

Solution

1. Mole fraction (x)

If the number of moles of A and B are n_A and n_B respectively, the mole fractions of A and B will be

$$x_A = \frac{n_A}{n_A + n_B}, \text{ and } x_B = \frac{n_B}{n_A + n_B}$$

$$x_A + x_B = 1$$

2. **Molarity (M)** = $\frac{\text{Moles of solute}}{\text{Volume of solution in litres}} \text{ mol L}^{-1}$

3. **Molality (m)** = $\frac{\text{Moles of solute}}{\text{Mass of solvent in kilograms}} \text{ mol kg}^{-1}$

4. **Parts per million (ppm)**

$$= \frac{\text{Number of parts of the component}}{\text{Total number of parts of all components of the solution}} \times 10^6$$

5. Raoult's law for a solution of volatile solute in volatile solvent :

$$p_A = p_A^\circ \cdot x_A$$

$$p_B = p_B^\circ \cdot x_B$$

Where p_A and p_B are partial vapour pressures of component 'A' and component 'B' respectively in solution. p_A° and p_B° are vapour pressures of pure components 'A' and 'B' respectively.

6. Raoult's law for a solution of non-volatile solute and volatile solvent :

$$\frac{p_A^\circ - p_A}{p_A^\circ} = i x_B \approx i \frac{n_B}{n_A} = i \frac{W_B \times M_A}{M_B \times W_A} \text{ (for dilute solutions)}$$

Where x_B is mole fraction of solute, i is van't Hoff factor and $\frac{p_A^\circ - p_A}{p_A^\circ}$ is relative lowering of vapour pressure.

NUMERICALS

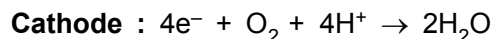
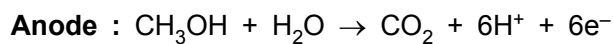
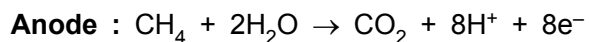
UNIT CELLS AND CRYSTAL LATTICES

1. In a fcc arrangement of A and B atoms, atoms of A are present at the corners of the unit cell and atoms of B are present at the face centres. If one atom of A is missing from its position at the corner, what is the formula of the compound? [Ans. : A_7B_{24}]
2. A compound made up of elements 'A' and 'B' crystallises in a cubic close packed structure. Atoms A are present on the corners as well as face centres, whereas atoms B are present on the edge-centres as well as body centre. What is the formula of the compound? [Ans. AB]
3. In a crystalline solid, anions 'C' are arranged in cubic close packing, cations 'A' occupy 50% of tetrahedral voids and cations 'B' occupy 50% of octahedral voids. What is the formula of the solid? [Ans. : A_2BC_2]
4. Magnetite, a magnetic oxide of iron used on recording tapes, crystallises with iron atoms occupying $\frac{1}{8}$ of the tetrahedral holes and $\frac{1}{2}$ of the octahedral holes in a closed packed array of oxygen ions. What is the formula of magnetite? [Ans. : Fe_3O_4]

DENSITY OF UNIT CELL

5. Sodium crystallises in a bcc unit cell. What is the approximate number of unit cells in 4.6 g of sodium? Given that the atomic mass of sodium is 23 g mol⁻¹. [Ans. : 6.022×10^{22}]
6. An element crystallises in a cubic close packed structure having a fcc unit cell of an edge 200 pm. Calculate the density if 200 g of this element contain 24×10^{23} atoms. [Ans. : 41.6 g cm^{-3}]
7. A metallic element has a body centred cubic lattice. Edge length of unit cell is 2.88×10^{-8} cm. The density of the metal is 7.20 g cm^{-3} . Calculate
 - (a) The volume of unit cell.
 - (b) Mass of unit cell.
 - (c) Number of atoms in 100 g of metal.[Ans. : (a) $2.39 \times 10^{-23} \text{ cm}^3$ (b) $1.72 \times 10^{-22} \text{ g}$, (c) 1.162×10^{24} atoms]
8. Molybdenum has atomic mass 96 g mol⁻¹ with density 10.3 g/cm^3 . The

12. A fuel cell is a voltaic cell that utilizes fuel such as H_2 , CH_4 , CH_3OH etc. in the cell reaction.



13. Corrosion of metals is essentially an electrochemical phenomenon. It slowly coats the surfaces of metallic objects with oxides or other salts of the metal.

VSA QUESTIONS (1 - MARK QUESTIONS)

1. What is a galvanic cell?
2. Give the cell representation for Daniell Cell.
3. Give the condition for a cell when there is no flow of electrons or current.
4. Can you store zinc sulphate solution in a copper container? Give suitable reason. ($E^\ominus \text{Zn}^{2+}/\text{Zn} = -0.76\text{V}$, $E^\ominus \text{Cu}^{2+}/\text{Cu} = 0.34\text{V}$)
5. Write Nernst equation for the electrode reaction : $\text{M}^{n+}(\text{aq}) + \text{ne}^- \rightarrow \text{M}(\text{s})$ at 298 K and 1 bar pressure.
6. List the two factors that influence the value of cell potential of a galvanic cell.
7. Show the direction of flow of electrons in the following cell :
 $\text{Zn}(\text{s}) \mid \text{Zn}^{2+}(\text{aq}) \parallel \text{Ag}^+(\text{aq}) \mid \text{Ag}(\text{s})$
8. Write the relation between $E^\ominus_{\text{cell}}$ and equilibrium constant (K) of a cell reaction.
9. Define cell constant. Write its SI unit.
10. How does specific conductance or conductivity of electrolytic solution vary with temperature?
11. What is the SI unit of (i) Conductance; (ii) Conductivity.
12. Represent a concentration cell with a suitable example.
13. Express the relation between conductivity and molar conductivity.
14. How many faradays are required to oxidise 1 mol of H_2O to O_2 .
15. Write the unit of Faraday constant.
16. State one difference between a primary battery and secondary battery.

NUMERICAL PROBLEMS

NERNST EQUATION

1. For concentration cell :



- (a) Calculate the cell potential.
(b) Will the cell generate emf when concentration becomes equal?

[Ans. : (a) 0.295V, (b) No.]

2. A zinc rod is dipped in 0.1M solution of ZnSO_4 . The salt is 95% dissociated at this dilution at 298K. Calculate the electrode potential

$$\left(E^\ominus_{\text{Zn}^{2+}/\text{Zn}} = -0.76\text{V} \right).$$

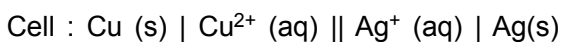
[Ans. : -0.7902V]

3. For the electrode $\text{Pt, H}_2 (\text{g, 1 atm}) | \text{H}^+_{(\text{aq})} (x \text{ M})$, the reduction electrode potential at 25°C is -0.34V . Write the electrode reaction and calculate the value of x. and the pH of solution.

[Ans. : $x = 1.807 \times 10^{-6}$, pH = 5.743]

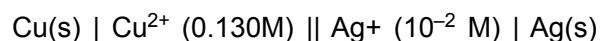
4. For what concentration of $\text{Ag}^+ (\text{aq})$ will the emf of the given cell be zero at 25°C if concentration of $\text{Cu}^{2+} (\text{aq})$ is 0.1M?

Given $E^\ominus_{\text{Ag}^+/\text{Ag}} = 0.80\text{V}$; $E^\ominus_{\text{Cu}^{2+}/\text{Cu}} = +0.34\text{V}$.



[Ans. : 5.3×10^{-9}]

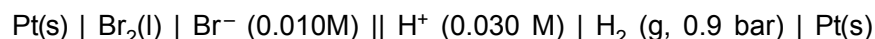
5. Write the Nernst equation and calculate the emf of the following cell at 298K.



Given $E^\ominus_{\text{Cu}^{2+}/\text{Cu}} = +0.34\text{V}$; $E^\ominus_{\text{Ag}^+/\text{Ag}} = +0.80\text{V}$

[Ans. : 0.37V]

6. Write the Nernst equation and emf of the following cell at 298K



Given $E^\ominus_{\text{Br}_2|\text{Br}^-|\text{Pt}} = 1.09\text{V}$

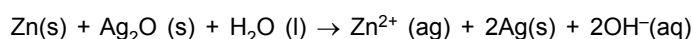
[Ans. : -1.29V]

(Given $E_{\text{Zn}^{2+}/\text{Zn}}^{\ominus} = -0.763\text{V}$, $E_{\text{Cd}^{2+}/\text{Cr}}^{\ominus} = -0.403\text{V}$,

$$1\text{F} = 96500 \text{ C mol}^{-1}. R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1}]$$

[Ans. : Cell emf = 0.3305 V; $\Delta G^{\ominus} = 69.48 \text{ kJ mol}^{-1}$]

13. In the button cell widely used in watches and other derices, the following reaction takes place :

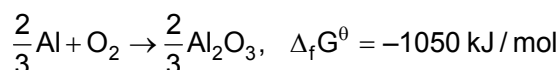


Determine $\Delta_r G^{\ominus}$ and $E^{\ominus}$ for the reaction.

Given $E_{\text{Zn}^{2+}/\text{Zn}}^{\ominus} = -0.76\text{V}$; $E_{\text{Ag}^{+}/\text{Ag}}^{\ominus} = 0.8\text{V}$

[Ans.: $-301.08 \text{ kJ / mol.}$, $E_{\text{cell}}^{\ominus} = 1.56\text{V}$]

14. The standard Gibbs energy of formation ($\Delta_f G^{\ominus}$) of Al_2O_3 is $-1050 \text{ kJ mol}^{-1}$ of O_2



Calculate voltage applied to carry out electrolysis of Al_2O_3 .

