- Applying the phase rule to this point
  $F = C - P + 2$
  $F = 1 - 3 + 2$
  $F = 0$

  Thus the degree of freedom at triple point is zero.
- It means that three phases can coexist in equilibrium only at a definite temperature and pressure which correspond to the point O.
- Thus the values of temperature and pressure which corresponds to point O are 0.0098^0C and 4.58 mm of Hg.

Metastable curve OB':
As water does not always freeze at 0ºC, so if the vessel containing water and vapour is perfectly clean and free from dust, it is possible to super-cool water several degrees below its freezing point O. The dotted curve OB' is a continuation of vaporization curve OA. It represents the vapour pressure curve of super cool water. This curve represents metastable system. On slight disturbance, the super cool water at once changes to solid ice. It may be noted that metastable vapour pressure of super cooled water is higher than the vapour pressure of ice.

Two Component Systems(eutectic system)

Introduction:

Eutectic System:
A binary system consisting of two substances, which are miscible in all proportions in the liquid phase, but which do not react chemically, is known as the "**eutectic** (easy to melt) **system**", e.g., a mixture of lead and silver comprises of such system.

Eutectic mixture:
It is a 'solid solution' of two or more substances having the lowest freezing point of all possible mixture of the components.

Eutectic point:
The minimum freezing point attainable corresponding to the eutectic mixture, is termed as **eutectic point**.

Condensed or reduced phase rule:
In a two component system, when P = 1, degree of freedom (F) has the highest value:
$F = C – P + 2$
$F = 2 – 1 + 2$
$F = 3.$

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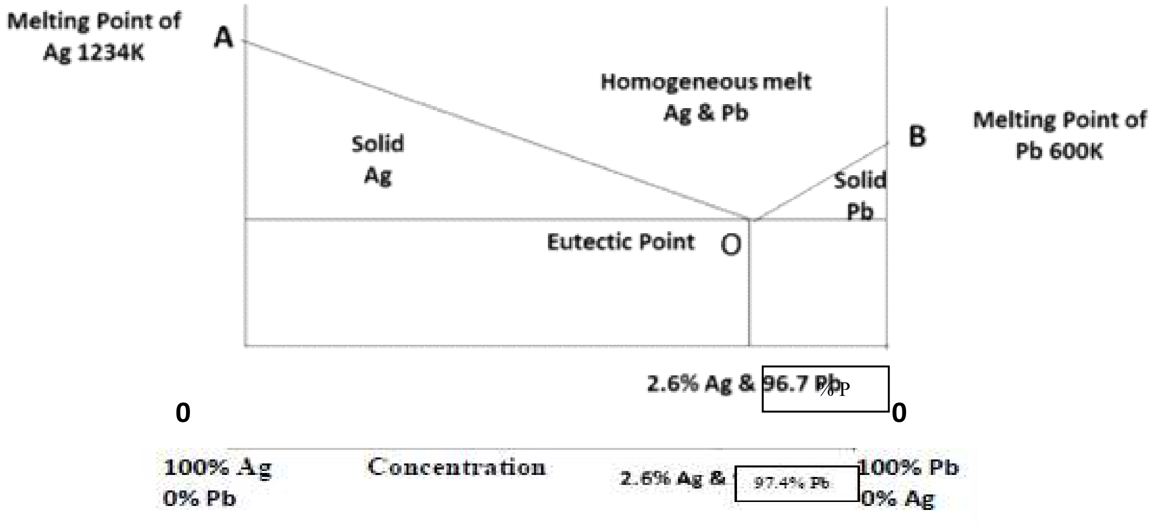
Since the maximum degrees of freedom in a two component system is three, so the phase behavior of a binary system may be represented by a three dimensional diagram of pressure, temperature and composition, which cannot be conveniently shown on paper. Solid-liquid equilibrium of an alloy has practically no gas phase and the effect of pressure is small on this type of equilibrium. Therefore, experiments are, usually conducted under atmospheric pressure. Thus, when the pressure is kept constant of a system, in which vapour phase is not considered, then, it is known as **condensed system**. It will reduce the degrees of freedom of the system by one and for such a system, the phase rule becomes: $\mathbf{F = C - P + 1}$

This is known as **reduced or condensed phase rule**, having two variables, namely, temperature and concentration (or composition) of the constituents.

Silver – lead system:

It is a two component system with four possible phases

1) Solid lead, 2) solid silver, 3) Solution of silver and lead and 4) vapour. Since the pressure has nearly no affect on equilibrium, so the system can be represented by a temperature-concentration diagram at constant atmospheric pressure. Also the vapour phase can be ignored as it is practically absent and the condensed phase rule equation can be made applicable: $\boxed{F = C - P + 1}$



Phase diagram for Pb-Ag eutectic system.

Explanation of phase diagram:

Curve AO:

- It is the freezing point(or melting point) curve of Ag. It shows effect of addition of lead on freezing point of silver.

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- Curve starts from point A (1234 K or 961ºC), which represents freezing point of pure Ag.
- From this curve it can be seen that the freezing point of Ag falls gradually on addition of Pb, along AO, till the lowest point O (576 K or 303º C)is reached, where the solution gets saturated with respect to lead and the freezing point of silver does not fall any further.
- Along this curve, solid Ag and liquid melt coexist and hence, according to reduced phase rule equation:
  F = C - P + 1
  F = 2 – 2 + 1
  F = 1.
  i.e. the system is univariant.

Curve BO:

- It is the freezing point (or melting point) curve of Pb. It shows effect of addition of silver on freezing point of lead.
- Curve starts from point B (600 K or 327ºC), which represents freezing point of pure Pb.
- From this curve it can be seen that the freezing point of Pb falls gradually on addition of Ag, along BO, till the lowest point O (576 K or 303º C) is reached where the solution gets saturated with respect to silver and the freezing point of, lead does not fall any further.
- Along this curve, solid Pb and solution coexist and hence, the system is univariant like AO.

Point O (eutectic point):

- The two curve AO and BO meet at O, where three phases (solid Ag, solid Pb and liquid melt) co-exist and according to condensed phase rule, the system will be invariant.

  F = C – P + 1
  F = 2 – 3 + 1
  F = 0.
- The point O (576 K or 303º C) represents a fixed composition (Ag = 2.6%; Pb = 97.4%) and is called eutectic composition.
- No mixture of lead and silver has a freezing point lower than the eutectic temperature.
- If the contents are further cooled, then, simultaneous crystallization of a mixture of Ag and Pb in relative amounts corresponding to eutectic point O takes place.

Area AOB:

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Region above AOB represents only one phase (liquid melt). Applying condensed phase rule, F = C – P + 1

F = 2 – 1 + 1

F = 2. i.e area is bivariant.

If a sample of lead containing less than 2.6% Ag is taken, say P. on allowing the mass to cool, the temperature gradually falls without any change in composition, till point P' is reached on the curve BO. On lowering the temperature, lead begins to separate out and the composition varies along P'O, till point O is reached. On further cooling, the whole mass solidifies to the eutectic composition.

Application of eutectic systems

- **Pattinson's process:** The above principle is used in pattinson's process of desilvarization of lead. If a sample of argentiferrous lead, containing Ag less than 2.6% is allowed to cool gradually, then, lead will separate out and the solution will become progressively richer in Ag till the percentage 2.6 of Ag is reached. On further cooling the whole mass will solidify and silver can thus be removed from lead.
- Some eutectic mixtures are used in preparing solders used for joining two metal pieces together. E.g. Pb-Sn solders.
- Eutectics are also used in safety fuses which are used in buildings to protect them against fire hazards. E.g Woods metal.

Advantages and limitations of phase rule:

Advantages of phase rule:

1. It gives a simple method of classifying equilibrium states of the system in terms of phases, components and degrees of freedom.
2. It confirms that the different systems having the same number of degrees of freedom behave in the similar manner.
3. It predicts the behavior of systems when subjected to changes in the variables such as pressure, temperature and volume.
4. It requires no information regarding molecular structure since it is applicable to macroscopic system.
5. It is applicable to physical as well as to chemical phase reactions.
6. Phase rule takes no account of nature or quantity of the reactants or products in phase reactions.

Limitations of the phase rule:

1. As the phase rule is applicable to heterogeneous system in equilibrium, it is therefore of no use for such systems which are slow in reaching the equilibrium state.
2. As the phase rule is applicable to a single equilibrium state, it never tells about the number of other equilibrium possible in the system.

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3. Phase rule considers only the number of phases rather than their amounts therefore, utmost care must be taken while deciding number of phases existing in an equilibrium state (even if a trace of phase is present, it accounts towards the total number of phases.).
4. All the phases in the system must be present under the same pressure, temperature.
5. According to phase rule, solid and liquid phases should not be in finely divided state, otherwise deviations occur.

Numericals on Phase Rule

Type 1

1. An alloy of Sn and Pb contains 73% Sn. Find the mass eutectic in 1 kg of solid alloy, if the eutectic contains 64% of Sn. (Ans-750g)
2. An alloy of Cd and Bi contains 25% Cd. Find the mass eutectic in 1 kg of solid alloy, if the eutectic contains 40% of Cd. (Ans-625g)
3. An alloy of Sn and Pb contains 80% Sn. Find the mass eutectic in 1 kg of solid alloy, if the eutectic contains 6o% of Sn. (Ans-500g)
4. An alloy of Cd and Bi contains 20% Sn. Find the mass eutectic in 1 kg of solid alloy, if the eutectic contains 50% of Cd. (Ans-800g)

Type 2

1. An alloy AB of 10 g weight contains 25% of A. The molten AB on cooling gave out B and an eutectic alloy with A and B at equal percentage. What is the amount of B that has formed? (Ans- 5g)
2. An alloy AB of 20 g weight contains 20% of A. The molten AB on cooling gave out and an eutectic alloy A and B with at equal percentage. What is the amount of B that has formed? (Ans- 12g)

Type 3

1. 1000 kg of a sample of argentiferrous Pb containing 0.1% Ag is melted and then allowed to cool. If eutectic contains, 2.6% Ag, what mass of (i) eutectic will be form, (ii) Pb will separate out?

University theory Question Bank (R-2019)

Engineering Chemistry- I

Polymer Classification:

1. Write short note on Thermoplastics and Thermosetting polymers.
2. What are thermoplastic polymers? Name any two thermoplastic polymers. Give preparation, properties and uses of any one thermoplastic polymer (PMMA).

3. Distinguish between Thermoplastics and thermosetting polymers.

4. Give reason: Thermosetting polymers cant be reshaped and reused.

5. What is degree of polymerization?

6. Give the classification of polymers.(On the basis of types and polymerization process)

Polymerization:

7. What is polymerization? What are the conditions for polymerization?

8. Distinguish between addition and condensation polymerization.

9. Write short note on Addition polymerization/ condensation.

Preparation properties and uses:

10. Explain the preparation, properties and uses of PMMA

11. Explain the preparation, properties and uses of Kevlar.

Glass transition temperature and viscoelasticity:

12. Explain the term "glass transition temperature" What is its significance?

13. Define glass transition temperature. What factors influence its value?

14. what is meant by viscoelasticity?

Compounding of plastic:

15. What are main constituents/ ingredients of plastic? Write the functions and examples of each constituent? **OR** What are the additives for plastic? **OR** What are the main constituents of plastic? Write the functions and examples of each constituent.
16. Write short note on compounding of Plastic.

17. What are plasticizers? Give their functions and examples **OR** What is the function of plasticizers in compounding of plastic. Give two examples.

18. Role of fillers, plasticizer and lubricant in compounding.

Fabrication of Plastic:

19. What is meant by Fabrication of plastic? Name the different methods of fabrication? Explain transfer molding with the help of a neat diagram?

20. What is meant by Fabrication of plastic? Name the different methods of fabrication? Explain any one with the help of a neat diagram?

21. Write short note on any 1 of the following 1) Injection molding 2) Compression molding.

22. What is meant by Fabrication of plastic? Explain transfer molding & Injection molding with the help of a neat diagram? **OR** Describe any one moulding method suitable for thermoplastic resin.

23. What is moulding? Explain with the help of a neat diagram extrusion moulding of an insulated cable.

OR Write short note on Extrusion molding. **OR** Describe any one moulding method suitable for thermoplastic resin.