($F = 96500 \text{ C mol}^{-1}$)

[Ans. : 2.720 V]

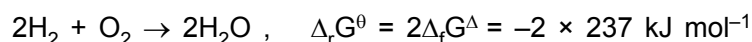
[Hint : $\frac{2}{3}\text{Al}_2\text{O}_3 \rightarrow \frac{4}{3}\text{Al} + \text{O}_2$, $\Delta_r G^{\ominus} = +1050 \text{ kJ / mol}$

$$\Delta_r G^{\ominus} = -nE^{\ominus}F \text{ and } n = 4]$$

15. Calculate the $E_{\text{cell}}^{\ominus}$ produced in $\text{H}_2 - \text{O}_2$ fuel cell if standard Gibbs energy of formation of water is -237 kJ/mol .

[Ans. : 1.228 V]

[Hint : The Cell reaction is :



The number of electrons involved = 4

$$\Delta_r G^{\ominus} = -n E_{\text{Cell}}^{\ominus} F.$$

CONDUCTANCE, CONDUCTIVITY & MOLAR CONDUCTIVITY

16. The conductivity of 0.2 M solution of KCl at 298K is 0.025 S cm^{-1} . Calculate its molar conductivity. [Ans. : $125 \text{ S cm}^{-2} \text{ mol}^{-1}$]
17. The molar conductivity of 0.1M CH_3COOH solution is $4.6 \text{ S cm}^2 \text{ mol}^{-1}$. Calculate the conductivity and resistivity of the solution.

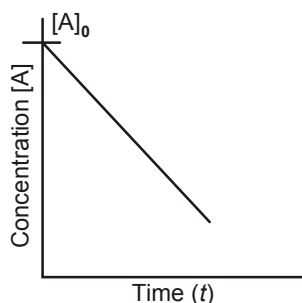
18. The resistance of a conductivity cell containing 0.01 M KCl solution at 298K is 1500Ω . What is the cell constant if the conductivity of 0.001 M KCl solution at 298K is $0.146 \times 10^{-3} \text{ S cm}^{-1}$? [Ans. : 0.219 cm^{-1}]

KOHLRAUSCH LAW

19. The molar conductivities of NH_4^+ ion and Cl^- ion are $73.5 \text{ S cm}^2 \text{ mol}^{-1}$ and $76.255 \text{ S cm}^2 \text{ mol}^{-1}$ respectively. The specific conductivity of 0.1 M NH_4Cl is $1.288 \times 10^{-2} \text{ S cm}^{-1}$. Calculate the dissociation constant of NH_4Cl . [Ans. : 7.396×10^{-2}]
20. Molar conductivity at infinite dilution for NH_4Cl , NaOH and NaCl solution at 298K are respectively 129.8, 218.4 and $108.9 \text{ S cm}^2 \text{ mol}^{-1}$ and Λ_m^c for 10^{-2} M solution of NH_4OH is $9.33 \text{ S cm}^2 \text{ mol}^{-1}$. Calculate the degree of dissociation of NH_4OH . [Ans. : 0.039]
21. Calculate the degree of dissociation of acetic at 298K, given that
- $$\Lambda_m^\circ(\text{CH}_3\text{COO}^-) = 40.9 \text{ S cm}^2 \text{ mol}^{-1}$$
- $$\Lambda_m^\circ(\text{H}^+) = 349.1 \text{ S cm}^2 \text{ mol}^{-1}$$
- $$\Lambda_m(\text{CH}_3\text{COOH}) = 11.7 \text{ S cm}^2 \text{ mol}^{-1}$$
- [Ans. : 3×10^{-2}]

VALUE BASED QUESTION (4-MARK QUESTIONS)

22. One afternoon when Preeti returned from her school she found that the main gate of her house was painted in green. She was very happy to see it. After about two months she noticed a brown and brittle solid deposited at a small portion of the gate. On looking minutely at it she found that there was no paint on that portion of the gate. Immediately she thought of its reason.
- Mention the reason of deposition of brown and brittle solid on the gate.
 - Name the brown solid and write its formula.
 - What is role of paint on gate.
 - Write the associated values.
23. Manu and his father went to a shop to purchase a battery for inverter. Shopkeeper showed them two types of batteries, one with lead plates and other with cadmium plates. Manu's father wanted to purchase lead battery as it was cheaper but Manu suggested cadmium battery.
- As a student of chemistry, give two reasons that why Manu suggested cadmium battery.



- (i) What is the order of the reaction ?
- (ii) Write the rate expression for the reaction.
9. What will be the order of reaction, if the rate of reaction does not depend on the concentration of any of the reactant.
10. For the elementary step of a chemical reaction :

$$\text{H}_2 + \text{I}_2 \rightarrow 2\text{HI}$$
 rate of reaction $\propto [\text{H}_2] [\text{I}_2]$
 What is the (i) molecularity and (ii) order of the reaction.
[Ans. : (i) 2 (ii) 1]
11. For a chemical reaction $\text{A} \rightarrow \text{B}$. The rate of the reaction is given as Rate = $k [\text{A}]^n$, the rate of the above reaction quadruples when the concentration of A is doubled. What is the value of n?
[Ans. : n = 2]
12. Mention one example of zero order reaction.
13. What is the order of radioactive decay?
[Ans. : First order]
- *14. Express the relation between the half-life period of a reactant and initial concentration of a reaction of n^{th} order.
[Ans. : $t_{1/2} \propto \frac{1}{[\text{R}]_0^{n-1}}$]
- *15. A reaction is 50% complete in 2 hours and 75% complete in 4 hours. What is the order of reaction?
[Ans : First order]
16. Suggest an appropriate reason for the observation : “On increasing temperature of the reacting system by 10 degrees, the rate of reaction

almost doubles or even sometimes becomes five folds.”

- *17. For a chemical reaction, activation energy is zero at 300K and rate constant is $5.9 \times 10^{-5} \text{ s}^{-1}$, what will be the rate constant at 400K?

[Ans. : $5.9 \times 10^{-5} \text{ s}^{-1}$]

- *18. Two reactions occurring at the same temperature have identical values of activation energy. Does this ensure that also they will have the same rate constant? Explain.

[Hint : Rate depends on the nature and concentrations of reactants and also pre-exponential factor.

19. The rate constant of a reaction is given by the expression $k = Ae^{-E_a/RT}$. Which factor in this expression should register a decrease so that the reaction proceeds rapidly?
20. For a chemical reaction, rate constant $k = 5.3 \times 10^{-4} \text{ mol L}^{-1} \text{ s}^{-1}$, what will be the order of reaction?

[Ans. : Zero order]

SA (I) TYPE QUESTIONS (2 - MARK QUESTIONS)

1. List four factors which affect the rate of a chemical reaction. State how each of these factors changes the reaction rate.
2. Differentiate between
- (a) Average rate and instantaneous rate of a chemical reaction.
 - (b) Rate of a reaction and specific rate of reaction, i.e., rate constant.
3. The rate law for the reaction : $A + B \rightarrow P$ is given by

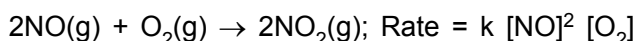
$$\text{Rate} = k [A]^n [B]^m$$

On doubling the concentration of A and reducing the concentration of B to half of its original concentration, calculate the ratio of the new rate to the previous rate of reaction.

[Ans. : 2^{n-m}]

$$\left[\text{Hint : } \frac{\text{New rate}}{\text{Previous rate}} = \frac{k [2A]^n \left[\frac{B}{2}\right]^m}{k [A]^n [B]^m} \right]$$

4. For the reaction in a closed vessel :



If the volume of the reaction vessel is doubled, how would it affect the rate of the reaction?

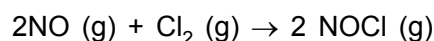
[Ans. : diminishes to 1/8 of initial value]

LONG ANSWER TYPE QUESTIONS (5-Mark Questions)

1. (a) A chemical reaction is of second order w.r.t. a reactant. How will the rate of reaction be affected if the concentration of this reactant is (a) doubled; (b) reduced to 1/8th?

[Ans. : (a) Four times (b) 1/64]

- (b) For the reaction



the following data were collected. All the measurements were taken at 263K

Experiment No.	Initial [NO] / M	Initial [Cl ₂] / M	Initial rate of disappearance of Cl ₂ [M / min]
1	0.15	0.15	0.60
2	0.15	0.30	1.20
3	0.30	0.15	0.60
4	0.25	0.25	?

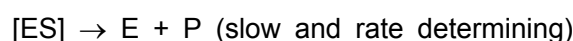
- (i) Write the expression for rate law.
 (ii) Calculate the value of rate constant and specify its units.
 (iii) What is the initial rate of disappearance of Cl₂ in exp. 4?

[Ans. : (i) Rate = k [NO]² [Cl₂], (ii) k = 177.7 L² mol⁻² min⁻¹,
 (iii) 2.7765 M/min]

2. (a) Draw a plot between log k and reciprocal of absolute temperature (T) and find the slope of the straight line.
 (b) The energy of activation for a chemical reaction is 100 kJ/mol. Presence of a catalyst lowers the energy of activation by 75%. What will be effect on the rate of reaction at 20°C, if other factors are equal?
3. (a) Derive the equation for rate constant of a first order reaction. What would be the units of the first order rate constant if the concentration is expressed in moles per litre and time in seconds?
 (b) For first order chemical reaction, half-life period (t_{1/2}) is concentration independent. Justify the statement by using integrated rate equation.

The plot of $\log x/m$ vs $\log P$ gives a straight line with slope = $\frac{1}{n}$ and y intercept = $\log k$.

11. Adsorption is generally temperature dependent. Generally adsorption is **exothermic** and, therefore, adsorption decreases with the increase in temperature.
12. For adsorption from solution, pressure (P) is replaced by equilibrium concentration (C).
13. A catalyst is a substance that increases the rate of reaction without being consumed in the reaction. In general, a catalyst functions by lowering the energy of activation which in turn makes the rate constant larger and, hence, the rate of reaction higher.
14. In **homogeneous catalysis**, the catalyst is in the same phase as are the reactants and in **heterogeneous catalysis**, the catalyst is in the different phase from the reactants.
15. **Enzymes** are biological catalysts. Their main characteristics are their high *specificity*, efficiency (even in traces) and activity at physiological temperature of 37°C and pH of 7.4.
16. Enzyme catalysed reaction takes place in two steps :



(E is enzyme, S is substrate and P is product)

17. **Colloidal solutions** are intermediate between true solutions and suspensions. Their size ranges in the order 1 nm to 1000 nm.
18. A colloidal system consists of two phases : the dispersed phase and dispersion medium.
19. **Lyophilic sols** are formed by organic substances like gum, starch, protein etc. These are reversible and more stable.

20. Why does sky appear blue to us?
21. What happens when hydrated ferric oxide and arsenious sulphide sols are mixed in almost equal proportions?
22. Gelatin is generally added to ice-cream. Why?
[Hint : Ice-cream is water in oil type (o/w) emulsion and gelatin acts as emulsifier].
23. Mention the two conditions for the formation of micelles. [Hint.: CMC & T_k]
24. How is Brownian movement responsible for the stability of sols?
25. Which of the following is more effective in coagulating positively charged hydrated ferric oxide sol : (i) KCl (ii) CaSO_4 (iii) $\text{K}_3[\text{Fe}(\text{CN})_6]$.
26. State the purpose of impregnating the filter paper with colloidal solution.
27. Mention one use of ZSM-5 catalyst.

SA (I) TYPE QUESTIONS (2-Mark Questions)

28. Explain the effect of temperature on the extent of physical and chemical adsorption.
29. Define the term peptization and mention its cause.
30. What will be the charge on colloidal solutions in the following cases.



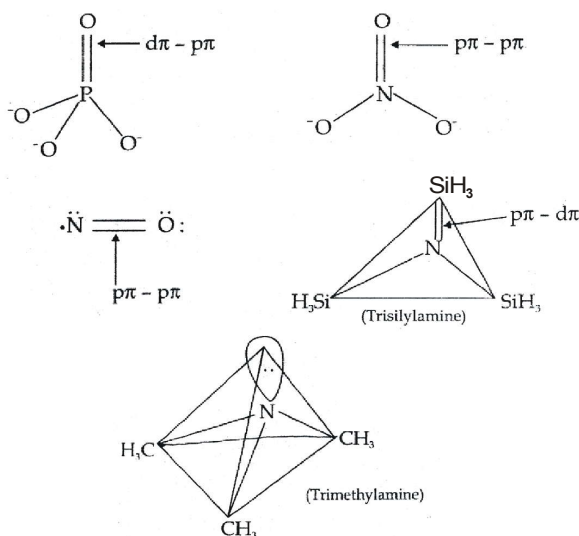
Give reasons for the origin of charge.

31. Write the factors upon which the catalytic reaction of shape-selective catalyst depends?
32. Mention two examples of emulsifying agents for o/w type emulsions and w/o type emulsions.
33. Suggest a mechanism of enzyme catalysed reaction.
34. A small amount of silica gel and a small amount of anhydrous calcium chloride are placed separately in two beakers containing water vapour. Name of phenomenon that takes place in both the beakers.
[Hint : Silica gel – Adsorption, Anhydrous CaCl_2 – Absorption, as it forms $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$]
35. Write the two points of difference between adsorption and absorption?

36. How can physisorption be distinguished from chemisorption?
37. In what way these are different : (a) a sol and a gel (b) a gel and an emulsion.
38. State "Hardy Schulze Rule" with one example.
39. What is an emulsifying agent? What role does it play in forming an emulsion?
40. Define the terms :
 - (a) Helmholtz electrical double layer.
 - (b) Zeta potential.
41. (a) In reference to Freundlich adsorption isotherm, write the expression for adsorption of gases on solids in the form of equation.
 (b) Write an important characteristic of lyophilic sols.
42. Mention the two necessary conditions for the observation of Tyndall Effect.
43. Account for the following :
 - (a) Artificial rain can be caused by spraying electrified sand or the clouds.
 - (b) Electrical precipitation of smoke.
44. Write chemical equations for the preparation of sols :
 - (a) Gold sol by reduction.
 - (b) hydrated ferric oxide sol by hydrolysis.
45. How can the two emulsions can be distinguished :
 - (a) oil in water type (o/w) and (b) water in oil type (w/o)
46. What are lyophilic and lyophobic colloids? Which of these sols can be easily coagulated on the addition of small amounts of electrolytes?

SA (II) TYPE QUESTIONS (3-Mark Questions)

47. Write the difference between
 - (a) catalysts and enzymes
 - (b) promoters and poisons
48. Write the steps of 'Modern Adsorption Theory of Heterogenous Catalysis.'
49. Mention the two important features of solid catalysts and explain with the help of suitable examples.
50. How are the following colloids different from each other in respect of dispersion medium and dispersed phase? Give one example of each type.
 - (a) An aerosol
 - (b) A hydrosol
 - (c) An emulsion.



Now, the following questions can be explained using the above mentioned reasoning :

- Nitrogen forms N_2 but phosphorus forms P_4 at room temperature. Why?
 - Oxygen exists as O_2 but sulphur as S_8 . Why?
 - Explain why $(\text{CH}_3)_3\text{P}=\text{O}$ is known but $(\text{CH}_3)_3\text{N}=\text{O}$ is not known.
3. Due to small size and high electronegativity and presence of lone pair(s) of elements N, O, F when bonded to hydrogen atom, forms hydrogen bonds which are stronger than other intermolecular forces. This results in exceptionally high m.p. and b.p. of the compounds having N-H/O-H/F-H bonds.

Isostructural species have same number of bond pairs and lone pairs if present around the central atom in a molecule/ion. Thus, they have the same geometry/shape/structure and the same hybridisation scheme. For example, $\text{ICl}_4^- / \text{XeF}_4$, $\text{BrO}_3^- / \text{XeO}_3$, $\text{BH}_4^- / \text{NH}_4^+$ are the pairs of isostructural species.

Inert pair effect : Due to poor shielding effect of intervening d and/ or f-electrons, the effective nuclear charge is increases. This increased nuclear charge holds the ns^2 electrons of heavier elements strongly and the tendency of ns^2 electrons to take part in bonding is more and more restricted down the group. Consequently, more stable lower oxidation state which is two units less than higher oxidation state becomes more and more stable than the higher oxidation state. Following questions can be explained with the help of inert pair effect.

[Hint : (b) $\text{XeF}_4 + 2\text{H}_2 \rightarrow \text{Xe} + 4\text{HF}$]

3. Write Chemical equations when :
 - (a) XeF_2 is hydrolysed
 - (b) PtF_6 and Xenon are mixed together.
4. Complete the reactions :
 - (i) $\text{XeF}_6 + \text{H}_2\text{O} \xrightarrow[\text{hydrolysis}]{\text{Complete}} \longrightarrow$
 - (ii) $\text{XeF}_6 + \text{H}_2\text{O} \xrightarrow[\text{hydrolysis}]{\text{Partial}} \longrightarrow$
5. Draw the structures of BrF_3 , XeOF_4 , XeO_3 using VSEPR theory.
6. Account for the following :
 - (a) XeF_2 has linear structure and not a bent structure.
 - (b) The majority of known noble gas compounds are those of Xenon. Why? (Hint : Xe has low ionization enthalpy as compared to other noble gases)
7. Write Chemical reactions :
 - (a) $\text{XeF}_2(\text{s}) + \text{H}_2\text{O}(\text{l}) \longrightarrow$
 - (b) $\text{XeF}_4 + \text{O}_2\text{F}_2 \xrightarrow[\text{4.4 K}]{\text{4.2 K}} \longrightarrow$

SA(II) TYPE QUESTIONS (3-Mark Questions)

1. Assign reason to the following :
 - (i) Noble gases have large positive values of electron gain enthalpy.
 - (ii) Helium is used by scuba divers.
 - (iii) No chemical compound of helium is known.
2. (i) How is XeO_3 prepared from XeF_6 ? Write the chemical equation for the reaction.
(ii) Draw the structure of XeF_4 .
3. Draw the structure of
 - (i) XeOF_4
 - (ii) XeF_6
 - (iii) XeO_3
4. Complete the reactions :
 - (i) $\text{XeF}_2 + \text{NaF} \longrightarrow$

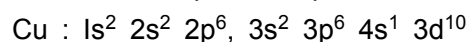
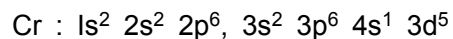
Unit - 8

d-and f-BLOCK ELEMENTS

Electronic Configuration of Transition Metals/Ions

The d-block element is called transition metal if it has partly filled d-orbitals in the ground state as well as in its oxidised state.

The general electronic configuration of transition metal is $(n-1) d^{1-10} ns^{1-2}$. Exceptions in electronic configuration are due to (a) very little energy difference between $(n-1) d$ and ns orbitals and (b) extra stability of half filled and completely filled orbitals in case of Cr and Cu in 3d series.