24. What is meant by Fabrication of plastic? Explain compression molding with the help of a neat diagram?

Conducting polymers:

25. Write short note on conducting polymers?

26. State applications of conducting polymers.

27. Advanced polymeric materials like conducting polymers have gained increasing importance in the recent years. Explain what their structural features with one example each are. (classification of conducting polymer.)

28. Define conducting polymer? Explain how polymers are made conductors with suitable examples.

University theory Question Bank (R-2019)

Engineering Chemistry- I

Atomic and Molecular Structure

Atomic Structure

1. What are the fundamental particles of an atom.

2. Explain the concept of shell and sub-shell with reference to the atom.

3. What are the orbitals?

4. Give the difference between the orbit(shell) and Orbitals (sub-shell). 5. Give the different shapes of the following orbitals

a. s- orbitals b. p- orbitals c. d- orbitals

Quantum Number

6.What are Quantum Numbers? Explain them in detail.

OR

6. Explain in detail the following Quantum Numbers

a. Principal quantum number.

b. Azimuthal quantum number

c. Magnetic quantum number

d. Spin quantum number

Electronic Configuration

7. What is meant by electronic configuration of an element (write electronic configuration from atomic no. 1 to 30)

8. What are the rules to be followed for filling the electrons.

OR

8. Explain the following rules which have to be followed for filling up of electrons in different orbitals.

a. Aufbau Principle

b. Pauli's Exclusion Principle

c. Hund's Rule of Maximum Multiplicity.

Molecular Orbital Theory

9. What is Molecular Orbital Theory?

10.Explain LCAO method with reference to MOT.

OR

10. How are molecular orbitals formed by addition and Subtraction.

11. Give diagrammatic representation of the Molecular Orbital Diagram.

12. What are bonding and anti-bonding molecular orbitals?

13. Differentiate between bonding MO and anti-bonding MO.

14. What are the conditions for the combination of atomic orbitals.

15. What are sigma and pi molecular orbitals.

16. Differentiate between Sigma and pi MO.

17. Explain the formation of molecular orbitals in diatomic molecules.

OR

17. What are the atomic orbitals which can combine for formation of diatomic molecule.

18. Give diagrammatic representation of the energy levels of the MO's in diatomic molecles.

19. What are the properties of a molecule that can be explained on the basis of molecular orbital energy diagram.

MO diagram for Homo-nuclear diatomic molecules

20. Explain in detail the MO diagram for Homo-nuclear Diatomic Molecule $Be_{2.}$

OR

20. On the basis of MOT, explain the bond order, Stability and Magnetic behavior of Be_2 Molecule.

21. Explain in detail the MO diagram for Homo-nuclear Diatomic Molecule O_2.

OR

22. On the basis of MOT, explain the bond order, Stability and Magnetic behavior of O_2 Molecule.

MO diagram for Hetero-nuclear diatomic molecules

22. Explain in detail the MO diagram for Hetero-nuclear Diatomic Molecule NO.

OR

22. On the basis of MOT, explain the bond order, Stability and Magnetic behavior of NO Molecule.

23. Explain in detail the MO diagram for Hetero-nuclear Diatomic Molecule CO.

OR

23. On the basis of MOT, explain the bond order, Stability and Magnetic behavior of CO Molecule.

24. Explain Why NO+ ion, nitrosyl ion, is more stable than NO molecule.

Chapter 1: Water

Impurities of water

I) Physical impurities II) Chemical impurities III) Biological impurities

I) Physical impurities

a) Colour:- Colour in water is mainly due to the presence of dissolved or colloidal or dispersed organic matter and metallic impurities like Fe, Mn, Cr etc.

Eg:- Yellowish tinge shows Presence of Cr and organic matter

Yellowish red shows presence of Fe

b) Turbidity:- Turbidity is due to colloidal, extremely fine suspension of clay, mud, dirt etc. It can be removed by sedimentation followed by coagulation, filtration etc.

C) Taste: It is due to presence of dissolved minerals in water.

E.g:-Bitter taste --- Presence of Fe, Al, Mn, sulphate or excess of lime

Soapy taste ---- Presence of $NaHCO_3$

d) Odour:- It is due to presence of living organism, dissolved gases, dead and decaying matter, industrial effluents containing aldehydes, phenols, ketones, esters etc.

II) chemical impurities:

a) Acidity:-It is caused by presence of free CO_2, mineral acid and weakly dissociated acids.

b) Gases:- All Natural water contains dissolved CO_2, its presence in water has no significance.

Presence of dissolved O_2 in industrial waste induces corrosion, but it is also essential for life of aquatic organism.

Dissolved NH_3 in water arises from decomposition of (aerobic and anaerobic) nitrogenous organic matter.

c) Mineral matter:- These includes salts of Ca^{2+}, Mg^{2+}, Na^+, K^+, Fe^{2+}, Mn^{2+}, CO_3^{2-}, HCO_3-, Cl^-, F^-, SO_4^{2-} etc. They are responsible for alkalinity and hardness of water.

III) Biological impurities:-

a) Microorganism:- They are abundant in surface water but their count is low in deep water. Their growth takes place at temperature between $20\text{-}35^{O}$ C.

In order to control microorganism chemical treatment like chlorination is done.

b) Water bodies: e.g Different groups of worms like flatworms, hair worms, tiny roundworms etc. They are harmful to human and fishes.

HARD WATER

"Water that produces very little lather and white curd like precipitate with soap is called hard water."
Hard water affects cleaning ability of soap. Hard water contains bicarbonate, chlorides and sulphates (any one or all) of calcium and magnesium.

SOFT WATER

"Water that produces lather with soap easily is called soft water. Soft water does not affect cleaning action of soap"

Hardness of water:

Q. What is meant by hardness of water? Distinguish between alkaline and non-alkaline water hardness.

- Hardness of water is the **characteristic of preventing lather formation of water with soap**.
- Generally salts like chlorides, bicarbonates and sulphates of Ca^{2+}, Mg^{2+} make water hard.
- This hard water on treatment with soap which is sodium or potassium salt of stearic or palmatic or oleic acid causes white precipitate formation of calcium or magnesium stearate or palmitate.

$$2C_{17}H_{35}COONa + CaCl_2 \longrightarrow Ca(C_{17}H_{35}COO)_2 \downarrow + 2NaCl$$

White ppt of calcium sterate

$$2C_{17}H_{35}COONa + MgSO_4 \longrightarrow Mg(C_{17}H_{35}COO)_2 \downarrow + Na_2SO_4$$

White ppt of magnesium sterate

$$2C_{17}H_{35}COONa + Ca(HCO_3)_2 \longrightarrow Ca(C_{17}H_{35}COO)_2 \downarrow + 2NaHCO_3$$

- Thus Hardness can be defined as, "**the soap consuming capacity of water sample**."
- Other metal ions like $Fe^{2+,}$ Mn^{2+}, and Al^{3+} also react with the soap in same manner, thus contributing to the hardness.
- But generally these are present in natural water only in traces.
- Hence, in practice, hardness of water sample is usually taken as a measure of its Ca^{2+}, Mg^{2+} content.
- When the hardness causing ions are removed as insoluble ppt, water becomes soft and forms lather.

Distinguish between hard water and soft water:

HARD WATER		**SOFT WATER**	
1	Water which does not produce lather with soap but forms a white curd, is called hard water.	**1**	Water which easily produces lather with soap is called soft water.
2	Hard water mainly contains dissolved salts of calcium and magnesium in it.	**2**	Soft water does not contain dissolved calcium and magnesium salts.
3	Hard water affects cleansing ability of soap and due to this a lot of soap is wasted during bathing and washing.	**3**	Soft water does not affect cleansing ability of soap and thus soap is not wasted.
4	Due to the presence of dissolved hardness causing salts, the boiling point of water is elevated. Hence more fuel and time are required for cooking.	**4**	Less fuel and time is required for cooking in soft water.
5	It is not safe for drinking as drinking hard water may affect digestive system.	**5**	It is safe for drinking.
6	Not suitable for industrial use.	**6**	Suitable for industrial use.

TYPES OF HARDNESS:

1. Temporary hardness
2. Permanent hardness

Temporary Hardness OR Carbonate Hardness OR Alkaline Hardness:

- Hardness due to bicarbonates and carbonates of Ca^{2+}, Mg^{2+} and other heavy metal ions is called as temporary hardness.
- Thus "Water that contains bicarbonates and carbonates of calcium and magnesium or of both is called temporary hard water."
- It is called alkaline hardness because the hardness causing salts like carbonates, bicarbonates and hydroxides of metals are alkaline in nature.
- Such hardness is removed by boiling followed by filtration.
- By boiling the bicarbonates are decomposed with the formation of insoluble carbonates with the evolution of CO_2.

$$Ca(HCO_3)_2 \xrightarrow{\Delta} CaCO_3\downarrow + H_2O + CO_2\uparrow$$

$$Mg(HCO_3)_2 \xrightarrow{\Delta} Mg(OH)_2\downarrow + 2CO_2\uparrow$$

Permanent Hardness OR Non-carbonate Hardness OR non-alkaline hardness:

- Hardness due to chlorides, sulphates or nitrates of calcium, magnesium or other heavy metal ions is referred as permanent hardness.
- Thus water that contains chlorides, sulphates or nitrates of calcium or magnesium or of both is called Permanent hard water.
- This type of hardness thus can be removed by addition of lime [$Ca(OH)_2$] and / or soda [Na_2CO_3] which precipitates the insoluble carbonate, which can be removed by filtration.

Total Hardness:

Total hardness = Permanent hardness + Temporary hardness.

Q. Distinguish between Permanent hardness & Temporary hardness

Temporary hardness		**Permanent hardness**	
1	Hardness due to bicarbonates of Ca^{2+}, Mg^{2+} and other heavy metal ions is called as temporary hardness.	1	Hardness due to chlorides or sulphates or nitrates of calcium, magnesium or other heavy metal ions is referred as permanent hardness.
2	It is called as carbonate hardness.	2	It is called as non carbonate hardness.
3	It is called alkaline hardness because the hardness causing salts like carbonates, bicarbonates and hydroxides of metals are alkaline in nature.	3	It is called non alkaline hardness.
4	Such hardness is removed by boiling followed by filtration.	4	Such hardness cannot be removed by boiling. It can be removed by various other processes like lime-soda method, ion exchange etc.
5	Temporary hardness leads to the formation of loose deposits of carbonates and hydroxides of Ca^{2+}, Mg^{2+} respectively if used in boilers.	5	Permanent hardness leads to the formation of adherent scales.

Degree of Hardness:

What is degree of hardness of water? Why do we express hardness of water in terms of calcium carbonate equivalent?

Degree of hardness is commonly defined as the total quantity of hardness causing salts present in water.

Hardness is usually reported as an equivalent quantity of calcium carbonate ($CaCO_3$) because, molecular weight of $CaCO_3$ is 100, so the calculation becomes easy and it is the most common insoluble precipitate formed in most of the water treatments.

The calcium carbonate equivalent of any hardness causing compound can be calculated as follows:

$$\text{Equivalent of } CaCO_3 = \frac{\begin{matrix}\text{Weight of hardness} \\ \text{producing substance}\end{matrix} \times \begin{matrix}\text{Chemical Equivalent} \\ \text{of } CaCO_3 \text{ (= 50)}\end{matrix}}{\text{[Chemical equivalent of hardness producing substance]}}$$

$$\text{Here, Multiplication factor} = \frac{\text{Chemical equivalents of } CaCO_3 \text{ (= 50)}}{\text{Chemical equivalent of hardness producing substance}}$$

Units of Hardness:

Mention the common units used for expressing hardness of water. Define ppm. What is the relation between ppm and mg/lit.