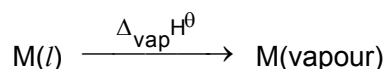
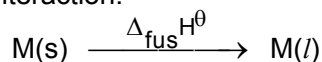
To write the electronic configuration of M^{n+} , the electrons are first removed from ns orbital and then from $(n-1) d$ orbitals of neutral atom (if required). For example, the outer electronic configuration of Cu^+ , Cu^{2+} and Cr^{3+} are respectively $3d^{10}$, $3d^9$ and $3d^3$.

The following questions can be answered with the help of above.

- (i) Scandium ($Z = 21$) is a transition element but zinc ($Z = 30$) is not.
- (ii) Copper ($Z = 29$) and silver ($Z = 47$) both have fully filled d-orbitals i.e., $(n-1) d^{10}$. why are these elements regarded as transition elements?
- (iii) Which of the d-block elements are not regarded as transition elements?

Understanding $\Delta_{\text{fus}} H^\theta$, $\Delta_{\text{vap}} H^\theta$, and $\Delta_a H^\theta$

In transition metals unpaired $(n-1)d$ electrons as well as ns electrons take part in interatomic bonding. Larger the number of unpaired $(n-1) d$ electrons, the stronger is the interatomic bonding and large amount of energy is required to overcome the interatomic interaction.



Participation of 5f electrons of actinoids in bonding.

5f orbitals in actinoids are not as buried as 4f orbitals in lanthanoids and hence 5f electrons can participate in bonding to a far greater extent.

There is a gradual decrease in the size of atoms or M^{3+} ions across the actinoid series. Since 5f orbitals are larger and more diffuse than 4f orbitals, their penetration towards the inner core of electrons is less than the penetration of 4f electrons. Hence, 5f electrons screen the nuclear charge less effectively than 4f electrons in lanthanoids. Consequently, effective nuclear charge in actinoids increases at a faster rate as compared with lanthanoids. Hence, actinoid contraction from element to element is more than the lanthanoid contraction.

VERY SHORT ANSWER TYPE QUESTIONS (1 - Mark Questions)

1. Write the electronic configuration of Cr^{3+} ion (atomic number of Cr = 24)?
2. Explain $CuSO_4 \cdot 5H_2O$ is blue while $ZnSO_4$ and $CuSO_4$ are colourless?
3. Why is the third ionisation energy of manganese (Z = 25) is unexpectedly high?

[Hint : The third electron is to be removed from stable configuration of Mn^{2+} ($3d^5$). It requires higher energy.]

4. Which element among 3d- transition elements exhibit the highest oxidation state? [Hint : Mn (+7)]
5. Silver (Ag) has completely filled d-orbitals ($4d^{10}$) in its ground state. How can you say that it is a transition element. [Hint : Ag^{2+} (d^9)]

6. In 3d series (Sc → Zn) the enthalpy of atomisation of Zn is low. Why? [Hint : Poor interatomic bonding in zinc due to all paired electrons in 3d subshell]

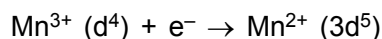
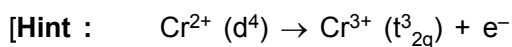
7. Out of the following elements, identify the elements which do not exhibit variable oxidation state?

Sc, Cr, Co, Zn.

8. The +3 oxidation state of lanthanum (Z = 57), gadolinium (Z = 64) and lutetium (Z = 71) are especially stable. Why?
9. Mention two consequences of Lanthanoid Contraction.
10. The first ionization enthalpies of 5d- series elements is higher than those of 3d- and 4d- series elements. why?

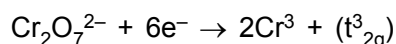
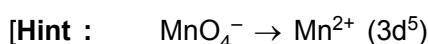
[Hint : Increasing value of effective nuclear charge due to lanthanoid contraction.]

26. Why is Cr^{2+} reducing and Mn^{3+} oxidising when both have d^4 configuration?



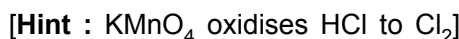
This is because extra stability is associated with half-filled t_{2g} level and half-filled d^5 configuration.]

27. How would you explain more oxidising power of MnO_4^- than $\text{Cr}_2\text{O}_7^{2-}$?



Stability of Mn^{2+} is more than that of Cr^{3+}]

28. Why can't hydrochloric acid be used to acidify KMnO_4 Solution?



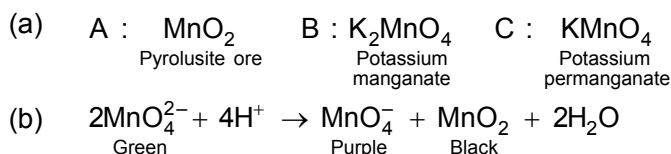
**29. Why MnO_4^- or $\text{Cr}_2\text{O}_7^{2-}$ is intensely coloured?

[Hint : $\text{Mn}^{7+} (3d^0)$ and $\text{Cr}^{6+} (3d^0)$ are intensely coloured because electronic transition i.e., charge transfer from O^{2-} ions Mn^{7+} in MnO_4^- or to Cr^{6+} in $\text{Cr}_2\text{O}_7^{2-}$ occurs upon the absorption of visible light radiations and therefore these oxoanions exhibit colour which is complementary to the colour absorbed by these ions.]

*30. Transition metals show low oxidation states like 0, -1, -2 etc with π -acceptor ligands like CO. Why?

[Hint : CO ligands not only donate electron pair to central atom but also accept electron through π -back donation from the central atom.]

[Hint :



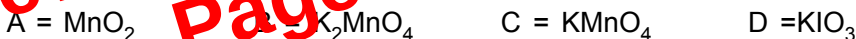
**11. A mixed oxide of iron and chromium $\text{FeO} \cdot \text{Cr}_2\text{O}_3$ is fused with sodium carbonate in the presence of air to form a yellow coloured compound (A). On acidification the compound (A) forms an orange coloured compound (B), which is a strong oxidizing agent.

- Identify the compounds (A) and (B).
- Write balanced chemical equation for each step.

[Hint :

- Compound A : Sodium chromate (Na_2CrO_4)
- Compound B : Sodium dichromate ($\text{Na}_2\text{Cr}_2\text{O}_7$).

**12. When an oxide of manganese (A) is fused with KOH in the presence of an oxidising agent and dissolved in water, it gives a dark solution of compound (B). Compound (B) disproportionates in neutral or acidic solution to give purple compound (C). An alkaline solution of compound (C) oxidizes potassium iodide solution to a compound (D) and compound (A) is also formed. Identify compounds A to D and also explain the reactions involved.



13. Give reasons for the following :

- Fe has higher melting point than Cu.
- Co(II) is stable in aqueous solution but in the presence of strong ligands and air, it can get oxidized to Co(III) .
- $[\text{Ti}(\text{H}_2\text{O})]^{3+}$ is coloured while $[\text{Sc}(\text{H}_2\text{O})_6]^{3+}$ is colourless.
- The 4d and 5d series of transition metals have more frequent metal-metal bonding in their compounds than do the 3d metals.
- Transition metals sometimes exhibit very low oxidation state such as +1.

**14. A violet compound of manganese (A) decomposes on heating to liberate oxygen and compounds (B) and (C) of manganese are formed. Compound (C) reacts with KOH in the presence of potassium nitrate to give compound

- Relation between stepwise and overall stability constant

$$\beta_n = K_1 \times K_2 \times K_3 \times K_4 \times \dots \times K_n$$

- The metal-carbon bond in metal carbonyls possesses both σ and π character. The ligand to metal is σ and metal to ligands is π bond. This unique synergic bonding provides stability to metal carbonyls.

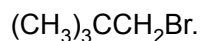
VSA QUESTIONS (1-Mark Questions)

1. Define the term 'coordination compound'.
2. Write the oxidation state of nickel in $[\text{Ni}(\text{CO})_4]$.
3. What is the coordination number of central atom in $[\text{Co}(\text{C}_2\text{O}_4)_3]^{3-}$?
4. What is the coordination number of iron in $[\text{Fe}(\text{EDTA})]^-$?
5. Write the IUPAC name of $[\text{Pt}(\text{NH}_3)_4\text{Cl}_2]\text{Cl}_2$.
6. Write the IUPAC name of $\text{O}_2^+ [\text{Pt F}_6]^-$
7. Give IUPAC name of ionisation isomer of $[\text{Ni}(\text{NH}_3)_3][\text{NO}_3]\text{Cl}$.
8. Write down the formula of tetramineaquachloride Coalt (III) chloride.
- *9. Write the IUPAC name of $[\text{Cr}(\text{NH}_3)_6][\text{Co}(\text{CN})_6]$.
10. Write the IUPAC name of $[\text{Pt Cl}(\text{en})_2]\text{NO}_3$.
- **11. Write IUPAC name of linkage isomer of $[\text{Cr}(\text{H}_2\text{O})_5(\text{SCN})]^{2+}$.
- **12. Arrange the following in the increasing order of conductivity in solution.
 $[\text{Ni}(\text{H}_3)_6]\text{Cl}_2$; $[\text{Co}(\text{NH}_3)_4]\text{Cl}_2$ and $[\text{CoCl}_2(\text{en})_2]\text{Cl}$
13. How many geometrical isomers are possible for the tetrahedral complex $[\text{Ni}(\text{CO})_4]$.
[Ans. : No isomer, as the relative positions of the unidentate ligands attached to the central metal atom are always the same with respect to each other].
- *14. Write the formula and the name of the coordinate isomer of $[\text{Co}(\text{en})_3][\text{Cr}(\text{CN})_6]$.
15. Give an example of coordination isomerism.
16. What is ambidentate ligand? Give an example.
17. Indicate the types of structural isomerism exhibited by the complex $[\text{Co}(\text{NH}_3)_5(\text{NO}_2)](\text{NO}_3)_2$.
18. Arrange the following ligands in increasing order of Δ_o (Crystal field splitting energy) for octahedral complexes with a particular metal ion.
 Cl^- , NH_3 , I^- , CO , $\text{H}_2\text{N}-\text{CH}_2-\text{CH}_2-\text{NH}_2$.

- (a) $[\text{Mn}(\text{CO})_5(\text{SCN})]$ and $[\text{Mn}(\text{CO})_5(\text{NCS})]$
- (b) $[\text{Co}(\text{NH}_3)_5(\text{NO}_3)] \text{SO}_4$
33. Draw the structures of geometrical isomers of the following coordination complexes : $[\text{Co}(\text{NH}_3)_3\text{Cl}_3]$ and $[\text{CoCl}_2(\text{en})_2]^+$
34. Calculate the magnetic moments of the following complexes :
- (i) $[\text{Fe}(\text{CN})_6]^{4-}$ (ii) $[\text{CoF}_6]^{3-}$
35. Explain the following :
- (a) $[\text{Fe}(\text{CN})_6]^{3-}$ is an inner orbital complex whereas $[\text{FeF}_6]^{3-}$ is an outer orbital complex.
- (b) NH_3 acts as complexing agent but NH_4^+ does not.
36. Explain on the basis of Valence Bond Theory that diamagnetic $[\text{Ni}(\text{CN})_4]^{2-}$ has square planar structure and paramagnetic $[\text{NiCl}_4]^{2-}$ ion has tetrahedral geometry.
37. Explain as to how the two complexes of nickel $[\text{Ni}(\text{CN})_4]^{2-}$ and $[\text{Ni}(\text{CO})_4]$ have different structures but do not differ in their magnetic behaviours. (At. no. of Ni = 28).
- **38. A complex is prepared by mixing CoCl_3 and NH_3 in the molar ratio of 1:4. 0.1 m solution of this complex was found to freeze at -0.372°C . What is the formula of the complex?
- K_f of water = 1.86°C/m
- Hint :** $\Delta T_f = K_f \times m = i \times 1.86 \times 0.1$
- $\Delta T_f(\text{obs}) = 0.373^\circ\text{C}$
- This means each molecule of complex dissociates into two ions. Hence the formula is $[\text{Co}(\text{NH}_3)_4\text{Cl}_2] \text{Cl}$
39. The $[\text{Mn}(\text{H}_2\text{O})_6]^{2+}$ ion contains five unpaired electrons while $[\text{Mn}(\text{CN})_6]^{4-}$ ion contains only one unpaired electron. Explain using Crystal Field Theory:
40. Explain the following terms—
- (a) crystal field splitting in an octahedral field
- (b) spectrochemical series
41. What do you understand by stepwise stability constant and overall stability constant of a coordination compound? How are these two constants related to one another?

16. Which will react faster in S_N2 displacement, 1-bromopentane or 2-bromopentane and why?

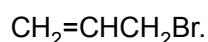
17. Write the IUPAC name of the following compound:



18. Write the structure of 1, 4-Dibromobut-2-ene.

19. Write the structure of 2(2-bromophenyl) butane.

20. Write the IUPAC name of the following compound :

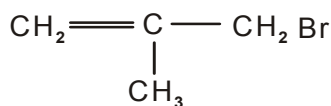


21. Write the structure of 2(2-chlorophenyl)-1-iodooctane.

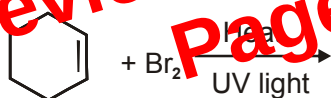
22. Write the structure of the following compound :

1-Bromo-4-sec.butyl-2-methylbenzene.

23. Give the IUPAC name of the following compound :

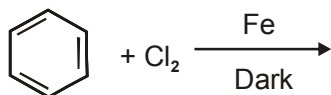


24. Draw the structure of major monohalogen product in the following reaction:

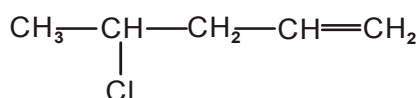


25. Predict the order of reactivity of four isomeric bromobutane in S_N1 reaction.

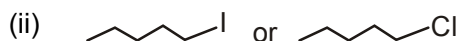
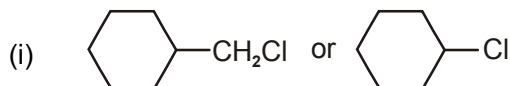
26. Draw the structure of major monohalogen product in the following reaction:



27. Write the IUPAC name of



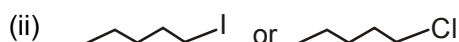
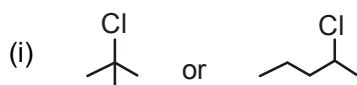
6. Which one in the following pairs of substances undergoes S_N2 substitution reaction faster and why?



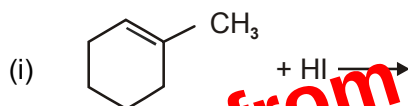
7. Suggest a possible reason for the following observations:

- (i) The order of reactivity of haloalkanes is $RI > RBr > RCl$.
(ii) Neo-pentyl chloride, $(CH_3)_3C-CH_2Cl$ does not follow S_N2 mechanism.

8. Which one in the following pairs undergoes S_N1 substitution reaction faster and why?



9. Complete the following chemical equations :



10. Explain why

- (i) the dipole moment of chlorobenzene is lower than that of cyclohexyl chloride.
(ii) Chloroform is stored in closed dark coloured bottles completely filled so that air is kept out?

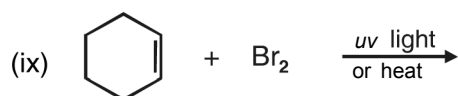
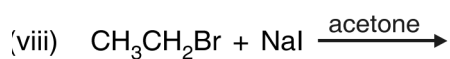
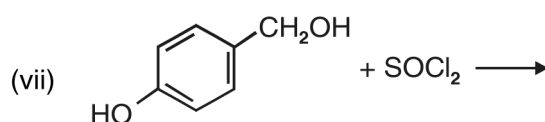
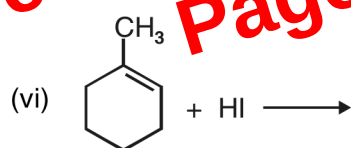
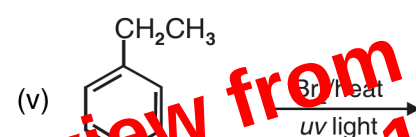
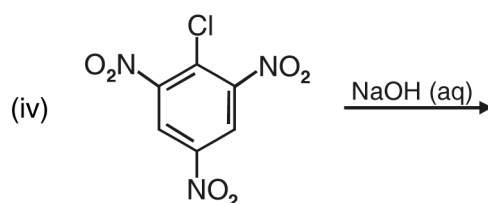
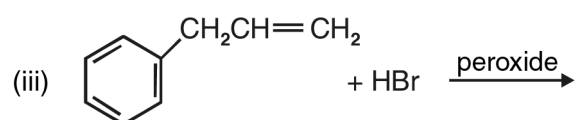
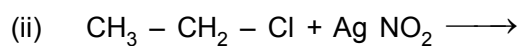
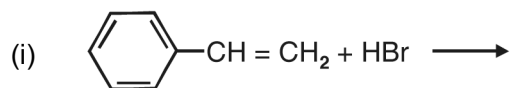
11. Explain as to why

- (i) alkyl halides, though polar, are immiscible with water?
(ii) Grignard's reagent should be prepared under anhydrous conditions?

12. What are ambident nucleophiles? Explain by giving an example.

13. Chlorobenzene is extremely less reactive towards nucleophilic substitution reaction. Give two reasons.

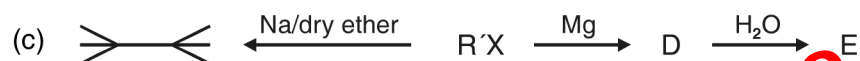
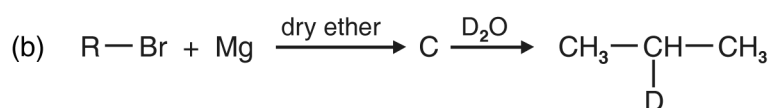
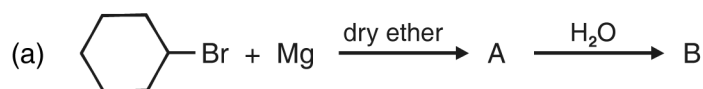
1. Complete the following reactions :



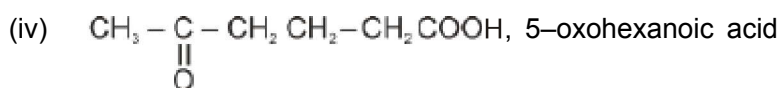
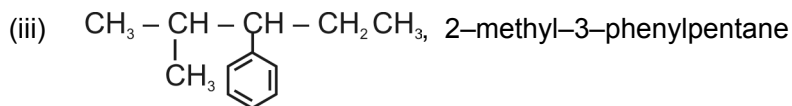
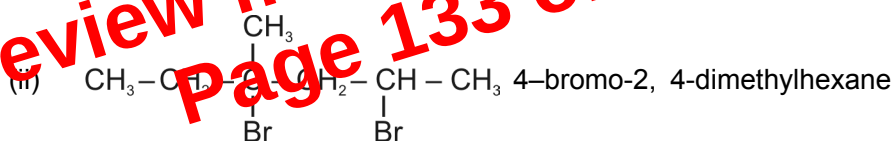
- **19. An organic compound (A) having molecular formula C_3H_7Cl on reaction with alcoholic solution of KCN gives compound B. The compound B on hydrolysis with dilute HCl gives compound C. C on reduction with H_2/Ni gives 1-aminobutane. Identify A, B and C.