Degree of hardness of given sample of water can be expressed in following different ways:

Parts per million (ppm)

It is the number of parts by weight of Calcium carbonate equivalent present per million parts by weight of water.

$$1 \text{ ppm} = \frac{\text{1 part by weight of } CaCO_3 \text{ equivalent}}{10^6 \text{ parts by weight of water}}$$

Milligram per litre (mg/lit)

It is the number of milligrams of Calcium carbonate equivalent hardness present per litre of water.

$$1 \text{ mg/L} = \frac{\text{1 mg of } CaCO_3 \text{ equivalent}}{\text{Litre of water}}$$

Relation between ppm and mg/L:

1 ppm = 1 mg/L

Numerical problems based on Calculation of hardness

Solved problem

1. Calculate the hardness of given sample of water containing following dissolved salts per litre.
   $CaSO_4$ = 15.2 mg/litre ,$Mg(HCO_3)_2$ = 2.4 mg/litre, $MgCl_2$ = 8.5 mg/litre

Solution:

Step I: Calculation of $CaCO_3$ equivalent

Constituents	Quantity	Molecular weight	Multiplication Factor	$CaCO_3$ Equivalent
$CaSO_4$	15.2mg/litre	136	100/2/136/2	15.2x100/136 = 11.18mg/litre
$Mg(HCO_3)_2$	2.4 mg/litre	146	100/2/146/2	2.4 x 100/146 = 1.64mg/litre
$MgCl_2$	8.5 mg/litre	95	100/2/95/2	8.5 x 100/95 = 8.94mg/litre

Step II: Calculation of Temporary hardness

Temporary hardness = Hardness due to Mg $(HCO_3)_2$

= 1.64 mg/litre or ppm

Step II: Calculation of permanent hardness

Permanent hardness = Hardness due to $CaSO_4$ and $MgCl_2$

= 11.18 + 8.94

= 20.12 mg/litre or ppm

Step III: Calculation of Total hardness

Total hardness = Temporary hardness + Permanent hardness

= 1.64 + 20.12

= 21.76 mg/litre or ppm

Problems for Practice

1. Calculate the temporary and permanent hardness in water from the following data.
$Mg(HCO_3)_2$ = 14.6 mg/litre, $Ca(HCO_3)_2$ = 8.1 mg/litre, $Mg(NO_3)_2$ = 29.6 mg/litre, $MgSO_4$ = 24 mg/litre , $MgCl_2$ = 19.0 mg/litre.

Ans: Temporary Hardness- 15 ppm, Permanent Hardness- 60 ppm

2. Calculate he temporary and total hardness of a sample of water containing following salts:
$Mg(HCO_3)_2$ = 7.3 mg/litre**,** $Ca(HCO_3)_2$ = 16.2 mg/litre**,** $MgCl_2$ = 9.5 mg/litre, $CaSO_4$ = 13.6 mg/litre.

Ans: Temporary Hardness- 15 ppm, Permanent Hardness- 20 ppm

3. Three water samples A, B, C were analyzed for their salt content. Sample A was found to contain 168 mg/litre $MgCO_3$ .Sample B was found to contain 82 mg/litre of $Ca(NO_3)_2$ and 2 mg/litre silica, sample C was found to contain 20 mg/litre of potassium nitrate and 20 mg of $CaCO_3$ per 500 ml. Determine the hardness in all the above three water samples A, B, C.

Ans: Hardness in A = 200 ppm, B = 50 ppm, C = 40 ppm.

4. Calculate the temporary and permanent hardness of a water sample having the following analysis.
$Mg(HCO_3)_2$ = 73 mg/litre, $MgCl_2$ = 95 mg/litre, $Ca(HCO_3)_2$ = 162 mg/litre, $CaSO_4$ = 136 mg/litre, $CaCl_2$ = 111 mg/litre, NaCl = 100 mg/litre.

5. A water sample contains: $Ca(HCO_3)_2$ = 32.4 mg/litre, $Mg(HCO_3)_2$ = 29.2 mg/litre, $CaSO_4$ = 13.5 mg/litre. Calculate the temporary, permanent and total hardness.

6. How many gms of $CaCl_2$ dissolved per liter gives 150 ppm of hardness? (Dec 2011) Ans:0.1665g/L

7. How many grams of $FeSO_4$ dissolved per litre gives 210.5ppm of hardness? (At. wt.: Fe – 56, S – 32, Ca -40, O -16, C – 12) Ans. 0.319g/L.

8. Two samples of water were analyzed for their salt content:
i) Sample A was found to contain 168mg $MgCO_3$ per litre.
ii) Sample B was found to contain 820mg $Ca(NO_3)_2$ per litre and 2mg SiO_2 per litre.
Calculate the total hardness of each sample and state which sample is more hard.
Ans. A= 200 ppm, B = 500ppm

9. Classify the following salts into temporary and perma' hardness causing salts and also calculate their calcium carbonate equivalent
1. $Ca(HCO_3)_2$ = 16.2 mg/litre
2. $MgSO_4$ = 1.2 mg/litre
3. $FeCl_2$ = 12.7 mg/litre
4. NaCl = 94 mg/litre

Estimation of Hardness of water by EDTA method (complexometric method)

This method is also called as complexometric methods since it involves metal complex with reagent used in the determination.

Principle:

The EDTA method for determination of total hardness of water is based on the fact that when blue dye Eriochrome Black T is added to hard water in alkaline medium (buffer pH 10), it gives a wine red coloured unstable complex with metal ions like Ca^{2+} and Mg^{2+}.

M^{n+} + EBT $\xrightarrow{\text{pH 10}}$ [M-EBT complex]
Blue (unstable complex)
Wine red

(M^{n+} - metal ions like Ca^{2+} and Mg^{2+})

When sodium salt of EDTA is added to the flask content, since EDTA has more affinity to form stable complex with metal ions, the metal-EBT unstable complex (wine red) dissociates to form more stable metal-EDTA complex (colourless), releasing the EBT dye (blue colour).

[M-EBT complex] [M-EDTA complex]
(Unstable complex) + EDTA $\longrightarrow$ (more stable complex) + EBT
Wine red **colourless** **Blue**

If some free metal ions are present in the flask solution, then they will react with this EBT dye forming M-EBT complex again which in turn reacts with EDTA to form stable complex. when all these free ions are reacted, the last drop of EDTA gives end point of the titration, i. e. colour change from wine red to blue. Thus amount of EDTA used corresponds to the hardness of water.

Why to use buffer of pH 10?

The colour of dye metal complex (M-EBT) and dye (EBT) are different. However change in pH is sharper at pH 10 than at other pH ranges. The metal dye complex has wine red colour at pH 10 while dye itself is blue colour at pH 10. Also the M-EDTA complex has high stability at pH 10.

Various steps involved in this are:

1. **Preparation of solutions:**
   This step involves preparation of standard hard water, buffer solution, EBT indicator and EDTA solution.
   {Preparation of standard hard water:

   Dissolve 1.0 gm of pure and dry $CaCO_3$ in minimum quantity dil. HCl and then evaporate the solution to dryness on a water bath. Dissolve the solution in a distilled water to make 1 litre solution. (So that each ml of this solution contains 1 mg. $CaCO_3$ equivalent hardness)

   Preparation of Buffer solution:
   Add 67.5 gm of NH_4Cl to 570 ml of concentrated (liquor) ammonia solution and then dilute with distilled water to 1 lit.

   Preparation Eriochrome Black T:
   Dissolve 0.5 gm of Eriochrome Black T in 100 ml of pure alcohol.2 to 3 drops of indicator are sufficient.

   Preparation of EDTA:
   Dissolve 4 gm of EDTA in 1 lit of distilled water & 0.1 gm of $MgCl_2$ is generally added to ensure proper colour development with dye.

   Student need not have to explain these steps. This is only for their understanding}

2. **Standardization of EDTA**

   Rinse and fill the Burette with EDTA solution. Pipette out 50 ml of standard hard water in a conical flask. Add to it 5-10 ml of buffer solution and 4-5 drops of indicator. Titrate the flask solution with EDTA solution till wine red colour changes to clear blue.

   Let the volume of EDTA solution used be V_1 ml.

3. **Titration of unknown hard water (for Total hardness)**
   Titrate 50 ml of sample water using Eriochrome Black T indicator exactly in the above manner.

   Let the volume of EDTA solution used be V_2 ml.

4. **Titration of boiled water sample (for permanent hardness)**
   Boil 250 ml of sample water in a beaker till the volume is reduced to 50 ml to convert all the bicarbonates into carbonate. Filter off the precipitate with distilled water and collect the filtrate and washings in 250 ml of measuring flask.

Make up the volume 250 ml with distilled water. Titrate 50 ml of this solution against EDTA solution using Eriochrome Black T as indicator.

Let the volume of EDTA solution used be V_3 ml.

Numerical problems based on Determination of hardness by EDTA method:

Solved problem

1. 50 ml of standard hard water containing 1 mg of pure $CaCO_3$ per ml consumed 20 ml of EDTA solution.50 ml of the given water sample required 25 ml of same EDTA solution. 50 ml of the boiled sample required 15 ml of EDTA solution. Calculate total, permanent and temporary hardness of water sample.

Solution:

Step I: Determination of strength of EDTA solution.

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

50 ml standard hard water = 50 mg of $CaCO_3$ ……… (1)

Also, 50 ml standard hard water = 20 ml EDTA solution ……… (2)

From equation (1) and (2),

20 ml EDTA solution = 50 mg $CaCO_3$

1 ml EDTA = 50 /20 = 2.5 mg of $CaCO_3$

Step II: Calculation of total hardness

50 ml of given water sample = 25 ml of EDTA solution………. (3)

But, 1 ml of EDTA solution = 2.5 mg of $CaCO_3$ 25 ml of EDTA solution = 2.5 x 25= 62.5 mg of $CaCO_3$…….. (4)

From equation (3) and (4),

50 ml of water sample = 62.5 mg of $CaCO_3$

$$1000 \text{ ml water sample} = \frac{1000 \times 62.5}{50}$$

$= 1250$ mg of $CaCO_3$

$= 1250$ mg/litre or ppm

Total hardness of water sample = 1250 ppm

Step III: Calculation of Permanent Hardness

50 ml of given water sample = 15 ml of EDTA solution………. (5)

But, 1 ml of EDTA solution = 2.5 mg of $CaCO_3$

15 ml of EDTA solution = 2.5 x 15 = 37.5 mg of $CaCO_3$…….. (6)

From equation (5) and (6),

50 ml of water sample = 37.5 mg of $CaCO_3$

$$1000 \text{ ml water sample} = \frac{1000 \times 37.5}{50}$$

$$= 750 \text{mg of } CaCO_3$$

$$= 750 \text{ mg/litre or ppm}$$

Permanent hardness of water sample = 750 ppm

Step IV: Determination of temporary hardness

Temporary Hardness = Total hardness — Permanent hardness
= 1250 - 750
= 500 mg/litre or ppm

Problems for practice

1. In the determination of hardness by EDTA method, 50 ml of standard hard water (containing 1 mg of $CaCO_3$ hardness per ml. of solution) required 45 ml of EDTA solution. While 50 ml of sample hard water consumed 20 ml of EDTA solution. After boiling and diluting, 50 ml of the same sample of water required 10 ml of EDTA solution. Calculate various hardness in ppm.

(Ans. Total Hardness = 444.44 ppm, Perm. Hardness = 222.22 ppm, Temp. Hardness = 222.22 ppm)

2. Calculate the hardness in ppm in a given sample of water from the following data:
   50 ml of standard hard water containing 1 mg of pure $CaCO_3$ per ml consumed 20 ml of EDTA.
   50 ml of water sample consumed 30 ml of EDTA solution using EBT indicator. 50 ml of sample of water after boiling and filtering consumed 20 ml of EDTA solution using EBT indicator.

(Ans. Total Hardness = 1500 ppm, Perm. Hardness = 1000 ppm, Temp. Hardness = 500 ppm)

3. 0.28 g of $CaCO_3$ was dissolved in HCl and solution is made up to 1 litre with distilled water. 100 ml of the above solution required 28 ml of EDTA solution. 100 ml hard water required 33 ml of same EDTA solution on titration. After boiling 100 ml of this was required 10 ml of EDTA solution on titration. Calculate the temporary and permanent hardness of water.

(Ans. Total Hardness = 330 ppm, Perm. Hardness = 100 ppm, Temp. Hardness = 230 ppm)

4. Calculate the hardness of water sample whose 20 ml required 30 ml of EDTA solution. 10 ml $CaCl_2$ solution (strength 300 mg $CaCO_3$ per 200 ml) required 20 ml of EDTA solution.
(Ans. Hardness = 1125 ppm)

5. 50 ml of hard water (1.1 mg of $CaCO_3$ per ml) requires 38 ml of disodium EDTA. 100 ml of a water sample consumes 21 ml of EDTA during titration. Find the degree of hardness of the water sample.
(Ans. Degree of Hardness = 303.9 mg/l)

6. Calculate the hardness in ppm of water sample from the following data. 100 ml of water containing 1 mg/ml of pure $CaCO_3$ consumed 40 ml of EDTA solution. 50 ml of water sample consumed 30 ml of EDTA solution using EBT indicator.