[Ans. : (A) $CH_3CH_2CH_2Cl$, (B) $CH_3CH_2CH_2CN$, (C) $CH_3CH_2CH_2CONH_2$

- *20. Identify A, B, C, D, E, R and R' in the following sequence of reactions :

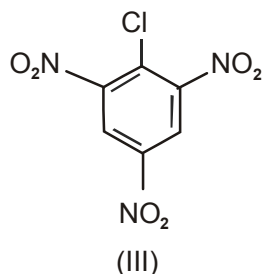
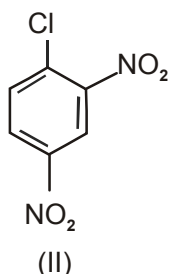
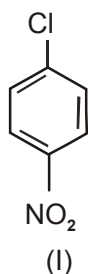


21. Which nomenclature is not according to IUPAC system.



- **22. Primary alkyl halide (A) C_4H_9Br reacted with alc.KOH to give 'B'. 'B' when reacted with HBr to give 'C', which is an isomer of 'A'. When 'A' reacted with Na metal, it gave a compound 'D' C_8H_{18} that was different from the compound, when n-butyl bromide was reacted with Na. Give the structural formulas of 'A' to 'D' and write the chemical equations of reactions involved.

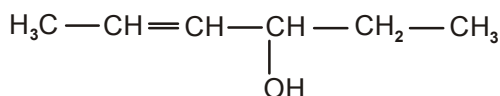
34. How will you obtain monobromobenzene from aniline?
35. Aryl halides are extremely less reactive towards nucleophilic substitution. Predict and explain the order of reactivity of the following compounds towards nucleophilic substitution:



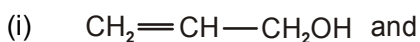
Hint: III > II > I

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13. Write the IUPAC name of the following compound:

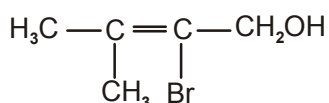


14. Of the two alcohols:



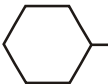
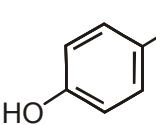
(ii) $\text{CH}_2=\text{CH}-\text{CH}_2-\text{CH}_2\text{OH}$, which one will react more easily with concentrated HCl in the presence of anhydrous ZnCl_2 ?

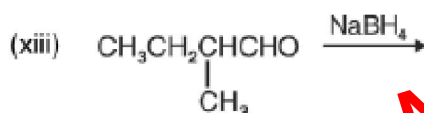
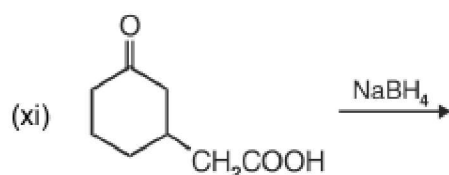
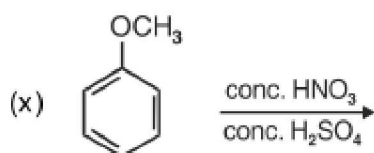
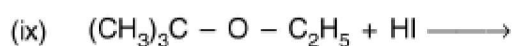
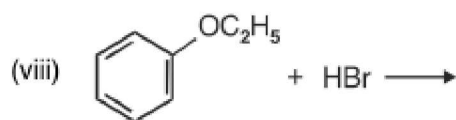
15. Write the IUPAC name of the following:



2-Mark Questions

1. Write the reactions and conditions involved in the conversion of
- propene to propan-1-ol
 - phenol to salicylic acid
2. How are the following conversions carried out?
- Propene to propan-2-ol
 - Ethyl magnesium chloride to propan-1-ol.
3. How are the following conversions carried out?
- Propene to propan-2-ol
 - Anisole to phenol
4. How could you account for
- Phenols are more acidic than alcohols?
 - The boiling points of ethers are much lower than those of the alcohols of comparable molar masses?
5. Give reason for the following:
- m*-Aminophenol is a stronger acid than *o*-aminophenol.
 - Alcohols act as weak bases.

6. Account for the following.
- Propanol has higher boiling point than butane.
 - ortho-Nitrophenol is more acidic than o-methoxyphenol.
7. Describe the mechanism of alcohols reacting both as nucleophiles and as electrophiles in their reactions.
8. Complete the following chemical equations.
- 
 $\text{OH} + \text{SOCl}_2 \longrightarrow$
 - 
 $+ \text{HCl} \longrightarrow$
9. Give one chemical test to distinguish between the following pairs of compounds.
- phenol and benzoic acid
 - 1-propanol and 2-propanol
10. Write the mechanism of hydration of ethene to ethanol.
11. How are the following conversions carried out ?
- Benzyl chloride to benzyl alcohol
 - Methyl magnesium bromide to 2-methylpropan-2-ol.
12. How would you obtain
- Picric acid from phenol?
 - 2-methylpropanol from 2-methylpropene?
13. Give a chemical test to distinguish between the following pair of compounds
- Ethanol and phenol
 - pentan-2-ol and pentan-3-ol.
14. Explain the mechanism of acid catalysed hydration of an alkene to form corresponding alcohol.



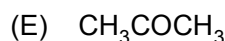
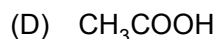
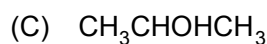
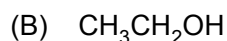
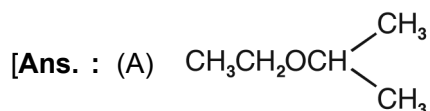
3. What happens when :

- aluminium reacts with tert-butyl alcohol
- cumene is oxidised in the presence of air and the product formed is treated with dilute acid.
- phenol is treated with conc. HNO_3 .
- phenol is treated with chloroform in presence of dilute NaOH .

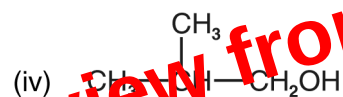
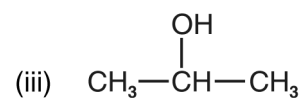
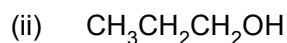
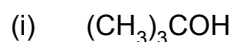
4. How will you convert

- propene to propan-1-ol.
- anisole to phenol

- **14. An ether A ($C_5H_{12}O$) when heated with excess of hot concentrated HI produced two alkyl halides which on hydrolysis form compounds B and C. Oxidation of B gives an acid D whereas oxidation of C gave a ketone E. Deduce the structures of A, B, C, D and E.

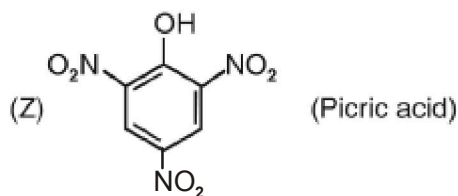
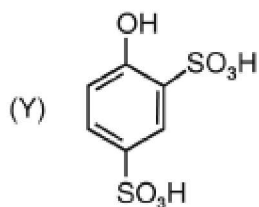


- **15. Which of the following compounds gives fastest reaction with HBr and why?



16. Phenol, C_6H_5OH when it first reacts with concentrated sulphuric acid, forms Y. The compound Y is reacted with concentrated nitric acid to form Z. Identify Y and Z and explain why phenol is not converted commercially to Z by reacting it with conc. HNO_3 .

[Ans. :



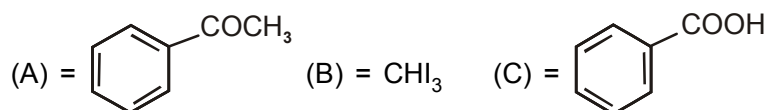
Phenol is not reacted directly with conc. HNO_3 because the yield of picric acid is very poor]

- (i) propan-2-ol and propanone
- (ii) ethyl acetate and methyl acetate
- (iii) benzaldehyde and benzoic acid
- (iv) benzaldehyde and acetaldehyde
- (v) formic acid and acetic acid
- (vi) propanal and propan-1-ol
- (vii) ethanoic acid and ethylethanoate
- (viii) $\text{C}_6\text{H}_5\text{CHO}$ and CH_3COCH_3
- (ix) CH_3CHO and HCHO
- (x) acetophenone and benzophenone
- (xi) ethanal and propanal.

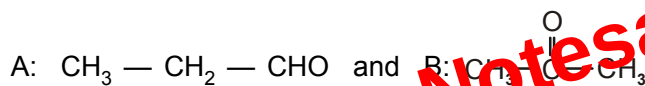
7. Give reason for the following:

- (i) Cyclohexanone form cyanohydrin in good yield but 2,2,6 trimethylcyclohexanone does not.
- (ii) Benzaldehyde does not give Fehling's test.
- (iii) The alpha H atom in ethanal are acidic in nature.
- (iv) p-nitrobenzaldehyde is more reactive than benzaldehyde towards nucleophilic addition reactions.
- (v) Acetic acid does not give sodium bisulphite addition product.
- (vi) For the formation of ethyl acetate from acetic acid and ethanol in presence of sulphuric acid, the reaction mixture is heated to remove water as fast as it is formed.
- (vii) Chloroacetic acid has lower pka value than acetic acid.
- (viii) Monochloroethanoic acid is a weaker acid than dichloroethanoic acid.
- (ix) Benzoic acid is stronger acid than ethanoic acid.
- (x) Aldehydes are more reactive towards nucleophilic reagents than ketones.
- (xi) Benzaldehyde does not undergo aldol condensation.

- **22. An aromatic compound 'A' (Molecular formula C_8H_8O) gives positive 2, 4-DNP test. It gives a yellow precipitate of compound 'B' on treatment with iodine and sodium hydroxide solution. Compound 'A' does not give Tollen's or Fehling's test. On drastic oxidation with potassium permanganate it forms a carboxylic acid 'C' (Molecular formula $C_7H_6O_2$), which is also formed along with the yellow compound in the above reaction. Identify A, B and C and write all the reactions involved.



- **23. Write down functional isomers of a carbonyl compound with molecular formula C_3H_6O . Which isomers will react faster with HCN and why? Explain the mechanism of the reaction also. Will the reaction lead to the completion with the conversion of whole reactant into product at reactions conditions? If a strong acid is added to the reaction mixture what will be the effect on concentration of the product and why?

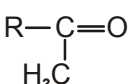


(A) is more reactive than (B)

The reaction will not proceed to completion since it is a reversible reaction. Addition of strong acid prevents the reaction because the formation of CN^- from weak acid, HCN , is prevented.

- *24. When liquid 'A' is treated with a freshly prepared ammoniacal silver nitrate solution, it gives bright silver mirror. The liquid forms a white crystalline solid on treatment with sodium hydrogensulphite. Liquid 'B' also forms a white crystalline solid with sodium hydrogensulphite but it does not give test with ammoniacal silver nitrate. Which of the two liquids is aldehyde? Write the chemical equations of these reactions also.

(A) = Aldehyde $R - CHO$

(B) = Methyl Ketone 

Unit - 13

AMINES

POINTS TO REMEMBER

1. Amines are alkyl and/or aryl derivatives of $\ddot{\text{N}}\text{H}_3$.
2. Functional groups of 1°, 2° and 3° amines are respectively as given below:
 $\text{—}\ddot{\text{N}}\text{H}_2$, $\text{—}\ddot{\text{N}}\text{H—}$ and $\text{—}\ddot{\text{N}}\text{—}$
3. Gabriel phthalimide synthesis can't be used for the preparation of 2° and 3° amines. It gives aliphatic primary amine only.
4. Hoffmann's bromamide reaction gives 1° amines having one carbon atom less than parent primary amide.
5. The order of basic strength of aliphatic amines is :
 - (i) Aliphatic amines are more basic than $\ddot{\text{N}}\text{H}_3$.
 - (ii) In aqueous medium, the order is $2^\circ > 1^\circ > 3^\circ$ (for CH_3 group) and $2^\circ > 3^\circ > 1^\circ$ for C_6H_5 group.
 - (iii) In non-aqueous medium or gaseous phase the order is $3^\circ > 2^\circ > 1^\circ$.
6. Basic strength of aromatic amines –
 - (i) Aromatic amines are weaker bases than $\ddot{\text{N}}\text{H}_3$.
 - (ii) ERGs like —CH_3 , —OR , —NH_2 etc. increase basic strength while EWGs like —NO_2 , —CN etc. decrease the basic strength. The effect of substituents is more at para positions and less at meta-position.
7. Basic strength of amines is expressed in terms of K_b or $\text{p}K_b$.
8. 1°, 2° and 3° amines can be distinguished by Hinsberg's Test.
9. Hinsberg's reagent is benzenesulphonyl chloride ($\text{C}_6\text{H}_5\text{SO}_2\text{Cl}$).
10. 3° amines like trimethylamine are used as insect attractants.
11. Diazonium salts are represented by the general formula $[\text{Ar N}\equiv\text{N}]^+ \text{X}^-$.

3-Mark Questions

37. Give complete reaction in each case.
- (i) Preparation of ethylamine from acetaldehyde.
 - (ii) Preparation of benzonitrile from aniline.
 - (iii) Preparation of ethyl isonitrile from ethylamine.
38. How could you carry out the following conversions?
- (i) Nitrobenzene to aniline
 - (ii) An alkyl halide to a quaternary ammonium salt
 - (iii) Aniline to benzonitrile
39. State reason for the following :
- (i) pK_b value for aniline is more than that for methylamine.
 - (ii) Ethylamine is soluble in water whereas aniline is not soluble.
 - (iii) Primary amines have higher boiling points than tertiary amines.
40. State the reactions and reaction conditions for the following conversions.
- (i) Benzenediazonium chloride to nitrobenzene
 - (ii) Aniline to benzenediazonium chloride
 - (iii) Ethylamine to methylamine
41. Complete the following chemical equations:
- (i) $C_6H_5NH_2 + CH_3COCl \longrightarrow$
 - (ii) $C_2H_5NH_2 + C_6H_5SO_2Cl \longrightarrow$
 - (iii) $C_2H_5NH_2 + HNO_2 \longrightarrow$
42. Complete the following chemical equations.
- (i) $C_6H_5N_2^+ Cl^- + C_6H_5NH_2 \longrightarrow$
 - (ii) $C_6H_5N_2^+ Cl^- + CH_3CH_2OH \longrightarrow$
 - (iii) $RNH_2 + CHCl_3 + Alc. KOH \longrightarrow$

- Giving an example of each, describe the following reactions :
 - Hoffman bromamide reaction
 - Gabriel phthalimide synthesis
 - Gatterman reaction
 - Coupling reaction
 - Carbylamine reaction or isocyanide test
 - Acetylation of aniline.
- Describe the Hinsberg's test for identification of primary, secondary and tertiary amines. Also write the chemical equations of the reactions involved.
- Arrange the following in the increasing order of given property indicated.
 - $\text{C}_2\text{H}_5\text{NH}_2$, $(\text{C}_2\text{H}_5)_2\text{NH}$, $(\text{C}_2\text{H}_5)_3\text{N}$ and NH_3 , (Basic strength in aqueous solution).
 - $\text{C}_2\text{H}_5\text{NH}_2$, $(\text{C}_2\text{H}_5)_2\text{NH}$, $(\text{C}_2\text{H}_5)_3\text{N}$ and CH_3NH_2 , (Basic strength in gaseous phase).
 - Aniline, *p*-toluidine, *p*-nitroaniline, (Basic strength).
 - $\text{C}_2\text{H}_5\text{OH}$, $(\text{CH}_3)_2\text{NH}$, $\text{C}_2\text{H}_5\text{NH}_2$, (Boiling point).
 - $\text{C}_2\text{H}_5\text{NH}_2$, $(\text{C}_2\text{H}_5)_2\text{NH}$, $\text{C}_2\text{H}_5\text{NH}_2$, (Increasing order of solubility)
- Identify A and B in the following reactions :
 - $\text{CH}_3\text{CH}_2\text{Cl} + \text{NH}_3 \text{ (Excess)} \xrightarrow[\text{OH}^-]{373\text{K}} \text{A}$
 - $\text{CH}_3\text{CH}_2\text{Cl (excess)} + \text{NH}_3 \xrightarrow[\text{OH}^-]{373\text{K}}$
- How will you bring about the following conversions?
 - benzene to aniline
 - aniline to benzene
 - ethanoic acid to ethanamine
 - p*-toluidine to 2-bromo-4-methylaniline.
 - methyl bromide to ethanamine
 - benzenediazonium chloride to nitrobenzene

[Hint : Chloroxylonol and Terpeneol].

12. What precaution should be taken before administering penicillin to a patient?

[Hint : To confirm beforehand that the patient is not allergic to penicillin.]

13. Explain why aspirin finds use in prevention of heart attacks?

[Hint : Due to anti blood clotting activity.]

14. Mention one use of drug meprobamate.

[Hint : Antidepressant drug.]

15. Name the derivative of sucrose which tastes like sugar and can be safely used by weight conscious people.

16. Why synthetic detergents are preferred over soaps for use in washing machines?

[Hint : They work well even with hard water and acidic medium.]

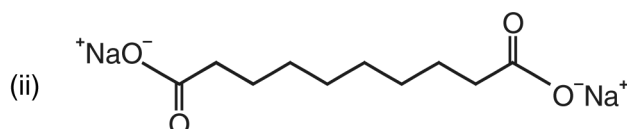
- *17. How is acidity cured with cimetidine or ranitidine?

[Hint. : Cimetidine or ranitidine prevents the interaction of histamines with the receptors present in stomach wall and therefore, secretion of acid is prevented].

- *18. While antacids and antiallergic drugs interfere with the function of histamines, why do these not interfere with the function of each other?

[Hint. : Antacids and antiallergic drugs bind to the different receptor sites. Therefore, they do not interfere with the function of each other).

19. Which of the following two compounds can be used as a surface agent and why?



[Hint : Compound (i) acts as a surface agent because its one end is hydrophobic while the other end is hydrophilic in nature.]

20. What type of drug is chloramphenicol?
21. Name a chemical used as an antiseptic as well as disinfectant.
22. Give two examples of antidepressants.
23. Name the antioxidants commonly used to increase the storage of butter.

[Hint : (i) anionic detergent. (ii) cationic detergent.
(iii) nonionic detergent.

- *11. How do enzyme inhibitors work? Distinguish between competitive and non-competitive enzyme inhibitors.

[Hint : An enzyme inhibitor either blocks the active site of enzyme or changes the shape of the active site by binding at an allosteric site. They are of two types.