(Ans. Hardness = 1500 ppm)

7. 0.5g of $CaCO_3$ was dissolved in HCl and solution is made up to 500ml with distilled water. 50ml of the above solution required 48 ml of EDTA solution. 50ml hard water required 15ml of same EDTA solution on titration. After boiling 50ml of this was required 10 ml of EDTA solution on titration. Calculate the temporary and permanent hardness of water.

(Ans. Total hardness = 312ppm, permanent hardness = 208ppm, temporary hardness = 104ppm)

8. 20ml of standard hard water containing 15g/L $CaCO_3$ required 25ml of EDTA solution. 100ml of hard water sample required 18ml of EDTA solution. Same sample on boiling required 12ml of EDTA solution. Calculate temporary hardness of the water.

(Ans. Total hardness = 2160ppm, permanent hardness = 1440ppm, temporary hardness = 720ppm)

9. 50 ml water sample required 6.2ml of N/20 EDTA for titration. After boiling and filteration the same volume required 4ml of EDTA. Calculate both the type of hardness. (Dec 2011)

(Ans. Total hardness = 310ppm, permanent hardness = 200ppm, temporary hardness = 110ppm)

10. 50 ml of sample hard water required 15ml of 0.01M EDTA for titration. After boiling and filteration the same sample required 5ml of same EDTA. Calculate the total, temporary and permanent hardness of water

(Ans. Total hardness = 300ppm, permanent hardness = 100ppm, temporary hardness = 200ppm)

Softening of water

Definition:

The process of removal of hardness of water, irrespective of whether it is permanent or temporary hardness is called softening.

The main principle involved in such softening is the conversion of soluble salts present in water to some insoluble ones which can then be easily removed by simple filtration.

Demineralization or Ion Exchange process

Principle:

In this process, cations like Ca^{2+}, Mg^{2+} of hard water are exchanged with H^+ ions of the cation exchanger resin (RH_2) and anions like Cl^-, SO_4^{-2} etc. of hard water are exchanged with OH^- of anion exchanger resin $R'(OH)_2$.

{Ion exchange resins

These are high molecular weight; cross linked, insoluble, long chain organic polymers with micro porous structure and the functional group attached to the chain are responsible for the ion exchanging properties.}

Process:

The process of softening in the ion exchange involves passing raw water first through the cation exchanger and then through the anion exchange resin.

The hard water is passed first through the cation exchange resin, it removes all the cations like Ca^{2+}, Mg^{2+} from it and equivalent amount of H^+ ions are released from this column to water.

$$RH_2 + Ca^{2+} \longrightarrow RCa + 2H^+$$

$$RH_2 + Mg^{2+} \longrightarrow RMg + 2H^+$$

The treated water is now free of cations but is too acidic and cannot yet be used in the boiler.

This acidic water emerging from cation exchanger is passed through the anion exchange which removes all the anions like SO_4^{2}, Cl^- etc. present in the water and equivalent amount of OH^- ions are released from this column to water.

Anion exchange

$$R'(OH)_2 + 2Cl^- \longrightarrow R'Cl_2 + 2OH^-$$

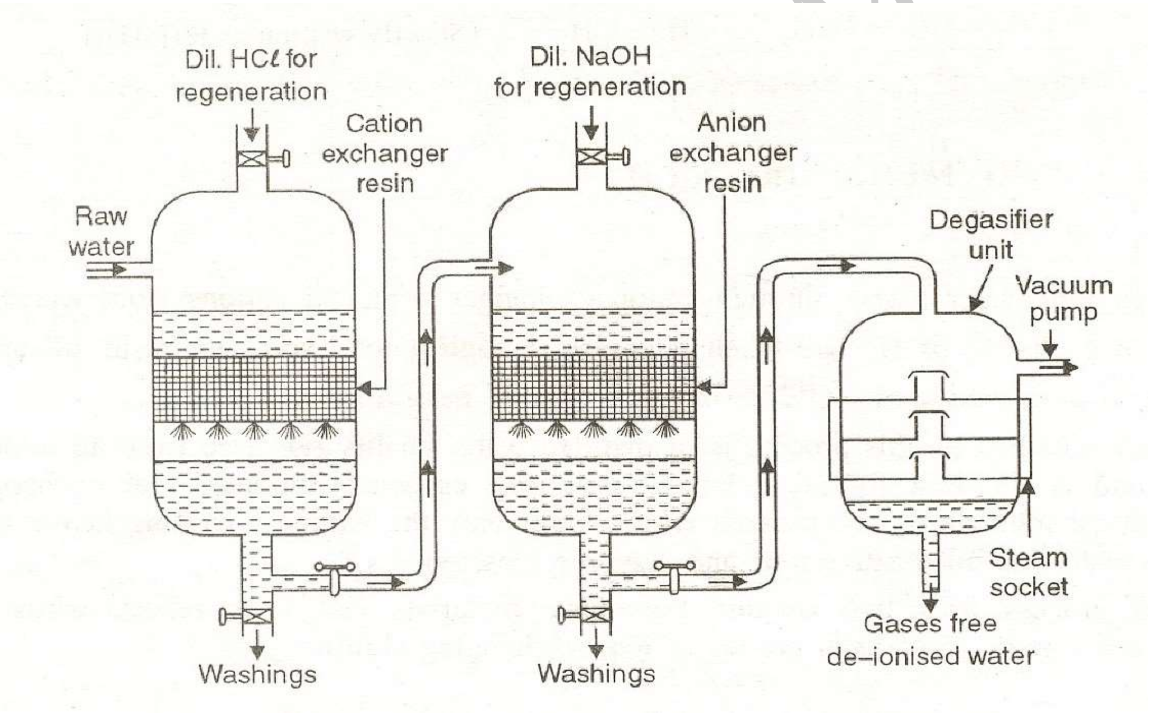
$$R'(OH)_2 + SO_4^{-2} \longrightarrow R'SO_4 + 2OH^-$$

In this way, the water coming out from both cation and anion exchanger is free from both cations and anions and is virtually distilled water.

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

It means it does not have any hardness at all. However water may contain some dissolved gases. In order to remove the dissolved gases, water is passed through degasifier.

{Degasifier is a tower whose both sides are heated with steam jacket and is connected to vacuum pump. High temperature and low pressure reduces the quantity of dissolved CO_2 and O_2 in water. Such softened water can be used for industrial purposes.}



The exhausted cation exchange is regenerated by passing dil. HCl or H_2SO_4 through the first tower. The reactions in regeneration can be represented as

$$R\text{-}Ca + H_2SO_4 \longrightarrow RH_2 + CaSO_4$$

$$R\text{-}Mg + 2HCl \longrightarrow RH_2 + MgCl_2$$

The washing containing $CaCl_2$, $MgCl_2$ or $CaSO_4$, $MgSO_4$ etc, is also passed to drain.

Regeneration of anion exchanger

The exhausted anion exchanger is regenerated by passing dilute solution of NaOH or KOH through the second tower. The reactions in regeneration can be represented as-

$$R'Cl_2 + 2NaOH \longrightarrow R'(OH)_2 + 2NaCl$$

$$R'SO_4 + 2NaOH \longrightarrow R'(OH)_2 + Na_2SO_4$$

Advantages of ion exchange process

1. The process can be used for highly acidic or alkaline water
2. By this process water of zero hardness can be obtained.
3. Water obtained can be used for high pressure boilers.

Disadvantages of ion exchange process

1. Capital cost is high since equipment and chemicals both are costly.
2. If water contains turbidity, then, the efficiency of the process reduced.

Problems for practice (Ion exchange)

1) An ion exchanger required 50 litres of N/20 HCL and 50 litres of N/20 NaOH for regeneration of cation and anion exchanger after softening 2000 litres of water. Find the hardness of the above water sample.

Ans: 62.5 mg/litre.

2) An ion exchanger required 20 litres of 1M HCL and 20 litres of 1M NaOH for regeneration of cation and anion exchanger after softening 10000 litres of water. Find the hardness of the above water sample.

Ans : 200 mg/litre

Desalination of Brackish water by Electrodialysis:

Principle:

Electrodialysis is an electrochemical process in which ions migrate through ion selective membrane as a result of their attraction towards two electrically charged electrodes.

Process:

- The unit consists of electrodes (anode & cathode) and thin rigid ion-selective membranes which are permeable to either cation or anion.

- The anode is placed near anion selective membrane while the cathode is placed near cation selective membrane.
- Under the influence of applied e.m.f. across the electrode, the cations (Na^+) move towards cathode through cation selective membrane while the anions (Cl^-) move towards anode through anion selective membrane.
- The net result is depletion of ions in the central compartment while increase in the concentration in the two side compartments.
- Desalinated water is periodically drawn out from central compartment, while the concentrated brackish water is replaced by fresh sample.

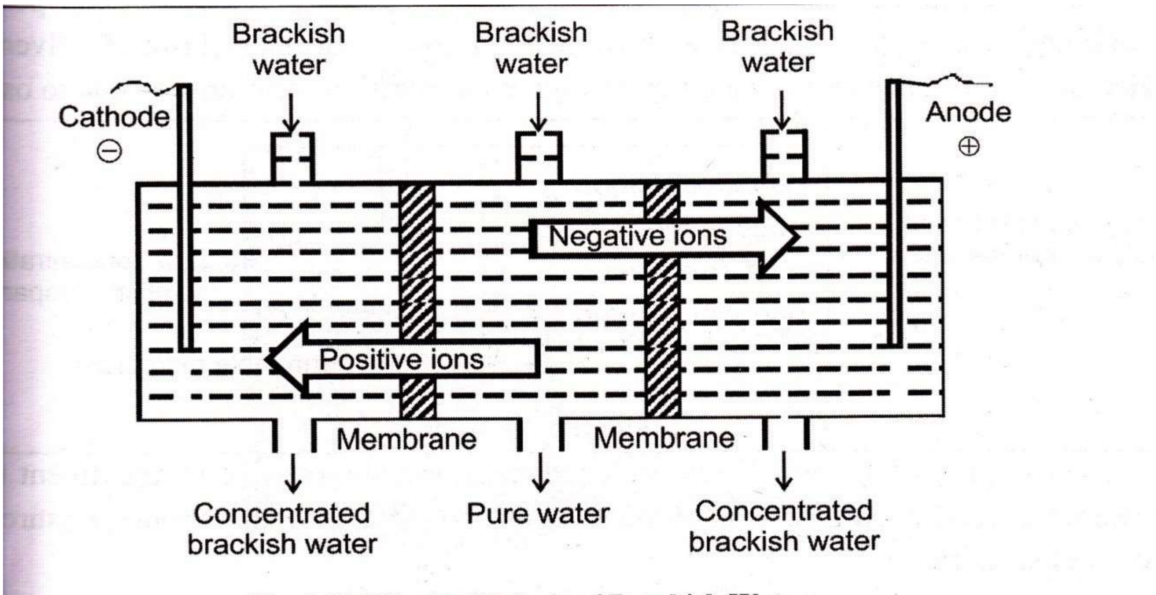


Fig. 1.10: Electro Dialysis of Brackish Water

Advantages:

1. The process is economical.
2. The unit is compact.

Reverse osmosis

What is osmosis?

During natural osmosis, water flows from a less concentrated solution through a semi permeable membrane to a more concentrated saline solution until concentrations on both sides of the membrane are equal

What is Reverse Osmosis (RO)?

Reverse osmosis is the reversal of the natural flow of osmosis. It occurs when the water is moved across the membrane from high concentration to lower concentration under the influence of applied pressure.

Method:

1. In this process, pressure is applied to impure water. Because of this pressure impure water is forced out through the semi permeable membrane; leaving behind the dissolved solids.

2. The membrane consists of very thin films of cellulose acetate, affixed to either side of a perforated tube.

3.The material of the membrane is semi-permeable; it allows water molecules to pass through while acting as a barrier to dissolved solids.

4.The remaining contaminants are concentrated and washed from the surface of the membrane down the drain.

5.Ultimately the membrane could become blocked by salt and other impurities.

6.To solve this problem, the membranes are configured to split the feed water into two streams. One part to be purified and the other part to wash away the particles rejected by the membrane.

Advantages of reverse osmosis:

1. Reverse osmosis possesses a distinct advantage of removing ionic as well as non ionic, colloidal and high molecular weight organic matter.
2. It removes colloidal silica, which is not removed by demineralization.
3. The maintenance cost is less.
4. The life time of membrane is quite high, about 2 years.
5. The membrane can be replaced within a few minutes, thereby providing nearly uninterrupted water supply.

Ultra filtration (UF)

Give an account of ultra-filtration. (3M) May 09.

1. Ultra filtration uses a membrane very similar in design to reverse osmosis systems except that the ultra filter's pores are slightly larger having pore size in the range of 0.0025 to 0.1 microns.
2. The ultra filter is used to remove pyrogens and other long chain organic molecules, salts, proteins and other impurities.

3. Because of the larger pore size in the membrane, UF requires a much lower operating pressure: 10 to 100 psi.
4. The type of membrane media determines how much pressure is needed to drive the water through and what sizes of micro-organisms can be filtered out.
5. Since a high percentage of the water passes through the ultra filters, it will eventually plug if not carefully maintained.
6. In a properly designed system, the ultra filter is regularly and tangentially washed free of contaminants.
7. With this type of design, ultra filtration is an outstanding technology for ensuring very consistent ultra pure water quality.

Advantages:

1. Effectively removes most particles, pyrogens, microorganisms, and colloids above their rated size.
2. Produces highest quality water for least amount of energy.
3. Regenerated using a hot (50°C) 5% caustic solution, solving the problem of fouling

Disadvantages:

It will not remove dissolved inorganic materials.

Applications:

1. Selective concentration of milk constituents (fat and true proteins)
2. Concentration of fruit juices.
3. Clarification of sugarcane juice.
4. Soya bean milk purification.
5. Removal of colloidal particles from surface water.
6. Purification of drinking water.

Methods to determine extent of water pollution:

1. Biological Oxygen Demand:

Definition:

BOD of sewage is defined as **"the amount of free oxygen in water required for the biological oxidation of organic matter under aerobic conditions at 20^0C and for a**

period of 5 days."BOD is expressed in Mg/liter or ppm. Drinking water has less than 1 ppm BOD. An average sewage has the BOD of 100-150 mg oxygen/litre.

Determination of BOD:

This test is based on determination of dissolved O_2. A known volume of sewage sample is diluted with a known volume of saline solution. (Water containing nutrients for the growth of bacteria), whose dissolved oxygen content is pre–determined. The whole solution is incubated in a closed bottle at 20ºC for a period of 5 days. After this, the unused oxygen is determined. The difference between the original oxygen content in saline solution and unused oxygen at solution after 5 days give BOD.

Importance or significance of BOD:

1. BOD test is the most important in sewage treatment as it indicates the amount of decomposable organic matter in sewage. Larger the concentration of decomposable matter, greater is the BOD and consequently, more the pollution of water.

2. It is also a means of checking on the quantity of effluents discharged into surface water.

BOD = [Dissolved Oxygen before incubation- Dissolved Oxygen after incubation] x Dilution Factor

OR

BOD = [DOb- DOa] x Dilution Factor

Dilution Factor = Volume of waste water after dilution/ Volume of waste water after dilution

Numericals On BOD

1. 100 mL of waste water(containing 920 ppm dissolved oxygen) was diluted with 100 mL of distilled water and kept in a bottle at 20º C for 5 days. The oxygen content of resulting water was then found to be 260 ppm. Calculate BOD of the sample.

BOD = [DOb- DOa] x Dilution Factor

BOD= [920-260] X 200/100

BOD= 1320 ppm.

2. A 50 mL Sample contains 840 ppm of dissolved oxygen after 5 days the dissolved oxygen value become 230 ppm after the sample has been diluted to 80 mL calculate BOD of the sample.

2. Chemical Oxygen Demand

Definition:

It is an amount of oxygen required for the chemical oxidation of organic matter in sewage". In other words, it is a measure of oxidisable impurities present in the sewage.

Determination of COD

The chemical oxygen demand is measure of the oxygen equivalent of that portion of organic matter in a sample that is susceptible to oxidation by a strong chemical oxidant. A measured quantity of the sample is reflux with a known amount of $K_2Cr_2O_7$ and H_2SO_4 (Most type of organic matter are completely oxidized by a boiling mixture of chromic and sulphuric acid to produce CO_2 and H_2O.) and the excess of dichromate remaining un-reacted is titrated with ferrous ammonium sulphate [$FeSO_4$ $(NH_4)_2SO_4$. $6H_2O$}]. The $K_2Cr_2O_7$ consumed is proportional to the amount of oxidisable organic matter measured as oxygen equivalent.

$$\text{COD of the sample water} = \frac{(V_{blank} - V_{sample})\ N \times 8000}{X}$$

Where V_{blank} = Volume of FAS solution run down in blank titration
V_{sample} = volume of FAS solution run down in the sample test titration.
N = normality of FAS solution.
X = Volume of test sample taken.

Importance of COD

1. BOD is just the measure of oxygen required for the oxidation of organic matter while COD is measure of both, the biologically oxidisable and the biologically inert organic matter (like cellulose). Thus, COD value is generally found higher than BOD.
2. COD determination gets completed in comparatively less time (i.e. 3hours) than BOD determination (which takes 5 days).
3. On the basis of COD value, approximate BOD value can be estimated.
4. It helps in designing water treatment plant.

Numericals On COD

1) A 25 ml of sewage water sample was refluxed with 10ml of 0.25N $K_2Cr_2O_7$. The unreacted dichromate required 6.5 ml of 0.1N FAS. 10 ml of same $K_2Cr_2O_7$ solution and 25 ml of distilled water under the same conditions required 27 ml of 0.1N FAS. Calculate COD of sewage water sample.

Given: V blank= 27ml

V sample=6.5 ml

Normality=0.1
Volume of sewage sample (X)=25ml

$$\text{COD} = \frac{(\text{Vblank} - \text{Vsample}) \text{X Normailty X } 8000}{\text{Volume of sewage sample}}$$

$$= \frac{(27-6.5) \text{ X } 0.1 \text{ X } 8000}{25}$$

=656mg/litre or 656 ppm

2) A 10 ml of waste water sample was refluxed with 20ml of $K_2Cr_2O_7$ solution after refluxing the excess unreacted dichromate required 26.2 ml of 0.1N FAS solution. A blank of 10 ml distilled water on refluxing with 20ml of $K_2Cr_2O_7$ solution required 36 ml of 0.1N FAS. Calculate COD of water sample.

Ans: 784 ppm

3) A 5 ml of waste water sample was refluxed with 30ml of $K_2Cr_2O_7$ solution after refluxing the excess unreacted dichromate required 23 ml of 0.1N FAS solution. A blank of 5 ml distilled water on refluxing with 30ml of $K_2Cr_2O_7$ solution required 36 ml of 0.1N FAS. Calculate COD of water sample.

Ans: 2080 ppm

Chapter 3: Polymers

- The word polymer is derived from a Greek word polymeros.
  Poly- many,
  Meros - parts.
- This term was introduced by Berzelius in 1833.

Definitions:

- **Polymer**- A complex giant molecule of high molecular mass, built by linking together a large number of monomers.
- **Monomer**-Small repeating unit in polymer are called monomers.

Examples of polymer: - polyethylene, polystyrene, rubber, starch, protein etc.

- **Polymerization**- A process of formation of high molecular weigh compound by reacting monomer molecules together in a chemical reaction.
- **Degree of polymerization-** It is the total number of monomers present in a given polymer.
- **Functionality-** It is the number of bonding sites present on a monomer.

Classification of polymers:-

There are different ways in which polymers can be classified. They are as follows.

1. Based on the origin-

- Natural polymers- polymers which are available from the natural sources are known as natural polymers.
  Example- Starch, Cellulose, Proteins, Natural rubber, cotton, jute, silk etc.
- Synthetic polymers- polymers which are synthesized in lab or industries are known as synthetic polymers or man-made polymers.
  Example- Nylon, Synthetic rubber, polyethylene, polypropylene, PVC etc.
- Semi-Synthetic polymers- polymers which are obtained by modifying natural polymers are called semi-synthetic polymers.
  Example- Cellulose acetate, Halogenated rubber, tericot etc..

2. Based on the monomer present:

They are classified as homopolymer and copolymer.

- Homopolymer: In this polymer the repeating units (monomers) are the same. E.g. rubber

$$\underset{\text{(A -Monomer)}}{nA} \longrightarrow -A-A-A-A-A-$$

- Copolymer: In this polymer, the repeating units are not same, but are derived from two or more molecules.

$$nA + mB \longrightarrow [-A-B-A-B-A-B-A-A-]_{n+m}$$

3. **Based on chemical composition:-**
    - Organic polymer: - A polymer whose backbone chain is essentially made of carbon atom is termed as organic polymer. The atoms attached to the side valencies of the backbone carbon atom are usually hydrogen, oxygen, nitrogen. The majority of synthetic polymers are organic. E.g :- polyethylene , polypropylene ,PVC.
      The body of the living organism contains organic polymer in the form of proteins, DNA, RNA etc.
    - Inorganic polymer: - If the backbone of the polymer chain contains atoms other than carbon, then it is called inorganic polymer.
      For E.g :- polysilane, polyphosphate

4. **Based on response to heat :-**
    - Thermo softening plastic: These are polymers which become soft on heating. They can be moulded into different shapes and shape is retained on cooling. They can be remoulded number of times by heat treatment. Hardness of such plastic is temporary.
      E.g:- Polyethylene, Polypropylene, Polystyrene, PVC
    - Thermosetting plastic: - These are polymers which cannot be reformed once they are set. They are also called as thermosetting resins. They have somewhat 3-D structure and high molecular weight.
      E.g:- Urea formaldehyde, Phenol formaldehyde.

Distinguish between **Thermoplastics and Thermosetting polymers**

Thermoplastics polymers		**Thermosetting polymers**	
1	Softens on heating and stiffen on cooling, reversibly by the action of heat.	1	On heating they are converted into an infusible mass and once set they cannot be reshaped.
2	They can be remoulded.	2	They cannot be remoulded.
3	Formed by addition polymerization.	3	Formed by condensation polymerization.
4	Soluble in organic solvents	4	Insoluble in organic solvents
5	They are soft, weak and less brittle.	5	They are hard, strong and more brittle.
6	They have low molecular weight as compared to thermosetting.	6	They have high molecular weight as compared to thermoplastics.

7	Chemical change does not occur on heating only physical changes are involved.	7	Chemical changes occur on heating.

Polymerization

Polymerization- A **process of formation of high molecular weigh compound by reacting monomer molecules together in a chemical reaction.**

Types of polymerization:-

1. Addition polymerization.
2. Condensation polymerization.
3. Co- polymerization.

Distinguish between addition polymerization and condensation polymerization
Properties of polymers

SR. No	Addition Polymerization	Condensation polymerization
1.	Monomer molecules having multiple bonds undergo addition reactions.	Monomers having simple polar groups condensed together by elimination of small molecule such as H_2O, CH_3OH etc.
2.	The monomer should contain one or more double bond (i.e. they should be bifunctional)	Monomers should have functionality more than two. They should have groups like - OH, -COOH, -COOR, NH_2.
3.	Also called as chain reaction.	Also known as step polymerization
4.	The reaction is very fast.	It is a slow reaction.
5.	No byproducts are formed.	Byproducts like H_2O, CH_3OH, NH_3, and HCl are formed.
6.	Addition polymers have comparatively low molecular weight.	High molecular weight products are formed.
7.	This polymerization takes place in three steps: - Initiation, propagation, termination.	Only one type of reaction i.e. condensation between two functional groups is involved.
8.	Polymers are thermosoftening (thermoplastic)	Polymers are thermosetting

9.	Eg: - polyethylene, polypropylene, polystyrene.	Eg: - urea and phenol formaldehyde.

Molecular Weight-

1.The important properties of polymers are influenced by the molecular weight of polymers as the intermolecular force of attraction between different polymeric chains increase with the length of the polymeric chains.

2. Higher molecular weight polymers are tougher and more heat resistant.
3. Their softening temperature are also higher compared to the low molecular weight polymers.

There are two methods for determining molecular weight of polymers

1. Number Average Molecular Weight
2. Weight Average Molecular Weight

1. Number Average Molecular Weight (M_n)

M_n is defined as the total weight (w) of all molecules in a polymer sample divided by the total number of molecules present.

$$M_n = \frac{N_1M_1 + N_2M_2 + N_3M_3}{N_1 + N_2 + N_3} = \frac{\Sigma N_iM_i}{\Sigma N_i}$$

$$M_n = \frac{\Sigma W_i}{\Sigma N_i}$$

$$M_n = \frac{\Sigma W_i}{\Sigma W_i/Mi}$$

Where, N_i is the number of molecules of molecular mass M_i

M_n is determined by measurement of colligative properties such as freezing point depression, Boiling point elevation, Osmotic pressure.

M_n is a good measure of physical properties such as tensile strength.

2. Weight Average Molecular Weight M_w

M_w is defined as the total weight (w) of all molecules multiply by molecular mass M_i in a polymer sample divided by the total weight of molecule (w)

$$M_w = \frac{N_1M_1^2 + N_2M_2^2 + N_3M_3^2}{N_1M_1 + N_2M_2 + N_3M_3} = \frac{\Sigma N_iM_i^2}{\Sigma N_iM_i}$$

$$M_w = \frac{W_1M_1 + W_2M_2 + W_3M_3}{W_1 + W_2 + W_3} \text{ .... } (NM = W)$$

$$M_w = \frac{\Sigma W_iM_i}{\Sigma W_i}$$

M_w is obtained from light-scattering and ultra-centrifugation techniques M_w is a good measure of molecular size.

Numericals

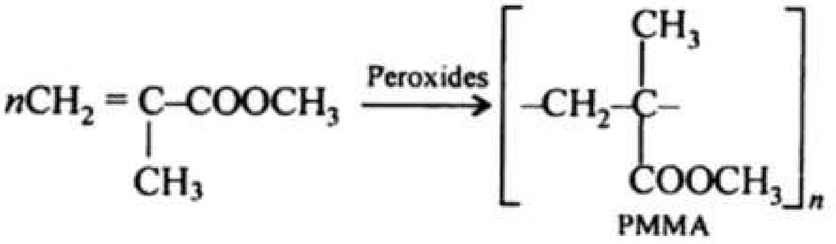
1. A polymer sample consists of 10% by weight of macromolecules of molecular weight 10,000 and 90% by weight of macromolecules with molecular weight 100,000. Calculate M_n and M_w.
2. A polymeric mixture is prepared by mixing three polymers A, B, C having M_n ,M_w and weight in mixture as given below

Polymer	M_n	M_w	Wt. in Mixture (gms.)
A	$1.2\text{x } 10^5$	$4.5\text{x } 10^5$	200
B	$5.6\text{x } 10^5$	$8.9\text{x } 10^5$	200
C	$10\text{x } 10^5$	$10\text{x } 10^5$	100

3. In a polymer, there are 100 molecules of molecular wight 100, 200 molecules of molecular weight 1000 and 300 molecules of molecular weight 10,000 find M_n and M_w.

The preparation, properties and uses of the following

1. ***Polymethyl methacrylate (PMMA) or Lucite or plexiyglass.***



$$n\mathrm{CH_2}=\underset{\mathrm{CH_3}}{\mathrm{C}}-\mathrm{COOCH_3} \xrightarrow{\text{Peroxides}} \left[-\mathrm{CH_2}-\overset{\mathrm{CH_3}}{\underset{\mathrm{COOCH_3}}{\mathrm{C}}}-\right]_n$$

PMMA

Properties:

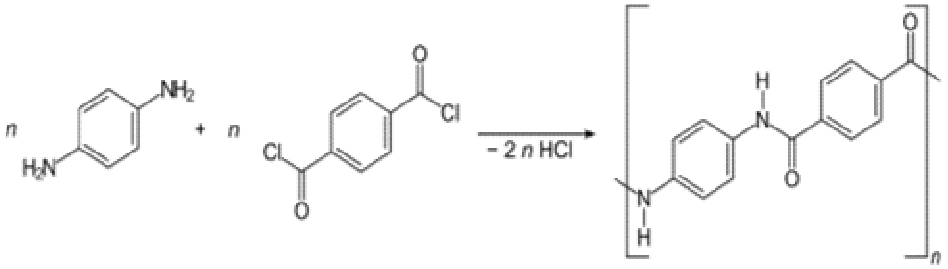
1. It is clear, colorless transparent plastic with high softening point.
2. Good impact strength, high tensile strength.
3. Good optical property i.e. it transmits 98% of the sunlight including ultra violet light.
4. Compared to glass, it weighs only one-third, hence can be easily moulded to any desired shape. Scratches on it can be easily removed by rubbing it with a cloth moistened with acetone. After cracking fragments formed are less sharp, and less harmful.

Uses:

1. It used for tail and signal light lenses.
2. It is an excellent substitute of glass (TV screens, wind screens)
3. It used to make artificial eyes, contact lenses, dentures.
4. It is used for making dome-shaped covers of solar collectors (i.e solar heaters).

2.Kevlar (Aromatic Amide):

Preparation:



Properties:

1. Highly strong, i.e. 5 times strong than steel, 10 times strong than Aluminium.
2. High heat stability and flexibility.
3. Rigid than nylon.

Uses:

1. Aerospace and aircraft industry
2. For making car parts such as tyres, brakes.

3. Protective clothing- bullet proof jackets, helmets etc.
4. For making ropes and cables.

Glass Transition Temperature:

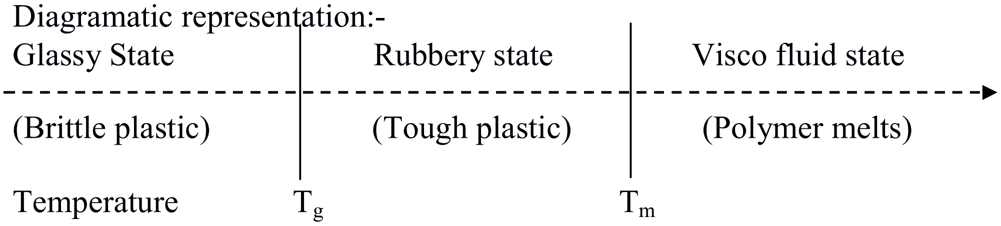
- This temperature below which a polymer is hard, brittle and glassy and above which it is soft, flexible and rubbery is called glass transition temperature. The hard brittle state is known as the **glassy state**

- The soft flexible state as **rubbery or viscoelastic state**.

- On further heating, the polymer becomes a highly viscous liquid and this state isknown as **viscofluid state**.

The glass transition is a property of only the amorphous portion of a semicrystalline solid. The crystalline portion remains crystalline during the glass transition.

Diagramatic representation:-



Factors Influencing Glass Transition Temperature:-

Mobility of the polymer chain is the main factor that affects glass transition temperature..

A polymer chain that can move easily will change from a glass to a rubber at a low

If the polymer chains don't move as easily, then it will require a relatively high temperature to change the compound into a rubbery form.

Thus lesser the mobility higher the T_g.

Value of Tg depends upon molecular characteristics that affect chain stiffness.

Chain flexibility is diminished and Tg is increased due to following

1. **<u>Presence of Polar side atoms or groups</u>** of atoms increases glass transition temperature.

For example: PVC Tg is **87°C**

PP Tg is – 18°C

PVC (poly vinyl chloride) has stronger intermolecular forces than polypropylene (PP) because of the dipole-dipole forces from the C-Cl bond.

2. **<u>Pendant Groups</u>**: The influence of pendant groups on the glass transition temperature is somewhat more complicated.

A) Bulky pendant groups, such as a benzene ring, can catch on neighboring chains like a "fish hook" and restrict rotational freedom. This increases T_g.

For example:-

PP is polypropylene **Tg – 18°C**

PS is polystyrene **Tg 100 °C**

Due to Presence of bulky side groups, Tg of polystyrene greater than polypropylene.

B)Flexible pendant groups, such as aliphatic chains, tend to limit how close chains can pack. This increases rotational motion and lowers T_g.

-

3. **Cross-Linking**:

The presence of cross-linksbetween chains restricts mobility and raises the Tg.

4. **Molecular weight:**Increase in the molecular weight tends to raise Tg

5. **Presence of Double chain bonds and aromatic chain groups**stiffen molecular backbone and raises the Tg.

6. **Plasticizers:**

Plasticizer molecules cause separation of polymer chains which results in increase in the mobility of the molecule. Hence Tg decreases.
Random copolymerization reduces molecular packing and inter-chain forces of attraction **7. Co-polymerization:**
which result in increase in chain mobility. Hence Tg decreases.

Significance of glass transition temperature:

1. It is used as a measure for evaluating the flexibility of a polymer molecule and type of response the polymeric material would exhibit to mechanical stress
2. Tg value along with Tm values gives an indication of temperature region at which a polymeric material transform from a rigid solid to a soft viscous state.
3. It helps in choosing the right processing temperature in which material can be converted into finished product.

Viscoelasticity

- Majority of the engineering polymers are **neither 100% crystalline nor 100% amorphous**
- They are combinations of amorphous and crystalline.
- Below Tg the polymer becomes hard brittle and glassy solid.
- Above Tg, the polymer becomes soft flexible and rubbery.
- On further heating at melting temperature Tm and beyond Tm the polymer become viscous liquids and start flowing.
  In case of polymers above Tg,There exists an intermediate stage where movement of the polymer chain is activated this corresponds to liquid state, but the movement of the polymer molecule as a whole is prevented or forbidden. This is solid state.
- This state is a combination of liquid and solid, and is called the rubbery state or viscoelastic state.

- Under the influence of applied stress it exhibits properties of a viscous fluid as well as an elastic solid. This property is known as viscoelasticity and the deformation is known as viscoelastic deformation.

Plastic:

1. The word plastic originated from Greek, meaning a material that can be moulded or formed into any shape of one's own choice.
2. The plastic is defined as, "An organic material of high molecular weight, which can be moulded into any desired form, when subjected to heat and under pressure". properties like,
3. They have gained lot of importance in every walk of life, due to their unique

- Lightness in weight.
- Good thermal and electrical insulation.
- Good corrosion resistivity.
- Low fabrication cost and decorative surface effect.
- Chemically inert to action of light, oils, acids and dampness.
- Low maintenance cost and high refractive index.

Compounding of Plastic:
(Additives of plastic or constituents of plastics)

- In order to impart certain definite properties to the finished product, plastic is compounded with other ingredients.
- These ingredients are known as additives.
- **The selection of additives and the operation of mixing them with the polymer constituent are known as compounding.**

The various additives/ingredients added are as follows,

1. Resin(Binder)

FUNCTIONS:

- It forms the major part of plastics and holds the different constituents of plastic together.

EXAMPLES:

- Binders are of two types: thermoplastic and thermosetting.
- Thermoplastic- PE, PP, PVC, Thermosetting- urea and phenol formaldehyde.

2. Fillers FUNCTIONS:

Fillers are added to plastics in order to,

- Reduce the cost of plastic.
- Reduce shrinkage on setting and brittleness.
- Improve hardness.
- Improve solvent resistance etc.

-

EXAMPLES:

The most common fillers are carbon black, calcium carbonate, calcium sulphate, talc, silica, alumina, clay, iron oxide, wood flour and metallic powders.

3. **Reinforcements**

FUNCTIONS:

- In some respects reinforcements may be regarded as fillers, but they are added mainly to improve the tensile strength properties of the plastic material.

EXAMPLES:

- Typical reinforcing materials available as fibers are glass, asbestos, boron, carbon, ceramic, cotton flock, jute, synthetic fibers of nylon, polyethylene terephthalate etc.

4. **Plasticizers FUNCTIONS:**

- To improve plasticity and flexibility.
- To improve processing and reduce brittleness of the end product.
- They lower the glass transition temperature below room temperature, so that the properties of a material change from hard, brittle, and glass-like to soft, flexible and tough.

EXAMPLES:

Phosphates, vegetable oil, camphor, esters of oleic acid.

5. **Lubricants FUNCTIONS:**

- They eliminate external friction between the polymer and the metal surface of the processing equipment.
- To impart flawless glossy finish to the product.

EXAMPLES:

Waxes, oils, stearates, oleates

6. **Stabilizers**

- Stabilizers provide protection against degradation caused by heat, oxidation, and solar radiation. Hence, they can be classified as heat (or thermal) stabilizers, antioxidants and UV light stabilizers.

EXAMPLES:

Heat stabilizers: lead compounds like lead chromate, white lead, stearate of Pb, Cd, and Ba.

- **Antioxidants**: substituted phenols, aromatic amines and sulphur compounds.
- **UV Light stabilizers:** substituted benzophenones; benzotriazoles and acrylonitriles, titanium dioxide and zinc oxide

7. **Fire Retardants**

FUNCTIONS:

Plastic compounds may also contain components that improve the fire resistance of the end product.

EXAMPLES:

The most commonly used fire retardants are compounds containing halogen, derivatives of antimony, phosphorous, boron, and nitrogen.

8. Colorants FUNCTIONS:

- Colorants are added to give colour to the plastic material and also to improve the appearance.

EXAMPLES:

Ultramarine- blue colour, $CaCO_3$ and zinc oxide- white, chromium trioxide- green, ferric oxide – red colour.

Fabrication of plastics:

Giving desired shape to plastic is known as fabrication of plastic.

The methods usually depend upon: - types of plastic or resins used i.e. whether thermosetting or thermo softening plastic. Commonly used fabrication methods are,

1. Compression moulding.
2. Injection moulding
3. Extrusion moulding
4. Transfer moulding

1.**Compression Moulding**

- Compression moulding is used for **thermoplastics as well as thermosetting polymers**.
- Compression moulding is the process that moulds molten plastic, through **compression**, into the desired shape of the moulding.
- The die used for moulding purpose consists of two parts:

  Upper cover part & Lower part

  In closed condition the gap between two halves gives the desired shape to the product.

  Generally lower part of the mould is fixed & upper part moves up & down. The movement being properly aligned because of guide pins present. The lower part of the die also has arrangement for heating & cooling by circulating fluid through pipe work.

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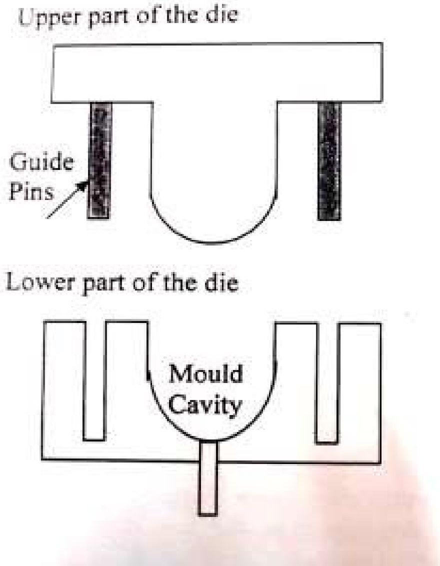
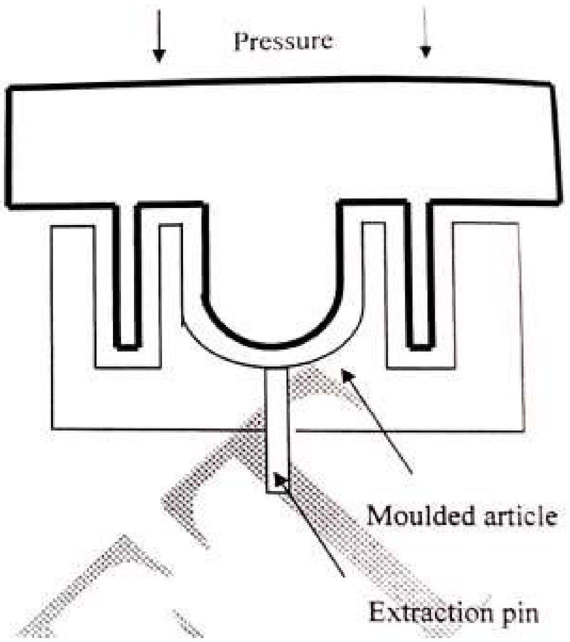




- The predetermined quantity of plastic ingredients in proper proportion is filled into the cavity. A slight excess of material is taken to ensure that the cavity gets completely filled with material.
- The charge in cavity is heated to make the moulding easier. Moulding temperature ranges from 130^0C to 180^0C with pressure varying from 100 to 500 kg/cm^2 depending upon kind of raw material.
- Due to heat and pressure, the cavity is filled with fluidized plastic. Then two halves are closed very slowly, to ensure the uniform distribution of plastic mass in the mould. It will take the shape of mould.
- Finally curing is done either by heating (in case of thermosetting plastic) or cooling(in case of thermo softening plastic).
- After curing, the moulded article is taken out by opening the mould parts.

Advantages:

- Relatively low capital and tooling cost.
- Low mould maintenance.
- The product has low residual stress.
- Retention of mechanical and electrical properties.

Applications:

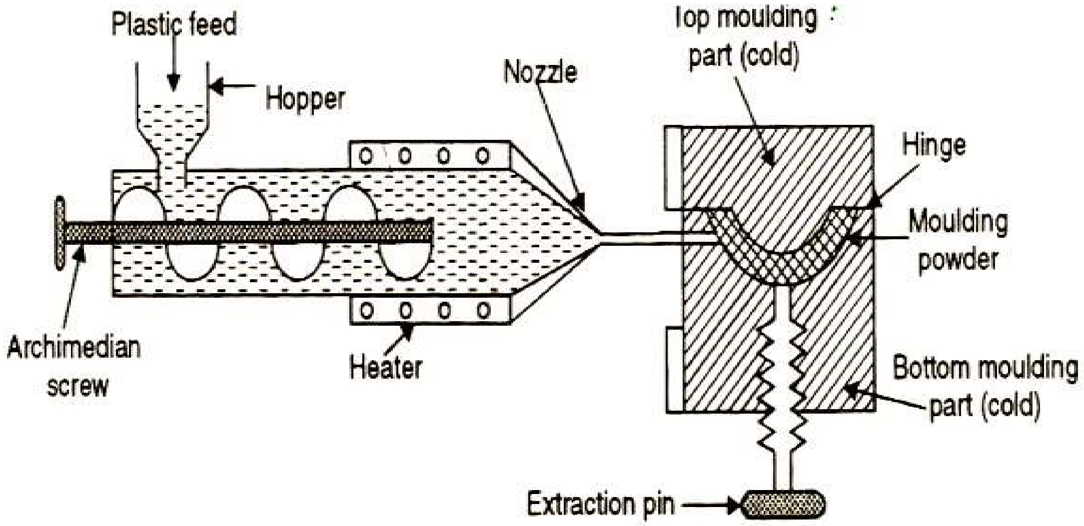
Familiar products manufactured by compression moulding include: 3-pin mains plugs, electrical switches, sockets and ashtrays, handles of electric irons etc.

- Thermoplastic products like gramophone records.
- Rubber products like springs, anti- vibration mounting pads

2. Injection moulding:

- **It is used for moulding thermoplastic polymers.**
- Injection moulding is a process where the hot, soft plastic is forced into a cavity in a steel die.
- The size and shape of the cavity is the same as the finished product.
- The shapes may be simple or complex.
- A pigment is added to the plastic powder or granules to produce the desired colour.
- The plastic is placed in a hopper so that it falls into the machine as the screw turned by the gear driven by an electric motor. that converts the plastic into a hot, almost liquid substance.
- As the screw turns it pushes the plastic along the machine and through the heater

- A split die is connected to the end of the machine.
- The screw is pushed into the machine and this forces the soft plastic through a small hole into the cavity of the die.
- **The die and plastic are cooled to harden the plastic (curing).**
- The die is separated and the plastic item is released. The process is then repeated to make another item.



Injection moulding

Advantages:

- High speed production,
- ow moulding cost,

- Loss of material is less and low finishing cost,

- ability to make complex shapes in single operation,

-

Limitations:
High capital cost of injection moulding machine.
Moulds are also costly.

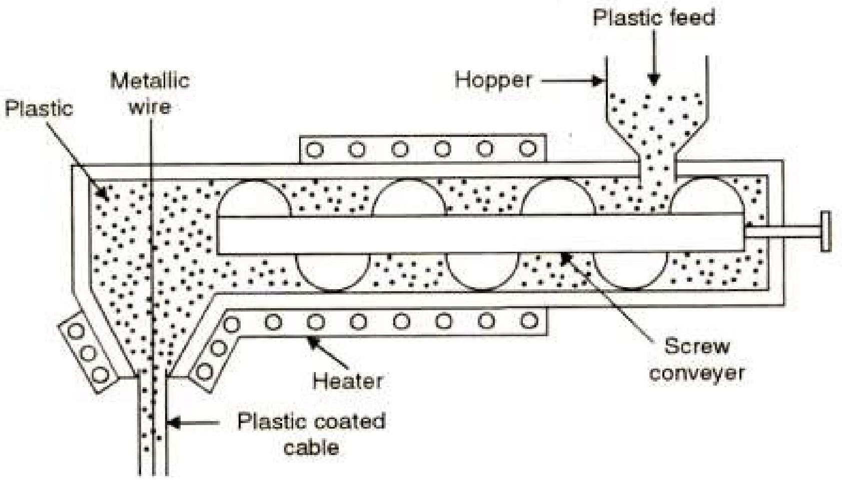
Applications:
Products such as the case of a mobile phone, computer parts, TV cabinets, mugs, buckets, milk crates, safety helmets, ice-block trays and food containers are prepared by injection moulding.

3. Extrusion moulding:.

- It is used for moulding **thermoplastic polymers**.
- In extrusion moulding the plastic powder (or granules) is placed in a hopper and then falls into the machine
- The screw turns and pushes the raw plastic along the machine where it is heated to soften the plastic.
- The softened plastic is then forced through a hole in the extrusion die.
- The extruding process is also very much like that of an old, hand operated meatmincer.
- **The extruded plastic is cooled (curing)** and then cut into the desired lengths.
- The shape and size of the extrusion is the same as the shape and size of the hole in the die.
- Changing the shape of the hole in the extrusion die will produce different shapes.

Advantages and applications:
It is most efficient and most rapid method for producing long continuous article such as tubing, tooth paste tubes, rods and filaments, pipes etc.

Limitation:
However this method can be used for obtaining linear shapes only.



Moulding of insulated electric cable of vertical extrusion moulding

4. Transfer moulding

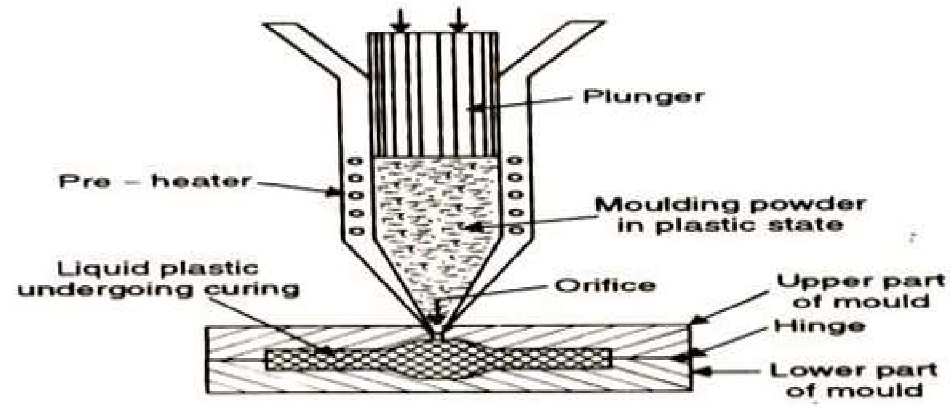
- The method is applicable for **thermosetting plastic** but the technique used is that of injection moulding.
- In this method the mould powder is kept in a heated chamber which is maintained at a temperature at which the moulding powder just starts to become plastic.
- This plastic is then injected through an orifice into mould by a plunger, working at a high temperature.
- The temperature of the material at the time of injection from the orifice becomes so high that moulding powder becomes liquid and flows quickly into the mould.
- **Mould is then heated up to the curing temperature required for setting.**
- The moulded article is then ejected mechanically.

Advantages:-

- Intricate shapes can readily be produced by transfer moulding.
- Article produced is free from flow marks.
- Even thick pieces cure almost completely and uniformly.
- Shrinkage and distortion are minimum due to uniform and through curing. Hence the mechanical strength and density of fabricated plastic pieces is higher.
- Moulding and finished cost are very less.
- Blistering is almost eliminated, since air and waste gases are expelled in the plasticizing chamber itself.

Limitations:

- Tooling is costly and complex
- It increases wear and maintenance cost.



Transfer moulding

Applications:
Utensil handles, electric appliance parts, electronic components, coils, integrated circuits, plugs, etc.

Conducting polymers

i) Most polymeric materials are poor conductor of electricity, because of the non availability of large no. of free electrons in the conduction process.
ii) Within past several years, polymeric materials have been synthesized which posses electrical conductance on par with metallic conductors.
iii) Polymers that conduct electricity are called conducting polymers.
iv) Conducting polymers are long, carbon-based chain, composed of simple repeating units called monomers & are capable of conducting electricity.
v) These polymers are widely used over conventional conducting materials because of their ease of processing, relative conductivity, & stability.
vi) Conducting polymers are much more electrically conductive than standard polymers, but much less than metals such as copper.

E.g. polyaniline, polythiophene

Classification:-

Intrinsic polymers (polymers containing conjugated pi electrons)

- ▪ This type of polymers contain conjugated-electron system in the backbone.
- Presence of delocalized electron pair increases the conductivity of polymer.
- E.g:- polyacetylene polymer, Polyaniline, Polythiophene.

A) Doped conducting polymer

- These polymers are obtained by exposing intrinsically conducting polymers like: polyacetylene, Polyaniline, Polythiophene with a charge transfer agent.
- These polymers are usually doped with appropriate impurities so that their conductivity increases.
- P-doping impurities are lewis acids like I_2 Br_2, AsF_5 and BF_3 etc which act as oxidizing agent.

$$\bullet\ (C_2H_2)_n + I_2 \longrightarrow (C_2H_2)_n^+ I_2^-$$

- N- Doping impurities are Li, Na, Ca, etc. here the polymer is treated with the impurity so that reduction takes place & negative charges are created on the backbone of the polymer.

$$(C_2H_2)_n + Li \longrightarrow (C_2H_2)_n^- Li^+$$

C)Extrinsic conducting polymers:

- **Conductive element filled polymer:** Here conductive element such as carbon black, metallic fibres and metal oxides are added to the polymer. Here the polymer acts as a binder to hold the conductive element together.
- **Blended conducting polymer**: Here a conventional polymer is blended with conducting polymer like polyacetylene, Polyaniline, Polythiophene either by physical or chemical change.
- **Co-ordination conducting polymer (inorganic polymer):**
  This is a charge transfer complex containing polymer obtained by combining a metal atom with a polydentate ligand

Applications:-

1) In rechargeable light weight batteries, these batteries are 10 times lighter than Pb-storage batteries.
2) In optically display devices.
3) Wiring in aircrafts & aerospace components.
4) In antistatic materials: To avoid static electricity in plastic, carpets in office, theaters, doped aniline is used as antistatic material.

5) They are used in construction of photovoltaic cells like, Al / conducting polymer / Pt 6)In telecommunication system.
7) Electronic devices like transistors and diodes.
8) In solar cells and drug delivery system for human body.

Chapter 4:Aromatic systems and their molecular structure

Many organic compounds obtained from natural sources like resins, balsams (tree gum), oil of wintergreen etc possessing pleasant fragrance (aroma- smell) are named as aromatic compounds.
Aromatic hydrocarbons also called arenes contains only carbon and hydrogen
Benzene is simplest aromatic hydrocarbon

Definition: Aromaticity

It is The property of certain planar, cyclic, conjugated molecules like benzene which behave like unsaturated molecules and undergo substitution reactions rather than addition reactions due to de-localization of electrons.

Characteristics of aromatic compound : ✓

1) Aromatic compounds contain higher percentage of carbon
2) They are cyclic compounds with alternate single and double bond
3) They burn with sooty flame
4) They prefer substitution reaction. Eg. Friedal-Crafts alkylation and acylation etc.
5) They are not attacked by normal oxidising and reducing agents
6) They do not undergo addition reaction easily.
7) They do not decolourise dilute aqueous solution of potassium permanganate

Q. Distinguish between aromatic & aliphatic compds.

Huckel rule:

Huckel rule for aromaticity states that, ' A cyclic system, containing (4n+2) π electrons where n is an integer equal to 0, 1, 2, 3, ...etc, would have special stability.'

This special stability is called Aromaticity.

× This rule can be applied successfully to cyclic polyenes, polycyclic compounds and nonbenzenoid compounds to predict aromaticity in them.

According to Huckel rule an aromatic compound must possess following characteristics

✓ a) It must be planar
✓ b) It must be cyclic.
✓ c) It must possess fully delocalized (4n+2) π electrons where n is equal to 0, 1, 2, 3, ...etc.

n=0 4n+2 = 2
n=1 4n+2 = 6
n=2 4n+2 = 10
n=3 4n+2 = 14 etc.

[Delocalizable electrons means-

a. One double bond will give 2 electrons.
b. Nonbonded electrons on N, S, O, X each one will give only one pair for delocalization.
c. – ve charge will give 2 electrons.
d. + ve charge will give 0 electrons
e. Radical will give 1 electron.

Full delocalization is possible when

a. The molecule is fully conjugated (alternate double and single bond)

b. In a cyclic system terminal C atom of pi network are separated by a sp3 hybridized carbon bearing + ve or – ve charge or radical site.]

Q. Predict the aromatic nature of following molecules.

①

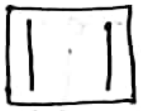
cyclopropene

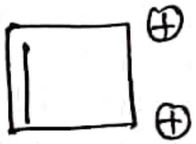
②

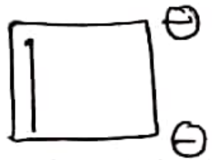
cyclopropenyl cation

③

—〃— anion

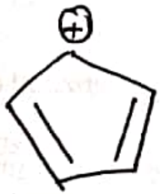
④

Cyclobutadiene

⑤

cyclobutadienyl cation

⑥

—〃— anion

⑦

cyclopentane.

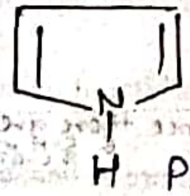
⑧

cyclopentadienyl cation

⑨

—〃— anion

⑩

benzene

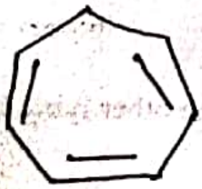
✓ ⑪

pyrrole

✓ ⑫

furan

✓ ⑬

thiophene

⑭

cycloheptatrien

✓ ⑮

Pyridine.

⑯

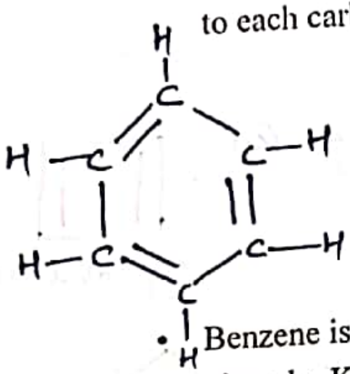
tropyllium cation
or
Cycloheptatrinyl catio

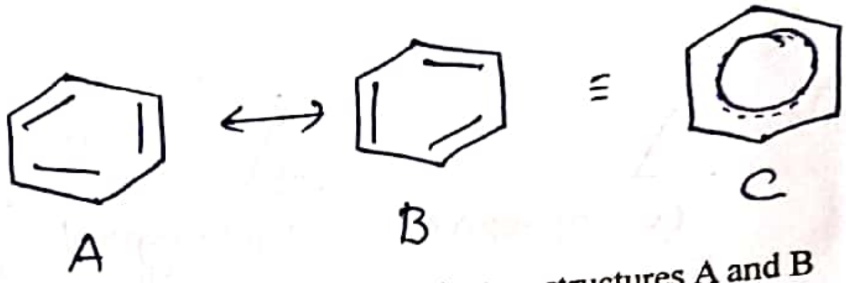
⑰

—〃— anion.

Structure and bonding of benzene

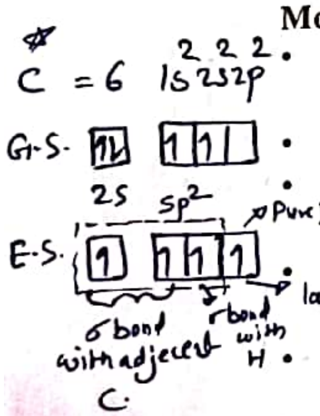
- Molecular formula of benzene C_6H_6.
- August Kekule suggested the structure for benzene having a cyclic planar ring of six carbon atoms with alternate single and double bond and hydrogen atom attached to each carbon Atom.





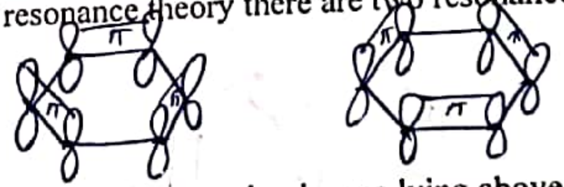
- Benzene is a hybrid of various resonance structures. The two structures A and B given by Kekule are the main contributing structures. The circle in structure C represents six electrons de-localized over the six carbon atoms of benzene ring.
- For benzene, stability due to resonance is so high that double bond of the molecule resist breaking. This explains lack of reactivity of benzene towards addition reactions.

Molecular orbital structure of benzene

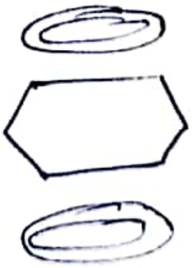


- The orbital picture of benzene show that all six carbon atoms in benzene are sp2 hybridised. ★
- Two sp2 hybrid orbitals of carbons overlap and form carbon- carbon sigma bond.
- Third sp2 hybrid orbital of each carbon overlap with s orbital of hydrogen atom to form 6CH sigma bonds.
- All the carbon atoms of the ring are in same plane with their bond separated by angle of 120 degrees actual in figure.
- The pure p orbital of carbon atom overlaps laterally with p orbital of adjacent carbon atom result in formation of ~~Three~~ π bonds. ★★ Hence there are 6 C–C σ bonds 6 C-H σ bonds. 3 C-C π bonds.
- According to resonance theory there are two resonance structure of benzene

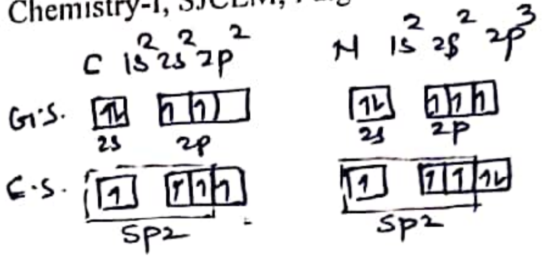
Q. Explain formation of π bond in benzene



This results in two pi electron clouds, one lying above and the other lying below the plane of the plane of the ring.

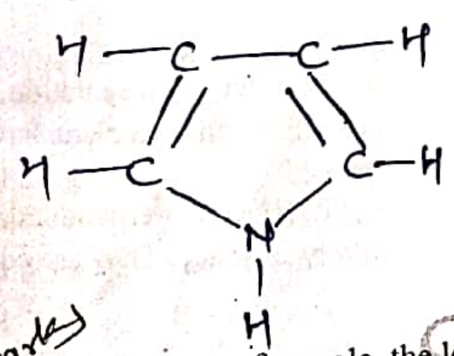


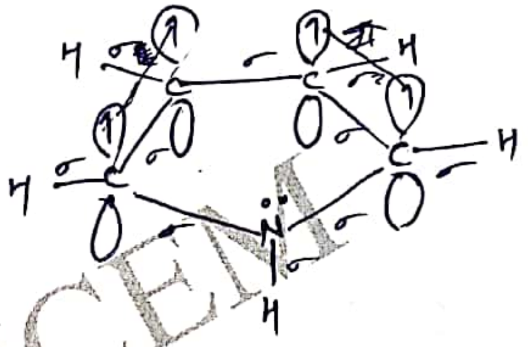
Explain formation of σ & π bond in pyrrole.



Structure and bonding of Pyrrole

- Molecular formula C_4H_5N.
- All the atoms of pyrrole rings are in the same plane.
- Angles between the bonds in the rings are 120°.
- All the atoms including N atom are sp2 hybridised. ☆
- Two orbitals ~~of each atom~~ from sp2 form sigma bond between carbon atom and also the N atom.
- Third sp2 orbital forms sigma bond ~~between Carbon and~~ with hydrogen atoms.
- The pure p orbital of carbon atom with one electron and the N atom with a pair of electrons overlaps laterally with adjacent atom result in formation of circular clouds of π electrons.
- ~~There will be delocalized circular cloud of six π electrons~~ above and below the plane of the rings.





Q. 2 marks) Why pyrrole is a weak base

- In the case of pyrrole, the lone pair of electrons on the N atom is also involved in the π electron cloud. Therefore it is not available to be shared with a proton. Hence, pyrrole is an extremely weak base.