- (i) Competitive enzyme inhibitor competes with natural substance for their attachment on the active sites of enzymes.
 - (ii) Non-competitive enzyme inhibitor binds at allosteric site and changes the shape of the active site in such a way that the substrate can not recognise it.]
12. (a) What class of drug is Ranitidine?
- (b) If water contains dissolved Ca^{2+} ions, out of soaps and synthetic detergents, which will you use for cleaning clothes?
- (c) Which of the following is an antiseptic?
0.2% phenol, or 1% phenol
13. What are detergents? How are they classified? Why are detergents usually preferred to soaps for washing clothes? Give an example of detergents.

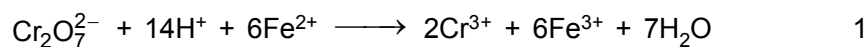
VALUE BASED QUESTION (4-Marks Question)

1. Mr. Naresh works in a multi-national company. He is stressed due to his hectic schedule. Mr. Amit, his friend, comes to know that he has started taking sleeping pills without consulting the doctor. Mr. Amit requested Naresh to stop this practice and took him to a Yoga Centre. With regular Yoga sessions Mr. Naresh is now a happy and relaxed man.

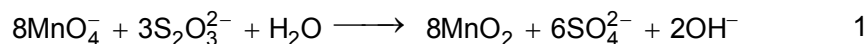
After reading the above passage answer the following questions:

- (i) Write the values shown by Mr. Amit.
- (ii) Which class of drugs is used in sleeping pills?
- (iii) Why is it not advisable to take sleeping pills without consultation with the doctor?
- (iv) Given an example of sleeping pills used commonly.

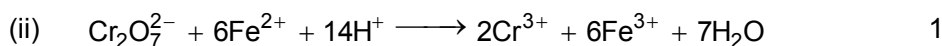
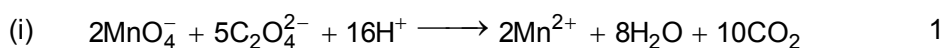
9. (i) Acidified $K_2Cr_2O_7$ oxidises iron(II) salt to iron (III)

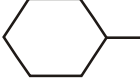


- (ii) In neutral aqueous medium, thiosulphate is oxidised to sulphate



OR



10. (a)  CH_2Cl , because it is primary halide. [1/2+1/2]

- (b)  I, because iodine is a better leaving group due to its large size, so it will be released at a faster rate. [1/2+1/2]

11. (i) For ccp, edge length of the unit cell

$$a = \frac{4r}{\sqrt{2}} = 2\sqrt{2} r \quad \frac{1}{2}$$

$$a = 2 \times 1.414 \times 125 \times 10^{-10} \text{ cm} \\ = 354 \times 10^{-10} \text{ cm} \quad 1$$

- (ii) Number of unit cells in 1 cm^3

$$= \frac{\text{Total Volume}}{\text{Volume of one unit cell}} = \frac{V}{a^3} \quad \frac{1}{2}$$

$$= \frac{1 \text{ cm}^3}{(354 \times 10^{-10})^3 \text{ cm}^3} \\ = 2.254 \times 10^{22} \text{ unit cells} \quad 1$$

12. Given $w_2 = 10.5 \text{ g}$, $w_1 = 200 \text{ g mol}^{-1}$

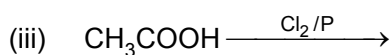
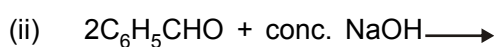
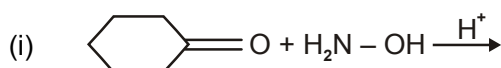
$$M_2 (\text{MgBr}_2) = 24 + 80 \times 2 = 184 \text{ g mol}^{-1}$$

$$K_f = 1.86 \text{ K kg mol}^{-1}$$

- (ii) Which transition metal of 3d series has positive $E^\circ(M^{2+}/M)$ value and why?
- (iii) Out of Cr^{3+} and Mn^{3+} , which is a stronger oxidizing agent and why?
- (iv) Name a member of the lanthanoid series which is well known to exhibit +2 oxidation state.
- (v) Complete the following equation :



26. Write the products of the following reactions :



(b) Give simple chemical tests to distinguish between the following pairs of compounds :

(i) Benzaldehyde and benzoic acid

(ii) Propanal and propanone

OR

(a) Account for the following :

(i) CH_3CHO is more reactive than CH_3COCH_3 towards reaction with HCN.

(ii) Carboxylic acid is a stronger acid than phenol.

(b) Write the chemical equations to illustrate the following name reactions.

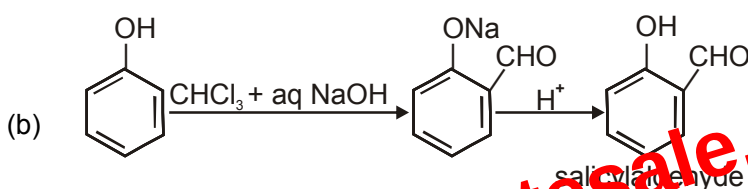
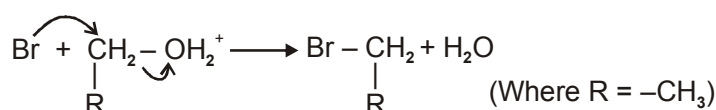
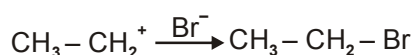
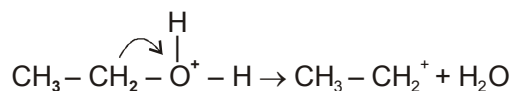
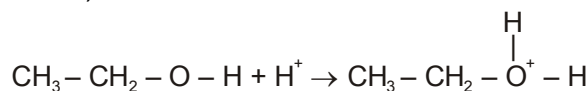
(i) Wolff-Kishner reduction

(ii) Aldol condensation

(iii) Cannizzaro reaction

5

10. Rate constant (k) is rate of the reaction when the concentration of each reactant is unity. Half-life period of the reaction is the time in which the concentration of the reactant is reduced to half of its initial concentration. 1+1



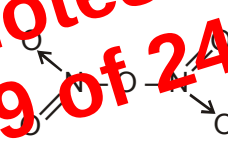
12. (a) (i)



(b) White phosphorus

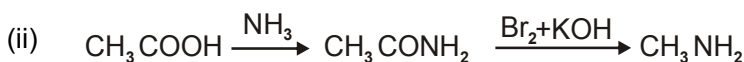
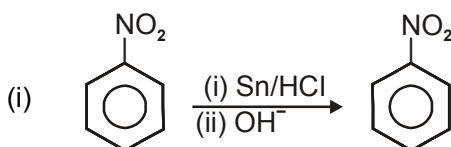
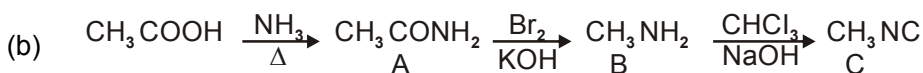
It exists as discrete tetrahedral P₄ unit

- (ii)



Red phosphorus

It exists in the form of polymeric chain.



$$E^\circ(\text{Cr}^{3+}/\text{Cr}^{2+}) = -0.4\text{V}, E^\circ(\text{Mn}^{3+}/\text{Mn}^{2+}) = 1.5\text{V}, E^\circ(\text{Fe}^{3+}/\text{Fe}^{2+}) = 0.8\text{V}$$

26. (a) Identify A, B and C in the following reaction :



- (b) Give reasons

- (i) *p*-Nitrobenzoic acid has higher K_a value than benzoic acid.
- (ii) Acetone is less reactive than acetaldehyde towards nucleophilic attack.

OR

- (a) An organic compound (A) has molecular formula ($\text{C}_5\text{H}_{10}\text{O}$). It does not reduce Tollens' reagent but forms an orange precipitate with 2,4-DNP reagent. It forms a carboxylic acid (B) with molecular formula ($\text{C}_3\text{H}_6\text{O}_2$) when treated with alkaline KMnO_4 and a yellow precipitate on treatment with NaOH and I_2 . On oxidation under vigorous conditions gives ethanoic acid and propanoic acid. Sodium salt of (B) gave a hydrocarbon (C) in Kolbe's Electrolytic Reduction. Identify (A), (B) and (C) and write the reactions involved.

- (b) Predict the products formed in the following cases.

- (i) (A) ($\text{C}_3\text{H}_6\text{O}$) reacts with PhMgBr and is then hydrolysed.
- (ii) (A) reacts with hydrazine and is then heated with KOH and ethylene glycol.
- (iii) (A) does not give Cannizzaro reaction.

15. PHBV (Poly- β -hydroxybutyrate-CO- β -hydroxyvalerate) is biodegradable polymer. It is a co-polymer of 3-hydroxybutanoic acid and 3-hydroxypentanoic acid.

- (a) How PHBV has found utility in medicines as capsule?
- (b) Is it an addition polymer or a condensation polymer?
- (c) Write the structure of PHBV

OR

Write the monomers of following polymers and mention one use of each polymer.

- (a) PAN
- (b) Nylon-6,6
- (c) Glyptal

16. Give reasons for the following:

- (a) *t*-Butyl bromide has lower boiling point than *n*-butyl bromide.
- (b) The dipole moment of chlorobenzene is lower than that of cyclohexyl chloride.
- (c) Draw the structure of Hex-3-enoic acid.

17. Give the pharmacological functions of the following type of drugs:

- (a) Analgesics (b) Tranquilizers (c) Antifertility drugs

18. (a) What happens when D-glucose is treated with the following reagents? Write chemical equations of the reactions involved.

- (i) HI (ii) Acetic anhydride

(b) The glucose is correctly named as D-(+)- glucose. What are represented by the letter 'D' and sign (+)?

19. (a) Give a chemical test to distinguish between the following pairs of compounds:

