SUPPORT STUDY MATERIAL

XII Chemistry

Study Material, Support Material, Study Notes, HOTS and VBQ

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Important Formulas of Physical Chemistry

THE SOLID STATE

1. **Calculation of numer of particles / atoms / ions in a Unit Cell :**

2.

Type of Unit Cell	Numer of particles per Unit Cell	Relationship between edge length (a) and radius (r) of atom/ion
Simple cubic	1	$a = 2r$
Body centred cubic	2	$a = \frac{4}{\sqrt{3}} r$
Face centred cubic	4	$a = 2\sqrt{2}\ r$

3. **Density of unit cell (d)**

$$d = \frac{Z \times M}{a^3 \times N_A}$$

Where **Z** is rank of unit cell (no. of atoms per unit cell), **m** is molar mass/ atomic mass, **'a'** is edge length of the cube, **'a^3'** is volume of cubic unit cell and $\mathbf{N_A}$ is Avogatro number.

4. **Packing efficiency** = $\frac{d \times N_A}{M} \times \frac{4}{3} \pi r^3 \times 100$

Here 'M' is molar mass 'r' is radius of atom, 'd' is density and N_A is Avogaotro's number (6.022×10^{23} mol^{-1}).

Rank of unit cell can be computed by packing efficiency value

Type of Unit Cell	Packing efficiency	Rank of Unit Cell
SC	52.4%	1
BCC	68.%	2
FCC	74%	4

Solution

1. Mole fraction (x)

if the number of moles of A and B are n_A and n_B respectrively, the mole fraction of A and B will be

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

$$x_A + x_B = 1$$

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

3. **Moality (m)** = $\frac{\text{Moles of solute}}{\text{Mass of solvent in kilograms}}$

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 :**

$$p_A = p_A^\circ \, x_A$$
$$p_B = p_B^\circ \, x_B$$

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

6. **Raoults law for a solution of non-volatile solute and volatile solvent :**

$$\frac{p_A^\circ - p_A}{p_A^\circ} = i x_B \simeq i \frac{n_B}{N_A} = i \frac{W_B \times M_A}{M_B \times W_A} \text{ (for dilute solution)}$$

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.

7. **Elevation in boiling point (ΔT_b)**

$$\Delta T_b = i.K_b\ m$$

where $\Delta T_b = T_b - T_b°$

K_b = molal boiling point elevation constant

m = molality of solution.

8. **Depression in freezing point (ΔT_f)**

$$\Delta T_f = i.K_f\ m$$

where $\Delta T_f = T_f° - T_f$

K_f = molal depression constant

m = molality of solution.

9. **Osmotic pressure (π) of a solution**

$$\pi V = inRT \quad \text{or} \quad \pi = i\ CRT$$

where π = osmotic pressure in bar or atm

V = volume in litres

i = Van't Hoff factor

c = molar concentration in moles per litres

n = number of moles

T = Temperature on Kelvin Scale

R = 0.083 L bar mol^{-1} K^{-1}

R = 0.0821 L atm mol^{-1} K^{-1}

10. **Van't Hoff factor (*i*)**

$$i = \frac{\text{Observed colligative property}}{\text{Theoretically calculated colligative property}}$$

$$i = \frac{\text{Normal molar mass}}{\text{Abnormal molar mass}}$$

$$\begin{cases} i > 1 & \text{For dissociation of molecules} \\ i < 1 & \text{For association of molecules} \\ i = 1 & \text{For ideal solution} \end{cases}$$

11. **Relationship between relative lowering in vapour prescure and elevation in b.p.**

$$\frac{\Delta p}{p_A^\circ} = i \frac{\Delta T_b}{K_b} M_A \times 1000$$

Here

Δp is lowering in vapour pressure, p_A° is vapour pressure of pure solvent, i is van't Hoff factor, ΔT_b is elevation in boiling point, K_b is molal elevation constant and M_A is molar mass of solvent

Electrochemistry

1. **Conductivity (k)**

$$K = \frac{1}{P} = \frac{1}{R} \times \frac{l}{A} = G \times G^*$$

Where R is resistance, l/A = cell constant (G*) and $\frac{1}{P}$ is resistivity.

2. Relationship between k and Λ_m

$$\Lambda_m = \frac{1000 \times k}{c}$$

Where Λ_m is molar conductance, k is conductivity and C is molar concentration.

Kohlrausch's law

(a) In general if an electrolyte on dissociation gives ν_+ cations and γ_- anions then, its limiting molar conductivity is given by

$$\Lambda^\circ_m = \gamma_+ \lambda^\circ_+ + \gamma_- \lambda^\circ_-$$

Here λ_+° and λ°_- are the limiting molar conductivities of cation and anion respectively and ν_+ and ν_- are the number of cations and anions furnished by one formula unit.

(b) **Degree of dissociation (α)** is given by :

$$\alpha = \frac{\Lambda_m^c}{\Lambda_m^\circ}$$

Here Λ°_m is molar conductivity at the concentration C and Λ°_m is limiting molar conductivity of the electrolyte.

(c) Dissociation constant (K.) of weak electrolyte

$$K = \frac{C\alpha^2}{1-\alpha} = \frac{C\left(\frac{\Lambda_m^c}{\Lambda_m^o}\right)^2}{\left(1-\frac{\Lambda_m}{\Lambda_m^o}\right)}$$

3. **Nernst Equation for electrode reaction :** $M^{n+} + ne^- \rightarrow M$.

$$E = E^\theta - \frac{2.303\ RT}{nF} \log \frac{1}{[M^{n+}]}$$

For Cell potential of electrochemical reaction aA : bB $\xrightarrow{ne^-}$ cC + dD

$$E_{cell} = E^\theta_{cell} - \frac{2.303RT}{nF} \log [Q_C]$$

4. **Relationship between E° cell and equilibrium constant (Kc)**

$$E^\theta\ cell = \frac{2.303RT}{nF} \log K_C$$

$$E^\theta\ cell = \frac{0.059v}{n} \log K_C$$

5. $\Delta G^\theta = -\ nF\ E^\theta cell$

Where ΔG^θ = standard Gibbs energy change and nF is the amount of charge passed.

$$\Delta G^\theta = -\ 2.303\ RT\ \log\ K_c$$

Chemical Kinetics

1. **Integrated rate law equation for zero order reaction**

(a) $k = \frac{[R]_\circ - [R]}{t}$

Where k is rate constant and $[R]_0$ is initial molar concentration.

(b) $t_{1/2} = \frac{[R]_\circ}{2k}$

$t_{1/2}$ is half life period of zero order reaction.

2. **Integrated rate law equation for first order reaction**

(a) $k = \frac{2.303}{t} \log \frac{[R]_\circ}{[R]}$

Where k is rate constant, $[R]_\circ$ is initial molar concentration and [R] is final concentration at time 't'.

(b) Half life period ($t_{1/2}$) for first order reaction :

$t_{1/2} = \frac{0.693}{k}$

3. **Anhenius epuation**

(a) $k = A\ e^{-Ea/RT}$

Where 'A' is frequency factor, Ea is the energy of activation, R is universal gas contant and T is absolute temperature.

$^{-Ea}/_{RT}$ gives the fraction of collisions having energy equal to or greater than Ea.

(b) $\log \frac{k_2}{k_1} = \frac{E_a}{2.303\ R} \left(\frac{T_2 - T_1}{T_1\ T_2} \right)$

Where k_1 is rate constant at temperature T_1 and k_2 is rate constant at temperature T_2.

Unit-1

THE SOLID STATE

QUESTIONS

VSA QUESTIONS (1 - MARK QUESTIONS)

1. What are anistropic substances.

2. Why are amorphous solids isotropic in nature?

3. Why glass is regarded as an amorphous solid?

4. Define the term 'crystal lattice.'

8. Define the term voids.

9. What type of stochiometric defect is shown by (i) ZnS and (ii) CsCl?

   [**Hint. :** (i) Frenkel defect (ii) Schottky defect]

*10. If the formula of a compound is A_2B, which sites would be occupied by A ions?

   [**Hint. :** Number of A ions is double to B ions, so ions will occupy tetrahedral voids]

11. What is the coordination number for

   (a) an octahedral void

   (b) a tetrahedral void.

   [**Hint. :** (a) 6; (b) 4]

*12. How many octahedral voids are there in 1 mole of a compound having cubic closed packed structure? [**Ans. :** 1 mole]

13. Arrange simple cubic, bcc and fcc lattice in decreasing order of the fraction of the unoccupied space.

   [**Hint. :** fcc < bcc < sc]

14. How much space is empty in a hexagonal closed packed solid?

15. An element crystallises separately both in hcp and ccp structure. Will the two structures have the same density? Justify your answer.

[**Hint :** Both crystal structures have same density because the percentage of occupied space is same.]

16. In NaCl crystal, Cl^- ions form the cubic close packing. What sites are occupied by Na^+ ions.

17. In Corundum, O^{2-} ions from hcp and Al^{3+} occupy two third of octahedral voids. Determine the formula of corundum. [**Ans. :** Al_2O_3]

18. Why is Frenkel defect not found in pure alkali metal halides?

19. Which point defect is observed in a crystal when a vacancy is created by an atom missing from a lattice site.

20. Define the term 'doping'.

21. Why does conductivity of silicon increase with the rise in temperature.

22. Name the crystal defect which lowers the density of an ionic crystal.

[**Ans. :** Schottky defect]

23. What makes the crystal of KCl sometimes appear violet?

[**Hint :** F-Centre]

24. Which point defect in ionic crystal does not alter the density of the relevant solid?

25. Name one solid in which both Frenkel and Schottky defects occur.

26. Which type of defects are known as thermodynamic defects?

[**Ans. :** Stoichiometric defects]

27. In a p-type semiconductor the current is said to move through holes. Explain.

28. Solid A is very hard, electrical insulator in solid as well as in molten state and melts at extremely high temperature. What type of solid is it?

[**Hint :** Covalent solid]

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

1. List four distinctions between crystalline and amorphous solids with one example of each.

2. Give suitable reason for the following–

   (a) Ionic solids are hard and brittle.

   (b) Copper is malleable and ductile.

3. Define F–centre. Mention its one consequence.

4. What is packing efficiency. Calculate the packing efficiency in body-centered cubic crystal.

5. Explain :

   (a) List two differences between metallic and ionic crystals.

   (b) Sodium chloride is hard but sodium metal is soft.

6. Account for the following :

   (a) Glass objects from ancient civilizations are found to become milky in appearance.

   (b) Window glass panes of old buildings are thicker at the bottom than at the top.

7. Why is graphite soft lubricant and good conductor of electricity?

8. What do you understand by the following types of stacking sequences :

   (a) AB AB ..... (b) A B CABC .....

   What kind of lattices do these sequences lead to?

9. Derive the formula for the density of a crystal whose length of the edge of the unit cell is known?

   $$\left[*\text{Hint : } d = \frac{zm}{a^3 \times n_A} \right]$$

10. Explain how much portion of an atom is located at (a) corner (b) body centre (c) face-centre and (d) edge centre of a cubic unit cell.

*11. In a fcc arrangement of A and B atoms A are present at the corners of the unit cell and 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}]

*12. 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]

13. Explain the terms :

(a) Intrinsic semiconductor

(b) Extrinsic semiconductor.

14. Explain how vacancies are introduced in a solid NaCl crystal when divalent cations are added to it.

15. What is meant by non-stoichiometric defect? Ionic solids which have anionic vacancies due to metal excess defect develop colour. Explain with the help of suitable example.

16. Define the term **'point defects'** Mention the main difference between stoichiometric and non-stoichiometric point defects.

THE SOLID STATE (2 - MARK QUESTIONS)

17. A compound M_pX_q has cubic close packing (ccp) arrangement of X. Its unit cell structure is show below :

Determine the empirical formula of the compound. [**Ans :** MX_2]

18. The concentration of cation vacancies in NaCl crystal doped with $CdCl_2$ is found to be 6.02 x 10^{16} mol^{-1}. What is the concentration of $CdCl_2$ added to it? [**Ans :** 10^{-5} mol% $CdCl_2$]

19. Iron changes its crystal structure from body contred to cubic close backed structure when heated to 916°C. Calculate the ratio of the density of the BCC crystal to that of CCP crystal. Assume that the metallic radius of the atom does not change. [**Ans :** 1]

SA (II) TYPE QUESTIONS (3 - MARK QUESTIONS)

1. Write the relationship between atomic radius (r) and edge length (a) of cubic unit cell for
   (a) Simple cubic unit cell
   (b) Body-centred cubic unit cell
   (c) Face-centred cubic unit cell

   [***Hint :** (a) $a = 2r$ (b) $a = \frac{4}{\sqrt{3}}r$ (c) $a = 2\sqrt{2}r$]

2. Define a semiconductor? Describe the two main types of semiconductors when it is doped with
   (a) group 13 element, (b) group 15 element.

3. Explain the following terms with one example each :
   (a) Ferrimagnetism (b) Antiferromagnetism
   (c) 13-15 compounds

*4. Examine the defective crystal lattice given below and answer the following questions :

   (a) Name the crystal defect present in ionic solid.
   (b) Out of AgCl and NaCl, which is most likely to show this type of defect and why?
   (c) Why this defect is also known as dislocation defect?

5. Tungsten crystallizes in body centred cubic unit cell. If the edge of the unit cell is 316. 5pm, calculate the radius of tungsten atom?

6. Iron has a body centred cubic unit cell with a cell dimension of 286.65 pm. The density of iron is 7.874 g cm^{-3}. Use this information to calculate Arogadro number.

   (At. Mass of Fe = 55.845u).

NUMERICALS

1. 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}]

*2. 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 octanedral voids. What is the formula of the solid? [**Ans. :** A_2BC_2]

*3. 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 oxides ions. What is the formula of magnetite? [**Ans. :** Fe_3O_4]

4. A metal crystalises into two cubic lattices fcc and bcc, whose edge length are 3.5Å and 3.0Å respectively. Calculate the ratio of the densities of fcc and bcc lattices.

5. An element of atomic mass 98.5 g mol^{-1} occurs in fcc structure. If its unit cell edge length is 500 pm and its density is 5.22 g cm^{-3}. Calculate the value of Avogadro constant. [**Ans. :** 6.03×10^{23} mol^{-1}]

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. Analysis shows that a metal oxide has a empirical formula $M_{0.96}O$. Calculate the percentage of M^{2+} and M^{3+} ions in this crystal.

   [**Ans. :** M^{2+} = 91.7%, M^{3+} = 8.3%]

8. AgCl is doped with 10^{-2} mol% of $CdCl_2$, find the concentration of cation vacancies. [**Ans. :** 10^{-4} mol]

9. A metallic element has a body centered cubic lattice. Edge length of unit cell is 2.88×10^{-8} cm. The density of the metal is 7.20 gcm^{-3}. Calculate

   (a) The volume of unit cell.

   (b) Mass of unit cell.

   (c) Number of atoms in 100 g of metal.

   [**Ans. :** (a) 2.39×10^{-23} cm^3 (b) 1.72×10^{-22} g, (c) 1.162×10^{24} atoms]

10. Molybednum has atomic mass 96 g mol^{-1} with density 10.3 g/cm^3. The

edge length of unit cell is 314 pm. Determine lattice structure whether simple cubic, bcc or fcc.

(Given N_A = 6.022 × 10^{23} mol^{-1}) [**Ans. :** Z = 2, bcc type]

*13. The density of copper metal is 8.95 g cm^{-3}. If the radius of copper atom is 127 pm, is the copper unit cell a simple cubic, a body-centred cubic or a face centred cubic structure?

(Given at. mass of Cu = 63.54 g mol^{-1} and N_A = 6.02 × 10^{23} mol^{-1}]

[**Ans. :** Z = 4, fcc type]

[**Hint :** d = $\frac{ZM}{a^3 \times N_A}$ calculate Z/a^3 by putting the values given in the question.

Calculate packing efficiency by $\frac{z \times \frac{4}{3}\pi r^3 \times 100}{a^3}$ using value of Z/a^3,which is 74%. This shows that Z = 4

14. The well known mineral fluorite is chemically calcium fluoride. It is known that in one unit cell of this mineral there are 4 Ca^{2+} ions and $8F^-$ ions and that Ca^{2+} ions are arranged in a fcc lattice. The F^- ions fill all the tetrahedral holes in the fcc lattice of Ca^{2+} ions. The edge of the unit cell is 5.46 × 10^{-8} cm in length. The density of the solid is 3.18 g cm^{-3}. Use this information to calculate Avogadro's number (Molar mass of CaF_2 = 78.08 g mol^{-1}]

[**Ans. :** 6.02 × 10^{23} mol^{-1}]

Unit - 2

SOLUTIONS

VSA QUESTIONS (1 - MARK QUESTIONS)

1. Give an example of 'liquid in solid' type solution.

2. Which type of solid solution will result by mixing two solid components with large difference in the sizes of their molecules?

3. What is meant by semimolar and decimolar solutions? $\left[\textbf{Ans.:}\ \frac{M}{2}, \frac{M}{10}\right]$

4. What will be the mole fraction of water in C_2H_5OH solution containing equal number of moles of water and C_2H_5OH? [**Ans. :** 0.5]

5. Which of the following is a dimensionless quantity : molarity, molality or mole fraction? [**Ans. :** mole fraction]

6. 10 g glucose is dissolved in 400 g. of solution. Calculate percentage concentration of the solution. [**Ans. :** 2.5% w/w]

7. Gases tend to be less soluble in liquids as the temperature is raised. Why?

8. State the conditions which must be satisfied if an ideal solution is to be formed.

9. A mixture of chlorobenzene and bromobenzene forms nearly ideal solution but a mixture of chloroform and acetone does not. Why?

10. How is the concentration of a solute present in trace amount in a solution expressed?

*12. N_2 and O_2 gases have K_H values 76.48 kbar and 34.86 kbar respectively at 293 K temperature. Which one of these will have more solubility in water?

*13. Under what condition molality and molarity of a solution are identical. Explain with suitable reason.

*14. Addition of H_gI_2 to KI (aq.) shows decrease in vapour pressure. Why?

15. What will happen to the boiling point of the solution formed on mixing two miscible liquids showing negative deviation from Raoult's law?

16. Liquid 'Y' has higher vapour pressure than liquid 'X', which of them will have higher boiling point?

17. When 50 mL of ethanol and 50 mL of water are mixed, predict whether the volume of the solution is equal to, greater than or less than 100 mL. Justify.

18. Which type of deviation is shown by the solution formed by mixing cyclohexane and ethanol?

19. A and B liquids on mixing produce a warm solution. Which type of deviation from Raoult's law is there?

20. Define cryoscopic constant (molal freezing point depression constant.)

21. Mention the unit of ebulioscopic constant (molal boiling point elevation constant.)

22. If k_f for water is 1.86 K kg mol^{-1}, what is the freezing point of 0.1 molal solution of a substance which undergoes no dissociation or association of solute?

[**Hint :** $\Delta T_f = iK_f \cdot m$]

24. What is reverse osmosis? Give one large scale use of it.

*25. What is the maximum value of van't Hoff factor (i) for $Na_2SO_4 \cdot 10H_2O$?

[**Ans. :** i = 3]

26. What is the value of van't Hoff factor (i) if solute molecules undergo dimerisation. [**Ans. :** i = 0.5]

27. Under what condition is van't Hoff factor less than one?

[**Ans. :** Association]

*28. The Phase Diagram for pure solvent and the solution containing nonvolatile solute are recorded below. The quantity indicated by 'X' in the figure is known as : [**Ans. :** ΔTb]

*29. $AgNO_3$ on reaction with NaCl in aqueous solution gives white precipitate. If the two solutions are separated by a semi-permeable membrane, will there be appearance of a white ppt. in the side 'X' due to osmosis?

0.1 M $AgNO_3$ X	S P M	0.01 M NaCl Y

[**Ans. :** No ppt, because only solvent particles moves through SPM]

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

1. Explain the following :
   (a) Solubility of a solid in a liquid involves dynamic equilibrium.
   (b) Ionic compounds are soluble in water but are insoluble in nonpolar solvents.
2. Give two examples each of a solution :
   (a) showing positive deviation from Raoult's Law.
   (b) showing negative deviation from Raoult's Law.
3. Draw vapour pressure vs composition (in terms of mole fraction) diagram for an ideal solution.
4. Define azeotropes with one example of each type.
5. Draw the total vapour pressure vs. mol fraction diagram for a binary solution exhibiting non-ideal behaviour with negative deviation.
6. The vapour pressure curve for three solutions having the same non-volatile solute in the same solvent are shown. The curves are parallel to each other and do not intersect. What is the correct order of the concentrations of the solutions. [**Hint. :** A < B < C]

7. Show that the relative lowering of vapour pressure of a solvent is a colligative property.

8. Benzene and toluene form a nearly ideal solution. At a certain temperature, calculate the vapour pressure of solution containing equal moles of the two substances.
[Given : $P°_{Benzene}$ = 150 mm of Hg, $P°_{Toluene}$ = 55 mm of Hg]

9. What is meant by abnormal molecular mass? Illustrate it with suitable examples.

*10. When 1 mole of NaCl is added to 1 litre water, the boiling point increases? When 1 mole of CH_3OH is added to 1 litre water, the boiling point decreases? Suggest reasons.

11. Can we separate water completely from HNO_3 solution by vapourisation? Justify your answer.

*12. 1 gram each of two solutes 'A' and 'B' (molar mass of A > molar mass of B) are dissolved separately in 100 g each of the same solvent. Which solute will show greater elevation in boiling point and Why?

Solution

2 - MARK QUESTIONS

13. Examine the following illustrations and answer the following questions

(a) Identify the liquid A and liquid B (pure water or sugar solution)

(b) Name the phenomenon involved in this experiment so that the level of liquid in this the funnel has risen after some time.

14. How relative lowering in vapour pressure is related with depression in freezing point and elevation in boiling point?

SA (II) TYPE QUESTIONS (3 - MARK QUESTIONS)

1. (a) State Henry's Law.

   (b) If O_2 is bubbled through water at 393 K, how many millimoles of O_2 gas would be dissolved in 1L of water? Assume that O_2 exerts a pressure of 0.95 bar.

   (Given K_H for O_2 = 46.82 bar at 393K).

2. Given reason for the following :–

   (a) Aquatic species are more comfortable in cold waters than in warm waters.

   (b) To avoid bends scuba divers use air diluted with helium.

   (c) Cold drinks bottles are sealed under high pressure of CO_2.

3. Why should a solution of a non-volatile and non-eletrolyte solute boil at a higher temperature? Explain with the help of a diagram. Derive the relationship between molar mass and elevation in boiling point.

4. Account for the following :–

   (a) $CaCl_2$ is used to clear snow from roads in hill stations.

   (b) Ethylene glycol is used as antifreeze solution in radiators of vehicles in cold countries.

   (c) The freezing point depression of 0.01 m NaCl is nearly twice that of 0.01 m glucose solution.

5. Why do colligative properties of solution of a given concentration are found to give abnormal molecular weight of solute. Explain with the help of suitable examples.

6. Give reasons for the following :–

   (a) RBC swell up and finally burst when placed in 0.1% NaCl solution.

   (b) When fruits and vegetables that have been dried are placed in water, they slowly swell and return to original form.

(c) A person suffering from high blood pressure is advised to take less amount of table salt.

*7. Glycerine, ethylene glycol and methanol are sold at the same price per kg. Which would be cheaper for preparing an antifreeze solution for the radiator of an automobile? [**Ans. :** Methanol]

*8. Determine the correct order of the property mentioned against them :

(a) 10% glucose (p_1), 10% urea (p_2), 10% sucrose (p_3) **[Osmotic pressure]**

(b) 0.1 m NaCl, 0.1 m urea, 0.1 m $MgCl_2$ [**Elevation in b.pt.**]

(c) 0.1 m $CaCl_2$, 0.1 m sucrose, 0.1 m NaCl [**Depression in f.pt.**]

9. For a dilute solution containing 2.5 g of a non-volatile non-electrolyte solute in 100 g of water, the elevation in boiling point at 1 atm pressure is 2°C. Assuming concentration of solute is much lower than the concentration of solvent, determine the vapour pressure (mm of Hg) of the solution.

[**Given :** K_b for water = 0.76 kg mol^{-1}] [**Ans.:** 724 mm of Hg]

[**Hind :** $\Delta T_b = K_b \cdot m \Rightarrow 0.76 \times \frac{2.5}{M_B} \times \frac{1000}{100} = 2k$

$M_b = 9.5 \text{ g mol}^{-1}$

$$\frac{p^\circ_A - p_A}{p^\circ_A} = \frac{25}{95} \times \frac{18}{100}$$

$$\frac{760 - p_A}{760} = \frac{25}{95} \times \frac{18}{100} \Rightarrow p_A = 724 \text{ mm of Hg}]$$

10. 15.0 g of an unknown molecular substance was dissolved in 450 g of water. The resulting solution was fund to freeze at –0.34°C. What is the molar mass of this substance. (K_f for water = 1.86 K kg mol^{-1}).

LONG ANSWER TYPE QUESTIONS (5 MARKS)

1. (a) What are ideal solutions? Write two examples.

(b) Calculate the osmoic pressure in pascals exerted by a solution prepared by dissolving 1.0g of polymer of molar mass 185000 in 450 mL of water at 37°C.

2. (a) Describe a method of determining molar mass of a non-volatile solute from vapour pressure lowering.

(b) How much urea (mol. mass 60 g mol^{-1}) must be dissolved in 50g of water so that the vapour pressure at the room temperature is reduced by 25%? Also calculate the molality of the solution obtained.

[**Ans. :** 55.55 g and 18.5 m]

3. (a) Why is the freezing point depression considered as a colligative property?

(b) The cryoscopic constant of water is 1.86 km^{-1}. Comment on this statement.

(c) Calculate the amount of ice that will separate out on cooling solution containing 50 g of ethylene glycol in 200 g H_2O to –9.3°C. (K_f for water = 1.86 K kg mol^{-1}) [**Ans. :** 38.71g]

4. (a) Define osmotic pressure.

(b) Why osmotic pressure is preferred over other colligative properties for the determination of molecular masses of macromolecules?

(c) What is the molar concentration of particles in human blood if the osmotic pressure is 7.2 atm at normal body temperature of 37°C?

[**Ans. :** 0.283 M]

NUMERICAL PROBLEMS

1. Calculate the mass percentage of benzene (C_6H_6) and carbon tetrachloride (CCl_4), If 22g of benzene is dissolved in 122g of carbon tetrachloride.

[**Ans. :** C_6H_6 = 15.3%, CCl_4 = 84.7%]

2. Calculate the molarity of a solution prepared by mixing 500 mL of 2.5 M urea solution and 500 mL of 2M urea solution. [**Ans. :** 2.25 m]

[**Hint :** $M = \frac{M_1 V_1 + M_2 V_2}{V_1 + V_2}$

3. The mole fraction of CH_3OH in an aqueous solution is 0.02 and density of solution 0.994 g cm^{-3}. Determine the molality and molarity.

[**Ans. :** 1.13m, 1.08m]

4. 200 mL of calcium chloride solution contains 3.011×10^{22} Cl^- ions. Calculate the molarity of the solution. Assume that calcium chloride is completely ionized. [**Ans. :** 0.125 M]

5. 6×10^{-3} g oxygen is dissolved per kg of sea water. Calculate the ppm of oxygen in sea water. [**Ans. :** 6 ppm]

6. The solubility of oxygen in water is 1.35×10^{-3} mol L^{-1} at 20°C and 1 atm pressure. Calculate the concentration of oxygen at 20°C and 0.2 atm pressure. [**Ans. :** 2.7×10^{-4} mol L^{-1}]

7. Two liquids X and Y on mixing form an ideal solution. The vapour pressure of the solution containing 2 mol of X and 1 mol of Y is 550 mm Hg. But when 4 mol of X and 1 mole of Y are mixed, the vapour pressure of solution thus formed is 560 mm Hg. What will be the vapour pressure of pure X and pure Y at this temperature?
[**Ans. :** X = 600 mm Hg; Y = 400 mm Hg]

8. An aqueous solution containing 3.12 g of barium chloride in 250 g of water is found to be boil at 100.0832°C. Calculate the degree of dissociation of barium chloride.

   [Given molar mass $BaCl_2$ = 208 g mol^{-1}, K_b for water = 0.52 K/m]
[**Ans. :** 83.3%]

9. The degree of dissociation of $Ca(NO_3)_2$ in a dilute aqueous solution, containing 7.0 g of salt per 100 g of water at 100°C is 70%. If the vapour pressure of water at 100°C is 760 mm of Hg, calculate the vapour pressure of the solution. [**Ans. :** 745.3 mm of Hg]

10. 2g of C_6H_5COOH dissolved in 25g of benzene shows depression in freezing point equal to 1.62K. Molar freezing point depression constant for benzene is 4.9 K kg mol^{-1}. What is the percentage association of acid if it forms a dimer in solution? [**Ans. :** 99.2%]

11. Calculate the amount of NaCl which must added to one kg of water so that the freezing point is depressed by 3K. Given K_f = 1.86 K kg mol^{-1}, Atomic mass : Na = 23, Cl = 35.5). [**Ans. :** 0.81 mol NaCl]

12. Three molecules of a solute (A) associate in benzene to form species A_3. Calculate the freezing point of 0.25 molal solution. The degree of association of solute A is found to be 0.8. The freezing point of benzene is 5.5°C and its K_f value is 5.13 K/m. [**Ans. :** 4.9°C]

13. A 5% solution of sucrose ($C_{12}H_{22}O_{11}$) is isotonic with 0.877% solution of urea. NH_2CONH_2) Calculate the molecular mass of urea.[**Ans. :** 59.99 g mol^{-1}]

14. Osmotic pressure of a 0.0103 molar solution of an electrolyte was found to be 0.75 atm at 27°C. Calculate Van't Hoff factor. [**Ans. :** i = 3]

*15. The maximum allowable level of nitrates in drinking water is 45 mg nitrate ions/dm^3. Express this level in ppm? [**Ans. :** 45 ppm]

16. 75.2 g of Phenol (C_6H_5OH) is dissolved in 1 kg solvent of K_f = 14 Km^{-1}, if the depression in freezing point is 7K, then find the % of phenol that dimerises. [**Ans. :** 75%]

*17. An aqueous solution of glucose boils at 100.01°C. The molal boiling point elevation constant for water is 0.5 K kg mol^{-1}. What is the number of glucose molecule in the solution containing 100 g of water.

[**Ans. :** 1.2×10^{21} molecules]

18. A bottle of commercial H_2SO_4 [density = 1.787 g/mL] is labelled as 86% by mass.

(a) What is the molarity of the acid?

(b) What volume of the acid has to be used to make 1 litre 0.2 M H_2SO_4?

(c) What is the molality of the acid?

[**Ans. :** 15.7 M, 12.74 mL, 62.86 m]

19. A solution containing 30g of non-volatile solute exactly in 90g of water has a vapour pressure of 2.8 kPa at 298 K. Furhter, 18 g of water is then added to the solution and the new vapour pressure becomes 2.9 kPa at 298 K. Calculate :

(i) molar mass of the solute

(ii) Vapour pressure of water at 298 K. [**Ans. :** 34 g mol^{-1}, 3.4 kPa]

20. The vapour pressure of pure liquids A and B are 450 and 750 mm Hg respectively, at 350K. Find out the composition of the liquid mixture if total vapour pressure is 600 mm Hg. Also find the composition of the vapour phase. [**Ans. :** X_A = 0.4, X_B = 0.6, Y_A = 0.3, Y_B = 0.7]

21. An aqueous solution of 2% non-volatile solute exerts a pressure of 1.004 bar at the normal boiling point of the solvent. What is the molar mass of the solute? [**Ans. :** 41.35 g mol^{-1}]

Unit - 3

ELECTROCHEMISTRY

VSA QUESTIONS (1 - MARK QUESTIONS)

1. What is a galvanic cell?
2. Give the cell representation for Daniell Cell.
3. Mention the purpose of salt-bridge placed between two half-cells of a galvanic cell?
4. Give the condition for Daniell Cell in which there is no flow of electrons or current.
5. How is electrode potential different from cell potential?
6. Can you store zinc sulphate solution in a copper container? Give suitable reason. ($E^{\theta}Zn^{2+}/Zn$ = – 01.76V, E^{θ} Cu^{2+}/Cu = 0.34v)
7. How does electrochemical series help us in predicting whether a redox reaction is feasible or not?
8. Write Nernst equation for the electrode reaction. $M^{n+}_{(aq)} + ne^{-} \rightarrow M_{(s)}$ at 298 K and 1 bar pressure.
10. List the two factors that influence the value of cell potential of a galvanic cell.
11. How is equilibrium constant of a reaction related to standard cell potential?
12. Write the relation between E^{θ}cell and equilibrium constant (K) of cell reaction.
13. Define cell constant. Write the SI unit of cell constant.
14 How does specific conductance or conductivity of electrolytic solution vary with temperature?
15. What is the SI unit of (i) Conductance; (ii) Conductivity.
16. Represent a concentration cell with a suitable example.

17. State one difference between a primary battery and secondary battery.

*18. Galvanized iron does not corrode even if the coating of zinc is broken. Explain why?

(Given : $\left(E^{\theta}\ Fe^{2+}/_{Fe} = -0.44V;\ E^{\theta}Zn^{2+}/_{Zn} = -0.76V\right)$

19. Write the unit of Faraday constant.

*20. Write the name of a chemical substance which is used to prevent corrosion.

[**Ans. :** Bisphenol]

21. Show is the direction of flow of electrons in the following cell :

$Zn\ (s)\ |\ Zn^{2+}\ (aq)\ ||\ Ag^{+}\ (aq)\ |\ Ag\ (s)$

22. Rusting of iron becomes quicker in saline water?

*23. Two metals A and B have reduction potential values of – 0.25V and 0.80V respectively. Which of these will liberate hydrogen gas from dilute H_2SO_4?

24. Express the relation between conductivity and molar conductivity.

25. Name the cell which was used in Apollo space programme.

26. How many faradays are required to oxidise 1 mole of H_2O to O_2.

[**Ans. :** 2F]

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

1. List two points of difference between metallic conductance and electrolytic conductance.

2. List two points of difference between electrochemical cell and electrolytic cell.

3. List two factors which affect the conductivity of ionic solutions.

4. A conventional method of representing a Daniel cell is :

   $Zn\ (s)\ |\ Zn^{2+}\ (1M)\ ||\ Cu^{2+}\ (1M)\ |\ Cu\ (s)$.

   (i) Draw a diagram of the cell and mark anode and cathode as current is drawn from the cell.

   (ii) Write the reactions taking place at the cathode and the anode during the operation of Daniel cell.

*5. Suggest a method to determine the Λ°_{m} value of water.

6. Write the cell reaction which occur in the lead storage battery (a) when the battery is in use (b) when the battery is on charging.

7. Why absolute value of electrode potential cannot be determined?

8. Account for the fact that when chlorine is passed through a fluoride solution, no reaction takes place. $\left(\text{Given } E^{\theta}\ F_2 / 2F^- = 2.87V;\ E^{\theta}_{Cl_2/2Cl^-}\ Cl_2 / 2Cl^- = 1.36V\right)$

9. Copper does not dissolve in HCl (*aq*) but dissolves in HNO_3 (aq) producing Cu^{2+} ions. Explain the difference in behaviour.

   [Given $E^{\theta}_{Cu^{2+}/Cu^-} = 0.34V$; $E^{\theta}_{Cl_2/2Cl^-} = 1.36V$ and $NO_3^- + 4H^+\ 3e^- \rightarrow$ NO (g) + $2H_2O$, $E^{\theta}_{NO_3^-/NO} = 0.97V$]

10. Explain the following observations :
    (a) The product of electrolysis of molten NaCl are sodium metal and chlorine gas.
    (b) The product of electrolysis of aqueous sodium chloride solution are NaOH, Cl_2 and H_2.

11. What are fuel cells? Describe the principle and overall reaction involved in the working of hydrogen–oxygen fuel cell or $CH_3OH - O_2$ fuel cell.

12. Explain the meaning of the terms
    (a) Ionic mobility. (b) Overvoltage.

*13. Some standard reduction potential are as given below :

Half Cell	E^{θ} Value
F_2/F^-	2.9V
Ag^+/Ag	0.8V
Cu^+/Cu	0.5V
Fe^{2+}/Fe	–0.4V
Na^+/Na	–2.7V
K^+/K	–2.9V

    (a) Arrange oxidising agents in order of increasing strength.
    (b) Which of these oxidising agents will oxidise Cu to Cu^+ under standard conditions?

14. Account for the following observations :

(a) In a dry cell, the build up of ammonia around the carbon cathode should disrupt the electric current, but in practice this does not happen.

(b) Ordinary dry cells are not rechargeable.

*15. The following figure shows two electrolytic cells connected in series.

(a) How much electricity is required for the reduction of 1 mole of Ag^+ ions to Ag?

(b) If three faradays of electricity is passed through these cells, what is the ratio of cations Ag^+ and Cu^{2+} deposited on cathodes?

[**Ans. :** (a) 1F, (b) 2:1]

16. You are aquainted with the construction and working of a lead storage battery. Give the plausible reasons for these facts.

(a) There is only a single compartment unlike other electrochemical cells which have two compartments

(b) Addition of water is necessary from time to time for maintenance

SA (II) TYPE QUESTIONS (3 - MARK QUESTIONS)

1. Using the standard electrode potential, predict the reaction, If any that occurs between the following :

   (a) $Fe^{3+}(aq)$ and $I^{-}(aq)$, $E^{\circ}_{Fe^{3+}/Fe^{2+}} = 0.77V$; $E^{\circ}_{I_2/2I^{-}} = 0.54V$

   (b) $Fe^{3+}(aq)$ and $Br^{-}(aq)$, $E^{\circ}_{Fe^{3+}/Fe^{2+}} = 0.77V$; $E^{\circ}_{Br_2/2Br^{-}} = 1.07V$

   (c) $Ag^{+}(aq)$ and $Cu(s)$, $E^{\circ}_{Cu^{2+}/Cu} = 0.34V$; $E^{\circ}_{Ag^{+}/Ag} = 0.8V$

2. State the relationship amongst cell constant of a cell, resistance of the solution in the cell and conductivity of the solution. How is molar conductivity of a solute related to conductivity of its solution?

3. Describe the composition of anode and cathode in a mercury cell. Write the electrode reactions for this cell. Why does it provide constant voltage throughout its life?

4. Give reasons for :

   (a) For a weak electrolyte, its molar conductivity of dilute solution increases as the concentration of solution is decreased.

   (b) Molar conductivity of a strong electrolyte like KCl decreases almost linearly while increasing concentration?

   (c) It is not easy to determine Λ°_{m} of a weak electrolyte by extrapolation of $\sqrt{c}$ υs Λ_m curves?

5. (a) Write the mechanism of the corrosion of metals.

   (b) How is underground iron pipe is protected from corrosion?

6. Formulate the galvanic cell in which the following reaction takes place :

   $$Zn(s) + 2Ag^{+}(aq) \rightarrow Zn^{2+}(aq) + 2Ag(s)$$

   State

   (a) Which one of its electrodes is negatively charged?

   (b) The reaction taking place at each of its electrode.

   (c) The direction of current within this cell.

*7. The standard reduction potentials are as given below :–

Half Cell	***E° Value***
$Zn(OH)_2/Zn$	– 1.245 V
$Mg(OH)_2/Mg$	– 2.690 V
$Fe(OH)_2/Fe$	– 0.877 V
$Fe(OH)_3/Fe$	– 2.30 V

Under standard conditions :

(a) Which is the strongest reducing agent?

(b) Which reducing agent could reduce $Zn(OH)_2$ to Zn?

(c) Which reducing agent could reduce $Fe(OH)_2$ to Fe?

LONG ANSWER TYPE QUESTIONS (5 MARKS)

1. (a) Explain with example the terms weak and strong electrolytes.

(b) Calculate the emf of the cell

$$Mg\,|Mg^{2+}(0.001M\,\|Cu^{2+}(0.001M)\,|Cu$$

$$E^{\varnothing}_{Cu^{2+}/Cu} = 0.34V; E^{\varnothing}_{Mg^{2+}/Mg} = -2.375V$$

[**Ans. :** 2.651 V]

2. (a) Explain Kohlrausch law of independent migration of ions. Mention two applications of this law.

(b) The conductivity of 0.001M CH_3COOH is 4.95×10^{-5} Scm^{-1}. Calculate its dissociation constant. Given for acetic acid Λ°_m is 390.5 S cm^2 mol^{-1}. [**Ans. :** = 0.126]

3. (i) Define molar conductivity. Draw the plots showing the variation of molar conductivity for strong and weak electrolyte with square root of concentation.

(ii) Resistance of a solution (A) is 50 ohm and that of solution (B) is 100 ohm, both solutions being taken in the same conductivity cell, if equal volumes of solutions (A) and (B) are mixed, what will be the resistance of the mixture, using the same cell? Assume that there is no increase in the degree of dissociation of (A) and (B) on mixing. [**Ans. :** 66.66 ohm]

[**Hint. :** k = Conductivity, y = Cell constant]

$k_1 = \frac{1}{50}$ y, $k_2 = \frac{1}{100}$ y : and specific conductance of mixture is given by

$$= \frac{k_1 + k_2}{2}$$

$$\frac{k_1 + k_2}{2} = \frac{1}{R} \times y, \frac{1}{2}\left[\frac{y}{50} + \frac{y}{100}\right] = \frac{1}{R} \times y \Rightarrow R = 66.66 \text{ ohm}$$

4. (a) State Faraday's first and second laws of electrolysis.

   (b) Silver is deposited on a metallic vessel of surface area 800 cm^2 by passing current of 0.2 ampere for 3 hours. Calculate the thickness of silver deposited.

   (Density of silver = 10.47 g cm^{-3}, Molar atomic mass of silver = 107.924 g mol^{-1}] [**Ans. :** 2.9×10^{-4} cm]

5. (a) Draw the diagram of standard hydrogen electrode. Write the electrode reaction.

   (b) Calculate the equilibrium constant for the reaction :

   $$Fe^{2+} + Ce^{4+} \rightleftharpoons Ce^{3+} + Fe^{3+}$$

   Given $E^{\circ}_{Ce^{4+}/Ce^{3+}} = 1.44V; E^{\circ}_{Fe^{3+}/Fe^{2+}} = 0.68V$

   [**Ans. :** 7.6×10^{12}]

NUMERICAL PROBLEMS

*1. The emf of the following cells are:

$$Ag|Ag^+(1M\|Cu^{2+}(1M)|Cu, E^{\circ} = 0.46V$$
$$Zn|Zn^{2+}(1M\|Cu^{2+}(1M)|Cu, E^{\circ} = 1.1V$$

Calculate emf of the cell :

$$An(s)|Zn^{2+}(1M\|Ag^{2+}(1M)|Ag(s)$$

2. For concentration cell

$$Cu\,(s)\,|\,Cu^{2+}\,(0.01M\,\|\,Cu^{2+}\,(0.1M)\,|\,Cu\,(s)$$

(a) Calculate the cell potential.

(b) Will the cell generate emf when concentration becomes equal?

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

3. Calculate the equilibrium constant for the reaction at 25°C.

$$Cu(s) + 2Ag^{+}\,(aq) \rightleftharpoons Cu^{2+}\,(aq) + 2Ag\,(s)$$

The standard cell potential for the reaction at 25°C is 0.46V.

[Given R = 8.314 $JK^{-1}\,mol^{-1}$] [**Ans. :** 4.0×10^{15}]

4. Calculate $\Delta G°$ for the reaction.

$$Cu^{2+}\,(aq) + Fe(s) \rightarrow Fe^{2+}\,(aq) + Cu(s)$$

$E^{\circ}_{Cu^{2+}/Cu} = +0.34\,V;\ E^{\circ}_{Fe^{2+}/Fe} = -0.44\,V$ [**Ans. :** –150, 540 kJ]

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

$$Cu(s)\ |\ Cu^{2+}\ (0.130M)\ ||\ Ag+\ (10^{-2}\ M)\ |\ Ag(s)$$

Given $E^{\circ}_{Cu^{2+}/Cu} = +0.34\,V;\ E^{\circ}_{Ag^{+}/Ag} = +0.80\,V$ [**Ans. :** 0.37V]

7. 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

$\left(E^{\circ}_{Zn^{2+}/Zn} = -0.76\,V\right)$. [**Ans. :** –0.7902V]

8. For the electrode Pt, H_2 (1 atm) | $H^{+}_{(aq)}$ (*xM*), 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 = 1.807×10^{-6}, pH = 5.743]

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

Given $E^{\circ}_{Ag^+/Ag} = 0.80\,V$; $E^{\circ}_{Cu^{2+}/Cu} = +0.34\,V$.

Cell : Cu (s) | Cu^{2+} (aq) || Ag^+ (aq) | Ag(s) [**Ans. :** 5.3×10^{-9}]

10. Zinc granules are added in excess to 500 mL of 1.0 M nickel nitrate solution at 25°C until the equilibrium is reached. If the standard reduction potential of Zn^{2+} | Zn and Ni^{2+} | Ni are –0.75 V and – 0.24 V respectively, find out the concentration of Ni^{2+} in solution at equilibrium.

[**Ans. :** 5.88×10^{-18}M]

11. The molar conductivity of 0.1M CH_3COOH solution is 4.6 S cm^2 mol^{-1}. Calculate the conductivity and resistivity of the solution.

[**Ans. :** .00046 S cm^{-1}, 2174 Ω cm]

12. The molar conductivities of NH^+_4 ion and Cl^- ion are 73.5 S cm^2 mol^{-1} and 76.255 cm^2 mol^{-1} respectively. The specific conductivity of 0.1 M NH_4Cl is 1.288×10^{-2} S cm^{-1}. Calculate the dissociation constant of NH_4Cl.

[**Ans. :** 7.396×10^{-2}]

13. Molar conductivity at infinite dilution for NH_4Cl, NaOH and NaCl solution at 298K are respectively 129.8, 218.4 and 108.9 Scm^2 mol^{-1} and m for 10^{-2} M solution of NH_4OH is 9.33 S cm^2 mol^{-1}. Calculate the degree of dissociation of NH_4OH. [**Ans. :** 0.039]

14. Write the Nernst equation and emf of the following cell at 298 K; Pt(s)/ Br_2(l)| Br^-(0.010M) || H^+(0.030M) | H_2(g) (0.9 bar) | Pt(s). $E^{\circ}_{Br_2/Br^-/Pt} = 1.09V$.

[**Ans. :** –1.297V]

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

$Zn(s) + Ag_2O\ (s) + H_2O\ (l) \rightarrow Zn^{2+}\ (ag) + 2Ag(s) + 2OH^-(aq)$

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

Given $E^{\circ}_{Zn^{2+}/Zn} = -0.76V$; $E^{\circ}_{Ag^+/Ag} = 0.8V$

[**Ans.:** –301.08 kJ / mol., $E^{\theta}_{cell} = 1.56V$]

Unit - 4

CHEMICAL KINETICS

VSA QUESTIONS (1 - MARK QUESTIONS)

1. Define the term 'rate of reaction'.

2. Mention the units of rate of reaction.

3. Express the rate of reaction in terms of Br^- (*aq*) as reactant and Br_2 (*aq*) as product for the reaction :

   $5\ Br^-(aq) + Br(aq) + 6H^+\ (aq) \rightarrow 3\ Br_2(aq) + 3H_2O(l)$

4. For a chemical reaction represented by R $\rightarrow$ P the rate of reaction is denoted by

   $$\frac{-\Delta[R]}{\Delta t} \text{ or } \frac{+\Delta[P]}{\Delta t}$$

   Why a positive sign (+) is placed before $\frac{\Delta[P]}{\Delta t}$ and negative sign (–) before $\frac{\Delta[R]}{\Delta t}$?

5. Express the rate of reaction in terms of disappearance of hydrogen and appearance of ammonia in the given reaction.

   $N_2(g) + 3\ H_2\ (g) \rightarrow 2NH_3\ (g)$

6. Why rate of reaction does not remain constant throughout?

7. Write the unit of first order rate constant of a gaseous reaction if the partial pressure of gaseous reactant is given in bar.

8. For a zero order reaction :

   R $\rightarrow$ P, the change in concentration of reactant w.r.t. time is shown by following graph.

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 :

$H_2 + I_2 \rightarrow 2HI$

rate of reaction α $[H_2]$ $[I_2]$

What is the (i) molecularity and (ii) order of the reaction.

[**Ans. :** (i) 2 (ii) 1]

11. For a chemical reaction A B. The rate of the reaction is given as Rate = k $[A]^n$, 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 value of the order of reaction of radioactive decay?

[**Ans. :** First order]

*14. Express the relation between the half life period of a reactant and initial concentration for a reaction of nth order.

[Ans : $t_{½}$ α $\frac{1}{[A]_0^{n-1}}$

*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 and at 300K rate constant is 5.9×10^{-5} s^{-1}, what will be the rate constant at 400K?

[**Ans. :** 5.9×10^{-5} s^{-1}]

*18. Two reactions occuring at the same temperature have identical values of Ea. 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 $k = Ae^{-Ea/RT}$ Which factor in this expression should register a decrease so that the reaction proceeds rapidly?

20. For a chemical reaction rate constant $k = 5.3 \times 10^{-4}$ mol L^{-1} s^{-1}, what will be the order of reaction? [**Ans. :** zero order]

21. Write the rate law and order for the following reaction :

$AB_2 + C_2 \rightarrow AB_2C + C$ (slow)

AB2 + C $\rightarrow$ AB_2C (Fast)]

[**Ans. :** Rate = k $[AB_2]$ $[C_2]$; Order = 1 + 1 = 2]

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

22. List four factors which affect the rate of a chemical reaction. State how each of these factors changes the reaction rate.

23. 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.

24. The rate law for the reaction : A + B $\rightarrow$ P is given by

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}]

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

25. For the reaction in a closed vessel :

$2NO(g) + O_2(g) \rightarrow 2NO_2(g)$; Rate = $k\,[NO]^2\,[O_2]$

If the volume of the reaction vessel is doubled, how would it affect the rate of the reaction? [**Ans. :** Diminish to 1/8 of initial value]

26. Explain with an example, what is a pseudo first order reaction?

27. Show that time required for 99.9% completion of the first order reaction is 10 times of $t_{1/2}$ for first order chemical reaction.

28. The graphs (1 and 2) given below are plots of rate of reaction verses concentration of the reaction. Predict the order from the graphs.

29. (a) For a reaction A + B Products, the rate law is given by

$$r = k\,[A]^{1/2}\,[B]^{2}$$

What is the order of reaction?

(b) the conversion of molecules X to Y follows second order kinetics. If concentration of X is increased to three times, how will it affect the rate of formation of Y? [**Ans. :** (a) 5/2; (b) 9 times]

SA (II) TYPE QUESTIONS (3 - MARK QUESTIONS)

31. What is meant by zero order reaction? Derive an integrated rate equation for a zero order reaction.

32. (a) Write two points of difference between order of reaction and molecularity of a reaction.

(b) Write one point of difference between rate of reaction and rate constant.

33. Draw a graph between fraction of molecules and kinetic energy of the reacting species for two different temperatures :

(a) Room temperature

(b) Temperature 10°C higher than the room temperature

(c) Indicate the fraction of additional molecules which react at (t +10)°C.

LONG ANSWER TYPE QUESTIONS (5 - MARK - QUESTIONS)

34. (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

$2NO\ (g) + Cl_2\ (g) \rightarrow 2\ NOCl\ (g)$

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

Experiment No.	*Initial [NO] / M*	*Initial [Cl_2] /M*	*Initial rate of disapperance of Cl_2 [M / min]*
1	0.15	0.15	0.60
2	0.15	0.30	1.20
3	0.30	0.15	2.40
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 disapperance of Cl_2 in exp. 4?

[**Ans.:** (i) Rate = k $[NO]^2\ [Cl_2]$, (ii) k = 177.7 $L^2\ mol^{-2}\ min^{-1}$, (iii) 2.7765 M/min

35. (a) Draw a plot between log k and reciprocal of absolute temperature (T).

(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?

36. (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.

NUMERICALS

37. The reaction $SO_2Cl_2(g) \xrightarrow{k} SO_2(g) + Cl_2(g)$ is a first order reaction with half life of 3.15×10^4 s at 575 K. What percentage of SO_2Cl_2 would be decomposed on heating at 575K for 90 min. [**Ans. :** 11.2%]

38. A certain reaction is 50% complete in 20 min at 300K and the same reaction is again 50% complete in 5 min at 350K. Calculate the activation energy if it is a first order reaction.

    (R = 8.314J K^{-1} mol^{-1}, log 4 = 0.602) [**Ans. :** 24.206 kJ/mol]

39. For a chemical reaction A $\rightarrow$ B, it was found that concentration of B increases by 0.2 mol L^{-1} in half an hour. What is the average rate of reaction.

    [**Ans. :** 0.0066 mol L^{-1} min^{-1}]

40. In the reaction R $\rightarrow$ P, the concentration of R decreases from 0.03M to 0.02 M in 25 minutes. Calculate the average rate of reaction using unit of time both in minutes and seconds.

    [**Ans. :** 4×10^{-4}M min^{-1}, 6.66×10^{-6} M s^{-1}]

41. A first order reaction has a rate constant 1.15×10^{-3} s^{-1}. How long will 5g of this reactant take to reduce to 3g? [**Ans. :** t = 444 s]

42. The rate of reaction triples when the temperature changes from 20°C to 50°C. Calculate the energy of activation. [R = 8.314 J K^{-1} mol^{-1}, log 3 = 0.48] [**Ans. :** 12.59 kJ]

43. A hydrogenation reaction is carried out at 550 K. If the same reaction is carried out in the presence of a catalyst at the same rate, the temperature required is 400 K. Calculate the activation energy of the reaction if the catalyst lowers the activation barrier by 20 kJ mol–1.

    [**Hint :** $k = Ae^{-E_a/RT}$. In the absence of catalyst, E_a = x kJ mol^{-1}. In the presence of catalyst, E_a = (x – 20) kJ mol^{-1}] [**Ans. :** E_a = 100 kJ mol^{-1}]

44. The rate constant for the first order decomposition of H_2O_2 is given by the following equation log k = 14.34 – 1.25×10^4 K/T. Calculate E_a for this reaction and at what temperature will its half-life be 256 minutes.

    [**Ans. :** E_a = 239.34 kJ; T = 670K]

45. Show that for a first order reaction, time required for 99% completion is twice for the time required for the 90% completion of reaction.

46. The experimental data for the reaction : $2A + B_2 \rightarrow 2AB$, are as follows. Write probable rate expression.

[A] mol/L^{-1}	*[B_2] mol/L^{-1}*	*Initial rate (mol L^{-1} sec^{-1})*
0.5	0.5	1.6×10^{-4}
0.5	1.0	3.2×10^{-4}
1.0	1.0	3.2×10^{-4}

[**Ans :** Rate = k [B_2]

47. A reaction is 20% complete in 20 minutes. Calculate the time required for 80% completion of reaction, If reaction follows the first order kinetics.

[**Ans. :** 144 min]

48. The decomposition of phosphine 4PH3(g) P4(g) + 6H2(g) has rate law; Rate = k [PH_3]. The rate constant is 6.0×10^{-4} s^{-1} at 300K and activation energy is 3.05×10^5 J mol^{-1}. Calculate the value of the rate constant at 310K. (R = 8.314 J K^{-1} mol^{-1}). [**Ans. :** 30.97×10^{-3} s^{-1}]

49. For the decomposition of azoisopropane to hexane and nitrogen at 543K, the following data is obtained.

t (sec.)	0	360	720
Pressure (atm.)	35.0	54.0	63.0

Calculate the rate constant.

[**Ans. :** $k_{360} = 2.17 \times 10^{-3}$ s^{-1} ; $k_{720} = 2.24 \times 10^{-3}$ s^{-1}]

50. The decomposition of hydrocarbon follows the equation

$k = (4.5\times10^{11}\ s^{-1})\ e^{-28000\ K/T}$,

Calculate activation energy (Ea). [**Ans. :** 232.79 $kJmol^{-1}$)

Unit - 5

SURFACE CHEMISTRY

VSA QUESTIONS (1 - MARK QUESTIONS)

1. Why does a gas mixed with another gas not form a colloidal system?
2. Why are adsorbate particles attracted and retained on the surface of adsorbent?
3. Explain the terms sorption and desorption.
4. "Chemisorption is highly specific." Illustrate with an example.
5. "Adsorbents in finely divided form are more effective." Why?
6. Name two compounds used as adsorbent for controlling humidity.
   [**Ans. :** Silica gel, Alumina gel]
7. Mention one shape selective catalyst used to convert alcohol directly into gasoline.
8. 'Generally high temperature is favourable for chemisorption.' Why?
9. Name the catalyst used in the following process :
   (a) Haber's process for the manufacture of NH_3 gas.
   (b) Ostwald process for the manufacture of nitric acid.
10. Explain the relationship given by Freundlich in adsorption isotherm.
11. Which group elements show maximum catalytic activity for hydrogenation reactions?
    [**Hint :** 7–9 group elements]
12. Why gas masks are used by miners in coal mines while working?
13. Write the chemical reaction involved in the preparation of sulphur sol.
14. Name the enzyme which converts milk into curd. [**Ans. :** lactobacilli]

15. What are the optimum temperature and pH at which enzymes are highly active. [**Ans. :** Temperature 298–310K and pH 5 to 7]

16. What are the physical states of dispersed phase and dispersion medium in foam rubber.

18. What is the composition of colloidion solution?

19. Why do colloidal particles show Brownian movement?

    [**Hint :** Due to unbalanced bombardment of the particles by the molecules of the dispersion medium]

21. State the sign of entropy change involved when the molecules of a substances get adsorbed on a solid surface. [**Ans. :** ΔS = –ve]

22. Why does sky appear blue to us?

23. What happens when hydrated ferric oxide and arsenious sulphide sols are mixed in almost equal proportions?

24. Gelatin is generally added to ice-cream. Why?

    [**Hint :** Ice-cream is water in oil type emulsion and gelatin acts as emulsifier].

25. How is lake test for aluminium ion based upon adsorption?

    [**Hint :** $Al_2O_3.xH_2O$ has the capacity to adsorb the colour of blue litmus from the solution]

26. What is saturation pressure in Freundlich's isotherm?

27. Mention the two conditions for the formation of micelles.

    [**Hint. :** CMC and T_k]

28. How is Brownian movement responsible for the stability of sols?

    [**Hint :** Stirring effect due to Brownian movement does not allow the particles to settle down.]

29. Which of the following is more effective in coagulating positively charged hydrated ferric oxide sol : (i) KCl (ii) $CaSO_4$ (iii) K_3 $[Fe(CN)_6]$.

30. State the purpose of impregnating the filter paper with colloidion solution.

31. Mention one use of ZSM–5 catalyst.

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

35. Explain the effect of temperature on the extent of physical and chemical adsorption.

36. Define the term peptization and mention its cause.

37. What will be the charge on colloidal solutions in the following cases.

Give reasons for the origin of charge.

38. Write the factors upon which the catalytic reaction of shape-selective catalyst depends?

[**Hint :** (a) Pore structure of the catalyst; (b) Size and shape of the reactant and product molecules.]

39. Mention two examples of emulsifying agents for o/w emulsions and w/o emulsions.

40. Suggest a mechanism of enzyme catalysed reaction.

41. 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 $CaCl_2 . 2H_2O$)

42. Write the differences between adsorption and absorption?

43. How can physisorption be distinguished from chemisorption?

44. Classify the following reactions as homogeneous and heterogeneous catalysis :

(a) Vegetable oil (*l*) + H_2 (g) $\xrightarrow{Ni(s)}$ Vegetable ghee (s)

(b) $C_{12}H_{22}O_{11}$ (aq) + H_2O (*l*) $\xrightarrow{H_2SO_4\ (aq)}$ $C_6H_{12}O_6$ (aq) + $C_6H_{12}O_6$ (aq)

45. In what way these are different : (a) a sol and a gel (b) a gel and an emulsion.

46. State “Hardy Schulze Rule” with one example.

47. What is an emulsifying agent? What role does it play in forming an emulsion?

48. Define the terms :

    (a) Helmholtz electrical double layer.

    (b) Zeta potential.

49. A graph between $\frac{x}{m}$ and log p is a straight line at an angle of 45° with intercept on the y-axis i.e. (log k) equal to 0.3010. Calculate the amount of the gas absorbed per gram of the adsorbent under a pressure of 0.5 atmosphere.

    [**Hint :** Refer to NCERT Text Book page 125, Fig. 5.2

    $\frac{1}{n} = \tan 45° = 1, \log k = 0.3010, k = 2, p = 0.5$ atm.

    $\frac{x}{m} = kp^{\frac{1}{n}} = 2 \times (0.5)^1 = 1.0$]

50. Mention the two necessary conditions for the observation of Tyndall Effect.

51. Account for the following :

    (a) Artificial rain can be caused by spraying electrified sand on the clouds.

    (b) Electrical precipitation of smoke.

52. Write chemical equations for the preparation of sols :

    (a) Gold sol by reduction.

    (b) hydrated ferric oxide sol by hydrolysis.

53. How can the two emulsions can be distinguished :

    (a) oil in water type (O/W) and

    (b) water in oil type (W/O)

SA (II) TYPE QUESTIONS (3 - MARK QUESTIONS)

54. Write the difference between

    (a) catalysts and enzymes

    (b) promoters and poisons

55. Write the steps of 'Modern Adsorption Theory of Heterogenous Catalysis.'

56. Mention the two important features of solid catalysts and explain with the help of suitable examples.

57. 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.

58. What happens :

    (a) by persistent dialysis of a sol.

    (b) when river water meets the sea water.

    (c) when alum is applied on cuts during bleeding.

59. Distinguish between multimolecular, macromolecular and associated colloids with the help of one example of each.

60. (a) Which property of colloids is responsible for the sun to look red at the time of setting?

    (b) C_2H_2 on addition with H_2 forms ethane in presence of palladium catalyst but if reaction is carried in the presence of barium sulphate and quinoline, the product is ethene and not ethane. Why?

[**Ans.** (a) Sun is at horizon and blue part of the light is scattered away by the dust particles as light has to travel a long distance through the atmosphere.

(b) $$CH = CH + H_2 \xrightarrow{Pd} CH_2 = CH_2 \xrightarrow[Pd]{H_2} CH_3 - CH_3$$

$$CH \equiv CH + H_2 \xrightarrow[BaSO_4,\ quinoline]{Pd} (CH_2 = CH_2)$$

($BaSO_4$ in presence of quinoline act as poison. The catalyst in this case is not effective in further reduction].

Unit - 6

GENERAL PRINCIPLES AND PROCESSES OF ISOLATION OF ELEMENTS

VSA QUESTIONS (1 - MARK QUESTIONS)

1. Name three metals which occur in native state in nature.

[**Ans. :** Au, Ag and Pt]

2. What are collectors in froth flotation process? Give one example.

[**Ex. :** Pine oil]

*3. Give the names and formulae of three ores which are concentrated by froth floatation process.

[**Ans. :** Galena (PbS), zinc blend (zns) cinnabar (HgS)]

4. Among Fe, Cu, Al and Pb, which metal (s) can not be obtained by smelting.

[**Ans. :** Al]

5. What is the thermodynamic criteria for the feasibility of a reaction?

[**Ans. :** ΔG should be –ve or log K = + ve]

8. Why can't aluminium be reduced by carbon?

[**Hint :** Al is stronger reducing agent than carbon]

9. Name the most important form of iron. Mention its one use.

[**Ans. :** Cast iron is used for making gutter pipes, castings, railway sleepers, toys etc.]

10. Name the impurities present in bauxite ore.

[**Ans. :** SiO_2, Fe_2O_3 and TiO_2]

11. What is the composition of copper matte?

[**Hint :** Cu_2S and FeS]

12. Which from of copper is called blister copper?

13. What are froth stabilizers? Give two examples.

[**Ex. :** Cresol and aniline].

14. A sample of galena is contaminated with zinc blend. Name one chemical which can be used to concentrate galena selectively by froth floatation method. [**Ans. :** NaCN]

15. What are the constituents of German silver?

[**Ans. :** Cu = 25-30%, Zn = 25-30%, Ni = 40-50%]

16. Why is froth floatation process selected for concentration of the sulphide ore?

[**Ans. :** Sulphide ore particles are wetted by oil (Pine oil) and gangue particles by water]

17. Write the reaction involved in the extraction of copper from low grade ores.

[**Ans. :** First step is leaching of ore with acid or bacteria then
Cu^{2+} (aq) + H_2 (g) $\rightarrow$ Cu(s) + $2H^+$ (g)]

18. Although aluminium is above hydrogen in the electrochemical series, it is stable in air and water. Why?

19. Which method of purification is represented by the following reaction

$$Ti(s) + 2I_2, (g) \xrightarrow{523K} Ti\ I_4(g) \xrightarrow{1700K} Ti(s) + 2I_2(g)$$

20. Zinc is used but not copper for the recovery of metallic silver from the complex $[Ag(CN)_2]^-$, although electrode potentials of both zinc and copper are less than that of Ag. Explain why?

[**Hint :** Zinc reacts at faster rate as compared with copper, further zinc is cheaper than copper].

21. Write the composition of motlen mixture which is electrolysed to extract aluminium.

SA (I) QUESTIONS (2 - MARK QUESTIONS)

*22. What is hydrometallurgy? Give one example where it is used for metal extraction.

[**Ans. :** Leaching followed by reduction is called hydrometallurgy. It is used in extraction and copper

*23. Name the process for the benefaction/concentration of (i) an ore having lighter impurities (ii) sulphide ore.

24. Mention the role of cryolite in the extraction of aluminium.

25. Mention the role of following :

(a) SiO_2 in the metallurgy of Cu.

(b) $CaCO_3$ in the metallurgy of Fe.

(c) CO in the metallergy of iron

(d) I_2 in the purification of zirconium.

26. Extraction of copper directly from sulphide ore is less favourable than from its oxide through reduction. Explain.

[**Ans. :** $2Cu\ S(s) + C(s) \rightarrow CS_2\ (l) + 2Cu(s)$

$CuO(s) + C(s) \rightarrow CO\ (g) + Cu(s)$

ΔG value is more –ve in second case as compared with first case]

27. The graphite electrodes in the extraction of 'alluminium' by Hall-Heroult process need to be changed frequently. Why?

28. Write the chemical formulae of the following ores (a) Haematite (b) Magnetite (c) Limonite (d) Siderite.

[**Ans. :** (a) Fe_2O_3 (b) Fe_3O_4 (c) $Fe_2O_3.2H_2O$ (d) $FeCO_3$]

29. Give equations for the industrial extraction of zinc from calamine.

[**Ans. :** $ZnCO_3 \rightarrow ZnO + CO_2$ (Calcination) $ZnO + C \rightarrow Zn + CO$ (Reduction)]

30. Name the elements present in anode mud during refining of copper. Why does it contain such elements?

[**Ans. :** Au and Ag. They are not oxidised at anode. They are less electropositive than copper.]

31. Write the Chemical reactions taking place in different zones in the blast furnace for the extraction of iron from its ore.

32. How are impurities separated from bauxite ore to get pure alumina?

33. Why is the reduction of a metal oxide easier if metal formed is in liquid state at the temperature of reduction?

[**Hint :** Entropy is more positive when the metal is in liquid state as compared with solid state, so ΔG becomes more –ve]

34. What is pyrometallurgy? Explain with one example.

[**Ans. :** A process of reducing a metal oxide by heating with either coke or some other reducing agent *e.g.*, Al, Mg etc.

$$ZnO + C \xrightarrow{975\ k} Zn + CO]$$

35. Write the method to produce Copper matte from copper pyrites.

*38. Copper can be extracted by hydrometallurgy but not zinc. Explain why?

[**Hint :** $E^{\circ}_{Zn^{2+}/Zn}$ is – ve, $E^{\circ}_{Cu^{2+}/Cu}$ is +ve]

*39. Gibbs energies of formation $\Delta_f G$ of MgO(s) and CO(g) at 1273K and 2273 K are given below:

$\Delta_f G$ [MgO(s)] = –941 kJ mol^{-1} at 1273 K.

$\Delta_f G$ [CO(g)] = –439 kJ mol^{-1} at 1273 K.

$\Delta_f G$ [MgO(s)] = –314 kJ mol^{-1} at 2273 K.

$\Delta_f G$ [CO(g)] = –628 kJ mol^{-1} at 2273 K.

On the basis of above data, predict the temperature at which carbon can be used as a reducing agent for MgO(s).

[**Ans. :** For the reaction, MgO(s) + C(s) $\rightarrow$ Mg(s) + CO(g)

At 1273K, $\Delta_r G = \Delta_f G[CO(g)] - \Delta_f G[MgO(s)]$ = –439 – (–941) KJ mol^{-1} = 502 kJ mol^{-1}

At 2273 K, $\Delta_r G$ = –628 – (–314) kJ mol^{-1} = –314 kJ mol^{-1}

The temperature is 2273 K]

SA (II) TYPE QUESTIONS (3 - MARK QUESTIONS)

*40. State the principles of refining of metal by the following methods.

(a) Zone refining (b) Electrolytic refining (c) Vapour phase refining.

41. How is pure copper obtained from its principle ore? Write the chemical reactions occurring during the extraction.

42. Name the method of refining of the following metals –

(a) Hg (b) Sn (c) Cu (d) Ge (e) Ni (f) Zr

[**Ans. :** (a) Distillation, (b) Liquation; (c) Electrolytic refining (d) Zone refining; (e) Mond Process (f) Van Arkel Processl]

*44. The native silver forms a water soluble compound (B) with dilute aqueous solution of NaCN in the presence of a gas (A). The silver metal is obtained by the addition of a metal (C) to (B) and complex (D) is formed as a byproduct. Write the structures of (C) and (D) and identify (A) and (B) in the following sequence –

$Ag + NaCN + [A] + H_2O \rightarrow [B] + OH^- + Na^+$.

$[C] + [B] \rightarrow [D] + Ag$.

[**Ans. :** [A] = O_2

[B] = Na $[Ag(CN)_2]$

[C] = Zn

[D] = Na_2 $[Zn\ (CN)_4]$].

45. In the cynamide extraction process of silver pon argentite ore, name the oxidising and reducing agents. Write the chemical equations of the reactions involved.

Unit - 7

Anomalous behaviour of first member of p-Block Elements

Anomalous behaviour of first element in the p-block elements is attributed to small size, large (charge/radius) ratio, high ionization enthapy, high electronegativity and unavailability of d-orbitals in its valance shell.

Consequences :

1. The first element in p-block element has four valence orbitals i.e. one 2s and three 2p, Hence maximum covalency of the first element in limited to four. The other elements of the p-block elements have vacant d-orbitals in their valence shell, e.g. elements of the third period have nine (9) one 3s, three 3p and five three 3d orbitals. Hence these show maximum covalence greater than four. Following questions can be answered -

   (i) Nitrogen (N) does not from pentahalide while P froms PCl_5, PF_5, and PF_6^-. Why?

   (ii) Sulphur (S) forms SF_6 but oxygen does not form OF_6. Why?

   (iii) Though nitrogen forms pentoxide but it does not form pentachloride. Explain. Why?

   (iv) Fluorine forms only one oxoacid while other halogens form a number of oxoacids. Why?

(2) The first member of p-block elements displays greater ability to from $p\pi$-$p\pi$ bond (s) with itself, (e.g., C = C, C ≡ C, N = N, N ≡ N) and with the other elements of second period (e.g., C = O, C ≡ N, N = O) compared to the subsequent members of the group.

   This is because p-orbitals of the heavier members are so large and diffuse that they cannot have effective sideways overlapping. Heavier members can form $p_\pi - d_\pi$ bonds with oxygen.

Nitrogen rarely forms $p\pi$–$d\pi$ bonds with heavier elements as in case of trisilylamine $(SiH_3)_3N$.

Now, the following questions can be explained using the above reasoning-

(i) Nitrogen forms N_2 but phosphorus forms P_4 at room temperature. Why?

(ii) Oxygen forms O_2 but sulphur exists as S_8. Why?

(iii) Explain why $(CH_3)_3$ P = O is known but $(CH_3)_3$ N = O is not known.

3. Due to small size and high electronegativity and presence of lone pair(s) of electrons, elements N, O, F when bonded to hydrogen atom, forms intermolecular hydrogen bonds which are stronger than other intermolcular forces. This results in exceptionally high m.p. and b.p. of the compounds having N–H/O–H/F–H bonds.

Shapes of some molecular/ionic species and hybridisation state of central atom.

Lewis structure	lone pairs + bond pairs and hydridisation of central atom	Electron-pair geometry	Shape of species
	0 + 4 = 4 (sp^3)	Tetrahedral	Tetrahedral
	1 + 3 = 4 (sp^3)	Tetrahedral	Pyramidal
	1 + 3 = 4 (sp^3)	Tetrahedral	Pyramidal
	1 + 2 = 3 (sp^2)	Trigonal planner	Bent

O = C = O	0 + 2 = 2 sp^2	Linear	Linear
	1 + 4 = 5 (sp^3d)	Trigonal-bipyramidal	 Sea-saw
	2 + 3 = 5 (sp^3d)	Trigonal-bipyramidal	 Bent T-shaped
	1 + 5 = 6 (sp^3d^2)	Octahedral	 Square Pyramidal
	2 + 4 = 6 (sp^3d^2)	Octahedral	 Square Planar

Note: Multiple bond is treated as single super pair. A π-bond shortens the bond length without affecting the geometry.

The state of hybridisation of the central atom is determined by sum of bond pairs and lone pair (s) if present arount the central atom in a molecule/ion.

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 ICl_4^- / XeF_4, BrO_3^-/XeO_3, BH_4^-/NH_4^+ are the pairs oi isostructural species.

Inert pair effect : Due to poor shielding effect of intervening d and/ or f–electrons, the effective nuclear charge is increased. This increased nuclear charge holds the ns^2 electrons of heavier elements to participate in bonding 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. For example, following questions can be exptalend with the help of inert pair effect.

(a) For N and P, + 5 oxidation state is more stable than + 3 oxidation state but for Bi, + 3 oxidation state is more stable than + 5. Explain why?

(b) $NaBiO_3$ is a strong oxidising agent. Why?
(**Hint :** Bi(v) is least stable O.S.).

(c) In group 16 stability of + 6 oxidiation state decreases and the stability of + 4 oxidation increases down the group. Why?

(d) SO_2 acts as reducing agent. Explain why?

(e) Why is BrO_4^- a stronger oxidising agent than ClO_4^- ?

[**Hint :** It is because + 7 oxidation state in less stable in BrO_4^- due to which Br – O bond becomes weaker.]

(f) $BiCl_5$ is highly unstable.

(g) The stability of highest oxidation state of 4p element is less than those of 3p and 5p elements of the same group?

Bond Length : Resonance averages bond lengths. The two oxygen–oxygen bond length are identical in the O_3 molecule because it is resonance hybrid of two cannonical forms.

In case of HNO_3, two nitrogen–oxygen bonds are identical and smaller than the third nitrogen–oxygen bond.

Now the following questions can be expained on the basis of this concept.

(i) In SO_2, the two sulphur-oxygen bonds are identical. Explain why?

(ii) In NO_3^-ion all the three N–O bonds are identical. Why?

Bond angle : In regular structures (where no lone pairs are present in the valence shell of the central atom in a molecule/ion), the bond angle does not depend upon the size/electronegativity of the central or terminal atoms.

In presence of lone pair(s) on the central atom, the geometry is distorted and the bond angle in changed.

Comparison of HNH and HPH bond angles

Since N is more electronegative than P, the bonding electron pair of N–H bond will shift more towards N atom than the bonding electron pair of P–H bond would shift towards P atom. This results in more bond pair-bond pair repulsion in NH_3

molecules than PH_3 molecule. Because of lp-bp repulsion the N–H are pushed closer to a less extent than in PH_3, Consequently, HNH bond angle is greater than HPH angle.

Now the following questions can be explained using the above mentioned concept.

(i) Bond angle in PH_4^+ ion is higher than in PH_3. Why?

(ii) H–O–H bond in H_2O in greater than H–S–H angle in H_2S. Why?

(iii) Cl–P–Cl bond angle in PCl_3 (100°) is less than F–N–F bond angle in NF_3 (102°). Explain why?

(iv) Bond angle in OF_2 (105°) molecule is less than in OCl_2 (110°). Why?

Boiling and melting points of hydrides depends upon the molar mass (or surface area) of molecules. More the molar mass, the higher in the m.p. and b.p. Hydrides forming intermolecular hydrogen bonds have exceptionally high m.p. and b.p. since intermolecular hydrogen bonds are stronger than the Van der waals forces.

Increasing order of melting point and boiling point of hybrides is as given below :

$PH_3 < AsH_3 < SbH_3 < NH_3$	; Melting point
$PH_3 < AsH_3 < NH_3 < SbH_3$	; Boiling point
$H_2S < H_2Se < H_2Te < H_2O$	; Melting point and Boiling point
$HCl < HBr < HI < HF$	; Boiling point
$HCl < HBr < HF < HI$	; Melting point

Thermal stability, reducing power and acid strength of hydrides depend upon bond dissociation enthalpy of E - H bond (E = group 15, group 16, and group 17 element). Due to the increase in size down the group, bond dissociation enthalpy of E - H bond decreases. Consequently, thermal stability, reducing power and acid strength of hydrides increases down the group.

The following questions can be explained using the above concepts.

Explain why :

(i) NH_3 has higher boiling point than PH_3.

(ii) H_2O is liquid and H_2S is gas or H_2S is more volatile than H_2O.

(iii) HE is weaker acid than HCl.

(iv) Among hydrogen halides, HI is the strongest reducing agent.

(v) H_2Te is more acidic than H_2S.

(vi) NH_3 is mild oxireducing agent while BiH_3 is the strongest reducing agent among the group-15 hydrides.

(vii) H_2S is weaker reducing agent than H_2Te.

Basic nature of hydrides EH_3 of group 15 elements

All the hydrides EH_3 has one lone pair of electron. In ammonia the lone pair of electron is present in, sp^3 hybrid orbital of the N-atom. The sp^3 hybrid orbital is directional and further N is more electronegtive than H, the bond pair of N - H is shifted towards N atom which further increases the electron density on N atom. In PH_3, the lone pair of electron is present in large and more diffuse 3s orbital which is non-directional. As a result PH_3 is less basic than NH_3 and basic character decreases down the group. NH_3 donates electron pair more readily than PH_3. $(SiH_3)_3N$ has less Lewis basic nature than that of $(CH_3)_3N$ because lone pair of electrons in p - orbital of N atom in $(SiH_3)_3N$ is transferred to the vacant d - orbital of Si atom forming $d\pi - p\pi$ fond.

COVALENT/IONIC CHARACTER OF HALIDES

Pentahalides are more covalent than trihalides since the element (E) in higher oridation state (+ 5) has more polarising power than element (E) in lower oxidation state (+ 3) in trihalides, Similarly $SnCl_4$, $PbCl_4$, $SbCl_5$ and UF_6 are more covalent than $SnCl_2$, $PbCl_2$, $SbCl_3$ and UF_4 respectively.

Following questions can be explained by using this concept. Explain why :

(i) $SnCl_2$ has more b.p. than $SnCl_4$.

(ii) $SbCl_5$ is more covalent than $SbCl_3$.

(iii) PCl_5 has lower boiling point than that of PCl_3.

Oxoacids of N, P and halogens :

Strength of oxoacid depends upon the polarity of O–H bond which in turn, depends on the electron with drawing power (or electronegativity) of the element E. Strength of oxoacids increase if the number of oxygen atom bonded with E increases.

Strength of oxoacid of halogens in the same oxidation state depends on the electronegativity of the halogen. The more the electrongeativeity, stronger is the oxoacid.

Stength of oxoacid of a halogen in different oxidation state increases with the increase in oxidation state. This is because the stabilisation of the oxoanion increases with the number of the oxygen atoms bonded to the halogen atom. More the number of oxygen atoms, the more the dispersal of –ve charge present on the oxoanion and stronger will be the oxoacid.

Oxidising power of halogens :

The more negative the value of $\Delta rH^\theta = \frac{1}{2}\Delta_{diss} H^\theta - \Delta_{eg} H^\theta - \Delta_{hyd} H^\theta$, the higher will be oxidising property of the halogen and more positive will be standard reduction potential E^θ_{red} of the halogen.

Following questions can be explained on the basis of parameters e.g., $\Delta_{diss} H^\theta$, eg H^θ and $\Delta_{hyd} H^\theta$.

(i) Why does F_2 have exceptionally low bond dissociation enthaply?

(ii) Although electron gain entharpy of fluorine(F) is less negative as compared to chlorine. (Cl), Flunorine (F_2) is a stronger oxidising agent than Cl_2. Why?

VSA QUESTIONS (1 - MARK QUESTIONS)

1. In group 15 elements, there is considerable increase in covalent radius from N to P but small increase from As to Bi. Why?

   [**Hint :** Due to completely filled d- and / or f-orbitals in As, Sb and Bi.

2. The tendency to exhibit – 3 oxidation state, decreases down the group in group 15 elements. Explain.

   [**Hint :** Due to increase in size and decrease in electronegativity down the groups].

3. Maximum covalence of Nitrogen is '4' but the heavier elements of group 15 show covalence greater than '4'. Why?

4. Nitrogen exists as a diatomic molecule with a triple bond between the two atoms, whereas the heavier elements of the group do not exist as E_2 at room temperature. Assign a reason.

   [**Hint :** $p_\pi - p_\pi$ multiple bonds are formed by N due to its small size.]

5. The ionization enthalpies of group 15 elements are higher than those of corresponding members of group 14 and 16 elements. Assign the reason.

6. The boiling point of PH_3 is lesser than NH_3. Why?

7. NO_2 dimerises to form N_2O_4. Why?

   [**Hint :** Due to presence of odd electron on N]

8. Draw the structure of N_2O_5 molecule.

9. How does ammonia solution react with Ag^+ (aq)? Write the balanced chemical equation.

10. Why does NH_3 forms intermolecular hydrogen bonds whereas PH_3 does not?

    [**Hint :** Due to strong electronegativity, small size of Nitrogen atom and presence of lone pair of electrons on N atom]

11. Write disproportionation reaction of H_3PO_3?

12. How does NH_3 acts as a complexing agent?

    [**Hint :** Metal hydroxides are dissolved in excess of NH_4OH. Ammonia acts as a Lewis base].

13. Why HF is the weakest acid and HI is the strongest.

    Hint : Ka : (HF) = 7×10^{-4} (HI) = 7×10^{11}

Intermolecular H–bonds in H–F and high bond dissociation enthalpy of H–F makes it weakest and weak bond in H–I makes it strogest.

14. Explain why halogens are strong oxidising agents.

[**Hint :** Ready acceptance of electron due to more negative eletron gain enthalpy.]

15. Why is Bi(V) a stronger oxidant than Sb(V)?

[**Hint :** +3 oxidation state is more stable than +5 oxidation state in Bi].

16. Why SF_4 is easily hydrolysed, whereas SF_6 is resistant to hydrolysis?

[**Hint :** Water molecule can not attack 'S' atom due to steric hinderance and 'S' atom is also coordinately saturated in SF_6 molecule.]

17. Bond dissociation enthalpy of F_2 is less than that of Cl_2. Why?

18. Write the reaction of PCl_5 with heavy water.

[**Hint :** $PCl_5 + D_2O \rightarrow POCl_3 + 2DCl$]

19. How many P – O – P bonds are there in cyclotrimetaphosphoric acid?

[**Hint :** 3 bonds]

20. In group 16, the stability of +6 oxidation state decreases and that of +4 oxidation state increases down the group. Why?

[**Hint :** due to inert pair effect]

21. Why we can not prepare HBr by heating KBr with sulphuric acid.

[**Hint :** As HBr readily reduces H_2SO_4 forming Br_2]

24. Fluorine exhibit only –1 oxidation state whereas other halogens exhibit +ve oxidation states also. Explain.

25. Arrange the following oxoacids of chlorine in increasing order of acidic strength.

$HOCl$, $HOClO$, $HOClO_3$, $HOClO_3$

*26. The majority of known noble gas compounds are those of Xenon. Why?

*27. "Hypophosphorus acid is a good reducing agent." Justify with an example.

[**Hint :** $4AgNO_3 + H_3PO_2 + 2H_2O \rightarrow 4Ag + HNO_3 + H_3PO_4$.

*28. Draw the structure of $H_4P_2O_7$ and find out its basicity?

[**Hint :** Tetrabasic]

*29. Arrange the following triatomic species in the order of increasing bond angle.

NO_2, NO_2^+, NO_2^-

[**Hint :**

NO_2 has one non-bonding electron, NO_2^- has two non-bonding electrons, NO_2^+ has no non-bonding electron on N atom. Bond angle of NO_2^+ is maximum that of NO_2^- minimum].

30. With what neutral molecule ClO^- is isoelectronic?

31. Draw the structure of $H_2S_2O_8$ and find the number of S–S bond if any.

32. What is cause of bleaching action of chlorine water? Explain it with chemical equation?

[**Hint :** Formation of nascent oxygen]

*33. Electron gain enthalpy of fluorine is more negative than that of chlorine.

[**Hint. :** Due to small size of F atom, there are strong interelectronic repulsions in the relatively smaller 2p orbitals of fluorine. So the incoming electron does experience less attraction than in Cl]

*34. Which one of the following is not oxidised by O_3. State the reason.

KI, $FeSO_4$, K_2MnO_4, $KMnO_4$

[**Hint. :** $KMnO_4$ since Mn is showing maximum oxidation state of +7.]

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

2. Why is red phosphorus denser and less chemically reactive than white phosphorus?

3. Give chemical reaction in support of the statement that all the bonds in PCl_5 molecule are not equivalent.

[**Hint :** $PCl_5 + H_2O \rightarrow POCl_3 + 2HCl$

4. Account for the following :

(a) XeF_2 has linear structure and not a bent structure.

(b) Phosphorus show marked tendency for Catenation.

5. Draw the structures of BrF_3, $XeOF_4$, XeO_3 using VSEPR theory.

6. Write the conditions that favour the formation of ammonia gas along with the reactions involved in Haber's Process.

7. Write the chemical equations of the following reactions

(a) Glucose in heated with conc. H_2SO_4.

(b) Sodium nitrate is heated with conc. H_2SO_4.

Complete the following reactions :

8. (i) $(NH_4)_2\ Cr_2O_7 \xrightarrow{heat}$

(ii) $N_4H\ Cl\ (aq) + NaNO_2\ (aq) \longrightarrow$

9. (i) $NH_2CONH_2 + H_2O \longrightarrow$

(ii) $FeCl_3\ (aq) + NH_4OH \longrightarrow$

10. (i) $Ca_3\ P_2 + H_2\ O\ (l) \longrightarrow$

(ii) $I_2 + HNO_3$ (conc.) $\longrightarrow$

11. (i) $Ba(N_3)_2 \xrightarrow{heat}$

(ii) $4H_3PO_3 \xrightarrow{heat}$

12. (i) $PH_4I + KOH \longrightarrow$

(ii) $HgCl_2 + PH_3 \longrightarrow$

13. (i) $PCl_3 + 3H_2O \longrightarrow$

(ii) $S + H_2SO_4$ (conc.) $\longrightarrow$

14. (i) $Al_2O_3(s) + NaOH\ (aq) + H_2O(l) \longrightarrow$

(ii) $HCl + O_2 \xrightarrow{CuCl_2}$

15. (i) $Ca(OH)_2 + Cl_2 \longrightarrow$

(ii) $XeF_4 + H_2O \longrightarrow$

16. (i) $Na_2SO_3 + Cl_2 + H_2O \longrightarrow$

(ii) $NaHCO_3 + HCl \longrightarrow$

17. (i) $XeF_6 + H_2O \xrightarrow[\text{hydrolysis}]{\text{Complete}}$

(ii) $XeF_6 + H_2O \xrightarrow[\text{hydrolysis}]{\text{Partial}}$

18. (i) $NO_3^- + Fe^{2+} + H^+ \longrightarrow$

(ii) $Zn + HNO_3\ (dil) \longrightarrow$

19. (i) $Zn + HNO_3\ (conc) \longrightarrow$

(ii) $P_4 + HNO_3\ (conc) \longrightarrow$

20. (i) $NH_3 + O_2 \xrightarrow{Pt/Rh}$

(ii) $P_4 + NaOH + H_2O \longrightarrow$

21. (i) $P_4 + SOCl_2 \longrightarrow$

(ii) $P_4 + SO_2Cl_2 \longrightarrow$

22. (i) $PbS + O_3 \longrightarrow$

(ii) $KI + H_2O + O_3 \longrightarrow$

23. (i) $MnO_4^- + SO_2 + H_2O \longrightarrow$

(ii) $Zn + HNO_3 \longrightarrow$
(dil)

24. (i) NH_3 (Excess) $+ Cl_2 \longrightarrow$

(ii) $NH_3 + Cl_2$ (Excess) $\longrightarrow$

25. (i) Cl_2 + NaOH (cold and dil) $\longrightarrow$

(ii) Cl_2 + NaOH (hot & conc) $\longrightarrow$

26. (i) $Fe + HCl \longrightarrow$

(ii) $Cl_2 + F_2$ (Excess) $\longrightarrow$

27. (i) $U + ClF_3 \longrightarrow$

(ii) $FeSO_4 + H_2SO_4 + Cl_2 \longrightarrow$

28. (i) What is the covalency of N in N_2O_5?

(ii) Explain why phosphorus forms pentachloride whereas nitrogen and bismuth do not?

29. (i) The acidic character of hydrides of group 15 increases from H_2O to H_2Te. Why?

(ii) Dioxygen is a gas while sulphur (S_8) is a solid. Why?

30. (i) Interhalogen compounds are more reactive than halogens except F_2. Why?

(ii) Give one important use of ClF_3.

31. (i) Write the composition of bleaching powder.

(ii) What happens when NaCl is heated with conc. H_2SO_4 in the presence of MnO_2. Write the chemical equation.

32. Arrange the following in the decreasing order of their basicity. Assign the reason :

PH_3, NH_3, SbH_3, AsH_3, BiH_3.

*33. A colourless and a pungent smelling gas which easily liquifies to a colourless liquid and freezes to a white crystalline solid, gives dense white fumes with ammonia. Identify the gas and write the chemical equation for its laboratory preparation. [**Hint :** HCl]

*34. Complete following disproportionation reactions.

(a) $P_4 + NaOH + H_2O \longrightarrow$

(b) $HNO_2 \xrightarrow{H^+}$

35. Arrange the following trichlorides in decreasing order of bond angle NCl_3 PCl_3, $AsCl_3$, $SbCl_3$

36. Suggest reason why only known binary compounds of noble gases are fluorides and oxides of Krypton, Xenon.

[**Hint :** F and O are most electronegative elements. Kr and Xe both have low Ionisation enthalpies.]

37. Which fluorinating agent are oftenly used instead of F_2? Write two chemical equations showing their use as fluorinating agents.

[**Hint :** $BrF_5 + 3H_2O \rightarrow HBrO_3 + 5HF$

$2IF_7 + SiO_2 \rightarrow 2IOF_5 + SiF_4$]

38. (a) Hydrolysis of XeF_6 is not regarded as a redox reaction. Why?

(b) Write a chemical equation to represent the oxidising nature of XeF_4.

[**Hint :** (b) $XeF_4 + 2H_2 \rightarrow Xe + 4HF$)]

39. Write Chemical equation :

(a) XeF_2 is hydrolysed

(b) PtF_6 and Xenon are mixed together.

SA (II) TYPE QUESTIONS (3 - MARK QUESTIONS)

1. (i) How is HNO_3 prepared commercially?

   (ii) Write chemical equations of the reactions involved.

   (iii) What concentration by mass of HNO_3 is obtained?

2. (i) How does O_3 react with lead sulphide? Write chemical equation.

   (ii) What happens when SO_2 is passed in acidified $KMnO_4$ solution?

   (iii) SO_2 behaves with lime water similar to CO_2.

3. Assign reason for the following :

   (i) Sulphur in vapour state exhibits paramagnetism.

   (ii) F_2 is strongest oxidising agent among halogens.

   (iii) In spite of having same electronegativity, oxygen forms hydrogen bond while chlorine does not.

4. Give appropriate reason for each of the following :

   (i) Metal fluorides are more ionic than metal chlorides.

   (ii) Perchloric acid is stronger than sulphuric acid.

   (iii) Addition of chlorine to KI solution gives it a brown colour but excess of Cl_2 makes it colourless.

   [Hint :

   (i) According to Fajan's Rule, bigger ions more are polarised than the smaller ion by a particular cation.

   (ii) ClO_4^- is more resonance stabilised than SO_4^{2-} since dispersal of negative charnge is more effective in ClO_4^- as compared with SO_4^{2-}

   (iii) $2KI + Cl_2 \rightarrow 2KCl + I_2$

   Excess $5Cl_2 + I_2 + 6H_2O \rightarrow 2HIO_3 + 10\ HCl$ (Colourless).

5. Explain why :

   (i) No chemical compound of helium is known.

   (ii) Bond dissociation energy of fluorine is less than that of chlorine.

   (iii) Two S–O bonds in SO_2 are identical.

6. Out of the following hydrides of group 16 elements, which will have :

   (i) H_2S (ii) H_2O (iii) H_2Te

(a) lowest boiling point

(b) highest bond angle

(c) highest electropositive hydrogen.

7. (i) How is XeO_3 prepared from XeF_6? Write the chemical equation for the reaction.

(ii) Draw the structure of XeF_4.

8. (i) Thermal stability of hydrides of group 16 elements decreases down the group. Why?

(ii) Compare the oxidising powers of F_2 and Cl_2 on the basis of bond dissociation enthalpy, electron gain ethalpy of hologens and hydration enthalpy of halide ions.

(iii) Write the chemical equation for the reaction of copper metal with conc. HNO_3.

*9. An unknown salt X reacts with hot conc. H_2SO_4 to produce a brown coloured gas which intensifies on addition on copper turnings. On adding dilute ferrous sulphate solution to an aqueous solution of X and then carefully adding conc. H_2SO_4 along the sides of the test tube, a brown complex Y is formed at the interface between the solution and H_2SO_4. Identify X and Y and write the chemical equation involved in the reaction.
[**Hint :** X is NO_3^- salt].

10. Assign reason to the following :

(i) Noble gases have large positive values of electron gain enthalpy.

(ii) Helium is used by scuba divers.

11. Arrange the following in the order of the property indicated for each set–

(a) F_2, Cl_2, Br_2, I_2 (Increasing bond dissociation energy).

(b) HF, HCl, HBr, HI (decreasing acid strength).

(c) NH_3, PH_3, ASH_3, SbH_3, BiH_3 (decreasing base strength).

[Hint :

(a) F_2 has exceptionally low bond dissociation enthalpy. Lone pairs in F_2 molecule are much closer to each other than in Cl_2 molecule. Larger electron–electron repulsions among the lone pairs in F_2 molecule make its bond dissociation enthalpy exceptionally low.

(b) Depends upon H–X bond dissociation enthalpy as the size of atom increases, bond dissociation enthalpy of H–X decreases.

(c) Electron availability on the central atom 'E' in EH_3 decreases down the group.

*12. A transluscent while waxy solid (A) on heating in an inert atmosphere is converted to its allotropic form (B), Allotrope (A) on reaction with very dilute aqueous NaOH liberates a highly poisonous gas (C) having a rotten fish smell, with excess of chlorine forms D which hydrolyses to form compound (E). Identify the compounds (A) to (E).

A : White phosphorus, B : Red phosphorus, C : PH_3, D : PCl_3, E : H_3PO_4

13. Write balanced equation for the following reactions :

(a) Zn is treated with dilute HNO_3.

(b) NaCl is heated with H_2SO_4 in the presence of MnO_2.

(c) Iodine is treated with conc. HNO_3.

14. X_2 is a greenish yellow gas with pungent offensive smell used in purification of water. It partially dissolves in H_2O to give a solution which turns blue litmus red. When X_2 is passed through NaBr Solution, Br_2 is obtained.

(a) Identify X_2, name the group to which it belongs.

(b) What are the products obtained when X_2 reacts with H_2O? Write chemical equation.

(c) What happens when X_2 reacts with hot and conc. NaOH? Give equation.

16. Assign the appropriate reason for the following:

(a) Nitrogen exists as diatomic molecule and phorphorous as P_4, Why?

(b) Why does $R_3P = 0$ exist but $R_3N = 0$ does not ? (R = an alkyl group).

(c) Explain why fluorine forms only one oxoacid, HOF.

[Hint :

(a) Due to its small size and high electronegativity N forms $p\pi - p\pi$ multiple bond ($N \equiv N$). whereas P does not form $p_\pi - p_\pi$ bonds but forms P – P single bond.

(b) Due to the absence of d-orbitals, N cannot expand its covalence beyond four.

In $R_3N = 0$, N should have a covalence of 5 so the compound $R_3N = 0$ does not exist since maximum covalence shown by N cannot exceed 4.

(c) F does not form oxoacids in which the oxidation state of F would be +3, +5, +7, it forms one oxoacid, because of unavailability of d orbitals in its valence shell.

LONG ANSWER TYPE QUESTIONS (5 - MARK QUESTIONS)

1. How is PH_3 prepared in the laboratory? How is it purified? How does the solution of PH_3 in water react on irradiation with light and on absorption in $CuSO_4$? How can you prove that PH_3 is basic in nature?

   Write the chemical equations for all the reactions involved.

2. Assign a possible reason for the following :

   (a) Stability of +5 oxidation state decreases and that of +3 oxidation state increases down the group 15 elements.

   (b) H_2O is less acidic than H_2S.

   (c) SF_6 is inert while SF_4 is highly reactive towards hydrolysis.

   (d) H_3PO_2 and H_3PO_3 act as good reducing agents while H_3PO_4 does not.

   (e) Noble gases have comparatively large size in their respective periods.

3. (a) How is XeF_6 prepared from the XeF_4? Write the chemical equation for the reaction.

   (b) Deduce the structure of XeF_6 using VSEPR theory.

   (c) How does XeF_2 reacts with PF_5?

   (d) Give one use each of helium and neon.

   (e) Write the chemical equation for the hydrolysis of XeF_4.

4. (a) Why does nitrogen show anomalous behaviour? Discuss the trend of chemical reactivity of group 15 elements with.

   (a) oxygen (b) halogens (c) metals

   (b) H_3PO_3 is a dibasic acid. Why?

5. (a) Arrange the following in the order of their increasing acid strength.

   (a) Cl_2O_7, SO_2, P_4O_{10}

   (b) How is N_2O gas prepared? And draw its structure.

   (c) Give one chemical reaction to show O_3 is an oxidising agent.

*6. Identify A, B, C, D and E in the following sequence of reactions

Complete the reactions of the above mentioned sequence.

[**Hint :** A is P_4].

*7. A white waxy, translucent solid, M, insoluble in water but soluble in CS_2, glows in dark. M dissolves in NaOH in an inert atmosphere giving a poisonous gas (N). Also M catches fire to give dense white fumes of Q :

(a) Identify M, N and Q and write the chemical equations of the reactions involved.

(b) M exists in the form of discrete tetrahedral molecules. Draw its structure.

(c) M on heating at 573 K is changed into other less reactive form, Q, which is non-poisonous, insoluble in water as well as in CS_2 and does not glow in dark, Identify Q and draw its structure.

8. Write the structure of A, B, C, D and E in the following sequence of reactions :

$$NH_3 + O_2 \xrightarrow{Pt/Rh} A + H_2O$$

$$A + O_2 \longrightarrow B \text{ (brown fumes)}$$

$$B + H_2O \longrightarrow C + A \text{ (C is an oxoacid)}$$

$$C + I^- \longrightarrow D \text{ (Violet vapours)}$$

Complete reactions of the above mentioned sequence and name the process by which 'C' is obtained.

[**Hint. :** A is NO and Ostwald process for the manufacture of HNO_3].

9. Give reason for each of the following :

(a) NH_3 is more basic than PH_3.

(b) Ammonia is a good complexing agent.

(c) Bleaching by SO_2 is temporary.

(d) PCl_5 is ionic in solid state.

(e) Sulphur in vapour state exhibits paramagnetism.

10. Knowing the electrons gain enthalpy value for $O \rightarrow O-$ and $O^- \rightarrow O^{2-}$ as –141 and 720 kJ mol^{-1} respectively, how can you account for the formation of large number of oxides having O^{2-} species and not O^-?

[**Hint :** Latlice enthalpy of formation of oxides having O^{2-} more than compensates the second $\Delta_{eg}H$ of oxygen.

d – AND f – BLOCK ELEMENTS

Electronic Configuration of Transition Metal/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 engery 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.

Cr : $Is^2\ 2s^2\ 2p^6,\ 3s^2\ 3p^6\ 4s^1\ 3d^5$

Cu : $Is^2\ 2s^2\ 2p^6,\ 3s^2\ 3p^6\ 4s^1\ 3d^{10}$

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 electronic configuration of Cu^+, Cu^{2+} and Cr^{3+} are respectively $3d^{10}\ 4s°$, $3d^9\ 4s°$ and $3d^3\ 4s°$.

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 are regarded as transition elements?

(iii) Which of the d-block elements are not regarded as transition elements?

UNDERSTANDING Δ_{fus} H^θ, Δ_{vap} H^θ, AND Δ_a H^θ

In transition metals unpaired (n - l)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.

$$M_{(s)} \xrightarrow{\Delta_{fus} H^\theta} M_{(1)}$$

$$M_{(1)} \xrightarrow{\Delta_{vap} H^\theta} M_{(vapour)}$$

$$M_{(s)} \xrightarrow{\Delta_a H^\theta} M_{(}g)$$

These enthalpies are related as

$$\Delta_{fus} H^\theta < D_{vap} H^\theta < \Delta a\ H^\theta$$

The following questions can be explained using the above reasoning.

(i) Which has higher m.p.? V (Z = 23) or Cr (Z = 24) ?

(ii) Explain why Fe (Z = 26) has higher m.p. than cobalt (Z = 27).

Metals of second (4d) and third (5d) transition series have greater enthalpies of atomisation than corresponding elements of first transition series on account of more frequent metal metal bonding due to greater spatial extension of 4d and 5d orbitals than 3d orbitals.

LANTHANOID CONTRACTION AND ITS CONSEQUENCE

The 4f orbitals screen the nuclear .charge less effectively because they are large and diffused. The filling of 4f orbitals before 5d orbitals results in the gradual increase in effective nuclear charge resulting in a regular decrease in atomic and ionic radii. This phenomenon is called lanthanoid contraction. The corresponding members of second and third transition series have similar radii because the normal size increase down the group of d-block elements almost exactly balanced by the lanthanoid contraction.

This reasoning is applied in answering the following questions.

(i) Elements in the'following pairs have identical (similar) radii : Zr/Hf, Nb/Ta and Mo/W. Explain why?

(ii) Why do Zr and Hf have very similar physical and chemical properties and occur together in the same mineral?

VARIATION IN IONISATION ENTHALPY

With the filling of (n - 1) d orbitals effective nuclear charge increases resulting in the increase in first ionisation enthalpy. There are some irregular variations.

The first ionisation enthalpy of chromium is lower because the removal of one electron produces extra stable d^5 configuration and that of zinc is higher because the removal of electron takes place from fully filled 4s orbital.

Second ionization enthalpy of Zn ($\Delta_i H_2$ = 1734 kj)/mol) is lower than second ionization enthalpy of Cu (1958 kj/mol). This is because removal of second electron in Zn produces stable d^{10} configuration while the removal of second electron in Cu disrupts the d^{10} configuration with a considerable loss in exchange energy to from less stable d^9 configuration.

Cr = $3d^5\ 4s^1$

Zn = $3d^{10}\ 4s^2$; Zn^{2+} = $3d^{10}$

Cu = $3d^{10}\ 4s^1$; Cu^{2+} = $3d^9$

Now the following questions can be accounted for :

(i) Why is second ionization enthalphy of Cr (Z = 24) more than that Mn (Z = 25) (Hint. Cr^+ ($d^5 \rightarrow d^4$), Mn^+ ($3d^5\ 4s^1 \rightarrow 3d^5$).

(ii) Which has more second ionisation enthalpy?

Cu (Z = 29) or Zn (Z = 30) (Hint. Cu^+ ($d^{10} \rightarrow d^9$), Zn^+ ($3d^{10}\ 4s^1 \rightarrow 3d^{10}$).

[iii) Second ionization enthalpy of Mn (Z = 25) is less than that of Fe (Z=26) but third ionisation enthalpy of Mn is more than that of Fe. Why?

Hint : Mn^+ ($3d^5\ 4s^1 \rightarrow 3d^5$) Fe^+ ($3d^6\ 4s^1 \rightarrow 3d^6$)

Mn^{2+} ($3d^5 \rightarrow 3d^4$) Fe^{2+} ($3d^6 \rightarrow 3d^5$)

Relationship between E^θ_{red} and stability of various oxidation states.

Transition metals show variable oxidation states due to incompletely filled d-orbitals. These variable oxidation states differ from each other by unity, e.g., Mn (II), Mn (III), Mn (IV), Mn (V), Mn (VI) and M (VII). Scandium is the only transition element which exclusively shows the oxidation state of +3.

Standard Electrode potential $E^\theta_{M^{2+}/M}$ can be calculated from the follwoing parameters :

The reducing property of a transition metal will be higher if $\Delta_r H^\theta$ has a large negative value which is possible if $\Delta_{hyd}\ H^\theta$ more than compensates ($\Delta_a\ H^\theta + \Delta_a\ H_1 + \Delta_i\ H_1 + \Delta_i\ H_2$).

More negative the $\Delta_r H^\theta$, the more positive will be standard oxidation potential and hence, more negative will be standrd reduction potential. $E^\circ_{Cu^{2+}/Cu}$ positive because ($\Delta_i H_1 + \Delta_i H_2$) i.e., energy required to produce Cu^{2+} is not balanced by $\Delta_{hyd} H^\theta$ of Cu^{2+}.

Since the sum of $\Delta_i H_1$ and $\Delta_i H_2$ generally increases with the increase in the atomic number of the transition metal, therefore $E^\circ_{M^{2+}/M}$ value becomes less and less negative.

$E^\circ_{M^{2+}/M}$ values for Mn, Zn and Ni are more negative than expected trend. This is because $\Delta_i H_2$ for Mn and Zn produces stable d^5 configuration (Mn^{2+}) and d^{10} configuration (Zn^{2+}) are produced and therefore requirement of energy is less.

whereas $E^\circ_{Ni^{2+}/Ni}$ is more negative due to highest negative $\Delta_{hyd} H^\theta$ which is – 2121 kj/mol for Ni^{2+}.

Example : Why is E^θ value for Mn^{3+} / Mn^{2+} couple much more positive than for Cr^{3}+ / Cr^{2+} or Fe^{3+} / Fe^{2+}.

Solution : Mn^{2+} (d^5) $\longrightarrow$ Mn^{3+} (d^4)

has much larger third ionisation energy due to disruption of extrastability of half filled d^5 configuration.

Cr^{2+} (d^4) $\longrightarrow$ Cr^{3+} (d^3)

Cr^{3+} has half-filled t_{2g} level. Hence Cr^{2+} is oxidised easily to stable Cr^{3+} ion. Hence E^θ value is compartively less.

Fe^{2+} (d^6) $\longrightarrow$ Fe^{3+} (d^5)

Comparatively low value of E^θ is also due to extra stability of d^5 configuration of Fe^{3+}.

Example : Which is stronger reducing agent Cr^{2+} or Fe^{2+} and why?

Solution : Cr^{2+} (d^4) $\longrightarrow$ Cr^{3+} (d^3 or half-filled t^3_{2g}

In water medium $[Cr(H_2O)_6]^{3+}$ has more CFSE than $[Fe(H_2O)_6]^{3+}$. Hence Cr^{2+} in a stronger reducing agent.

Stability of Higher Oxidation States :

Higher oxidation states are shown by transition metals in fluorides, oxides, oxocations and oxoanions. The ability of fluorine to stablise the highest oxidation state is due to either higher lattice energy as in case of CoF_3 or higher bond enthalpy terms for higher covalent compounds, e.g., VF_5 and CrF_6.

Transition metals show highest oxidation state in oxides and oxocations and oxoanions, e.g., VO_4^+ and VO_4^-. The ability of oxygen to stabilise these high oxidation states exceeds that of fluorine due to its ability to form multiple bonds to metals.

The following questions can be explained using the above concepts.

(i) All Cu (II) halides are known except the iodides. Why?

[**Hint :** $2Cu^{2+} + 4I^- \longrightarrow Cu_2I_2 + I_2$]

(ii) Why do Cu (I) compounds undergo disproportionation in water?

[**Hint :** $\Delta_{hyd} H^\theta$ of Cu^{2+} more than compensates the $\Delta_1 H_2$ of copper]

(iii) Highest fluoride of Mn is MnF_4 but the highest oxide is Mn_2O_7.

(iv) E^θ values of 3d series varies irregularly.

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

[**Hint :** Cr^{2+} $(d^4) \longrightarrow Cr^{2+}$ (t^3_{2g}; half filled t_{2g} level)

Mn^{3+} $(d^4) + e^- \longrightarrow Mn^{2+}$ (d^5; half filled d-level)

(vi) Why is highest oxidation state shown in oxocations and oxoanions?

Properties of Transition Elements

Transition matals with partly filled d-orbitals exhibit certain characterstic properties. For example they display a variety of oxidtion states, form coloured ions and enter into complexe formation. Transition metals and their compounds exhibit catalytic properties and are generally paramagnetic in nature.

Crystal Field Theory :

d orbitals splitting in an octahedral crystal-field

Calculation of CFSE : Each electron occupying t_{2g} orbital results in the lowering of energy by – 0.40 Δ_0 and each electron occupying the e_g orbital increases the energy by + 0.60 Δ_0. If x is the no. of electrons occupying t_{2g} orbitals and 'y' is the no. of electrons occupying the e_g orbitals, then CFSE is given by

$$\text{CFSE} = (-0.40\ \Delta_0\ x + 0.60\ \Delta_0 y)$$
$$= (-0.40\ x + 0.60\ y)\ \Delta_0$$

Formation of Coloured Ions : Degeneracy of d-orbitals is lifted in presence of the field of ligands approaching the central metal ion. For example, in the octahedral crystal field of ligands, the d-orbitals are split into two set of d-orbitals (i) t_{2g} orbitals of lower energy : these are d_{xy} $dy_{z,}$ d_{xz} and (ii) e_g orbitals of higher energy i.e., $d_{x^2-y^2}$ and d_{z^2}.

When visible light is incident on the octahedral transition metal complex, an electron is excited from t_{2g} level to e_g level. During this d-d transition, a characteristic wave length of visible light is absorbed and therefore transmitted light appears coloured. The colour of complex is complementry to the colour absorbed by the transition metal complex.

No d-d transition occurs if d-orbitals are empty or fully filled and therefore, such ions may be colourless.

Exceptions : AgBr, AgI, have fully filled d-orbitals but are coloured due to transference of electron cloud from Br^- or I^- to Ag^+ (d^{10}) when white light is incident on AgBr / AgI. During this process also characteristic wave length of visible light is absorbed. Similarly MnO_4^- (purple), CrO_4^{2-} (yellow) and $Cr_2O_7^{2-}$ (orange) are coloured due to charge transfer from oxide ions to the central metal ions although they have no d-electrons.

Comparison of oxidising powers of $KMnO_4$ and $K_2Cr_2O_7$

$$MnO_2^- + 2H_2O + 3e^- \longrightarrow Mn_2 + 4OH^- \qquad E^\theta = +1.69\ V$$

$$MnO_4^- + 8H^+ + 5e^- \longrightarrow Mn^{2+} + 4H_2O \qquad E^\theta = +1.52\ V$$

$$Cr_2O_7^{2-} + 14H^+ + 6e^- \longrightarrow 2Cr^{3+} + 7H_2O \qquad E^\theta = +1.33\ V$$

Electrode potential values shows that acidified $KMnO_4$ is a stronger oxidising agent than acidified $K_2Cr_2O_7$. But $KMnO_4$ in faint alkaline medium is a stronger oxidising agent than acidified $KMnO_4$.

For example, $KMnO_4$ oxidises KI to I_2 in acidic medium but to KIO_3 in alkaline medium.

(a) $$MnO_4^- + 8H^+ + 5e^- \longrightarrow Mn^{2+} + 4H_2O] \times 2$$

$$2I^- \longrightarrow I_2 + 2e^-] \times 2$$

Overall : $$2Mn_4^- + 10\ I_- + 16\ H^- \longrightarrow 2Mn^{2+} + 8H_2O + 5I_2$$

(b) $$MnO_4^- + 2H_2O + 3e^- \longrightarrow MnO_2 + 4OH^-] \times 2$$

$$I^- + 6\ OH^- \longrightarrow IO_3^- + 3H_2O + 6e^-$$

Overall : $$2Mn_4^- + H_2O + I^- \longrightarrow 2MnO_2 + IO_3^- + 2OH^-$$

Following questions involving the oxidising actions of KMnO4 and $K_2Cr_2O_7$ may be answered

(i) How do acidified $KMnO_4$ and acidified $K_2Cr_2O_7$ reacts separately with (a) SO_2, (b) H_2S (c) $FeSO_4$?

(ii) Write the ionic equations of $KMnO_4$ (acidified) with (a) oxalate ion (b) Mohr salt (c) NO_2^- and (d) Iron (II) oxalate.

[**Hint :** (d) Both Fe^{2+} and $C_2O_4^{2-}$ are oxidised to Fe^{3+} and CO_2 respectively.]

Oxidation States of Lanthanoids and Actinoids

The most common and most stable oxidation state of lanthanoids is +3. They also show oxidation states of +2, and +4 if the corresponding lanthanoid ions have extra stable $4f^0$, $4f^7$ and $4f^{14}$ configuration.

$Ce^{4+} + e^- \longrightarrow Ce^{3+}$, + 3 more stable O.S. than + 4

$Tb^{2+} + e^- \longrightarrow Tb^{3+}$, + 3 more stable O.S. than + 4

Hence Ce^{4+} and Tb^{4+} are strong oxidants.

$Eu^{2+} \longrightarrow Eu^{3+} + e^-$, +3 more stable O.S. than +2

$Yb^{2+} \longrightarrow Yb^{3+} + e^-$, + 3 more stable O.S. than + 3

Hence, Eu^{2+} and Yb^{2+} are strong reducing agents.

Actinoids also show most common O.S. of + 3 but it is not always most stable. Actinoids also show higher oxidation states, e.g., Th (+4), Pa (+5), U (+ 6) and Np (+ 7).

Example : La ($5d^16s^2$), Gd ($4f^75d^16s^2$) and Lu ($4f^{14}$ $5d^16s^2$) have abnormally low third ionisation enthalpies. Why?

Solution : La^{3+}, Gd^{3+} and Lu^{3+} have stable configurations $4f^0$, $4f^7$ and $4f^{14}$ respectively.

Answer the following question –

(i) Name the two members of lanthanoid series which show + 2 oxidation state

(ii) Name the lanthanoid element which shows +4 O.S.

Participation of 5f electrons of actinoids in bonding.

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

There in a gradual decrease in the size of atoms or M^{3+} ions across the actionoid 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 elecrons. Hence 5f electrons screen the nuclear charge less effectively than 4f electrons in lanthanoids. Consequently effective nuclear charge in actinoids increases at faster rate as compared with lanthanoids. Hence actinoid contraction from element to element is more than the lanthanoid contraction.

The following question can explained with the above reasoning :

Explain why Actinoid contraction from element to element is greater than lanthanoid contraction.

VERY SHORT ANSWER TYPE QUESTIONS

(1 - MARK QUESTIONS)

1. Write the electronic configuration of Cr^{3+} ion (atomic number of Cr = 24)?

3. Explain $CuSO_4 . 5H_2O$ is blue while $ZnSO_4$ and $CuSO_4$ are colourless?

4. Why is the third ionisation energy of Manganese (Z = 25) is unexpectedly high?

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

5. Which element among 3d– transition elements, exhibit the highest oxidation state?

   [**Hint :** Mn (+7)]

6. Silver (Ag) has completely filled d-orbitals ($4d^{10}$) in its ground state. How can you say that it is a transition element.

7. In 3d series (Sc $\longrightarrow$ Zn), the enthalpy of atomisation of Zn is low. Why?

   [**Hint :** Poor interatomic bonding in zinc.]

8. Out of the following elements, identify the element which does not exhibit variable oxidation state?

   Cr, Co, Zn.

9. The +3 oxidation state of lanthanum (*Z* = 57), gadolinium (Z = 64) and lutetium (Z = 71) are especially stable. Why?

10. Mention one consequence of Lanthanoid Contraction?

11. The first ionization enthalpies of 5*d*– series elements is higher than those of 3*d* and 4*d* series elements why?

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

12. Why Mn^{2+} compounds are more stable than Fe^{2+} compounds towards oxidation to their +3 state?

14. Calculate the magnetic moment of Cu^{2+} (Z = 29) on the basis of "spin-only" formula.

[**Hint :** $\mu = \sqrt{n(n+2)}$ B.M.]

15. What is the shape of chromate ions?

[**Hint :** Tetrahedral]

16. Why does vanadium pentoxide act a catalyst?

[**Hint :** In V_2O_5, Vanadium shows variable oxidation sates.]

17. What are interstitial compounds?

18. The transition metals and their compounds are known for their catalytic activity. Give two specific reasons to justify the statement.

19. Write the chemical equation for the reaction of thiosulphate ions and alkaline potassium permanganate.

[**Hint :** $8MnO_4^- + 3S_2O_3^{2-} + H_2O \longrightarrow 8MnO_2 + 2OH^- + 6SO_4^{2-}$].

20. Mention the name and formula of the ore from which potassium dichromate is prepared.

[**Hint :** $FeCr_2O_4$ (Chromite)].

21. Write the electronic configuration of Lu^{3+} (At. No. = 71).

22. What is the most common oxidation state of actinoids?

23. Write the names of the catalyst used in the :

(a) Manufacture of sulphuric acid by contact process.

(b) Manufacture of polythene.

24. Mention the name of the element among lanthanoids known to exhibit +4 oxidation state.

25. Name one ore each of manganese and chromium.

26. Why is Cd^{2+} ion white?

*27. Draw the structure of dichromate anion.

*28. Arrange the following monoxides of transition metals on the basis of decreasing basic character TiO, VO, CrO, FeO.[Hint : TiO > VO > CrO > FeO]

SHORT ANSWER TYPE QUESTIONS
(2 - MARK QUESTIONS)

1. Write the chemical equation, when the yellow colour of aqueous solution of Na_2CrO_4 changes to orange on passing CO_2 gas?

2. The stability of Cu^{2+} (aq) is more than that of Cu+ (aq). Why?

3. Indicate the steps in the preparation of

   (a) $K_2Cr_2O_7$ from Chromite ore.

   (b) $KMnO_4$ from Pyrolusite ore.

4. Give reason for : –

   (a) In permanganate ions, all bonds formed between manganese and oxygen are covalent.

   (b) Permanganate titrations in presence of hydrochloric acid are unsatisfactory.

5. Write complete chemical equations for

   (a) oxidation of Fe^{2+} by $Cr_2O_7^{2-}$ in acidic medium

   (b) oxidation of Mn^{2+} by MnO_4^- in neutral or faintly alkaline medium.

6. (a) Why do transition metals show high melting points?

   (b) Out of Fe and Cu, which one would exhibit higher melting point?

   [**Hint.** (i) Strong interatomic bonding arising from the participation of *ns* and unpaired (*n* – 1) *d*-electrons.

   (ii) Fe has higher melting point due to presence of more unpaired electrons 3*d*-orbitals.

7. Describe giving reason which one of the following pairs has the property indicated :

   (a) Cr^{2+} or Fe^{2+} (stronger reducing agent).

   (b) Co^{2+} or Ni^{2+} (lower magnetic moments).

8. Of the ions Co^{2+}, Sc^{3+}, Cr^{3+} which one will give colourless aqueous solution and how will each of them respond to magnetic field and why?

   [**Hint :** Co^{2+} ($3d^7$); Cr^{3+} ($3d^4$); Sc^{3+} ($3d^{\circ}$)]

9. Complete the following equations :

   (a) $MnO_2 + KOH + O_2 \longrightarrow$ (b) $Na_2Cr_2O_7 + KCl \longrightarrow$

10. Transition metals show low oxidation states with carbon monoxide.

[Hind : CO is a π acceptor ligand capable of forming a π bond by accepting π electrons from the filled d-orbitals of transition metal and CO also form σ bond by donating σ electrons to transition metal orbital.

11. For the first row transition metals the enthalpy of atomisation value are :

	Sc	*Ti*	*V*	*Cr*	*Mn*	*Fe*	*Co*	*Ni*	*Cu*	*Zn*
$\Delta_a H^\theta$/kJ mol^{-1}	326	473	515	397	281	416	425	430	339	26

Assign reason for the following :

(a) Transition elements have higher values of enthalpies of atomisation.

(b) The enthalpy of atomisation of zinc is the lowest in 3d - series.

12. Account for the following :

(a) Copper shows its inability to liberate hydrogen gas from the dilute acids.

(b) Scandium (Z = 21) does not exhibit variable oxidation states.

13. Copper (I) compounds undergo disproportionation. Write the chemical equation for the reaction involved and give reason.

14. Iron (III) catalyses the reaction :

$$2I^- + S_2O_8^{2-} \xrightarrow{Fe^{3+}} I_2 + 2SO_4^{2-}$$

15. Complete the equations :

(a) $MnO_4^- + NO_2^- + H^+ \longrightarrow$

(b) $KMnO_4 \xrightarrow{513\ k}$

16. The following two reactions of MNO_3 with Zn are given.

(a) $Zn + \text{conc. } HNO_3 \longrightarrow Zn(NO_3)_2 + X + H_2O$

(b) $Zn + \text{dil.}HNO_3 \longrightarrow Zn(NO_3)_2 + Y + H_2O$

Identify X and Y and write balanced equations.

[**Hint :** X is NO_2 and Y is N_2O].

17. Titanium shows magnetic moment of 1.73 BM in its compound. What is the oxidation number of Ti in the compound?

[**Hint :** O.N. of Ti = +3].

18. Account for the following :

(a) Transition metals and majority of their compounds act as good catalysts.

(b) From element to element, actionoid contraction is greater than lanthanoid contraction

19. Calculate the number of electrons transferred in each case when $KMnO_4$ acts as an oxidising agent to give

(i) MnO_2 (ii) Mn^{2+} (iii) $Mn(OH)_3$ (iv) MnO_4^{2-} respectively.

[**Hint :** 3, 5, 4, 1].]

20. Calculate the number of moles of KM_nO_4 that is needed to react completely with one mole of sulphite ion in acidic medium.

[**Hint :** 2/5 moles].

SHORT ANSWER TYPE QUESTIONS (3 - MARK QUESTIONS)

1. Account for the following :

(a) $La(OH)_3$ is more basic than $Lu(OH)_3$

(b) Zn^{2+} salts are white.

(c) Cu(I) compounds are unstable in aqueous solution and undergo disproportination.

2. Describe the oxidising action of potassium dichromate with following. Write ionic equations for its reaction with.

(a) Iodide ion (b) Iron (II) (c) H_2S.

3. (a) Deduce the number of 3d electrons in the following ions : Fe^{3+}, Cu^{2+} and Sc^{3+}.

(b) Why do transition metals form alloys.

(c) Write any two characteristics of interstitial compounds.

*4. In the following reaction, Mn(VI) changes to Mn(VII) and Mn(IV) in acidic solution.

$$3Mn^{VI}O_4^{2-} + 4H^+ \longrightarrow 2Mn^{VII}O_4^- + Mn^{IV}O_2 + 2H_2O$$

(a) Explain why Mn(VI) changes to Mn(VII) and Mn(IV).

(b) What special name is given to such type of reactions?

5. What happens when

(a) thiosulphate ions react with alkaline $KMnO_4$.

(b) ferrous oxalate reacts with acidified $KMnO_4$.

(c) sulphurous acid reacts with acidified $KMnO_4$

Write the chemical equations for the reactions involved.

7. Name the catalysts used in the

(a) manufacture of ammonia by Haber's Process

(b) oxidation of ethyne to ethanol

(c) photographic industry.

*8. Among $TiCl_4$, VCl_3 and $FeCl_2$ which one will be drawn more strongly into a magnetic field and why?

[**Hint :** Among these halides the transition metal ion having maximum number of unpaired electrons will be drawn strongly into the magnetic field.

$Ti^{4+} = 3d^0$	no. of unpaired $e^- = 0$	$\mu = 0$
$V^{3+} = 3d^2$	no. of unpaired $e^- = 2$	$\mu = 2.76$ BM
$Fe^{2+} = 3d^6$	no. of unpaired $e^- = 4$	$\mu = 4.9$ BM]

9. Complete the following equations

(a) $Mn0_4^{2-} + H+ \longrightarrow$ ..... + ...+ .....

(b) $KMnO_4 \xrightarrow{Heat}$

(c) $H^+ + MnO_4^- + Fe^{2+} + C_2O_4^{2-} \longrightarrow$

10. How do you account for the following?

(a) With the same d-orbital configuration (d^4), Cr^{2+} is a reducing agent while Mn^{3+} is an oxidiising agent.

(b) The actinoids exhibit a larger number of oxidation states than the corresponding members in the lanthanoid series.

(c) Most of transition metal ions exhibit characteristic colours in aqueous solutions.

LONG ANSWER TYPE QUESTIONS (5 - MARK QUESTIONS)

1. A green compound 'A' on fusion with NaOH in presence of air forms yellow compound 'B' which on acidification with dilute acid, gives orange solution of compound 'C'. The orange solution when reacted with equimolar ammonuim salt gives compound 'D' which when heated liberates nitrogen gas and compound 'A'. Identify compounds A to D and write the chemical equation of the reactions involved.

   [**Hint :** 'A' = CrO_3; 'B' = Na_2CrO_4; 'C' = $Na_2Cr_2O_7$ 'D' = $(NH_4)_2\ Cr_2O_7$

2. Assign reasons for the following :

   (a) There is no regular trends in E° values of M^{2+}/M systems in 3d series.

   (b) There is gradual decrease in the ionic radii of M^{2+} ion in 3d series.

   (c) Majority of transition metals form complexes.

   (d) Ce^{3+} can be easily oxidised to Ce^{4+}

   (e) Tantalum and palladium metals are used to electroplate coinage metals.

3. Account for the following :

   (a) Actinoids display a variety of oxidation states.

   (b) Yb^{2+} behaves as a good reductant.

   (c) Cerium (iv) is a good analytical reagent.

   (d) Transition metal fluorides are ionic in nature while chlorides and bromides are covalent in nature.

   (e) Hydrochloric acid attacks all the actinoids.

*4. Explain by giving suitable reason :

   (a) Co(II) is stable in aqueous solution but in the presence of complexing agent it is readily oxidised.

   (b) Eu^{2+}, Yb^{2+} are good reductants whereas Tb^{4+} is an oxidant.

   (c) AgCl dissolves in ammonia solution

   (d) Out of Cr^{2+} or Fe^{2+}, which one is a stronger reducing agent?

   (e) The highest oxidation state is exhibited in oxoanions of a transition metal.

5. When a white crystalline compound A is heated with $K_2Cr_2O_7$ and conc. H_2SO_4, a reddish brown gas B is evolved, which gives a yellow coloured solution C when passed through NaOH. On adding CH_3COOH and $(CH_3COO)_2$ Pb to solution C, a yellow coloured ppt. D is obtained. Also on heating A with NaOH and passing the evolved gas through K_2HgI_4 solution, a reddish brown precipitate E is formed.

Identify A, B, C, D and E and write the chemical equations for the reactions involved.

[Hint : (A) NH_4Cl, (B) CrO_2Cl_2 (g), (C) Na_2CrO_4

(D) $PbCrO_4$, (E) NH_2 $\begin{matrix} \diagup \text{HgO} \\ \diagdown \text{HgI} \end{matrix}$]

*6. (a) Describe the preparation of potassium dichromate ($K_2Cr_2O_7$). Write the chemical equations of the reactions involved.

(b) "The chromates and dichromates are interconvertible by the change in pH of medium." Why? Give chemical equations in favour of your answer.

7. Explain giving reasons :

(a) Transition metals are less reactive than the alkali metals and alkaline earth metals.

(b) $E^{\circ}_{Cu^{2+}/Cu}$ has positive value

(c) Elements in the middle of transition series have higher melting points.

(d) The decrease in atomic size of transition elements in a series is very small.

8. (a) Compare the chemistry of the actinoids with that of lanthanoids with reference to—

(i) electronic configuration

(ii) oxidation states

(iii) chemical reactivity.

(b) How would you account for the following :

(i) of the d^4 species, Cr^{2+} is strongly reducing while Mn^{3+} is strongly oxidising.

(ii) the lowest oxide of a transition metal is basic whereas highest is amphoteric or acidic.

9. (a) What is meant by disproportionation of an oxidation state. Give one example.

(b) Explain why europium (II) is more stable than Ce(II)?

[**Hint :** (a) When particular state becomes less stable relative to other oxidation states, one lower and one higher, it is said to undergo disproportionation, for example,

$$3\overset{VI}{MnO_4^{2-}} + 4\overset{+}{H} \longrightarrow 2\overset{VII}{MnO_4^{-}} + \overset{IV}{MnO_2} + 2H_2O$$

(b) Eu (II)= [Xe] $4f^7$ $5d^0$ (4f subshell is half filled)

Ce (II)= [Xe] $4f^1$ $5d^0$ (5d Subshell is empty and 4f subshell has only one electron which can be easily lost.)]

10. (a) For M^{2+}/M and M^{3+}/M^{2+} systems, the E^{θ} values for some metals are as follows :

$Cr^{2+}/Cr = -0.9V$ and $Cr^{3+}/Cr^{2+} = -0.4V$

$Mn^{2+}/Mn = -1.2\ V$ and $Mn^{3+}/Mn^{2+} = +1.5V$

$Fe^{2+}/Fe = -0.4V$ and $Fe^{3+}/Fe^{2+} = +0.8V$

Use this data to comment upon :

(i) the stability of Fe^{3+} in acid solution as compared to that of Cr^{3+} and Mn^{3+}

(ii) the ease with which iron can be oxidised as compared to a similar process for either chromium or manganese.

(b) How is the variability in oxidation states of transition metals different from that of the non-transition metals? Illustrate with examples.

Unit - 9

CO-ORDINATION COMPOUNDS

QUESTIONS

VSA QUESTIONS (1 - MARK QUESTIONS)

1. Define the term coordination compound?

2. Write the names of counter ions in

   (i) Hg [Co $(SCN)_4$] and (ii) $[Pt(NH_3)_4]$ Cl_2.

3. Write the oxidation state of nickel in $[Ni(CO)_4]$

*4. What is the coordination number of central atom in $[Co(C_2O_4)_3]^{3-}$?

   [**Ans. :** 6]

5. What is the coordination number of iron in $[Fe\ (EDTA)]^-$? [**Ans. :** 6]

6. Write the name of a complex compound used in chemotherapy.

   [**Ans. :** Cis–Platin. $[Pt(NH_3)_2\ Cl_2]$

7. Name the compound used to estimate the hardness of water volumetrically.

8. Give the IUPAC name of $[Pt\ Cl_2\ (NH_2CH_3)\ (NH_3)_2]$ Cl.

*9. How many geometrical isomers are possible for the tetrahedral complex $[Ni(CO)_4]$.

   [**Ans. :** No isomer, as the relative positions of the unidentate ligands attached to the central metal atom are same with respect to each other].

10. Arrange the following in the increasing order of conductivity in solution.

    $[Ni(NH_3)_6]Cl_2$; $[Co(NH_3)_6]Cl_3$ and $[CoCl_2(en)_2]$ Cl

11. 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, en.

12. Write I.U.P.A.C. name of Tollens' reagent.

13. Which is more stable? $K_3[Fe(CN)_6]$ or $K_4[Fe(CN)_6]$

14. Calculate the overall dissociation equilibrium constant for the $[Cu(NH_3)_4]^{2+}$ ion. Given that overall stability constant (β_4) for this complex is 2.1×10^{13}.
[**Ans. :** 4.7×10^{-14}]

*15. What is a chelate ligand? Give one example.

16. Write the I.U.P.A.C. name of $Li[AlH_4]$.

17. Name one homogeneous catalyst used in hydrogenation of alkenes.

*18. Name the types of isomerism shown by coordination entity : $[CrCl_2(Ox)_2]^{3-}$

*19. $[Ti(H_2O)_6]Cl_3$ is coloured but on heating becomes colourless. Why?

*20. Write the IUPAC name of ionization isomer of $[Co(NH_3)_5(SO_4)]$ Br

*21. Write the formula and the name of the coordinate isomer of $[Co(en)_3]$ $[Cr(CN)_6]$.
[**Ans. :** $[Cr(en)_3]$ $[Co(CN)_6]$ Tris- (ethane –1, 2, diammine) chromium (III) hexacyanocobaltate (III)]

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

*22. Write two differences between a double salt and a coordination compound with the help of an example of each.

23. Mention the main postulates of Werner's Theory.

24. Define (a) Homoleptic and (b) Heteroleptic complexes with the help of one example of each.

25. In the following coordination entity : $[Cu(en)_2]^{2+}$

(a) Identify the ligand involved and

(b) Oxidation state of copper metal.

27. Calculate the magnetic moments of the following complexes :

(i) $[Fe(CN)_6]^{4-}$ (ii) $[CoF_6]^{3-}$

28. Explain the following :

(a) $[Fe(CN)_6]^{3-}$ is an inner orbital complex whereas $[FeF_6]^{3-}$ is an outer orbital complex.

(b) NH_3 acts as complexing agent but NH_4^+ does not.

29. What type of structural isomerism is represented by the following complexes:

(a) $[Mn(CO)_5(SCN)]$ and $[Mn(CO)_5(NCS)]$

(b) $[Co(NH_3)_5(NO_3)]\ SO_4$

30. How are complex compounds applicable in (a) electroplating of silver, gold or other noble metals (b) in photography.

31. Explain on the basis of Valance Bond Theory that diamagnetic $[Ni(CN)_4]^{2-}$ has square planar structure and paramagnetic $[NiCl_4]^{2-}$ ion has tetrahedal geometry.

23. Explain as to how the two complexes of nickel $[Ni(CN)_4]^{2-}$ and $Ni(CO)_4$ have different structures but do not differ in their magnetic behaviours. (At. no. of Ni = 28).

34. Draw the structures of geometrical isomers of the coordination complexes– $[Co(NH_3)_3Cl_3]$ and $[CoCl_2(en)_2]^+$

35. Write the IUPAC name of the complexes :

(a) $[NiCl_2\ (PPh_3)_2]$ (b) $[Co(NH_3)_4\ Cl(NO_2)]\ Cl$

(c) $K[Cr(H_2O)_2\ (C_2O_4)_2]$

[**Hint. :** (a) Dichloridobis(triphenylphosphine)nickel (II);

36. Using IUPAC norms write the formulae for the following :

(a) Terabromidocuprate (II)

(b) Pentaamminenitrito–O– Cobalt (III)

*37. How does EDTA help as a cure for lead poisoning?

[**Ans. :** Calcium in Ca–EDTA complex is replaced by lead in the body. The more soluble complex lead-EDTA is eliminated in urine].

37. 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 :** $\Delta T_f = i\ K_f \times m = i \times 1.86 \times 0.1$

$\Delta T_f(obs) = 0.373°C$

This means each molecule of complex dissociates into two ions. Hence the formula is i = 2

*38. The $[Mn(H_2O)_6]^{2+}$ ion contains five unpaired electrons while $[Mn(CN)_6]^{4-}$ ion contains only one unpaired electron. Explain using Crystal Field Theory:

SA (II) TYPE QUESTIONS (3 - MARK QUESTIONS)

39. Account for the following —

(i) $[NiCl_4]^{2-}$ is paramagnetic while $[Ni(CO)_4]$ is diamagnetic though both are tetrahedral.

(ii) $[Fe(H_2O)_6]^{3+}$ is strongly paramagnetic whereas $[Ni(NH_3)_6]^{2+}$ weakly paramagnetic.

(iii) $[Co(NH_3)_6]^{3+}$ is an inner orbital complex whereas $[Ni(MH_3)_6]^{2+}$ is in outer orbital complex.

40. Compare the following complexes with respect to their shape, magnetic behaviours and the hybrid orbitals involved.

(a) $[CoF_6]^{3-}$

(b) $[Cr(NH_3)_6]^{3+}$

(c) $[Fe(CN)_6]^{4-}$

[Atomic Number : Co = 27, Cr = 24, Fe = 26]

41. Draw the structure of

(a) cis-dichloridotetracyanochromate (II) ion

(b) mer-triamminetrichloridocobalt (III)

(c) fac-triaquatrinitrito–N–cobalt (III)

42. Name the central metal atom/ion present in (a) Chlorophyll (b) Haemoglobin (c) Vitamin B-12. [**Ans. :** (a) Mg (b) Fe; (c) Co.]

43. A metal complex having composition $Cr(NH_3)_4\ Cl_2Br$ has been isolated in two forms 'A' and 'B'. The form 'A' reacts with $AgNO_3$ solution to give white precipitate which is readily soluble in dilute aqueous ammonia, whereas 'B' gives a pale yellow precipitate which is soluble in concentrated ammonia solution. Write the formula of 'A' and 'B'. Also mention the isomerism which arises among 'A' and 'B'.

[**Hint :** A = $[Cr(NH_3)_4\ BrCl]\ Cl$; B = $[Cr(NH_3)_4Cl_2]\ Br$ are ionisation isomers].

44. Write the limitations of Valence Bond Theory.

45. Draw a sketch to show the splitting of d-orbitals in an octahedral crystal field state for a d^4 ion. How the actual electronic configuration of the split

d-orbitals in an octahedral crystal field is decided by the relative values of Δ_0 and pairing energy (P)?

*46. For the complex $[Fe(en)_2Cl_2]Cl$ identify

(a) the oxidation number of iron.

(b) the hybrid orbitals and the shape of the complex.

(c) the magnetic behaviour of the complex.

(d) the number of geometrical isomers.

(e) whether there is an optical isomer also?

(f) name of the complex. [At. no. of Fe = 26]

48. A chloride of fourth group cation in qualitative analysis gives a green coloured complex [A] in aqueous solution which when treated with ethane –1, 2-diamine (en) gives pale yellow solution [B] which on subsequent addition of ethane –1, 2-diamine turns to blue/purple [C] and finally to violet [D]. Identify [A], [B], [C] and [D] complexes,

[**Hint. :** Nickel, [A] = $[Ni(H_2O)_6]^{2+}$; [B] = $[Ni(H_2O)_4\ (en)]^{2+}$;

[C] = $[Ni(H_2O)_2\ (en)_2]^{2+}$; [D] = $[Ni(en)_3]^{2+}$.

ORGANIC CHEMISTRY

SOME NOTEWORTHY POINTS

2. If there are two or more functional groups, the order of decreasing priority is : –COOH > $–SO_3H$ > anhydride > Ester > Acid halide > nitrile > aldehyde > ketone > alcohol > amine >> C = C < > – C ≡ C –

3. Anti Markownikov's addition takes place only with HBr in presence of a peroxide.

4. Order of reactivity of hydrohalic acid : HI > HBr > HCl.

5. Order of reactivity of alcohols with Lucas reagent : 3° > 2° > 1°.

6. $R – H + X_2 \xrightarrow{h\nu} R – X + HX$. The order of reactivity of halogens $Cl_2 > Br_2 > I_2$. Order of reactivity of hydrogen atom substracted is 3° > 2° > I°.

Example : $CH_3—CH_2—CH_3 \xrightarrow[Cl_2]{h\nu} CH_3—\underset{\underset{Cl}{|}}{CH}—CH_3 + CH_3—CH_2—CH_2Cl$

(Major) (Minor)

7.

(Electrophillic Aromatic Substitution)

8. Order of reactivity in S_N1 and S_N2 mechanism are as follows :

For S_N1 reactions

3° 2° 1° CH_3X

For S_N2 reactions

R – I > R – Br > R – Cl.

9. In case of optically active alkyl halide, S_N2 mechanism results in the inversion of configuration while S_N1 mechanism in racemisation.

10. Aryl halides are much less reactive towards nucleopillic substitution reactions. Presence of electron withdrawing groups (like $-NO_2$, –CN, –COOH etc.) at o– and/or *p*-position to halogen increases the rate of reaction.

12. All the three types of monohydric alcohols (1°, 2° or 3°) except methanol can be prepared from Grignard Reagent

13. Alcohols

14. Presence of electron withdrawing group increases the acid strength of alcohol, phenol and carboxylic acid while presence of electron donating group decreases the acid strength.

E.W.G. : NO_2, –X, –CN, –COOH, etc., E.D.G. : –R, –OR, –OH, $-NH_2$ etc.

15. In electrophilic aromatic substitution reaction, ring activating groups like –OH, $-NH_2$, –OR, are o– and *p*– directing whereas ring deactivating groups like –CHO, > C = 0, –COOH, $-NO_2$, $-SO_3H$ are m-directing. Halogens (F, Cl, Br and I) are deactivating but are o– and p– directing groups.

16. 3° alcohols are resistant to oxidation due to lack of α-hydrogen.

17. Order of Acid strength : Alcohol < Phenol < Carboxylic acid, it is because of resonance stabilization of phenoxide and carboxylate ion. In carboxylate ion negative charge is delocalised over two oxygen atoms. while in phenoxide ion it is delocalised over one oxygen atom and the less electronegative C atom of benzene ring.

18. All organic compounds which form intermolecular H-bonds with water are soluble in water.

19. Intermolecular H-bonds of p- and m- nitrophenol increases water solubility/ Acid strength while intramolecular H-bonds in o-nitrophenol decreases

these properties.

20. In the reaction of alkyl aryl ether (Anisole) with HI, the products are always alkyl halide and phenol, because O–R bond is weaker than O–Ar bond.

22. In reaction of toluene with CrO_3 in presence of acetic anhydride is used to protect benzaldehyde as benzylidenediacetate to avoid further oxidation to benzoic acid.

23. Order of reactivity of aldehydes and ketones towards nuclerphilic attack

    HCHO > CH_3CHO > CH_3CH_2CHO

    RCHO > R COR ; ArCHO > Ar COR > Ar CO Ar.

    because of (i) +I Inductive effect of alkyl groups. (ii) steric hindrance of alkyl and aryl group reactivity of ketones is less than aldelydes.

24. Bioling and melting points of various organic compounds depend on intermolecular forces of attraction which depend on the following :

    (a) Inter molecular/intramolecular H-bonding.

    (b) dipole-dipole interaction

    (c) Molecular size

    (d) Surface area. (branching decreases surface area of molecules).

25. Benzaldehyde does not reduce Fehling's reagent.

26. The more the Ka value, the lesser is the pk_a, a stronger acid always has higher Ka but a lower pk_a value.

27. Order of Acid strength : HCOOH > C_6H_5COOH > $C_6H_5CH_2COOH$ > CH_3COOH, CH_3CH_2COOH

28. group in carboxylic acid is not a true carbonyl group because of resonance.

Hence, carboxylic acids do not give addition reaction of aldehydes and ketones.

(a) In aqueous solution order of basicity is :

$(C_2H_5)_2NH > (C_2H_5)_3N > C_2H_5NH_2 > NH_3$.

$(CH_3)_2NH > CH_3NH_2 > (CH_3)_3N > NH_3$.

(b) In gaseous (vapour) state order of basicity is :

$RNH_2 < R_2NH < R_3N$.

30. Basic character of aromatic amine

31. Hinsberg's reagent ($C_6H_5SO_2Cl$) is used to separate the mixtures of 1°, 2° and 3° amines.

32. Sulphanilic acid exists as zwitter ion, therefore it is amphoteric in nature.

33. Aryl diazonium salts are more stable than alkyl diazonium salts.

34. Aniline, phenol and benzoic acid do not show Friedel-Crafts Reaction.

35. The more the basic character, the more is the K_b value and lesser will be its pk_b value.

35. In phenol and aniline, electron donating or electron withdrawing groups when present in ortho position, always have acid strenghening effect. This is called ortho effect.

USEFUL TIPS FOR IDENTIFICATION OF FUNCTIONAL GROUPS

For identification of chloro, bromo or Iodo alkanes, aq. KOH is added followed by $AgNO_3$ solution then precipitate of AgX is formed.

Iodoform Test is given by all organic compounds having

$CH_3-\overset{\overset{\large O}{\|}}{C}-$ or $CH_3-\underset{\underset{\large OH}{|}}{CH}-$ when heated with NaOH (aq) and I_2, produces yellow iodoform (CHI_3)

Tollens' reagent test is given by organic compound having $-\overset{\overset{\large O}{\|}}{C}-H$ group

(formic acid $H-\overset{\overset{\large O}{\|}}{C}-O-H$ also gives this test).

Tollens' reagent test is given by aldehydes

Methanoic acid and ethanoic acid gives deep red colour solution with iron (III) chloride solution.

Benzoic acid gives buff coloured precipitate with iron (III) chloride solution

Acid chlorides and esters may be recognised after hydrolysis. The resultant acid and alcohol may be tested for.

Amides are recognised by the liberation of ammonia on heating with alkali (NaOH or KOH) whereas ammonum salts liberate ammonia with alkali in the cold.

1°, 2° and 3° alcohols are distinguished by Lucas test.

1°, 2° and 3° amines can be distinguished with the help of Hinsberg reagent.

1° and 2° anines can be distinguished by Carbylamine test

Unit - 10

HALOALKANES AND HALOARENES

1. Write the IUPAC names of the following compounds.

(i)

(ii)

(iii)

(iv)

(v) $CH_2Br - CH = CH - CH_2 - C \equiv CH$

(vi)

(vii)

(ix) $(CCl_3)_3\ CCl$

2. Write the structure of following halogen compounds

(i) 2-chloro-3-methylpentane

(ii) 2-(2-chlorophenyl)-1-iodooctane

(iii) 1-bromo-4-sec-butyl-2–methylebenzene.

(iv) p-bromotoluene.

(v) chlorophenylmethane

3. Arrange the following in the increasing order of properly indicated :

(i) bromomethane, chloromethane, dichloromethane. (Increasing order of boiling points).

(ii) 1-chloropropane, isopropyl chloride, 1-chlorobutane (Increasing order of boiling point)

(iii) dichloromethane, chloroform, carbon terachloride. (Increasing order of dipole moment.

(iv) CH_3F, CH_3Cl, CH_3Br, CH_3I (Increasing reactivity towards nucleophilic substitution and increasing order of dipole moment)

(v) *o,m.p*-dichlorobenzenes (Increasing order of melting points).

4. Complete the following reactions :

(i)

(ii) $CH_3 - CH_2 - Cl + Ag\ NO_2 \longrightarrow$

(iii)

(iv)

(v)

$\xrightarrow[\text{uv light}]{Br_2/\text{heat}}$

(vi)

+ HI $\longrightarrow$

(vii)

+ $SOCl_2$ $\longrightarrow$

(viii) $CH_3CH_2Br + NaI \xrightarrow{\text{acetone}}$

(ix)
+ Br_2 $\xrightarrow{UV\ \text{light}}$

(x) $(CH_3)_3\ CBr + KOH \xrightarrow[\text{heat}]{\text{ethanol}}$

(xi) $CH_3CH_2Br + KCN \xrightarrow{aq.\ EtOH}$

(xii)

+ Mg $\xrightarrow[\text{Ether}]{\text{dry}}$

(xiii) $C_6H_5ONa + C_2H_5Cl \longrightarrow$

(xiv) $CH_3-\overset{\overset{Br}{|}}{C}H-CH_2-CH_3 + Na \xrightarrow{\text{dry ether}}$

(xv) $CH_3\overset{\overset{Br}{|}}{C}H-CH_2-CH_3 + NaOH\ (aq) \longrightarrow$

(xvi) $C_6H_5N_2^+Cl^- + KI \longrightarrow$

5. How will you bring about the following conversions?

(i) benzene to 3-bromonitrobenzene

(ii) ethanol to but-1-yne

(iii) 1-bromopropane to 2-bromopropane

(iv) benzene to 4-bromo-1-nitrobenzene

(v) aniline to chlorobenzene

(vi) 2-methyl-1-propene to 2-chloro-2-methylpropane

(vii) ethyl chloride to propanoic acid

(viii) but-1-ene to n-butyl iodide

(ix) benzene to phenylchloromethane.

(x) tert-butyl bromide to isobutyl bromide.

6. Identify the products formed in the following sequence :

(i)

(ii)

(iii) $C_6H_5CH_2CHBrCH_3 \xrightarrow{\text{alc. KOH}} A \xrightarrow{HBr} B$

(iv) $CH_3\underset{\underset{Br}{|}}{CH}-CH_3 \xrightarrow{\text{alc. KOH}} X \xrightarrow[H_2O_2]{HBr} Y$

(v) $CH_3CH_2CH = CH_2 + Br_2 \xrightarrow{CCl_4} A$

(vi) $CH_3CH_2CH = CH_2 + Br_2 \xrightarrow[\text{UV light}]{\text{heat}} B$

(vii)

(viii) $CH_3Br \xrightarrow{KCN} A \xrightarrow{H_3O^+} \xrightarrow[ether]{Li\,Al\,H_4}$

7. Explain the following reactions with suitable example :

   (i) Finkelstein reaction.

   (ii) Swarts reaction.

   (iii) Wurtz reaction.

   (iv) Wurtz-Fitting reaction

   (v) Friedel-Craft's alkylation reaction.

   (vi) Friedel-Craft's acylation reaction

   (vii) Sandmeyer reaction.

8. Write the major products and name the rule responsible for the formation of the product.

   (i) $CH_3-CH_2-\underset{\underset{Br}{|}}{CH}-CH_3 \xrightarrow[EtOH]{KOH}$

   (ii) $CH_3-CH_2-CH = CH_2 + HBr \xrightarrow{\text{organic peroxide}}$

9. Write the difference between

   (i) enantiomers and diastereomers

   (ii) retention and inversion of configuration.

   (iii) electrophilic and nucleophilic substitution reactions.

10. Give a chemical test to distinguish between the following pairs of compounds:

   (i) chlorobenzene and cyclohexylchloride.

   (ii) vinyl chloride and ethyl chloride.

   (iii) n-propyl bromide and isopropyl bromide.

11. Give mechanism of the following reactions :

   (i) $(CH_3)_3C - Cl + \bar{O}H \longrightarrow (CH_3)_3\,C - OH$

   (ii) $CH_3 - Cl + OH^- \longrightarrow CH_3 - OH$

(iii)

(iv)

(v)

12. Which compound in each of the following pairs will react faster in S_N2 reaction with OH^- and why?

    (i) CH_3Br or CH_3I

    (ii) $(CH_3)_3$ CCl or CH_3Cl

13. In the following pairs which halogen compound undergoes faster SN1 reaction?

    (i)

    (ii)

    (iii) $(CH_3)_3C - Cl$ and $C_6H_5CH_2Cl$

    (iv) $C_6H_5CH_2Cl$ and $C_6H_5C(Cl)C_6H_5$

    (v) $CH_2 = CH - Cl$ and $CH_2 = CH - CH_2Cl$

14. Give reasons for the following :

    (i) The bond length of C–Cl bond is larger in haloalkanes than that in haloarenes.

    (ii) Although alkyl halides are polar in nature but are not soluble in water.

(iii) tert-butyl bromide has lower boiling point than n-Butyl bromide.

(iv) haloalkanes react with KCN to form alkyl cyanide as main product while with AgCN alkyl isocyanide is the main product.

(v) sulphuric acid is not used in the reaction of alcohol with KI.

(vi) thionyl chloride is the preferred reagent for converting ethanol to chloroethane.

(vii) haloalkanes undergo nucleophilic substitution reaction easily but haloarenes do not undergo nucleophilic substitution under ordinary conditions.

(viii) chlorobenzene on reaction with fuming sulphuric acid gives ortho and para chlorosulphonic acids.

(ix) 2, 4-dinitro chlorobenzene is much more reactive than chlorobenzene towards hydrolysis reaction with NaOH.

(x) Grignard reagent should be prepared under anhydrous conditions.

(xi) the dipole moment of chlorobenzene is lower than that of cyclohexyl chloride.

(xii) neopentyl bromide undergoes nucleophilic substitution reactions very slowly

(xiii) vinyl chloride is unreactive in nucleophilic substitution reaction.

(xiv) An optically inactive product is obtained after the hydrolysis of optically active 2- bromobutane.

[**Hint :** The hydrolysis reaction occurs by S_N1 pathway. The carbocation is formed first which gives a mixture of (±) butan-2-ol in the second step].

I.

II.

(xv) methyl iodide is hydrolysed at faster rate than methyl chloride.

15. Write the different products and their number formed by the monochlorination of following compounds :

(i) $CH_3CH_2CH_2CH_3$

(ii) $(CH_3)_2CHCH_2CH_3$

(iii) $(CH_3)_2CHCH(CH_3)_2$

[**Hint :** (i) Two, (ii) four, (iii) three

16. (a) When 3-methylbutan-2-ol is treated with HBr, the following reaction takes places :

Give the mechanism for this reaction.

(b) In the following reaction :

major and minor products are :

(i)

(ii)

(iii)

(iv)

Ans. Major (iii) minor (i)

17. Give one use of each of following :

(i) Freon-12 (ii) DDT

(iii) Carbon tetrachloride (iv) Iodoform

18. An optically active compound having molecular formula $C_7H_{15}Br$ reacts with aqueous KOH to give $C_7H_{15}OH$, which is optically inactive. Give mechanism for the reaction.

[**Ans. :** (i)

(Slow)

(ii)

product with inversion of configuration

product having retention of configuration

A racemic mixture is obtained which is optically inactive.]

19. An organic compound C_8H_9Br has three isomers A, B and C. A is optically active. Both A and B gave the white precipitate when warmed with alcoholic $AgNO_3$ solution in alkaline medium. Benzoic acid, terephthalic and p-bromobenzoic acid were obtained on oxidation of A, B and C respectively. Identify A, B and C.

[**Ans. :** (A)

(B)

(C)

*20. An alkyl halide X having molecular formula $C_6H_{13}Cl$ on treatment with potassium tert-butoxide gives two isomeric alkenes Y and Z but alkene y is symetrical. Both alkenes on hydrogenation give 2, 3-dimethylbutane. Identify X, Y and Z.

[**Ans.**

*21. 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) $CH_3CH_2CH_2CONH_2$

*22. Identify A, B, C, D, E, R and R´ in the following sequence of reactions :

(a)

(b)

(c)

23. Which nomenclature is not occording to IUPAC system.

(i) $Br - CH_2\ CH = CH_2$; 1–bromoprop-2-ene

(ii)

4–bromo-2, 4-dimethylhexane

(iii)

2–methyl–3–phenylpentane

(iv)

5–oxohexanoic acid

Unit - 11

ALCOHOLS, PHENOLS AND ETHERS

1. Write IUPAC names of the following compounds :

(i)

(ii)

(iii) $CH \equiv C–CH_2OH$

(iv)

(v)

(vi)

(vii)

(viii)

(ix) $C_6H_5OC_3H_7$

(x) $CH_3CH_2OCH_2CH_2CH_2Cl$

2. Write the structures of the compounds whose names are given below :

(i) 3, 5-dimethoxyhexane-1, 3, 5-triol

(ii) cyclohexylmethanol

(iii) 2-ethoxy-3-methylpentane

(iv) 3-chloromethylpentan-2-ol

(v) p-nitroanisole

3. Describe the following reactions with example :

(i) Hydroboration oxidation of alkenes

(ii) Acid catalysed dehydration of alcohols at 443K.

(iii) Williamson synthesis

(iv) Reimer-Tiemann reaction.

(v) Kolbe's reaction

(vi) Friedel-Crafts acylation of Anisole.

4. Complete the following reactions :

(i) $CH_3CH_2CH_2CHO \xrightarrow{Pd/H_2}$

(ii) $CH_3CHO \xrightarrow[\text{(ii) } H^+/H_2O]{\text{(i) } CH_3MgBr}$

(iii) $CH_3CH_2OH \xrightarrow{Cu/573K}$

(iv) $C_6H_5OH + Br_2 \xrightarrow{H_2O}$

(v)

(vi)

(vii) $CH_3CH_2CH_2O - CH_3 + HBr \longrightarrow$

(viii)

(ix) $(CH_3)_3C - O - C_2H_5 + HI \longrightarrow$

(x)

(xi)

(xiii)

(xiv)

5. What happens when :

(i) aluminium reacts with tert-butyl alcohol

(ii) phenol is oxidised with chromic acid

(iii) cumene is oxidised in the presence of air and the product formed is treated with dilute acid.

(iv) phenol is treated with conc. HNO_3.

(v) phenol is treated with chloroform in presence of dilute NaOH.

6. How will you convert

(i) propene to propan-l-ol.

(ii) anisole to phenol

(iii) butan-2-one to butan-2-ol

(iv) ethanal to ethanol

(v) phenol to ethoxybenzene

(vi) 1-phenylethene to 1-phenylethanol

(vii) formaldehyde to cyclohexylmethanol

(viii) butyl bromide to pentan-1-ol.

(ix) toluene to benzyl alcohol

(x) 1-propoxypropane to propyl iodide

(xi) ethyl bromide to 1-ethoxyethane

(xii) methyl bromide to 2-methoxy-2-methylpropane

(xiii) ethyl bromide to ethoxybenzene

(xiv) ethanol to benzyl ethyl ether.

7. Identify the missing reactant or product A to D in the following equations:

(i) (A) + HNO_3 + H_2SO_4 ⟶

(ii) + dil. H_2SO_4 ⟶ (B)

(iii) (C) + H_2O $\xrightarrow{H^+}$ $CH_3(CH_2)_2\ C(CH_3)\ (OH)\ (CH_2)_2CH_3$

(vi) $CH_3OC_6H_5$ + HI ⟶ (D)

8. Identify X, Y and Z in the following sequence of reactions :

(i) Phenol $\xrightarrow{\text{Zn dust}}$ X $\xrightarrow[\text{Anhyd. } AlCl_3]{CH_3Cl}$ Y $\xrightarrow[OH^-]{KMnO_4}$ Z

(ii) Ethanol $\xrightarrow{PBr_3}$ X $\xrightarrow{\text{alc. KOH}}$ Y $\xrightarrow{\text{dil.}H_2SO_4}$ Z

(iii) $\xrightarrow{HI}$ X + CH_3I

X + conc. HNO_3 ⟶ Y (a dinitro compound)

X + Br_2(aq) ⟶ Z (a tribromo product)

10. Write the mechanism for following reactions :

(i)

(acid catalysed hydration of alkenes)

(ii) $CH_3 - CH_2 - OH \xrightarrow[443\ K]{H^+} CH_2 = CH_2$
(acid catalysed dehydration of alcohols)

(iii) $2CH_3CH_2OH \xrightarrow[413\ K]{H^+} CH_3CH_2OCH_2CH_3$
(acid catalysed nucleophilic substitution reaction)

(iv) $CH_3OCH_3 + HI \longrightarrow CH_3OH + CH_3I$

(v) $(CH_3)_3C - O - CH_3 + HI \longrightarrow CH_3OH + (CH_3)_3\ CI$

11. Give reason for the following :

(i) The C–O–C bond angle in dimethyl ether is (111.7°)

(ii) Alcohols have higher boiling points than ethers of comparable molecular masses.

(iii) Phenols are more acidic than alcohols.

(iv) Nitrophenol is more acidic than o-methoxyphenol.

(v) Phenol is more reactive towards electrophilic substitution reaction than benzene.

(vii) The following is not an appropriate method for the preparation of t-butyl ethyl ether :

(a) What would be the major product of this reaction?

(b) Write suitable reaction for the preparation of t–butyl ethyl ether.

(viii) The following is not an appropriate method for the preparation of 1-methoxy-4-nitrobenzene;

(x) Write the suitable reaction for the preparation of 1–methoxy–4–nitrobenzene

(ix) o-nitrophenol is steam volatile but p-nitrophenol is not.

(x) phenol is less polar than ethanol.

(xi) The phenyl methyl ether reacts with HI fo form phenol and iodomethane and not iodobenzene and methanol.

(xii) methanol is less acidic than water.

(xiii) alcohols can act as weak base as well as weak acids.

(xiv) phenols do not give protonation reaction readily.

(xvi) absolute ethanol can not be obtained by factional distillation of ethanol and water mixture.

12. Arrange the following in the increasing order of property shown :

(i) methanol, ethanol, diethylether, ethyleneglycol. (Boiling points)

(ii) phenol, o-nitrophenol, m-nitrophenol, p-nitrophenol. (Acid strength)

(iii) dimethylether, ethanol, phenol. (Solubility in water)

(iv) n-butanol, 2-methylpropan-1-ol, 2-methylpropan-2-ol. (Acid strength)

13. Give a chemical test to distinguish between the following pair of compounds.

(i) n-propyl alcohol and isopropylalcohol

(ii) methanol and ethanol

(iii) cyclohexanol and phenol.

(iv) propan-2-ol and 2-methylpropan-2-ol.

(v) phenol and anisole

(vi) ethanol and diethyl ether

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

(i) $(CH_3)_3COH$

(ii) $CH_3CH_2CH_2OH$

(iii)

(iv)

*15. What is the function of $ZnCl_2$ (anhyd) in Lucas test for distinction between 1°, 2° and 3° alcohols.

16. An alcohol A ($C_4H_{10}O$) on oxidation with acidified potassium dichromate gives carboxylic acid B ($C_4H_8O_2$). Compound A when dehydrated with conc. H_2SO_4 at 443 K gives compound C. Treatment of C with aqueous H_2SO_4 gives compound D ($C_4H_{10}O$) which is an isomer of A. Compound D is resistant to oxidation but compound A can be easily oxidised. Identify A, B, C and D and write their structures.

[**Ans. :** [A] : $(CH_3)_2CHCH_2OH$ [B] : $CH_3CH(CH_3)COOH$

[C] : $(CH_3)_2C = CH_2$ [D] : $(CH_3)_3C - OH$

*17. An organic compound A having molecular formula C_6H_6O gives a characteristic colour with aqueous $FeCl_3$. When A is treated with NaOH and CO_2 at 400 K under pressure, compound B is obtained. Compound B on acidification gives compound C which reacts with acetyl chloride to form D which is a popular pain killer. Deduce the structure of A, B, C and D. What is the common name of Drug D?

[**Ans. :**

(A)

(B)

(C)

(D)

Aspirin

19. An ether A ($C_5H_{12}O$) when heated with excess of hot concentrated HI produced two alkyl halides which on hydrolysis from 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.

[**Ans. :** (A)

(B) CH_3CH_2OH

(C) $CH_3CHOHCH_3$

(D) CH_3COOH

(E) CH_3COCH_3

20. Phenol, C_6H_5OH when it first reacts with concentrated sulphuric acid, forms Y.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. :**

(Y)

(Z) (Picric acid)

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

21. Synthesise the following alcohols from suitable alkenes.

(a)

(b)

22. How are the following ethers prepared by williumson synthesis?

(a) Ethoxybenzene (b) 2–methoxy–2–methylpropane

Unit - 12

ALDEHYDES, KETONES AND CARBOXYLIC ACIDS

1. Indicate the electrophilic and nucleophilic centres in acetaldehyde.

2. Write the IUPAC names of the following organic compounds :

(i)

(ii) $CH_3-\overset{\overset{O}{\|}}{C}-CH_2-\overset{\overset{Cl}{|}}{CH}-CHO$

(iii) $HOOC-CH_2-CH=\overset{\overset{Br}{|}}{C}-CHO$

(iv)

(v) $CH_3\overset{\overset{Br}{|}}{C}HCH_2\overset{\overset{O}{\|}}{C}-NHCH_3$

(vi)

(vii) $[(CH_3)_2CH-CH_2CO]_2O$

(viii)

(ix)

(x)

(xi)

(xii)

(xiii)

(xiv)

3. Explain the following reactions giving one example of each :
   (i) Rosenmund reduction reaction
   (ii) Stephen reaction
   (iii) Etard reaction
   (iv) Gatterman-Koch reaction
   (v) Aldol condensation
   (vi) Cross aldol condensation
   (vii) Cannizzaro reaction
   (viii) Decarboxylation reaction

(ix) Kolbe's reaction

(x) Hell-Volhard-Zelinsky reaction

(xi) Clemmensen reduction

(xii) Wolff-Kishner reduction

(xii) Haloform reaction.

4. How will you convert :

(i) Isopropyl chloride to 2-methylpropionaldehyde.

(ii) benzene to benzaldehyde

(iii) benzoic acid to acetophenone

(iv) propene to propanal

(v) butanoic acid to 2-hydroxybutanoic acid

(vi) benzoic acid to m-nitrobenzyl alcohol

(vii) propanol to propene

(viii) propanol to butan-2-one.

(ix) methyl magnesium bromide to ethanoic acid

(x) benzoic acid to benzyl chloride

(xi) acetone to chloroform

(xii) acetylene to acetic acid

(xiii) formaldehyde to propanol

(xiv) acetophenone to 2-phenylbutan-2-ol

5. Complete the following reactions :

(i)

(ii) $CH_2{=}CH{-}CH_2{-}CN \xrightarrow[\text{(ii) } H_2O]{\text{(i) AlH } (i\text{–Bu})_2}$

(iii)

(iv)

$+ \text{HCHO} \xrightarrow{50\% \text{ NaOH}}$

(v)

$\xrightarrow[\text{(ii) } H_3O^+]{\text{(i) } LiAlH_4}$

(vi)

$\xrightarrow{KMnO_4/KOH}$

(vii)

$+ CrO_3 + (CH_3CO)_2O \longrightarrow$

(viii)
$\xrightarrow{KMnO_4/H_2SO_4}$

(ix) $CH_3—CH_2—COOH \xrightarrow{Br_2/P} X$

(x) $CH_3—C\equiv CH \xrightarrow{Hg^{2+}/H_2SO_4}$

6. How will you prepare the following derivatives of acetone?
   (i) 2, 4-DNP derivative
   (ii) Schiff's base
   (iii) Oxime

7. Arrange the following in the increasing order of the property indicated

(i) CH_3CHO, HCHO, CH_3COCH_3, C_6H_5CHO (reactivity towards HCN)

(ii) propan-1-ol, propanone, propanal (boiling point)

8. Give the reaction mechanism for following reactions :

(i) $CH_3CHO + HCN \longrightarrow CH_3-CH(OH)(CN)$

(ii) $CH_3COOH + C_2H_5OH \xrightarrow{H_2SO_4} CH_3COOC_2H_5 + H_2O$

(iii) $CH_3COCH_3 \xrightarrow[\text{(ii) } H_2O]{\text{(i) } CH_3MgBr} CH_3-C(OH)(CH_3)-CH_3$

9. Give one chemical test to distinguish between following pair of compounds: Write the chemical reaction involved.

(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) CH_3CHO and CH_3COCH_3

(ix) CH_3CHO and HCHO

(x) acetophenone and benzophenone

10. 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 atoms 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.

(xii) Formic acid reduces Tollens' reagent.

(xiii) Electrophilic substitution in benzoic acid takes place at m-position.

(xiv) Carboxylic acids do not give characteristic reactions of carbonyl group.

(xv) Formaldehyde gives Cannizzaro reaction whereas acetaldehyde does not.

(xvi) tert-butyl benzene cannot be oxidised with $KMnO_4$.

(xviii) There are two $–NH_2$ groups in semicarbazide. However, only one $–NH_2$ group is involved in the formation of semicarbazones.

(xix) Benzoic acid is less soluble in water than acetic acid.

(xx) Formic acid is a stronger acid than acetic acid.

*11. You are given four different reagents Zn–Hg/HCl, NH_2 NH_2/OH^- in Glycol, H_2/Ni and $NaBH_4$. Select one reagent for the following transformation and give reasons to justify your answer.

[**Hint :** OH group and alkene are sensitive groups to HCl so clemmeson reduction cannot be used. Hence NH_2 NH_2/OH^- in glycol will be used.

*12. An organic compound (A) having molecular formula $C_5H_{10}O$ gives a positive 2, 4-DNP test. It does not reduce Tollens' reagent but forms an addition compound with sodium hydrogen sulphite. On reaction with I_2 in alkaline medium, it forms a yellow precipitate of compound B and another compound C having molecular formula $C_4H_7O_2Na$. On oxidation with $KMnO_4$, [A] forms two acids D and E having molecular formula $C_3H_6O_2$ and $C_2H_4O_2$ respectively. Identity A, B, C, D and E.

A : $CH_3CH_2CH_2COCH_3$ B : CHI_3 C : $CH_3CH_2CH_2COONa$

D : CH_3CH_2COOH E : CH_3COOH

*13. Formaldehyde and acetaldehyde on treatment with dil. NaOH form A which on heating changes to B. When B is treated with HCN, it forms C. Reduction of C with DIBAL- H yields D which on hydrolysis gives E. Identify A, B, C, D and E.

[Ans. : A : $HOCH_2CH_2CHO$ B : $CH_2 = CH - CHO$

C :

D :

E :

*14. Identify the missing reagent/products in the following reactions :

(i) $CH_3CH_2\overset{\overset{O}{\|}}{C}-CH_3 + A \longrightarrow CH_3CH_2COONa + B + NaI + H_2O$

(ii)

(iii)

(iv) $C_6H_5COCH_3 + A \longrightarrow C_6H_5-\overset{\overset{OMgBr}{|}}{\underset{\underset{CH_3}{|}}{C}}-CH_2C_6H_5 \xrightarrow{H_3O^+} B \xrightarrow{\Delta} C$

15. Identify A, B, C, D and E in the following sequences of reactions :

$$\underset{\text{Acyclic compound}}{A\left(C_6H_{12}\right)} \xrightarrow{HCl} \underset{\text{major}}{B} + \underset{\text{minor}}{C}$$

$$A\left(C_6H_{12}\right) \xrightarrow[\text{(ii) } Zn/H_2O]{\text{(i) } O_3} D + E \left(\begin{array}{l}\text{both give Tollens' test but}\\ \text{do not respond to iodoform test}\end{array}\right)$$

$$D + E \xrightarrow{\text{conc. NaOH}} HCOONa + \left(CH_3\right)_3 C - CH_2OH$$

*16. A tertiary alcohol 'A' on acid catalyzed dehydration gave product 'B'. Ozonolysis of 'B' gives compounds 'C' and 'D'. Compound 'C' on reaction with KOH gives benzyl alcohol and compound 'E'. Compound 'D' on reaction with KOH gives $\alpha.\beta$ – unsaturated ketone having the following structure.

Identify A, B, C, D and E

[**Ans. :** (A)

(B) , (C) PhCHO, (D) $PhCOCH_3$, (E) PhCOOH

*17. Identify A, B, C, D and E in the following sequence of reactions :

[**Ans. :** (A) CH_3CH_2Cl (B) $CH_2 = CH_2$ (C) $CH \equiv CH$

(D) CH_3CHCl_2 (E) CH_3CHO

*18. Arrange the following acids in the order of increasing acid strength

(i) formic acid, benzoic acid, acetic acid

(ii)

(iii) CH_3CH_2COOH, C_6H_5COOH, CH_3COOH, $C_6H_5CH_2COOH$

*19. During the reaction of a carbonyl compound with a weak nucleophile, H^+ ions are added as catalyst. Why?

[**Ans. :** $>C{=}O + H^+ \longrightarrow >C^+{-}OH$

H^+ ions get attached to oxygen atom and make carbonyl carbon more electrophilic in nature.]

*20. During reaction of carbonyl compound with 2, 4-DNP reagent, the pH of the reaction mixture has to be maintained between 3 and 4. Why?

[**Ans. :** H^+ ions increase the electrophilicity of carbonyl carbon. When H^+ ions are in excess, they protonate the NH_2 group of 2, 4-DNP. After protonation $-N^+H_3$ group does not act as nucleophile.]

*21. An aromatic compound X with molecular formula C_9H_{10} gives the following chemical tests :

(i) Forms 2, 4-DNP derivative

(ii) Reduces Tollens' reagent

(iii) Undergoes Cannizzaro reaction

(iv) On vigorous oxidation gives 1, 2-benzenedicarboxylic acid.

Identify X and write its IUPAC name. Also write the reactions involved in the formation of above mentioned products.

[**Ans. :** (X)

2-Ethylbenzaldehyde

22. Iodoform can be prepared from, all except.

(i) Ethyl methyl ketone (ii) Isopropyl alcohol

(iii) 3-methylbutan-2-one (iv) Isobutyl alcohol Ans : (iv)

Unit - 13

AMINES

1. Write IUPAC names of the following :

(i)

(ii) $CH_3NHCH(CH_3)_2$

(iii) $(CH_3)_3\ N$

(iv) $C_6H_5NHCH_3$

(v)

(vi)

(vii)

(viii) $H_2N\ (CH_2)_6NH_2$

(ix)

(x)

2. Giving an example of each, describe the following reactions :

(i) Hoffman bromamide reaction

(ii) Gabriel phthanlimide synthesis

(iii) Gatterman reaction

(iv) Coupling reaction

(vi) Carbylamine reaction

(vii) Acetylation of aniline.

3. Describe the Hinsberg's test for identification of primary, secondary and tertiary amines. Also write the chemical equations of the reactions involved.

4. Arrange the following in the increasing order of given property indicated.

   (i) $C_2H_5NH_2$, $(C_2H_5)_2NH$, $(C_2H_5)_3N$ and NH_3, (Basic strength in aqueous solution).

   (ii) $C_2H_5NH_2$, $(C_2H_5)_2NH$, $(C_2H_5)_3N$ and CH_3NH_2. (Basic strength in gaseous phase).

   (iii) Aniline, p-toluidine, p-nitroaniline. (Basic strength).

   (iv) C_2H_5OH, $(CH_3)_2$ HN, $C_2H_5NH_2$ (Boiling point)

5. Identify A and B in the following reactions :

   (i) $CH_3CH_2Cl + NH_3$ (Excess) $\xrightarrow[OH^-]{373K}$ A

   (ii) $CH_3CH_2Cl + NH_3 \xrightarrow[OH^-]{373K}$

   (excess)

6. How will you bring about the following conversions?

   (i) benzene to Aniline

   (ii) aniline to benzene

   (iii) ethanoic acid to ethanamine

   (iv) p-toluidine to 2-bromo-4-methylaniline.

   (v) methylbromide to ethanamine

   (vi) benzenediazonium chloride to nitrobenzene

   (vii) ethylamine to methylamine

   (ix) benzene to sulphanilic acid

   (x) hexanenitrile to 1-aminopentane.

7. Write the products formed in the following sequence of reactions :–

$$CH_3CH_2I \xrightarrow{NaCN} A \xrightarrow[\text{Partial hydrolysis}]{OH^-} B \xrightarrow{Br_2/NaOH} C$$

8. Identify the missing reagent/product in the following reactions :

(i)

(ii)

(iii) $C_6H_5N_2^+Cl^- \xrightarrow{CuCN} A \xrightarrow{H_2O/H^+} B$

(iv) $C_6H_5NO_2 \xrightarrow{Fe/HCl} A \xrightarrow{H_2SO_4} B \xrightarrow{heat} C$

(v)

9. Give one chemical test to distinguish between the following pairs of compounds :

(i) methylamine and dimethylamine

(ii) secondary and tertiary amines

(iii) ethylamine and aniline

(iv) aniline and benzylamine

(v) methylamine and methanol

(vi) methylamine and N, N-dimethylamine

(vii) ethanol and ethanamine

10. Explain why :

(i) The C–N–C bond angle in trimethyl amine is 108°

(ii) the quaternary ammonium salts having four different alkyl groups are optically active

(iii) alkylamines are more basic than ammonia

(iv) aniline cannot be prepared by Gabriel phthalimide synthesis

(v) Garbriel phthalimide synthesis is preferably used for synthesising primary amines.

(vi) ethylamine is soluble in water but aniline is not

(vii) amines are soluble in dilute HCl.

(viii) amines have lower boiling point than alcohols of comparable molecular masses.

(ix) 1° amines have higher boiling points than 2° amines which in turn, are higher boiling than 3° amines.

(x) The pK_b value of benzeneamine is 9.33 while that of ammonia is 4.75.

(xi) aniline does not undergo Friedel-Crafts reaction.

(xii) aniline readily forms 2, 4, 6-tribromoaniline on reaction with bromine water.

(xiii) sulphanilic acid is soluble in water.

(xiv) methylamine in water reacts with ferric chloride to precipitate hydrated ferric oxide.

(xv) diazonium salt of aromatic amines are more stable than the diazonium salts of aliphatic amines.

(xvi) Although amino group is o, p-directing in aromatic electrophilic substitution reactions, aniline on nitration gives a substantial amount of m-nitroaniline.

11. Why do amines act as nucleophiles? Give example of a reaction in which methylamine acts as a nucleophile.

*12. Three isomeric amines A, B and C have the molecular formula C_3H_9N. Compound A on reaction with benzene sulphonyl chloride forms a product which is soluble in NaOH. Compound B on reaction with benzene sulphonyl chloride forms a product which is insoluble in NaOH and compound C

does not react with benzene sulphonyl chloride. Identify A, B and C.

[**Ans. :** (A) $CH_3CH_2CH_2NH_2$ (B) $CH_3CH_2NHCH_3$ (C) $(CH_3)_3N$]

13. An organic compound A (C_2H_3N) is used as a solvent of choice for many organic reactions because it is not reactive in mild acidic and basic conditions. Compound A on treatment with Ni/H_2 forms B. When B is treated with nitrous acid at 273K, ethanol is obtained. When B is warmed with chloroform and NaOH, a foul smelling compound C formed. Identify A, B and C.

[**Ans. :** (A) CH_3CN (B) $CH_3CH_2NH_2$ (C) CH_3CH_2NC

14. An organic compound [A] $C_3H_6O_2$ on reaction with ammonia followed by heating yield B. Compound B on reaction with Br_2 and alc. NaOH gives compound C (C_2H_7N). Compound C forms a foul smelling compound D on reaction with chloroform and NaOH. Identify A, B, C, D and the write the equations of reactions involved.

[**Hint :** (A) CH_3CH_2COOH (B) $CH_2CH_2CONH_2$

(C) $CH_3CH_2NH_2$ (D) CH_3CH_2NC.]

Unit - 14

BIOMOLECULES

POINTS TO REMEMBER

1. Carbohydrates are optically active polyhydroxy aldehydes or ketones or molecules which provide such units on hydrolysis.
2. Corbohydrates are classified into three groups (i) monosaccharides, (ii) oligosaccharides and (iii) polysaccharides.
3. Glucose, the most important source of energy for mammals, is obtained by the digestion of starch.
4. Monosaccharides are held together by glycosidic linkages to form disaccharides or polysaccharides.
5. Proteins are the polymers of about twenty different amino acids which are linked by peptide bonds. Ten amino acids are called essential amino acids because they can not be synthesised in our body, hence must be provided through diet.
6. Proteins perform various structural and dynamic functions in the organisms. Proteins which contain only amino acids, are called simple proteins.
7. The secondary or tertiary structure of proteins get disturbed on change of pH or temperature and they are not able to perform their functions. This is called denaturation of proteins.
8. Enzymes are biocatalysts which speed up the reactions in biosystems. They are very specific and selective and efficient in their actions and chemically all enzymes are proteins.
9. Vitamins are necessory food factors required in the diet. They are classified as fat soluble (A, D, E and K) and water soluble (B group and C).
10. Nucleic acid are responsible for the transfer of characters from parents to offsprings.
11. There are two types of nucleic acids DNA and RNA. DNA contains a five carbon sugar molecule called 2-deoxyribose and RNA contains ribose.
12. Both DNA and RNA contain adenine, guanine and cytosine. The fourth base is thymine in DNA and uracil in RNA. The structure of DNA is double

stranded while that of RNA is a single stranded molecule.

13. DNA is the chemical basis of heredity and has the coded message for proteins to be synthesised.

14. There are three types of RNA, *i.e.,* m-RNA, r-RNA and t-RNA which actually carry out the protein synthesis in the nucleus.

15. Human stomach does not have any enzyme capable of breaking cellulose molecules and thus we cannot digest cellulose.

QUESTIONS

VSA TYPE QUESTIONS (1 - MARK QUESTIONS)

1. Name polysaccharide which is stored in the liver of animals.

2. What structural feature is required for a carbohydrate to behave as reducing sugar?

   [**Hint :** The carbonyl group of any one monosaccharide present in carbohydrate should be free]

3. How many asymmetric carbon atoms are present in D (+) glucose?

4. Name the enantiomer of D-glucose.

   [**Hint :** L-glucose]

5. Give the significance of (+)-sign in the name D-(+)-glucose.

   [**Hint :** (+) sign indicates dextrorotatory nature of glucose].

6. Give the significance of prefix 'D' in the name D-(+)-glucose.

   [**Hint :** 'D' Signifies that –OH group on C-5 is on the right hand side]

7. Glucose is an aldose sugar but it does not react with sodium hydrogen sulphite. Give reason.

   [**Hint :** The –CHO group reacts with –OH group at C–5 to form a cyclic hemiacetal].

8. Why is sucrose called invert sugar?

   [**Hint :** When sucrose is hydrolysed by water, the optical rotation of solution changes from positive to negative.]

9. Name the building blocks of proteins.

10. Give the structure of simplest optically active amino acid.

11. Name the amino acid which is not optically active.

12. Write the Zwitter ionic form of aminoacetic acid.

13. Name the enzyme which catalyses the hydrolysis of maltose into glucose.

14. Give reason : Amylase present in the saliva becomes inactive in the stomach.

    [**Hint :** HCl present in stomach decreases the pH]

15. How would you explain the amphoteric behavior of amino acids.

    [**Hint :** Amino acids are amphoteric due to the presence of both acidic and basic functional groups.]

16. Which forces are responsible for the stability of α – helical structure of proteins.

17. How are polypeptides different from proteins.

18. Which nucleic acid is responsible for carrying out protein synthesis in the cell.

19. The two strands in DNA are not identical but complementary. Explain.

    [**Hint :** H-bonding is present between specific pairs of bases present in stands.]

20. When RNA is hydrolysed, there is no relationship among the quantities of different bases obtained. What does this fact suggest about the structure of RNA.

    [**Hint :** RNA is single stranded].

21. What type of linkage holds together the monomers of DNA and RNA.

    [**Hint :**Phosphodiester linkage]

22. Mention the number of hydrogen bonds between adenine and thymine.

23. A child diagnosed with bone deformities, is likely to have the deficiency of which vitamin?

24. What is meant by the term DNA fingerprinting?

25. List two important functions of proteins in human body.

26. Name the vitamin responsible for coagulation of blood.

27. Except vitamin B_{12}, all other vitamins of group B, should be supplied regularly in diet. Why?

28. How is glucose prepared commercially?

29. What is the structural difference between glucose and fructose?

30. What is the difference between an oligosaccharide and a polysaccharide.

31. Give the Haworth projection of D-glucopyranose.

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

1. What are anomers. Give the structures of two anomers of glucose.

2. Write the hydrolysed products of
   (i) maltose (ii) cellulose.

3. Name the two components of starch? Which one is water soluble?

4. (i) Acetylation of glucose with acetic anhydride gives glucose pentaacetate. Write the structure of the pentaacetate.
   (ii) Explain why glucose pentaacetate does not react with hydroxylamine?
   [**Hint :** The molecule of glucose pentaacetate has a cyclic structure in which –CHO is involved in ring formation with OH group at C–5]

5. What are vitamins? How are they classified?

6. (i) Why is sucrose called a reducing sugar?
   (ii) Give the type of glycosidic linkage present in sucrose.

7. Classify the following as monosaccharides or oligosaccharides.
   (i) Ribose (ii) Maltose
   (iii) Galactose (iv) Lactose

8. Write the products of oxidation of glucose with
   (a) Bromine water (b) Nitric acid

9. State two main differences between globular and fibrous proteins.

10. Classify the following α-amino acids as neutral, acidic or basic.
    (i) $HOOC - CH_2 - CH(NH_2)COOH$
    (ii) $C_6H_5 - CH_2 - CH(NH_2)COOH$
    (iii) $H_2N - (CH_2)_4 - CH(NH_2) - COOH$
    (iv) $HN = \underset{\underset{NH_2}{|}}{C} - (CH_2)_3 - CH(NH_2)COOH$

11. You have two amino acids, *i*,e. glycine and alanine. What are the structures of two possible dipeptides that they can form?

12. What are essential and non essential amino acids? Give one example of each type.

13. Name four type of intermolecular forces which stabilize 2° and 3° structure of proteins.
    [**Hint :** Hydrogen bonds, disulphide linkages, vander Waals and electrostatic forces of attraction.]

14. Classify the following as globular or fibrous proteins.
(i) Keratin (ii) Myosin
(iii) Insulin (iv) Haemoglobin.

15. What do you understand by

(a) denaturation of protein (b) specificity of an enzyme.

16. On electrolysis in acidic solution amino acids migrate towards cathode while in alkaline solution they migrate towards anode.

[**Hint :** In acidic solution, COO^- group of zwitter ion formed from α-amino acid is protonated and NH_3^+ groups is left unchanged while in basic solution deprotonation converts NH_3^+ to NH_2 and COO^- is left unchanged.]

17. (i) Name the disease caused by deficiency of vitamin D.

(ii) Why cannot vitamin C be stored in our body?

18. Define the terms hypervitaminosis and avitaminosis.

[**Hint :** Excess intake of vitamin A and D causes hypervitaminosis while multiple deficiencies caused by lack of more than one vitamins are called avitaminosis]

19. Explain what is meant by :
(i) a peptide linkage (ii) a glycosidic linkage?

[**Hint :** (i) Peptide linkage refers to the –CONH– linkage formed by reaction between –COOH group of one amino acid with $–NH_2$ group of the other amino acid.
(ii) Glycosidic linkage refers to –C–O–C– linkage between two sugars formed by loss of H_2O.]

20. Give the sources of vitamin A and E and name the deficiency diseases resulting from lack of vitamin A and E in the diet.

21. What are the main functions of DNA and RNA in human body.

SA(II) TYPE QUESTIONS (3 - MARK QUESTIONS)

1. How are carbohydrate classified?

2. (i) Name four bases present in DNA.

(ii) Which of them is not present in RNA.

(iii) Give the structure of a nucleotide of DNA.

3. Differentiate between the following :

(i) secondary and tertiary structure of protein.

(ii) α-Helix and β-pleated sheet structure of protein.

(iii) fibrous and globular proteins.

Unit - 15

POLYMERS

Points to Remember

1. Polymers are defined as high molecular mass macromolecules which consist of repeating structural units derived from the appropriate monomers.
2. In presence of an organic peroxide initiator, the alkenes and their derivatives undergo addition polymerisation or chain growth polymerisation through a free radical mechanism. Polythene, teflon, orlon etc. are formed by addition polymerisation of an appropriate alkene or its derivative.
3. Condensation polymerisation reactions are shown by the addition of bi– or poly functional monomers containing $–NH_2$, –OH and –COOH groups. This type of polymerisation proceeds through the elimination of certain simple molecules such as H_2O, NH_3 etc.
4. Formaldehyde reacts with phenol and melamine to form the corresponding condensation polymer products. The condensation polymerisation progresses through step by step and is called also step growth polymerisation.
5. Nylon, bakelite and dacron are some of the important examples of condensation polymers.
6. A condensation of two different unsaturated monomers exhibits copolymerisation. A copolymer like Buna-S contains multiple units of 1, 3-Butadiene and styrene.
7. Natural rubber is cis-1, 4-polyisoprene. It can be made more tough by the process of vulcanization with sulphur.
8. Synthetic rubbers like Buna-N are usually obtained by copolymerisation of alkene and 1, 3-Butadiene derivatives.
9. In view of potential environmental hazards of synthetic polymeric wastes, certain biodegradable polymers such as PHBV and Nylon-2-Nylon-6 are developed as alternatives.

QUESTIONS

VSA TYPE QUESTIONS (1 - MARK QUESTIONS)

1. Define the term copolymer.
2. Identify homopolymer from the following examples Nylon-66, Nylon-6, Nylon- 2-Nylon-6.
3. Give example of a natural polyamide which is an important constituent of diet.

   [**Hint :** Proteins]
4. Classify polythene and bakelite as thermosetting plastics or thermoplastics.
5. Among fibres, elastomers and thermosetting polymers, which one has strongest intermolecular forces of attraction?
6. Why is bakelite called a thermosetting polymer.
7. Give the monomers of bakelite.
8. Identify the monomer in the following polymeric structure.

9. Nylon-2-Nylon-6 is a biodegradable polymer obtained from glycine, $H_2N - CH_2 - COOH$ and aminocaproic acid, $H_2N–(CH_2)_5–COOH$. Write the structure of this polymer.
10. Give two uses of teflon.
11. Name the polymer used for making insulation material for coating copper wire. [**Hint :** PVC].
12. Write the name and structure of monomer of the polymer which is used as synthetic wool.
13. How is vulcanized rubber obtained?
14. Name the polymer used for making radio television cabinets and feeding bottles of children.
15. What do the digits 6 and 66 represent in the names nylon-6 and nylon-66?
16. Write the full form of PHBV.

17. Which of the following sets has all polymers capable of repeatedly softening on heating and hardening on cooling?

(i) Glyptal, Melamine, PAN.

(ii) PVC, Polystyrene, polythene.

(iii) Polypropylene, urea formaldehyde resin, teflon.

*18. Why benzoyl peroxide is used as an initiator for chain growth polymerisation?

[**Hint :** It easily generates free radicals required for initiation of reaction.]

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

1. Give the structure of monomer of neoprene. What is the advantage of neoprene over the natural rubber?

2. Classify the following as homopolymer or copolymer. Also classify them as addition or condensation polymers.

(i) $-(NH\ CH\ (R)\ CO)_n-$

(ii) $-(CH_2 - CH = CH - CH_2 - \underset{\underset{C_2H_5}{|}}{CH} - CH_2)_n$

3. Give the mechanism of polymerisation of ethene to polythene in presence of benzoyl peroxide.

4. Complete the following reactions :

5. (i) What is the difference between step growth polymer and chain growth polymer?

(ii) Give one example of each type.

6. How can you differentiate between thermosetting and thermoplastic polymers.

7. Mention the type of intermolecular forces present in nylon-66. What properties do they impart to nylon?

   [**Hint :** Strong intermolecular forces of attraction like Hydrogen bonding. This results in close packing of chains and thus impart crystalline nature to the fibres.]

8. What is the difference between linear chain and branched chain polymers. Explain giving examples.

9. Identify the polymer whose structure are given and mention one of their important use.

   (i) $\left[CO-(CH_2)_5-NH\right]_n$

   (ii)

10. Arrange the following polymers in the order of increasing intermolecular forces :

    (i) Nylon-6,6, Buna-S, Polythene.

    (ii) Nylon-6, Neoprene, Polyvinylchloride

11. Write the expanded form and give the structures of monomers for the following polymers:

    (i) PAN (ii) PTFE

12. Novolac is the linear polymer which on heating with formaldehyde forms cross-linked bakelite. Write the structures of monomers and the polymer novolac.

13. Write the structure of following polymers and also give their main uses :

    (a) Polystyrene (ii) Melamine - formaldehyde resin.

14. Identify the polymers used in the manufacture of paints and lacquers. Write the structure of the polymer and its monomers.

15. Can a copolymer be formed by both addition and condensation polymerisation? Explain with the help of examples.

16. What is the difference between an elastomer and a fibre? Give one example of each.

17. Write the structure of the monomers used in the synthesis of :

(i) Nylon-6 (ii) Nylon-6, 6

SA (II) TYPE QUESTIONS (3 - MARK QUESTIONS)

1. Differentiate between the following pairs :

(i) Branched chain polymers and cross linked polymers.

(ii) Thermoplastic and thermosetting polymers.

(iii) Chain growth and step growth polymerisation.

2. List two uses each of the following polymers :

(i) Nylon-2-Nylon-6. (ii) Urea-formaldehyde resin

(iii) Glyptal

3. (i) What is meant by biodegradabhle polymers?

(ii) A biodegradable polymer is used in speciality packaging, orthopaedic devices and in controlled release of drugs. Identify the polymer and give its structure.

4. Write the name and formula of the following polymers.

(a) Nylon 5, 6 (b) Nylon 6

(c) PHBV (d) Terylene

(e) Buna–S (f) Bakelite

Unit - 16

CHEMISTRY IN EVERYDAY LIFE

Points to Remember

1. A drug is a chemical agent which affects human metabolism and provides cure from ailment. If taken in doses higher than recommended, these may have poisonous effect.
2. Use of chemicals for therapeutic effect is called chemotherapy.
3. Drugs usually interact with biological macromolecules such as carbohydrates, proteins, lipids and nucleic acids. These are called target molecules.
4. Drugs are designed to interact with specific targets so that these have the least chance of affecting other targets. This minimises the side effects and localises the action of the drug.
5. Drugs like analgesics, antibiotics, antiseptics, disinfectants, antacids and tranquilizers have specific pharmacological functions.
6. Antifertility drugs are used to control population. These contain a mixture of synthetic estrogen and progesterone derivatives.
7. Chemicals are added to food for preservation, enhancing their appeal and adding nutritive value in them.
8. Artificial sweetening agents like aspartame, saccharin etc. are of great value to diabetic persons and people who need to control their calories.
9. These days detergents are much in vogue and get preference over soaps because they work even in hard water.
10. Synthetic detergents are classified into three main categories namely anionic, cationic and non- ionic.
11. Detergents with straight chain of hydrocarbons are preferred over branched chain as the latter are non-biodegradable and consequently cause environmental pollution.
12. The unbranched hydrocarbon side chains of the detergent molecule are prone to attack by bacteria, so the detergents are bio-degradable and pollution is prevented.

VSA QUESTIONS (1 - MARK QUESTIONS)

1. Write the formula and IUPAC name of aspirin.

   [**Hint :**

   [IUPAC name : 2-Acetoxybenzoic acid.]

2. Name two types of the drugs classified on the basis of pharmacological effect.

3. What is the role of Bithional in toilet soaps?

4. Why is sodium benzoate added to packed containers of jams and pickles?

5. Name the type of drugs having following structural formula :

   [**Hint :** Sulpha Drugs].

6. Why the receptors embedded in cell membrances show selectivity for one chemical messenger over the other?

   [**Hint :** The active site of receptor has specific shape and specific functional groups which can bind only specific messenger which fits in.]

7. With reference to which classification has the statement 'ranitidine is an antacid' been given?

   [**Hint :** Classification based on pharmacological effect.]

8. Give the name of medicine used for the treatment of syphilis.

   [**Hint :** Salvarsan].

9. Give the composition of tincture of iodine.

10. How does aspirin act as analgesic?

    [**Hint :** Aspirin inhibits the synthesis of prostaglandins which cause pain.]

11. Name the antiseptic agents present in dettol.

[**Hint :** Chloroxylenol and Terpineol].

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

[**Hint :** To confirm, beforehand that the patient is not allergic to penicilin.]

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 not form any scum.]

*17. How is acidity cured with cimetidine?

[**Hint. :** Cimetidine prevents the interaction of histamines with the receptors present in stomach wall.]

*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?

(i)

(ii)

[**Hint :** Compound (i) acts as a surface agent because its one end is hydrophobic while the other end is hydrophillic 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.

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

1. What are antihistamines. Give two examples.
2. What are narcotic and non-narcotic analgesics? Give one example of each.
3. Explain the following terms as used in medicinal chemistry :

   (i) Target molecules (ii) Enzyme inhibitors.
4. Give one important use of each of following :

   (i) Equanil (ii) Morphine
5. What are neurologically active drugs. Give two examples.
6. (i) What are antibiotics?

   (ii) What is meant by the term broad spectrum antibiotic?
7. From the given examples ciprofloxacin, phenelzine, morphine, ranitidine. Choose the drug used for

   (i) treating allergic conditions (ii) to get relief from pain
8. Why a drug should not be taken without consulting a doctor? Give two reasons.
9. State the main difference between bacteriostatic and bacteriocidal antibiotics. Give one example of each.
10. What are antifertility drugs? Name the constituents of an oral contraceptive.
11. What do you mean by non-biodegradable detergents? How can we make biodegradable detergents?

*12. If water contains dissolved calcium hydrogencarbonate, which out of soap and detergent, will you prefer to use? Why?

[**Hint :** We will use detergent because it will not form insoluble precipitate with Ca^{2+}]

*13. What are barbiturates? What is the action of barbiturates on human body?

[**Hint :** Barbaturic acid derivatives are called barbiturates. They are highly effective pain relieving agents.]

*14. Write the structures of soaps obtained by the hydrolysis of following fats:

(i) $(C_{15}H_{31}\ COO)_3\ C_3H_5$ Glyceryl palmitate

(ii) $(C_{17}H_{33}\ COO)_3\ C_3H_5$ Glyceryl oleate.

[**Hint :** (i) $C_{15}H_{31}COO^{-}Na^{+}$ (ii) $C_{17}H_{33}COO^{-}Na^{+}$]

SA (II) TYPE QUESTIONS (3 - MARK QUESTIONS)

1. (i) Why are artificial sweeting agents harmless when taken?

   (ii) Name one such artificial sweeting agent.

   (iii) Why is the use of aspartame as an artificial sweetener limited to cold foods?

2. Pick out the odd one amongst the following on the basis of their medicinal properties. Give suitable reason.

   (i) Luminal, seconal, terfenadine, equanil.

   (ii) Chloroxylenol, phenol, chloamphenicol, bithional.

   (iii) Sucralose, aspartame, alitame, sodium benzoate.

   [**Hint :**

   (i) Terfenadine is antihistamine other three are used as tranquilisers.

   (ii) Chloramphenicol is a broad spectrum antibiotic. Other three have antiseptic properties.

   (iii) Sodium benzoate is a food preservative. Other three are artificial sweetners.]

3. Give the main function of following in the body of human beings.

   (i) Enzymes

   (ii) Receptor proteins

   (iii) Neurotransmitter

4. Identify the class of drug :

   (i) Phenelzine (Nardin)

   (ii) Aspirin

   (iii) Cimetidine

5. Give the pharmacological function of the following type of drugs:

   (i) Analgesics

   (ii) Tranquilizers

   (iii) Antifertility drugs

6. Give the name of medicine used in the treatments of following diseases:

(i) Typhoid

(ii) Joint pain (in Arthritis)

(iii) Hypertension

7. Give the class of drugs to which these substances belong :

(i) Bithional

(ii) Amoxycillin

(iii) Salvarsan

8. How are antiseptics different from disinfectants? How does an antibiotic different from these two? Give one example of each of them.

9. Explain the following terms with suitable examples :

(i) Cationic detergents

(ii) Anionic detergents

(iii) Nonionic detergents

*10. Label hydrophilic and hydrophobic part in the following compounds :

(i) $CH_3(CH_2)_{10}CH_2OSO_3^-$ Na+

(ii) $CH_3(CH_2)_{15}N^+(CH_3)_3$ Br^-

(iii) $CH_3(CH_2)_{16}COO$ $(CH_2CH_2O)_n$ CH_2CH_2OH

[**Hint :** (i) $\underbrace{CH_3(CH_2)_{10}CH_2}_{\text{hydrophobic}}$ $\underbrace{OSO_3^-Na^+}_{\text{hydrophilic}}$

(ii) $\underbrace{CH_3(CH_2)_{15}}_{\text{hydrophobic}}$ $\underbrace{N^+ (CH_3)_3 Br^-}_{\text{hydrophilic}}$

(iii) $\underbrace{CH_3(CH_2)_{16}}_{\text{hydrophobic}}$ $\underbrace{COO (CH_2CH_2O)_4 CH_2CH_2OH}_{\text{hydrophobic}}$

*11. Classify the following as cationic detergents, anionic detergents or nonionic detergents:

(i) $CH_3(CH_2)_{10}$ CH_2 OSO_3^- Na^+

(ii) $[CH_3 - (CH_2)_{15} N(CH_3)_3]^+$ Br^-

(iii)

Where (n = 5 – 10)

[**Hint :** (i) Anionic detergent. (ii) Cationic detergent.

(iii) Nonionic detergent.

*12. 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 – It 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.]

MODEL TEST PAPER-I (SOLVED)

(FOR SR. SCHOOL CERTIFICATE EXAMINATION-2012)

Chemistry (Theory)

Time : 3 hours **Total Marks : 70**

General Instruction

(i) *All questions are compulsory.*

(ii) *Question number 1 to 8 are very short answer questions, carrying 1 mark each. Answer these in one word or about one sentence each.*

(iii) *Question number 9 to 18 are short answer questions, carrying 2 marks each. Answer these in about 30 words each.*

(iv) *Question number 19 to 27 are short answer questions, carrying 3 marks each. Answer these in about 40 words each.*

(v) *Question number 28 to 30 are long answer questions, carrying 5 marks each. Answer these in about 70 words each.*

(vi) *Use log table, if necessary.*

(vii) *Use of calculator is not permitted.*

1. Name the non-stoichiometric point defect responsible for colour in alkali metal halides. 1

2. Write the IUPAC name of coordination isomer of the compound

   $[CO(NH_3)_6]\ [Cr(CN)_6]$ 1

3. Write IUPAC name of the following compound

4. Chloroacetic acid has lower pKa value than acetic acid. 1

5. Write the structural formula of N, N–dimethylethanamine. 1

6. What happens when D-glucose is treated with the bromine water? 1

7. How does vulcanisation change the character of natural rubber? 1

8. Differentiate between antagonists and agonists. 1

9. Explain the following terms with suitable examples :–

(i) Non-ionic detergents

(ii) Tranquilizers 2

10. Write the names and structures of the monomers used for getting the following polymers.

(i) PAN

(ii) Nylon-6 2

11. Which one in the following pairs undergoes S_N2 reaction faster and why?

(i)

(ii)

12. Give suitable reasons for the following :

(i) Alkyl halides give cyanides with KCN but isocyanide with AgCN.

(ii) The dipole moment of chlorobenzene is lower than that of cyclohexyl chloride. 2

13. Compare the following complexes with respect to shape and magnetic behaviour

(i) $[Ni(CN)_4]^{2-}$

(ii) $[NiCl_4]^{2-}$ 2

14. Compare the chemistry of actinoids with that of lanthanoids with special reference to

(a) oxidation state

(b) chemical reactivity 2

15. Explain the following terms with a suitable example in each case

(a) Shape selective catalysts 2

(b) electroosmosis

Or

15. Write the difference between

(a) Physisorption and Chemisorption

(b) Catalyst and enzyme 2

16. What type of cell is the lead storage battery? Write the anode and the cathode reactions and the overall reaction occurring in a lead storage battery while operating or in use. 2

17. Account for the following – 2

(a) The vapour pressure of a solution of glucose in water is lower than that of pure water.

(b) Mixture of phenol and aniline shows (–)ve deviation from Raoults law.

18. Write chemical equations for the preparation of sols :

(a) Gold sol by reduction

(b) hydrated ferric oxide sol by hydrolysis 2

19. An element has a bcc structure with a cell edge of 288 pm. The density of the metal is 7.2 g cm^{-3}. How many atoms and unit cells are there in 208g of the element. 3

20. At 300K, two solutions of glucose in water with concentration 0.01M and 0.001 M are separated by semipermeable membrane. On what solution pressure need to be applied to prevent osmosis? Also calculate magnitude of this applied pressure. [R = 0.821 L atm mol^{-1} K^{-1}] 3

21. Calculate the standard cell potential of the galvanic cell in which the following reaction take place :

$$2Cr(s) + 3Cd^{2+}(aq) \longrightarrow 2Cr^{3+}(aq) + 3Cd(s)$$

Also calculate $\Delta_r G°$ value for the reaction.

[Given $E^{\circ}_{Cr^{3+}/Cr} = -0.74\,V$; $E^{\circ}_{Cd^{2+}/Cd} = -0.4\,V$

F = 96500C mol^{-1}]. 3

22. State briefly the principles which serve as basis for the following operations in metallurgy :

(a) Zone refining

(b) Vapour phase refining

(c) Froth floatation process 3

Or

22. Describe the role of the following :

(a) Depressant in froth floatation process

(b) Cryolite in the metallurgy of aluminium

(c) Silica in the extraction of copper from copper pyrities ore. 3

23. Arrange the following in the order of property indicated for each set :

(a) NH_3, PH_3, AsH_3, SbH_3, BiH_3 (Decreasing basic strength)

(b) F_2, Cl_2, Br_2, I_2 (Increasing bond dissociation enthalpy)

(c) H_2O, H_2S, H_2Se, H_2Te (Increasing bond angle) 3

24. Assign reason for the following :

(i) The enthalpies of atomisation of transition elements are high.

(ii) The metallic radii of the third (5d) series of transition elements are virtually the same as those of the corresponding members of the second series.

(iii) With the same d-orbital configuration [d^4] Cr^{2}+ ion is a reducing agent but Mn^{3+} ion is an oxidising agent. 3

25. How will you convert :

(i) Phenol to ethoxybenzene

(ii) butan-2-one to but-2-ene

(iii) 1-propoxypropane to propyl alcohol 3

26. (a) Explain with suitable reasons :

(i) Gabriel phthalimide synthesis is not used for the synthesis of aniline.

(ii) Although amino group is *o*, *p*-directing in aromatic electrophilic substitution reactions, aniline on nitration gives a substantial amount of m-nitroaniline.

(b) Identify the A and B in the following reactions :

$$C_6H_5N_2^+Cl^- \xrightarrow[\text{KCN}]{\text{Cu CN}} A \xrightarrow[\text{Partial hydrolysis}]{H_2O/H^+} B$$

27. (a) How are vitamins classified? Mention the deficiency diseases caused by lack of vitamin A and K.

(b) Write the zwitter ionic form of amino acids. 3

28. (a) List two main differences between order and molecularity of a reaction.

(b) A certain reaction is 50% complete in 20 minutes at 300K and the same reaction is again 50% complete in 5 minutes at 350K. Calculate the activation energy if it is a first order reaction

($R = 8.314\ J\ K^{-1}\ mol^{-1}$; log 4 = 0.6020] 5

Or

28. (a) Justify the statement that for a first order reaction half-life period ($t_{1/2}$) is independent of the initial concentration of the reactant.

(b) For a chemical reaction at 800°C, $2NO + 2H_2 \longrightarrow N_2 + 2H_2O$ the following data were obtained.

[NO] × 10^{-4} mol L^{-1}	*[H_2] × 10^{-3} mol L^{-1}*	*Initial rate (mol L^{-1} s^{-1})*
1.5	4.0	4.4 × 10–4
1.5	2.0	2.2 × 10–4
0.5	2.0	0.24 × 10–4

What is the order of reaction w.r.t. NO and H_2? Also calculate the rate constant at 800°C. 5

29. (a) Assign reasons for the following :

(i) H_3PO_2 and H_3PO_3 act as good reducing agents while H_3PO_4 does not.

(ii) ICl is more reactive than I_2.

(iii) H_2S is less acidic than H_2Te.

(b) Draw the structure of

(i) $XeOF_4$

(ii) $H_2S_2O_7$ 5

Or

29. (a) Complete the following chemical equations

(i) $P_4(s) + NaOH\ (aq) + H_2O\ (l) \longrightarrow$

(ii) $I^-\ (aq) + H_2O(l) + O_3\ (g) \longrightarrow$

(b) Assign a reason for each of following :

(i) Bi(V) is a stronger oxidising agent than Sb(V).

(ii) Fluorine does not exhibit any positive oxidation state.

(iii) In solution of H_2SO_4 in water, the second dissociation constant Ka_2 is less than the first dissociation constant K_{a1}.

30. (a) Describe the following reactions

(i) Cannizzaro reaction

(ii) Cross Aldol condensation

(b) Give chemical tests to distinguish between :

(i) Phenol and benzoic acid

(ii) Acetophenone and benzophenone

(c) Arrange the following in increasing order of acid strengths :

$(CH_3)_2CHCOOH$, $CH_2CH_2CH(Br)\ COOH$, $CH_3CH(Br)CH_2COOH$ 5

Or

30. An organic compound (A) $C_5H_{10}O$ gives positive 2, 4-DNP Test. It does not reduce Tollens' reagent but forms an addition compound with sodium hydrogen sulphite. On reaction with iodine in presence of sodium hydroxide, yellow precipitate B and another compound C is formed. On oxidation with $KMnO_4$ it forms two acids D and E. Identify A, B, C, D and E.

MARKING SCHEME

Q. No.	*Value Points*	*Marks*
1.	F–Center or Metal excess defect	1
2.	$[Cr(NH_3)_6]$ $[Co(CN)_6]$ Hexaamminechromium (III) hexacyanocobatate (III)	1
3.	4-Phenylbut-2-en-1–ol	1
4.	Chloroacetic acid is stronger acid than acetic acid due to –I effect of chlorine atom. Therefore, it has lower pk_a value.	1
5.	$CH_3—CH_2—N(CH_3)—CH_3$	1
6.	Gluconic acid	1
7.	In vulcanisation, sulphur forms cross links at the reactive sites of double bonds and thus the rubber gets stiffened.	1
8.	Drugs that bind to the receptor site and inhibit its natural function, are called antagonists. Drugs that mimic the natural messenger by switching on receptor, are called agonists.	1
9.	(a) Non-ionic detergents do not contain any ion in their constitution. One such detergent is formed when stearic acid reacts with polyethylene glycol.	1

1

(b) Tranquilizers are a class of chemical compounds used for the treatment of stress, and mild or even severe mental diseases, e.g., chlordiazepoxide and meprobamate. 1

10. (a) $CH_2 = CH - CN$

(Acrylonitrile)

(b)

(Caprotactum)

11. (a)

As iodine is a better leaving group because of its large size, It will be released at a faster rate in the presence of incoming nucleophile. 1

(b)

It is primary halide and therefore undergoes SN2 reaction faster. 1

12. (a) KCN is ionic compound and produces CN^-, so it combines with RX and gives cyanides as major product because of higher bond enthalpy of C–C bond than that of C – N bond, while with AgCN it gives isocyanide due to convalent nature of Ag-C bond by attacking through N atom. 1

(b) In chlorobenzene carbon is sp^2 hybridised while in cyclohexane it is sp^3 hybridised. Due to the more electronegativity difference in cyclohexyl chloride, its dipole moment is higher than that of chlorobenzene. 1

13. (a) $[Ni(CN)_4]^{2-}$

Ni_{28} $[Ar]^{18}$ $4s^2$ $3d^8$

Ni(II) $[Ar]^{18}$ $3d^8$

dsp^2 hydridization 1
(Square Planar)
(Diamagnetic)

(b) $[NiCl_4]^{2-}$

Ni_{28} $[Ar]^{18}$ $4s_2$ $3d^8$

Ni (II) $[Ar]^{18}$ $3d^8$

sp^3 hydridization 1
tetrahedral
(paramagnetic)

14. (a) All the lanthanoids exhibit a common stable oxidation state of +3. In addition some lanthanoids also show oxidation states of +2 and +4 where L_n^{2+} and L_n^{4+} have more stable 4f°, $4f^7$ or $4f^{14}$ confiquration. Members of the actinoids family exhibit more variable oxidation states as compared to the elements belonging to lanthanoids. 1

(b) Actinoids are more reactive than lanthanoids due to bigger size.1

15. (a) Zeolites are known as shape selective catalysts, because their activity depends on pore size and shape and size of reactant and product molecules. 1

(b) Electroosmosis : When the movement of colloidal particles is prevented by some suitable means, it is obsvered that the dispersion medium begins to move in an electric field. This phenomenon is called electroosmosis. 1

Or

15. (a) Physisorption have weak van der Waal attraction forces while in chemisorption there are stronger chemical bonds [40 kJ to 200 kJ/mol.] 1

(b) Almost all the enzymes are globular proteins and used as biochemical catalyst while catalysts are chemical substance used for increasing the rate of chemical reactions. 1

16. (a) Lead storage battery is a secondary battery. ½

Anode : $Pb(s) + SO_4^{2-}(aq) \longrightarrow PbSO_4(s) + 2e^-$ ½

Cathode : $PbO_2(s) + SO_4^{2-}(aq) + 4H^+(aq) + 2e^- \longrightarrow PbSO_4(l) + 2H_2O(l)$ ½

Overall reaction :

$Pb(s) + PbO_2(s) + 4H^+(aq) + 2SO_4^{2-}(aq) \longrightarrow 2PbSO_4(s) + 2H_2O(l)$

½

17. (a) Vapour pressure of pure water gets decreased by addition of nonvolatile glucose, which covers some surface area and lesser surface area is available for vapourisation of water molecules. 1

(b) In this case the intermolecular hydrogen bonding between phenolic proton and lone pair on nitrogen atom of anline is stronger than the respective intermolecular hydrogen bonding between similar molecules. 1

18. (a) $2\,AuCl_3 + 3SnCl_2 \longrightarrow 3SnCl_4 + 2Au$ (Gold sol). 1

(b) $FeCl_3 + 3H_2O \longrightarrow \underset{\text{sol}}{Fe_2O_3.XH_2O} + 3HCl$ 1

19. Volume of the unit cell = $(288 \times 10^{-10}\ cm)^3$
$= 2.39 \times 10^{-23}\ cm^3$

Volume of 208 g of the element $= \dfrac{\text{Mass}}{\text{Density}} = \dfrac{208g}{7.2g\ cm^{-3}}$ 1

$= 28.88\ am^3$

No. of unit cells $= \dfrac{28.88\ cm^3}{2.39 \times 10^{-23}\ cm^3/\text{unit cell}}$ 1

$= 12.08 \times 10^{23}$ unit cells

Since the unit cell is bcc therefore, number of atoms per unit cell is 2

Total number of atoms in 208 of element $= 2 \times 12.08 \times 10^{23}$ 1

$= 24.16 \times 10^{23}$

20. (a) For 0.01 M solution

$\pi_1 = C_1RT$

$\pi_1 = 0.01 \times 0.0821 \times 300 = 0.2463$ atm. 1

For 0.001 M solution.

$\pi_2 = 0.001 \times 0.0821 \times 300$

$= 0.02463$ atm. .

(b) The solvent particles pass from dilute to concentrate solution, i.e., from 0.001M to 0.01 M solution. Therefore, pressure should be applied on 0.01m solution to prevent osmosis. ½

(c) The magnitude of pressure applied = 0.2463 atm
1

21. $Cr \mid Cr^{3+} \parallel Cd^{2+} \mid Cd$

$E^{\theta}_{cell} = E^{\theta}_{R} - E^{\theta}_{L}$

$= -V0.4V - (-V0.74V) = 0.34$ V 1

$\therefore \Delta G^{\circ} = -nF\ E^{\theta}_{cell}$

$\Delta G^{\circ} = -6 \times 96500\ C\ mol^{-1} \times 0.34\ V = -6 \times 96500 \times 0.34$

$CV\ mol^{-1}$ 1

$\Delta G^{\circ} = -196860\ J\ mol^{-1}$

$\Delta G^{\circ} = -196.86\ kJ\ mol^{-1}$ 1

22. (a) **Zone Refining :** Impure metal rod is heated with circular heater from one end. The metal melts and on cooling the pure metal gets solidified while impurities go into the molten zone. 1

(b) **Vapour Phase Refining :** The metal is converted to a volatile compound which on further heating breaks down to give pure metal.

$$Ni\ (s) + 4CO\ (g) \xrightarrow[300-350]{} \underset{\left(\text{Volatitle compound}\right)}{Ni\ (CO)_4}$$

$$Ni\ (CO)_4\ (g) \xrightarrow{450-700\ K} Ni\ (s) + 4CO$$ 1

(c) Froth Floatation Process : In this process sulphide ore particles are wetted with oil and rise to the surface along with the froth and are separated. The earthy matter wetted by water settles down at the bottom. 1

Or

22. (a) Depressant prevents the formation of froth of one ore in a mixture of two sulphide ores. 1

(b) Cryolite is added to lower the melting point of the mix and brings conductivity. 1

(c) Silica is used for removal of FeO as slag, $FeSiO_3$ in the metallurgy of copper. 1

23. Arrangement of the following compound in the order of property indicated for each set.

(a) $NH_3 > PH_3 > AsH_3 > SbH_3 > BiH_3$ [Decreasing basic strength] 1

(b) $I_2 < F_2 < Br_2 < C^{l2}$ [Increasing bond dissociation enthalpy] 1

(c) $H_2Te < H_2Se < H_2S < H_2O$ [Increasing bond angle] 1

24. (a) Strong M–M interactions due to participation both ns and (n – 1) d electrons, the enthalpies of atomisation of transition elements are high. 1

(b) Due to lanthanoid contraction the sizes of 5d series do not increase and remain almost the same as corresponding members of 4d series. 1

(c) Cr^{2+} is reducing agent because $E^{\varnothing}_{Cr^{3+}/Cr^{2+}}$ is negative. This is because of stable. configuration of Cr^{3+} ion. On the other hand $E^{\varnothing}_{Mn^{3+}/Mn^{2+}}$ is positive due to extra stability of Mn^{2+} which has [Ar] $3d^5$ configuration. 1

25. (a)

(b)

(c) $CH_3CH_2CH_2O\ CH_2CH_2CH_3 \xrightarrow[\text{Excess}]{HI} 2\ CH_3CH_2CH_2I$

$$\downarrow \text{Aq. KOH}$$

$$2\ CH_3CH_2CH_2OH$$

26. (a) Ar–X does not exhibit nucleophilic substitution reaction readily due to partial double bond character of C – X bond, therefore $ArNH_2$ cannot be prepared by Gabriel phthalimide process. 1

(b) Amino group is *o, p*–directing towards electrophilic substitution reaction but due to the formation of anilinium ion $–N^+H_3$ it gives *m*–product also. 1

(c)

1

27. (a) Vitamins are broadly classified as water soluble and fat soluble vitamins,

Water soluble : B, C

Fat soluble : A, D, E and K 1

Deficiency disease of vitamin A is night blindness

Deficiency disease of Vitamin K is increases blood clotting time.

½ × 2

(b)

28. (a)

Order of Reaction	*Molecularity of Reaction*	
Order of reaction corresponds to sum of. the exponents to which the concentration terms is raised in rate law expression.	Molecularity corresponds to no. of reacting species in elementary reaction.	
It may be zero.	It can never be zero.	
It may be fractional.	It can never be fractional	
It is experimentally determined.	It is a theoretical term.	½ × 4

(b) $k = \frac{0693}{t_{\frac{1}{2}}} \Rightarrow k_1 = \frac{0693}{20 \text{ min}} = 0.03465 \text{ min}^{-1}$ ½

$$k_2 = \frac{0693}{5 \text{ min}} \quad 0.1386 \text{ min}^{-1}$$

$$\log \frac{k_2}{k_1} = \frac{E_a}{2.303R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

$$\log\left[\frac{0.1386}{0.03465}\right] = \frac{E_a}{2.303 \times 8.314 \text{ JK}^{-1} \text{ mol}^{-1}} \times \left(\frac{1}{300\text{K}} - \frac{1}{350\text{K}}\right)$$

1

$E_a = 24205.8 \text{ J mol}^{-1} = 24.2 \text{ kJ mol}^{-1}$ ½

Or

28. (a) As per first order integrated rate law

$$t = \frac{2.303}{k} \log \frac{[A]_0}{[A]}$$

half-life period $t = t_{1/2}$

when $[A] = \frac{[A]_0}{2}$

$$\Rightarrow t_{1/2} \frac{2.303}{k} \log \frac{[A]_0}{[A_0]} \times 2$$

$$\Rightarrow \quad t_{1/2} \quad \frac{2.693}{k}$$

It means half life period (t1/2) is independent of the initial concentration. 2

(b) According to data using in a hypothetical equation :
Rate = $k[NO]^x [H_2]^y$

$Rate_1 = 4.4 \times 10^{-4} = k\ [1.5]^x\ [4.0]^y$

$Rate_2 = 2.2 \times 10^{-4} = k\ [1.5]^x\ [2.0]^y$

$Rate_3 = 0.24 \times 10^{-4} = k\ [0.5]^x\ [2.0]^y$

Compare $Rate_1$ with $Rate_2$

$$\frac{Rate_1}{Rate_2} = \frac{4.4 \times 10^{-4}}{2.2 \times 10^{-4}} = \frac{k\,[1.5]^x\,[4.0]^y}{k\,[1.5]^x\,[2.0]^y}$$

$2 = (2)^y$

$y = 1$

Similarly by comparing $Rate_2$ and $Rate_3$

$3^x = 3^2 \quad \Rightarrow \quad x = 2$

Rate = $k\ [NO]^2\ [H_2]^1$

$0.24 \times 10^{-4} = k[0.5]^2 \times [2.0]^1$

$k = 4.88 \times 10^{-8}\ mol^{-2}\ litre^2\ min^{-1}$ 1

29. (a) (i) H_3PO_4 exhibit +5 oxidation state which is highest oxidation state for phosphorus, so it does not act as a good reducing agent and also no H is directly attached to P atom. 1

(ii) I–Cl bond is weaker than I – I bond because the extent of overlapping is less. 1

(iii) In H_2Te, H–Te bond is weaker than H–S bond in H_2S. So it is more acidic than H_2S. 1

(b) (i)

(ii)

29. (a) (i) $P_4 + 3NaOH + 3H_2O \longrightarrow PH_3 + 3NaH_2PO_2$ 1

(ii) $2I^- (aq) + H_2O(l) + O_3(g) \longrightarrow 2OH^- + I_2(s) + O_2(g)$ 1

(b) (i) Bi(V) is stronger oxidising agent due to greater magnitude of inert pair effect as compared to Sb(V) because of more diffused 4f orbitals present in bismuth. 1

(ii) Fluorine always exhibits –1 oxidation state due to its highest electronegativity (4.0) in the periodic table. 1

(iii) First ionisation of H_2SO_4 to H_3O^+ and HSO_4^- occurs almost completely. The ionisation of HSO_4^- to H_3O^+ and SO_4^{2-} is very difficult because HSO_4^- in an ionic species. That is why $K_{a2} << K_{a1}$. 1

30. (a) (i) Cannizzaro reaction

$HCHO + HCHO + \text{conc. } KOH \longrightarrow CH_3OH + HCOOK$ 1

(ii) Cross Aldol Condensation

1

(b)

	Phenol	*Benzoic acid*	
(i)	It does not react with $NaHCO_3$ solution	It gives brisk effervescence of CO_2 gas.	1
(ii)	**Acetophenone** Add NaOH and I_2 $\xrightarrow{heat}$ yellow coloured ppt. of CHI_3 is formed.	**Benzophenone** Add NaOH and I_2 $\xrightarrow{heat}$ No ppt. is formed	1

(c) Increasing order of acid strengths. $(CH_3)_2CHCOOH$ <

$CH_3CH(Br)CH_2COOH$ < $CH_3CH_2\underset{\underset{Br}{|}}{C}H—COOH$

Or

30. $CH_3—CH_2—CH_2—\overset{\overset{O}{\|}}{C}—CH_3$ (A)

$\xrightarrow[\text{NaOH/I}_2]{\text{heat}}$

$\underset{\text{yellow ppt (B)}}{CHI_3}$ + $\underset{\text{(C)}}{CH_3CH_2CH_2COONa}$ 1

$CH_3CH_2CH_2\overset{\overset{O}{\|}}{C}—CH_3$ (A)

$\xrightarrow{\text{oxidation}}$

$\underset{\text{(D)}}{CH_3CH_2\underset{\underset{O}{\|}}{C}—OH}$ + $\underset{\text{(E)}}{CH_3—\underset{\underset{O}{\|}}{C}—OH}$ 2

MODEL TEST PAPER-II

Chemistry (Theory)

Time : 3 hours **Total Marks : 70**

General Instruction

(i) *All questions are compulsory.*

(ii) *Question number 1 to 8 are very short answer questions, carrying 1 mark each. Answer these in one word or about one sentence each.*

(iii) *Question number 9 to 18 are short answer questions, carrying 2 marks each. Answer these in about 30 words each.*

(iv) *Question number 19 to 27 are short answer questions, carrying 3 marks each. Answer these in about 40 words each.*

(v) *Question number 28 to 30 are long answer questions, carrying 5 marks each. Answer these in about 70 words each.*

(vi) *Use log table, if necessary.*

(vii) *Use of calculator is not permitted.*

1. 'Crystalline solids are anisotropic in nature.' What does this statement mean?

2. Express the relation between conductivity and molar conductivity of a solution held in a cell.

3. Define 'electrophoresis.'

4. Draw the structure of XeF_2 molecule.

5. Write the IUPAC name of the following compound : $(CH_3)_3\ CCH_2Br$

6. Draw the structure of 3-methylbutanal.

7. Arrange the following compounds in an increasing order of their solubility in water : $C_6H_5NH_2$, $(C_2H_5)_2NH$, $C_2H_5NH_2$

8. What are biodegradable polymers?

9. The chemistry of corrosion of iron is essentially an electrochemical phenomenon. Explain the reactions occurring during the corrosion of iron in the atmosphere.

10. Determine the values of equilibrium constant (K_C) and Go for the following reaction :

$$Ni(s) + 2Ag^+ (aq) \longrightarrow Ni^{2}+(aq) + 2Ag(s),\ E^{\theta} = 1.05\ V$$

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

11. Distinguish between 'rate expression' and 'rate constant' of a reaction.

12. State reasons for each of the following :

(i) The N – O bond in NO_2^- is shorter than the N – O bond in NO_3^-.

(ii) SF_6 is kinetically an inert substance towards hydrolysis.

OR

State reasons for each of the following :

(i) All the P-Cl bonds in PCl_5 molecule are not equivalent.

(ii) Sulphur has greater tendency for catenation than oxygen.

13. Assign reasons for the following :

(i) Copper (I) ion is not known in aqueous solution.

(ii) Actinoids exhibit greater range of oxidation states than lanthanoids.

14. Explain the following giving one example for each :

(i) Reimer-Tiemann reaction

(ii) Friedel – Craft's acetylation of anisole.

15. How would you obtain

(i) Picric acid (2, 4, 6-trinitrophenol) from phenol,

(ii) 2-Methylpropene from 2-methylpropanol?

16. What is essentially the difference between α form of glucose and β form of glucose? Explain.

17. Describe what you understand by primary structure and secondary structure of proteins.

18. Mention two important uses of each of the following :

(i) Bakelite (ii) Nylon 6

19. Silver crystallizes in face-centered cubic unit cell. Each side of this unit cell has a length of 400 pm. Calculate the radius of the silver atom. (Assume the atoms just touch each other on the diagonal across the face of the unit cell. That is each, face atom is touching the four corner atoms.)

20. Nitrogen pentoxide decomposes according to equation : $2N_2O_5(g) \longrightarrow 4\ NO_2(g) + O_2(g)$.

This first order reaction was allowed to proceed at 40 °C and the data below were collected :

$[N_2O_5]$/M	(M) Time/(min)
0.400	0.00
0.289	20.0
0.209	40.0
0.151	60.0
0.109	80.0

(a) Calculate the rate constant. Include units with your answer.

(b) What will be the concentration of N_2O_5 after 100 minutes?

(c) Calculate the initial rate of reaction.

21. Explain how the phenomenon of adsorption finds application in each of the following processes:

(i) Production of vacuum

(ii) Heterogeneous catalysis

(iii) Froth Floatation process

OR

Define each of the following terms :

(i) Micelles

(ii) Peptization

(iii) Desorption

22. Describe the principle behind each of the following processes :

(i) Vapour phase refining of a metal.

(ii) Electrolytic refining of a metal.

(iii) Recovery of silver ore was leached with NaCN.

23. Complete the following chemical equations :

(i) $MnO_4^- + C_2O_4^{2-} + H^+ \longrightarrow$

(ii) $KMnO_4 \xrightarrow{\text{heat}}$

(iii) $Cr_2O_7^{2-} + H_2S + H^+ \longrightarrow$

24. Write the name, stereochemistry and magnetic behaviour of the following: (At.nos. Mn = 25, Co = 27, Ni = 28)

(i) K_4 $[Mn(CN)_6]$

(ii) $[Co(NH_3)_5$ Cl] Cl_2

(iii) K_2 $[Ni(CN)_4]$

25. Answer the following :

(i) Haloalkanes easily dissolve in organic solvents, why?

(ii) What is known as a racemic mixture? Give an example.

(iii) Of the two bromoderivatives,
$C_6H_5CH(CH_3)Br$ and $C_6H_5CH(C_6H_5)$ Br,
which one is more reactive in S_N1 substitution reaction and why?

26. (a) Explain why an alkylamine is more basic than ammonia.

(b) How would you convert

(i) Aniline to nitrobenzene

(ii) Aniline to iodobenzene?

27. Describe the following giving one example for each :

(i) Detergents

(ii) Food preservatives

(iii) Antacids

28. (a) Differentiate between molarity and molality for a solution. How does a change in temperature influence their values?

(b) Calculate the freezing point of an aqueous solution containing 10.50 g of $MgBr_2$ in 200 g of water. (Molar mass of $MgBr_2$ = 184 g mol^{-1}).

K_f for water = 1.86 K kg mol^{-1})

OR

(a) Define the terms osmosis and osmotic pressure. Is the osmotic pressure of a solution a colligative property? Explain.

(b) Calculate the boiling point of a solution prepared by adding 15.00 g of NaCl to 250.0 g of water. (K_b for water = 0.512 K kg mol^{-1},

Molar mass of NaCl = 58.44 g mol^{-1}

29. (a) Given chemical tests to distinguish between

(i) propanal and propanone,

(ii) benzaldehyde and acetophenone.

(b) How would you obtain

(i) but-2-enal from ethanal,

(ii) butanoic acid from butanol,

(iii) benzoic acid from ethylbenzene?

OR

(a) Describe the following giving linked chemical equations :

(i) Cannizzaro reaction

(ii) Decarboxylation

(b) Complete the following chemical equations :

(i)

(ii)

(iii) $C_6H_5CONH_2 \xrightarrow[\text{heat}]{H_3O^+}$

30. (a) Explain the following :

(i) NF_3 is an exothermic compound whereas NCl_3 is not.

(ii) F_2 is most reactive of all the four common halogens.

(b) Complete the following chemical equations :

(i) $C + H_2SO_4 \text{ (conc)} \longrightarrow$

(ii) $P_4 + NaOH + H_2O \longrightarrow$

(iii) $Cl_2 + \underset{\text{(excess)}}{F_2} \longrightarrow$

OR

(a) Account for the following :

(i) The acidic strength decreases in the order $HCl > H_2S > PH_3$

(ii) Tendency to form pentahalides decreases down the group in group 15 of the periodic table.

(b) Complete the following chemical equations :

(i) $P_4 + SO_2Cl_2 \longrightarrow$

(ii) $XeF_2 + H_2O \longrightarrow$

(iii) $I_2 + \underset{\text{(conc)}}{HNO_3} \longrightarrow$

MODEL TEST PAPER (III)

Chemistry (Theory)

Time : 3 hours **Total Marks : 70**

General Instruction

(i) *All questions are compulsory.*

(ii) *Question number 1 to 8 are very short answer questions, carrying 1 mark each. Answer these in one word or about one sentence each.*

(iii) *Question number 9 to 18 are short answer questions, carrying 2 marks each. Answer these in about 30 words each.*

(iv) *Question number 19 to 27 are short answer questions, carrying 3 marks each. Answer these in about 40 words each.*

(v) *Question number 28 to 30 are long answer questions, carrying 5 marks each. Answer these in about 70 words each.*

(vi) *Use log table, if necessary.*

(vii) *Use of calculator is not permitted.*

1. Wirte a point of distinction between a metallic solid and an ionic solid other than metallic lustre. 1

2. Which one of PCl_4^+ and PCl_4^- is not likely to exist and why? 1

3. What is the role of graphite in the electrometallurgy of aluminium? 1

4. Arrange the following compounds in an increasing order of their reactivity in mucleophilic addition reactions : ethanal, propanal, propanone, butanone.

5. Draw the structural formula of 2-methylpropan -2-ol molecule. 1

6.

   Give the IUPAC name of the following compound.

7. Define the term, 'homopolymerisation' giving an example.

8. Arrange the following in the dereaing order of their basic strength in aqueous solutions.

   CH_3NH_2, (CH_3) NH, $(CH_3)_3$ and NH_3

9. A 1.00 molal aqueous solution of trichloroacetic acid (CCl_3COOH) is heated to its boiling point. The solution has the boiling point of 100.18 °C. Determine the van't Hoff factor for trichloroacetic acid. (K_b for water = 0.512 K kg mol^{-1})

OR

Define the following terms :

(i) Mole fraction

(ii) Isotonic solutions

(iii) Van't Hoff factor

(iv) Ideal solution

11. Describe a conspicuous change observed when

(i) a solution of NaCl is added to a sol of hydrated ferric oxide.

(ii) a beam of light is passed through a solution of NaCl and then through a sol.

12. What is meant by caugulation of a colloidal solution? Describe briefly any three methods by which coagulation of lyophobic sols can be carried out.

13. Describe the following :

(i) The role of cryolite in electro metallurgy of aluminium.

(ii) The role of carbon monoxide in the refining of crude nickel.

14. What is meant by (i) peptide linkage (ii) biocatalysts?

15. Explain the following giving an appropriate reason in each case.

(i) O_2 and F_2 both stabilize higher oxidation states of metals but O_2 exceeds F_2 in doing so.

(ii) Structures of Xenon fluorides cannot be explained by Valence Bond approach.

16. Complete the following chemical equations :

(i) $Cr_2O^2{}_7 + H^+ + I^- \longrightarrow$

(ii) $MnO_4^- + NO_2^- + H^+ \longrightarrow$

17. Draw the structure of the monomer for each of the following polymers :

(i) Nylon 6

(ii) Polypropene

18. Write the main structural difference between DNA and RNA. Of the two bases, thymine and uracil, which one is present in DNA?

19. Tungsten crystallizes in body centred cubic unit cell. If the edge of the unit cell is 316.5 pm, what is the radius of tungsten atom?

OR

Iron has a body centred cubic unit cell with a cell dimension of 286.65 pm. The density of iron is 7.874 g cm^{-3}. Use this information to calculate Avogadro's number. (At mass of Fe=55.845u).

20. A solution of glycerol ($C_3H_3O_3$) in water was prepared by dissolving some glycerol in 500 g of water. This solution has a boiling point of 100.42 °C while pure water boils at 100°C. What mass of glycerol was dissolved to make the solution?

(K_b for water = 0.512 K kg mol^{-1})

21. For reaction

$$2NO_{(g)} + Cl_{2(g)}\ 2NOCl_{(g)}$$

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

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	2.40
4	0.25	0.25	?

(a) Write the expression for rate law.

(b) Calculate the value of rate constant and specify its units.

(c) What is the initial rate of disappearnce of Cl_2 in exp. 4?

22. State a reason for each of the following situations :

(i) Co^{2+} is easily oxidized to Co^{3+} in presence of a strong ligand.

(ii) CO is a stronger complexing reagent than NH_3.

(iii) The molecular shape of $Ni(CO)_4$ is not the same as that of $[Ni(CN)_4]^{2-}$

23. How would you account for the following?

(i) With the same d-orbital configuration (d^4) Cr^{2+} is a reducing agent while Mn^{3+} is an oxidizing agent.

(ii) The actionoids exhibit a larger number of oxidation states than the corresponding members in the lanthanoid series.

(iii) Most of the transition metal ions exhibit characteristic in colours in aqueous solutions.

24. Write chemical equations for the following onversions :

(i) nitrobenzene to benzonic acid.

(ii) benzyl chloride to 2-phenylethanamine.

(iii) aniline to benzyl alcohol.

25. What ate the following substances? Give one example of each one of them.

(i) Tranquilizers

(ii) Food preservatives

(iii) Synthetic detergents

26. Draw the structure and name the product formed if the following alcohols are oxidized. Assume that an excess of oxidizing agent is used.

(i) $CH_3CH_2CH_2CH_2OH$

(ii) 2-butenol

(iii) 2-methyl-1-propanol

27. Although chlorine is an electron withdrawing group, yet it is ortho-, para-directing in electrophilic aromatic substitution reaction. Explain why it is so? 3

28. (a) complete the following chemical reaction equations :

(i) $P_4 + SO_2Cl_2 \longrightarrow$

(ii) $XeF_6 + H_2O \longrightarrow$

(b) Predict the shape and the asked angle (90° or more or less) in each of the following cases :

(i) SO_3^{2-} and the angle O – S – O

(ii) ClF_3 and the angle F – Cl – F

(iii) XeF_2 and the angle F – Xe – F

OR

(a) Complete the following chemical equations :

(i) $NaOH + Cl_2 \longrightarrow$ (hot and conc.)

(ii) $XeF_4 + O_2F_2 \longrightarrow$

(b) Draw the sturcture of the following molecules :

(i) H_3PO_2

(ii) $H_2S_2O_7$

(iii) $XeOF_4$

29. (a) What type of a batter is lead storage batter? Write the anode and the cathode reactions and the overall reaction occurring in a lead storage batter when current is drawn from it.

(b) In the button cell, widely used in watches, the following reaction takes place

$$Zn_{(s)} + Ag_2O_{(s)} + H_2O(l) \rightarrow Zn^{2+}_{(aq)} + 2Ag_{(s)} + 2OH^-_{(aq)}$$

Determine E^θ and $\Delta G°$ for the reaction.

(given : $E^\circ_{Ag^+/Ag} = +0.80\,V$; $E^\circ_{Zn^{2+}/Zn} = -0.76\,V$

OR

(a) Define molar conductivity of a solution and explain how molar conductivity changes with change in concentration of solution for a weak and a strong electrolyte.

(b) The resistance of a conductivity cell containing 0.001 M KCl solution at 298 K is 1500 Ω. What is the cell constant if the conductivity of 0.001 M KCl solution at 298 K is 0.146×10^{-3} S cm^{-1}?

30. Give a plausible explanation for each one of the following :

(i) There are two – NH_2 groups in semicarbazide. However, only one such group is involved in the formation of semicarbazones.

(ii) Cyclohexanone forms cyanohydrin in good yield but 2, 4, 6–trimethylcyclohexanone does not.

(b) An organic compound with molecular formula $C_9H_{10}O$ forms 2, 4, –DNP derivative, reduces Tollens' reagent and undergoes Cannizzaro's reaction. On vigorous oxidation it gives 1, 2-benzenedicarboxylic acid. Idenfify the compound.

OR

(a) Give chemical tests to distinguish between

(i) phenol and benzoic acid

(ii) benzophenone and acetophenone

(b) Write the structures of the main products of following reactions :

(i)

(ii) $H_3C - C \equiv C - H \xrightarrow[]{Hg^{2+},\ H_2SO_4}$

(iii)

CHEMISTRY

SET I

Time : 3 Hrs. **Max Marks : 70**

General Instructions

1. All questions are compulsory.
2. Question nos. 1 to 8 are very short answer questions and carry 1 mark each.
3. Question nos. 9 to 18 are short answer questions and carry 2 marks each.
4. Question nos. 19 to 27 are also short answer questions and carry 3 marks each.
5. Question nos. 28 to 30 are long answer questions and carry 5 marks each.
6. Use log tables if necessary, use of calculators is not allowed.

(1) Why is ferric chloride preferred over potassium chloride in case of a cut, leading to bleeding? 1

(2) Why does a tetrahedral complex of the type $[MA_2 B_2]$ not show geometrical isomerism? 1

(3) How do you account for the miscibility of ethoxyethane with water. 1

(4) Give the IUPAC name of the organic compound

$$(CH_3)_2 C = CH - \underset{\underset{O}{\|}}{C} - CH_3$$

(5) Name the monomers of nylon 2 or nylon 6 polymer. 1

(6) Give one example of an artificial sweetener used by the diabetic patients. 1

(7) Direct nitration of aniline is not carried out. Explain why? 1

(8) What type of linkage holds together the monomers of D.N.A.? 1

(9) Examine the illustration of a portion of the defective crystal given below and answer the following questions.

(i) What are these type of vacancy defects called?
(ii) How is the density of a crystal affected by these defects?
(iii) Name one ionic compound which can show this type of defect in the crystalline state.
(iv) How is the stoichiometry of the compound affected? 2

10. Analysis shows that a metal oxide has the empirical formula $M_{0.96} O_{1.00}$. Calculate the percentage of M^{2+} and M^{3+} ions in this crystal? 2

OR

In an ionic compound the anion (N^-) form cubic close type of packing. While the cation (M^+) ions occupy one third of the tetrahedral voids. Deduce the empirical formula of the compound and the coordination number of (M^+) ions. 2

11. Given below is the sketch of a plant for carrying out a process.

(i) Name the process occurring in the above plant.
(ii) To which container does the net flow of solvent take place?
(iii) Name one SPM which can be used in this plant.
(iv) Give one practical use of the plant. 2

12. Write the chemical equations for all the steps involved in the rusting of iron. Give any one method to prevent rusting of iron. 2

13. A metal ion M^{n+} having d^4 valence electronic configuration combines with three didentate ligands to form a complex compound. Assuming $D_o > P$
(i) Draw the diagram showing d orbital splitting during this complex formation.
(ii) Write the electronic configuration of the valence electrons of the metal M^{n+} ion in terms of t_{2g} and e_g.
(iii) What type of hybridisation will M^{n+} ion have?
(iv) Name the type of isomerism exhibited by this complex. 2

14. A mixed oxide of iron and chromium $FeO.Cr_2O_3$ 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 oxidising agent. Identify

(i) The compounds (A) and (B).

(ii) Write balanced chemical equation for each step. 2

15. An optically active compound having molecular formula $C_7H_{15}Br$ reacts with aqueous KOH to give a racemic mixture of products. Write the mechanism involved for this reaction. 2

16. Write the formula of main product formed in the following chemical reactions.

(i) $2(CH_3)_2\ CH\text{-}Cl \xrightarrow[\text{dry ether}]{Na}$

(ii) $CH_3Br + AgF \xrightarrow{\Delta}$

(iii) $CH_3CH_2Br + NaI \xrightarrow{\text{dry acetone}}$

(iv)

2

17. Differentiate the following pair of polymers based on the property mentioned against each.

(i) Novolac and Bakelite (structure).

(ii) Buna-S and Terylene (intermolecular forces of attraction). 2

18. In order to wash clothes with water containing dissolved calcium hydrogen carbonate, which cleaning agent will you prefer and why: soaps or synthetic detergents? Give one advantage of soaps over synthetic detergents. 2

19. Heptane and octane form an ideal solution at 373 K, The vapour pressures of the pure liquids at this temperature are 105.2 kPa and 46.8 kPa respectively. If the solution contains 25g of heptane and 28.5g of octane, calculate,

(i) vapour pressure exerted by heptane.

(ii) vapour pressure exerted by solution.

(iii) mole fraction of octane in the vapour phase. 3

20. The following chemical reaction is occurring in an electrochemical cell.

$Mg_{(s)} + 2\ Ag^+_{0.0001\ M}$ ® $Mg^{2+}_{0.10M} + 2\ Ag_{(s)}$

The E^0 electrode values are

$Mg^{2+} / Mg = -2.36$ V

$Ag^+ / Ag = 0.81$ V

For this cell calculate / write

(a) (i) E^0 value for the electrode: $2Ag^+ / 2Ag$

(ii) Standard cell potential, E^0_{cell}.

(b) Cell potential $(E)_{cell}$.

(c) (i) Symbolic representation of the above cell.

(ii) Will the above cell reaction be spontaneous? 3

21. Consider the adsorption isotherms given below and interpret the variation in the extent of adsorption (x/m) when,

(a) (i) temperature increases at constant pressure

(ii) pressure increases at constant temperature

(b) Name the catalyst and the promoter used in Haber's process for the manufacture of ammonia.3

22. Account for the following facts.

(a) The reduction of a metal oxide is easier if the metal formed is in liquid state at the temperature of reduction.

(b) The reduction of Cr_2O_3 with Al is thermodynamically feasible, yet it does not occur at room temperature.

(c) Pine oil is used in froth floatation method. 3

23. Explain the following facts.

(a) Transition metals act as catalysts.

(b) Chromium group elements have the highest melting points in their respective series.

(c) Transition metals form coloured complexes. 3

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

(i)

(ii) $CH_3 - \underset{\underset{OH}{|}}{CH} - CH_3$ and

(b) Why is phenol more acidic than ethanol?

25. Account for the following observations

(i) Among the halogens, F_2 is the strongest oxidising agent?

(ii) Fluorine exhibits only – 1 oxidation state whereas other halogens exhibit higher positive oxidation states also.

(iii) Acidity of oxoacid of chlorine is
$HOCl < HOClO < HOClO_2 < HOClO_3$ 3

26. (a) Give plausible explanation for each of the following.
(i) The presence of a base is needed in the ammonolysis of alkyl halides.
(ii) Aromatic primary amines cannot be prepared by Gabriel phthalimide synthesis.
(b) Write the IUPAC name of

27. An optically active compound having molecular formula $C_6H_{12}O_6$ is found in two isomeric forms (A) and (B) in nature. When (A) and (B) are dissolved in water they show the following equilibrium.

(A) Þ Equilibrium mixture Ü (B)
$[a]_D = 111^0$ 52.2^0 19.2^0

(i) What are such isomers called?
(ii) Can they be called enantiomers? Justify your answer.
(iii) Draw the cyclic structure of isomer (A).

OR

An optically active amino acid (A) can exist in three forms depending on the pH of the medium. If the molecular formula of (A) is $C_3H_7NO_2$ write,
(i) structure of compound (A) in aqueous medium. What are such ions called?
(ii) In which medium will the cationic form of compound (A) exist?
(iii) In alkaline medium, towards which electrode will the compound (A) migrate in electric field? 3

28. For a certain chemical reaction variation in the concentration in [R] Vs. time (s) plot is given below.

For this reaction write / draw
(i) What is the order of the reactions?
(ii) What are the units of rate constant k?
(iii) Give the relationship between k and $t_{½}$ (half life period).
(iv) What does the slope of the above line indicate?
(v) Draw the plot log $[R]_0$ / [R]Vs time t(s) 5

OR

For a certain chemical reaction
A + 2B ® 2C + D
The experimentally obtained information is tabulated below.

Experiment	$[A]_0$	$[B]_0$	Initial rate of reaction
1	0.30	0.30	0.096
2	0.60	0.30	0.384
3	0.30	0.60	0.192
4	0.60	0.60	0.768

For this reaction,
(i) Derive the order of reaction with respect to both the reactants A and B.
(ii) Write the rate law.
(iii) Calculate the value of rate constant k.
(iv) Write the expression for the rate of reaction in terms of A and C.

29. A translucent white waxy solid (A) on heating in an inert atmosphere is converted to its allotropic form (B). Allotrope (A) on reaction with very dilute aqueous KOH liberates a highly poisonous gas (C) having rotten fish smell. With excess of chlorine, it forms (D) which hydrolyses to compound (E). Identify compounds (A) to (E). 5

OR

Concentrated sulphuric acid is added followed by heating to each of the following test tubes labelled (i) to (v)

Identify in which of the above test tube the following change will be observed. Support your answer with the help of a chemical equation.
(a) formation of black substance.
(b) evolution of brown gas.

(c) evolution of colourless gas.

(d) formation of brown substance which on dilution becomes blue.

(e) disappearance of yellow powder along with evolution of colourless gas.

30. Identify the unknown organic compounds (A) to (E) in the following series of chemical reactions.

(i)

$\xrightarrow[Zn/H_2O]{O_3}$ (A) + (B)

(ii) (A) + (B) $\xrightarrow{\text{dil NaOH}}$ C + H_2O

(iii) (C) $\xrightarrow[2.\ Zn/H_2O]{1.\ O_3}$ (A) + (D)

(iv) (D) $\xrightarrow[\Delta]{H_2/Ni}$ (E)

OR

An organic compound (A) having molecular formula $C_9H_{10}O$ forms an orange red precipitate (B) with 2, 4 - DNP reagent. Compound (A) gives an yellow precipitate (C) when heated in the presence of iodine and NaOH along with a colourless compound (D). (A) does not reduce Tollen's reagent or Fehling's solution nor does it decolorise bromine water. On drastic oxidation of (A) with chromic acid, a carboxylic acid (E) of molecular formula $C_7H_6O_2$ is formed. Deduce the structures of the organic compounds (A) to (E).

SET II

General Instructions same as set 1

1. Give IUPAC name of the following organic compound.

$$CH_3CH = \underset{\underset{CH_3}{|}}{C} - \underset{\underset{Br}{|}}{CH} - CH_3$$

2. What are the physical states of dispersed phase and dispersion medium of froth? 1

3. Write the balanced equation for complete hydrolysis of XeF_6 . 1

4. Write the structure of :
4 - methyl pent - 3 - en - 2 - one 1

5. A compound contains two types of atoms - X and Y. It crystallises in a cubic lattice with atom X at the corners of the unit cell and atomsY at the body centres. What is the simplest possible formula of this compound? 1

6. What is the Van't Hoff factor for a compound which undergoes tetramerisation in an organic solvent? 1

7. An ore sample of galena (PbS) is contaminated with zinc blende (ZnS). Name one chemical which can be used to concentrate galena selectively by froth floatation method. 1

8. Predict the shape of ClF_3 on the basis of VSEPR theory. 1

9. Ethylene glycol (molar mass = 62 g mol^{-1}) is a common automobile antifreeze. Calculate the freezing point of a solution containing 12.4g of this substance in 100 g of water. Would it be advisable to keep this substance in the car radiator during summer?
Given : K_f for water = 1.86 Kkg/mol
K_b for water = 0.512 Kkg/mol 2

10. Consider the reaction A $\xrightarrow{k}$ P. The change in concentration of A with time is shown in the following plot:

(i) Predict the order of the reaction.

(ii) Derive the expression for the time required for the completion of the reaction.

11. Free energies of formation (D_fG)of $MgO_{(s)}$ and $CO_{(g)}$ at 1273 K and 2273K are given below
D_fG ($MgO_{(s)}$) = - 941 kJ/mol at 1273K
D_fG ($MgO_{(s)}$) = - 314 kJ/mol at 2273K
D_fG ($CO_{(g)}$) = - 439 kJ/mol at 1273K
D_fG ($CO_{(g)}$) = - 628 kJ/mol at 2273K
On the basis of above data, predict the temperature at which carbon can be used as a reducing agent for $MgO_{(s)}$. 2

12. Name the two components of starch. How do they differ from each other structurally? 2

13. (a) What changes occur in the nature of egg proteins on boiling?
(b) Name the type of bonding which stabilises a-helix structure in proteins. 2

14. Describe the mechanism of the formation of

diethyl ether from ethanol in the presence of concentrated sulphuric acid. 2

15. Complete and name the following reactions:
    (a) $RNH_2 + CHCl_3 + 3KOH$ ®
    (b) $RCONH_2 + Br_2 + 4NaOH$ ® 2
16. Give chemical tests to distinguish between compounds in each of the following pairs:
    (i) Phenol and Benzyl alcohol
    (ii) Butane-2 -ol and 2- Methyl propan - 2- ol 2
17. Predict, giving reasons, the order of basicity of the following compounds in (i) gaseous phase and (ii) in aqueous solutions $(CH_3)_3N$, $(CH_3)_2NH$, CH_3NH_2, NH_3. 2

OR

Account for the following:

(a) Aniline does not undergo Friedel Crafts alkylation
(b) Although - NH_2 group is an ortho and para-directing group, nitration of aniline gives along with ortho & para derivatives, meta-derivative also.

18. Give reasons for the following :
    (a) At higher altitudes, people suffer from a disease called anoxia. In this disease, they become weak and cannot think clearly.
(b) When mercuric iodide is added to an aqueous solution of KI, the freezing point is raised. 2
19. An element X with an atomic mass of 60g/mol has density of 6.23 gcm^{-3}. If the edge length of its cubic unit cell is 400 pm, identify the type of cubic unit cell. Calculate the radius of an atom of this element. 3
20. Write names of monomer/s of the following polymers and classify them as addition or condensation polymers.
    (a) Teflon (b) Bakelite (c) Natural Rubber 3
21. (a) Give the IUPAC name of :
    $[Cr\,Cl_2\,(H_2O)_4]\,Cl$
    (b) Give the number of unpaired electrons in the following complex ions: $[FeF_6]^{4-}$ and $[Fe(CN)_6]^{4-}$
    (c) Name the isomerism exhibited by the following pair of coordination compounds:
    $[Co(NH_3)_5\,Br]\,SO_4$, $[Co(NH_3)_5\,SO_4]Br$
    Give one chemical test to distinguish between these two compounds. 3
22. Explain the following observations.
(a) Ferric hydroxide sol gets coagulated on addition of sodium chloride solution.
(b) Cottrell's smoke precipitator is fitted at the mouth of the chimney used in factories.
(c) Physical adsorption is multilayered, while chemisorption is monolayered. 3
23. Account for the following:
    (a) Chlorine water has both oxidising and bleaching properties.
    (b) H_3PO_2 and H_3PO_3 act as as good reducing agents while H_3PO_4 does not.
    (c) On addition of ozone gas to KI solution, violet vapours are obtained. 3
24. The decomposition of $N_2O_{5(g)}$ is a first order reaction with a rate constant of 5×10^{-4} sec^{-1} at 45° C. ie. $2N_2O_{5\,(g)}$ ® $4NO_{2\,(g)} + O_{2\,(g)}$. If initial concentration of N_2O_5 is 0.25M, calculate its concentration after 2 min. Also calculate half life for decomposition of $N_2O_{5\,(g)}$.
(b) For an elementary reaction 2A + B ® 3C
    the rate of appearance of C at time 't' is
    1.3×10^{-4} mol L^{-1} s^{-1}. Calculate at this time
    (i) rate of the reaction.
    (ii) rate of disappearance of A. 3
25. (a) Which of the following two compounds would react faster by S_N^2 path way : 1 - bromobutane or 2 - bromobutane and why?
    (b) Allyl chloride is more reactive than n - propyl chloride towards nucleophilic substitution reaction. Explain why.
    (c) Haloalkanes react with KCN to give alkyl cyanide as main product while with AgCN they form isocyanide as main product. Give reason. 3
26. Give reasons for the following:
    (a) CN^- ion is known but CP^- ion is not known.
    (b) NO_2 dimerises to form N_2O_4
    (c) ICl is more reactive than I_2

OR

An element 'A' exists as a yellow solid in standard state. It forms a volatile hydride 'B' which is a foul smelling gas and is extensively used in qualitative analysis of salts. When treated with oxygen, 'B' forms an oxide 'C' which is a colourless, pungent smelling gas. This gas when passed through acidified $KMnO_4$ solution, decolourises it. 'C' gets oxidised to another oxide 'D' in the presence of a heterogeneous catalyst. Identify A,B,C,D, and also give the chemical equation of reaction of 'C' with

acidified $KMnO_4$ solution and for conversion of 'C' to 'D'.

27. Account for the following:

(a) Aspirin drug helps in the prevention of heart attack.

(b) Diabetic patients are advised to take artificial sweetners instead of natural sweetners.

(c) Detergents are non-biodegradable while soaps are biodegradable. 3

28. (a) An organic compound 'A' with molecular formula $C_5H_8O_2$ is reduced to n-pentane on treatment with Zn-Hg/HCI. 'A' forms a dioxime with hydroxylamine and gives a positive iodoform test and Tollen's test. Identify the compound A and deduce its structure.

(b) Write the chemical equations for the following conversions: (not more than 2 steps)

(i) Ethyl benzene to benzene

(ii) Acetaldehyde to butane - 1, 3 - diol

(iii) Acetone to propene 5

OR

(a) An organic compound 'A' with molecular formula C_8H_8O gives positive DNP and iodoform tests. It does not reduce Tollen's or Fehling's reagent and does not decolourise bromine water also. On oxidation with chromic acid (H_2CrO_4), it gives a carboxylic acid (B) with molecular formula $C_7H_6O_2$. Deduce the structures of A and B.

(b) Complete the following reactions by identifying A, B and C.

(i) $A + H_{2(g)} \xrightarrow{Pd/BaSO_4} (CH_3)_2CH - CHO$

(ii)

29. (a) Calculate the equilibrium constant for the reaction

$Cd^{2+}_{(aq)} + Zn_{(s)} \rightarrow Zn^{2+}_{(aq)} + Cd_{(s)}$

If $E^0_{cd^{2+}/cd} = -0.403$ V

$E^0_{Zn^{2+}/Zn} = -0.763$ V

(b) When a current of 0.75A is passed through a $CuSO_4$ solution for 25 min, 0.369 g of copper is deposited at the cathode. Calculate the atomic mass of copper.

(c) Tarnished silver contains Ag_2S. Can this tarnish be removed by placing tarnished silver ware in an aluminium pan containing an inert electrolytic solution such as NaCl. The standard electrode potential for half reaction :

$Ag_2S_{(s)} + 2\bar{e} \rightarrow 2Ag_{(s)} + S^{2-}$ is –0.71V

and for $Al^{3+} + 3\bar{e} \rightarrow Al_{(s)}$ is –1.66 V

OR

(a) Calculate the standard free energy change for the following reaction at 25°C

$Au_{(s)} + Ca^{2+}_{(aq, 1m)} \rightarrow Au^{3+}_{(aq, 1m)}$

$E^0_{Au^{3+}/Au} = +1.50$V

$E^0_{Ca^{2+}/Ca} = -2.87$ V

Predict whether the reaction will be spontaneous or not at 25°C. Which of the above two half cells will act as an oxidising agent and which one will be a reducing agent?

(b) The conductivity of 0.001M acetic acid is 4×10^{-5}S / cm. Calculate the dissociation constant of acetic acid, if Λ^0_m for acetic acid is 390.5 S cm²/mol.

30. (a) A blackish brown coloured solid 'A' when fused with alkali metal hydroxides in presence of air, produces a dark green coloured compound 'B', which on electrolytic oxidation in alkaline medium gives a dark purple coloured compound C. Identify A, B and C and write the reactions involved.

(b) What happens when an acidic solution of the green compound (B) is allowed to stand for some time? Give the equation involved. What is this type of reaction called? (3 + 2 = 5)

OR

Give reasons for the following:

(a) Transition metals have high enthalpies of atomisation.

(b) Among the lanthanoids, Ce(III) is easily oxidised to Ce(IV).

(c) Fe^{3+}/Fe^{2+} redox couple has less positive electrode potential than Mn^{3+}/Mn^{2+} couple.

(d) Copper (I) has d^{10} configuration, while copper (II) has d^9 configuration, still copper (II) is more stable in aqueous solution than copper (I).

(e) The second and third transition series elements have almost similar atomic radii. 5

SET III

General instructions same as set 1.

1. Name the type of point defect that occurs in a crystal of zinc sulphide. 1
2. The decomposition reaction of ammonia gas on platinum surface has a rate constant $k = 2.5 \times 10^{-4}$ mol L^{-1} s^{-1}. What is the order of the reaction? 1
3. Give the IUPAC name of the following compound

4. How many octahedral voids are there in l mole of a compound having cubic close packed structure? 1
5. What is the molecularity of the reaction?

$$Cl \rightarrow \frac{1}{2}Cl_{2(g)}$$ 1

6. In each of the following pairs of organic compounds, identify the compound which will undergo S_N^1 reaction faster? 1

(a)

(b)

7. In the ring test for identification of nitrate ion, what is the formula of the compound responsible for the brown ring formed at the interface of two liquids? 1
8. Except for vitamin B_{12}, all other vitamins of group B, should be supplied regularly in diet. Why? 1
9. An element E crystallises in body centered cubic structure. If the edge length of the cell is 1.469×10^{-10} m and the density is 19.3 gcm^{-3}, calculate the atomic mass of this element. Also calculate the radius of an atom of this element. 2
10. The following curve is obtained when molar conductivity (Y-axis) is plotted against the square root of concentration (X - axis) for two electrolytes A and B.

(a) What can you say about the nature of the two electrolytes A and B?

(b) How do you account for the increase in molar conductivity l_m for the electrolytes A and B on dilution? 2

11 (a) Adsorption of a gas on the surface of solid is generally accompanied by a decrease in entropy. Still it is a spontaneous process. Explain.

(b) How does an increase in temperature affect both physical as well as chemical adsorption? 2

12. A colloidal solution of AgI is prepared by two different methods shown below:-

(i) What is the charge of AgI colloidal particles in the two test tubes (A) and (B)?

(ii) Give reasons for the origin of charge. 2

13. (a) What is the covalence of nitrogen in N_2O_5?

(b) Explain why both N and Bi do not form pentahalides while phosphorus does. 2

OR

When conc. H_2SO_4 was added into an unknown salt present in a test tube, a brown gas (A) was evolved. This gas intensified when copper turnings were also added into this test-tube. On cooling, the gas (A) changed into a colourless gas (B).

(a) Identify the gases A and B.

(b) Write the equations for the reactions involved.

14. Which is a stronger acid - Phenol or Cresol? Explain. 2
15. (a) How can you convert an amide into an amine having one carbon less - than the starting compound?

(b) Name the reaction.

(c) Give the IUPAC name and structure of the amine obtained by the above method if the amide is 3- chlorobutanamide. 2

16. (a) Why does chlorine water lose its yellow colour on standing?

(b) What happens when Cl_2 reacts with cold dilute solution of sodium hydroxide? Write equation only. 2

17. How will you distinguish between:

(a) and CH_3NH_2

(b) $CH_3-\underset{\underset{CH_3}{|}}{N}-H$ and $(CH_3)_3N$

18. Give mechanism of preparation of ethoxyethanol from ethanol. 2

19. (a) A current of 1.50 amp was passed through an electrolytic cell containing $AgNO_3$ solution with inert electrodes. The weight of Ag deposited was 1.50g. How long did the current flow?

(b) Write the reactions taking place at the anode and cathode in the above cell.

(c) Give reactions taking place at the two electrodes if these are made up of Ag. 3

20.

Answer the following questions on the basis of the above curve for a first order reaction A ® P:-

(a) What is the relation between slope of this line and rate constant? (1)

(b) Calculate the rate constant of the above reaction if the slope is $2 \times 10^{-4}\ s^{-1}$

(c) Derive the relationship between half life of a first order reaction and its rate constant.

21. (a) Name the method used for refining of

(i) Nickel (ii) Zirconium

(b) The extraction of Au by leaching with NaCN involves both oxidation and reduction. Justify giving equations. 3

22. Write down the equations for hydrolysis of XeF_4 and XeF_6. Which of these two reactions is a redox reaction? 3

23. Give the electronic configuration of the

(a) d- orbitals of Ti in $[Ti(H_2O)_6]^{3+}$ ion in an octahedral crystal field.

(b) Why is this complex coloured? Explain on the basis of distribution of electrons in the d- orbitals.

(c) How does the colour change on heating $[Ti(H_2O)_6]^{3+}$ ion? 3

24. (a) Which will have a higher boiling point?

1 - Chloroethane or 2 methyl -2- chlorobutane Give reasons.

(b) p - nitrochlorobenzene undergoes nucleophilic substitution faster than chlorobenzene. Explain giving the resonating structures as well. 3

25. Despite having an aldehyde group

(a) Glucose does not give 2,4 - DNP test. What does this indicate?

(b) Draw the Haworth structure of a - D - (+) – Glucopyranose.

(c) What is the significance of D and (+) here? 3

26. (a) What is the role of Benzoyl peroxide in polymerisation of ethene?

(b) What are LDPE and HDPE? How are they prepared? 3

27. Classify synthetic detergents giving an example in each case.

OR

What are antihistamines? Give two examples. Explain how they act on the human body. 3

28. (a) Derive the relationship between relative lowering of vapour pressure and mole fraction of the volatile liquid.

(b) (i) Benzoic acid completely dimerises in benzene. What will be the vapour pressure of a solution containing 61g of benzoic acid per 500g benzene when the vapour pressure of pure benzene at the temperature of experiment is 66.6 torr?

(ii) What would have been the vapour pressure in the absence of dimerisation?

(iii) Derive a relationship between mole fraction and vapour pressure of a component of an ideal solution in the liquid phase and vapour phase. 5

OR

(a) Which aqueous solution has higher concentration -1 molar or 1 molal solution of the same solute? Give reason.

(b) 0.5g KCl was dissolved in 100g water and the solution originally at 20°C, froze at – 0.24°C. Calculate the percentage ionisation of salt. K_f per 1000g of water = 1.86K.

29. (a) Out of Ag_2SO_4, CuF_2 , MgF_2 and CuCl, which compound will be coloured and why?

(b) Explain :

(i) CrO_4^{2-} is a strong oxidising agent while MnO_4^{2-} is not.

(ii) Zr and Hf have identical sizes.

(iii) The lowest oxidation state of manganese is basic while the highest is acidic.

(iv) Mn (II) shows maximum paramagnetic character amongst the divalent ions of the first transition series. 5

OR

(a) In the titration of $FeSO_4$ with $KMnO_4$ in the acidic medium, why is dil H_2SO_4 used instead of dil HCl?

(b) Give reasons:

(i) Among transition metals, the highest oxidation state is exhibited in oxoanions of a metal.

(ii) Ce^{4+} is used as an oxidising agent in volumetric analysis.

(iii) Transition metals form a number of interstitial compounds.

(iv) Zn^{2+} salts are white while Cu^{2+} salts are blue.

30. An unknown Aldehyde 'A' on reacting with alkali gives a b-hydroxy –aldehyde, which losses water to form an unsaturated aldehyde, 2- butenal. Another aldehyde 'B' undergoes disproportionation reaction in the presence of conc. alkali to form products C and D. C is an arylalcohol with the formula C_7H_8O.

(i) Identify A and B.(ii) Write the sequence of reactions involved.(iii) Name the product, when 'B' reacts with Zinc amalgum and hydrochloric acid.5

OR

A compound 'X' (C_2H_4O) on oxidation gives 'Y' ($C_2H_4O_2$). 'X' undergoes haloform reaction. On treatment with HCN 'X' forms a product 'Z' which on hydrolysis gives 2- hydroxy propanoic acid.

(i) Write down structures of 'X' and 'Y'.

(ii) Name the product when 'X' reacts with dil NaOH.

(iii) Write down the equations for the reactions involved.

Answers

SET I

1. Fe^{3+} (ferric ion) is a better coagulating ion than K^+ ion.
2. In a tetrahedral complexes of the type $[MA_2B_2]$, unidentate ligands are equidistant from each other.
3. Ethoxyethane is miscible in water because of intermolecular hydrogen bonding between ether and water molecule.
4. 4 - Methylpent – 3 – en – 2 – one
5. Glycine and aminocaproic acid

OR

$H_2N – CH_2 – COOH$ and $H_2N – (CH_2)_5 COOH$

6. Saccharin / Aspartame
7. During direct nitration of aniline besides ortho, para substituted products,oxidised tarry products and meta substituted products are formed.
8. Phosphodiester linkages
9. (i) Schottky defects

   (ii) The density of a crystal decreases.

   (iii) Na^+Cl^-

   iv) Not affected
10. The formula $M_{0.96}O_{1.00}$ shows that there is 0.96 M atoms are associated with 1 oxygen atom.

    Let number of M^{2+} ions = x.

    Then, number of M^{3+} ions = (0.96 – x)

    We know that charge of oxygen atom = –2

    Then total charge of metal oxide

    $x \times 2 + (0.96 – x)\, 3 + (1 \times –2) = 0$

    ie $2x + 2.88 – 3x – 2 = 0$

    ie $–x + 0.88 = 0$; ie $x = 0.88$.

    % of M^{2+} ion = $\frac{0.88}{0.96} \times 100$ = 91.67%

    % of M^{3+} ion = $\frac{0.08}{0.96} \times 100$ = 8.33%

    OR

    Number of N^- ion in each F.C.C. unit cell = 4

    Number of tetrahedral voids = 2 × 4 = 8

    Fraction occupied tetrahedral voids = $\frac{1}{3} \times 8 = \frac{8}{3}$

    Empirical formula of compound = $M_{8/3}N_4 = M_2N_3$

    Coordination number of M^+ ions = 4
11. (i) Reverse osmosis

    (ii) Fresh water container

    (iii) Cellulose acetate placed on a suitable support

    (iv) Desalination of sea water.
12. Oxidation : $Fe_{(s)} \rightarrow Fe^{2+}_{(aq)} + 2e^-$

    Reduction : $O_{2\,(g)} + 4H^+_{(aq)} + 4e^- \rightarrow 2H_2O$

    Atmospheric oxidation :

    $$2Fe^{2+}_{(aq)} + 2H_2O_{(l)} + \frac{1}{2}O_{2(g)} \rightarrow Fe_2O_{3(s)} + 4H^+_{(aq)}$$

Prevention : Applying a coating of more reactive metal like Zn.

13. (i)

(ii) $t^4_{2g}\ e^0_g$ or t^4_{2g}

(iii) d^2sp^3

(iv) Optical isomerism

14. Compound (A) is sodium chromate or Na_2CrO_4

Compound (B) is sodium dichromate or $Na_2Cr_2O_7$

$4FeO.\ C_2O_3 + 8Na_2CO_3 + 7O_2 \rightarrow 8Na_2CrO_4 + 2Fe_2O_3 + 8CO_2$

$2Na_2CrO_4 + 2H^+ \rightarrow Na_2Cr_2O_7 + 2Na^+ + H_2O$

15. Undergoes S_N^1 mechanism

(Optically active)

16. (i) $(CH_3)_2\ CH - CH - (CH_3)_2$

(ii) CH_3F (iii) CH_3CH_2I

(iv)

17. (i) Novolac is a straight chain linear polymer but bakelite is cross linked polymer.

(ii) Buna-S is an elastomer having weak van der Waal's intermolecular forces whereas terylene is a fibre having strong intermolecular hydrogen bonding.

18. Calcium ions form insoluble calcium soaps which separate as scum in water, hence detergents preferred.

Soaps are biodegradable, detergents are not easily biodegradable.

19. Moles of heptane = $\dfrac{\text{Mass of heptane}}{\text{Molar mass of heptane}}$

$= \dfrac{25g}{100g\ mol^{-1}} = 0.25$ moles

Moles of octane = $\dfrac{\text{Mass of octane}}{\text{Molar mass of octane}}$

$= \dfrac{28.5g}{114g\ mol^{-1}} = 0.25$ moles

Total moles = 0.25 + 0.25 = 0.50 moles

Mole fraction of heptane

$= \dfrac{\text{No. of moles of heptane}}{\text{Total No. of moles}} = \dfrac{0.25}{0.50} = 0.5$

Mole fraction of octane

$= \dfrac{\text{No. of moles of octane}}{\text{Total No. of moles}} = \dfrac{0.25}{0.50} = 0.5$

(i) Partial pressure of heptane, $P = p^0_{heptane} \times X_{heptane}$

$= 105.2\ kPa \times 0.5 = 52.6\ kPa$

(ii) Partial pressure of octane, $P = p^0_{octane} \times X_{octane}$

$= 46.8\ kPa \times 0.5$

$= 23.4\ kPa$

$P_{solution} = P_{heptane} + P_{octane}$

$= 52.6\ kPa + 23.4\ kPa$

$= 76.0\ kPa$

(iii) Mole fraction of octane in vapour phase

$= \dfrac{P_{octane}}{P_{solution}} = \dfrac{23.4kPa}{76.0kPa} = 0.3078$

20. (a) (i) 0.81 V

(ii) $E^0_{cell} = E^0_{right} - E^0_{left} = 0.81\ V - (-2.36\ V) = 3.17V$

(b) $E_{cell} = E^0_{cell} - \dfrac{0.0591}{n} \log \dfrac{[Mg^{2+}]}{[Ag^+]^2}$

$= 3.17 - \dfrac{0.0591}{2} \log \dfrac{(0.1)}{(0.0001)^2} = 2.96\ V$

(c) (i) $Mg_{(s)} \mid Mg^{2+}_{(0.01M)} \| Ag^+_{(0.0001M)} \mid Ag_{(s)}$

(ii) Yes

21. (a) (i) (x / m) extent of adsorption decreases.
    (ii) (x / m) extent of adsorption increases.
    (b) Catalyst : iron
    Promoter : molybdenum / Al_2O_3 / K_2O

22. (a) In liquid state entropy is higher than the solid form, this makes $\Delta_r G$ more negative.
    (b) By increasing temperature, fraction of activated molecules increase which help in crossing over the energy barriers.
    (c) Pine oil enhances non-wetting property of ore particles and acts as a froth collector.

23. (a) Transition metals acts as catalysts due to their abilities to show multiple oxidation states and form complexes.
    (b) Chromium group elements have maximum number of unpaired electrons in d orbitals because of which maximum d - d interactions are possible. Therefore these elements have the highest melting points in their respective series.
    (c) Transition metals complexes are coloured due to d- d transitions.

24. (a) (i) Add bromine water to both the containers containing phenol and cyclohexanol. The container in which white precipitate is formed contains phenol while the container in which no precipitate is formed contains cyclohexanol.

(ii) Add iodine and sodium hydroxide to both the containers containing $CH_3 - \underset{\underset{OH}{|}}{CH} - CH_3$ (isopropyl alcohol) and (benzyl alcohol).

The container in which yellow precipitate is formed contains, $CH_3 - \underset{\underset{OH}{|}}{CH} - CH_3$ while the container in which no yellow precipitate is formed contains

(b)

$$CH_3 - CH_2 - OH \rightleftharpoons CH_3COO^- + H^+$$

(i) Phenol has electron withdrawing phenyl group, but ethanol has electron releasing ethyl group, hence extent of forward reaction is higher in phenol in aqueous medium.
(ii) Phenoxide ion is resonance stabilised, ethoxide ion is not resonance stabilised, hence extent of backward reaction is more in ethanol than phenol.

25. (i) Low bond dissociation enthalpy and high hydration (solvation) enthalpy among the halogens.
    (ii) Due to high electronegativity of fluorine atom which exhibits only –1 oxidation state.
    (iii) Higher the oxidation state of chlorine in oxo acid, stronger the acid.

26. (a) (i) To remove HX formed so that the reaction shifts in the forward direction.
    (ii) Aryl halides do not undergo nucleophillic substitution with the anion formed by phthalimide.
    (b) N – ethyl – N – methyl ethanamide.

27. (i) Anomers
    (ii) No, they are not enantiomers because stereoisomers related to each other as non-superimposable mirror images are enantiomers. Anomers differ only at C_1 configuration (or carbonyl carbon).

OR

(i) $H_2N - \underset{\underset{H}{|}}{\overset{\overset{CH_3}{|}}{C}} - \overset{\overset{O}{||}}{C} - O^-$, Zwitter ion

(ii) Acidic medium (iii) Anode

28. (i) First order

(ii) time $^{-1}$ (s^{-1}) (iii) $k = \dfrac{0.693}{t_{1/2}}$

(iv) Rate constant k of reaction.

(v)

OR

(i) Rate = k $[A]^x \times [B]^y$

$0.096 = k\,(0.30)^x \times (0.30)^y$ ---------- (i)

$0.384 = k\,(0.60)^x \times (0.30)^y$ ---------- (ii)

dividing eqn. (ii) by (i), we get x = 2

$0.192 = k\,(0.30)^x \times (0.60)^y$ ---------- (iii)

dividing eqn. (iii) by (i) we get

y = 1

(ii) Rate = k $[A]^2 [B]^1$

(iii) $0.096 = k\,(0.30)^2\,(0.30)^1$

\ k = 3.56

(iv) Rate of reaction = $-\left\{\frac{\Delta[A]}{\Delta t}\right\} = \frac{1}{2}\left\{\frac{(\Delta C)}{\Delta t}\right\}$

29. $P_4 \xrightarrow[N_2]{\Delta} P_4$; $P_4 + 3\,KOH + 3H_2O$ ® $PH_3 + 3KH_2PO_2$

White (A) Red (B) white (C)

$P_4 + 10Cl_2$ ® $4PCl_5$; $PCl_5 + 4H_2O$ ® $H_3PO_4 + 5HCl$

(D) (E)

(A) : white phosphorus

(B) : red phosphorus

(C) : phosphine or PH_3

(D) : phosphorus pentachloride or PCl_5

(E) : phosphoric acid or H_3PO_4

OR

(a) (i) $C_{12}H_{22}O_{11}$ ® $12\,C + 11\,H_2O$

(white) (black substance)

(b) (ii) $2NaBr + 2\,H_2SO_4$

® Br_2 - + $Na_2SO_4 + SO_2 + 2H_2O$

(Brown gas)

(c) (v) $2KCI + H_2SO_4$ ® 2HCI - + K_2SO_4

(colourless gas)

(d) (iii) $Cu + 2\,H_2SO_4$ ® $CuSO_4 + SO_2 + 2H_2O$

(e) (iv) $3\,S + 2\,H_2SO_4$ ® $3\,SO_2$ - + $2H_2O$

(colourless gas)

30. (A) :

(B)

(C)

(D)

(E)

OR

(A)

(B)

(C) CHI_3 (yellow precipitate)

(D)

(E)

SET II

1. 4 – Bromo – 3– methyl pent – 2– ene.
2. Dispersed phase : gas
   Dispersion medium : liquid
3. $XeF_6 + 3H_2O$ ® $XeO_3 + 6HF$
4. $H_3C - \underset{\underset{CH_3}{|}}{C} = CH - \underset{\underset{O}{\|}}{C} - CH_3$
5. XY
6. $i = \frac{1}{4}$
7. NaCN, Sodium cyanide, used as a depressant.
8.

T - shape

9. $DT_f = K_f \times \frac{W_B}{M_B} \times \frac{1000}{W_A}$

$= 1.86 \times \frac{12.4}{62} \times \frac{1000}{100} = 3.76$ K

Since water freezes at 0°C, so freezing point of the solution containing ethylene glycol will be –3.76° C

$DT_b = K_b \times \frac{W_B}{M_B} \times \frac{1000}{W_A}$

$= 0.512 \times \frac{12.4}{62} \times \frac{1000}{100} = 1.024$ K

Since water boils at 100°C, so a solution containing ethylene glycol will boil at 101.024°C, so it is advisable to keep this substance in car radiator during summer.

10. (i) The reaction $A \xrightarrow{k} P$ is a zero order reaction.

(ii) For the reaction $A \xrightarrow{k} P$

Rate = $\frac{-d[A]}{dt} = k[A]^0$

$-d[A] = k\,dt$

Integrating both the sides :

$[A] = kt + C$ ----------(i)

where C = constant of integration at t = 0,

$[A] = [A]_0$

Substituting this in equation (i)

$C = [A]_o$

Substituting the value of 'C' in equation (i)

$[A] = -kt + [A]_o$

$kt = [A]_o - [A]$

$$t = \frac{[A]_o - [A]}{k}$$

11. The reaction for reducing action of carbon is :

$MgO_{(s)} + C_{(s)} \rightarrow Mg_{(s)} + CO_{(g)}$

At 2273K, $D_rG = D_fG\,(CO) - D_fG\,(MgO)$

$= -628 - (-314) = -314$kJ/mol

At 1273K, $D_rG = -439 - (-941)$

$= +502$ kJ/mol

So carbon can be used as reducing agent with $MgO_{(s)}$ at 2273k.

12. The two components of starch are:

(a) Amylose (b) Amylopectin

Amylose is a straight chain polymer a – D – (+) of glucose, while amylopectin is a branched chain polymer of a – (D) (–) glucose.

13. (a) On boiling, protein of egg gets denatured or coagulated and water of egg get absorbed in it.

(b) Hydrogen bonding between $-\underset{\underset{O}{\|}}{C}-$ and - NH- groups of peptide bond.

14. $2CH_3CH_2-\ddot{\underset{..}{O}}H \xrightarrow{conc.H_2SO_4} CH_3-CH_2-\ddot{\underset{..}{O}}-CH_2CH_3$

Mechanism:

(i)

(ii)

$\rightarrow CH_3-CH_2-\overset{\oplus}{\underset{H}{O}}-CH_2-CH_3 + H_2O$

(iii)

15. (a) $RNH_2 + CHCl_3 + 3KOH \rightarrow RNC + 3KCl + 3H_2O$

Carbylamine reaction

(b) $RCONH_2 + Br_2 + 4NaOH \rightarrow RNH_2 + Na_2CO_3 + 2NaBr + 2H_2O$

Hoffmann bromamide degradation reaction

16. (i) Addition of neutral ferric chloride solution to phenol will give a violet colouration, while no such colouration will be observed in case of benzyl alcohol.

(ii) On addition of Luca's reagent (a mixture of concentrated hydrochloric acid and anhydrous zinc chloride) to 2 - methyl - 2- propanol will give a white turbidity immediately while 2 - butanol will give turbidity after five minutes.

17. In gaseous phase, basic character of amines increases with increase in number of electron releasing alkyl groups, due to + I effect, so trend of basic character is $3^0 > 2^0 > 1^0$. But in aqueous phase, solvation of ammonium cation occurs by water molecules, greater the size of ion, lesser will be the solvation, and lesser will be the stability of ion, so on combining + I effect and solvation effect, in aqueous phase trend changes to $2^o > 3^o > 1^o$.

OR

(a) During Friedal craft's alkylation, aluminium chloride acts as a catalyst, as well as a Lewis acid, it forms salt with - NH_2 group of aniline, so that - NH_2 group acquires a positive charge, and acts as a deactivating group, so aniline does not undergo Friedal Craft's Alkylation.

(b) During nitration, in strongly acidic medium aniline is protonated to form anilinium ion, which is a meta directing group, so along with o- & p- isomers, meta isomer is also obtained.

18. (a) At higher altitudes, partial pressure of oxygen is less than that at ground level, so that oxygen concentration becomes less in blood or tissues. Hence people suffer from anoxia.

(b) Due to the formation of complex $K_2(Hg\,I_4)$, number of particles in the solution decreases and hence the freezing point is raised.

19. $d = \frac{z \times M}{a^3 \times N_A}$

$$6.23 = \frac{z \times 60}{(400)^3 \times 10^{-30} \times 6.023 \times 10^{23}}$$

z = 4

The unit cell is face centered cubic.

$$\text{radius 'r'} = \frac{a}{2\sqrt{2}} = \frac{400}{2\sqrt{2}} = 141.4 \text{ pm}$$

20. (a) Tetraflouro ethene
Addition polymer
(b) Phenol and formaldehyde
Condensation polymer
(c) Isoprene
Addition polymer

21. (a) Tetraaquadichlorochromium(III) chloride.
(b) $[FeF_6]^{4-}$ has 4 unpaired electrons as I^- is a weak field ligand.
$[Fe(CN)_6]^{4-}$ has zero unpaired electron as CN^- is a strong field ligand.
(c) Ionisation isomerism. On addition of dilute HCl followed by aqueous $BaCl_2$, $[Co(NH_3)_5Br]SO_4$ will give a white precipitate while the other coordination compound will not give any white precipitate.

22. (a) As ferric hydroxide, $Fe(OH)_3$ is a positively charged sol, so it gets coagulated by chloride ions, Cl^-, released by NaCl solution.
(b) Cottrell's smoke precipitator, neutralises the charge on unburnt carbon particles coming out of chimney and they get precipitated and settle down at the floor of the chamber.
(c) As physical adsorption, involves only weak van der Waal's force of interaction, so many layers of adsorbate get attached, while chemisorption involves chemical bond formation between adsorbate and adsorbent, so monolayer is formed.

23. (a) Chlorine water produces nascent oxygen which is responsible for bleaching action and oxidation.
$Cl_2 + H_2O$ ® $2\,HCl + [O]$
(b) Both H_3PO_2 and H_3PO_3 have P- H bonds, so they act as reducing agents, but H_3PO_4, has no P-H bond but has O-H bonds, so it cannot act as a reducing agent.
(c) Ozone gas acts as a strong oxidising agent, so it oxidises iodide ions to iodine.
$2I^{\ominus}_{(aq)} + H_2O_{(l)} + O^{\ominus}_{3(g)}$ ® $2\,OH^{\ominus}_{(aq)} + I_{2(g)} + O_{2(g)}$
I_2 vapours evolved have violet colour.

24. (a) For first order reaction

$$k = \frac{2.303}{t}\log\frac{[R]_0}{[R]_t}$$

$$5 \times 10^{-4} = \frac{2.303}{2\times 60}\log\frac{0.25}{[R]_t}$$

\ $[R]_t = 0.23$ M

$$t_{1/2} = \frac{0.693}{5\times 10^{-4}}\text{sec} = 1386 \text{ sec}$$

(b) (i) $\text{Rate} = \frac{1}{3}\frac{d[C]}{dt} = \frac{1}{3}\times 1.3\times 10^{-4}$
$= 0.43 \times 10^{-4}$ mol L^{-1} sec^{-1}

(ii) $\text{Rate} = \frac{-d[A]}{dt} = \frac{2}{3}\times\frac{d[C]}{dt}$
$= 0.86 \times 10^{-4}$ mol L^{-1} sec^{-1}

25. (a) 1- Bromo butane, being a primary alkyl halide would react faster by S_N^2 pathway, due to less steric hinderance.
(b) In allyl chloride, $CH_2 = CH - CH_2Cl$, the carbocation $CH_2 = CH - CH_2^+$ formed is stabilised due to resonance while the carbocation formed from n - propyl chloride ie. $CH_3CH_2CH_2^+$ is less stable, so allyl chloride is more reactive towards nucleophilic substitution reaction.
(c) KCN, being ionic, CN^- ions liberated reacts with haloalkanes forming alkyl cyanides but in AgCN , being covalent, does not release CN^- ion but lone pair on nitrogen acts as a nucleophile, resulting in formation of isocyanides.

26. (a) Nitrogen being smaller in size forms pp – pp multiple bonding with carbon, so CN^- ion is known, but phosphorus does not form pp – pp bond as it is larger in size.
(b) Since NO_2 is an odd electron molecule and therefore gets dimerised to stable N_2O_4.
(c) Because ICl has less bond dissociation enthalpy than I_2.

OR

'A' = Sulphur
B = H_2S gas
C = SO_2 gas
D = SO_3 gas
$5SO_{2(g)} + 2MnO_4^- + 2H_2O$ ® $5SO_4^{2-} + 4H^+ + 2Mn^{2+}$
$2SO_{2(g)} + O_{2(g)} \xrightarrow{V_2O_5} 2SO_{3(g)}$

27. (a) Due to antiblood clotting action, aspirin is used for prevention of heart attacks.
(b) As artificial sweetners provide less calories than natural sweetners.

(c) Detergents have highly branched hydrocarbon chain, which cannot be degraded by bacteria, so they get accumulated while soap containing straight hydrocarbon chain can be degraded easily.

28. (a) As 'A' gives positive iodoform test, so it has

$CH_3 - \underset{\underset{O}{\|}}{C}$ – group

As 'A' gives positive Tollen's test, so it must have – CHO group.

So A is $CH_3 - \underset{\underset{O}{\|}}{C} - CH_2CH_2CHO$

(b)

Ethyl benzene

Benzene

(ii) $2CH_3CHO \xrightarrow[NaOH]{dilute} CH_3\underset{\underset{OH}{|}}{CH} - CH_2CHO$

$CH_3\underset{\underset{OH}{|}}{CH} - CH_2CHO \xrightarrow{NaBH_4} CH_3\underset{\underset{OH}{|}}{CH} - CH_2\underset{\underset{OH}{|}}{CH_2}$

Butane-1,3-diol

(iii) $CH_3 - \underset{\underset{O}{\|}}{C} - CH_3 \xrightarrow{NaBH_4} CH_3\underset{\underset{OH}{|}}{CH} - CH_3$

Acetone

$CH_3 - \underset{\underset{OH}{|}}{CH} - CH_3 \xrightarrow{conc.H_2SO_4} CH_3CH = CH_2$

Propene

OR

(a) As 'A' does not give Fehling's or Tollen's test, so it does not have – CHO group but it gives positive iodoform test and DNP test so it has $CH_3 - \underset{\underset{O}{\|}}{C}$ group.

So 'A' is:

Acetophenone

B is carboxylic acid obtained by oxidation of A with H_2CrO_4.

So 'B' is

Benzoic acid

(b) A = $(CH_3)_2CH - \underset{\underset{O}{\|}}{C} - Cl$

B = $CH_3 - \underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}} - COONa$

C = CHI_3

29. (a) $E^o_{cell} = E^o_c - E^o_a = -0.403 - (-0.763) = 0.360$ V

As $\log K_c = \left(\frac{nE^0_{cell}}{0.059}\right) = \left(\frac{2\times0.360}{0.059}\right)$

$= \left(\frac{0.720}{0.059}\right) = 12.20$

K_c = antilog (12.20) = 1.585×10^{12}

(b) M = ZIt

$0.369 = \frac{x}{2\times96500}\times0.75\times25\times60$ (x = molar mass of copper)

x = 63.3g/mol.

(c) E^0_{cell} for reaction of tarnished silver ware with aluminium pan is

(–0.71 V) – (–1.66V) ie, + 0.95 V

Tarnished silver ware, therefore, can be cleaned by placing it in an aluminium pan E^0_{cell} as it is positive.

OR

(a) E^0_{cell} = (–2.87 V) – (1.50 V) = - 4.37 V

DG^0_{cell} = – 6 × 96500 × – 4.37 V

= + 2350.230 kJ/mol

Since D_rG^0 is positive, reaction is non spontaneous. Au^{3+}/Au half cell will be a reducing agent, Ca^{2+}/Ca half cell will be an oxidising agent.

(b) $\Lambda^o_m = K \times \frac{1000}{\text{molarity}}$

K = specific conductance

$= \frac{4\times10^{-5} S/cm \times 1000}{0.001} = 40\ Scm^2\ mol^{-1}$

$\alpha = \frac{\Lambda_m}{\Lambda^0_m}$, $\alpha = \frac{40}{390.5} = 0.103$

$K_c = \frac{c\alpha^2}{1-\alpha} = \frac{0.001\times(0.103)^2}{1-0.103} = 1.19\times10^{-5}$

30. (a) A = MnO_2

B = K_2MnO_4

C = $KMnO_4$

$2MnO_2 + 4KOH + O_2$ ® $2K_2MnO_4 + 2H_2O$
(A) (B)

$$MnO_4^{2-} \xrightarrow[\text{oxidation in alkaline solution}]{\text{electrolytic}} MnO_4^-$$

(b) In acidic medium, K_2MnO_4 changes to give purple coloured compound along with black precipitate.

$$3MnO_4^{2-} \xrightarrow{4H^+} 2MnO_4^- + MnO_2 + 2H_2O$$

Green compound — purple compound — Black

It is called disproportionation reaction.

OR

(a) Due to strong interatomic interaction between unpaired valence electrons.

(b) Because Ce(IV) has extrastability due to empty f^0 orbital.

(c) In Mn^{2+} d^5 configuration leads to extrastability of half filled configuration, so Mn^{3+} / Mn^{2+} (d^4) tends to get converted to stable d^5, configuration of Mn^{2+}, by accepting an electron so Mn^{3+}/Mn^{2+} redox couple has more positive potential than couple.

(d) Due to more negative enthalpy of hydration of $Cu^{2+}_{(aq)}$ than $Cu^+_{(aq)}$ which compensates for second ionisation enthalpy of copper.

(e) In the third transition series after lanthanum there is lanthanoid contraction, due to ineffective shielding by intervening f- orbital electrons and hence second and third transition series elements have similar atomic radii.

SET III

1. Frenkel defect
2. Zero order reaction
3. 2 - Methylcyclopent -3- ene carboxylic acid
4. 1 Mole or 6.02×10^{23}
5. One
6. (a)

(b)

7. $[Fe(H_2O)_5NO]^{2+}$
8. Except for B_{12}, no other vitamin of group B can be stored in the body and is readily excreted in urine.
9. $d = \frac{zM}{a^3N_0}$ gcm^{-3}

   $a = 1.469 \times 10^{-10}$ m $= 146.9 \times 10^{-10}$ cm

   $$M = \frac{da^3N_0}{z} g = \frac{19.3 \times (146.9 \times 10^{-10})^3 \times 6.02 \times 10^{23}}{2}$$

   $= 19.3 \times 3.17 \times 3.01 = 183.5g$

   $r = 0.634 \times 10^{-8}$ cm
10. (a) A is a strong electrolyte.
    B is a weak electrolyte.

    (b) Molar conductivity of a strong electrolyte increases with dilution as ionic mobility increases. In a weak electrolyte molar conductivity increases steeply with dilution as degree of dissociation increases.
11. (a) According to the equation DG = DH – TDS for a process to be spontaneous DG should be negative. Even though DS is negative here, DG is negative because reaction is highly exothermic.ie, DH is negative.

    (b) On increasing temperature desorption occurs in physical adsorption. Chemical adsorption increases first and then decreases with increase in temperature.
12. (i) The AgI colloidal particles in test tube (A) has negative charge.

    The AgI colloidal particles in test tube (B) has positive charge.

    (ii) In test tube (A)I^- is adsorbed on Ag. [or AgI / I^- is formed]

    In test tube (B)Ag^A is adsorbed on AgI. [or AgI / Ag^+ is formed]
13. (a) 4

    (b) Unlike P, N has no vacant d-orbitals in its valence shell.

    Bi prefers +3 oxidation state due to inert pair effect.

    OR

    (a) A is NO_2 gas
    B is N_2O_4 gas

    $MNO_3 + H_2SO_4$ ® $MHSO_4 + HNO_3$

    $Cu + 4HNO_3$ ® $Cu(NO_3)_2 + 2H_2O + 2NO_2$

    $2NO_2 \rightleftharpoons N_2O_4$

    Brown gas — Colourless gas
14. Phenol is a stronger acid, methyl group due to +I effect concentrates the negative charge on the oxygen, thus destabilising the intermidiate phenoxide ion in cresol.
15. (a) By reacting it with NaOH and Br_2.

    (b) Hoffmann bromamide degradation reaction.

    (c) $CH_3 - \overset{Cl}{\overset{|}{C}H} - CH_2 NH_2$

    2-Chloropropanamine

16. (a) Chlorine water loses its yellow colour on standing due to the formation of HCl and HClO.

$Cl_2 + H_2O$ ® $HCl + HClO$

(b) $Cl_2 + 2NaOH$ ® $NaCl + NaClO + H_2O$

(cold & dilute)

17. (a) By reacting with $NaNO_2$ and HCl or HNO_2 at temperature 0-5°C, aniline will form diazonium salt; CH_3NH_2 will form methanol and bubbles of N_2 gas will come out of the solution.

(b) By using Hinsberg's reagent. ($C_6H_5SO_2Cl$) $(CH_3)_3N$ will not react with Hinsberg's reagent while $(CH_3)_2NH$ will form a product insoluble in alkali.

18. (i)

(ii)

®

(iii)

19. (a) According to Faraday's first law, charge required

to deposit 1.50 g Ag = $\frac{96500}{108} \times 1.50$

= 1331.70 coulombs

Time taken = $\frac{1313.70}{1.50} = 887.15$ sec

(b) Inert electrodes

At Anode; $2H_2O_{(g)}$ ® $O_{2(g)} + 4H^+_{(aq)} + 4e^-$

At Cathode; $Ag^+_{(aq)} + e^-$ ® $Ag_{(s)}$

(c) Ag electrodes

At Anode : $Ag_{(s)}$ ® $Ag^+_{(aq)} + e^-$

At Cathode : $Ag^+_{(aq)} + e^-$ ® $Ag_{(s)}$

20. (i) Slope = $\frac{k}{2.303}$

(ii) As slope = $2 \times 10^{-4}\ s^{-1}$

$k = 2.303 \times 2 \times 10^{-4}\ s^{-1}$

$k = 4.606 \times 10^{-4}\ s^{-1}$

(iii) For a first order reaction $t = \frac{2.303}{k} \log \frac{[R]_0}{[R]}$

At $t_{1/2}$, $[R] = \frac{[R]_0}{2}$

$$t_{1/2} = \frac{2.303}{k} \log \frac{[R]_0}{\frac{[R]_0}{2}} = \frac{2.303}{k} \log 2$$

$$t_{1/2} = \frac{0.693}{k}$$

21. (a) (i) Mond's Process

(ii) Van Arkel Method

(b) $4Au_{(s)} + 8CN^-_{(aq)} + 2H_2O_{(aq)} + O_{2(g)}$

® $4[Au(CN)_2]^-_{(aq)} + 4OH^-_{(aq)}$

$2[Au(CN)_2]^-_{(aq)} + Zn_{(s)}$ ® $2Au_{(s)} + [Zn(CN)_4]^{2-}_{(aq)}$

In the first reaction Au changes into Au^+ ie. oxidation takes place. In the second case

Au^+ ® Au^0

ie, reduction takes place.

22. $6XeF_4 + 12H_2O$ ® $4Xe + 2XeO_3 + 24HF + 3O_2$

$XeF_6 + 3H_2O$ ® $XeO_3 + 6HF$

Hydrolysis of XeF_4 is a redox reaction. Here Xe^{4+} is changing into Xe and Xe^{6+}

ie, Xe^{4+} ® $Xe^o + Xe^{6+}$

23. (a) In $[Ti(H_2O)_6]^{3+}$ ion Ti is in +3 oxidation state. There is only 1 electron in the d-orbital and its configuration is $t^0_{2g}eg^1$.

(b) This complex is coloured due to d-d transition, configuration becomes $t^1_{2g}eg^o$.

(c) On heating $[Ti(H_2O)_6]^{3+}$ ion becomes colourless as there is no ligand (H_2O) left in heating. In the absence of ligand, crystal field splitting does not occur.

24. (a) 2-methyl-2-chlorobutane.

Larger molecular mass and has high magnitude of van der Waal forces.

Surface area and hence Van der Waal's forces of attraction decreases on branching.

(b) In nucleophilic substitution reaction, a carbanion intermediate is formed. This is stabilised by resonance as shown below in p-nitrochlorobenzene.

The -I effect of nitro group further stabilizes the intermediate.

Hence p- nitrochlorobenzene reacts faster than chloro benzene.

25. (a) This indicates that the aldehyde group in glucose is not free.

(b)

a – D – (+) – Glucopyranose

(c) 'D' gives the configuration ie. the – OH group at carbon 5 is on the right hand side (+) indicates that the isomer is dextro rotatory.

26. (a) Benzoyl peroxide working as an initiator in the polymerisation of ethene. It forms a free radical.

(b) LDPE :- Low Density Polyethylene

LDPE is obtained by the polymerisation of ethene under high pressure of 1000 to 2000 atm at 350K to 570 K temperature in the presence of an initiator.

HDPE:- High Density Polyethylene. It is obtained when polymerisation is done in the presence of Ziegler Natta Catalyst at 333 K to 343 K under 6 - 7 atm pressure.

27. Synthetic detergents are classified into three.

Anionic detergents : These are sodium salts of sulphonated long chain alcohols or hydrocarbons.

Eg : Sodium Salt of alkyl benzene sulphonates.

Cationic detergents : These are quarternary ammonium salts of amines with acetates, chlorides or bromides as anions.

Non-ionic detergents : They do not contain any ion in them. eg : Ester of stearic acid and polyethylene glycol.

OR

Antihistamines are drugs that interfere with the natural action of histamines. eg : (1) Bromopheniramine (2) Terfenadine - They interfere with the natural action of histamine by competing with histamine binding sites of receptor where histamine exerts its effect.

28. (a) $P_A = P_A^0 \times X_A$, X_A - Mole fraction of A

P_A- Partial vapour pressure of A

P_A^0 - Vapour pressure of pure A

According to Dalton's law of partial pressure, total pressure $P = P_A + P_B$ or $P = X_A P^0_A + X_B P^0_B$

Here for a solution containing non volatile solute

$P = P_A = X_A P^0_A$

But for a binary solution, $X_A + X_B = 1$ or $X_A = 1 - X_B$

Hence the above equation becomes $P = 1 - X_B$

where X_B = mole fraction of solute

ie, $P = P^0_A - X_B P^0_A$

$X_B P^0_A = P^0_A - P$ or $X_B = \frac{P^0_A - P}{P^0_A}$

(b) $\frac{\Delta P}{P^0} = iX_B$, $i = \frac{1}{2}$

$$X_B = \frac{n_B}{n_A + n_B} = \frac{61/122}{61/122 + \frac{500}{78}} = \frac{0.5}{0.5 + 6.41} = \frac{0.5}{6.91}$$

$$\frac{\Delta P}{66.6} = \frac{1}{2} \times \frac{50}{691}, \quad \Delta P = \frac{50 \times 66.6}{691 \times 2} = 2.41$$

$P^o - P = 2.41$, $P = 66.6 - 2.40 = 64.20$ torr

(ii) In the absence of dimerisation

$i = 1$; $\frac{\Delta P}{P^o} = X_B$

$Dp = \frac{50}{691} \times 66.6 = 4.82$

$P = 66.6 - 4.82 = 61.78$ torr

(iii) From Raoult's law

X_1 = mole fraction of liquid 1

X_2 = mole fraction of liquid 2

$P_1 = X_1 P_1^0$; $P_2 = X_2 P^0_2$

Y_1 = Mole fraction of component -1 in vapour phase.

Y_2 = Mole fraction of component - 2 in vapour phase.

$$Y_1 = \frac{P_1}{P_{total}} = \frac{P_1}{P_1 + P_2} \qquad Y_2 = \frac{P_2}{P_{total}} = \frac{P_2}{P_1 + P_2}$$

$$Y_1 = \frac{X_1 P_1^0}{X_1 P_1^0 + X_2 P_2^0} = \frac{X_1 P_1^0}{X_1 P_1^0 + (1 - X_1) P_2^0}$$

$$Y_2 = \frac{X_2 P_2^0}{X_1 P_1^0 + X_2 P_2^0}$$

OR

(a) 1 M has higher concentration than 1m.

1 m solution = 1 mole in 1000 g solvent

or

1 mole in 1000 cm^3 of solvent if d = 1 g / cm^3

But 1 M solution = 1 mole in 1000 cm^3 of solution ie, solvent is less here,

(b) $\Delta T_f = 0 - (-0.24) = +0.24^o$ C

$$M_2 = \frac{1000 K_f W_2}{\Delta T_f W_1} = \frac{1000 \times 1.86 \times 5}{0.24 \times 100} g\,mol^{-1} = 38.75\,g\,mol^{-1}$$

Theoretical molecular mass of KCl

= 39 + 35.5 = 74.5 g mol^{-1}

$$i = \frac{\text{Calculated mol. mass}}{\text{Theoretical mol. mass}} = \frac{74.5}{38.75} = 1.92$$

	$KCl \rightleftharpoons$	K^+	Cl^-
Initial moles:	1 mole	0	0
After dissociation:	$1 - a$	a	a

Total no. of moles after dissociation

$= 1 - a + a + a = 1 + a$

$$i = \frac{1 + \alpha}{1}$$

$a = i - 1 = 1.92 - 1 = 0.92$

Percentage dissociation = 92%

29. (a) CuF_2

In CuF_2, Cu^{2+} ($3d^9$) has an unpaired electron.

(b) (i) Oxidation state of Cr in CrO_4^{2-} is +6. This is its maximum oxidation state and it can only gain electrons. Oxidation state of Mn in MnO_4^{2-} is +6. Mn can further lose electron to become +7 which is its highest oxidation state.

(ii) This is due to lanthanoid contraction.

(iii) In its highest oxidation state, manganese can only accept electrons and so is acidic in behaviour. Similarly in its lowest oxidation state, it can donate electrons and hence is basic.

(iv) Mn (II) has maximum number of unpaired electrons ie. $3d^5$.

OR

(a) Dil. H_2SO_4 is an oxidising agent and oxidises $FeSO_4$ to $Fe_2(SO_4)_3$.

Dil.HCl is a reducing agent and liberates chlorine on reacting with $KMnO_4$ solution. Thus, part of the oxygen produced from $KMnO_4$ is used up by HCl.

(b) (i) In oxoanions, the oxygen atoms are directly bonded to the transition metal. Since oxygen is highly electronegative, the oxoanions bring out the highest oxidation state of the metal.

(ii) Ce^{4+} has the tendency to attain +3 oxidation state and so it is used as an oxidising agent in volumetric analysis.

(iii) This is due to the presence of voids of appropriate sizes in their crystal lattices.

(iv) Zn^{2+} ion has all its orbitals completely filled where as in Cu^{2+} ion, there is one half-filled 3d-orbital. It therefore has a tendency to form coloured salts where as Zn^{2+} has no such tendency.

30. (i) A is CH_3CHO or ethanal

B is C_6H_5CHO or benzaldehyde.

(ii) $$\underset{[A]}{2CH_3CHO} \xrightarrow{NaOH} CH_3 - \underset{}{\overset{OH}{\overset{|}{CH}}} - CH_2CHO \xrightarrow{-H_2O} CH_3 - CH = CH - CHO$$

2 -Butenal

(iii)

(iii) Toluene

OR

(i) X is CH_3CHO; Y is CH_3COOH

(ii) 3 - Hydroxybutanal.

(iii) $$\underset{\text{[Haloform test]}}{CHI_3} \xleftarrow{I_2/NaOH} \underset{[X]}{CH_3CHO} \xrightarrow{[O]} \underset{[Y]}{CH_3COOH}$$

$$CH_3 - \underset{CN}{\underset{|}{CH}} - OH \xrightarrow{H_2O/H^+} CH_3 - \underset{COOH}{\underset{|}{CH}} - OH$$

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UNIT - 1

THE SOLID STATE

1-Mark Questions

1) In the normal spinel structure, the oxide ions are arranged in CCP pattern. The Zn^{2+} ions occupy one eighth of the tetrahedral holes and one half of the octahedral voids are occupied by Al^{3+}. Give the formula of the spinel.

2) Metallic gold crystallizes in FCC lattice. How many nearest neighbours do each gold atom has?

3) When a crystal of NaCl is heated in sodium vapour, it acquires a yellow colour. The yellow colour is due to non stoichiometric defect. Name the defect.

4) In the face centered cubic arrangement of A and B atoms where A atoms are at the corner of the unit cell and B atoms at the face centres. One of the A atom is missing from one corner in the unit cell. What is the simplest formula of the compound?

5) For the structure given below identify the site marked as S.

6) In BCC lattice, what are the numbers of the nearest and next nearest neighbours?

7) What type of magnetism is shown by the substance whose magnetic moments are aligned as given below:

↑↑↓↑↓↑↑

8) A solid 'X' conducts electricity in solid state as well as in molten state. Its conductance decreases with increase in temperature. Identify the solid X.

9) In Chromium(III) Chloride, $CrCl_3$, chloride ions have cubic close packed arrangement and Cr(III) ions are present in the octahedral holes. What is the fraction of octahedral holes occupied? What is the fraction of total number of holes occupied?

2 **Marks Questions**

10) A compound AB crystallizes in BCC lattice with unit cell edge length of 480Pm. If the radius of B is 225Pm. Calculate the radius of A^+.
Hint:

For BCC structure: $2(r_A+r_B) = \sqrt{3}\, a$

11) In the close packing arrangement of atoms does a face centred atom touch the face centred atom of an adjacent face? Give reason for your answer.

12) Identify the crystal systems which have the following crystallographic dimensions:

$a \neq b \neq c$ $\alpha=\beta=\gamma=90°$

$a=b\neq c$ $\alpha=\beta=90°$ $\gamma=120°$

13) Identify the unit cell and calculate the number of atoms per unit cell.

14)

a. What are the types of close packing shown in figure 1 and 2?

b. Write one example for each type of close packing in metals.

15) The composition of a sample of wustite is $Fe_{0.93}O_{1.00}$. What percentage of Fe is present as Fe(III)?

16) Iron changes its crystal structure from body centred to cubic close packed structure when heated to 916°C. Calculate the ratio of the density of the BCC crystal to that of CCP crystal. Assume that the metallic radius of the atom does not change.
Hint:
Volume same, so ratio of density is also same
i.e. d(bcc)/d(ccp)

17) A compound forms hexagonal close packed structure. What is the total number of voids in 0.5 mol of it? How many of these are tetrahedral voids?

18) The electrical conductivity of Zinc oxide increases on heating. Give reason.

19) Both the ionic solids NaF and MgO have the same number of electrons and about the same inter nuclear distances. But the melting point of NaF is 992°C and that of MgO is 2642°C. Give plausible reason for this observation.
Hint:- charge of ions and lattice enthalpy.

20) The concentration of cation vacancies in NaCl crystal doped with $CdCl_2$ is found to be 6.02×10^{16} mol^{-1}. What is the concentration of $CdCl_2$ added to it?

3 Marks Questions

21) Calcium crystallizes in a face centred cubic unit cell with a=0.556nm. Calculate the density if

i. It contains 0.1% Frenkel defects.
ii. It contains 0.1% Schottky defects.

Hint:

Frenkel defect does not affect density.

$d=zM/a^3N_A$

Schottky defect reduces the density by 0.1%, assuming that volume remains constant.

$d'=d(1-0.1/100)$

$d'=0.999d$

22) You are given marbles of diameter 10mm. They are to be placed such that their centres are lying in a square bound by four lines each of length 40mm. What will be the arrangements of the marbles in a plane so that maximum number of marbles can be placed inside the area? Sketch the diagram and calculate the number of spheres per unit area.

23)

i. Name the defect shown in the figure.
ii. How does it affects the density of the solid
iii. Name a solid which shows this defect.

24) In the mineral, spinel, having the formula $MgAl_2O_4$, oxide irons are arranged in the cubic close packing. Mg^{2+}ions occupy the tetrahedral voids while Al^{3+}ions occupy the octahedral voids.

(i) What is the percentage of tetrahedral voids occupied by Mg^{2+}ions?
(ii) What is the percentage of octahedral voids occupied by Al^{3+}ions?

25) Metallic magnesium has a hexagonal close packed structure and has a density 1.74g cm^{-3}. Assuming magnesium atoms to be spherical, calculate the radius of magnesium atom. (Atomic mass of Magnesium= 24.3).

Hints: Consider 1cm^3 Mg and calculate mass of 1cm^3 of Mg. Then calculate the No: of atoms in that much mass of Mg. Calculate the volume occupied by the Mg Atoms and that occupied by 1 Mg atom. Then using the formula $4/3\pi r^3$ radius of Mg, r can be calculated

UNIT - 2

SOLUTIONS

1 Marks Questions

1. A 500 gm of toothpaste sample has 0.2 g of fluoride concentration. What is the concentration of fluoride in terms of ppm level?

2. Two liquids A and B boil at 135^0C and 185^0C respectively. Which of them has a higher vapour pressure at 80^0C?

3. Write the possible structural arrangement of a mixture of chloroform and acetone to form a solution.

4. What is Van't Hoff's factor for a compound which undergoes tetramerization in an organic solvent?

5. Aquatic species are more comfortable in cold waters rather than in warm water. Give reason.

2 marks questions

6. RBC's are placed in the given solutions as in figure (i)and (ii). What happens to RBC in test tube (i) and test tube (ii).

7. Given below is the sketch of a plant carrying out a process.

(i) Name the process occurring in the above plant.

(ii) To which container does the net flow of the solvent takes place?

(iii) Name one SPM which can be used in this plant.

(iv) Give one practical use of the plant.

8. A solution of sucrose (Molar mass 342 g mol^{-1}) is prepared by dissolving 68.4 g in 1000 g of water. What is the

   (i) Vapour pressure of the solution at 293k .

   (ii) Osmotic pressure at 293k.

   (iii) Boiling point of the solution.

   (iv) Freezing point of the solution.

   The vapour pressure of the water at 293k is 0.023atm. k_b=0.52k kg mol^{-1} & k_f=1.86k kg mol^{-1} . Assume the solution to behave ideally.

9. Why calculations based on colligative properties of solutions sometimes do gives abnormal molecular mass values for solute? What are the nature of the abnormalities. 2g of C_6H_5COOH dissolved in 25g of benzene shows a depression in freezing point equal to 1.62k. Molal depression constant for benzene is 4.9k kg mol^{-1}. What is the Percentage(%) of association of acid, if it forms a dimer in solution?

10. Assuming complete dissociation, calculate the freezing point of a solution prepared by dissolving 6 g of glaubers salt ($Na_2SO_4.10H_2O$) in 0.100 kg of H_2O. Given k_f = 1.86k kg mol^{-1} Atomic mass of H_2O : 18 , Na : 23 , S : 32 , O : 16 , H : 1 all in amu units.

3 Marks Questions

11. A) Addition of HgI_2 to aq. KI solution shows an increase in the vapour pressure why?

    B) A person suffering from high blood pressure is advised to take minimum quantity of common salt. Give reason.

12. A) Why the vapour pressure of a solution of glucose in water lower than that of water?

B) 0.1 molal solution of glucose and NaCl respectively. Which one will have higher boiling point?

13. H_2S, a toxic gas with rotten egg like smell is used for qualitative analysis. If the solubility of H_2S in water at STP is 0.195 m, calculate Henry's law constant (k_H=282 bar)

14. Examine the following illustrations and answer the following questions

1) Identify the liquid A (pure water or sugar solution).

2) Identify the liquid B (pure water or sugar solution).

3) Why the level of liquid in thistle funnel has risen after sometime?

4) Name the phenomenon involved in this experiment and define it.

15. A storage battery contains a solution of H_2SO_4 38% by weight. At this concentration van't Hoff factor is 2.50. At what temperature will the battery contents freeze?

(k_f for water =1.86k kg/ mol)

16. Following are the graphs for the vapour pressure of two component system as a function of composition. Answer the following questions.

Fig (a) Fig. (b)

(i) What type of deviation is shown in fig.(a) and (b)?

(ii) Give one example of solutions showing deviations in fig (a) (b).

(iii) What change in the volume and temperature is observed in solutions of this type?

17. How does osmotic pressure depend on temperature and atmospheric pressure, what is the molar concentration of solute particles in the human blood, if the osmotic pressure is 7.2 atm at the body temperature of 37^0C?

18. The vapour pressure of dilute aqueous solution of glucose ($C_6H_{12}O_6$) is 750 mm of mercury at 373K. Calculate

1) Molality

2) Mole fraction of the solute

5 Marks Questions

19. The elements A and B form purely covalent compounds having molecular formulae AB_2 and AB_4. When dissolved in 20g of benzene, 1g of AB_2 lowers the freezing point by 2.3K, whereas 1g of AB_4 lowers it by 1.3K. the molal depression constant for benzene is 5.1 K kg/mol, calculate the atomic mass of A and atomic mass of B. (**A=25.59, B=42.64**)

20. a) Why constant boiling mixtures behave like a single component when subjected to distillation.

b) What type of Azeotropic mixtures are formed by the following solution

i) H_2O and HCl ii) H_2O and C_2H_5OH

c) Give one practical application of depression of freezing point?

d) A Solid solution is formed between two substances. One whose particles are very large and the other particles are very small. What type of solid solution is this likely to be?

e) Write the Raoults Law for each component of a binary solution and show that the total vapour pressure of the solution may be expressed as $P = P^0A + (P^0B - P^0A) X_B$

21. Vapour pressure of pure benzene at a certain temperature is 640 mm Hg. A non-volatile non-electrolyte solid weighing 2.175g is added to 39.0 of benzene. The vapour pressure of solution is 600 mm Hg. What is the molecular mass of solid substance? (**65.9g mol^{-1}**)

22. The degree of dissociation of $Ca(NO_3)_2$ in dilute solution aqueous solution containing 7.0g of the solute per 100g of water at 100^0 C is 70 percent. If the vapour pressure of water at 100^0 C is 760mm, calculate the vapour pressure of the solution. (**746.02mm**)

23. What mass of a non-volatile solute urea (NH_2CONH_2) need to be dissolved in 100g of water in order to decrease the vapour pressure of water by 25%? also calculate the molality of the solution. (**18.52m**)

24. 8.0575×10^{-2} kg of Glauber's salt is dissolved in water to obtain 1 dm^3 of a solution of density 1077.2 kg m^{-3}. Calculate the molarity, molality & mole fraction of Na_2SO_4 in the solution. (**0.2508m, 0.0045, 0.25M**)

25. To 500 cm^3 of water 3.0×10^{-3} kg of acetic acid is added. If 23% of acetic acid is dissociated, what will be the depression in freezing point? K_f and density of water are 1.86 K kg mol^{-1} & 0.997 g cm^{-3} respectively.(**0.229K**)

UNIT - 3

ELECTROCHEMISTRY

2 Marks Questions

1 How many faraday of charge is required for conversion of $C_6H_5NO_2$ into $C_6H_5NH_2$?

2 Explain why Zn dissolves in dil. HCl to liberate $H_2(g)$ but from conc. H_2SO_4, the gas evolved is SO_2.

3 Cu does not dissolve in HCl but dissolves in nitric acid. Explain why?

4 Fluorine has a low electron gain enthalpy compared to chlorine, yet it is a more powerful oxidant. Explain why?

5 If Zn2+/Zn electrode is diluted 100 times, then what will be the change in emf?

6 You are aquainted with the construction and working of a lead-storage battery. Give the plausible reasons for these facts:

1. There is only a single compartment unlike other electrochemical cells.
2. Replacement of water is necessary for maintenance.

7 For what concentration of Ag+(aq.), will the emf of given cell be zero at \ 25 ^oC , if the concentration of Cu(s) | Cu^{2+}(0.1M) || Ag^+(aq.) | Ag(s)? Given , $E^0_{Ag+/Ag}$=0.80V; $E^0_{Cu2+/Cu}$=0.34V.

8 In a small town along the costal area, it is observed that iron objects rust easily. Being an industrial town, it also faces air pollution problem. Identify any 4 factors which are contributing to rusting phenomenon.

9 Iodine(I_2) and Bromine(Br_2) are added to a solution containing iodide(I-) and bromide ions(Br-). What reaction would occur if the concentration of each species is 1M? The electrode potentials are $E^0_{I2/I-}$=0.54V and $E^0_{Br2/Br-}$=1.08V

3 Marks Questions

10 In an industrial plant, aluminium is produced by elecrolysis of alumina dissolved in cryolite. This takes a current of 20000A. If the current efficiency is 90%, how much Al will be produced per day?

11 In an experiment 0.04 F was passed through 400 mL of 1M soln. of NaCl. What would be pH of the soln. after elecrolysis.

12 Estimate the minimum P.D. needed to reduce Al_2O_3 at 500 0 C. The free energy change for the decomposition reaction is 960 kJ.
$2/3\ Al_2O_3 \qquad 4/3\ Al + O_2;\ \Delta G = 960\ kJ$

13. A cell with N/50 KCl soln. offered a resistance of 550 ohms at 298 K. The specific conductance of N/50 KCl at 298 K is 0.002768 ohm-1cm-1. When the cell is filled with N/10 ZnSO4 soln, it offered a resistance of 72.18 ohms at 298 K. Find the cell constant and molar conductance of $ZnSO_4$ soln. at 298K.

14. Which of the following has larger molar conductance:
    a. 0.08 M soln. having conductivity equal to 2×10^{-2} $ohm^{-1}cm^{-1}$.
    b. 0.10 M soln. having resistivity equal to 5.8 ohm cm.

15. The K_{sp} of AgCl at 298 K is 1×10^{-10}. Calculate electrode potential of Ag electrode immersed in 1 M KCl soln..
[Given: $E^0\ Ag^+/Ag = 0.799$ V]

16. Tarnished siver contains Ag_2S. Can this tarnish be removed by immersing the tarnished silverware in an Al pan containing an inert electrolyte soln. such as NaCl?
Given that standard electrode potentials for half reactions are:
$Ag_2S(s) + 2e^- \qquad 2Ag(s) + S^{2-}(aq.)$ is -0.71 V
$Al^{3+}(aq.) + 3e^- \qquad Al(s)$ is -1.66 V.

5 **Marks Questions**

17 Observe the diagram carefully and answer the questions below:

An external opposite potential is applied such that it exceeds the cell potential.

a. Is this an electrochemical cell or electrolytic cell?
b. Which substance gets dissolved?
c. Which substance gets deposited and where?
d. Write half cell reactions.
e. Is the needle in the voltmeter correctly marked?

18 2 beakers A and B contain 1 M $ZnSO_4$ solution. To A , Strip of Mg is dipped, while in B, A zinc rod is put. If both are connected to a standard hydrogen electrode, which cell would show a deflection? Explain with suitable reason.

19 The standard electrode potentials of different electrodes are given as $E^0_{Co^{3+}/Co^{2+}} = 1.81$ V, $E^0_{Al^{3+}/Al} = -1.66$ V, $E^0_{Fe^{2+}/Fe} = -0.44$ V, $E^0_{Br2/Br-} = 1.01$ V

a. Identify all the possible combination for construction of a feasible electrochemical cell?
b. Write their electrochemical cell representation.
c. Calculate the emf in each case.

20 a. During electrolysis of NaOH, Cl_2 and H_2 while for molten NaCl only Na metal and Cl_2 gas are obtained. Explain these observations with suitable eqn.
b. Electrolysis of conc. and dil. sulphuric acid are different. Explain with eqn.

21 An Aq. solution of $AuCl_3$ was electrolysed with a current of 0.5A until 1.20g of Au had been deposited on the cathode. At another electrode in series with this, the only reaction was evolution of O_2. Find—

1. The no. of moles
2. The volume at NTP
3. The mass of O_2 liberated
4. the no. of coulombs passed through the solution and
5. the duration of electrolysis

UNIT – 4

CHEMICAL KINETICS

1 Mark Questions

1. If rate law is; rate = $[A]^{3/2}\ [B]^{-1}$, determine the order.

2.A gas decomposition of AB follows the rate law; rate = $K[AB]^{3/4.}$ Write units of K.

3. State any one condition under which a bimolecular reaction may be kinetically of first order.
4. In some cases, it is found that a large number of colliding molecules have energy more than threshold energy, yet the reaction is slow. Why?
5. Variation of concentration of a reactant with time for a given reaction is shown below. What is its order of reaction?

6. Variation of concentration of a reactant, ln[R] with time for a given reaction is shown below. What is its order of reaction?

2 / 3 Mark Questions

7. The kinetics of the reaction: A + 2B $\rightarrow$ Products; obeys the rate equation Rate = k $[A]^X$ $[B]^{Y.}$ For it, find
   a) Order of the reaction
   b) Apparent molecularity of reaction
   c) Order of reaction when B is in large excess.

8.Following reaction takes place in one step

$$2NO\ (g) + O_{2\ (g)} \rightarrow 2\ NO_2\ (g)$$

How will the rate of above reaction change if the volume of the reaction vessel is diminished to one third of its original volume? Will there be any change in order of reaction with the reduced volume?

9. For the reaction

$NO_2 + CO \rightarrow CO_2 + NO$

Mechanism of reaction is

a) $NO_2 + NO_2 \rightarrow NO + NO_3$ (slow)

b) $NO_3 + CO \rightarrow CO_2 + NO_2$ (fast)

Write its rate law.

10. The activation energy of a first order reaction is 30 kJ/mol at 298K. The activation energy for the same reaction in the presence of a catalyst is 24 kJ/mol at 298K. How many times the reaction rate has changed in the presence of a catalyst?

11. A reaction is carried out at two different initial concentrations of a reactant. The initial concentrations are 1mol L^{-1} and 2mol L^{-1}. The half-life values obtained were20minutes and 40 minutes respectively. What is the order of reaction?

12. In the Arrhenius equation fora certain reaction, the value of A and Ea are 4×10^{13} s^{-1} and 98.6 kJ mol^{-1} respectively. If the reaction is of first order; at what temperature will its half life period be ten minutes?

13. The time required for 10% completion of a first order reaction at 298 K is equal to that required for its 25% completion at 308K. If the pre-exponential factor for the reaction is 3.56×10^{9} sec^{-1}, calculate its rate constants at 318K and also the energy of activation.

5 Mark Questions

14. Following is a graph between reaction co-ordinate and potential energy. Explain how a catalyst influence the reaction.

15. In a given graph**, i**f 'E' is the activation energy for a given reaction, explain how temperature influences the rate of reaction.

16. In the following figure, orientations of reaction molecules are shown. Explain the influence of orientation of molecules in a chemical reaction?

UNIT-5

SURFACE CHEMISTRY

2 Marks Questions

1 Explain how activated charcoal adsorbs organic dye.

2. A graph between log(x/m) and log p is a straight line at angle of 45^0 with intercept on the y-axis(log k) equal to 0.301. Calculate the amount of the gas adsorbed per gram of the adsorbent under a pressure of 0.4 Atmosphere

3 Adsorption is always exothermic in nature. Comment.

4 Critical temperatures of N_2, CO, CH_4 are 126, 134, and 110 K respectively. Arrange them in increasing order of adsorption on the surface of activated charcoal?

5 Consider the adsorption isotherms given below and interpret the variation in the extent of adsorption (x/m) when:
   (i) Temperature increases at constant pressure.
   (ii) Pressure increases at constant temperature

6 If the flocculation values of NaCl and $AlCl_3$ are respectively 52 and 0.093, compare their coagulating powers.

7. Explain how soap solution stabilizes an emulsion of oil in water?

8 What happens when a freshly precipitated $Fe(OH)_3$ is shaken with little dil. $FeCl_3$ solution? Explain with possible reactions.

9 A methanol poisoned patient is treated by giving intravenous infusion of dil. ethanol. Explain.
[Hint: Influence of inhibitors]

10 How does a 'collector' separate the ore from gangue in the froth floatation process?

3 Marks Questions

11 A colloidal solution of AgI is prepared by 2 different methods as shown:

(i) What is the charge of AgI colloidal particles in the two test tubes (A) and (B)?

(ii) Give reasons for the origin of charge.

12 SnO_2 forms a positively charged colloidal sol in the acidic medium and negatively charged sol in basic medium. Explain.

13 1 g of charcoal adsorbs 100 ml of 0.5 M CH_3COOH to form a monolayer and thereby the molarity of acetic acid is reduced to 0.49 M. Calculate the surface area of the charcoal adsorbed by each molecule of acetic acid. Surface area of charcoal = 3.01×10^2 m^2/g.

14 To 100 ml of M/2 oxalic acid solution 2 g of active charcoal is added. After adsorption the strength of solution is reduced to M/4. Calculate the acid adsorbed by 1 g of charcoal.

15 Explain why:

(i) At sunset an orange colour develops in the sky.

(ii) Bleeding due to a small cut can be stopped by rubbing alum.

Activated charcoal is used in gas masks used by coal miners.

UNIT - 6

GENERAL PRINCIPLES AND PROCESS OF ISOLATION OF ELEMENTS

1 Mark questions

1. During metallurgical process, in the extraction of metal, flux is added. Why?
2. 'Reduction of a metal oxide is easier if the metal formed is in liquid state at the temperature of reduction. Why?
3. Although thermodynamically feasible, in practice, magnesium metal is not used for the reduction of alumina in the metallurgy of aluminium. Why?
4. Can Mg reduce Al_2O_3 and Al reduces MgO? State the conditions required for this reduction process.

2/ 3 Marks Questions

5. At a site, low grade copper ores are available and zinc and iron scraps are also available. Which of the two scraps would be more suitable for reducing the leached copper ore and why?
6. The value of $\Delta_f G^o$ for formation of Cr_2O_3 is – 540 kJ mol^{-1} and that of Al_2O_3 is – 827 kJ mol^{-1}. Is the reduction of Cr_2O_3 possible with Al?
7. Why is zinc not extracted from zinc oxide through reduction using CO?
8. Cinnabar (HgS) abd Galena (PbS) on roasting often give their respective metals but Zinc blende (ZnS) does not. Why?
9. The choice of a reducing agent in a particular case depends upon thermodynamic factor. How far do you agree with this statement? Explain?
10. "The extraction of Ag by leaching with NaCN involves both oxidation and reduction". Explain?
11. Out of C and CO which is a better reducing agent at 673 K?

UNIT-7

p- BLOCK ELEMENTS

1 Mark Questions

1. Which amongst the following is the strongest oxidizing agent?

   ClO_4^-, BrO_4^-, IO_4^-

2. A student wanted to draw his school building on a glass sheet, which acid he should use?

3. Nitrogen and P give negative ions, while As, Sb and Bi do not. Why?

4. Sea weeds are the sources of which halogen?

5. When NaBr is heated with conc H_2SO_4 ,Br_2 is produced but when NaCl is heated with conc H_2SO_4, HCl is produced. Why?

6. Which oxo-acid of Phosphorus contains P-P linkage?

7. Out of $HClO_3$ and $HClO_4$, which has lower Pka value and why?

8. Name the acidic hydride of N_2?

9. State the difference between the nature of Pi bonds in H_3PO_3 and HNO_3 molecules?

10. Name the gas liberated when Ammonium Nitrate is strongly heated.

11. Give one disproportionation reaction of H_3PO_3.

2 Mark Questions

12. Oxides of Nitrogen have open chain structure, while those of Phosphorous have closed chain or cage structures. Why is it so?

13. Complete the following :

    I. $HNO_3 + P_4O_{10} \rightarrow$

    II. $IO_3^- + I^- + H^+ \rightarrow$

III. $NH_3 + NaOCl \rightarrow$

IV. $SbCl_3 + H_2O \rightarrow$

14. Calculate the amount of 0.1 M NaOH solution required to neutralize the solution produced by dissolving 1.1 g of P_4O_6 in water.

15. Explain giving reason. Nitrogen exists as a diatomic molecule whereas Phosphorous exists as tetra atomic molecule.

16. Name the hydrogen halide which is liquid at room temperature and why?

17. Which oxide of sulphur is capable of acting as oxidizing as well as reducing agent? Why?

18. $(SiH_3)_3N$ is a weaker base than $(CH_3)_3N$. Give reason.

19. CN^- ion is known but is CP^- not known. Give reason.

20. Explain giving reason. NF_3 is an exothermic compound but NCl_3 is an endothermic compound.

21. Which halogen will produce O_2 and O_3 as passed through water?

22. Nitrogen forms a large no. of oxides than Phosphorous. Explain.

3 marks question

23. Account for the following

    I. Chlorine water has both oxidizing and bleaching properties.

    II. H_3PO_2 and H_3PO_3 act as good reducing agents while H_3PO_4 doesn't.

24. An organic compound A gives a brick red flame on performing flame test. The compound gives the following tests also

    I. It gives smell of chlorine when placed in moist air.

    II. If KI and CH_3COOH are added to the solution of the compound a violet colour is observed.

    Identify the compound and write the chemical reactions for the steps (I) and (II).

25. Give reasons for each of the following observations

    I. Only higher members of the group 18 of the periodic table are expected to form compounds.

    II. NO_2 readily forms a dimer whereas ClO_2 doesn't.

26. Give reasons for the following observations

    I. SF_6 is used as gaseous electrical insulators.

    II. S exhibit greater tendency for catenation than selenion.

    III. The electron gain enthalpy value of F_2 is less negative than chlorine.

27. Bleaching of flowers by Cl_2 is permanent, by SO_2 it is temporary. Explain?

28. Hydrogen halides are covalent compounds but their aqueous solutions can conduct electric current. Explain.

29. Which of the halogens (except At)

    I. Forms the weakest acid?

    II. Has the largest atom?

    III. Has the minimum ionization enthalpy?

    IV. Has the maximum electron affinity?

30. Knowing the electron gain enthalpy values for $O \rightarrow O^-$ and $O \rightarrow O^{2-}$ as

    -141 KJ/mol and 702 Kj/mol respectively, how can you account for the formation of a large no. of oxides having O^{2-} species and not O^- (clue: Lattice Enthalpy).

31. What happens when SO_2 is passed through an aq. Solution of Fe (III) salt. Give equation.

5 Marks Question

32. An element 'A' exists as a yellow solid in standard state. It forms a volatile hydride 'B' which is a foul smelling gas and is extensively used in qualitative analysis of salts.

When treated with oxygen, ‘B’ forms an oxide ‘C’ which is colourless, pungent smelling gas. This gas when passed through acidified $KMnO_4$ solution, decolourizes it. ‘C’ gets oxidized to another oxide ‘D’ in the presence of a Heterogeneous catalyst. Identify A, B, C, D and also give the chemical equation of reaction of ‘C’ with acidified KMnO4 solution and for conversion of ‘C’ to ‘D’.

33. Concentrated sulphuric acid is added followed by heating to each of the following test tubes labelled (i) to (v)

Identify in which of the above test tube the following change will be observed. Support your answer with the help of a chemical equation.

(a) Formation of black substance

(b) Evolution of brown gas

(c) Evolution of colourless gas

(d) Formation of brown substance which on dilution becomes blue

(e) Disappearance of yellow powder along with evolution of colourless gas.

34. When conc. sulphuric acid was added to an unknown salt present in a test tube, a brown gas (A) was evolved. This gas intensified when copper turnings were also added into this tube. On cooling, the gas ‘A’ changed into a colourless gas ‘B’.

(a) Identify the gases A and B.

(b) Write the equations for the reactions involved.

35. A translucent white waxy solid ‘A’ on heating in an inert atmosphere is converted in to its allotropic form (B). Allotrope ‘A’ on reaction with very dilute aqueous KOH librates a highly poisonous gas ‘C’ having rotten fish smell. With excess of chlorine ‘A’ forms ‘D’ which hydrolysis to compound ‘E’. Identify compounds ‘A’ to ‘E’ .

36. A colourless inorganic salt (A) decomposes completely at about 25^0 C to give only two products, (B) and (C), leaving no residue. The oxide (C) is a liquid at room temperature and neutral to moist litmus paper while the gas (B) is a neutral oxide. White phosphorus burns in excess of (B) to produce a strong white dehydrating agent. Write balanced equations for the reactions involved in the above process.

Gradual addition of KI to $Bi(NO_3)_3$ solution initially produces a dark brown precipitate which dissolves in excess of KI to give a clear yellow solution. Write chemical equations for the a

UNIT - 8
THE d- and f- BLOCK ELEMENTS

1 Mark Questions

1. Ce^{4+} has a noble gas electronic configuration, but it is used as an oxidizing agent in volumetric analysis. Give reason.

2 State why Flourine stabilizes higher oxidation states?
3. CrO_4^{2-} is a strong oxidizing agent while MnO_4^{2-} is not. Why?
4. Why is Cu_2Cl_2 colourless and $CuCl_2$ coloured?
5. Which is stronger base $La(OH)_3$ or $Lu(OH)_3$? Why?
6. It is found that Ce^{4+} is a good oxidizing agent whereas Sm^{2+} is a good reducing agent. State the reason for this difference.
7. Actinoid contraction is greater from element to element than lanthanoid contraction. Why?
8. Mn^{2+} is more stable than Mn^{3+}. Give the reason?
9. Observe the following equation and identify the phenomenon takes place:
   $3MnO_4^{2-} + 4H^+ \longrightarrow 2MnO_4^- + MnO_2 + 2H_2O$
10. $Cr_2O_7^{2-} \rightleftharpoons 2CrO_4^{2-}$
    How does this equilibrium can be shifted to right?

2 Marks Questions

11. An yellow translucent solution is obtained on passing H_2S gas through an acidified solution of $KMnO_4$. Identify the solution and write the balanced chemical equation.

12. Electronic configuration of Cu(I) is $[Xe]3d^{10}$ and that of Cu(II) is $[Xe]3d^9$. Which is more stable in aqueous solution? Why?

13. Electronic configuration of four metals A,B and C are give below:

A:	$1S^2$	$2S^2$	$2P^6$	$3S^2$	$3P^6$	$4S^1$	$3d^{10}$
B:	$1S^2$	$2S^2$	$2P^6$	$3S^2$	$3P^6$	$4S^2$	$3d^{10}$
C:	$1S^2$	$2S^2$	$2P^6$	$3S^2$	$3P^6$	$4S^2$	$3d^5$

    Identify the transition metals among them.
14. Zr (4d series) and Hf (5d series) have similar radi and have similar physical and chemical properties. Explain why?

15. In a given series the difference in the ionization enthalpies between any two successive d block elements is very much less than that in case of s and p block elements. Give the explanation.
16. Cu^{+} is unstable in aqueous solution and disproportionate as
$2Cu^{+} \longrightarrow Cu^{2+} + Cu$
Why does Cu^{+} disproportionate in aqueous solution?
17. Observe the following reaction:

$$2Fe^{3+} + 2I^{-} \longrightarrow 2Fe^{2+} + I_2$$

$$2Fe^{2+} + S_2O_8^{\ 2-} \longrightarrow 2Fe^{3+} + 2SO_4^{2-}$$

(i) Identify the role of Fe^{3+} in this reaction

(ii) Which property of Fe is used up here.

18. Among the oxides of Chromium CrO_3 is acidic, Cr_2O_3 is amphoteric and CrO is basic. State reasons for these observations.

19. For the first row of transition metals the $E^{\ominus}$ values are

Elements	V	Cr	Mn	Fe	Co	Ni	Cu
$E^{\ominus}(M^{2+}/M)$ in volts	-1.18	-0.91	-1.18	-0.44	-0.28	-0.25	+0.34

Observe the values and write the reasons for irregularities.
20. Give reasons for the following:

(i) Mn^{2+} is more stable than Mn^{3+}

(ii) The colour of $CuCr_2O_7$ in water is green.

3 Marks Questions

21. The structure of chromate ion and dichromate ion are given below;

They are interconvertible in aqueous solution depending upon P^{H} of the solution. Give the possible reason for this phenomenon along with the balanced chemical equations.

22. When an orange coloured crystalline compound ‘A’ was heated with common salt and concentrated H_2SO_4, an orange red coloured gas ‘B’ was evolved. The gas ‘B’ on passing through NaOH solution gave an yellow solution C

(i) Identify A,B and C.

(ii) Write balanced chemical equation involved in the reactions.

23. Observe the following graph and answer the questions given below:

(i) Why melting point of transition elements generally increases towards middle in each series.

(ii) Why Mn and Tc in 3d and 4d series respectively have low values of melting points.

(Hint: d^5 – stable electronic configuration; electrons held tightly by nucleus; delocalization is less and metallic bond is weak)

(iii) Why the last members of each series show low values of melting points?

24.

Elements	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
$\Delta_i H^{\ominus}$II	1235	1309	1414	1592	1509	1561	1644	1752	1988	1734
$\Delta_i H^{\ominus}$III	2393	2657	2833	2990	3266	2962	3243	3462	3556	3829

Observe the table and give plausible reasons for the following trends:

(i) The second ionization enthalpy values of Cr and Cu are unusually high.

(ii) The second ionization enthalpy of Zn is comparatively low.

(iii) The third ionization enthalpy of Mn and Zn are unusually high.

25. Observe the following table and explain the statements given below:

Elements	Ti	V	Cr	Mn	Fe	Co
$E^{\ominus}(M^{3+}/ M^{2+})$ in volts	-0.37	-0.26	-0.41	1.57	0.77	1.97

(i) Mn has high $E^{\ominus}$ value.

(ii) Comparatively low $E^{\ominus}$ value of V.

(iii) Comparatively low $E^{\ominus}$ value of Fe.

26. A mixed oxide of iron and chromium $FeOCr_2O_3$ is fused with Sodium Carbonate in 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.
(i) Identify the compounds (A) and (B)
(ii) Write balanced chemical equations for each step.

5 Marks Questions

27. (a) A blackish brown coloured solid (A) when fused with alkali metal hydroxides in presence of air produces a dark green compound (B), which on electrolytic oxidation in alkaline medium gives a dark purple compound (C). Identify (A), (B) and (C) and write balanced chemical equations for the reactions involved.
(b) What happens when an acidic solution of the green coloured compound (B) is allowed to stand for some time? Give the equation of the reaction involved. What is this type of reaction called?
(Hint: MnO_4^{2-} changes to MnO_4^-)

28. (A) reacts with H_2SO_4 to form purple coloured solution (B) which reacts with KI to form colourless compound (C). The colour of (B) disappears with acidic solution of $FeSO_4$. With concentrated H_2SO_4 (B) forms (D) which can decompose to give a black compound (E) and O_2. Identify (A) to (E) and write equations for the reactions involved.

UNIT - 9

CO-ORDINATION COMPOUNDS

1 Mark Questions

1. Write the IUPAC name of the complex $Na_3[Cr(OH)_2F_4]$.
2. Write the IUPAC name of $[CO(en)_2Cl(ONO)]^+$
3. Which of these cannot act as ligand and why: NH_3, H_2O, CO, CH_4. Give reason?
4. NH_3 is strong ligand NH_4^+ ion is not, why?
5. Which of the two is more stable $K_4[Fe(CN)_6]$ or $K_3[Fe(CN)_6]$.

2 / 3 Mark Questions

1. A coordination compound has a formula ($CoCl_3$. $4NH_3$). It does not liberate NH_3 but precipitates chloride ion as AgCl. Give the IUPAC name of the complex and write its structural formula.
2. How is stability of co-ordination compounds determined in aqueous solution? Select a complex formation reaction and write an expression for the stability constant of the complex. Mention the factors affecting stability of complexes.
3. Why do tetrahedral complex not show geometrical isomerism?
4. Write the correct formula for the following co-ordination compounds.
   $CrCl_3$. $6H_2O$ (Violet, with 3 Chloride ions/ Unit formula)
   CrCl3 . $6H_2O$ (Light green colour with 2 Chloride ions/ unit formula)
   $CrCl_3$. $6H_2O$ (Dark green colour, with 1 Chloride ion/ unit formula)
5. Aqueous copper sulphate solution (blue in colour) gives:
   a. a green precipitate with aqueous potassium flouride
   b. a bright green solution with aqueous potassium chloride. Explain these experimental results.
6. Identify complexes with different geometries depending upon the type of hybridization.
   (a) $[Co(NH_3)_6]^{3+}$ (b) $[CoF_6]^{3-}$
7. One mole of complex compound $Co(NH_3)_5Cl_3$ gives 3 moles of ions on dissolution in water. One mole of same complex reacts with 2 moles of AgCl(s). What is the structure of the complex and write its formula.
8. When an aquous solution of Nickel (II) chloride is mixed with ethane-1,2 diamine(en) in the molar ratios en : Ni=1:1, 2:1 and 3:1, the green coloured solution finally turns violet. Explain the chemical reactions based on the data provided.

UNIT - 10
HALOALKANES AND HALOARENES

1 Iodoform gives the precipitate with $AgNO_3$ on heating while chloroform does not. Give reasons

2 The following reaction give 2 products.
Write their structures
.

$$C_6H_5CH_2CHClC_6H_5 \xrightarrow[\text{Heat}]{\text{Alc.KOH}}$$

[hint: the 2 are geometrical isomers]

3 Predict the products of the following reactions:

a. HCl with $CH_3CCl{=}CH_2$
b. HBr with $CH_3CH{=}C(CH_3)_2$

4 Monochlorination of ethane to ethyl chloride is more practical than chlorination of n-pentane. Give reasons

5 An optically active compound having molecular formula $C_7H_{15}Br$ reacts with aq. KOH to give racemic mixture of products. Write the mechanism involved in the reaction.
[hint: a carbocation being planar, allows attack of nucleophile from either direction.]

6 a. Which of the following 2 compounds would react faster by S_N2 pathway:- 1-bromobutane or 2-bromobutane and why?

b. Allyl chloride is more reactive than n-propyl chloride towards nucleophilic substitution reaction. Explain why?

c. Haloalkanes react with KCN to give alkyl cyanides as main product while with AgCN, they form isocyanide as the main product. Give reasons.

7 In each of the following pairs of organic compounds, identify the compound which will undergo $S_N1$reaction faster. Also give reason with related structures.

8 p-nitrobenzene undergoes nucleophilic substitution faster than chlorobenzene. Explain giving the resonating structures as well.

9 the structural formulas of the organic compounds. A, B, C, D in the following sequence of reactions

10 Rearrange the following in order of increasing ease of dehydrohalogenation: $CH_3CH_2CH_2Cl$, $CH_3CHClCH_3$, $CH_3CCl(CH_3)_2$. Give reasons.

11 Write formulae for structural and geometrical isomers of $C_3H_4Cl_2$.
[HINT: total 7 structures

12 When toluene is chlorinated:
a. in presence of sunlight
b. in dark, in the presence of lewis acid, two separate compounds are obtained.
Explain with suitable mechanism.

13 Predict the order of reactivity of the following compounds in S_N1 and S_N2 reactions, giving reasons-
a. $C_6H_5CH_2Br$, $C_6H_5CH(C_6H_5)Br$, $C_6H_5CH(CH_3)Br$, $C_6H_5C(CH_3)(C_6H_5)Br$
The 4 isomeric bromobutanes

14 Arrange the following isomeric substituted haloarenes in ascending order of their reactivity towards NaOH to form corresponding substituted phenols.

15 Arrange the following halocompounds in decreasing order of reactivity towards S_N1 nucleophilic substitution reaction, Vinyl chloride, Benzyl chlorides, iso propyl bromide.

UNIT-11

ALCOHOLS, PHENOLS & ETHERS

1 Marks Questions

1. Write the IUPAC name of the product formed by the catalytic reduction of Butanal.
2. How can you prepare Phenol from Aminobenzene.
3. Para-amino phenol is less acidic than phenol. Give reason.
4. Arrange the following alcohols in the order of increasing reactivity towards Lucas reagent:

   2-butanol, 1-butanol, 2-methyl-2-propanol.
5. Which bond of alcohol is cleaved during its reaction with carboxylic acid?
6. Which structural isomer of butanol cannot be dehydrogenated by copper at 573K?

2 Marks Questions

7. Anisole reacts with HI to give phenol and methyl iodide and not iodobenzene and methylalcohol. Give reason.
8. Write the equations of the reactions which takes place when

   I. Thionyl chloride is treated with 2-propanol.

   II. Cumene hydroperoxide is treated with dil. H_2SO_4.
9. Why is that the phenol is acidic and hexanol is neutral towards a solution of NaOH.
10. Out of bezene and phenol which is more easily Nitrated and why?
11. A) di-tert-butyl ether cannot be made by williamson's synthesis. Explain why?

    B) name the carbocation formed when 3,3 di-2-butanol is treated with dilute acid.
12. Write the steps involved in the mechanism of acid catalysed hydration of propene.

13. Give a chemical test to distinguish between the following pairs of compounds

    I. Phenol and cyclohexanol.

    II. Propan-2-ol and benzylalcohol.

3 Marks Questions

14. An organic compound (A) having molecular formula C_6H_6O gives a characteristic colour with aqueous $FeCl_3$ solution (A) on treatment with CO_2 and NaOH at 400 K under high pressure gives (B) which on acidification gives a compound (C). C reacts with acetyl chloride to give (D), which is a popular Pain Killer. Deduce the structures of (A), (B), (C) and (D).

15. Write the chemical equations and reaction conditions for the conversion of
    I. Phenol to salicylaldehyde.
    II. Methanol to ethanol
    III. Anisole to 4-methoxyacetophenone
16. Name the reagents for the following
    I. Oxidation of primary alcohol to aldehyde.
    II. Oxidation of primary alcohol to carboxylic acid.
    III. Dehydration of prapan-2-ol to propene.
    IV. Reduction of butan-2-one to butan-2-ol.
17. Complete the following reaction

18. Compound (A) reacts with $SOCl_2$ to give compound (B). B reacts with Mg to form Grignard reagent which is treated with acetone and the product is hydrolyzed to give 2-methylbutan-2-ol. What are A and B compounds?

UNIT-12
ALDEHYDES KETONES AND CARBOXYLIC ACIDS

1-Mark Questions

1) Identify X.

2) Identify B and C in the following reaction.

3) Arrange the following compounds in the increasing order of their boiling points.
$CH_3CH_2CH_2CH_3$, $CH_3OCH_2CH_3$, CH_3CH_2CHO, CH_3COCH_3, $CH_3CH_2CH_2OH$

4) Propanal is more reactive than propanone. Give the reason.

5) a

Observe the reactions and state why the compound A is oxidized where as compound B is not oxidized by alkaline $KMnO_4$?

6) Which one among the following is the strongest acid?

7) Identify the reagent used in the following conversion.

8) Fluorine is more electronegative than Chlorine even then P-Fluorobenzoic acid is weaker acid than P-Chlorobenzoic acid. State the plausible reason for this.

9) Identify A and B in the following reaction:

2- Mark Questions

10) For the reaction:

The position of equilibrium lies largely to the right hand side for most Aldehydes and to the left for most ketones. Find out the reason.

11) Identify the following named reactions and write the reagents used:

$CH_3CHO \longrightarrow CH_3\text{-}CH_3 + H_2O$

$CH_3COCH_3 \longrightarrow CH_3-C(CH_3)=NNH_2 \longrightarrow CH_3CH_2CH_3 + N_2$

12) Aldol condensation of a ketone in presence of dilute alkali gives 4-Hydroxy -4-methylpentan-2-one.Write the structure of ketone and its IUPAC name.

13) Which among the following compounds give Cannizzaro reaction and state the reason?

, CH_3CHO, CH_3COCH_3.

14) Predict the products of the following reactions:

$$R\text{-}CH{=}CH\text{-}CHO + NH_2\text{-}\underset{\underset{O}{\|}}{C}\text{-}NH\text{-}NH_2 \xrightarrow{H^+}$$

15) The decreasing order of acidity of a few carboxylic acids is given below:
$C_6H_5COOH > C_6H_5CH_2COOH > CH_3COOH > CH_3CH_2COOH$.
Explain plausible reason for the order of acidity followed.

16) An organic compound A, Molecular Formula $C_9H_{10}O$ forms 2,4 DNP derivative, reduces Tollens reagent and undergoes Cannizaros reaction. On vigorous oxidation it gives 1,2-benzene dicarboxylic acids. Identify A.
(Hint: An aldehyde which do not contain α hydrogen atom.)

17) Do the following conversion using suitable reagents not more than two steps:

a. Ethanol to 3-Hydroxy butanal.
b. Bromobenzene to 1-phenyl ethanol.

18) Compound A $C_4H_8Cl_2$ is hydrolysed to a compound B C_4H_8O which form an oxime with NH_2OH and give negative Tollens test. What are the structures of A and B. Write balanced chemical equations for the reactions involved.
(Hint: A is a gemdihallide and B is a ketone)

19) Write the structure of the product and name the reaction.

20) Give reasons for the following:

i) Iodoform is obtained when methyl ketones react with hypoiodite but not with iodide.
(Hint: Hypoiodite ion being stronger base than iodide ion, can easily remove acidic hydrogen atom.)

ii) Hydrazones of aldehydes and ketones are not prepared in highly acidic medium.
(Hint: In strong acidic medium N of reagent gets protonated to get an electrophile which cannot react.)

21) Both and give addition reactions. How do the addition reactions differ in both the cases and explain why?

Hint: Formed between two similar atoms having same electronegativity.

Formed between two different atoms with different electronegativities.

22) Benzaldehyde gives positive test with Tollens reagent but not with Fehlings solution. State the reason.
Hint:+R effect increases electron density on carbonyl group and C-H become strong.
$Ag(NH_3)_2^+$is a stronger oxidizing agent than Cu^{2+} + tartarate + base.

23) Write the structures of the products in the following reactions:

3-Mark Questions

24)

a. Write the structures of A and B.
b. Identify any two important features of this reaction.
(Hint: - Structural characteristics of compounds giving haloform reaction.)

25)

Write the structures of A, B and C.

26) Compound X, containing Chlorine on treatment with strong ammonia gives a solid Y which is free from Chlorine. Y on analysis gives C=49.31%, H=9.59% and N=19.18% and reacts with Br_2 and caustic soda to give a basic compound Z. Z reacts with HNO_2 to give ethanol. Suggest structures for X, Y and Z.

Hint:
Calculate the empirical formula of the compound. Y reacts with Br_2 and alkali indicates that it is amide.

27) Complete the following equation and write the structures of A, B, C, D, E and F.

$$A \xrightarrow{P/Br_2} CH_3CH_2CH_2Br \xrightarrow{Alc.KOH} B \xrightarrow{Br_2|CCl_4} C \xrightarrow[(ii)\ NaNH_2]{(i)\ Alc.KOH} D \xrightarrow[dil.\ H_2SO_4]{Hg2+} E \xrightarrow{NH_2OH\ |\ H^+} F$$

28) A compound X (C_2H_4O) on oxidation gives Y ($C_2H_4O_2$). X undergoes haloform reaction. On treatment with HCN, X forms a product Z which on hydrolysis gives 2-hydroxy propanoic acid.

a. Write down the structures of X and Y.
b. Name the product when X reacts with dil. NaOH.
c. Write down the equations for the reactions involved.

Hint: - X is an aldehyde since it has general formula $C_nH_{2n}O$ and has only two carbon atoms.

5- Mark Questions

29) An alkene (A with molecular formula C7H14) on ozonolysis yields an aldehyde. The aldehyde is easily oxidized to an acid (B). When B is treated with Bromine in presence of Phosphorous it yields a compound (C) which on hydrolysis gives a hydroxy acid (D). This acid can also be obtained from acetone by the reaction with hydrogen cyanide followed by hydrolysis. Identify A, B, C and D and write the chemical equations for the reactions involved.

30) Five isomeric para-di- substituted aromatic compounds, A to E with molecular formula $C_8H_8O_2$ were given for identification. Based on the following observations give the structures of the compounds:

Both A and B form silver mirror with Tollens reagent, also B gives a positive test with $FeCl_3$.
C gives positive Iodoform test.
D is readily extracted in aqueous $NaHCO_3$ solution.
E on acid hydrolysis gives 1,4-dihydroxy benzene.

Hint: A and B contain CHO groups since they've shown positive Tollens test. B has phenolic group as it reacts with $FeCl_3$ solution. C should have $–CH_3CO$ group. D should have –COOH group. E should be p-hydroxy phenyl vinyl ether.

UNIT – 13

AMINES

1 / 2 / 3 Marks Questions

1. Arrange the following in order of decreasing basic strength
   (a) Ethyl amine, Ammonia, Triethyl amine
   (b) Aniline, p- Nitroaniline , p- Toluidine
2. Amine group in aniline is ortho and para directing. Why does then aniline on nitration give substantial amount of m-nitroaniline
3. Primary amines have higher boiling points than tertiary amines. Why?
4. 'Amide are more acidic than amines'. Why?
5. Arrange the following amines in the ascending order of basic strength giving reason-$EtNH_2$, Et_2NH, Et_3N, in aqueous solution?
6. Explain the role of mineral acid in the reaction of a carbonyl compound with KCN (aq)?
7. Why is acetonitrile preferred as a solvent for running organic reaction?
8. Why aniline is acetylated first to prepare mono bromo derivative?
9. Ammonolysis of alkyl halide does not give a corresponding amine in pure state. Explain?
11. Explain why methyl bromide reacts with KCN go give mostly methyl cyanide but it reacts with AgCN to give mostly methyl isocyanide.
12. Why is necessary to maintain the temperature between 273 K and 278 K during diazotization?
13. Why does silver chloride dissolve in aqueous methyl amine solution?
14. How can the following conversion be carried out :-
    (a) p-toluidine to 2- bromo-4- methylanline
    (b) Aniline to iodobenzene
    (c) Aniline to benzonitrile

UNIT-14

BIOMOLECULES

1 Mark Question

1 How many chiral centres are there in D-(-)-Fructose?

2 Where does the water present in the egg go after boiling the egg?

3 Why do monosaccharides form cyclic structures?

4 Name the α-amino acids obtained when tripeptide(Gly-Ala-Leu) is hydrolysed.

5 Explain how curdling of milk occurs. What structural changes take place?

6 Drugs which are proteins such as insulin cannot be taken by mouth but must be injected. Why?

7 .Amino acids show amphoteric behavior. Explain

8 In alkaline solution, an amino acid contains 2 basic groups – NH_2 and –COO^-, which is more basic? If acid is added to the solution, what will happen?

9 In a quite acidic solution, the AA contains 2 acidic groups- NH_3 and -COOH , which is more acidic? If a base is added to the solution, what will happen?

10 Sucrose is dextrorotary. Its structure is given as:

a. What happens when sucrose solution is treated with tollen's reagent and why?
b. Its aqueous solution exhibits a change in rotation . Why?

11 Starch forms an emulsion rather than solution with water. Explain.

12 The melting points and solubility in water of amino acids are generally higher than that of corresponding lab acids. Explain.

13 Activation energy for acid hydrolysis of sucrose is 6.22 kJ mol-1 while it is only 2.15 kJ mol-1 when hydrolysed by enzyme sucrose.
a) Write the mechanism of the enzyme catalysed reaction
b) Also depict the progress of reaction against energy in both cases, diagrammatically.

14 When DNA is hydrolysed, there is a definite relation among the quantities of different bases obtained. But for hydrolysis of RNA, it is not so. What does this suggest about the structure of DNA and RNA?

15 Identify and explain the various forces which stabilize protein structure.

UNIT - 15

POLYMERS

1 Mark Questions

1. Arrange the following polymers in the increasing order of their intermolecular forces. Also classify them as additional and condensation polymers: Nylon 66, Buna-S, Polythene
2. Give name and structure of reagent used for initiating a free radical chain reaction?
3. Why is cationic polymerisation preferred in case of Vinylic monomers containing electron donating groups?
4. Arrange the following in the increasing order of their intermolecular forces Nylon – 66, Buna-S, Polythene.

2 / 3 Marks Questions

1. State the significance of numbers in the polymer name nylon –6 and nylon – 66.
2. What are linear polymer and branched chain polymers. How do these differ from cross-linked polymers?
3. Write the difference between polyacrylates and polyesters.
4. Differentiate between chain growth and step growth polymerization.
5. Write the structure of a reagent used for initiating a free radical chain reaction.
6. Will you prefer to polymerize, acrylonitrile under anionic or cationic polymerization?
7. How does the presence of $\dot{C}Cl_4$ influence the course of vinyl free radical polymerization?
8. Why does styrene undergo anionic polymerization easily?
9. How vulcanization does changes the character of natural rubber?

UNIT -16
CHEMISTRY IN EVERYDAY LIFE

1 Mark Question

1) Which among the following is a semi synthetic modification of penicillin
Erythromycin, ampicillin, tetracycline, ofloxacin.

2) Substances produced wholly or partly by chemical synthesis, which in low concentrations inhibits the growth or destroys microorganisms by intervening in their metabolic processes. Identify the substance.

3) Drugs are classified as

Aspirin	–	analgesic
Chlordiazepoxide	–	tranquilizer
Penicillin	–	antibiotic

Mention on what basis the above classification is done?

4)

Identify the type of detergent given in the above structure.

5) Which of the following drug combinations is not correct and state why?

Chloramphenicol	–	broad spectrum antibiotic.
Equanil	–	sedative.
Phenacetin	–	antipyretic.
Bithional	–	tranquilizer.

2 Mark Questions

6) Analysis of water in a place shows that the water contains Magnesium Chloride. The people in that place are advised to use detergents for washing clothes. Why?

7) Pick out the odd one from the following and mention why?

Erythromycin, penicillin, tetracycline, chloramphenicol

8) Antiallergics and antacids are antihistamines. Can antiallergics be used to reduce the acidity of the stomach? Give plausible reason for your answer.

9) Following drugs are used as analgesics. One among them is different from others. Identify it and state the reason.

Morphine, Heroin, Aspirin, Codeine.

10)

i. Identify the compound.
ii. What is its use?

11) Birth control pills essentially contain a mixture of synthetic estrogen and progesterone. What are estrogen and progesterone? Why are they used in birth control pills?

12) Sodium and Potassium soaps are only used for cleaning purposes. Why?

13) Detergents containing unbranched chains are more preferable than those containing branched chains. State the reason.

14) Low level of noradrenalin is the cause of depression. Suggest drugs to cure this problem?

3 Mark Questions

15) Observe the diagram and answer the questions given below:

i. Name the drug target.
ii. What is meant by allosteric site?
iii. Mention the role of inhibitors.

16) Observe and identify the steps a, b, c from the diagram given below:

17) Sodium hydrogen carbonate and ranitidine are used as antacids. Which one is a better choice? Why?

18) Identify the following substances:

i. It is about 550 times as sweet as cane sugar and excreted from body in urine unchanged.

ii. It is 100 times as sweet as cane sugar and its use is limited to cold food and soft drinks as it is unstable at cooking temperature.

iii. It is a trichloro derivative of Sucrose and it is stable at room temperature.

VALUE BASED QUESTIONS IN CHEMISTRY FOR CLASS - XII

Scuba divers when come towards the surface, the pressure gradually decreases resulting in the released of dissolved gases leading to formation of bubbles of nitrogen gas in the blood which blocks the capillaries and thus harmful kinds are created. To avoid bends and toxic effects of high concn of nitrogen gas, the air is diluted with helium. After reading the above passage, answer the following questions.

i) Why is the harmful condition of bends overcome by the use of helium.

ii) Which law is used to calculate the concentration of gases in solution.

iii) Mention the value associated with providing divers air diluted with helium.

(2) Ram takes a open pan to cook vegetables at a hill station while shyam cook the same vegetables in a pressure cooker at the same place.

(a) Explain with reason who will cook vegetable faster.

(b) Mention the reason for the delay in cooking.

(c) Which value is learnt by the student in the process of cooking food in the pressure cooker.

(3)

$p_B > \pi$

a) Name the process observed when pressure on solution side is more than osmotic pressure.

(b) Write main use of this process.

(c) Mention the values associated with the above process.

(4) Reena planted neem tree in school premisses and Meena planted Neem tree in marshy land near railway line.

(a) Which student planted Neem tree correctly and why?

(b) Name the chemical substances used to stop decay of such plants.

(c) Mention the values by the plantation.

(5) People are advised to limit the use of fossil fuels resulting in Green House Effect leading to a rise in the temperature of earth. Hydrogen provides an ideal alternative and its combustion in fuel cells.

1. White electrode reaction in H_2-O_2 fuel cell.
2. How is green house effect reduced by the use of fuel cells?
3. Write the values associated with preference of using fuel cells to fossil fuel.

(6) In Apollo Space programs, hydrogen-oxygen fuel cell was used.

(a) Explain why, fuel cell is preferred in space programme.?

(b) Mention the values associated with the decision of using fuel cell?

(7) Ira a student of science went with her grandfather to buy a battery for their inverter and camera. They found two types of batteries, one a lead storage battery and other a Nickel-Cadmium storage battery. Later was more expensive but lighter in weight. Ira insisted to purchase costlier Nickels-Cadmium battery.

(a) In your opinion, why Ira insisted for Nickel-Cadmium battery? Give reasons

(b) Write the values associated with above decision?

(8) Shyam's father wants to buy a new car. In the market various options are available. Shyam persuades his father to buy a hybrid car which can run both on electricity as well as on petrel.

(i) Mention the values associated with this decision.

(ii) Name the battery used for running the car.

(iii) Write the reactions taking place at the anode and cathode of battery.

(9) Ajay, a student of chemistry, was performing chemical reaction between sodium thiosulfate and HCI. He found that time required to appear turbidity increases when concentration of HCI or sodium thiosulfates or both decreases.

(a) Mention the season for appearance of turbidly.

(b) Write the chemical reaction involved.

(c) Mention the values associated with above experiment.

(10) Smoke is colloidal solution of solid particles such as Carbon, arsenic compounds dust, etc. in air. Precipitation of smoke particles coming form the chimney of factories is carried out by Cottrel Precipitator and Carbon free air passes out through the chimney.

(a) Name the principle used in the Cottrel Precipitator.

(b) How smoke precepitator causes precipitation and settling of smoke particles.

(c) Name the value learnt by the use of this Cottrel Precipitator.

(11) While coming back from school, a student witnesses an accident on road. A person on bike had suffered injures due to skidding of bike. The student rushed to the aid of biker with the help of some people, the biker was taken to a nearby hospital. The student discovered that the bike skidded due to oil spilled on road. The student arranged for an old cloth and wiped the oil from the road.

i) Mention the values shown by the student in the above case.

ii) The oil spill can also be washed with soap and water. Explain the cleaning action of soap.

(12) Chlorofluorocarbons (CFC) and gas emitted from the exhaust system of supersonics aeroplanes might be slowly depleting the concentration of the ozone layer in the upper atmosphere.

(a) Name the gas emitted by the exhaust of supersonic jet aeroplanes.

(b) write the chemical reactions involved in the ozone layer depletion.

(c) Mention the values that are learnt by the students in this depletion of ozone layer.

(13) A student accidently spills concentrated H_2SO_4 on his hand. Before the teacher gets to know , his friend washed his hands with water and also with soap but the burning sensation on hand was still going on. The friend then rubs solid sodium bicarbonate on his hand and then washed with water, finally the burning sensation is releived.

(i) Mention the values shown by student's friend.

(ii) Can you recommend any other substance available in the laboratory which can be used instead of sodium bicarbonate?

(iii) Write the chemical reaction involved in the treatment of acid burn with sodium bicarbonate.

(14) Ramu, a caretaker of swimming pool was using chlorine for disinfecting swimming pool water. His friend Jagat an another swimming pool caretaker was using ozone in place of chlorine.

(a) In your opinion, which is better way of disinfecting water in a swimming pool.

(b) Mention reason and values associated with your reply.

(15) A trainee pilot was flying his plane in stratosphere. His senior advised him not to fly the aeroplane in the stratosphere.

(a) In your opinion, why the senior pilot advised his trainee pilot not to fly his plane in the strostosphere.

(b) Write the possible chemical reaction.

(c) Mention the values associated with your reply.

(16) During world war II, mustard gas was used to kill innocent people by Adolf Hitler, though science should always be used for betterment of human race.

(i) Write the formula of mustard gas.

(ii) Name the value obtained from the above mentioned paragraph.

(17) Police usually disperse the indisciplined mob by using tear gas shells. One of the person in the mob advised the people either to use water wetted cloth on eyes or to avoid the smoke

(i) Write the chemical formula of compound used in tear gas and reaction involved.

(ii) Write the value involved as advised by one person present in the mob.

(18) Recently a blanket ban is imposed on use of any kind of ploythene bags in Delhi. Polythene is supposed to be non-biodegradable and creates an environmental garbage but some poythene manufacturing units opposed this decision.

(i) Which value is missing in the polythene manufacturing traders?

(ii) Name one important catalyst used in the manufacturing of polythene.

(iii) Write the chemical formula of polythene, polypropylene and PVC.

(19) Recently Delhi Police launched a special drive to curb the crimes and accidents related to “Drunken-Driving” An instrument known as “Alcometer” is used to test whether a driver has consumed alcohol or not.

(i) Write the name and chemical formula of the compound used in alcometer.

(ii) By preventing alcohol drinking during driving. Name the value, which Delhi Police tries to inculcate in drivers and general public.

(iii) Write the chemistry involved in the above test.

(20) A group of students was smoking cigarettes in college premises. A social activist, noticed and advised them not to smoke as smoking is injurious to health.

(i) By forbidding them not to smoke, which value social activist want to be inculcated among the youth.

(ii) As a chemistry student, write the name of “Alloy” used in lighter’s flint.

(iii) Mention diseases caused by smoking.

(21) In a terrorist activity in the Mumbai nearly ten persons were killed and 50 injured due to continuous showering of bullets on them by terrorists. A group of persons rushed to the spot immediately and helped the injured to reach the nearby hospital.

(i) Which kind of value is reflected by these persons by doing this?

(ii) Which alloy is used in the preparation of bullet?

(22) It is a general belief that we should not come out of the house to see “Solar Eclipse” because it can have evil impact on life but nowadays educated people allow their children to see solar eclipse, treating it as a natural science phenomenon, but children are advised to see them by U.V. protected sun glasses (crooke’s lenses) to avoid harmful impact of UV light on eyes.

(i) Write the name of transition metal oxide used in making U.V protected lens.

(ii) By allowing the children to see solar eclipse using U.V. protected lens which value the educated people trying to inculcate in the children.

(iii) Which rays are present in the light which can damage the eye while viewing solar eclipse with naked eye.

(23) Hard water does not form leathers with soap. Rita uses a washing powder containing sodium metapolyphosphate and ethylenediamine tetracetate (EDTA) while Sita is using ordinary washing power.

(a) Which washing powder is move effective for washing clothes in hard water and why?

(b) Name the values associated with the above passage.

(24) A lots of children, working in a lead industry were rescued by NGO's activists. The children sent to the hospital and found to be excess exposure to lead so called lead poisoning.

(i) Name the ligand (compound) used for treatment of Lead poisoning.

(ii) During this rescue operation which values are shown by NGO's activists?

(iii) Write the reaction involved for removal of lead from living organism.

(25) Cancer is not a communicable disease. It occurs due to unlimited growth of body cells leading to tumours. We should shake hand, eat together with people suffering from cancer. These activities boost up the confidence in them for living.

(i) Write the name of coordination compound used as a chemotherapeutic agent to curb the growth of tumours.

(ii) By showing such attitude to cancer patients, mention the values reflected by us.

(26) Ravi Prasad, a farmer has 25 acres of land. He noticed some infection on the leaves of his crops. He called his friend Raghav, who advised him to use DDT. However, Ravi Prasad preferred to use dry powder of neem leaves as an insecticide.

(a) Mention reason why Ravi Prasad prefer using neem powder?

(b) In your opinion, who took right decision?

(c) Write values associated with above decision?

(27) A manufacturer dealing in A.C plant was using Freon-12 in his AC plant. His friend Raju, who also deals in similar business, was using liquid ammonia in place of Freon-12.

(i) In your opinion, Who is using right compound in refrigeration plants.

(ii) Mention values associated with above opinion.

(28) In a locality a large number of people fell ill after drinking liquor sold by a local vender. Many people started vomiting, some shouted that they are not able to see properly and some others went unconscious. Ram's father also

suffered from severe stomach ache after consuming liquor. Everyone in Ram's family peaked. Neighbours family was also weeping loudly. Ram calmed down his mother and helped her to call ambulance for his father and also for other people. They also informed the police about the incident.

(i) Mention the values shown by Ram.

(ii) Write the probable cause of poisoning by liquor.

(iii) Write the reaction showing the conversion of ,mollases to Ethyl alcohol using yeast.

(29) Some students enter the chemistry lab for doing practical. Some students are not serious about learning and want to create trouble. They remove the lables from two bottles containing methanol and dimethyl ether. Mohan approaches the teacher and informs about the incident.

(i) Mention the values shown try Mohan.

(ii) If the teacher asks the some students to perform chemical test to identify methanol and demethyl ether, write the reaction involved for the test.

(30) An owner of a paint company who was using ethanol as solvent noted that his stock of ethand was misused by his employee.

To prevent this misuse, he decided to add small amount of a bule colour compound (A) and another nitrogen containing heterocyclic base (B) which gives a foul smell to alcohol.

(a) Do you think that he took right decision?

(b) Write the names of compound A& B ? Name process of adding compound A & B to ethanol ?

(c) Mention the values associated with above decision.

(31) Arpita wanted to buy vanilla ice cream from a local ice cream vendor. Her friend Amita told her that these vendor use synthetic chemical compound vanillin whose flavor is similar to that of vanilla. They decided not to buy such ice creams.

(i) Write the Chemical formula and IUPAC name of vanillin.

(ii) Write values that are associated with above decision.

(32) Kabir is fond of eating too much of chowmein loaded with cabbage leaves. At the age of fifteen his teeth got rotten and he started complaining of severe headache. His mother took him to a doctor who after examining found that Kabir is suffering from neurocysticercosis, a mental disease caused

by larvae of tape warm.

After reading the above paragraph, answer the questions.

(a) Name the chemical substance responsible for damaging Kabir's teeth.

(B) Is there any link between eating of too much of chowmein and his head-ache.

(c) Mention the values conveyed by above paragraph.

(33) Sushil's friend want to play Holi with synthetic colours, eggs, muddy water etc. Sunil persuades his friends to play Holi with natural colours. He reminds them that last time one of their friends had developed skin allergy after playing Holi with synthetic colours. It took him a long time to recover. Sushil's friends agreed and prepared natural colours using leaves and flowers.

(i) Mention the values shown by Sushil.

(ii) Write the names and reaction of preparation of two azo dyes (synthetic)

(iii) Write the name of two pigments present in natural colours.

(34) Nita's mother fell ill and the doctor diagnosed her with pernicious anemia. She felt lethargic and did not have the energy to do work. Nita helped her mother in household work till she recovered.

(i) Name the vitamin whose deficiency caused pernicious anemia.

(ii) Name the sources which will provides this vitamin.

(iii) Mention the values shown by Nita.

(35) Two shopkeepers are using LDP (Low Density Polythene) and HDP (High density Polythene) polymers for packing of materials.

(i) Name the ploythene preferred for packaging.

(ii) Name the catalyst used in the synthesis of HDP.

(iii) Mention the values associated with the use of a specific polymer.

(36) PHBV (Poly-B-Hydroxybutyrate-Co-β-hydroxy valerate) is a biodegradable polymer. It is a copolymer of 3-hydroxy valerate acid and 3-hydroxy pentanic acid.

(a) How PHBV has found utility in medicines as Capsule?

(b) Write the name of polymer used in artificial limb popularly known as Jaipur foot.

(c) Mention the values associated with the use of such polymers.

(37) In a school, lot of emphasis is given to the 3R principle of Reduce, refuse and Recycle. The students observe their teachers following it and they are made to follow it in school. Rita also follows at home and always tries to save paper. She also keeps waste paper and waste items separately so that they be sent for recycling. She does not use plastic bags and takes a jute bag with her while going to the market.

(i) Mention the values shown by Rita.

(ii) If the jute bag is made of cellulose polymer, and name the monomer.

(iii) Name the chemical substance used in cotton, Jute and Rayon fibre.

(38) In order to wash clothes with water containing dissolved calcium hydrogen carbonate, which cleansing agent will you prefer and why, soap or detergent? Give one advantage of soap and synthetic detergent.

(i) Mention the values associated with the use of soap.

(ii) Name the chemical used in shaving soaps.

(39) Rama's younger brother is suffering from cold, caugh and fever. Rama's father did not take him to the doctor and wanted to give medication on his own. Rama tells her father that he should not give medicines to her brother on his own but should take him to a doctor.

(/8) Mention the values shown by Rama?

(ii) Why should not medicines be taken without consulting doctors?

(iii) While antacids and antiallergic drugs interfere with the action of histamines, why do these not interfere with the function of each other?

(40) Ravi observed that his classmate Manish was showing a change in behaviour over some time , Manish stayed aloof, did not mix with friends and had become easily irritable. He avoided going to any type of get-together also. Ravi shares his concerns with his class teacher who has also observed these things about Manish. The teacher calls Manish's parents and advise them to consult a doctor. Doctor prescribes antidepressant drugs for him.

(i) Name the antidepressant drugs? How are they classified. Give examples of each class.

(ii) Mention the values shown by Ravi.

(41) Harish was feeling headache. His friend Vikram observed that Harish had fever. He advises him to take two tablets oflaxin-200 mg

(a) In you opinion , is it right to take medicine as per your friend advice?

(b) Give reasons for your reply.

(c) Write values associated with his friend decision.

(42) Rajni asked her maid to prepare halwa for her diabetic mother-in-law. Her maid added sugar free tablet containing two amino acids in the boiling contents. Rajni scolded her maid for this action.

Q. In your opinion, why Rajni did so?

Q Mention values associated with your opinion.

(43) A laundry engaged in washing cloths has been pouring waste water directly into river. Over a period of time, it was found that large number of fish were dying in the river.

Q. Mention the reasons for above problem. Can it be avoided?

Q. Mention values associated with above situation.

VARIOUS VALES ASSOCIATED

1 Critical thinking and self awareness.

2 Energy conservation

3 Water conservation

4 Environmental conservation

5 Environmental conservation

6 Environmental conservation

7 Environmental conservation

8 Environmental conservation

9 Critical thinking & problem analysis

10 Environmental conservation

11 Social responsibility

12 Environmental conservation

13 Inclusion and dignity of individual

14 Self awareness and decision making

15 Critical thinking and decision making

16 Dignity of individual

17 Social responsibility and social justice
18 Environmental conservation
19 Appreciation of cultural values and dignity of individual
20 Interplay of different cultures.
21 Principle of equality and social justice
22 Scientific attitude
23 Water and Environmental conservation
24 Dignity of individual
25 Self awareness
26 Environmental conservation
27 Environmental conservation
28 Social justice, awareness, respect for diversity
29 Inclusion
30 Critical thinking and decision making.
31 Self awareness, critical thinking.
32 Self awareness, dignity of individual.
33 Environmental conservation, respect of multireligious and multicultural country.
34 Self awareness.
35 Environmental conservation
36 Dignity of individual
37 Environmental conservation
38 Environmental conservation
39 Self awareness and dignity of individual
40 Principle of equality and social justice
41 Critical thinking
42 Self awareness
43 Environmental conservation

SOLID STATE

KEY CONCEPTS

As we know that matter exists in different physical states under different conditions of temperature and pressure. For example solid state, liquid gases plasma and BEC etc. Now we will study about different aspects of solid state.

Introduction:

1. The state of matter whose M.P is above room temp is solid state. Solids have definite shape and volume, having high density and constituent particles are held strongly.
2. Based on arrangement of particles types of solid : 1: Crystalline

   2:Amorphous
3. Crystalline solids have regular arrangement of constituent particles throughout, melting point is sharp, Anisotropic in nature and give clear cut cleavage.
4. Amorphous solids have no regular arrangement, no sharp M.P, isotropic in nature they do not exhibit cleavage property.
5. Amorphous silica is used in photovoltaic cells.(Applications of amorphous solid)
6. Space lattice is the regular 3D, arrangement of constituent particles in the crystalline solid. It shows how the constituents particles(atoms, molecules etc.) are arranged.
7. Smallest repeating unit in a space lattice is called unit cell.
8. There are 4 types of unit cells, 7 crystal systems and 14 bravais lattices.
9. Types of unit cell No. of atoms per unit cell

i. Simple cubic unit cell 8*1/8=1

ii. FCC (Face centered cubic) 8*1/8+6*1/2=4

iii. BCC (Body centered cubic) 8*1/8+1*1=2

10. Hexagonal close packing and cubic close packing have equal efficiency i.e 74%
11. Packing efficiency =volume occupied by spheres (Particles)/volume of unit cell *100
12. For simple cubic unit cell the p.f.=$1*4/3 *\pi r^3/8*r^3 *100$ =52.4
13. The packing efficiency in **fcc** =$4*4/3 *\pi r^3/16*2^{1/2} r^3 *100$ =74

14. The packing efficiency in **bcc** $=2*4/3*\pi r^3/64*3^{3/2} r^3*100 =68$

15. The packing efficiency in **hcp =74**

16. Packing efficiency in bcc arrangement in 68% and simple cubic unit cell is 52.4%

17. Unoccupied spaces in solids are called interstitial voids or interstitial sites.

18. Two important interstitial voids are (I). Tetrahedral void and (II). Octahedral void.

19. Radius ratio is the ratio of radius of void to the radius of sphere.

    a. For tetrahedral void radius ratio=0.225

       For octahedral void radius ratio=0.414

20. No. of tetrahedral void=2*N (N=No. of particles)

21. No. of octahedral void=N

22. Formula of a compound depends upon arrangement of constituent of particles.

23. Density of unit cell

    $D=Z*M/a^3*NA$

D=density, M=Molar mass, a=side of unit cell, $NA=6.022*10^{23}$

24. The relationship between edge length and radius of atom and interatomic or interionic distance for different types of unit is different as given below

    a. Simple cubic unit cell a=2R

    b. F C C $a=4R/\sqrt{2}$

    c. B C C $a=4R/\sqrt{3}$

25. Interatomic distance=2R

26. Interionic distance=Rc+Ra (Rc=Radius of cation, Ra=Radius of anion)

27. Imperfection is the ir-regularty in the arrangement of constituent particles.

28. Point defect or Atomic defect-> it is the deviation from ideal arrangement of constituent atom. Point defects are two types (a) Vacancy defect (b) Interstitial defect

29. Vacancy defect lowers the density and

30. Interstitial defect increases the density of crystal.

31. Point defects in the ionic crystal may be classified as:

a. Stoichiometric defect (Ratio of cation and anion is same).

b. Non Stoichiometric defect (disturb the ratio).

c. Impurity defects (due to presence of some impurity ions at the lattice sites)

32. Schottky defect lowers the density of crystal it arises due to missing of equal no. of cations of anions from lattice sites e.g. Nacl.

33. Frenkel defectis the combination of vacancy and interstitial defects. Cations leave their actual lattice sites and come to occupy the interstitial space density remains the same eg. Agcl.

34. Non stoichiometric defect

    a. Metal excess defect due to anion vacancy.

    b. Metal excess due to presence of interstitial cation.

    c. Metal deficiency due to absence of cation.

SHORT ANSWER QUESTION (2)

Q1. What do you mean by paramagnetic substance?

Ans: - Attracted by pragnetic field and these substances are made of atoms or ions with unpaired electrons.

Q2. Which substance exhibit schottky and Frenkel both defects.

Ans: - AgBr

Q3. Name a salt which is added to Agcl so as to produce cation vacancies.

Ans:-Cdcl2

Q4. Why Frenkel defects not found in pure Alkali metal halide.

Ans: - Due to larger size of Alkali metal ion.

Q5. What is the use of amorphous silica?

Ans. Used in Photovoltaic cell.

Q6. Analysis shows that a metal oxide has the empirical formula $Mo.98^{0}1.00$. Calculate the percentage of M^{2+} and M^{3+} ions in the crystal.

Ans: - Let the M^{2+} ion in the crystal be x and $M3^{+}$ =0.98-x

Since total change on the compound must be zero

2x+3(0.098-x)-z=0

X=0.88

%of M^{2+} 0.88/0.96*100=91.67

% of $M3^{+}$ =100-91.91.67=8.33

Q7. What is the co-ordination no. of cation in Antifluorite structure?

Ans: - 4

Q8. What is the Co.No. of cation and anion in Caesium Chloride.

Ans: 8 and 8

Q9. What is F centre?

Ans:- It is the anion vacancy which contains unpaired electron in non-stoichiometric compound containing excess of metal ion.

Q10. What makes Alkali metal halides sometimes coloured, which are otherwise colourless?

<u>Very Short Answers(1 marks) :</u>

1. How does amorphous silica differ from quartz?

In amorphous silica, SiO_4 tetrahedral are randomly joined to each other whereas in quartz they are linked in a regular manner.

2. Which point defect lowers the density of a crystal?

Schottky defect.

3. Why glass is called supper cooled liquids?

It has tendency to flow like liquid.

4. Some of the very old glass objects appear slightly milky instead of being transparent why?

Due to crystallization.

5. What is anisotropy?

Physical properties show different values when measured along different in crystalline solids.

6. What is the coordination number of atoms?

a) in fcc structure b) in bcc structure

a) 12 b) 8

7. How many lattice points are there in one cell of -

a) fcc b) bcc c) simple cubic

a) 14 b) 9 c) 8

8. What are the co-ordination numbers of octahedral voids and tetrahedral voids?

6 and 4 respectively.

9. Why common salt is sometimes yellow instead of being of being pure white?

Due to the presence of electrons in some lattice sites in place of anions these sites act as F-centers. These electrons when excited impart color to the crystal.

10. A compound is formed by two elements X and Y. The element Y forms ccp and atoms of X occupy octahedral voids. What is formula of the compound?

No. of Y atoms be N No. of octahedral voids N

No. of X atoms be =N Formula XY

HOTS Very Short Answers:

1. **Define F centers.**
2. **What type of stoichiometric defect is shown by**
    a. **Zns**
    b. **AgBr**
3. **What are the differences between frenkel and schottky defect?**
4. **Define the following terms with suitable examples**
    - **Ferromagnetism**
    - **Paramagnetism**
    - **Ferrimagnetism**
    - **12-16 and 13-15 group compound**
5. **In terms of band theory what is the difference**
    - **Between conductor and an insulator**
    - **Between a conductor and a semi-conductor**

Short Answers (2 Marks):HOTS

1. **Explain how electrical neutrality is maintained in compounds showing Frenkel and Schottky defect.**

   In compound showing Frenkel defect, ions just get displaced within the lattice. While in compounds showing Schottky defect, equal number of anions and Cations are removed from the lattice. Thus, electrical neutrality is maintained in both cases.

2. **Calculate the number of atoms in a cubic unit cell having one atom on each corner and two atoms on each body diagonal.**
   8 corner *1/8 atom per unit cell = 1atom

   There are four body diagonals in a cubic unit cell and each has two body centre atoms.

   So **4*2=8 atoms** therefore total number of atoms per unit cell =1+8=9

3. **Gold crystallizes in an FCC unit cell. What is the length of a side of the cell(r=0.144mm)**
   r=0.144nm

   a=2*√2r

   =2*1.414*0.144nm

   =0.407nm

4. **Classify each of the following as either a p-type or n-type semi-conductor.**
   a) Ge doped with In

   b) B doped with Si

(a) Ge is group 14 elements and In is group 13 element. Therefore, an electron deficit hole is created. Thus semi-conductor is p-type.

(b) Since b group 13 element and Si is group 14 elements, there will be a free electron, thus it is n-type semi-conductor.

5. **In terms of band theory what is the difference between a conductor, an insulator and a semi-conductor?**

The energy gap between the valence band and conduction band in an insulator is very large while in a conductor, the energy gap is very small or there is overlapping between valence band and conduction band.

6. **$CaCl_2$ will introduce Scotty defect if added to AgCl crystal. Explain**

Two Ag+ ions will be replaced by one Ca^{2+} ions to maintain electrical neutrality. Thus a hole is created at the lattice site for every Ca^{2+} ion introduced.

7. **The electrical conductivity of a metal decreases with rise in temperature while that of a semi-conductor increases. Explain.**

In metals with increase of temperature, the kernels start vibrating and thus offer resistance to the flow of electrons. Hence conductivity decreases. In case of semi-conductors, with increase of temperature, more electrons can shift from valence band to conduction band. Hence conductivity increases.

8. **What type of substances would make better permanent magnets, ferromagnetic or ferromagnetic, why?**

Ferromagnetic substances make better permanent magnets. This is because the metal ions of a ferromagnetic substance are grouped into small regions called domains. Each domain acts as tiny magnet and get oriented in the direction of magnetic field in which it is placed. This persists even in the absence of magnetic field.

9. **In a crystalline solid, the atoms A and B are arranged as follows:-**
   a. **Atoms A are arranged in ccp array.**
   b. **Atoms B occupy all the octahedral voids and half of the tetrahedral voids. What is the formula of the compound?**

Let no. of atoms of A be N

No. of octahedral voids = N

No. of tetrahedral voids= 2N

i) There will be one atom of b in the octahedral void
ii) There will be one atom of B in the tetrahedral void (1/2*2N)
Therefore, total 2 atoms of b for each atom of A

Therefore formula of the compound $=AB_2$

10. In compound atoms of element Y forms ccp lattice and those of element X occupy 2/3rd of tetrahedral voids. What is the formula of the compound?

No. of Y atoms per unit cell in ccp lattice=4

No. of tetrahedral voids= 2*4=8

No. of tetrahedral voids occupied by X= 2/3*8=16/3

Therefore formula of the compound $=X_{16/3}Y_4$

$=X_{16}Y_{12}$

$=X_4Y_3$

HOTS Short Answer:

1. **How many lattice points are there in one unit cell of the following lattices?**
   - **FCC**
   - **BCC**
   - **SCC**

2. **A cubic solid is made of two elements X and Y. Atom Y are at the corners of the cube and X at the body centers. What is the formula of the compound?**
3. **Silver forms ccp lattice and X –ray studies of its crystal show that the edge length of its unit cell is 408.6 pm. Calculate the density of silver (Atomic wt= 107.9u).**
4. **A cubic solid is made up of two elements P and Q. Atoms of the Q are present at the corners of the cube and atoms of P at the body centre. What is the formula of the compound? What are the co-ordination number of P and Q.**
5. **What happens when:-**
   - **CsCl crystal is heated**
   - **Pressure is applied on NaCl crystal.**

Short Answers (3 marks):

1. **The density of chromium is 7.2g cm^{-3}. If the unit cell is a cubic with length of 289pm, determine the type of unit cell (Atomic mass of Cr=52 u and N_A = 6.022*10^{23} atoms mol^{-1}).**

d= Z * M

$a^3 * N_A$

Z=? , a= 289 pm =28910^{-10} cm, M=52g mol^{-1}, d=7.2g cm^{-3}

$$Z = \frac{d * a^3 * N}{M} = \frac{7.2(g\ cm^{-3}) * [289 * 10^{-10}\ cm]^3 * 6.022 * 10^{23}(atom\ mol^{-1})}{52\ g\ mol^{-1}}$$

2. **An element crystallizes in FCC structure; 200 g of this element has $4.12*10^{24}$ atoms. If the density of A is 7.2g cm^{-3}, calculate the edge length of unit cell.**
3. **Niobium crystallizes in bcc structure. If its density is 8.55 cm^{-3}, calculate atomic radius of [At. Mass of Niobium = 92.9u, N_A = $6.022*10^{23}$ atoms mol^{-1}].**
4. **If radius of octahedral void is r and radius of atom in close packing is R, derive the relationship between r and R.**
5. **Non stoichiometric cuprous oxide can be prepared in the laboratory. In this oxide, copper to oxygen ratio is slightly less than 2:1 can u account for the fact that the substance is a p=type semiconductor?**
6. **The unit cell of an element of atomic mass 50u has edge length 290pm. Calculate its density the element has bcc structure (N_A $6.02*10^{23}$ atoms mol^{-1}).**
7. **Calculate the density of silver which crystallizes in face centered cubic form. The distance between nearest metal atoms is 287pm (Ag= 107.87g mol^{-1}, N_A= $6.022*10^{23}$).**

8. **What is the distance between Na^+ and Cl-ions in NaCl crystal if its density 2.165g cm^{-3}. NaCl crystallizes in FCC lattice.**

9. **Analysis shows that Nickel oxide has $Ni_{0.98}O_{1.00}$ what fractions of nickel exist as Ni^{2+} ions and Ni^{3+} ions?**

10. **Find the type of lattice for cube having edge length of 400pm, atomic wt. = 60 and density =6.25g/cc.**

<u>HOTS Short Answer:</u>

1. **Aluminium crystallizes in cubic closed pack structure. Its metallic radius is 125 pm**
   - **What is the length of the side of the unit cell?**
   - **How many unit cell are there in 100 cm^3 of Aluminium.**

2. **Classify the following as either p-type or n-type semiconductors.**

   Ge doped with In

   B doped with Si

3. **Zinc oxide is white but it turns yellow on heating. Explain.**

Long Answer(5 Marks):

1. **It is face centered cubic lattice A metal has cubic lattice. Edge length of lattice cell is $2A^0$. The density of metal is 2.4g $cm^{-3.}$ How many units cell are present in 200g of metal.**

2. **A metal crystallizes as face centered cubic lattice with edge length of 450pm. Molar mass of metal is 50g mol^{-1}. The density of mental is?**

3. **A compound forms hexagonal close packed structure. What is the total number of voids in 0.5 mol of it? How many of these are tetrahedral voids?**

4. **Copper Crystallizes into FCC lattice with edge length $3.61*10^{-8}$ cm. Show that calculated density is in agreement with measured value of 8.92g/cc.**

5. **Niobium crystallizes in bcc structure with density 8.55g/cc, Calculate atomic radius using atomic mass i.e. 93u.**

HOTS Long Answer:

1. The compound CuCl has Fu structure like ZnS, its density is 3.4g cm^{-3}. What is the length of the edge of unit cell?

Hint: d=Z X M /a3 X NA

a^3=4X99 / 3.4 X 6.022 X $10^{2.3}$

a^3=193.4 X 10-24 cm^3

a=5.78 X 10^{-8}cm

2. If NaCl is dropped with 10^{-3} mol% $SrCl_2$. What is the concentration of cation valancies?

3. If the radius of the octahedral void is r and the radius of the atom in the close packing is R. derive relationship between r and R.

4. **The edge length of the unit cell of mental having molecular weight 75g/mol is A^0 which crystallizes into cubic lattice. If the density is 2g/cm^3 then find the radius of metal atom (N_A = $6.022*10^{23}$)**
5. **The density of K Br. Is 2.75 gm cm^{-3}. the length of edge of the unit cell is 654 pm. Predict the type of cubic lattice to which unit cell of KBr belongs.**
   NA=$6.023*10^{23}$; at mass of K=39: Br. = 80
   Ans. Calculate value of z= 4 so it has fcc lattice

6. **CsCl has bcc arrangement and its unit cell edge lenth is 400 pm . calculate the interionic distance of CsCl. Ans. 34604 pm**
7. **The radius of an Iron atom is 1.42 A^0 . It has rock salt structure. Calculate density of unit cell. Ans. 5.74 g cm^{-3}**
8. **What is the distance between na^+ and Cl^- in a NaCl crystal if its density is 2.165 gcm^{-3} NaCl crystalline in the fcc lattice. Ans.281PM**
9. **Copper crystalline with fcc unit cell. If the radius of copper atom is 127.8 pm. Calculate the density of copper metal. At. Mass of Cu=63.55u NA= $6.02*10^{23}$ Ans.a=2√2 .r , a3=$4.723*10^{-23}$, d=8.95 5.74 g cm^{-3}**

Solution

KEY CONCEPTS

Solution is the homogeneous mixture of two or more substances in which the components are uniformly distributed into each other. The substances which make the solution are called components. Most of the solutions are binary i.e., consists of two components out of which one is solute and other is solvent. Ternary solution consists of three components

Solute - The component of solution which is present in smaller quantity.

Solvent – The component of solution present in larger quantity or whose physical state is same as the physical state of resulting solution.

Types of solutions: Based on physical state of components solutions can be divided into 9 types.

Solubility - The amount of solute which can be dissolved in 100grm of solvent at particular temp. to make saturated solution.

Solid solutions are of 2 types -

1. Substitutional solid solution e.g. Brass (Components have almost similar size)

2. Interstitial solid solution e.g. steel (smaller component occupies the interstitial voids)

Expression of concentration of solution

1. **Mass percentage**= amount of solute present in 100grm solution.

   Percentage = $\frac{mass\ of\ solute W_B}{mass\ of\ solution (W_A + W_B)} \times 100$

For liquid solutions percentage by volume is expressed as = $\frac{Volume\ of\ solute (V_B)}{volume\ of\ solution (V_A + W_B)} \times 100$

2**. Mole fraction** it is the ratio of no. of one component to the total no. of moles of all components. It is expressed as 'x'. For two component system made of A and B ,$X_A = n_A + n_B$, $X_B = n_A + n_B$, Sum of all the components is 1 ; $X_A + X_B = 1$

3. **Molarity (M)** = $\frac{no.of\ moles\ of\ solute}{volume\ of\ solution (L)}$

It decreases with increase in temperature as volume of solution increases with temperature.

4. **Molality (m)** = $\frac{No.of\ moles\ of\ solute}{Mass\ of\ solvent (in\ kg)}$

No effect of change of temperature on molality as it is mass to mass ratio.

5**. Normality (N)** = $\frac{no.of\ gram\ equivalent\ of\ solute}{volume\ of\ solution (L)}$

It changes with changes temperature.

6. **Parts per million (ppm)** concentration of very dilute solution is expressed in ppm.

Ppm = $\frac{w_B}{w_B + w_A} \times 10^6$

Vapor pressure – It is defined as the pressure exerted by the vapour of liquid over the liquid over the liquid in equilibrium with liquid at particular temperature vapour pressure of liquid depends upon nature of liquid and temperature.

Roult's Law –

1. For the solution containing non-volatile solute the vapor pressure of the solution is directly proportional to the mole fraction of solvent at particular temperature
   $P_A \propto X_A$
   $P_A = P^0_A.X_A$
2. For the solution consisting of two miscible and volatile liquids the partial vapor pressure of each component is directly proportional to its own mole fraction in the solution at particular temperature.
   $P_A=P^0_A. X_A,$ $P_B=P^0_B .X_B$
   And total vapor pressure is equal to sum of partial pressure. $P_{total} = P_A + P_B$

Ideal solution – The solution which obeys Roult's law under all conditions of temperature and concentration and during the preparation of which there is no change in enthalpy and volume on mixing the component.

Conditions –

$P_A = P^0_A X_A,$ $P_B = P^0_B.X_B$

$\Delta H_{Mix} = 0,$ $\Delta V_{mix} = 0$

This is only possible if A-B interaction is same as A-A and B-B interaction nearly ideal solution are –

1. Benzene and Toluene
2. Chlorobenzene and Bromobenzene

Very dilute solutions exhibit ideal behavior to greater extent.

Non-ideal solution –

(a) $P_A \neq P^0_A.X_A$ (b) $P_B \neq P^0_B.X_B$
(b) $\Delta H_{mix} \neq 0$ (d) $\Delta V_{mix} \neq 0$

For non-ideal solution the A-B interaction is different from A-A and B-B interactions

i. For solution showing positive deviation
   $P_A > P^0_A$, $P_B > P^0_B. X_B$
   ΔH_{Mix} = positive, ΔV_{mix}=positive (A-B interaction is weaker than A-A and B-B)
   E.g. alcohol and water

ii. For the solution showing negative deviation

$P_A < P^0_A.X_A$, $P_B<P^0_B.X_B$

ΔH_{Mix}= negative, ΔV_{mix} = negative'

A-B interaction is stronger than A-A and B-B interactions

E.g. Chloroform, acetone, HCl and water

What is Azeotrope? – The mixture of liquids at particular composition which has constant boiling point which behaves like a pure liquid and cannot be separated by simple distillation. Azeotropes are of two types:

(a) minimum boiling Azeotrope (mixture which shows +ve deviations) ex. alcohol and water
(b) maximum boiling Azeotrope (which shows –ve deviations) ex. acetone and chloroform

Colligative Properties - Properties of ideal solution which depends upon no. of particles of solute but independent of the nature of particle are called colligative property

<u>Relative lowering in vapour pressure:</u>

$$(P^o_A - P_A)/ P^o_A = X_B$$

Determination of molar mass of solute

$$M_B =(W_A\times M_A\times P^o_A)/W_A\times(P^o_A - P_A)$$

<u>Elevator in Boiling Point</u>

$$\Delta T_B = Kb.\ m$$

Where $\Delta T_B = T'_B - T^o_B$

Kb = molal elevator constant

M = molality

$$M_B =(Kb\times1000\times W_B)/\Delta T_B\times W_A$$

<u>Depression in Freezing Point:</u>

$$\Delta T_f = k_f.\ m$$

Where $\Delta T_f - T'_f$; m = molality

K_f = molal depression constant

unit = $k.kgmol^{-1}$

Osmotic Pressure

The hydrostatic pressure which is developed on solution side due movement of solvent particles from lower concentration to higher concentration through semipermeable membrane denoted as **π** and it is expressed as

$$\Pi = \frac{n}{V} RT$$

$$\Pi = CRT$$

n = No. of moles; v = volume of solution (L)

R = 0.0821 $Latmmol^{-1}$; T = temperature in kelvin.

Isotonic solutions have same osmotic pressure and same concentration.

Hypertonic solutions have higher osmotic pressure and hypotonic solutions have lower osmotic pressure.

0.91% solutions have sodium chloride solution RBC swells up or burst.

Q1- What do you mean by Henry's Law? The Henry's Law constant for oxygen dissolved in water is 4.34×10^4 atm at 25° C. If the partial pressure of oxygen in air is 0.2 atm, under atmospheric pressure conditions. Calculate the concentration in moles per Litre of dissolved oxygen in water in equilibrium with water air at 25° C.

Ans: Partial pressure of the gas is directly proportional to its mole fraction in solution at particular temperature.

$P_A \alpha X_A$; K_H = Henry's Law of constant

$P_A = K_H \times A$

$K_H = 4.34\times10^4$ atm

$PO_2 = 0.2$ atm

$Xo_2 = PO_2 / K_H \quad = 0.2 / 4.34\times10^4 = 4.6\times10^{-6}$

If we assume 1L solution = 1L water

n water = 1000/18 = 55.5

$XO_2 = nO_2 / (nO_2 + n\ H_2O) \sim = nO_2 / nH_2O$

$nO_2 = 4.6 \text{ X } 10^{-6} \text{ X } 55.5 = 2.55 \text{ X } 10^{-4}$ mol

$M = 2.55 \text{ X } 10^{-4}$ M

Q.2. What is Vant Hoff factor?

Ans. It is the ratio of normal molecular mass to observed molecular mass . H is denoted as 'i'

i = normal m.m / observed m.m

= no. of particles after association or dissociation / no. of particles before

Q.3. What is the Vant Hoff factor in $K_4[Fe(CN)_6]$ and $BaCl_2$?

Ans 5 and 3

Q.4. Why the molecular mass becomes abnormal?

Ans. Due to association or dissociation of solute in given solvent .

Q.5. Define molarity, how it is related with normality ?

Ans. N = M x Basicity or acidity.

Q.6. How molarity is related with percentage and density of solution ?
Ans. M = P x d x10/M.M

Q.7. What role does the molecular interaction play in the solution of alcohol and water?

Ans. Positive deviation from ideal behavior .

Q.8. What is Vant Hoff factor , how is it related with

a. degree of dissociation b. degree of association

Ans. a. $\alpha = i - 1/n-1$ b. $\alpha = i - 1 / 1/n - 1$

Q.9. Why NaCl is used to clear snow from roads ?

Ans. It lowers f.p of water

Q10. why the boiling point of solution is higher than oure liquid

Ans. Due to lowering in v.p

HOTS

Q1. Out of 1M and 1m aqueous solution which is more concentrated

Ans. 1M as density of water is 1gm/Ml

Q2. Henry law constant for two gases are 21.5 and 49.5 atm ,which gas is more soluble .

Ans. KH is inversely proportional to solubility .

Q.3. Define azeotrope , give an example of maximum boiling azeotrope.

Q.4. Calculate the volume of 75% of H_2SO_4 by weight (d=1.8 gm/ml) required to prepare 1L of 0.2M solution

Hint: $M_1 = P \times d \times 10 / 98$

$M_1 V_1 = M_2 V_2$

14.5ml

Q.5. Why water cannot be completely separated from aqueous solution of ethyl alcohol?

Ans. Due to formation of Azeotrope at (95.4%)

SHORT ANSWERS (2 MARKS)

Q.1. How many grams of KCl should be added to 1kg of water to lower its freezing point to -8.0^0C (kf = 1.86 K kg /mol)

Ans. Since KCl dissociate in water completely L=2

$\Delta Tf = i\,kf \times m$; m =$\Delta Tf/ikf$

m= 8 / 2X1.86 = 2.15mol/kg.

Grams of KCl= 2.15 X 74.5 = 160.2 g/kg.

Q.2. With the help of diagram: show the elevator in boiling point colligative properties ?

Q.3. what do you mean by colligative properties, which colligative property is used to determine m.m of polymer and why?

Q.4. Define reverse osmosis, write its one use.

Ans. Desalination of water.

Q.5. Why does an azeotropic mixture distills without any change in composition.

Hint: It has same composition of components in liquid and vapour phase.

Q.6. Under what condition Vant Hoff's factor is

a. equal to 1 b. less than 1 c. more than 1

Q.7. If the density of some lake water is 1.25 gm /ml and contains 92gm of Na^+ ions per kg of water. Calculate the molality of Na^+ ion in the lake .

Ans. n = 92/23 = 4

m= 4/1 = 4m

Q.8. An aqueous solution of 2% non-volatile exerts a pressure of 1.004 Bar at the normal boiling point of the solvent . What is the molar mass of the solute .

Hint: $P^0_A - P_A/P^0_A = w_B X m_A / m_B X w_A$

1.013 – 1.004 / 1.013 = 2X 18 /m_B X 98

m_B = 41.35gm/mol

Q.9. Why is it advised to add ethylene glycol to water in a car radiator in hill station?

Hint: Anti- freeze.

Q.10. what do you mean by hypertonic solution, what happens when RBC is kept in 0.91% solution of sodium chloride?

Q 11. (a). define the following terms.

1. Mole fraction
2. Ideal solutions

(b)15 g of an unknown molecular material is dissolved in 450 g of water. The resulting solution frrezez at -0.34 ^{0}c . what is the molar mass of material? Kf for water= 1.86 K Kg mol^{-1} .

Ans. 182.35 glmol

Q 12.(a) explain the following :

1. Henry's law about dissolution of a gas in a liquid .
2. Boling point elevation constant for a solvent

(b)a solution of glycerol ($C_3h_80_3$) in water was prepared by dissolving some glycerol in in 500 g of water. The solution has a boiling point of 100.42 ^{0}c . what mass of glycerol was dissolved to make this solution?

Kb for water = 0.512 k Kg mol^{-1}

(hint: $atb = \frac{b*wb*1000}{Mb*Wa}$

Ans. 37.73 gm

Q 13. 2 g of benzoic acid (c_6h_5cooh) dissolved in 25 g of benzene shows a depression in freezing point equal to 1.62 K . KF for benzene is 4.9 K Kg mol^{-1}. What is the percentage association of acid if it forms dimer in solution. Ans. 99.2%

Q14. Osmotic pressure of a 0.0103 molar solution of an electrolite is found to be 0.70 atm at 27^{0}c . calculate Vant Hoff factor.(R=0.082 L atom mol^{-1} K^{-1}) Ans. 2.76

UNIT-3

ELECTROCHEMISTRY CONCEPTS

Electrochemistry may be defined as the branch of chemistry which deals with the quantitative study of interrelation ship between chemical energy and electrical energy and inter-conversion of one form into another.relationships between electrical energy taking place in redox reactions.

A cell is of two types:-

I. Galvanic Cell
II. Electrolytic cell.

In Galvanic cell the chemical energy of a spontaneous redox reaction is converted into electrical work.

In Electrolytic cell electrical energy is used to carry out a non-spontaneous redox reaction.

The Standard Electrode Potential for any electrode dipped in an appropriate solution is defined with respect to standard electrode potential of hydrogen electrode taken as zero. The standard potential of the cell can be obtained by taking the difference of the standard potentials of cathode and anode.

$$E^0_{cell} = E^0_{cathode} - E^0_{anode}$$

The standard potential of the cells are related of standard Gibbs energy.

$$\Delta_r G = -nFE^0_{cell}$$

The standard potential of the cells is related to equilibrium constant.

$$\Delta_r G = -RTink$$

Concentration dependence of the potentials of the electrodes and the cells are given by Nernst equation.

$$aA + bB \xrightarrow{ne^-} cC + dD$$

Nernst equation can be written as

$$E_{cell} = E^0_{cell} - \frac{RT}{nF} \frac{\ln[C]^c[D]^d}{[A]^a[B]^b}$$

The conductivity, K of an electrolytic solution depends on the concentration of the electrolyte, nature of solvent and temperature.

Molar Conductivity, Δm, is defined by K/C where C is the concentration in Mol L^{-1}

$$\Delta M = \frac{k*1000}{m}$$

the unit of molar conductivity is Ω^{-1} cm^2 mol^-1. Conductivity decrease but molar conductivity increases with decrease in concentration. It increases slowly with decrease in concentration for strong electrolyte while the increase is very dilute solutions.

Kohlrausch law of independent migration of ions. The law states that limiting conductivity of an electrolyte can be represented as the sum of the individual contribution to the anion and cation of the electrolyte.

Faraday's laws of Electrolysis

I. The amount of chemical reaction which occurs at any electrode during electrolysis by a current is proportional to the quantity of electricity passed through the electrolyte.
II. The amount of different substances liberated by the same quantity of electricity passing through the electrolytic solution is proportional to their chemical equivalent weights.

Batteries and full cells are very useful forms of galvanic cells
There are mainly two types of batteries.

Corrosion of metals is an electrochemical phenomenon
In corrosion metal is oxidized by loss of electrons to oxygen and formation of oxides.

Anode (Oxidation): $2Fe(s) \rightarrow 2Fe^{2+} + 4e^-$
Cathode (Reduction): $O_2(g) + 4H^+(aq) + 4e^- \rightarrow 2H_2O$

Atmospheric Oxidation:
$2Fe^{2+}(aq) + 2H_2O(l) + 1/2O_2(g) \rightarrow Fe_2O_3(s) + 4H^+(aq)$

QUESTION CARRING 1 MARK

1. What is the effect of temperature on molar conductivity?

Ans. Molar conductivity of an electrolyte increases with increase in temperature.

2. Why is it not possible to measure single electrode potential?

Ans. (It is not possible to measure single electrode potential because the half cell containing single electrode cannot exist independently, as charge cannot flow on its own in a single electrode.)

3. Name the factor on which emf of a cell depends:-

Ans. Emf of a cell depends on following factor-

a. Nature of reactants.
b. Concentration of solution in two half cells.
c. Temperature

d. Pressure of gas.

4. What are the units of molar conductivity?
(cm^2 ohm^{-1} mol^{-1} or Scm^2mol^{-1})

5. Write Nernst equation –
For the general cell reaction
aA+bB→cC+dD

Ans. $$E_{cell} = E^0_{cell} - \frac{RT}{nF} \ln \frac{[C]^c[[D]^d}{[A]^a[B]^b}$$

6. What is the EMF of the cell when the cell reaction attains equilibrium?
Ans. Zero

7. What is the electrolyte used in a dry cell?
Ans. A paste of NH_4Cl, MnO_2 and C

8. How is cell constant calculated from conductance values?
Ans. Cell constant= specific conductance/ observed conductance.

9. What flows in the internal circuit of a galvanic cell.
Ans. Ions

10. Define electrochemical series.
Ans. The arrangement of various electrodes in the decreasing or increasing order of their standard reduction potentials is called electrochemical series.

QUESTIONS CARRYING TWO MARKS

1. How can you increase the reduction potential of an electrode.?
For the reaction

$M^{n+}(aq) + ne^- \rightarrow M(s)$

Ans. Nernst equation is:

$$E^0_{M\,n+/M} = E_{M\,n+/M} - \frac{2.303RT}{nF} \log \frac{1}{[Mn^+]}$$

$E_{M\,n+/M}$ can be increased by

a. increase in concentration of M^{n+} ions in solution
b. by increasing the temperature.

2. Calculate emf of the following cell at 298K

Zn/Zn^{2+} (10^{-4} M) || Cu^{2+} (10^{-2}M)/Cu

Given E^0 Zn^{2+}/Zn=-0.76V

E^0Cu^{2+}/Cu=+0.34V

Ans. Cell reaction is as follows.

$Zn(s) + Cu^{2+}(aq) \rightarrow Zn^{2+}(aq) + Cu(s)$

N=2

T=298K

$$Ecell=(E^0Cu^{2+}/Cu-E0Zn^{2+}/Zn)-0.0591V \log\frac{[Zn^{2+}(aq)]}{[Cu^{+}(aq)]}$$

$$= 0.34V-(-0.76)-0.02955V\log\frac{10^{-4}}{10^{-2}}$$

= 1.10V-0.02955V log 10-2

= 1.10V+2 X 0.02955V

= 1.10V + 0.0591 V

= 1.1591V

Q 3. Electrolysis of KBr(aq) gives Br_2 at anode but KF(aq) does not give $F^{2.}$ Give reason.

Ans. Oxidation takes place at anode. Now higher the oxidation Potential, easier to oxidize. Oxidation potential of Br^-, H2O,F^- are in the following order.

Br->H_2O>F-

Therefore in aq. Solution of KBr. Br^- ions are oxidized to Br_2 in preference to H_2O. On the other hand, in aq. Solution of KF, H_2O is oxidized in preference to F^-. Thus in this case oxidation of H_2O at anode gives O_2 and no F_2 is produced.

3. What happens when a piece of copper is added to (a) an aq solution of $FeSO_4$(b) an Aq solution of $FeCl_3$?

a. Nothing will happen when the piece of copper is added to FeSo4 because reduction potential E0 Cu2/Cu(0.34) is more than the reduction potential E0(Fe2+/Fe) (0.44V).

b. Copper will dissolve in an aq solution of $FeCl_3$ because reduction potential E^0Fe^{3+}/Fe^{2+}(0.77V) is more than the reduction potential of E^0Cu_2/Cu(0.34)

$Cu(s)+ 2FeCl_3 (aq) \rightarrow Cu_2(aq) + 2 FeCl_2(aq)$

4. Define corrosion. Write chemical formula of rust.
   Corrosion is a process of determination of metal as a result of its reaction with air and water, surrounding it. It is due to formulation of sulphides, oxides, carbonates, hydroxides, etc.
   Formula of rust- $Fe_2O.XH_2O$
5. Write short notes on reduction and oxidation potentials.
6. How are standard electrode potentials measured?
7. What is cell constant? How it is determined?
8. what is conductivity water

9. Why it is necessary to platinize the electrodes of a conductivity cell before it is used for conductance measurement?
10. Why mercury cell gives the constant voltage.
11. What is fuel cell, write reaction involved in h_2-o_2 fuel cel.

QUESTION CARRYING THREE MARKS

1. Write any three differences between potential difference and e.m.f.

E.M.F	POTENTIAL DIFFERENCE
1.It is difference between electrode potential of two electrodes when no current is flowing through circuit.	1.it is difference of potential between electrode in a closed circuit.
2. it is the maximum voltage obtained From a cell.	2.it is less than maximum voltage Obtained from a cell.
3. it is responsible for steady flow of Current.	3.it is not responsible for steady Flow of current.

2. Why an electrochemical cell stops working after sometime?
The reduction potential of an electrode depends upon the concentration of solution with which it is in contact.

As the cell works, the concentration of reactants decrease. Then according to Le chatelier's principle it will shift the equilibrium in backward direction. On the other hand if the concentration is more on the reactant side then it will shift the equilibrium in forward direction. When cell works concentration in anodic compartment in cathodic compartment decrease and hence E^0 cathode will decrease. Now EMF of cell is
$E^0_{cell} = E^0_{cathode} - E^0_{anode}$

A decrease in $E^0_{cathode}$ **and a corresponding increase in** E^0 anode wil mean that EMF of the cell will decrease and will ultimately become zero i.e., cell stops working after some time.

3. for the standard cell
$Cu(s)/Cu^+(aq)|| Ag^+(aq)/Ag(s)$
E^0_{cell} $^{2+/}Cu = +0.34$ V
E^0_{cell} $^{2+} = +0.34$ V

E^0 $Ag^+/Ag = +0.80$ V

i. identify the cathode and the anode as the current is drawn from the cell.
ii. Write the reaction taking place at the electrodes.
iii. Calculate the standard cell potential.

Ans. 1.From the cell representation

Ag/Ag^+ electrode is cathode and Cu/Cu^+ electrode is anode .

1. At anode :

$Cu(s) \rightarrow$
Cu^{2+} (aq)+$2e^- \rightarrow Ag(s)$

$$E^0_{cell} = E^0_{cathode} - E^0_{anode}$$
$$= E^0_{Ag+/Ag} - E^0_{Cu2+/Cu}$$
$$= +.80\ V - (+0.34V)$$
$$= +0.80V - 0.34V$$
$$= 0.46V$$

2. Can we store copper sulphate in (i)Zinc vessel (ii) Silver vessel? Give reasons.
   Given E^0 Cu^{2+}/Cu = +0.34V, E^0Zn^{2+}/Zn= -0.76V) , $E0Ag^+/Ag$ = +0.80V

   Ans. A metal having lower reduction potential can displace a metal having higher reduction potential from solution of its salt.of Cu^{2+}(E^0Cu^{2+}/C

   I. Since standard reduction potential of Zn^{2+}(E^0Zn^{2+}/Zn = -0.76V) is less than the standard reduction potentialof Cu^{2+} (E^0Cu^{2+}/Cu=+0.34V), Zn can displace copper from copper sulphate solution. Thus, $CuSo_4$ solution can be stored in silver vessel.

3. How many grams of chlorine can be produced by the electrolysis of matters NaCl with a current of 1.02 A for 15 min?
   $2NaCl(l) \rightarrow 2Na^+(l)+2Cl^-(l)$
   $2\ Cl^- \rightarrow Cl_2(g) + 2e^-$
   2 mole 1mol
   Q= nf
   Q= 2 x 96500 C/mol= 1.93 x 10^5C

   Quantity of electricity used = IT
   = 1.02 A X (15 X 60)sec
   = 900C
   Molar mass of Cl2 = 2 X 35.5 = 71 $gmol^{-1}$ X 10^5 C of charge produce chlorine = 71g
   1.93 X 10^5 C of charge produce chlorine = 71gm
   900 C of charge produce chlorine $\frac{71 \times 900}{1.93 \times 10^5}$
   = 0.331 gm
4. What is understood by a normal hydrogen electrode? Give its significance.
5. Define electrode potential. Why absolute value of reduction potential of electrode cannot be determined?
6. Write the equation showing the effect of concentration on the electrode potential.

7. Derive the relationship between Gibb's free energy change and the cell potential.
8. How Nernst equation can be applied in the calculation of equilibrium constant of any cell reaction.?
9. The cell reaction as written is spontaneous if the overall EMF of the cell is positive. Comment on this statement.

QUESTIONS CARRYING 5 MARKS

1. Explain the term electrolysis. Discuss briefly the electrolysis of (i) molten NaCl (ii) aqueous sodium chloride solution (iii) molten lead bromide (iv) water.
2. state and explain Faraday's laws of electrolysis. What is Electrochemical equivalent?
3. What do you understand by 'electrolytic conduction'? what are the factors on which electrolyte conduction depends.? What is the effect of temperature on electrolytic conduction?
4. How is electrolytic conductance measured experimentally?
5. Describe normal hydrogen electrode and its applications.

HOT QUESTIONS

<u>1 Mark questions</u>:-

1. Why in a concentrated solution, a strong electrolyte shows deviations from Debye-Huckle- Onsagar equation?
Ans:- Because interionic forces of attractions are large.

2. What is the use of Platinum foil in the hydrogen electrode?
A: It is used for inflow and outflow of electrons.
3. Corrosion of motor cars is of greater problem in winter when salts are spread on roads to melt ice and snow. Why?

4. Is it safe to stir $AgNO_3$ solution with copper spoon? ($E^0_{Ag+/Ag}$ = 0.80 Volt; $E^0_{Cu+/Cu}$ = 0.34 Volt)
Ans: No it is not safe because reacts with $AgNO_3$ Solution (Emf will be positive.)
5. Why is it necessary to use salt bridge in A galvanic cell?
Ans: To complete inner circuit and to maintain electrical neutrality of the solution.

<u>2 mark questions</u>:-

1. Why is Li best reducing agent where as Fluorine is best oxidizing agent ?

2. Equilibrium constant is related to Eθ cell but not to Ecell. Explain.
3. Why sodium metal is not obtained at cathode when aq NaCl is electrolysed with Pt electrodes but obtained when molten NaCl is electrolysed ? 2
4. Zn rod weighing 25 g was kept in 100 mL of 1M copper sulphate solution. After certain time interval, the molarity of Cu^{2+} was found to be 0.8 M. What is the molarity of SO_4^{-2} in the resulting solution and what should be the mass of Zn rod after
cleaning and drying ?
5. Which will have greater molar conductivity and why? Sol A. 1mol KCl dissolved in 200cc of the solution or Sol B. 1 mol KCl dissolved in 500cc of the solution.

<u>3/ 5 mark questions</u>:-
1. What do you mean by (i) negative standard electrode potential and
(ii) positive standard electrode potential ?
2. Which cell is generally used in hearing aids?Name the material of the anode, cathode and the electrolyte. Write the reactions involved.
3. Iron does not rust even if Zinc coating is broken in agalvanised iron pipe but rusting occurs much faster if tin coating over iron is broken.Explain.
4. ‘ Corrosion is an electrochemical phenomenan’, explain.

5. Calculate the pH of following cell: Pt, H_2/ H_2SO_4, if its electrode potential is0.03V.
6 . A cell contains two hydrogen electrodes. The negative electrode is in contact witha solution of 10^{-5} M H+ ions. The emf of the cell is 0.118 V at 298 K. Calculate theconcentration of the H+ ions at the positive electrode.

7. Crude copper containing Fe and Ag as contaminations was subjected to electro refining by using a current of 175 A for 6.434 min. The mass of anode was found to decrease by 22.260 g, while that of cathode was increased by 22.011 g. Estimate the % of copper, iron and silver in crude copper.

8 Zinc electrode is constituted at 298 K by placing Zn rod in 0.1 M aq solution of zinc sulphate which is 95 % dissociated at this concentration. What will be the electrode potential of the electrode given that EθZn2+/Zn= - 0.76 V. 3

9. At what pH will hydrogen electrode at 298 K show an electrode potential of -0.118 V, when Hydrogen gas is bubbled at 1 atm pressure ? 3

10 Electrolysis of the solution of MnSO4 in aq sulphuric acid is a method for the preparation of MnO2 as per the chemical reaction
Mn2+ + 2H2O → MnO2 + 2H+ + H2
Passing a current of 27 A for 24 Hrs gives 1 kg of MnO2. What is the current efficiency ? What are the reactions occurring at anode and cathode ?

Electrochemistry

Q 1.What do you mean by kohlrauch's law: from the following molar conductivities at infinite dilution

$\Delta m\infty$ $Ba(OH)_2$ =457.6 Ω^{-1} cm^2 mol^{-1}

$\Delta m\infty$ Ba Cl_2 = 240.6 Ω^{-1} cm^2 mol^{-1}

$\Delta m\infty$ NH_4Cl= 129.8 Ω^{-1} cm^2 mol^{-1}

Calculate $\Delta m\infty$ for NH_4OH

Ans. 238.3 $\Omega^{-1}cm^2$ mol^{-1}

Q2. Calculate the equilibrium constant for the reaction

$Zn + Cd^{2+} \longleftrightarrow Zn^{2+} + Cd$

If E^0 Cd^{++}/Cd =-.403 v

E^0 Zn^{++}/Zn= -0.763 v

Antilog 12.1827

Ans.$1.52*10^{12}$

Q3. Predict the products of electrolyzing of the following

(a) a dil. Solution of h^2So^4 with Pt. electrode

(b). An aqueous solution of AgNO3 with silver electrode

UNIT-4

CHEMICAL KINETICS

CONCEPT

Thermodynamics helps us to predict the feasibility of chemical reaction by using ΔG as parameter but it cannot tell everything about the rate of reaction. Rate of chemical reaction is studied in another branch of chemistry called Chemical Kinetics**.**

Chemical kinetics- The branch of physical chemistry which deals with the study of rate of reaction and their mechanism is called chemical kinetics.

Rate of chemical reaction- The change in concentration of any reactant or product per unit time is called rate of reaction.

TYPES OF RATE OF REACTION-

1. **Average rate of reaction-** The rate of reaction measured over the long time interval is called average rate of reaction.

$$\text{Avg rate } \Delta x/\Delta t = -\Delta[R]/\Delta t = +\Delta[p]/\Delta t$$

2. **Instantaneous rate of reaction-** The rate of reaction measured at a particular time is called instantaneous rate of reaction.

$$\text{Instantaneous rate } dx/dt = -d[R]/dt = +d[P]/dt$$

FACTORS AFFECTING RATE OF REACTION-

1. **Concentration of reactant**
2. **Surface area**
3. **Temperature**
4. **Nature of reactant**
5. **Presence of catalyst**
6. **Radiation**

RATE CONSTANT (k)- It is equal to the rate of reaction when molecular concentration of reactant is at unity.

RATE LAW- The rate of reaction is directly proportional to the product of concentration of reactant and each concentration is raised to some power which may or may not be equal to stereochemistry experimentally.

For a reaction

$aA+bB \rightarrow cC+dD$

Rate law = $k[A]^p[B]^q$
Where powers P and Q are determined experimentally
MOLECULARITY – The total no. of reactants taking part in elementary chemical reaction is called molecularity.

ORDER OF REACTION- The sum of powers to which the concentrations terms are raised in a rate law expression is called order of reactions. For above case order = P+Q: orders of r^n is determined experimentally

HALF-LIFE PERIOD- The time during which the concentration of the reactant is reduced to half of its initial concentration is called half-life period.

ACTIVATION ENERGY- The minimum extra amount of energy absorbed by reactant molecules so that their energy becomes equal to the threshold energy is called activation energy.

Activation energy = Threshold energy – kinetic energy

TEMPERATURE COEFFICIENT- The ratio of rate constant at two temperatures having difference of 10^0C is called temperature coefficient.

Temperature coefficient = Rate constant at T+10^0C/Rate constant at T^0C

Arhenius Equation-

$$K = Ae^{-Ea/RT}$$

K-rate constant
A-Arrhenius energy
E_a-Activation energy
R- Rate constant
T-Temperature

$$\text{Log } K = \text{Log } A - \frac{Eq}{2.303RT}$$

Energy of activation can be evaluated as

1. Log [K2/K1] **= Ea(1/T1-1/T2)/ 2.303RT**
   Log [K2/K1] **= Ea(1/T1-1/T2)/ 19.15**

1 MARKS QUESTION

1. The gas phase decomposition of acetaldehyde

$$CH_3CHO \rightarrow CH_4 + CO$$

Follows the rate law.

What are the units of its rate constant.

Ans. $Atm^{-1/2}sec^{-1}$

2. State the order with respect to each reactant and overall reaction.

$$H_2O + 3I^- + 2H^+ \rightarrow 2H_2O + I_3^-$$

Rate = $k[H_2O_2]^1[I^-]^1$

Ans. Order of reaction= 1+1= 2

3. Give one example of pseudo first order reaction**.**

Ans. Hydrolysis of an ester

$$CH_3COOC_2H_5 + H_2O \rightarrow CH_3COOH + C_2H_5OH$$

4. The conversion of molecules X to Y follows the second order of kinetics. If concentration of X is increased 3 times, how will it affect the rate of formation of Y.

Ans. Rate = $k\,[A]^2$
= $k\,[3A]^2$
= $k\,[9a]^2$

The rate of formation will become nine times.

5. The rate law for a reaction is

Rate = $K\,[A]\,[B]^{3/2}$

Can the reaction be an elementary process? Explain.

Ans. No, an elementary process would have a rate law with orders equal to its molecularities and therefore must be in integral form.

6. What do you understand by 'rate of reaction'?
7. Name the factors on which the rate of a particular reaction depends.
8. Why rate of reaction does not remain constant throughout?
9. Define specific reaction rate or rate constant.

10. What is half-life period of a reaction?

2 MARKS QUESTION

1. The rate of a particular reaction quadruples when the temperature changes from 293K to 313K. Calculate activation energy.

Ans. $K_2/K_1 = 4$,

T1= 293K T2 = 313K

Log [K2/K1] = Ea[T2-T1]/19.15

Thus on calculating and substituting values we get…..

Ea = 52.86 KJ mol^{-1}

2. If the decomposition of nitrogen oxide as

$2N_2O_5 \longrightarrow 4NO_2 + O_2$

follows a first order kinetics.

(i) Calculate the rate constant for a 0.05 M solution if the instantaneous rate is 1.5×10^{-6} mol/l/s?

Ans. Rate = K $[N_2O_5]$

$$K = \frac{Rate}{[N_2O_5]}$$

$$K = \frac{1.5 \times 10^{-6}}{0.05}$$

$K = 3.0 \times 10^{-5}$

ii) What concentration of N_2O_6 would give a rate of 2.45×10^{-5} mol $L^{-1}s^{-1}$

Rate = 2.45×10^{-5} mol $L^{-1}s^{-1}$

$$[N_2O_5] = \frac{Rate}{K} = \frac{2.45 \times 10^{-5}}{3.0 \times 10^{-5}}$$

= 0.82 M

3) Write the difference between order and molecularity of reaction.

Ans.

ORDER	MOLECULARITY
It is the sum of the powers of concentration terms in the rate law expression.	It is the number of reacting speci--es undergoing simultaneously Collision in a reaction.
It is determined experimentally	it is a theoretical concept
Order of reaction need not be a whole number	It is whole no. only
Order of reaction can be zero.	It can't be zero or fractional

4) Define Threshold energy and activation energy. How they are related?
Ans. Threshold Energy: It is the minimum amount of energy which the reactant molecules must possess for the effective collision in forming the products.

Activation Energy: It is the excess energy required by the reactants to undergo chemical reaction.

Activation energy = Threshold energy – Average kinetic energy of molecules.

5(a). Draw a schematic graph showing how the rate of a first order reaction changes in concentration of reactants.

Variation of rate of first of first order reaction with concentration.

(b). rate of reaction is given by the equation
Rate = k [A] 2[B]
What are the units of rate constant for this reaction?
Ans. Rate = k [A] 2[B]

$$K = \frac{mol\ L^{-1}s^{-1}}{(mol\ L^{-1})^2(mol^{-1})}$$

$$K = mol^{-2}L^{2}s^{-1}$$

6. List the factors affecting the rate of reaction.
7. Explain with suitable example, how the molecularity of a reaction is different from the order of a reaction.

8. Define the term 'rate constant' of 'specific reaction rate'.
9. What are Pseudo unimolecular reactions? Explain with the help of a suitable example.
10. What is half life period? Derive and expression for half-life period in case of a first order reaction.

3 marks question

Q1. The rate constant for first order reaction is 60/s. How much time will it take to reduce the concentration of the reaction to 1/10 of its initial value.
Ans:-

$$t = \frac{2.303}{K} \log \frac{[R_0]}{[R]}$$

$$t = \frac{2.303}{\frac{1}{10}} \log \frac{[R0]}{[R]}$$

$$t = \frac{2.303}{60} \log 10$$

$$t = \frac{2.303}{60} = 3.38 X\ 10^{-2} s^{-1}$$

2. The rate of most of reaction double when their temperature is raised from 298k to 308k. Calculate the activation energy of such a reaction.
Ans:-

$$\text{Log} \frac{K_2}{K_1} = \frac{E_a}{2.303\ R} \frac{1 - 1}{T_1\ T_2}$$

$$Ea = \frac{2.303 X 8.314 X 298 X 308 X 0.3010}{1000}$$

Ea = 52.89KJ/mol

3. A first order reaction takes 69.3 min for 50% completion. Set up on equation for determining the time needed for 80% completion.
Ans. $K = \frac{0.693}{T^{1/2}}$
= 0.693/69.3min
= $10^{-2} min^{-1}$

$$T = \frac{2.303}{K} \log \frac{[R_0]}{[R]}$$

$T = 2.303/10^{-2} \log 5$

T= 160.9min

4. Following reaction takes place in one step

$$2NO + O_2 \rightarrow 2NO_2$$

How will the rate of the reaction of the above reaction change if the volume of reaction vessel is diminished to 1/3 of its original volume? Will there be any change in the order of reaction with reduced volume?

Ans. $2NO + O_2 \rightarrow 2NO_2$

$dx/dt = k*[NO]_2[O_2]1$

[Since it is one step]

If the volume of reaction vessel is diminished to 1/3, conc. Of both NO and O2 will become 3 time, the rate of reaction increased 27 times.
In the order of reaction with the reduced volume.

5. The decomposition of NH_3 on platinum surface is a zero order reaction. What are the rate of production of N_2 and H_2.
If $k = 2.5 \times 10^{-4}$

Ans. $2NH_3 \rightarrow N_2 + 3H_2$

$$\frac{-1}{2}\frac{d[NH_3]}{dt} = \frac{d[NH_2]}{dt} + \frac{1}{3}\frac{d[H_2]}{dt}$$

$$\frac{-d[NH_3]}{dt} = \text{rate} = k \times [NH_3]^0$$

$$= 2.5 \times 10^{-4}\ molL^{-1}sec^{-1}$$

$$\frac{d[N_2]}{dt} = -\frac{1}{2}\frac{d[NH_3]}{dt}$$

$$= 1/2 \times 2.5 \times 10^{-4}\ molL^{-1}sec^{-1}$$

$$d[H_2] = -\frac{3}{2}\frac{d[NH_3]}{dt} = 3/2 \times 2.5 \times 10^{-4}$$

$$= 3.75 \times 10^{-44} molL^{-1}sec^{-1}$$

$$\text{Rate} = -\frac{d[NH3]}{dt} = k \times [NH3]^0$$

$$= 2.5 \times 10^{-4}\ molL^{-1}sec^{-1}$$

Rate of production of $N_2 = 2.5 \times 10^{-4}\ molL^{-1}sec^{-1}$

6. How is the rapid change in concentration of reactants/products monitored for fast reactions.
7. What are photochemical reactions? Give two examples,
8. What is the effect of temperature on the rate of reaction? Explain giving reasons.
9. Comment on free energy change of ‘photochemical reactions’.
10. State the role of activated complex in a reaction and state its relation with activation energy.

QUESTIONS CARRYING 5 MARKS

1. What do you understand by the rate of a reaction? How it is expressed? How it is the rate of reaction determined?
2. What do you understand by order of a reaction? How does rate law differ from law of mass action? Give two example of each of the reactions of (i) zero order (ii) first order (iii) second order
3. Derive the equation for the rate constant for a first order reaction. What would be the units of the first order rate constant if the concentration is expressed in mole per litre and time in seconds.
4. Explain why the rate of reaction increases with increase in temperature.
5. Briefly explain the effect of temperature on the rate constant of a reaction.

HOTS

1. The half-life period of two samples are 0.1 and 0.4 seconds. Their initial Concentrations are 200 and 50 mol L^{-1} respectively. What is the order of reaction?

2. What is the ratio of $t_{3/4} : t_{1/2}$ for a first order reaction ?

3. Higher molecularity reactions (viz. molecularity, 4 and above) are very rare. Why?

4. Consider the reaction 2A + B _____> Products

When concentration of B alone was doubled, half life time does not change. When conc. of A alone is doubled, the rate increases by two times. What is the unit of K and what is the order of the reaction?

5. For the reaction, the energy of activation is 75KJ / mol. When the energy of activation of a catalyst is lowered to 20KJ / mol. What is the effect of catalyst on the rate of reaction at 20^0C.

6. The gas phase decomposition of CH_3OCH_3 follows first order of kinetics

$CH_3OCH_3 \rightarrow CH_4 (g) + H_2 (g) + CO (g)$

The reaction is carried out at a constant volume of the container at 500^0 C and has $t_{1/2}$ =14.5min.

Initially only dimethyl ether is present at a pressure of 0.40 atm. What is the total pressure of the system after 12 min? Assume ideal behavior.

Q 7. See the graph and answer the following question

1). What is the order of r^n

2) what is the value of a and b

q 8. 1) what is the order of r^n
2) what is the value of slope and intercept

q 9.1). what is the value of slope

Chapter-5 SURFACE CHEMISTRY

The branch of the Chemistry wich deals with the study of surface phenomena is called surface Chemistry.

POINTS TO BE REMEMBERED: ---

1. ***Adsorption***: - *The accumulation of molecules species at the surface rather in the bulk of a solid or liquid is termed adsorption.*

2. ***Desorption:***-Removal of *adsorbate from the surface of adsorbent is known as Desorption.*

3. ***Sorption:***-*When adsorption and absorption both takes place simultaneously.*

4. ***Type of adsorption***: - On *the basis of interaction between adsorption and absorption, adsorbate are of two types*:

(i)***Physical adsorption/physisorption:*** - *When weak vander waal interaction involve between adsorbate and adsorbent.*

(ii) ***Chemical adsorption/chemisortion***:-*When chemical bonds form between adsorbate and adsorbent.*

5. ***Adsorption isotherm***:-*The variation in the amount of gas adsorbed by the adsorbent with pressure at constant temperature can be expressed by means of a curve termed as adsorption isotherm.*

6. ***Application of adsorption***:-

(a) *Removal of colouring matter from solution using animal charcoal.*

(b)Chromatographic analysis is based on adsorption.

7. ***Freundlich adsorption isotherm***:-*It is a graph which shows relationship between the quality of gas adsorbed by unit mass of solid adsorbent and pressure at a particular temperature.*

$x/m = kp^{1/n}$

8 .Factors affecting adsorption:-

(i)**Surface area**: - *Adsorption increases with increases of surface area of adsorbent.*

(ii)**Nature of adsorbate**:- *Easily liquefiable gases are readily adsorbed.*

(iii)**Temperature**:-*Low temperature is favorable for physical adsorption and High temperature for chemisortion.*

(iv)**Pressure:** - *Pressure increases, adsorption increases.*

9. CATALYSIS:- *Substances which alter the rate of chemical reaction and themselves remain chemically and quantitatively unchanged after the reaction are known as catalyst and the phenomenon is known as catalysis.*

10. PROMOTERS AND POISONS

Promoters are substance that enhance the activity of catalyst while poisons decrease the activity of catalyst.

$$N_2 + 3H_2 \xrightarrow[\text{Mo}]{\text{Fe}} 2NH_3\,(g)$$

Fe =catalyst *Mo= promoter*

11. Homogenous catalyst – *when reactants and catalyst are in same phase.*

e.g. $2\,SO_{2\,(g)} + O_{2\,(g)} \xrightarrow{NO(g)} 2SO_{3(G)}$

12. Heterogeneous catalyst – *the catalytic process in which the reactants and catalyst are in different phase.*

e.g. $SO_2 + O_2 \xrightarrow{Pt} 2SO_3\,(g)$

13. Adsorption theory of Heterogeneous catalysis – *It explains the mechanism of heterogeneous catalyst.*

The mechanism involves 5 steps:-

a. Diffusion of reactants to the surface of catalyst.

b. Adsorption of reactant molecules on the surface of catalyst.
c. Chemical reaction on the catalyst surface through formation of an intermediate.
d. Desorption of reaction product from the catalyst surface.
e. Diffusion of reaction product away from the catalyst surface.

14. IMPORTANT FEATURES OF SOLID CATALYST

Activity - *The activity of a catalyst depend on the strength of chemisorption. Catalytic activity increases from group 5 to group 11 elements of the periodic table.*

$$2H_2 + O_2 \xrightarrow{Pt} 2H_2O$$

Selectivity – *The selectivity of a catalyst is its ability to direct a reaction to yield a particular product.*

1. $CO + 3H_2 \xrightarrow{Ni} CH_4 + H2O$
2. $CO + H_2 \xrightarrow{Cu} HCHO$

15. SHAPE SELECTIVE CATALYSIS

The catalytic reaction that depends upon the pure substance of the catalyst and the size of reactant and product molecules is called shape selective catalysis.

e.g. Zeolites are good shape selective catalyst.

16. ENZYME CATALYSIS

Enzymes are protein molecules of high molecular mass which catalyse the biochemical reaction.

e.g. Inversion of cane sugar by invertase enzyme.

17. Characteristic of enzyme catalysis –

a. **Enzymes are specific to substrate.**
b. **Enzymes are highly active under optimum temperature.**
c. **Enzymes are specific to pH. e.g. Pepsin act in acidic medium**
d. **Enzymes are inhabited by the presence of certain substance.**

Mechanism of enzyme catalysis –

1. *Binding of enzyme to substrate to form an activated complex.*

$$E + S \rightarrow ES^*$$

2. *Decomposition of activated complex to form product.*

$$ES^* \rightarrow E + P$$

18. ***Colloid***-a colloid is a heterogeneous system in which one substance is dispersed(dispersed phase)in another substance called dispersion medium and size of dispersed phase is from 1nm-1000 nm.

19. TYPES OF COLLOIDS

(1) On the basis of nature of interaction between dispersed phase and dispersion medium.

(a) Lyophobic colloid-solvent , hating colloid, these colloids can not be prepared by simply mixing of dispersed phase into dispersion medium.

e.g. metallic sols.

(b) Lyophobic colloid-solvent loving these colloids can be prepared by simply mixing of dispersion phase into dispersion medium.

e.g. Starch sol.

(2) On the basis of types of particles of the dispersed phase

(a) Multimolecular colloid-on dissolution, a large number of atoms or smaller molecules of a substance aggregate together to form species having size in colloidal range. The species thus formed are called Multimolecular colloids.

e.g. Sulphur sol.

(b) Macromolecular colloids -macromolecules are suitable solvent from solution in which size of the particles are in range of colloidal range.

e.g. starch sol.

(c) Associated colloids (micelles)-some substances in law concentration behaves as normal strong electrolyte but at higher concentration exhibit colloidal behavior due to formation of aggregates. The aggregated particles are called micelles and also known as associated colloids.

(3) Kraft temperature- Temp. above which formation of micelles takes places.

(4) Critical micelle concentration (cmc) - concentration above which micelle formation takes place is known as cmc.

(5) ***PREPERATION OF COLLOIDS***

(a) Chemical methods- By double decomposition, oxidation reaction or hydrolysis

OXIDATION

e.g. $SO_2 + 2H_2S \rightarrow 3S\,(SOL) + 2H_2O$

HYDROLYSIS

e.g. $FeCl_3 + 3H_2O \rightarrow Fe(OH)_3 + 3HCl$ (sol)

(b) Bredig's arc method- For preparation of metallic sol. It involves dispersion as well as condensation.

(c) Peptization- Process of converting a precipitate into colloidal sol. By shaking it with dispersion medium in the presence of a small amount of electrolyte.

(6)*PURIFICATION OF COLLIODAL SOLUTION* :-

(a) Dialysis-it is a process of removing a dissolved substance from a colloidal solution by membrane.

(b)Electro dialysis-when dialysis is carried out with an electric field applied around the membrane.

(c) Ultra filtration- Use of special filters which are permeable to all ionic substances except colloidal particles.

(7)*PROPERTIES OF COLLOIDAL SOLUTION:-*

(1) They show colligative properties

(2) Brownian movement-zig-zag motion of colloidal particles

(3) Tyndall effect-scattering of light by colloidal particles by which path of beam becomes clearly visible. This effect is known as tyndall effect.

1. Charge on colloidal particles – Colloidal particles which carry on electric charge and nature of charge is same on all particles.
2. Electrophoresis - Movement of Colloidal particles towards opposite electrode in presence of external electric field.
3. Coagulation – The process of setting of colloidal particles is called coagulation of the sol.
4. Hardy Sehulze Law – Coagulating value of a coagulating ion is directly proportional to the charge on the ion.

Eg: $Na^+ < Ca^{++} < Al^{3+}$ for negatively charged sol.

$Cl^- < CO^{2-}_3 < PO^{3-}_4 < [Fe(CN)_6]^{4-}$ for positive sol.

5. Emulsion – Liquid – liquid colloidal system is known as Emulsion.

There are two types of Emulsion.

a) O/W type - Oil dispersed in water. Eg: milk, vanishing cream.
b) W/O type – Water dispersed in oil. Eg: Butter & Cream.

6. Emulsifying Agent – The substance which stabilizes emulsion.

VERY SHORT ANSWER TYPE QUESTION

(1 marks)

1. What are the physical states of dispersed phase and dispersion medium of froth?

Ans - Dispersed phase is gas, dispersion medium is liquid.

2. What is the cause of Brownian movement among colloidal particles?

Ans - Due to collision between particles.

3. Arrange the solutions: True solution, colloidal solution, suspension in decreasing order of their particles size?
   Ans – Suspension > colloidal > true solution.
4. Give an example of micelles system?
   Ans – Sodium stearate ($C_{17}H_{35}COO^{-}Na^{+}$)
5. Why is it necessary to remove CO when ammonia is obtained by Haber's process?
   Ans- CO acts as poison catalyst for Haber's process therefore it will lower the activity of solution therefore it is necessary to remove when NH_3 obtained by Haber's process.
6. How is adsorption of a gas related to its critical temperature?
   Ans- Higher the critical temperature of the gas. Greater is the ease of liquefaction.
   i.e. greater Vander walls forces of attraction and hence large adsorption will occur.
7. What is meant by Shape Selective Catalyst?
   Ans – On the Shape Selective Catalyst, the rate depends upon pore size of the catalyst and the shape & size of the reactant and products molecules.
8. Of the physiorption & chemisorptions, which type of adsorption has higher enthalpy of adsorption?
   Ans - chemisorptions.
9. Write down the Example of Positive Sol?
   Ans – Ferric hydro-oxide sol.
10. Write down the Example of Negative Sol?
   Ans – Arsenic sulphide.

SHORT ANSWER TYPE QUESTION

(2 marks)

1. Differentiate between physical & chemical adsorption?
   Ans –

Physical adsorption	**Chemical adsorption**
a) Forces between adsorbate & adsorbent are week Vander waal forces. b) Low heat of Adsorption.	a) Forces between adsorbate & adsorbent are strong chemical forces. b) High heat of Adsorption.

2. Differentiate between Lyophobic & Lyophilic colloids**?**
3. Ans –

Lyophilic colloids	**Lyophobic colloids**
a) These are easily formed by direct mixing. b) Particles of colloids are not easily visible even under ultra microscope. c) These are very stable.	a) These are easily formed by Special method. b) Particles of colloids are easily visible under ultra microscope. c) These are unstable.

4. Differentiate between multi molecular, macromolecular and associated colloids?
5. Ans**:-**

Multi molecular colloids	**Macromolecular colloids**	**Associated colloids**
a) They consist of	a) They consist of	a) Behave as colloidal

aggregates of atoms or molecules which generally have diameter less than 1nm. b) They are usually lyophobic	large molecules. b) They are hydrophilic.	size particles at higher conc. b) They have both lyophobic character & Lyophilic

6. What is difference between Sol. & Gel?
Ans – Both are colloidal solutions. Sol has solid as 'dispersed phase & liquid as dispersion medium'. While 'Gel' has liquid as dispersed phase and solid as dispersion medium.

7. Action of Soap is due to Emulsification & Micelle formation? Comment.
Ans – soaps are sodium & potassium salts of higher fatty acids.
Eg: $C_{17}H_{35}COONa$ oil & Grease in dirt adhere firmly to clothing and is undisturbed by washing in tap water. Soap acts as an Emulsifying agent and brings the Greasy dirt into colloidal dispersion the hydrocarbon chain of soap molecule is soluble in oil or grease. It dissolves in grease and encapsulates. It to form micelle. The anionic ends of chain protrude from droplets and interact with water molecules, preventing coalescence of droplets.

SHORT ANSWER TYPE QUESTION

(3 marks)

8. Discuss the effect of pressure & temperature on the adsorption of gases on solids?
Ans – Effect of pressure on adsorption: - At constant temp the extent of adsorption of gas(x/m) in the solid increases with pressure. A graph between x/m and the pressure P of a gas at constant temp is called adsorption isotherm.

Freundlich adsorption isotherm -

i) At lower range of pressure, (x/m) is directly proportional to the applied pressure.

$X/m \propto p^{I}$

ii) At high pressure range, the extent of adsorption of a gas (x/m) is independent of the applied pressure i.e.

$X/m \propto p^{o}$

iii) At intermediate pressure range, the value of (x/m) is proportional to the fractional power of pressure i.e.

$X/m \propto p^{1/n}$

Where 1/n is fraction. Its value may be between 0 and 1

$X/m = kp^{1/n}$

$\log(x/m) = \log k + 1/n \log p$

Effect of temp on Adsorption – Adsorption is generally temp. depended. Mostly adsorption processes are exothermic and hence, adsorption decreases with increasing temp. However for an endothermic adsorption process adsorption increases with increase in Temperature.

1. Explain What is observe when

i) An electrolyte, NaCl is added to hydrate ferric oxide sol.

ii) Electric current is passed through a colloidal sol.

iii) When a beam of light is passed through a colloidal sol.

Ans –(i) The positively charged colloidal particles of $Fe(OH)_3$ get coagulated by the positively charged Cl^- ions provided by NaCl.

(ii) On passing direct current, colloidal particles move towards the positively charged electrode where they lose their charge and get coagulated.

(iii) Scattering of light by the colloidal particles takes place and the path of light becomes visible (Tyndall effect).

2. Describes some features of catalysis by Zeolites?

Ans – Features of catalysis by Zeolites:-

I) Zeolites are hydrated alumino silicates which have a three dimensional network structure containing water molecules in their pores.

II) To use them as catalysts, they heated so that water of hydration present in the pores is lost and the pores become vacant.

III) The size of pores varies from 260 to 740 pm. Thus, only those molecules can be adsorbed in these pores and catalyzed whose size is small enough to enter these pores. Hence, they act as molecular sieves or shape selective catalysts.

An important catalyst used in petroleum industries in zsm-5. It converts alcohols into petrol by first dehydrating them to form a mixture of hydro carbons.

$$\text{Alcohols} \xrightarrow[\text{Dehyderation}]{ZSm-5} \text{Hydro carbons}$$

3. Comment on the statement that "colloid is not a substance but state of a substance"?

Ans – The given statement is true. This is because the statement may exist as a colloid under certain conditions and as a crystalloid under certain other conditions.e.g:NaCl in water behaves as a crystalloid while in benzene, behaves as a colloid (called associated colloid). It is the size of the particles which matters i.e. the state in which the substance exist. If the size of the particles lies in the range 1nm to 1000nm it is in the colloid state.

4. Write short notes on followings:-

(a) Tyndall effect

(b) Brownian Movement

(c) Hardy Schulze Rule

Ans- (a) Tyndall effect-scattering of light by colloidal particles by which path of beam becomes clearly visible. this effect is known as tyndall effect

(b) Brownian movement-zig-zag motion of colloidal particles.

(c) Hardy Sehulze Law – Coagulating value of a coagulating ion is directly proportional to the charge on the ion.

e.g: $Na^+ < Ca^{++} < Al^{3+}$ for negatively changed sol.

$Cl^- < CO^{2-}_3 < PO^{3-}_4 < [Fe(CN)_6]^{4-}$ for positive sol.

Chapter:-6 General Principles & Process of Isolation of Elements

Important Points :

1. The chemical substances in the earth's crust obtained by mining are called Minerals.
2. Minerals, which act as source for metal, are called Ore. From ore metal can be obtained economically .
3. The unwanted impurities present in ore are called Gangue.
4. The entire process of extraction of metal from its ore is called Metallurgy.
5. Removal of gangue from ore is called Concentration, Dressing or Benefaction of ore.
6. Concentration by Hydraulic washing is based on the difference in gravities of ore and gangue particles.
7. Concentration by Magnetic separation is based on differences in magnetic properties of ore components. If either of ore or gangue is capable of attracted by a magnet field, then such separation is carried out.
8. Concentration by Froth Flotation Process is based on the facts that sulphide ore is wetted by oil & gangue particles are wetted by water.
9. Concentration by Leaching is based on the facts that ore is soluble in some suitable reagent & gangue is insoluble in same reagent. e.g. Bauxite ore contains impurities of silica, iron oxide & TiO_2 .The powdered ore is treated with NaOH which dissolve Al & impurities remains insoluble in it.

$$Al_2O_3 + 2NaOH + 3\,H_2O \longrightarrow 2\,Na\,[Al(OH)_4].$$

10. Calcination involves heating of ore in absence of air below melting point of metal. In this process volatile impurities escapes leaving behind metal oxide.

$$Fe_2O_3.xH_2O \longrightarrow Fe_2O_3 + xH_2O$$

$$ZnCO_3 \longrightarrow ZnO + CO_2$$

$$CaCO_3.MgCO_3 \longrightarrow CaO + MgO + 2CO_2$$

11. Roasting involves heating of ore in presence of air below melting point of metal in reverberatory furnace. In this process volatile impurities escapes leaving behind metal oxide and metal sulphide converts to metal oxide.

$$2\,ZnS + 3\,O_2 \longrightarrow 2ZnO + 2SO_2$$

$$2PbS + 3\,O_2 \longrightarrow 2\,PbO + 2\,SO_2$$

$$2\,Cu_2S + 3\,O_2 \longrightarrow 2Cu_2O + 2\,SO_2$$

12. Reduction of metal oxide involves heating of metal in presence of suitable reagent Coke or CO_2.

13. Reactions taking place at different zones of blast furnace in extraction of iron:-

(i) Zone of reduction:- Temperature range 250^oC-700^oC

$$3Fe_2O_3 + CO \longrightarrow 2Fe_3O_4 + CO_2$$

$$Fe_3O_4 + CO \longrightarrow 3FeO + CO_2$$

$$FeO + CO \longrightarrow Fe + CO_2$$

(ii) Zone of slag formation:- Temperature range 800^oC-1000^oC

$$CaCO_3 \longrightarrow CaO + CO_2$$

$$CaO + SiO_2 \longrightarrow CaSiO_3, \qquad P_4O_{10} + 10C \longrightarrow 4P + 10CO,$$

$$SiO_2 + 2C \longrightarrow Si + 2CO, \qquad MnO_2 + 2C \longrightarrow Mn + 2CO$$

(iii) Zone of fusion: - Temperature range 1150°C-1350°C

$$CO_2 + C \longrightarrow 2CO$$

(iv) Zone of fusion: - Temperature range 1450°C-1950°C

$$C + O_2 \longrightarrow CO_2$$

14. **FLOW SHEET FOR EXTRACTION OF IRON:-**

Iron ore(Magnetite Fe_3O_4)(Haematite Fe_2O_3)

↓

Concentration is done by Gravity separation followed by magnetic separation

↓

Calcination &Roasting i.e. Ore + Air +Heat→Moisture,CO_2,SO_2, As_2O_3 removed And FeO oxidized to Fe_2O_3

↓

Smelting of charge i.e. mixture of ore, coke & $CaCO_3$ takes place in long BLAST FURNACE. Following reaction take place at different zones:-
(refer to point 13)

↓

Pig iron is obtained, which is remelted and cooled then cast iron is obtained

15. Pig Iron: - It contains Fe 93-95%, Carbon 2.5-5%, and Impurities 3%.
16. Cast Iron: - It contains Fe 99.5-99.8%, Carbon 0.1-0.2% Impurities 0.3%.
17. Spongy iron: - Iron formed in the zone of reduction of blast furnace is called spongy iron. It contains impurities of C, Mn , Si, etc.

18**. FLOW SHEET FOR EXTRACTION OF COPPER:-**

Copper Pyrites $CuFeS_2$

↓

Concentration is done by Froth floatation process
Powdered ore + water +pine oil +air→ Sulphide ore in the froth

↓

Roasting is presence of air. following reactions take place:-
$S + O2 \rightarrow SO_2$, $4As + 3O_2 \rightarrow 2As_2O_3$, $2CuFeS_2 + O_2 \rightarrow Cu_2S + 2FeS + SO_2$

↓

Smelting in small blast furnace of a mixture of Roasted ore, coke, and silica.
$2FeS + 3O_2 \rightarrow 2FeO + 2SO_2$, $FeO + SiO_2 \rightarrow FeSiO_3$(slag)

↓

A mixture of Cu_2S, FeS & silica is obtained from blast furnace known as Copper matte

↓

Bessemerisation of copper matte is done in Bessemer converter in presence of air. Following reactions take place:-

$2FeS + 3O_2 \rightarrow 2FeO + 2\ SO_2$, $FeO + SiO_2 \rightarrow FeSiO_3$ (slag),

$2Cu_2S + 3O_2 \rightarrow 2Cu_2O + 2SO_2$, $2Cu_2O + 2Cu_2S \rightarrow 6Cu + SO_2$

↓

Melted copper is cooled, and then SO_2 is evolved. such copper is known as BLISTER COPPER(98%Cu+2% impurities)

19. **FLOW SHEET FOR EXTRACTION OF ALUMINIUM:-**

Bauxite $Al_2O_3.2H_2O$

↓

Concentration of ore is done by leaching .Bauxite is treated with NaOH .Following reaction takes place:-

$Al_2O_3 + 2NaOH + 3\ H_2O \longrightarrow 2\ Na\ [Al\ (OH)_4]$ and impurities of Fe_2O_3, TiO2 &SiO_2 are removed.

↓

Na $[Al\ (OH)_4]$,then reacts with CO_2 then pure Alumina is obtained.

$Na\ [Al(OH)_4] + 2CO_2 \rightarrow Al_2O_3.xH_2O + 2NaHCO_3$

↓

Electrolytic reduction of pure alumina takes place in iron box (cathode) with cryolite (Na_3AlF_6) & fluorspar CaF_2.Graphide rods act as anode. Following reactions take place:-

At cathode:- $Al^{3+} + 3e \rightarrow Al$, At Anode:- $2O^{2-} \rightarrow O_2 + 4e$

↓

By this process 98.8% pure Aluminum is obtained.

20. Vapour phase refining is used for extraction of Nickel (MOND PROCESS) and Zirconium &Titanium (VAN ARKEL PROCESS).

21. Zone refining is used for extraction of Si, Ge, Ga, etc.

22. Chromatography method is based on selective distribution of various constituents of a mixture between two phases, a stationary phase and a moving phase. The stationary phase can be either solid or liquid on solid support.

22. Column chromatography is based on adsorption phenomenon. This method is useful for those elements, which are available in small amounts and the impurities are not much different in chemical properties from the element to be purified.

VERY SHORT ANSWER TYPE QUESTION

(1 marks)

Q.1- What is slag?

A.1- It is easily fusible material fusible material, which is formed when gangue still present in roasted ore combines with the flux.

e.g. CaO (flux) + SiO2 (gangue) $\rightarrow CaSiO_3$ (slag)

Q.2- Which is better reducing agent at 983K, carbon or CO?

A.2- CO, (above 983K CO being more stable & does not act as a good reducing agent but carbon does.)

Q.3- At which temperature carbon can be used as a reducing agent for Foe ?

A.3- Above 1123K, carbon can reduce FeO to Fe.

Q.4- What is the role of graphite rods in electrometallurgy of aluminium ?

A.4- Graphite rods act as anode, are attacked by oxygen to form CO_2 and so to be replace time to time.

Q.5- What is the role of cryolite in electrometallurgy of aluminium?

A.5- alumina cannot be fused easily because of high melting point. Dissolving of alumina in cryolite furnishes Al^{3+} ions, which can be electrolyzed easily.

Q.6- What are depressants?

A.6- It is possible to separate two sulphide ore by adjusting proportion of oil to water in froth flotation process by using a substance known as depressant.

e.g. NaCN is used to separate ZnS and PbS.

Q.7- Copper can be extracted by hydrometallurgy but not Zn. Why?

A.7- The E^0 of Zn is lower than that of Cu thus Zn can displace Cu^{2+} ion from its solution. On other hand side to displace Zn from Zn^{2+} ion, we need a more reactive metal than it.

Q.8- Give name and formula of important ore of iron .

A.8- Haematite – Fe_2O_3, Magnetite –Fe_3O_4, Iron pyrites FeS_2.

Q.9- Give name and formula of important ore of Copper .

A.9- Copper pyrites $CuFeS_2$, Malachite $CuCO_3$. Cu $(OH)_2$, Cuprite Cu_2O.

Q.10- Give name and formula of important ore of Zinc .

A.10- Zinc blende - ZnS, Calamine- $ZnCO_3$, Zincite – ZnO .

SHORT ANSWER TYPE QUESTION

(2 marks)

Q.1 Describe the method of refining of nickel.

A.1- In the Mond Process, Ni is heated in a stream of CO forming a volatile complex, which then decomposes at higher temperature to give Ni.

At 330-350K: - $Ni + 4CO \rightarrow Ni(CO)_4$

At 450-470K $Ni(CO)_4 \rightarrow Ni + 4CO$

Q.2- What is Zone Refining? Explain with example.

A.2- Zone refining is a method of obtaining a metal in very pure state. It is based on the principal that impurities are more soluble in molten state of metal than solidified state.

In this method, a rod of impure metal is moved slowly over circular heater. The portion of the metal being heated melts & forms the molten zone. As this portion of the rod moves out of heater, it solidified while the impurities pass into molten zone. The process is repeated to obtain ultrapure metal and end of rod containing impure metal cutoff.

Q.3 Write the principal of electro-refining.

A.3- In this method of purification impure metal is made Anode and pure metal is made the cathode. On passing electricity, pure metal is deposited at the cathode while the impurities dissolve dissolve in solution as anode mud. E.g. electro- refining of copper:-

At Cathode: - $Cu^{2+} + 2e \rightarrow Cu$

At Anode: - $Cu \rightarrow Cu^{2+} + 2e$

Q.4- Write difference between calcinations and roasting .

A.4- Refer points no 10 &11.

Q.5- Describe the method of refining of Zirconium and Titanium.

A.5- Van Arkel process is used for obtaining ultrapure metal. The impure metal is converted into volatile compound, which then decomposes electrically to get pure metal.

At 850K: - Zr impure) + 2 $I_2 \rightarrow ZnI_4$

At 2075K:- $ZnI_4 \rightarrow$ Zr (pure) + 2 I_2

Q.6- Out of C & CO, which is better reducing agent for ZnO?

A.6- Since free energy of formation of CO from C is lower at temperature above 1120K while that of CO_2 from carbon is lower above 1323K than free energy of formation 0f ZnO. However, the free energy of formation of CO_2 from CO is always higher than that of ZnO. Hence, C is better reducing agent of ZnO.

Q.7- The value of $\Delta_f G^0$ for Cr_2O_3 is -540kJ/mole & that of Al_2O_3 is -827kJ/mole. Is the reduction of Cr_2O_3 possible with aluminium?

A.7- The desired conversion is

$$4\,Al + 2Cr_2O_3 \rightarrow 2Al_2O_3 + 4Cr$$

It is obtained by addition of following two reactions:-

$4Al + 3O_2 \rightarrow 2\,Al_2O_3 \quad \Delta_f G^0$=-827kJ/mole

$2Cr_2O_3 \rightarrow 4Cr + 3O_2 \quad \Delta_f G^0$==+ 540 kJ/mole

Therefore, ΔG^0 for desired reaction is -827+540=-287, as a result reduction is possible.

Q.8:- Why copper matte is put in silica lined converter?

A.8:- Copper matte consists of Cu_2S and FeS. When blast of air is passed through molten matte in silica-lined converter, FeS present in matte is oxidized to FeO, which combines with silica to form slag.

(i) $2FeS + 3O_2 \rightarrow 2FeO + 2\,SO_2$, (ii) $FeO + SiO_2 \rightarrow FeSiO_3$ (slag),

(III) $2Cu_2S + 3O_2 \rightarrow 2Cu_2O + 2SO_2$, (IV) $2Cu_2O + 2Cu_2S \rightarrow 6Cu + SO_2$

Q.9- What is meant by term chromatography?

A.9-Chromato means Colour and graphy means writing because the method was first used for separation of coloured substance. It is based on selective distribution of various constituents of a mixture between two phases, a stationary phase and a moving phase. The stationary phase can be either solid or liquid on solid support.

Q.10-Why is reduction of metal oxide easier if metal formed is in liquid state at temperature of reduction.

A.10- The entropy of a substance is higher in liquid state than solid state. In the reduction of metal oxide, the entropy change will be positive if metal formed is in liquid state. Thus, the value of ΔG^0 becomes negative and reduction occurs easily.

SHORT ANSWER TYPE QUESTION

(3 marks)

Q.1- Explain the following:-

(i) Zinc but not copper is used for recovery of Ag from the complex $[Ag(CN)_2]^-$.

(ii) Partial roasting of sulphide ore is done in the metallurgy of copper.

(iii) Extraction of Cu from pyrites is difficult than that from its oxide ore through reduction.

A.1- (i) Zn is more powerful reducing agent in comparison to copper.Zn is also cheaper than Cu.

(ii) Partial roasting of sulphide ore forms some oxide. This oxide then reacts with remaining sulphide ore to give copper i.e. self-reduction occurs.

$$2Cu_2S + 3O_2 \rightarrow 2Cu_2O + 2SO_2,$$
$$2Cu_2O + 2Cu_2S \rightarrow 6Cu + SO_2.$$

(iii) Though carbon is good reducing agent for oxide but it is poor reducing agent for sulphides. The reduction of metal sulphide does not have large negative value.

Q.2- Explain the method for obtaining pig iron from magnetite.

A.2- Extraction of iron from Magnetite takes place in following steps:-

(i) Concentration of ore: - It is done by Gravity separation followed by magnetic separation process.

(ii) Calcination: - It involve heating when the volatile matter escapes leaving behind metal oxide.

$$Fe_2O_3.xH_2O \rightarrow Fe_2O_3 + xH_2O.$$

(iii) Roasting: - It involves heating of ore in presence of air, thus moisture, CO_2, SO_2, As_2O_3 removed And FeO oxidized to Fe_2O_3.

(iv) Smelting of roasted ore: - A mixture of ore, coke & $CaCO_3$ is smelted in long BLAST FURNACE. Following reaction takes place at different temperature zones:-

(i) Zone of reduction: - Temperature range 250^oC-700^oC

$$3Fe_2O_3 + CO \longrightarrow 2Fe_3O_4 + CO_2$$
$$Fe_3O_4 + CO \longrightarrow 3FeO + CO_2$$
$$FeO + CO \longrightarrow Fe + CO_2$$

(ii) Zone of slag formation:- Temperature range 800^oC-1000^oC

$$CaCO3 \longrightarrow CaO + CO2$$
$$CaO + SiO_2 \longrightarrow CaSiO_3, \qquad P_4O_{10} + 10C \longrightarrow 4P + 10CO,$$
$$SiO_2 + 2C \longrightarrow Si + 2CO, \qquad MnO_2 + 2C \longrightarrow Mn + 2CO$$

(iii) Zone of fusion:- Temperature range 1150^oC-1350^oC

$$CO_2 + C \longrightarrow 2CO$$

(iv) Zone of fusion:- Temperature range 1450^oC-1950^oC

$$C + O_2 \longrightarrow CO_2$$

Thus, Pig iron is obtained from Blast Furnace.

Q.3- Describe the principles of extraction of copper from its ore .

A.3- Refer points no 18. For steps, involve in the extraction.

Q.4- Name the principal ore of aluminium and describe how Al is extracted from its ore.

A.4- Important ores -(i) Bauxite $Al_2O_3.xH_20$ (ii) Corrundum Al_2O_3. Bauxite is commercially important ore Al.

Extraction from Bauxite ore involves the following two stages:-

(i) Purification of bauxite to get pure alumina (Al_2O_3)

(ii) Electrolysis of pure alumina in molten cryolite

Step:-1 Bauxite is treated with NaOH .Following reaction takes place:-

$$Al_2O_3 + 2NaOH + 3H_2O \longrightarrow 2Na[Al(OH)_4]$$

and impurities of Fe_2O_3, TiO_2 & SiO_2 are removed . Na $[Al(OH)_4]$,then reacts with CO_2 then pure Alumina is obtained.

$$Na[Al(OH)_4] + 2CO_2 \rightarrow Al_2O_3.xH_2O + 2NaHCO_3$$

Step:-2 Electrolytic reduction of pure alumina takes place in iron box (cathode) with cryolite (Na_3AlF_6) & fluorspar CaF_2.Graphide rods act as anode. Following reactions take place:-

At cathode:- $Al^{3+} + 3e \rightarrow Al$, At Anode:- $2O^{2-} \rightarrow O_2 +$ By this process 98.8% pure Aluminum is obtained.

Q.5- Describe the principles of extraction of Zinc from zinc blende .

A.5- Important ores of Zn:-Zinc blende - ZnS, Calamine- $ZnCO_3$, and Zincite – ZnO. ZnS is commercially important ore of Zn.Various stages involved in the extraction of Zn from ZnS are as following:-
(i) Concentration of ore:-It is concentrated by Froth flotation process followed by gravity separation process.
(ii) Roasting:- The concentrated ore is roasted in presence of air. Following reactions take place:-

$$2ZnS + 3O_2 \rightarrow 2ZnO + 2SO_2$$

The mass obtained during roasting is porous and is called porous clinker.
(iii) Reduction of ZnO to Zn: - ZnO is made into bricketts with coke and clay and heated ai1163K.Zn formed distills off and is collected by rapid cooling of zinc vapours.

$$ZnO + C \rightarrow Zn + CO$$

Unit-16 CHEMISTRY IN EVERYDAY LIFE

POINTS TO BE REMEMBERED

1. **DRUGS – Drugs are chemical of low molecular masses, which interact with macromolecular targets and produce a biological response.**
2. **CHEMOTHERAPY- The use of chemicals for therapeutic effect is called chemotherapy.**
3. **CLASSIFICATION OF DRUGS –**

(a) ***ON THE BASIS OF PHARMACOLOGICAL EFFECT*-drugs for a particular type of problem as analgesics-----for pain relieving.**
(b) ***ON THE BASIS OF DRUG ACTION*-Action of drug on a particular biochemical process.**
(c) ***ON THE BASIS OF CHEMICAL ACTION*-Drugs having similar structure .eg-sulpha drugs.**
(d) ***ON THE BASIS OF MOLECULAR TARGETS*- Drugs interacting with biomolecules as lipids, proteins.**

4. **ENZYMES AS DRUG TARGETS**

(i) ***CATALYTIC ACTION OF EN ZYMES*-**
(a) **Enzymes have active sites which hold the substrate molecule .it can be attracted by reacting molecules.**
(b) **Substrate is bonded to active sites through hydrogen bonds, ionic bonds, Vander Waal or dipole –dipole interactions.**
(ii) ***DRUG- ENZYME INTERACTIONS*-**
(a)Drug complete with natural substrate for their attachments on the active sites of enzymes .They are called competitive inhibitors.
(b)Some drugs binds to a different site of the enzyme called allosteric sites which changes the shape of active sites.

5. **ANTAGONISTS- The drugs that bind to the receptor site and inhibit its natural function.**
6. **AGONISTS-Drugs mimic the natural messenger by switching on the receptor.**

7. **ANTACIDS-These are compounds which neutralize excess acid of stomach.eg-Aluminium hydroxide, Magnesium hydroxide.**
8. **ANTI HISTAMINES-The drugs which interfare with the natural action of histamines and prevent the allergic reaction. eg- rantidine,tegarnet, avil.**
9. **TRANQULIZERS-The class of chemical compounds used for the treatment of stress,mild or even severe mental diseases. Eg-idardil, iproniagid, luminal, second equaqnil .**
10. **ANALGESICS-They reduce pain without causing impairment of consciousness, mental confusion or some other disturbance of the nervous system.**

Eg - aspirin, seridon , phenacetin.

11. **ANTIMICROBIALS-They tend to prevent/destroy or inhibit the pathogenic action of microbes as bacteria ,virus ,fungi etc .They are classified as**

(i)*ANTIBIOTICS*-Those are the chemicals substances which are produced by micro-organisms.

Eg- Pencillin , ofloxacin .

***NARROW SPECTRUM ANTI-BIOTICS*-These are effective mainly against gram positive or gram negative bacteria. Eg- Penicillin , streptomycin.**

***BROAD SPECTRUM ANTI-BIOTICS*-They kill or inhibit a wide range of micro-organisms.**

eg- chloramphenicol , tetracydine .

(ii)*ANTISEPTICS OR DISINFECTANT*-These are which either kill/inhibit the growth of micro-organisms

Antiseptics are applied to the living tissuses such as wounds, cuts, ulcers etc. eg-furacine,chloroxylenol & terpinol(dettol) .Disinfectant are applied to inanimate objects such as floors , drainage , system.

Eg- 0.2% solution of phenol is an antiseptic while 1% solution is an disinfectant.

12. **ANTIFERTILITY DRUGS- These is the chemical substances used to control the pregnancy. They are also called oral contraceptives or birth control pills.**

Eg-Mifepristone, norethindrone.

13. **ARTIFICIAL SWEETNING AGENTS-These are the chemical compounds which give sweetening effect to the food without adding calorie.**

They are good for diabatic people eg- aspartame, saccharin, alitame , sucrolose.

14. **FOOD PRESERVATIVES- They prevents spoilage of food to microbial growth.eg-salt, sugar, and sodium benzoate.**
15. **CLEANSING AGENTS-**

(i) *SOAPS*- They is sodium or potassium salts of long chain fatty acids.They are obtained by the soapnification reaction, when fatty acids are heated with aqueous sodium hydroxide.

They do not work well in hard water.

(iii) *TOILETS SOAP*-That are prepared by using better grade of fatty acids and excess of alkali needs to be removed .colour & perfumes are added to make them attractive.

(iv) *MEDICATED SOAPS*- Substances of medicinal value are added.eg- Buthional , dettol.

16. SYNTHETIC DETERGENTS-They are cleaning agents having properties of soaps, but actually contain no soap .They can used in both soft and hard water .They are-

(i)*ANIONIC DETERGENTS*-They are sodium salts of sulphonated long chain alcohols or hydrocarbons.eg-sodium lauryl sulphonate . They are effective in acidic solution.

$CH_3 (CH_2) CH2OH \rightarrow CH_3 (CH_2)_{10}CH_2OSO_3H$

(laurylalchol)

$\rightarrow CH_3 (CH_2)_{10}CH_2SO_3^-Na^+$

(Sodium lauryl sulphonate)

(ii)*CATIONIC DETERGENTS*- They are quarternary ammonium salts of amines with acetates , chlorides, or bromides.They are expensive used tolimited extent.eg- cytyltrimethylammoniumbromide

(iii)*NON-IONIC DETERGENTS*- They does not contain any ions. Some liquid dishwashing detergents which are of non-ionic type .

17. BIODEGREDABLE DETERGENTS- The detergents which are linear and can be attacked by micro-organisms are biodegradable.

Eg -sodium 4-(1-dodecyl) benzene \ sulphonate.

18. NON-BIODEGREDABLE DETERGENTS- The detergents which are branched and cannot be decomposed by micro-organisms are called non-biodegdradable.eg-sodium 4-(1,3,5,7 tetramethyloctl)-benzene sulphonate .It creates water pollution.

VERY SHORT ANSWER TYPE QUESTION

(1 marks)

Q-1 Define the term chemotherapy?

Ans-1 Treatment of diseases using chemicals is called chemotherapy.

Q-2 why do we require artificial sweetening agents?

Ans-2 To reduce calorie intake.

Q-3 what are main constiuent of Dettol?

Ans-3 Choloroxylenol & Terpinol .

Q-4 what type drug phenaticinis?

Ans-4 It is antipyretics.

Q-5 Name the drug that are used to control allergy?

Ans-5 Antihistamines.

Q-6Why is the use of aspartame limited to cold food and drinks?

Ans-6 It is unstable at cooking temperature and decompose.

Q-7What is tranquilizers? Give an example?

Ans-7 They is the drug used in stress, mild severe mental disease.

Q-8 what type of drug chloramphenicol?

Ans-8 It is broad spectrum antibiotic.

Q-9Why is biothional is added to the toilet soap?

Ans-9It acts as antiseptics.

Q-10 what are food preservatives?

Ans-10 The substances that prevent spoilage of food due to microbial growth. eg- sodium benzonate.

SHORT ANSWER TYPE QUESTION

(2 marks)

Q-1 Mention one important use of the following-

(i) Equanil (ii)Sucrolose

Ans-1 (i) Equanil- It is a tranquilizer.

(ii) Sucrolose-It is an artificial sweetener.

Q-2 Define the following and give one example-

(i)Antipyretics (ii) Antibiotics

Ans-2 (i) Antipyretics- Those drugs which reduce the temperature of feveral body are called Antipyretics.

Eg - Paracetamol

(ii) Antibiotics-The drugs which prevent the growth of other micro-organisms. Eg- Pencillin.

Q-3 Name the medicines used for the treatment of the following-

(i) Tuberculosis (ii) Typhoid Tuberculosis- Sterptomycin

Typhoid- Cholororophenicol

Q-4 what are tincture of iodine?

Ans-4 2-3% iodine solution of alcohol water is called tincture of Iodine. It is a powerful antiseptics and is applied on wounds.

Q- 5 What is artificial sweetening agent? Give two examples?

Ans-5 The substances which give sweetening to food but don't add calorie to our body .

Eg- Saccharin, alitame.

Q-6 How is synthetic detergents better than soaps?

Ans- 6 (i) Detergents can be used in hard water but soaps cannot be used.

(ii) Detergents have a stronger cleansing action than soaps.

Q-7 what are sulpha drugs? Give two examples?

Ans-7 a group of drugs which are derivatives of sulphanilamide and are used in place of antibiotics is called sulpha drugs.

Eg- sulphadizine, sulphanilamide.

Q-8 what forces are involved in holding the active sites of the enzymes?

Ans-8 The forces are involved in holding the active sites of the enzymes are hydrogen bonding , ionic bonding , dipole-dipole attractions or Vander waals force of attractions.

Q-9 Describe the following giving an example in each case- (i) Edible colours

(ii) Antifertility drugs

(i) Edible colours- They are used for dying food.

Eg- saffron is used to colour rice.

(ii) Antifertility drugs- Those drugs which control the birth of the child are called antifertility drugs.

Q-10 Give two examples of organic compounds used as antiseptics?

Ans-10 Phenol (0.2%), iodoform

SHORT ANSWER TYPE QUESTION

(3 marks)

Q-1 what are Biodegredable and non-biodegdredable detergents? Give one example of each.

Ans-1 Detergents having straight hydrocarbon chain and are easily decomposed by micro-organisms are called Biodegredable detergents.The detergents having branched hydrocarbon chain and are not easily decomposed by micro-organisms are called Non-Biodegredable detergents.

Q-2 what are barbiturates? To which class of drugs do they belong? Give two examples.

Ans-2 Derivatives of barbituric acid are called barbiturates.They are tranquilizers. They also act as hypnotics. eg- luminal , seconal.

Q-3 what is the use of –

(i) Benadryl (ii) sodium benzoate (iii) Progesterone

Ans-3 (i) Antihistamines

(ii) Preservatives

(iii) Antifertility drug

Q-4 Identify the type of drug-

(i) Ofloxacin (ii) Aspirin (iii) Cimetidine

Ans- 4 (i) Antibiotic (ii) Analgesics & Antipyretics

(iii) Antihistamines & antacid

Q-5 Describe the following with suitable example-

(i) Disinfectant (ii) Analgesics

(iii) Broad spectrum antibiotics

(i) Disinfectant- chemicals used to kill the micro-organisms can applied on non living articles.

(ii) Analgesics- They are the drugs which are used to relieve pain . eg – Aspirin , Ibuprofen.

(iii) Broad spectrum antibiotics- They kill the wide range of gram positive and gram negative bacteria.

Eg- Chloramphenicol , ofloxacin.

7. p-Block Elements

Points to remember:-

The general valence shell electronic configuration of p-block elements $ns^2\ np^{1-6}$

GROUP 15 ELEMENTS:-

Group 15 elements ; N, P, As, Sb & Bi

General electronic configuration: ns^2np^3

Physical Properties:-

- Dinitrogen is a diatomic gas while all others are solids.
- N & P are non-metals. As & Sb metalloids & Bi is a metals . this is due to decrease in ionization enthalpy & increase in atomic size .
- Electro negativity decreases down the group .

Chemical properties:-

- Common oxidation states : -3, +3 & +5.
- Due to inert effect, the stability of +5 state decreases down the group & stability of +3 state increases .
- In the case of Nitrogen all Oxidation states from +1 to +4 tend to disproportionate in acid solution , e.g.:- $3HNO_3 \rightarrow H_2O + 2NO$

  Anamalous behavior of Nitrogen :- due to its small size, high electronegativity, high ionization enthalpy and absence of d-orbital.

  N_2 has unique ability to pπ-pπ multiple bonds whereas the heavier of this group do not form pπ –pπ because there atomic orbitals are so large & diffuse that they cannot have effective overlapping.

  Nitrogen exists as diatomic molecule with triple bond between the two atoms whereas other elements form single bonds in elemental state.

  N cannot form dπ-pπ due to the non availibility of d-orbitals whereas other elements can.

Trends In Properties:-

Stability - $NH_3>PH_3>AsH_3>SbH_3>BiH_3$

Bond Dissociation Enthalpy- $NH_3>PH_3>AsH_3>SbH_3>BiH_3$

Reducing character - $NH_3>PH_3>AsH_3>SbH_3>BiH_3$

Basic character- $NH_3>PH_3>AsH_3>SbH_3>BiH_3$

Acidic character- $N_2O_3>P_2O_3>As_2O_3>Sb_2O_3>Bi_2O_3$

Dinitrogen:-

Preparation

- Commercial preparation – By the liquification & fractional distillation of air.
- Laboratory preparation – By treating an aqueous solution NH_4Cl with sodium nitrate .

  $NH_4Cl + NaNO_2 \rightarrow N_2 + 2H_2O + NaCl$

- Thermal decomposition of ammonium dichromate olso gise N_2.
  $(NH_4)_2Cr_2O_7 \rightarrow N_2 + 4H_2O + Cr_2O_3$
- Thermal decomposition of Barium or Sodium azide gives very pure N_2.

PROPERTIES

At high temperature nitrogen combines with metals to form ionic nitride (Mg_3N_2) & with non-metals , covalent nitride.

AMMONIA PREPARATION

- In laboratory it is prepared by heating ammonium salt with NaOH or lime.
  $2NH_4Cl + Ca(OH)_2 \rightarrow 2NH_3 + 2H_2O + CaCl_2$
- In large scale it is manufactured by Haber 'process
  $N_2 + 3H_2 = 2NH_3$
  $\Delta H^0 = -46.1 kJ/mol$
  Acc.to Lechatelier's principle the favourable conditions for the manufacture of NH_3 are:-
  Optimum temperature : 700 K
  High pressure : 200 atm

Catalytst: Iron Oxides

Promoter : K_2O & Al_2O_3

PROPERTIES

Ammonia is a colorless gas with pungent odour.

Highly soluble in water.

In solids & liquid states it exists as an associated molecule due to hydrogen bonding witch accounts for high melting & boiling points of NH_3

Trigonal Pyramidal shape NH_3 molecule.

Aqueous solution of ammonia is weakly basic due to the formation of OH^- ion .

$ZnSO_4 + 2NH_4OH \rightarrow Zn(OH)_2 + (NH_4)_2SO_4$

Ammonia can form coordinate bonds by donating its lone on nitrogen, ammonia forms complexes.

$CuSO_4 + 4NH_3 \rightarrow [Cu(NH_3)_4]_2SO_4$

Name	Formula	Oxidation state	Chemical nature
Nitrous oxide or Laughing gas	N_2O	+1	Neutral

Nitric oxide	NO	+2	Neutral
Dinitrogen trioxide	N_2O_3	+3	Acidic
Dinitrogen tetra oxide	N_2O_4or NO_2	+4	Acidic
Dinitrogen pentaoxide	N_2O_5	+5	Acidic

NITRIC ACID

PREPARATION:ostwald's procees – it is based upon catalytic oxidation of ammonia by atmospheric oxidation . The main steps are

1) $4NH_3 + 5O_2 \xrightarrow[500K,\ 9BAR]{-PT} 4NO + 6H_2O$
2) $2NO+O_2 \rightarrow 2HNO_3 + NO$

PROPERTIES:-

(i)conc. HNO_3 is a strong oxidizing agent & attacks most metals gold & Pt. .

(ii)Cr & Al do not dissolve HNO_3 because of the formation of a positive film of oxide on the surface.

(iii)it oxidises non metals like I_2 to HNO_3, C to CO_2 , S to H_2so_4

(iv)brown ring tes is used to detect NO^-.

PHOSPHOROUS:-

ALLOTROPIC FORMS: White , red α-black &β-black .

White phosphorous is more reactive red phosphorous because white P exists as discrete P_4 molecules . in red P several P_4molecules are linked to formed polymeric chain.

PHOSPHINE

Preparation:It is prepared in laboratory by heating white P with concentrated naoh solution in an Inert atmosphere of CO_2 [$P_4+3NaOH+3H_2O \rightarrow PH_3+3NaH_2PO_2$]

Phosphorous halides

Phosphorous forms two types of halides PX_3& PX_5 (X=F,I,Br)

Trihalides have pyramidal shape and pentahalides have trigonal bipyramidal structure.

OXOACIDS OF PHOSPHOROUS

- **The acids in +3 oxidation state disproportionate to higher & lower oxidation.**

  $4H_3PO_3 \rightarrow 3H_3PO_4+PH_3$

- **Acids which contains P-H bond have strong reducing properties.EX:-H_3PO_2**

  Are ionisable and cause the basicity.

- **Hydrogen atom which are attached with oxygen in P-OH form are ionisable**

GROUP-16 ELEMENTS (CHALCOGENS)

Grouo 16 Elements:O,S,SE,TE,PO

General electronic configuration:ns^2np^4

Element	Occurence
Oxygen	Comprises 20.946% by volume of the atmosphere.
Sulphur	As sulphates such as gypsum $CaSO_4.2H_2O$,Epsom salt $MgSO_4.7H_2O$ and sulphides Such as galena PbS,zinc blende ZnS,copper pyrites $CuFeS_2$ As metal selenides and tellurides in sulphide ores.
Se&Te	as a decay product of thorium and uranium minerals.

ATOMIC & PHYSICAL PROPERTIES

- **Ionisation enthalpy decreases from oxygen to polonium.**
- **Oxygen atom has less negative electron gain enthalpy than S because of the compact nature of the oxygen atom.However from the S onwards the value again becomes less negative upto polonium.**
- **Electronegativity gradually decreases from oxygen to polonium,metallic character increases from oxygen to polonium.**
- **Oxygen & S are non-metals,selenium and telerium are metalloids.Po is a radioactive metal.**
- **Oxygen is a diatomic gas while S,Se&Te are octa atomic S_8,Se_8&Te_8 molecules which has puckered ' ring' structure.**

CHEMICAL PROPERTIES

- **Common oxidation state:- -2,+2,+4 &+6.**
- **Due to inert effect,the stability of +6 decreases down the group and stability of +4 increases.**

Oxygen exhibits +1 state in O_2F_2,+2 in OF_2.

Anamolous behavior of oxygen-due to its small size,high electronegativity and absence of d-orbitals.

TREND IN PROPERTIES

Acidic character-$H_2O<H_2S<H_2Se<H_2Te$

Thermal stability-$H_2O>H_2S>H_2Se>H_2Te$

Reducing character-$H_2S<H_2Se<H_2Te$

Boiling point-$H_2S<H_2Se<H_2Te<H_2O$

Reducing property of dioxides-$SO_2>SeO_2>TeO_2$

Stability of halides-F>Cl>Br>I

HALIDES

DI HALIDES:sp^3 hybridisation but angular structure.

TETRA HALIDES:sp3 hybridisation-see-saw geometry

HEXA HALIDES:sp^3d^2,octahedral SF_6

DIOXYGEN

Prepared by heating oxygen containing salts like chlorates,nitrares

$$2KClO_3 \xrightarrow{heat} 2KCl+3O_2$$

$$2Fe^{3+}+SO_2+2H_2O \rightarrow 2Fe^{2+} + SO_4^{2-} + 4H^+$$

$$5SO_2+2MnO_4^- +2H_2O \rightarrow 5SO_4^{2-} +4H^+ +2Mn^{2+}$$

SO2 molecule is angular.

OXIDES

A binary compound of oxygen with another element is called oxide. Oxides can be classified on the basis of nature

- **Acidic Oxides:- Non metallic oxides. Aqueous solutions are acids. Neutralize bases to form salts.Ex:So_2,Co_2,N_2O_5 etc.**
- **Basic Oxides:metallic oxides.Aqueous solutions are alkalis. Neutralize acids to form salts.Ex:Na_2O,K_2o,etc.**
- **Amphoteric oxides:-some metallic oxides exhibit a dual behavior. Neutralize bothacids & bases to form salts.**
  Ex:-Al_2O_3,SbO_2,SnO,etc……..

OZONE

PREPARATION

Prepared by subjecting cold, dry oxygen to silent electric discharge.
$3O_2 \rightarrow 2O_3$

PROPERTIES

Due to the ease with which it liberates atoms of nascent oxygen, it acts as a powerful oxidizing agent. For eg:- it oxidiseslead sulphide to lead sulphate and iodide ions to iodine.
$PbS+4O_3 \rightarrow PbSO_4+4O_2$

<u>SULPHUR DIOXIDE</u>

PREPARATION

Burning of S in air
$S+O_2 \rightarrow SO_2$
Roasting of sulphide minerals
(Iron pyrites)
$4FeS_2+110_2 \rightarrow 2Fe_2O_3+8SO_2$
(Zinc blend)$2ZnS+3O_2 \rightarrow 2ZnO+2SO_2$

PROPERTIES

- **Highly soluble in water to form solution of sulphurous acid**
  $SO_2+H_2O \rightarrow H_2SO_3$
- **SO_2 reacts with Cl_2 to form sulphuryl chloride**
  $SO_2+Cl_2 \rightarrow SO_2Cl_2$

- **It reacts with oxygen to form SO_3 in presence of V_2O_5 catalyst**
  $2SO_2+O_2 \rightarrow 2SO_3$

- **Moist SO_2 behaves as a reducing agent. It converts Fe(III) ions to Fe(II) ions& decolourises acidified potassium permanganate (VII) solution(It is the test for the gas).**

<u>SULPHURIC ACID</u>

<u>PREPARATION</u>

It is manufactured by contact process which involves 3 steps

1. **Burning of S or Sulphide ores in air to generate SO_2.**
2. **Conversion of SO_2 to SO_3 in presence of V_2O_5 catalyst**
3. **Absorption of SO_3 in H_2SO_4 to give oleum.**

<u>PROPERTIES</u>

1. **In aqeous solution it ionizes in 2 steps**

$H_2SO_4+H2O \rightarrow H3O++HSO4-$

$HSO_4^- + H_2O \rightarrow H_3O^+ + SO_4^{2-}$

2. **It is a strong dehydrating agent Eg:-charring action of sugar**

$C12H22O11 \xrightarrow{H2SO4} 12C+11H_2O$

3. **It is a moderately strong oxidizing agent.**

$Cu+2H_2SO_4(conc.) \rightarrow CuSO_4+SO_2+2H_2O$

$C+2H_2SO_4(conc.) \rightarrow CO_2+2SO_2+2H_2O$

<u>GROUP 17 ELEMENTS(HALOGENS)</u>

Group 17 elements: F,Cl,Br,I,At

General electronic configuration:ns^2np^5

Element	Occurence
Fluorine	As insoluble fluorides(fluorspar CaF_2,Cryolite and fluoroapattie)
Cl.Br,I	Sea water contains chlorides, bromides and iodides of Sodium,potassium magnesium and calcium, but is mainly sodium chloride solution(2.5% by mass). Certain forms of marine life(various seaweeds)

ATOMIC & PHYSICAL PROPERTIES

i. Atomic & ionic radii increase from fluorine to iodine.
ii. Ionization enthalpy gradually decreases from fluorine to iodine due to increase in atomic size.
iii. Electron gain enthalpy of fluorine is less than that of chlorine. It is due to small size of fluorine & repulsion between newly added electron &electrons already present in its small 2p orbital.
iv. Electronegativity decreases from fluorine to iodine. Fluorine is the most electronegative element in the periodic table.
v. The color of halogens is due to absorption of radiations in visible region which results in the excitation of outer electrons to higher energy level.
vi. Bond dissociation enthalpy of fluorine is smaller than that of chlorine is due to electron-electron repulsion among the lone pair in fluorine molecules where they are much closer to each other than in case of chlorine. The trend: Cl-Cl>Br-Br>F-F>I-I.

CHEMICAL PROPERTIES

OXIDATION STATES:-1.However, chlorine, bromine &iodine exhibit +1, +3, +5, +7 oxidation states also.

Fluorine forms two oxides OF_2 and O_2F_2. These are essentially oxygen fluorides because of the higher electronegativity of fluorine than oxygen.

Anomalous behavior of fluorine- due to its small size, highest electronegativity, low F-F bond dissociation enthalpy and absence of d-orbitals.

TRENDS IN PROPERTIES

Oxidizing property – $F_2>Cl_2>Br_2>I_2$
Acidic strength- HF<HCl<HBr<HI
Stability & bond dissociation enthalpy- HF>HCl>HBr>HI
Stability of oxides of halogens- I>Cl>Br
Ionic character of halides –MF>MCl>MBr>MI

CHLORINE

PREPARATION

1. $MnO_2 + 4HCl \rightarrow MnCl_2 + Cl_2 + 2H_2O$
2. $4NaCl + MnO_2 + 4H_2SO_4 \rightarrow MnCl_2 + 4\ NaHSO_4 + 2H_2O + Cl_2$
3. $2KMnO_4 + 16HCl \rightarrow 2KCl + 2MnCl_2 + 8H_2O + 5Cl_2$
4. **DEACON'S PROCESS**

   $4HCl + O_2 \xrightarrow{CuCl_2} 2Cl_2 + 2H_2O$

5. By electrolysis of brine solution. Cl_2 is obtained at anode.

PROPERTIES

i. With cold and dilute Cl_2 produces a mixture of chloride and hypochlorite but with hot and concentrated alkalis it gives chloride and chlorate.

$2NaOH+Cl_2 \rightarrow NaCl+NaOCl+H_2O$

$6NaOH+3Cl_2 \rightarrow 5NaCl+NaClO_3+3H_2O$

ii. With dry slaked lime it gives bleaching powder.

$2Ca(OH)_2+2Cl_2 \rightarrow Ca(OH)_2+CaCl_2+2H_2O$

iii. It is a powerful bleaching agent; bleaching action is due to oxidation

$Cl_2+H_2O \rightarrow 2HCl+(O)$

Colored substance+(O)→colorless substance

iv. Action of concentrated H_2SO_4 on NaCl give HCl gas.

$NaCl+H_2SO_4 \xrightarrow{420K} NaHSO_4+HCl$

3:1 ratio of conc. HCl & HNO_3 is known as aquaregia & it is used for dissolving noble metals like Au and Pt.

OXOACIDS OF HALOGENS (SEE TABLE 7.10& FIG.7.8)

Interhalogen compounds are prepared by direct combination of halogens.

Ex: ClF, ClF3, BrF5, IF7

They are more reactive than halogens because X-X' is weaker than X-X bonds in halogens (except F-F).

TYPE	STRUCTURE
XX'_3	Bent T-shaped
XX'_5	Square pyramidal
XX'_7	Pentagonal bipyramidal

GROUP 18 ELEMENTS

GROUP 18 ELEMENTS: He, Ne, Ar,Kr,Xe &Rn

General electronic configuration:ns^2np^6

Atomic radii- large as compared to other elements in the period since it corresponds to Vander Waal radii.

Inert – due to complete octet of outermost shell, very high ionization enthalpy & electron gain enthalpies are almost zero.

The first noble compound prepared by Neil Bartlett was $XePtF_6$&Xenon.

$O_2^+PtF_6^-$.led to the discovery of $XePtF_6$ since first ionization enthalpy of molecular oxygen (1175kJmol^{-1}) was almost identical with that of xenon (1170kJmol^{-1}).

PROPERTIES

$Xe+F_2$--------673K, 1bar--→XeF_2

Xe (g) +$2F_2$ (g) ----873k, 7bar→XeF_4(s)

Xe (g) +$3F_2$ (g) ----573k, 6070bar→XeF_6(s)

XeF_6+MF→M^+ $[XeF_7]^-$

XeF_2+PF5→$[XeF]^+[PF_6]^-$

XeF_6+2H_2O→XeO_2F_2+4HF(partial hydrolysis)

SOLVED QUESTIONS

1 MARK QUESTIONS

1. Ammonia has higher boiling point than phosphine. Why?

   -AMMONIA FORMS INTERMOLECULAR H-BOND.

2. Why BiH_3 the strongest reducing agent amongst all the hydrides of group 15 elements ?

3. Why does PCl_3 fume in moisture ?

   In the presence of (H_2O) , PCl_3 undergoes hydrolysis giving fumes of HCl .

   $PCl_3 + 3H_2O$→ H_3PO_3 + 3HCl

4. What Happens when H_3PO_3 is Heated ?

   It disproportionate to give orthophosphoric acid and Phosphine .

$4H_3PO_3 \rightarrow 3H_3PO_4$ PH_3

5. Why H_2S is acidic and H_2S is neutral ?

   The S---H bond is weaker than O---H bond because the size of S atomis bigger than that of O atom . Hence H_2S can dissociate to give H^+ Ions in aqueous solution .

6. Name two poisonous gases which can be prepared from chlorine gas ?

Phosgene ($COCl_2$) , tear gas (CCl_3NO_2)

7. Name the halogen which does not exhibit positive oxidation state .

   Flourine being the most electronegative element does not show positive oxidation state .

8. Iodine forms I_3^- but F_2 does not form F_3^- ions .why?

   Due to the presence of vacant D-orbitals , I_2 accepts electrons from I-ions to form I_3- ions , but because of d-orbitals F_2 does not accept electrons from F-ions to form F_3 ions.

9. Draw the structure of peroxosulphuric acid .

10. Phosphorous forms PCl_5 but nitrogen cannot form NCl_5. Why?

    Due to the availability of vacant d-orbital in p.

2 MARK QUESTION (SHORT ANSWER TYPE QUESTION)

1. Why is HF acid stored in wax coated glass bottles?

This is because HF does not attack wax but reacts with glass.It dissolves SiO_2 present in glass forming hydrofluorosilicic acid.

$SiO_2 + 6HF \rightarrow H_2SiF_6 + 2H_2O$

2. What is laughing gas? Why is it so called?How is it prepared?

Nitrous oxide (N_2O) is called laughing gas, because when inhaled it produced hysterical laughter. It is prepared by gently heating ammonium nitrate.

$NH_4NO_3 \rightarrow N_2O + 2H_2O$

3. Give reasons for the following:

(i) Conc.HNO_3 turns yellow on exposure to sunlight.

(ii) PCl_5 behaves as an ionic species in solid state.

(i)Conc HNO_3 decompose to NO_2 which is brown in colour & NO_2 dissolves in HNO_3 to it yellow.

(ii)It exists as $[PCl_4]^+[PCl_6]^-$ in solid state.

4. What happens when white P is heated with conc.NaOH solution in an atmosphere of CO_2? Give equation.

Phosphorus gas will be formed.

$P_4 + {}_3NaOH + 3H_2O \rightarrow PH_3 + 3NaH_2PO_2$

5. How is ozone estimated quantitatively?

When ozone reacts with an excess of potassium iodide solution

Buffered with a borate buffer (Ph9.2), Iodide is liberated which can be titrated against a standard solution of sodium thiosulphate . This is a quantitative method for estimating O_3gas.

6. Are all the five bonds in PCl_5 molecule equivalent? Justify your answer.

PCl5 has a trigonal bipyramidal structure and the three equatorial P-Cl bonds are equivalent, while the two axial bonds are different and longer than equatorial bonds.

7. NO2 is coloured and readily dimerises.Why ?

NO2 contains odd number of valence electrons.It behaves as a typical odd molecules .On dimerization; it is converted to stable N_20_4 molecule with even number of electrons.

8. Write the balanced chemical equation for the reaction of Cl2 with hot and concentrated NaOH .Is this reaction a dispropotionation reaction? Justify:

$3Cl_2+6NaOH \rightarrow 5NaCl+NaClO_3+3H_2O$

Yes, chlorine from zero oxidation state is changed to -1 and +5 oxidation states.

9. Account for the following.

(i)SF_6 is less reactive than.

(ii) 0f the noble gases only xenon chemical compounds.

(i)In SF_6 there is less repulsion between F atoms than In SF_4.

(II)Xe has low ionisation enthalpy & high polarising power due to larger atomic size.

10. With what neutral molecule is ClO^-Isoelectronic? Is that molecule a Lewis base?

CiF .Yes, it is Lewis base due to presence of lone pair of electron.

3 MARK QUESTIONS

1(i) why is He used in diving apparatus?

(ii)Noble gases have very low boiling points.Why?

(iii)Why is ICl moe reactive than I_2?

(I)It is not soluble in blood even under high pressure.

(ii)Being monoatomic they have weak dispersion forces.

(ii)I-Cl bond is weaker than l-l bond

2. Complete the following equations.

(i)XeF4+H2O→

(ii)$Ca_3P_2+H_2O \rightarrow$

(iii)$AgCl_{(s)}$ +NH3 (aq)→

(i) 6XeF4+12H_2O→4Xe+2XeO_3+24HF+3O_2

(ii)Ca_2P_2+6H_2O→3Ca (OH) $_2$+2PH_3

(iii)$AgCl_{(s)}$ +2$NH_{3\ (aq)}$→$[Ag(NH_3)_2]Cl_{(aq)}$

3. (i)How is XeOF4 prepared ?Draw its structure.

(ii)When HCL reacts with finely powdered iron, it forms ferrous chloride and not ferric chloride .Why?

(i)Partial hydrolysis of $XeOF_4$

XeF_6+H_2O→$XeOF_4$+2HF

Structure-square pyramidal. See Fig7.9

(ii) Its reaction with iron produces h2

Fe+2HCl→$FeCl_2$+H_2

Liberation of hydrogen prevents the formation of ferric chloride.

5 MARK QUESTION

1. Account for the following.

(i)Noble gas form compounds with F_2&O_2 only.

(ii)Sulphur shows paramagnetic behavior.

(iii)HF is much less volatile than HCl.

(iv)White phosphorous is kept under water.

(v)Ammonia is a stronger base than phosphine.

(i)F_2&O_2 are best oxidizing agents.

(ii)In vapour state sulphur partly exists as S_2 molecule which has two unpaired electrons in the antibonding pi *orbitals like O_2 and, hence, exhibit paramagnetism.

(iii)HF is associated with intermolecular H bonding.

(iv) Ignition temperature of white phosphorous is very low (303 K). Therefore on explosure to air, it spontaneously catches fire forming P_4O_{10}. Therefore to protect it from air, it is kept under water.

(v)Due to the smaller size of N, lone pair of electrons is readily available.

2. When Conc. H_2SO_4 was added to an unknown salt present in a test tube, a brown gas (A) was evolved. This gas intensified when copper turnings were added in to test tube. On cooling gas (A) changed in to a colourless gas (B).

(a)Identify the gases 'A' and 'B'

(b)Write the equations for the reactions involved

The gas 'A' is NO_2 whereas 'B' is N_2O_4.

$XNO_3 + H_2SO_4 \rightarrow XHSO_4 + HNO_3$

Salt (conc.)

$Cu + 4HNO_3$ (Conc.) $\rightarrow Cu\ (NO_3)2 + 2NO_2 + 2H_2O$

Blue Brown (A)

$2NO_2$ (on cooling) $\rightarrow N_2O_4$

Colourless(B)

3. Arrange the following in the increasing order of the property mentioned.

(i)HOCl, $HClO_2$, $HClO_3$, $HClO_4$ (Acidic strength)

(ii)As_2O_3, ClO_2, GeO_3, Ga2O3 (Acidity)

(iii)NH_3, PH_3, AsH_3, SbH_3 (HEH bond angle)

(iv)HF, HCl, HBr, HI (Acidic strength)

(v)MF, MCl, MBr, MI (ionic character)

(i)Acidic strength:$HOCl<HClO_2<HClO_3<HClO_4$

(ii)Acidity: $Ga2O3<GeO_2<AsO_3<ClO_2$

(iii)Bond angle: $SbH_3<AsH_3<PH_3<NH_3$

(iv)Acidic strength: HF<HCl<HBr<HI

(v)Ionic character: MI<MBr<MCl<MF

ASSIGNMENTS

Very shot answer type questions:

1) PH3 has lower boiling point than NH_3. Explain.

2) Why are halogens coloured.

3) What are chalcogens?

4) Which noble gas is Radioactive?

5) Explain why fluorine always exhibit an oxidation state of - 1 only.

6) Which compound led to the discovery of compounds of noble gas?

7) Name the most electronegative element.

8) Why is OF6 compound not known?

9) Why is N2 not particularly reactive?

10) Ammonia acts as aligned. Explain.

Short answer type questions:

1) Write Phosphorous is more reactive than red phosphorous. Explain.

2) Why do noble gases have comparatively large atomic sizes?

3) Arrange in decreasing order of Ionic character

M – F, M – Cl, M – Br, M – I

4) Phosphinic acid behaves as a monoprotic acid

5) Arrange the following in the order of property indicated:

a)AS_2O_3, ClO_2, GeO_2, Ga_2O_3__Increasing acidity

b) H_2O, H_2S, H_2Se, H_2Te__Increasing acid strength.

6) Arrange in decreasing order of bond energy:

F_2, Cl_2, Br_2, I_2

7) Complete the following:

i) $HNO_3 + P_4O_{10} \rightarrow$

ii) $IO^-_3 + I^- + H^+ \rightarrow$

8) Give the chemical reactions in support of following observations:

a) The +5 oxidation state of Bi is less stable than +3 oxidation state.

b) Sulphur exhibits greater tendency for catenation than selenium.

9) How would you account for following?

i)Enthalpy of dissociation of F_2 is much less than that of Cl_2.

ii)Sulphur in vapour state exhibits paramagnetism.

10) Draw structures of following:

a)Pre-oxomonasalphuric acid H_2SO_5

b)XeF_4

Level – III

1. Complete and balance:

i) $F_2 + H_2O$ Cold →

ii) $BrO^-_3 + F_2 + OH^-$ →

iii) $Li + N_2$ (cold) →

iv) $NH_3 + NaOCl$ →

2) Despite lower electron affinity of F_2, is stronger oxidising agent than Cl_2. Explain.

3) Give reasons:

a) Nitric oxide becomes brown when released in air.

b) PCl5 is ionic in nature in the solid state.

4) Which of the two is more covalent $SbCl_3$ or $SbCl_5$?

5) Addition of Cl_2 to Kl solution gives if brown colour but excess at if turns it colourless. Explain.

Identify hybridization state of central atom and use conceot of VSEPR theory . also its shape (geometry) and draw the structure.

PCl_3	sp^3	bp=3	lp=1	
PCl_5	sp^3d	bp=5	lp=0	
BrF_3	sp^3d	bp=3	lp=2	
XeF_2	sp^3d	bp=2	lp=3	
XeF_4	sp^3d^2	bp=4	lp=2	
$XeOF_4$	sp^3d^2	bp=5	lp=1	
XeO_3	sp^3	bp=3	lp=1	
XeF_6	sp^3d^3	bp=6	lp=1	
SF_4	sp^3d	bp=4	lp=1	

Formula	Resonance Structures	Bond Parameters
N_2O	$\ddot{N}=N=\ddot{O} \longleftrightarrow :N\equiv N-\ddot{O}:$	N — N — O 113 pm 119 pm Linear
NO	$:N=\ddot{O}: \longleftrightarrow :\dot{N}=\ddot{O}:$	N — O 115 pm
N_2O_3		 Planar
NO_2		 Angular
N_2O_4		 Planar
N_2O_5		 Planar

Fig. 7.4
Structures of some important oxoacids of phosphorus

Fig. 7.6: Structures of some important oxoacids of sulphur

Chromate ion

Dichromate ion

Tetrahedral manganate (green) ion

Tetrahedral permanganate (purple) ion

Chapter:-8 The d-and f-Block Elements

***POINTS TO BE REMEMBERED*: ---**

1. The elements of periodic table belonging to group 3 to 12 are known as d-Block elements.
2. The general electronic configuration of these elements is $(n-1)d^{1-10}\ ns^{1-2}$
3. d- Block elements are collectively known as Transition Elements because properties of these elements vary in between s-Block and p-Block elements.
4. A transition element should have partially filled (n-1) d orbital.
5. Group 12 elements i.e. Zn, Cd, Hg have completely filled (n-1) d-orbital in atomic & ionic state & thus these elements are considered as Typical Transition Elements.
6. All these elements are metals. They are less electropositive than s-block elements & more electropositive than p-block elements.
7. The atomic radii decreases from group 3 to 6 (i.e. Sc to Cr) because of increase in effective nuclear charge gradually.
8. The atomic radii of group 7,8 9 &10 elements (i.e. Fe,Co,Ni) is almost same because pairing of electrons take place in (n-1)d orbital causing repulsion i.e. shielding of (n-1)d orbital.
9. Group 11 &12 elements i.e. Cu & Zn have bigger size due to strong shielding of completely filled (n-1)d orbital.
10. The transition elements show variable oxidation state due to small energy difference between (n-1)d &ns orbital as a result both (n-1)d &ns electrons take part in bond formation.
11. The highest oxidation state of an element is equal to number of unpaired electrons present in (n-1)d &ns orbital.
12. Transition elements have high enthalpy of atomization/ sublimation Because of large number of unpaired electrons in their atoms, they have stronger interatomic interaction and hence strong metallic bonding is present between atoms.
13. Most of transition elements are paramagnetic due to presence of unpaired electrons in (n-1) d orbital.
14. Most of transition elements are used as catalyst. It is due to (i) partially filled (n-1) d orbital (ii) Variable oxidation state (iii) Ability to change oxidation state frequently.
15. Most of transition elements form coloured compounds due to presence of unpaired electrons in (n-1) d orbital & thus they can undergo d-d transition.
16. Most of transition elements form complex compounds due to (i) small size (ii) high charge (iii) presence of vacant d-orbital of suitable energy.
17. Transition elements have lower value of Reduction Potential due to high ionization potential, high heat of sublimation & low enthalpy of hydration.
18. Transition elements form interstitial compounds because size of interstitial voids is similar to size of non- metals C, N, O, H.
19. Transition elements form alloys due to similar ionic radii.
20. The oxides of transition metals in lower oxidation state are BASIC, intermediate oxidation state are AMPHOTERIC, highest oxidation state are ACIDIC.

LANTHANOIDS: ---

1. The 14 elements after Lanthanum having atomic number 58 to 71 are collectively known as Lanthanoids.
2. The general electronic configuration of these elements is [Xe] $4f^{1-14}$, $5d^{0-1}$,$6s^2$.
3. Most common oxidation state of these elements is +3, but Ce shows +4, Eu +2, because they acquire stable configuration.
4. The size of Lanthanoids and its trivalent ion decreases from La to Lu due to poor shielding of 4f electrons. It is known as lanthanoids contraction.

ACTINOIDS:--

1. The 14 elements after Actinium having atomic number 90 to 113 are collectively known as Actinoids.

2. The general electronic configuration of these elements is [Rn] $5f^{1-14}$, $6d^{0-1}$,$7s^{2.}$
3. The size of actinoids and its trivalent ion decreases from Ac to Lw due to poor shielding of 5f electrons. It is known as actinoids contraction.
4. The elements after U (92) are man made known as transuranic elements.

POTASSIUM DICHROMATE:--

Preparation: - It takes place in three steps-

(i) Conversion of chromite ore to sodium chromate.
(ii) Conversion of sodium chromate to sodium dichromate.
(iii) Conversion of sodium dichromate to potassium dichromate
Following reaction take place:--

$$4\ FeCr_2O_4 + 4\ Na_2CO_3 + 7O_2 \longrightarrow 2\ Na_2CrO_4 + 2Fe_2O_3 + 8\ CO_2$$

$$2Na_2CrO_4 + 2\ H^+ \longrightarrow Na_2Cr_2O_7 + 2\ Na^+ + H_2O$$

$$Na_2Cr_2O_7 + 2\ KCl \longrightarrow K_2Cr_2O_7 + 2\ NaCl$$

The chromates and dichromates are interconvertible in aqueous solution depending upon Ph of the solution.

A) In Acedic medium(PH<7)

$$2CrO_4^{2-} + 2H^+ \quad Cr_2O_7^{2-} + H_2O$$

B) In basic medium (PH >7)

C) $2CrO_7^{2-} + 2OH^- \quad Cr_2O_4^{2-} + H_2O$

Chromate ion Dichromate ion

POTASSIUM PERMANGNATE:--

Preparation: --
It takes place in two steps:-

(i) Conversion of pyrolusite ore into potassium magnate
(ii) Conversion of potassium magnate to potassium permaganate
Following reactions take place:-

$$2\ MnO_2 + 4\ KOH + O_2 \longrightarrow 2\ K_2MnO_4 + 2H_2O$$

$$3\ MnO_4^{2-} + 4H^+ \longrightarrow 2\ MnO_4^- + MnO_2 + 2H_2O$$

QUESTION ANSWERS

(TWO MARK QUESTIONS)

Q.1-Explain briefly how +2 oxidation state becomes more and more stable in the first half of the first row transition elements with increasing atomic number.
A.1-In M^{2+} ions, 3d-orbitals get occupied gradually as the atomic number increases. Since, the number of empty d-orbitals decreases, the stability of cations increases from Sc^{2+} to Mn^{2+} .Mn^{2+} is most stable as all d-orbitals are singly occupied.

Q.2- Explain why transition elements have many irregularities in their electronic configurations?
A.2-In the transition elements, there is a little difference in the energy of (n-1) d-orbitals and ns-orbitals. Thus, incoming electron can occupy either of shell. Hence, transition elements exhibit many irregularities in their electronic configurations.
Q.3-What are different oxidation states exhibited by Lanthanides?
A.3-The common stable oxidation state of lanthanides is +3.However some members also show oxidation states of +2 & +4.
Q.4-How is the variability in oxidation states of transition metals different from that of the non-transition metals? Illustrate with examples.
A.4-The transition elements use its (n-1)d, ns and np orbital and the successive oxidation states differ by unity. For example, Mn shows all the oxidation states from +2 to +7. On other hand non transition elements use its ns, np and nd orbitals and the successive oxidation states differ by two units e.g. Sn^{2+}, Sn^{4+} etc.
Q.5- Why do transition elements show variable oxidation states?
A.5- The transition elements show variable oxidation state due to small energy difference between (n-1) d &ns orbital as a result both (n-1)d &ns electrons take part in bond formation.
Q.6-Why are Mn^{2+} compounds more stable than Fe^{2+} compounds towards oxidation to +3 state?
A.6-The electronic configuration of Mn^{2+} is [Ar] $3d^5$, i.e. all five d-orbitals are singly occupied. Thus this is stable electronic configuration and further loss of electron requires high energy .on other hand side the electronic configuration of $Fe^{2+}$is [Ar] $3d^6$, i.e. Loss of one electron requires low energy.
Q.7-To what extend do the electronic configuration decide the stability of oxidation state in the first series of the transition elements? Illustrate your answer with an example.
A.7-In a transition series, the oxidation state which lead to exactly half filled or completely filled orbitals are more stable.e.g. the electronic configuration of Fe is [Ar] $3d^6$,$4s^2$. It shows various oxidation state but Fe(III) is more stable than Fe(II).
Q.8-What is meant by disproportionation? Give two examples.
A.8-Those reactions in which same substance undergoes oxidation as well as reduction are called disproportionation reactions.e.g.

$$2Cu^+ \rightarrow Cu^{2+} + Cu$$

$$3\ MnO_4^{2-} + 4\ H^+ \rightarrow 2\ MnO_4^- + MnO_2 + 2\ H_2O$$

Q.9- Which metal in the first series of transition metals exhibits +1 oxidation state most frequently and why?
A.9- Copper with configuration [Ar] $3d^{10}$ $4s^1$ exhibits +1 oxidation state. Copper loses $4s^1$ electron easily and achieved a stable configuration $3d^{10}$ by forming Cu^+.
Q.10- What are inner transition elements?
A.10- The f-block elements in which the last electron accommodated on (n-2) f-subshell are called inner transition elements. These include atomic numbers 58 to 71 and from 90 to 103.
Q.11- The paramagnetic character in 3d-transition series elements increases upto Mn and then decreases. Explain why?
A.11- In the 3d-transition series as we move from Sc (21) to Mn (25) the number of unpaired electrons increases and hence paramagnetic character increases. After Mn, the pairing of electrons in the d-orbital starts and the number of unpaired electrons decreases and hence, paramagnetic character decreases.
Q.12- Comment on the statement that elements of the first transition series possess many properties different from those of heavier transition metal
A.12-The following points justify that the given statement is true:-
(i) Ionization enthalpies of heavier transition elements are higher than the elements of 3d series. Consequently, heavier transition elements are less reactive in comparison to 3d-elements.
(ii) Melting points of heavier transition elements are higher than 3d-elements.
(iii) Higher oxidation states of heavier transition elements are stable whereas lower oxidation states are stable in 3d-elements.
Q.13-What are transition elements? Which d-block elements are not regarded as transition elements and why?

A.13- An element which has partially filled (n-1) d orbital is known as transition elements. Group 12 elements i.e. Zn, Cd, Hg have completely filled (n-1) d-orbital in atomic & ionic state & thus these elements are not considered as Transition Elements.

Q.14-What are interstitial compounds? Why are such compounds well known for transition metal?

A.14- Compounds of transition metal with relatively smaller non-metals are known as interstitial compounds. These compounds are well known for transition metals because size of C, N, O, and B is similar to size of interstitial voids of transition metal

Q.15-For the first row of transition metals the E^0 values are:-

E^0 values	V	Cr	Mn	Fe	Co	Ni	Cu
M^{2+}/M	-1.18	-0.91	-1.18	-0.44	-0.28	-0.25	+0.34

Explain the irregularity in the above values.

A.15-The E^0 (M^{2+}/M) values are not regular which can be explained from the irregular variation of ionization energy and sublimation energy of Mn due to half-filled orbitals.

(THREE MARK QUESTIONS)

Q.1- Decide giving reason which one of the following pairs exhibits the property indicated:

(i)Sc^{3+} or Cr^{3+} exhibits paramagnetism

(ii)V or Mn exhibits more number of oxidation states

(iii)V^{4+} or V^{5+} exhibits colour

A.1- (i) Sc=[Ar] $3d^1 4s^2$; Sc^{3+}=[Ar] ; it has no unpaired electron so diamagnetic

Cr=[Ar] $3d^5 4s^1$; Cr^{3+}=[Ar]$3d^3$; it has three unpaired electrons paramagnetic

(ii) V=[Ar] $3d^3 4s^2$ Mn=[Ar] $3d^5 4s^2$ Thus V exhibit oxidation states of +2, +3, +4, +5 Whereas Mn exhibit oxidation states of +2 to +7.

(iii) V^{4+}=[Ar] $3d^1$ → coloured V^{5+}=[Ar] → colourless

Q.2-(a) Describe the general trends in the following properties of the first series of the transition elements:-

(i) Stability of +2-oxidation state

(ii) Formation of oxometal ions

(b) Write steps involved in the preparation of $KMnO_4$ from K_2MnO_4

A.2- (a) i-The elements of first transition series show decreasing tendency to form divalent cation as we move left to right in the series. This trend is due to general increase in the first and second ionization energy. The greater stability of Mn^{2+} is due to half filled d^5 configuration and that of zinc is due to d^{10} configuration.

(ii) All metal except Sc from oxide of type MO which are basic. The highest oxidation number in all oxide, coincide with the group number and is attain in Sc_2O_3 to Mn_2O_7. Formation of oxoanions is due to high electro negativity and small size of oxygen atom.

2-(b) It takes place in two steps:-

(iii) Conversion of pyrolusite ore into potassium mangnate.

(iv) Conversion of potassium mangnate to potassium permanganate.

Following reactions take place:-

$2\ MnO_2 + 4\ KOH + O_2 \longrightarrow 2\ K_2MnO_4 + 2H_2O$

$3\ MnO_4^{2-} + 4H^+ \longrightarrow 2\ MnO_4^- + MnO_2 + 2H_2O$

Q.3-(a) Write the steps involve in the preparation of K2Cr2O7 from chromite ore.

(b) What is the effect of pH on dichromate ion solution?

A.3-(a):- It takes place in three steps-

(iv) Conversion of chromite ore to sodium chromate.

(v) Conversion of sodium chromate to sodium dichromate.

(vi) Conversion of sodium dichromate to potassium dichromate

Following reactions take place:--

$4\ FeCr_2O_4 + 4\ Na_2CO_3 + 7O_2 \longrightarrow 2\ Na_2CrO_4 + 2Fe_2O_3 + 8\ CO_2$

$2Na2CrO4 + 2\ H^+ \longrightarrow Na2Cr2O7 + 2\ Na^+ + H2O$

$Na2Cr2O7 + 2\ KCl \longrightarrow K2Cr2O7 + 2\ NaCl$

(b) Dichromate ion is orange in acidic solution (pH<7) and turns yellow in basic solution. It is due to interconversion of dichromate ion to chromate ion. Following reactions take place:-

$$2\ CrO_4^{2-}\ (\text{yellow}) + 2\ H^+ \rightarrow Cr_2O_7^{2-}\ (\text{orange}) + H_2O$$

$$Cr_2O_7^{2-}\ (\text{orange}) + 2\ OH^- \rightarrow 2\ CrO_4^{2-}\ (\text{yellow}) + H_2O.$$

Q.4- (a) What is lanthanide contraction? What effect does it have on the chemistry of the elements, which follow lanthanoids?

(b) The chemistry of actinoid elements is not so much smooth as that of lanthanoids. Justify these statements by giving some examples from the oxidation state of these elements.

A.4- (a)The size of Lanthanoids and its trivalent ion decreases from La to Lu. It is known as lanthanoids contraction.

Cause: - It is due to poor shielding of 4f electrons.

Consequences of lanthanide contraction: - (i) Basic strength of hydroxide decreases from $La(OH)_3$ TO $Lu(OH)_3$. (ii) Because of similar chemical properties lanthanides are difficult to separate.

(b) Lanthanoids show limited number of oxidation states i.e. +2, +3, +4 (out of which +3 is most common) . This is because of a large energy gap between 4f, 5d and 6s subshell. The dominant oxidation state of actinides is also +3 but they show a number of other oxidation state also e.g. +4, +5, and +7. This is due to small energy difference between 5f, 6d and 7s orbitals.

Q.5- Give examples and suggest reasons for the following features of the transition metal chemistry:

(i) The lowest oxide of transition metal is basic, the highest is amphoteric/acidic.

(ii) A transition metal exhibits highest oxidation state in oxides and fluorides.

(iii) Of the d^4 species, Cr^{2+} is strongly reducing while manganese(III)is strongly oxidizing.

A.5-(i) The oxide of transition metals in lower oxidation states are generally basic while those in the higher oxidation states are acidic. Acidic character increases with increase in oxidation state is due to decrease in size of metal ion and increase in charge density.e.g. MnO (basic), Mn_3O_4 (amphoteric), Mn_2O_7 (acidic).

(ii) A transition metal exhibits higher oxidation states in oxides and fluorides because oxygen and fluorine are the most electronegative elements and thus easily can unpair electrons of metal atom.

(iii) Because oxidizing and reducing property depends on E^0 value. Since E^0 value of Cr^{3+}/Cr^{2+} is negative while that of Mn^{3+}/Mn^{2+} is positive, as a result Cr(II) act as reducing agent and Mn(III) is strong oxidizing.

Q.6-For M^{2+}/M and M^{3+}/M^{2+} systems ,the E^o values for some metals are as follows:

Cr^{2+}/Cr	-0.9V	Cr^{3+}/Cr^{2+}	-0.4V
Mn^{2+}/Mn	-1.2V	Mn^{3+}/Mn^{2+}	+ 1.5V
Fe^{2+}/Fe	-0.4V	Fe^{3+}/Fe^{2+}	+0.8V

Use this data to comment upon :-

(i)the stability of Fe^{3+} in acid solution as compared to Cr^{3+} or Mn^{3+} and

(ii)the ease with which iron can be oxidized as compared to a similar process for either chromium or manganese metal.

A.6- (i)E^o for Cr^{3+}/Cr^{2+} is -0.4V i.e. negative, this means Cr^{3+} ions in the solution cannot be reduced to Cr^{2+} easily i.e. Cr^{3+} is stable. As Mn^{3+}/Mn^{2+} is +1.5V i.e positive means Mn^{3+} can easily reduced to Mn^{2+} ions in comparison to Fe^{3+} ions. Thus relatively stability of these ions is:-

$$Mn^{3+} < Fe^{3+} < Cr^{3+}$$

(ii) The oxidation potentials for the given pairs will be +0.9V, +1.2V and 0.4V. Thus, the order of their getting oxidized will be in the order Mn>Cr>Fe.

Q.7-Account for the following statements:

(i)Cobalt (II) is stable in aqueous solution but in the presence of strong ligands and air, it can be oxidized to Co (III).

(ii)The d^1 configuration is very unstable in ions.

(iii)One among the lanthanides, Ce (III) can be easily oxidized to Ce (IV).

A.7- (i) Strong ligands force cobalt (II) to lose one more electron from 3d-subshell and thereby induced d^2sp^3 hybrisation.

(ii) The ion with d^1 configuration try to lose the only electron in order to acquire inert gas configuration.
(iii) The configuration of Ce is [Xe] $4f^1$, $5d^1$,$6s^2$. There is no much difference between the energy of 4f, 5d and 6s orbitals and thus, Ce can utilize electrons present in these orbitals and hence oxidation state of +4.
Q.8- Compare the chemistry of actinides with that of the lanthanoids with special reference to:
(i) electronic configuration
(ii) atomic and ionic sizes and
(iii) oxidation state
(iv) chemical reactivity

A.8- **Comparison of Lanthanoids and Actinides**

Properties	Lanthanoids	Actinides
Electronic configuration	[Xe] $4f^{1-14}$, $5d^{0-1}$,$6s^2$	[Rn] $5f^{1-14}$, $6d^{0-1}$,$7s^{2.}$
Atomic/ionic sizes	Size decreases from La to Lu, and size is more than actinides.	Size decreases from Ac to Lw, and size is smaller than lanthanoids due to poorer shielding of 5f electrons
Oxidation states	Common oxidation is +3 where other oxidation states are +2, +4.It is due to a large energy gap between 4f, 5d and 6s subshell	Common oxidation is +3 where other oxidation states are +2, +4,+5 and+7 due to due to small energy difference between 5f, 6d and 7s orbitals
Chemical reactivity	The earlier member quite reactive but with increasing atomic number they behave like aluminum.	The actinides highly reactive ,especially in finely divided.
Complex formation	Less tendency to form complex due to less charge density.	More tendency to form complex due to high charge density.

Q.9-(a) What is actinides contraction? What effect does it have on the chemistry of the elements, which follow actinides?
(b) Name an important alloy, which contains some of the lanthanide metals. Mention its uses.
A.9- (a) The size of actinoid and its trivalent ion decreases from Ac to Lw. It is known as l actinides contraction.
Cause: - It is due to poor shielding of 5f electrons.
Consequences of actinides contraction: - (i) Basic strength of hydroxide decreases from $Ac(OH)_3$ To $Lw(OH)_3$. (ii) Because of similar chemical properties l actinides are difficult to separate.
(b) An important alloy containing lanthanoid metals is mischmetal, which contains 95% lanthanide metal and 5% Fe along with traces of S, C, Ca and Al. It is used in Mg-based alloy to produce bullets, shells and lighter flint.
Q.10- Complete following reactions:-

(i) $MnO_4^- + H^+ + Fe^{2+} \rightarrow$ ----------+----------+----------

(ii) $MnO_4^- + C_2O_4^{2-} + H^+ \rightarrow$ ----------+----------+----------

(iii) $MnO_4^- + OH^- + I^- \rightarrow$ ----------+----------+----------

A.10-(i) $MnO_4^- + 8H^+ + 5Fe^{2+} \rightarrow Mn^{2+} + 5Fe^{3+} + 4H_2O$

(ii) $2MnO_4^- + 5C_2O_4^{2-} + 16H^+ \rightarrow 2Mn^{2+} + 10CO_2 + 8H_2O$

(iii) $2MnO_4^- + H_2O + I^- \rightarrow 2MnO_2 + 2OH^- + IO_3^-$

(FIVE MARK QUESTIONS)

Q.1-Explain giving reasons:
(i) Transition metals and many of their compounds show paramagnetic behaviour.

(ii) The enthalpies of atomisation of the transition metals are high.
(iii) The transition metals generally form coloured compounds.
(iv) Transition metals and their many compounds act as good catalyst.
(v)Transition metals have a strong tendency to form complexes.

A.1- (i)Transition metals and many of their compounds show paramagnetic behaviour due to presence of unpaired electrons in (n-1) d orbital.

(ii) The enthalpies of atomisation of the transition metals are high Because of large number of unpaired electrons in their atoms, they have stronger interatomic interaction and hence strong metallic bonding is present between atoms.

(iii) The transition metals generally form coloured compounds due to presence of unpaired electrons in (n-1) d orbital & thus they can undergo d-d transition.

(iv) Transition metals and their many compounds act as good catalyst It is due to (i) partially filled (n-1) d orbital (ii) Variable oxidation state (iii) Ability to change oxidation state frequently.

(v) Transition metals have a strong tendency to form complexes Most of transition elements form complex compounds due to (i) small size (ii) high charge (iii) presence of vacant d-orbital of suitable energy.

Q.2- Give reasons for the following:-

(i) Fe has higher melting point than Cu.
(ii) $[Ti (H_2O)_6]^{3+}$ is coloured while $[Sc(H_20)_6]$ is colourless.
(iii)The 4d and 5d series of transition metals have more frequent metal-metal bonding in their compound than do the 3d metals.
(iv)Transition metals some time exhibit very low oxidation state such as +1and 0.
(v)Hg is not considered a transition metal.

A.2-(i) This is because Fe ($3d^6$, $4s^1$) has four unpaired electrons in 3d-subshell. While Cu ($3d^{10}$, $4s^1$) only one unpaired electron in 4s shell. Hence metallic bonding is stronger in Fe than those in Cu.

(ii) The oxidation state of Ti in $[Ti (H_2O)_6]^{3+}$ is +3 and its configuration is [Ar] $3d^1$ i.e one unpaired electron and hence it is coloured. Whereas the oxidation state of Sc in $[Sc (H_2O)_6]^{3+}$ is +3 and its configuration is [Ar] $3d^0$ i.e no unpaired electron and hence it is colourless.

(iii)In the same group of d-block elements, the 4d and 5d transition elements are larger size than that of 3d elements. Hence, the valence electrons are less tightly held and form metal-metal bond more frequently.

(iv)+1 oxidation state is shown by elements like Cu because after loss of one electron, it acquire stable configuration. Zero oxidation state is shown in metal carbonyl, because $\prod$ -electrons donated by CO are accepted into the empty orbital.

(v)The characteristic properties of transition metal are due to partially filled d-orbitals.Hg has completely filled d-orbital, as a result it doesn't show properties of transition metals and hence is not considered as transition metal.

Q.3-(a) write electronic configuration of element having atomic number 101.
(b) Which element show maximum oxidation state in 3d transition series?
(c) What is mischmetal?
(d) Explain why Cu^+ ion is not stable in aqueous solution?
(e) Name the transition metal which is well known to exhibit +4 oxidation state?

A.3-(a) [Rn] $5f^{13}$,$6d^0$, $7s^2$.
(b) Mn, Which shows +7 oxidation state in $KMnO_4$.
(c) It is an important alloy, which contains 95% lanthanide metal and 5% Fe along with traces of S, C, Ca and Al. It is used in Mg-based alloy to produce bullets, shells and lighter flint.
(d) Water is a good complexing agent and thus Cu forms complex by losing one more electron from 3d orbital.
(e)Cerium (Z=58)

Q.4-(a) Write the preparation of potassium dichromate from iron chromite. What happens when potassium dichromate reacts with (i) Hydrogen sulphide (ii) $FeSO_4$?
(b) Why do Zr and Hf exhibit almost similar properties?
(c)Why is $La(OH)_3$ stronger base than $Lu(OH)_3$.

A.4- (a) Preparation:- It takes place in three steps-

(i) Conversion of chromite ore to sodium chromate.

(ii) Conversion of sodium chromate to sodium dichromate.

(iii) Conversion of sodium dichromate to potassium dichromate

Following reaction takes place:--

$$4\ FeCr_2O_4 + 4\ Na_2CO_3 + 7O_2 \longrightarrow 2\ Na_2CrO_4 + 2Fe_2O_3 + 8\ CO_2$$

$$2Na_2CrO_4 + 2\ H^+ \longrightarrow Na_2Cr_2O_7 + 2\ Na^+ + H_2O$$

$$Na_2Cr_2O_7 + 2\ KCl \longrightarrow K_2Cr_2O_7 + 2\ NaCl$$

Reactions: - (i) $Cr_2O_7^{\ 2-} + 8\ H^+ + 3\ H_2S \rightarrow 2Cr^{3+} + 7\ H_20 + 3S$

(ii) $Cr_2O_7^{\ 2-} + 14\ H^+ + 6\ Fe^{2+} \rightarrow 2Cr^{3+} + 7\ H_20 + 6\ Fe^{3+}$.

(b) Because both have similar ionic size

(c)Due to lanthanoid contraction size of La^{3+} is smaller than Lu^{3+} as a result Lu-O bond will stronger than La-O bond.

Q.5- Give reasons for the following:-

(i) Transition metals have high enthalpy of hydration.

(ii) Zn, Cd and Hg are not regarded as transition metal.

(iii) d block elements exhibit a large number of oxidation state than f block elements.

(iv)The second and third members in each group of transition element have similar atomic radii.

(v) $K_2\ [PtCl_6]$ is well known compound whereas the corresponding Ni compound is not known.

A.5-(i) Transition metal ions are smaller and have higher charge, therefore have high enthalpy of hydration.

(ii) Group 12 elements i.e. Zn, Cd, Hg have completely filled (n-1) d-orbital in atomic & ionic state & thus these elements are not considered as transition elements.

(iii)The difference in the energy of (n-1) d orbital and ns orbital is very small and thus both sub-shells are used for bond formation. Whereas in f block elements (n-2)f orbitals lie underneath and hence are not available for bond formation.

(iv) The second and third members in each group of transition element have similar atomic radii due to lanthanoid contraction. It arises due to poor shielding of d and f electron.

(v)The oxidation state of Pt in is +4 which is stable for Pt. The +4 oxidation state for Ni is very difficult to achieve because the sum of first four ionization energies is very high. Hence ,the corresponding Ni(II) compound is known.

UNIT 9: CO-ORDINATION COMPOUNDS

The compounds which contain dative bonds between metal atom and surrounding species is called co-ordination compounds .

The branch of inorganic chemistry which deals with hte study of preparation properties of coordination compound is called co-ordination chemistry.

$K_4[Fe(CN)_6]$, $[CuNH_3)_4]SO_4$

POINTS TO REMEMBER:

1. **Coordination compounds**

Coordination compounds are compounds in which a central metal atom or ion is linked to a number of ions or neutral molecules by coordinate bonds or which contain complex ions.

Examples- $K_4[Fe(CN)_6]$; $[Cu(NH_3)_4]SO_4$; $Ni(CO)_4$

2.**ThemainpostulatesofWerner'stheoryofcoordinationcompounds**

i) In coordination compounds metals show two types of linkages or valencies- Primary and Secondary.

ii) The primary valencies are ionisable and are satisfied by negative ions.

iii) The secondary valencies are non- ionisable and are satisfied by neutral molecules or negative ions. The secondary valence is equal to the C.N and is fixed for a metal.

iv) The ions or groups bound by secondary linkages to the metal have characteristic spatial arrangements corresponding to different coordination nos.

3.Difference between a double salt and a complex

Both double salts as well as complexes are formed by the combination of two or more stable compounds in stoichiometric ratio. However, double salts such as carnallite, $KCl.MgCl_2.6H_2O$, Mohr's salt, $FeSO_4.(NH_4)_2SO_4.6H_2O$, potash alum, $KAl(SO_4)_2.12H_2O$, etc. dissociate into simple ions completely when dissolved in water. However, complex ions such as $[Fe(CN)^6]^{4-}$ of $K4[Fe(CN)_6]$, do not dissociate into Fe^{2+} and CN^- ions.

IMPOTANT TERMINOLOGY

(i) Coordination entity: It constitutes the central metal ion or atom bonded to a fixed number of ions or molecules represented within a square bracket.

(ii) Central atom/ ion: In a coordination entity, the atom/ion to which a fixed number of ions/groups are bound in a definite geometrical arrangement around it, is called the central atom or ion.

iii) **Ligands**: The neutral or negative ions bound to the central metal or

ion in the coordination entity. These donate a pair/s of electrons to the central metal atom /ion. Ligands may be classified as-

a) **Monodentate/Unidentate**: Ligands bound to the central metal atom/ion through a single donor atom. Ex- Cl^- ; H_2O ; NH_3 ; NO_2^-.
b) **Didentate**: Ligates through two donor atoms. Ex- $C_2O_4^{2-}$ (ox); $H_2NCH_2CH_2NH_2$(en)
c) **Polydentate**: which ligates through two or more donor atoms present in a single ligand. Ex- $(EDTA)^{4-}$
d) **Chelating ligands**: Di- or polydentate ligands that uses two or more donor atoms to bind to a single metal ion to form ring- like complexes. (Ox); (edta)
e) **Ambidentate ligand**: A ligand that can ligate through two different atoms, one at a time. Ex-NO_2^- ; SCN^-
v) **Coordination number**: The no. of ligand donor atoms to which the metal is directly bonded through sigma bonds only. It is commonly 4 or 6.
vi) **Counter ions**: The ionisable groups written outside the square bracket. Ex- K+ in $K_4[Fe(CN)_6]$ OR $3Cl^-$ in $[Co(NH_3)_6]Cl_3$
vii) **Coordination Polyhedron**: The spatial arrangement of the ligand atoms which are directly attached to the central metal atom/ion. They are commonly Octahedral, Square-planar or Tetrahedral

Oxidation number: The charge that the central atom would carry if all the ligands are removed along with their pairs of electrons shared with the central atom. It is represented in parenthesis.

viii) **Homoleptic complexes**: Complexes in which a metal is bonded to only one kind of donor groups. Ex- $[Co(NH_3)_6]^{3+}$

ix) **Heteroleptic complexes**: Complexes in which a metal is bonded to more than one kind of donor groups. Ex- $[Co(NH_3)_4\ Cl_2]^+$

5. NAMING OF MONONUCLEAR COORDINATION COMPOUNDS

The principle of additive nomenclature is followed while naming the coordination compounds. The following rules are used-

i The cation is named first in both positively and negatively charged coordination entities.

ii The ligands are named in an alphabetical order before the name of the central atom/ion

iii The name of the anionic ligands end in –o, those of neutral and cationic ligands are

the same except aqua for H_2O, ammine for NH_3, carbonyl for CO and nitrosyl for NO. these are placed within enclosing marks .

iv When the prefixes mono, di, tri, etc., are used to indicate the number of the

individual ligands in the coordination entity. When the names of the ligands include a numerical prefix, then the terms, bis, tris , tetrakis are used, the ligand to which they refer being placed in parenthesis.

v Oxidation state of the metal in cation, anion, or neutral coordination entity is

indicated by roman numeral in parenthesis.

vi If the complex ion is a cation , the metal is same as the element.

vii The neutral complex molecule is named similar to that of the complex cation.

6.NAMES OF SOME COMMON LIGANDS

NEGATIVE LIGANDS		CHARGE	NEUTRAL LIGANDS		CHARGE
CN-	Cyano	-1	NH_3	Ammine	0
Cl-	Chlorido	-1	H_2O	Aqua/aquo	0
Br-	Bromido	-1	NO	Nitrosyl	0

F-	Fluoride	-1	CO	Carbonyl	0
SO_4^{2-}	Sulphato	-2	PH_3	Phosphine	0
$C_2O_4^{2-}$	Oxalato	-4	CH_2-NH_2 CH_2NH_2	(1,2-Ethane diamine)	0
NH_2^-	Amido	-1	POSITIVE LIGANDS		
NH^{2-}	Imido	-2	NH_2-$NH3^+$	Hydrazinium	+1
ONO^-	Nitrito-O	-1	NO^+	Nitrosonium	+1
NO_2^-	Nitro	-1	NO_2^+	Nitronium	+1
NO_3^-	Nitrato	-1			
SCN^-	Thiocyanato	-1			
NCS^-	Isothiocyanato	-1			
$CH_2(NH_2)COO^-$	Glycinato	-1			
-OH	Hydroxo	-1			

7. ISOMERISM IN COORDINATION COMPOUNDS

Two or more substances having the same molecular formula but different spatial arrangements are called isomers and the phenomenon is called isomerism. Coordination compounds show two main types of isomerism-

A) Structural Isomerism B) Stereoisomerism

STRUCTURAL ISOMERISM:- It arises due to the difference in structures of coordination compounds. It is further subdivided into the following types-

1) **Ionisation isomerism :** This form of isomerism arises when the counter ion in a complex salt is itself a potential ligand and can displace a ligand which can then become the counter ion. An example is provided by the ionization isomers $[Co(NH_3)_5SO_4]Br$ and $[Co(NH_3)_5Br]SO_4$.

2) **Hydrate or solvate isomerism**: This form of isomerism is known as ‗hydrate isomerism' in case where water is involved as a solvent. This is similar to ionisation isomerism. Solvate isomers differ by whether or not a solvent molecule is directly bonded to the metal ion or merely present as free solvent molecules in the crystal lattice. An example is provided by the aqua complex $[Cr(H_2O)_6]Cl_3$ (violet) and its solvate isomer $[Cr(H_2O)_5Cl]Cl_2.H_2O$ (grey-green).

3) **Linkage Isomerism**: Linkage isomerism arises in a coordination compound containing ambidentate ligand. A simple example is provided by complexes containing the thiocyanate ligand, NCS^-, which may bind through the nitrogen to give M–NCS or through sulphur to give M–SCN.

4) **Coordination isomerism:** It arises from the interchange of ligands between cationic and anionic entities of different metal ions present in a complex .
Example $[Co(NH_3)_6][Cr(CN)_6]$ & $[Cr(NH_3)_6][Co(CN)_6]$

STEREOISOMERISM: Stereo isomers have the same chemical formula and chemical bonds but they have different spatial arrangement. They are of two kinds

A. Geometrical isomerism

B. Optical isomerism

GEOMETRICAL ISOMERISM- This type of isomerism arises in heteroleptic complexes due to different possible geometric arrangements of the ligands. Important examples of this behaviour are found with coordination numbers 4 and 6. In a square planar complex of formula $[MX_2L_2]$ (X and L are unidentate), the two ligands X may be arranged adjacent to each other in a cis isomer, or opposite to each other in a trans isomer [MABXL]-Where A,B,X,L are unidentates Two cis- and one trans- isomers are possible.

cis

trans

cis

trans

Another type of geometrical isomerism occurs in octahedral coordination entities of the type $[Ma_3b_3]$ like $[Co(NH_3)_3(NO_2)_3]$. If three donor atoms of the same ligands occupy adjacent positions at the corners of an octahedral face, we have the facial (fac) isomer. When the positions are around the meridian of the octahedron, we get the meridional (mer) isomer.

fac–

mer–

b) **OPTICAL ISOMERISM:** Optical isomers are mirror images that cannot be superimposed on one another. These are called as enantiomers. The molecules or ions that cannot be superimposed are called chiral. The two forms are called dextro (d) and laevo (l) depending upon the direction they rotate the plane of polarised light in a polarimeter (d rotates to the right, l to the left). Optical isomerism is common in octahedral complexes involving didentate ligands. In a coordination entity of the type $[CoCl_2(en)_2]^{2+}$, only the cis-isomer shows optical activity

TYPES OF HYBRIDISATION

Coordination number	Type of hybridisation	Acquired geometry
4	sp^3	Tetrahedral
4	dsp^2	Square planar
5	sp^3d	Trigonal bipyramidal
6	sp^3d^2	Octahedral
6	d^2sp^3	Octahedral

8.CRYSTAL FIELD THEORY:

1. The metal-ligand bond is ionic arising purely from electrostatic interactions between the metal ion and the ligand.
2. Ligands are treated as point charges or dipoles in case of anions and neutral molecules.
3. In an isolated gaseous metal atom or ion the five d-orbitals are degenerate.
4. Degeneracy is maintained if a spherically symmetrical field of negative charges surrounds the metal /ion.
5. In a complex the negative field becomes asymmetrical and results in splitting of the

d-orbitals.

A) **CRYSTAL FIELD SPLLITING IN OCTAHEDRAL COORDINATION ENTITIES**

d orbital splitting in an octahedral crystal field

1. For d^4 ions, two possible patterns of electron distribution arise:

(i) If $\Delta_o < P$, the fourth electron enters one of the e_g orbitals giving the

configuration $t^3_{2g} e^1_g$. Ligands for which $\Delta_o < P$ are known as weak

field ligands and form high spin complexes.

(ii) If $\Delta o > P$, it becomes more energetically favourable for the fourth electron to occupy a t_{2g} orbital with configuration $t^4_{2g} e^0_g$. Ligands which produce this effect are known as strong field ligands and form low spin complexes.

B) **CRYSTAL FIELD SPLLITING IN TETRAHEDRAL COORDINATION ENTITIES**

1. The four surrounding ligands approach the central metal atom/ion along the planes between the axes.
2. The t_{2g} orbitals are raised in energy (2/5) $_t$.
3. The two e_g orbitals are lowered in energy (3/5) $_t$
4. The splitting is smaller as compared to octahedral field splitting, $_t$=(4/9) $_0$.

5. Pairing of electrons is rare and thus complexes have generally high spin configurations.

BONDING IN METAL CARBONYLS

The metal-carbon bond in metal carbonyls possess both σ and π character. The M–C σ bond

is formed by the donation of lone pair of electrons on the carbonyl carbon into a vacant orbital of the metal. The M–C π bond is formed by the donation of a pair of electrons from a filled d orbital of metal into the vacant antibonding π* orbital of carbon monoxide. The metal to ligand bonding creates a synergic effect which strengthens the bond between CO and the metal .

SOLVED QUESTIONS

1 MARK QUESTIONS

1. What are ambidentate ligands? Give two examples for each.

ANS. Ambidentate ligands are ligands that can attach themselves to the central metal atom through two different atoms. For example:

(a)

(The donor atom is N)

(The donor atom is oxygen)

(b)

(The donor atom is S) (The donor atom is N)

Q2. Using IUPAC norms write the formula for the following: Tetrahydroxozincate(II)
ANS. $[Zn(OH)_4]^{2-}$

Q3. Using IUPAC norms write the formula for the following: Hexaamminecobalt(III) sulphate
ANS. $[Co(NH_3)_6]_2\ (SO_4)_3$

Q4. Using IUPAC norms write the formula for the following: Pentaamminenitrito-O-cobalt(III)
ANS. $[Co(ONO)\ (NH_3)_5]^{2+}$

Q5. Using IUPAC norms write the systematic name of the following: [Co(NH3)6]Cl3

ANS. Hexaamminecobalt(III) chloride

Q6. Using IUPAC norms write the systematic name of the following: [Pt(NH3)2Cl(NH2CH3)]Cl

ANS. Diamminechlorido(methylamine) platinum(II) chloride

Q7. Using IUPAC norms write the systematic name of the following: $[Co(en)_3]^{3+}$

ANS. Tris(ethane-1, 2-diammine) cobalt(III) ion

Q8. Draw the structures of optical isomers of: c$[Cr(C_2O_4)_3]^{3-}$

ANS .

Q9. What is meant by the chelate effect? Give an example.
ANS. When a ligand attaches to the metal ion in a manner that forms a ring, then the metal-ligand association is found to be more stable.

2 / 3 MARK QUESTIONS

Q1. What is spectrochemical series? Explain the difference between a weak field ligand and a strong field ligand.

ANS. A spectrochemical series is the arrangement of common ligands in the increasing order of their crystal-field splitting energy (CFSE) values.

$I^- < Br^- < S^{2-} < SCN^- < Cl^- < N_3 < F^- < OH^- < C_2O_4^{2-} \sim H_2O < NCS^- \sim H^- < CN^- < NH_3 < en \sim SO_3^{2-} < NO_2^- < phen < CO$

Q2. $[Cr(NH_3)_6]^{3+}$ is paramagnetic while $[Ni(CN)_4]^{2-}$ is diamagnetic. Explain why?

ANS. Cr is in the +3 oxidation state i.e., d^3 configuration. Also, NH_3 is a weak field ligand that does not cause the pairing of the electrons in the 3d orbital.

Cr^{3+} :

Therefore, it undergoes d^2sp^3 hybridization and the electrons in the 3d orbitals remain unpaired. Hence, it is paramagnetic in nature.
In $[Ni(CN)_4]^{2-}$, Ni exists in the +2 oxidation state i.e., d^8 configuration.

Ni^{2+}:

CN^- is a strong field ligand. It causes the pairing of the 3d orbital electrons. Then, Ni^{2+} undergoes dsp^2 hybridization.

Q3. A solution of $[Ni(H_2O)_6]^{2+}$ is green but a solution of $[Ni(CN)_4]^{2-}$ is colourless. Explain.

ANS. In $[Ni(H_2O)_6]^{2+}$, $H_2\ddot{O}$ is a weak field ligand. Therefore, there are unpaired electrons in Ni^{2+}. In this complex, the d electrons from the lower energy level can be excited to the higher energy level i.e., the possibility of d−d transition is present. Hence, $Ni(H_2O)_6]^{2+}$ is coloured.

In $[Ni(CN)_4]^{2-}$, the electrons are all paired as CN^- is a strong field ligand. Therefore, d-d transition is not possible in $[Ni(CN)_4]^{2-}$. Hence, it is colourless. As there are no unpaired electrons, it is diamagnetic.

Q2. Draw all the isomers (geometrical and optical) of:

(i) $[CoCl_2(en)_2]^+$
(ii) $[Co(NH_3)Cl(en)_2]^{2+}$
(iii) $[Co(NH_3)_2Cl_2(en)]^+$

<u>ANS.</u> **(i)** $[CoCl_2(en)_2]^+$

In total, three isomers are possible.

Trans-isomers are optically inactive.

Cis-isomers are optically active.

(iii) $[Co(NH_3)_2Cl_2(en)]^+$

Q3. Write all the geometrical isomers of $[Pt(NH_3)(Br)(Cl)(py)]$ and how many of these will exhibit optical isomers?

<u>**ANS.**</u> $[Pt(NH_3)(Br)(Cl)(py)$

From the above isomers, none will exhibit optical isomers. Tetrahedral complexes rarely show optical isomerization. They do so only in the presence of unsymmetrical chelating agents.

Q4. What is meant by stability of a coordination compound in solution? State the factors which govern stability of complexes.

<u>**ANS.**</u> The stability of a complex in a solution refers to the degree of association between the two species involved in a state of equilibrium. Stability can be expressed quantitatively in terms of stability constant or formation constant.

$$M + 3L \longleftrightarrow ML_3$$

$$\text{Stability constant, } \beta = \frac{[ML_3]}{[M]\,[L]^3}$$

For this reaction, the greater the value of the stability constant, the greater is the proportion of ML_3 in the solution.

5 MARKS QUESTIONS

Q1. (a) Discuss the nature of bonding in the following coordination entities on the basisof valence bond theory:

(i) $[Fe(CN)_6]^{4-}$ (ii) $[FeF_6]^{3-}$ (iii) $[Co(C_2O_4)3]^{3-}$ (iv) $[CoF_6]^{3-}$

ANS. (i) $[Fe(CN)_6]^{4-}$In the above coordination complex, iron exists in the +II oxidation state.Fe^{2+} : Electronic configuration is $3d^6$ Orbitals of Fe^{2+} ion:

As CN^- is a strong field ligand, it causes the pairing of the unpaired 3d electrons.Since there are six ligands around the central metal ion, the most feasible hybridization is d^2sp^3. d^2sp^3 hybridized orbitals of Fe^{2+} are:

6 electron pairs from CN^- ions occupy the six hybrid d^2sp^3orbitals.Then,

Hence, the geometry of the complex is octahedral and the complex is diamagnetic (as there are no unpaired electrons).

(ii) $[FeF_6]^{3-}$

In this complex, the oxidation state of Fe is +3.

Orbitals of Fe^{+3} ion:

There are 6 F^- ions. Thus, it will undergo d^2sp^3 or sp^3d^2 hybridization. As F^- is a weak field ligand, it does not cause the pairing of the electrons in the 3d orbital. Hence, the most feasible hybridization is sp^3d^2.sp^3d^2 hybridized orbitals of Fe are:

Hence, the geometry of the complex is found to be octahedral.

(iii) $[Co(C_2O_4)_3]^{3-}$

Cobalt exists in the +3 oxidation state in the given complex.Orbitals of Co^{3+} ion:Oxalate is a weak field ligand. Therefore, it cannot cause the pairing of the 3d orbital electrons. As there are 6 ligands, hybridization has to be either sp^3d^2 or d^2sp^3 hybridization.sp^3d^2 hybridization of Co^{3+}:

The 6 electron pairs from the 3 oxalate ions (oxalate anion is a bidentate ligand) occupy these sp^3d^2 orbitals.

Hence, the geometry of the complex is found to be octahedral.

(iv) $[CoF_6]^{3-}$Cobalt exists in the +3 oxidation state.

Orbitals of Co^{3+} ion:

Again, fluoride ion is a weak field ligand. It cannot cause the pairing of the 3d electrons. As a result, the Co^{3+} ion will undergo sp^3d^2 hybridization.sp^3d^2 hybridized orbitals of Co^{3+} ion are:

Hence, the geometry of the complex is octahedral and paramagnetic.

Q3. Write down the IUPAC name for each of the following complexes and indicate the oxidation state, electronic configuration and coordination number. Also give stereochemistry and magnetic moment of the complex:

(i) $K[Cr(H_2O)_2(C_2O_4)_2].3H_2O$ (ii) $[Co(NH_3)_5Cl]Cl_2$ <u>**ANS.**</u> **(i)** Potassium diaquadioxalatochromate (III) trihydrate.

Oxidation state of chromium = 3 Electronic configuration: $3d^3$: t_{2g}^3
Coordination number = 6 Shape: octahedral

Stereochemistry:

Trans

Cis

Trans is optically inactive

Cis is optically active

Magnetic moment, μ $= \sqrt{n(n+2)}$

$= \sqrt{3(3+2)}$

$= \sqrt{15}$

~ 4BM

(ii) $[Co(NH_3)_5Cl]Cl_2$

IUPAC name: Pentaamminechloridocobalt(III) chloride
Oxidation state of Co = +3
Coordination number = 6
Shape: octahedral.

Electronic configuration: d^6: t_{2g}^6.

Stereochemistry:

2 isomers

Magnetic Moment = 0

LEVEL 1

1.Why do tetrahedral complex not show geometrical isomerism?

2. Why does the colour changes on heating $[Ti(H_2O)_6]^{3+}$.

3. $[Fe(H_2O)_6]^{3+}$ is strongly paramagnetic whereas $[Fe(CN)_6]^{3-}$ is weakly paramagnetic. Explain.

4. What happens when potassium ferrocyanide solution is added to a ferric salt solution?

LEVEL 2

5. A coordination compound has a formula ($CoCl_3$. $4NH_3$). It does not liberate NH_3but precipitates chloride ion as AgCl. Give the IUPAC name of the complex and write its structural formula.

6. Write the correct formula for the following co-ordination compounds. $CrCl_3$. $6H_2O$ (Violet, with 3 Chloride ions/ Unit formula) $CrCl_3$. $6H_2O$ (Light green colour with 2 Chloride ions/ unit formula)

7. Give the electronic configuration of the d-orbitals of Ti in $[Ti(H_2O)_6]^{3+}$ ion in anoctahedral crystal field.

8. Co(II) is stable in aqueous solution but in the presence of strong ligands and air, it can get oxidized to Co(III). (Atomic Number of cobalt is 27). Explain.

9. Give a chemical test to distinguish between $[Co(NH_3)_5Br]SO_4$ and $[Co(NH_3)_5Br]SO_4Br$. Name the type of isomerism exhibited by these compounds.

10. What is the coordination entity formed when excess of aqueous KCN is added to an aqueous solution of copper sulphate? Why is that no precipitate of copper sulphate is obtained when H_2S (g) is passed through this solution?

LEVEL 3

11. Aqueous copper sulphate solution (blue in colour) gives a green precipitate with aqueous potassium fluoride, a bright green solution with aqueous potassium chloride. Explain these experimental results.

12. A metal complex having the composition $Cr(NH)_4Cl_2Br$ has been isolated in two forms, A and B. The form A reacts with $AgNO_3$ solution to give a white precipitate readily soluble in dilute aqueous ammonia whereas B give a pale yellow precipitate soluble in concentrated ammonia solution. Write the formulae of A and B and write their IUPAC names.

13. Explain the following

i. All octahedral complexes of Ni^{2+}must be outer orbital complexes. ii.

NH_4^+ ion does not form any complex.

iii. $(SCN)^{-1}$ ion is involved in linkage isomerism in co-ordination compounds.

14. A metal ion Mn^+ having d^4 valence electronic configuration combines with three didentate ligands to form complexes. Assuming $\Delta_o > P$ Draw the diagram showing d orbital splitting during this complex formation. Write the electronic configuration of the valence electrons of the metal Mn^+ ion in terms of t_{2g} and e_g. What type of the hybridization will Mn^+ ion have? Name the type of isomerism exhibited by this complex.

15. The coordination no. of Ni^{2+} is 4.

$NiCl_2$ + KCN(excess) → A(a cyano complex)

A + Conc HCl(excess) → B (a chloro complex)

i) Write IUPAC name of A and B

ii) Predict the magnetic nature of A and B

iii) Write hybridization of Ni in A and B

16. Explain the following
i. $Cu(OH)_2$ is soluble in ammonium hydroxide but not in sodium hydroxide solution. ii.

EDTA is used to cure lead poisoning

iii. Blue coloured solution of $[CoCl_4]^{2-}$ changes to pink on reaction with $HgCl_2$.

1 MARK QUESTIONS

Q1. Write the formula for the following coordination compound:
Tetraamineaquachloridocobalt(III) chloride

Q2. Write the IUPAC name of the following coordination compound:

$[CoCl_2(en)_2]Cl$

Q3. Why is geometrical isomerism not possible in tetrahedral complexes having two different types of unidentate ligands coordinated with the central metal ion ?

Q4. Out of the following two coordination entities which is chiral (optically active)?

(a) *cis*-$[CrCl_2 (ox)_2]^{3-}$ (b) *trans*-$[CrCl_2 (ox)_2]^{3-}$

Q5. The spin only magnetic moment of $[MnBr_4]^{2-}$ is 5.9 BM. Predict the geometry of the complex ion?

Q6. $[NiCl_4]^{2-}$ is paramagnetic while $[Ni(CO)_4]$ is diamagnetic though both are tetrahedral. Why?

2 MARKS QUESTIONS

Q1. Draw structures of geometrical isomers of $[Fe(NH_3)_2(CN)_4]^-$

Q2. Indicate the type of isomerism exhibited by the following complex and draw the structures for these isomers:

$[Co(en)_3]Cl_3$

Q3. Give evidence that $[Co(NH_3)_5 Cl]SO_4$ and $[Co(NH_3)_5 SO_4]Cl$ are ionization isomers.

Q4. Calculate the overall complex dissociation equilibrium constant for the $[Cu(NH_3)_4]^{2+}$ ion, given that β_4 for this complex is 2.1×10^{13}.

Q5. What is meant by unidentate ligand? Give two examples.

Q6. What is meant by didentate ligand? Give two examples.

Q7. What is meant by ambidentate ligands? Give two examples.

Q8. Draw the structures of optical isomers of:

$[Cr(C_2O_4)_3]^{3-}$

Q9. Discuss the nature of bonding in metal carbonyls.

Q10. What is meant by the *chelate effect*? Give an example.

Q11. Draw the structures of:

(i) $Ni(CO)_4$ (ii) $Fe(CO)_5$

3 MARKS QUESTIONS

Q1. Discuss the nature of bonding in the following coordination entities on the basis of valence bond theory:

(i)$[Fe(CN)_6]^{4-}$ (ii) $[FeF_6]^{3-}$ (iii) $[Co(C_2O_4)_3]^{3-}$

Also predict their magnetic behaviour.

Q2. What is crystal field splitting energy? Draw figure to show the splitting of *d* orbitals in an octahedral crystal field. How does the magnitude of Δ_o decide the actual configuration of *d* orbitals in a coordination entity?

Q3. Discuss briefly giving an example in each case the role of coordination compounds in:

(i) biological systems (iii) analytical chemistry

(ii) medicinal chemistry .

UNIT 13:
AMINES

2.	Amines	1. Ammonolysis of alkylholids, Gabriel Phthalimide synthesis, Hoffmann Bromamide Degradation. 2. Basic character of Amines(pK_b) and comparisons in gaseous and aqueous phase. 3. Carbylomine Reaction ,Hinsberg's Test. 4. Electrophilic substitution. 5. Diazonium salts –reactions

<u>IUPAC NOMENCLATURE</u>

IUPAC NOMENCLATURE

Amine	IUPAC name
$CH_3-CH_2-NH_2$	Ethanamine
$CH_3-CH_2-CH_2-NH_2$	Propan-1-amine
$CH_3-CH(NH_2)-CH_3$	Propan-2-amine
$CH_3-N(H)-CH_2-CH_3$	N-Methylethanamine
$CH_3-N(CH_3)-CH_3$	N,N-Dimethylmethanamine
$C_2H_5-N(C_2H_5)-\overset{1}{C}H_2-\overset{2}{C}H_2-\overset{3}{C}H_2-\overset{4}{C}H_3$	N,N-Diethylbutan-1-amine
$NH_2-\overset{1}{C}H_2-\overset{2}{C}H=\overset{3}{C}H_2$	Prop-2-en-1-amine
$NH_2-(CH_2)_6-NH_2$	Hexane-1,6-diamine
	Aniline or Benzenamine
	2-Aminotoluene
	4-Bromobenzenamine or 4-Bromoaniline
	N,N-Dimethylbenzenamine

NAME REACTIONS

1. Gabriel phthalimide synthesis

Gabriel synthesis is used for the preparation of primary amines. Phthalimide on treatment with ethanolic potassium hydroxide forms potassium salt of phthalimide which on heating with alkyl halide followed by alkaline hydrolysis produces the corresponding primary amine. Aromatic primary amines cannot be prepared by this method because aryl halides do not undergo nucleophilic substitution with the anion formed by phthalimide.

2. Hoffmann bromamide degradation reaction

Hoffmann developed a method for preparation of primary amines by treating an amide with bromine in an aqueous or ethanolic solution of sodium hydroxide. The amine so formed contains one carbon less than that present in the amide.

$$R-\overset{\overset{\displaystyle O}{\|}}{C}-NH_2 + Br_2 + 4NaOH \longrightarrow R-NH_2 + Na_2CO_3 + 2NaBr + 2H_2O$$

3. Carbylamine reaction

Aliphatic and aromatic primary amines on heating with chloroform and ethanolic potassium hydroxide form isocyanides or carbylamines which are foul smelling substances. Secondary and tertiary amines do not show this reaction. This reaction is known as carbylamine reaction or isocyanide test and is used as a test for primary amines.

$$R-NH_2 + CHCl_3 + 3KOH \xrightarrow{Heat} R-NC + 3KCl + 3H_2O$$

4. Hinsberg Test:

Benzenesulphonyl chloride ($C_6H_5SO_2Cl$), which is also known as Hinsberg's reagent, reacts with primary and secondary amines to form sulphonamides.

(a) The reaction of benzenesulphonyl chloride with primary amine

yields N-ethylbenzenesulphonyl amide.

N-Ethylbenzenesulphonamide
(soluble in alkali)

The hydrogen attached to nitrogen in sulphonamide is strongly acidic due to the presence of strong electron withdrawing sulphonyl group. Hence, it is soluble in alkali.

(b) In the reaction with secondary amine, N,N-diethylbenzenesulphonamide

is formed.

N,N-Diethylbenzenesulphonamide

Since N, N-diethylbenzene sulphonamide does not contain any hydrogen atom attached to nitrogen atom, it is not acidic and hence insoluble in alkali.

(c) Tertiary amines do not react with benzenesulphonyl chloride. This property of amines reacting with benzenesulphonyl chloride in a different manner is used for the distinction of primary, secondary and tertiary amines and also for the separation of a mixture of amines.

5. Sandmeyer Reaction

The Cl–, Br– and CN– nucleophiles can easily be introduced in the benzene ring of diazonium salts in the presence of Cu(I) ion.

6. Gatterman Reaction

Chlorine or bromine can be introduced in the benzene ring by treating the diazonium salt solution with corresponding halogen acid in the presence of copper powder.

7. Coupling reactions

The azo products obtained have an extended conjugate system having both the aromatic rings joined through the –N=N– bond. These compounds are often coloured and are used as dyes. Benzene diazonium chloride reacts with phenol in which the phenol molecule at its para position is coupled with the diazonium salt to form p-hydroxyazobenzene. This type of reaction is known as coupling reaction.

Similarly the reaction of diazonium salt with aniline yields p-aminoazobenzene.

DISTINCTION BETWEEN PAIRS OF COMPOUNDS

Give one chemical test to distinguish between the following pairs of compounds.

(i) Methylamine and dimethylamine
(ii) Secondary and tertiary amines
(iii) Ethylamine and aniline

(iv) Aniline and benzylamine
(v) Aniline and N-methylaniline.

ANS. (i) Methylamine and dimethylamine can be distinguished by the carbylamine test. Carbylamine test: Aliphatic and aromatic primary amines on heating with chloroform and ethanolic potassium hydroxide form foul-smelling isocyanides or carbylamines. Methylamine (being an aliphatic primary amine) gives a positive carbylamine test, but dimethylamine does not.

$$\underset{\text{Methylamine}(1^0)}{CH_3-NH_2} + CHCl_3 + 3KOH \xrightarrow{\Delta} \underset{\text{Methyl isocyanide (foul smell)}}{CH_3-NC} + 3KCl + 3H_2$$

$$(CH_3)_2NH + CHCl_3 + 3KOH \xrightarrow{\Delta} \text{No reaction}$$

(ii) Secondary and tertiary amines can be distinguished by allowing them to react with Hinsberg's reagent (benzenesulphonyl chloride, $C_6H_5SO_2Cl$).Secondary amines react with Hinsberg's reagent to form a product that is insoluble in an alkali. For example, N, N−diethylamine reacts with Hinsberg's reagent to form N, N−diethylbenzenesulphonamide, which is insoluble in an alkali. Tertiary amines, however, do not react with Hinsberg's reagent.

(iii) Ethylamine and aniline can be distinguished using the azo-dye test. A dye is obtained when aromatic amines react with HNO_2 ($NaNO_2$ + dil.HCl) at 0-5°C, followed by a reaction with the alkaline solution of 2-naphthol. The dye is usually yellow, red, or orange in colour. Aliphatic amines give a brisk effervescence due (to the evolution of N_2 gas) under similar conditions.

$$CH_3CH_2-NH_2 + HONO \xrightarrow{0\text{-}5^\circ C} C_2H_5OH + N_2\uparrow + H_2O$$

(iv) Aniline and benzylamine can be distinguished by their reactions with the help of nitrous acid, which is prepared in situ from a mineral acid and sodium nitrite.

Benzylamine reacts with nitrous acid to form unstable diazonium salt, which in turn gives alcohol with the evolution of nitrogen gas.

On the other hand, aniline reacts with HNO_2 at a low temperature to form stable diazonium salt. Thus, nitrogen gas is not evolved.

(v) Aniline and N-methylaniline can be distinguished using the Carbylamine test. Primary amines, on heating with chloroform and ethanolic potassium hydroxide, form foul-smelling isocyanides or carbylamines. Aniline, being an aromatic primary amine, gives positive carbylamine test. However, N-methylaniline, being a secondary amine does not.

REASONING QUESTIONS

Q1. Account for the following:

(i) pKb of aniline is more than that of methylamine.

(ii) Ethylamine is soluble in water whereas aniline is not.

(iii) Methylamine in water reacts with ferric chloride to precipitate hydrated ferric oxide.

(iv) Although amino group is o– and p– directing in aromatic electrophilic substitution reactions, aniline on nitration gives a substantial amount of m-nitroaniline.

(v) Aniline does not undergo Friedel-Crafts reaction.

(vi) Diazonium salts of aromatic amines are more stable than those of aliphatic amines.

(vii) Gabriel phthalimide synthesis is preferred for synthesising primary amines.

ANS. (i) pK_b of aniline is more than that of methylamine:

Aniline Methylamine

Aniline undergoes resonance and as a result, the electrons on the N-atom are delocalized over the benzene ring. Therefore, the electrons on the N-atom are less available to donate.

On the other hand, in case of methylamine (due to the +I effect of methyl group), the electron density on the N-atom is increased. As a result, aniline is less basic than methylamine. Thus, pK_b of aniline is more than that of methylamine.

(ii) Ethylamine is soluble in water whereas aniline is not:

Ethylamine when added to water forms intermolecular H−bonds with water. Hence, it is soluble in water.

Ethylamine

But aniline does not undergo H−bonding with water to a very large extent due to the presence of a large hydrophobic $-C_6H_5$ group. Hence, aniline is insoluble in water.

(iii) Methylamine in water reacts with ferric chloride to precipitate hydrated ferric oxide:

Methylamine Water

Due to the +I effect of $-CH_3$ group, methylamine is more basic than water. Therefore, in water, methylamine produces OH^- ions by accepting H^+ ions from water.

$$CH_3-NH_2 + H-OH \longrightarrow CH_3-\overset{+}{N}H_3 + OH^-$$

Ferric chloride ($FeCl_3$) dissociates in water to form Fe^{3+} and Cl^- ions.

$$FeCl_3 \longrightarrow Fe^{3+} + 3Cl^-$$

Then, OH^- ion reacts with Fe^{3+} ion to form a precipitate of hydrated ferric oxide.

$$2Fe^{3+} + 6OH^- \longrightarrow \underset{\text{Hydrated ferric oxide}}{Fe_2O_3 \cdot 3H_2O}$$

(iv) Although amino group is o,p− directing in aromatic electrophilic substitution reactions, aniline on nitration gives a substantial amount of m-nitroaniline:

Nitration is carried out in an acidic medium. In an acidic medium, aniline is protonated to give anilinium ion (which is meta-directing).

For this reason, aniline on nitration gives a substantial amount of m-nitroaniline.

(v) Aniline does not undergo Friedel-Crafts reaction:

A Friedel-Crafts reaction is carried out in the presence of $AlCl_3$. But $AlCl_3$ is acidic in nature, while aniline is a strong base. Thus, aniline reacts with $AlCl_3$ to form a salt (as shown in the following equation).

Due to the positive charge on the N-atom, electrophilic substitution in the benzene ring is deactivated. Hence, aniline does not undergo the Friedel-Crafts reaction.

(vi) Diazonium salts of aromatic amines are more stable than those of aliphatic amines:

The diazonium ion undergoes resonance as shown below:

This resonance accounts for the stability of the diazonium ion. Hence, diazonium salts of aromatic amines are more stable than those of aliphatic amines.

(vii) Gabriel phthalimide synthesis is preferred for synthesising primary amines:

Gabriel phthalimide synthesis results in the formation of 1° amine only. 2° or 3° amines are not formed in this synthesis. Thus, a pure 1° amine can be obtained. Therefore, Gabriel phthalimide synthesis is preferred for synthesizing primary amines.

Q2. Why cannot aromatic primary amines be prepared by Gabriel phthalimide

synthesis?

ANS. Gabriel phthalimide synthesis is used for the preparation of aliphatic primary amines. It involves nucleophilic substitution (S_N2) of alkyl halides by the anion formed by the phthalimide.

But aryl halides do not undergo nucleophilic substitution with the anion formed by the phthalimide.

Hence, aromatic primary amines cannot be prepared by this process.

Q3. Give plausible explanation for each of the following:

(i) Why are amines less acidic than alcohols of comparable molecular masses?

(ii) Why do primary amines have higher boiling point than tertiary amines?

(iii) Why are aliphatic amines stronger bases than aromatic amines?

ANS. (i) Amines undergo protonation to give amide ion.

$$R-NH_2 \longrightarrow R-\bar{N}H + H^+$$

Amide ion

Similarly, alcohol loses a proton to give alkoxide ion.

$$\underset{\text{Alcohol}}{R-OH} \longrightarrow \underset{\text{Alkoxide ion}}{R-\bar{O}} + H^+$$

In an amide ion, the negative charge is on the N-atom whereas in alkoxide ion, the negative charge is on the O-atom. Since O is more electronegative than N, O can accommodate the negative charge more easily than N. As a result, the amide ion is less stable than the alkoxide ion. Hence, amines are less acidic than alcohols of comparable molecular masses.

(ii) In a molecule of tertiary amine, there are no H−atoms whereas in primary amines, two hydrogen atoms are present. Due to the presence of H−atoms, primary amines undergo extensive intermolecular H−bonding.

As a result, extra energy is required to separate the molecules of primary amines. Hence, primary amines have higher boiling points than tertiary amines.

(iii) Due to the −R effect of the benzene ring, the electrons on the N- atom are less available in case of aromatic amines. Therefore, the electrons on the N-atom in aromatic amines cannot be donated easily. This explains why aliphatic amines are stronger bases than aromatic amines.

SOLVED QUESTIONS

1 MARK QUESTIONS

Q1. Give the IUPAC name of the compound and classify into primary, secondary or tertiary amines.

$(CH_3)_2CHNH_2$ 1-Methylethanamine (1^0 amine)

Q2. Give the IUPAC name of the compound and classify into primary, secondary or tertiary amines.

$CH_3(CH_2)_2NH_2$ Propan-1-amine (1^0 amine)

Q3. Give the IUPAC name of the compound and classify into primary, secondary or tertiary amines.

$CH_3NHCH(CH_3)_2$ N−Methyl-2-methylethanamine (2^0 amine)

Q4. Give the IUPAC name of the compound and classify into primary, secondary or tertiary amines.

$(CH_3)_3CNH_2$ 2-Methylpropan-2-amine (1^0 amine)

Q5. Give the IUPAC name of the compound and classify into primary, secondary or tertiary amines.

$C_6H_5NHCH_3$ N−Methylbenzamine or N-methylaniline (2^0 amine)

Q6. Write short notes on diazotization

Aromatic primary amines react with nitrous acid (prepared in situ from $NaNO_2$ and a mineral acid such as HCl) at low temperatures (273-278 K) to form diazonium salts. This conversion of aromatic primary amines into diazonium salts is known as diazotization. For example, on treatment with $NaNO_2$ and HCl at 273−278 K, aniline produces benzenediazonium chloride, with NaCl and H_2O as by-products.

Q7. Write short notes on ammonolysis

When an alkyl or benzyl halide is allowed to react with an ethanolic solution of ammonia, it undergoes nucleophilic substitution reaction in which the halogen atom is replaced by an amino ($-NH_2$) group. This process of cleavage of the carbon-halogen bond is known as ammonolysis.

When this substituted ammonium salt is treated with a strong base such as sodium hydroxide, amine is obtained.

Though primary amine is produced as the major product, this process produces a mixture of primary, secondary and tertiary amines, and also a quaternary ammonium salt

$$\underset{(1^\circ)}{RNH_2} \xrightarrow{RX} \underset{(2^\circ)}{R_2NH} \xrightarrow{RX} \underset{(3^\circ)}{R_3N} \xrightarrow{RX} \underset{\text{Quaternary ammonium salt}}{R_4\overset{+}{N}\overset{-}{X}}$$

Q8. Write short notes on acetylation.

Acetylation (or ethanoylation) is the process of introducing an acetyl group into a molecule. Aliphatic and aromatic primary and secondary amines undergo acetylation reaction by nucleophilic substitution when treated with acid chlorides, anhydrides or esters. This reaction involves the replacement of the hydrogen atom of $-NH_2$ or > NH group by the acetyl group, which in turn leads to the production of amides. To shift the equilibrium to the right hand side, the HCl formed during the reaction is removed as soon as it is formed. This reaction is carried out in the presence of a base (such as pyridine) which is stronger than the amine.

$$C_2H_5NH_2 + CH_3COCl \xrightarrow{\text{pyridine}} C_2H_5NHCOCH_3 + HCl$$

Q9.Why are amines basic in character?

<u>ANS</u>. Like ammonia, the nitrogen atom in amines RNH_2 is trivalent and bears an unshared pair of electrons. Thus it acts like a Lewis base and donates the pair of electrons to electron-deficient species which further increases due to +I effect of alkyl radical.

Q10. Arrange the following in decreasing order of their basic strength:

$C_6H_5NH_2$, $C_2H_5NH_2$, $(C_2H_5)_2NH$, NH_3

The decreasing order of basic strength of the above amines and ammonia

follows the following order:

$(C_2H_5)_2NH$ > $C_2H_5NH_2$ > NH_3 > $C_6H_5NH_2$

<u>SOLVED EXAMPLES</u> (2 Marks)

Q1. Write chemical equations for the following reactions:

(i) Reaction of ethanolic NH_3 with C_2H_5Cl.

(ii) Ammonolysis of benzyl chloride and reaction of amine so formed

with two moles of CH_3Cl

ANS.

(i) $C_2H_5–Cl \xrightarrow{NH_3} C_2H_5–NH_2 \xrightarrow{C_2H_5-Cl} C_2H_5–\overset{\overset{H}{|}}{N}–C_2H_5 \xrightarrow{C_2H_5-Cl} C_2H_5–\underset{\underset{C_2H_5}{|}}{N}–C_2H_5$

Chloroethane Ethanamine N-Ethylethanamine N,N-Diethylethanamine

(ii) $C_6H_5–CH_2–Cl \xrightarrow{NH_3} C_6H_5–CH_2NH_2 \xrightarrow{2CH_3Cl} C_6H_5–CH_2–\underset{\underset{CH_3}{|}}{N}–CH_3$

Benzylchloride Benzylamine N,N-Dimethylphenylmethanamine

Q2. Write chemical equations for the following conversions:

(i) CH_3 –CH_2 –Cl into CH_3 –CH_2 –CH_2 –NH_2

(ii) C_6H_5–CH_5 –Cl into C_6H_5 –CH_2 –CH_2 –NH_2

(i) $CH_3–CH_2–Cl \xrightarrow{\text{Ethanolic NaCN}} CH_3–CH_2–C\equiv N \xrightarrow{\text{reduction}} CH_3–CH_2–CH_2–NH_2$

Chloroethane Propanenitrile Propan-1-amine

(ii) $C_6H_5–CH_2–Cl \xrightarrow{\text{Ethanolic NaCN}} C_6H_5–CH_2–C\equiv N \xrightarrow{H_2/Ni} C_6H_5–CH_2–CH_2–NH_2$

Chlorophenylmethane (Benzyl chloride) Phenylethanenitrile (Benzyl cyanide) 2-Phenylethanamine

Q3.Write structures and IUPAC names of

(i) the amide which gives propanamine by Hoffmann bromamide

reaction.

(ii) the amine produced by the Hoffmann degradation of benzamide.

ANS. (i) Propanamine contains three carbons. Hence, the amide molecule must contain four carbon atoms. Structure and IUPAC name of the starting amide with four carbon atoms are given below:

$CH_3–CH_2–CH_2–\underset{\underset{O}{||}}{C}–NH_2$ (Butanamide)

(ii) Benzamide is an aromatic amide containing seven carbon atoms. Hence, the amine formed from benzamide is aromatic primary amine containing six carbon atoms.

(Aniline or benzenamine)

Q4. How will you convert 4-nitrotoluene to 2-bromobenzoic acid?

ANS.

Q5. Write the reactions of (i) aromatic and (ii) aliphatic primary amines with nitrous acid.

ANS. (i) Aromatic amines react with nitrous acid (prepared in situ from $NaNO_2$ and a mineral acid such as HCl) at 273 − 278 K to form stable aromatic diazonium salts i.e., NaCl and H_2O.

(ii) Aliphatic primary amines react with nitrous acid (prepared in situ from $NaNO_2$ and a mineral acid such as HCl) to form unstable aliphatic diazonium salts, which further produce alcohol and HCl with the evolution of N_2 gas.

Q6. How will you convert:

(i) Ethanoic acid into methanamine

(ii) Hexanenitrile into 1-aminopentane

ANS. (i)

(ii)

Q7. How will you convert:

(i) Methanol to ethanoic acid

(ii) Ethanamine into methanamine

ANS. (i)

(ii)

Q8. How will you convert

(i) Ethanoic acid into propanoic acid

(ii) Methanamine into ethanamine

<u>ANS.</u> (i)

(ii)

Q9. How will you convert

(i) Nitromethane into dimethylamine

(ii) Propanoic acid into ethanoic acid?

(i)

(ii)

Q10. An aromatic compound ‗A' on treatment with aqueous ammonia and heating forms compound ‗B' which on heating with Br_2 and KOH forms a compound ‗C' of molecular formula C_6H_7N. Write the structures and IUPAC names of compounds A, B and C.

ANS. It is given that compound ‗C' having the molecular formula, C_6H_7N is formed by heating compound ‗B' with Br_2 and KOH. This is a Hoffmann bromamide degradation reaction. Therefore, compound ‗B' is an amide and compound ‗C' is an amine. The only amine having the molecular formula, C_6H_7N is aniline, ($C_6H_5NH_2$).The given reactions can be explained with the help of the following equations:

3 MARKS QUESTIONS

Q1. Arrange the following:

(i) In decreasing order of the pKb values:
$C_2H_5NH_2$, $C_6H_5NHCH_3$, $(C_2H_5)_2NH$ and $C_6H_5NH_2$

(ii) In increasing order of basic strength:

$C_6H_5NH_2$, $C_6H_5N(CH_3)_2$, $(C_2H_5)_2$ NH and CH_3NH_2

(iii) In increasing order of basic strength:

Aniline, p-nitroaniline and p-toluidine

ANS. (i) The order of increasing basicity of the given compounds is as follows:
$C_6H_5NH_2 < C_6H_5NHCH_3 < C_2H_5NH_2 < (C_2H_5)_2NH$
We know that the higher the basic strength, the lower is the pK_b values.
$C_6H_5NH_2 > C_6H_5NHCH_3 > C_2H_5NH_2 > (C_2H_5)_2NH$
(ii)The increasing order of the basic strengths of the given compounds is as follows:
$C_6H_5NH_2 < C_6H_5N(CH_3)_2 < CH_3NH_2 < (C_2H_5)_2NH$
(iii) The increasing order of the basic strengths of the given compounds is :
p-Nitroaniline < Aniline < p-Toluidine

Q2. Arrange the following
(i) In decreasing order of basic strength in gas phase:
$C_2H_5NH_2$, $(C_2H_5)_2NH$, $(C_2H_5)_3N$ and NH_3
(ii) In increasing order of boiling point:
C_2H_5OH, $(CH_3)_2NH$, $C_2H_5NH_2$
(iii) In increasing order of solubility in water:
$C_6H_5NH_2$, $(C_2H_5)_2NH$, $C_2H_5NH_2$.

ANS. (i) The given compounds can be arranged in the decreasing order of their basic strengths in the gas phase as follows:
$(C_2H_5)_3N > (C_2H_5)_2NH > C_2H_5NH_2 > NH_3$
(ii) The given compounds can be arranged in the increasing order of their boiling points as follows:
$(CH_3)_2NH < C_2H_5NH_2 < C_2H_5OH$
(iii) The more extensive the H−bonding, the higher is the solubility. $C_2H_5NH_2$ contains two H-atoms whereas $(C_2H_5)_2NH$ contains only one H-atom. Thus, $C_2H_5NH_2$ undergoes more extensive H−bonding than $(C_2H_5)_2NH$. Hence, the solubility in water of $C_2H_5NH_2$ is more than that of $(C_2H_5)_2NH$.

Q3. Accomplish the following conversions:
(i) Nitrobenzene to benzoic acid
(ii) Benzene to m-bromophenol
(iii) Benzoic acid to aniline

ANS. (i)

(ii)

(iii)

Q4. Accomplish the following conversions:
(i) Aniline to 2,4,6-tribromofluorobenzene
(ii) Benzyl chloride to 2-phenylethanamine
(iii) Chlorobenzene to p-chloroaniline

ANS. (i)

NH2
Br2/H2O
Aniline
NH2
Br
Br
Br
2, 4, 6-Tribromoaniline
NaNO2/HCl
273–278 K
N2Cl
Br
Br
Br
2, 4, 6-Tribromobenzene diazonium chloride
HBF4
N2BF4
Br
Br
Br
Δ
–N2, –BF3
F
Br
Br
Br
2, 4, 6-Tribromofluorobenzene

(ii)

CH2Cl
Ethanolic NaCN
–NaCl
CH2CN
H2/Ni
CH2CH2NH2
Benzyl chloride
Phenylethanenitrile
2-Phenylethanamine

(iii)

Q5. Accomplish the following conversions:
(i) Aniline to p-bromoaniline
(ii) Benzamide to toluene
(iii) Aniline to benzyl alcohol.

<u>ANS.</u> (i)

(ii)

(iii)

5 MARKS QUESTIONS

Q1. Give the structures of A, B and C in the following reactions:

(i) $CH_3CH_2I \xrightarrow{NaCN} A \xrightarrow[\text{Partial hydrolysis}]{OH^-} B \xrightarrow{NaOH + Br_2} C$

(ii) $C_6H_5N_2Cl \xrightarrow{CuCN} A \xrightarrow{H_2O/H^+} B \xrightarrow[\Delta]{NH_3} C$

(iii) $CH_3CH_2Br \xrightarrow{KCN} A \xrightarrow{LiAlH_4} B \xrightarrow[0^0C]{HNO_2} C$

(iv) $C_6H_5NO_2 \xrightarrow{Fe/HCl} A \xrightarrow[273K]{NaNO_2 + HCl} B \xrightarrow[\Delta]{H_2O/H^+} C$

(v) $CH_3COOH \xrightarrow[\Delta]{NH_3} A \xrightarrow{NaOBr} B \xrightarrow{NaNO_2/HCl} C$

ANS. (i)

(ii)

(iii)

(iv)

(v)

Q2. Complete the following reactions:

(i) $C_6H_5NH_2 + CHCl_3 + alc.KOH \rightarrow$

(ii) $C_6H_5N_2Cl + H_3PO_2 + H_2O \rightarrow$

(iii) $C_6H_5NH_2 + H_2SO_4(conc.) \rightarrow$

(iv) $C_6H_5N_2Cl + C_2H_5OH \rightarrow$

(v) $C_6H_5NH_2 + Br_2(aq) \rightarrow$

<u>ANS.</u> (i)

(ii)

$$C_6H_5N_2Cl + H_3PO_2 + H_2O \rightarrow C_6H_6 + N_2 + H_3PO_3 + HCl$$

Benzenediazonium chloride — Benzene

(iii)

$$C_6H_5NH_2 + conc.H_2SO_4 \rightarrow C_6H_5\overset{+}{N}H_3HS\overset{-}{O}_4$$

Aniline — Anilinium hydrogen sulphate

(iv)

$$C_6H_5N_2Cl + C_2H_5OH \rightarrow C_6H_6 + CH_3CHO + N_2 + HCl$$

Benzenediazonium chloride — Ethanol — Benzene — Ethanal

(v)

Assignments

Level 1

1. Write IUPAC Name of $C_6H_5N(CH_3)_3Br$?
2. Which reaction is used for preparation of pure aliphatic & aralkyl primary amine ?
3. Name one reagent used for the separation of primary, secondary & tertiary amine ?
4. What amine salts are used for determing their molecular masses ?
5. What is the directive influence of amino group in arylamines?
6. Why are benzene diazonium salts soluble in water ?
7. Which is more basic: CH_3NH_2 & $(CH_3)_3N$?
8. Which is more acidic, aniline or ammonia ?
9. Write the IUPAC name of $C_6H_5NHCH_3$?
10. Mention two uses of sulphanilic acid?

Level 2

1. What for are quaternary ammonium salts widely used ?
2. What product is formed when aniline is first diazotized and then treated with Phenol in alkaline medium ?
3. How is phenyl hydrazine prepared from aniline ?
4. What is the IUPAC name of a tertiary amine containing one methyl, one ethyl And one n-propyl group ?
5. Explain why silver chloride is soluble in aqueous solution of methylamine ?
6. Write the IUPAC name of $C_6H_5N(CH_3)_3$ Br ?
7. Primary amines have higher boiling points then tertiary amines why ?

8. Why is it necessary to maintain the temperature between 273 K & 278 K during diazotization?
9. Arrange the following in order of decreasing basic strength : Ethyl amine, Ammonia, Triethylamine ?
10. Why aniline is acetylated first to prepare mono bromo derivative?

LEVEL 3

1. Arrange the following in decreasing order of their basic strength.

   $C_6H_5NH_2$, C2H5NH2, $(C_2H_5)_2NH$, NH_3

2. Write chemical equation for the conversion

   CH_3-CH_2-Cl into CH_3 –CH_2-CH_3-NH_2

3. Write the equation involved in Carbylamines reactions?

4. How will you distinguish the following pairs? (i) Methanamine and N-methyl methane amine (ii) Aniline and ethyl amine

5. Write chemical sections involved in following name reactions. (i) Hoffmann Bromoamide reaction. (ii) Diazotisation reaction.

COMMON ERRORS

Basic character of amines in aqueous and in gaseous state, p_{ka} and p_{kb} values

1 MARK QUESTIONS

Q1. Arrange the following in decreasing order of their basic strength:
$C_6H_5NH_2$, $C_2H_5NH_2$, $(C_2H_5)_2NH$, NH_3
Q2. Arrange the following in decreasing order of the p*Kb* values:
$C_2H_5NH_2$, $C_6H_5NHCH_3$, $(C_2H_5)_2NH$ and $C_6H_5NH_2$
Q3. p*Kb* of aniline is more than that of methylamine. Why?
Q4. Ethylamine is soluble in water whereas aniline is not. Give reason.
Q5. Methylamine in water reacts with ferric chloride to precipitate hydrated ferric oxide. Why?
Q6. Although amino group is *o*– and *p*– directing in aromatic electrophilic substitution reactions, aniline on nitration gives a substantial amount of
m-nitroaniline. Give reason.
Q7. Aniline does not undergo Friedel-Crafts reaction. Why?
Q8. Diazonium salts of aromatic amines are more stable than those of aliphatic amines. Why?
Q9. Gabriel phthalimide synthesis is preferred for synthesising primary amines. Give reason
Q10. Why cannot aromatic primary amines be prepared by Gabriel phthalimide synthesis?
Q11. Why do primary amines have higher boiling point than tertiary amines?
Q12. Why are aliphatic amines stronger bases than aromatic amines?
Q13. Direct nitration of aniline is not carried out. Give reason.
Q14. The presence of base is needed in the ammonolysis of alkyl halides. Why?

2 MARKS QUESTIONS

Q1. Write structures and IUPAC names of
(i) the amide which gives propanamine by Hoffmann bromamide reaction.
(ii) the amine produced by the Hoffmann degradation of benzamide.
Q2. Give one chemical test to distinguish between the following pairs of compounds.
(i) Methylamine and dimethylamine (ii) Ethylamine and aniline

Q3. Write short notes on the following:
(i) Carbylamine reaction (ii) Diazotisation
Q4. Explain the following with the help of an example.
(i) Hofmann's bromamide reaction (ii) Coupling reaction
Q5. Explain the following with the help of an example.
(i) Ammonolysis (ii) Gabriel phthalimide synthesis
Q6. How can you convert an amide into an amine having one carbon less than the starting compound? Name the reaction.
Q7. Give a chemical test to distinguish between:
(a) $C_6H_5NH_2$ & CH_3NH_2
(b) CH_3NHCH_3 & $(CH_3)_3N$
Q8. Give the IUPAC names of:
(a) $(CH_3)_2CHNH_2$
(b) $(CH_3CH_2)_2NCH_3$
Q9. Write the structures of:
(a) 3-Bromobenzenamine
(b) 3-Chlorobutanamide

<u>3 MARKS QUESTIONS</u>

Q1. How will you convert
(i) Benzene into aniline (ii) Benzene into N, N-dimethylaniline
(iii) Aniline to Sulphanilic acid

Q2. An aromatic compound 'A' on treatment with aqueous ammonia and heatingforms compound 'B' which on heating with Br_2 and KOH forms a compound 'C'of molecular formula C_6H_7N. Write the structures and IUPAC names of compounds A, B and C.

Q3. How will you carry out the following conversions (Write Chemical equations and reaction conditions):
(a) Aniline to Phenol
(b)Acetamide to Ethylamine
(c) Aniline to *p*-nitroaniline

GENERAL ORGANIC CHEMISTRY

(1) When two half filled atomic orbitals to same or different atoms are brought near to each other, they overlap (combine) and form new orbitals called molecular orbitals. The molecular orbitals that are formed encompass both nuclei, and in them , the electrons can move about both nuclei. the electrons are not restricted to the vicinity of one nucleus or the other as they were in the separate atomic orbital

(2) When atomic orbitals combine to form molecular orbitals , the number of molecular orbitals that result always equals the number of atomic orbitals that combine.
Thus in the formation of hydrogen molecule the two atomic orbitals of two hydrogen atoms combine to produce two molecular orbitals . Two molecular orbitals result because the mathematical properties of wave function permit them to be combined by liner combination. Linear combination of atomic orbital may be either addition or subtraction,i.e., they can combine either in phase or out of phase.

(3) When orbitals with like sine (in phase combination or addition) overlap, a bonding molecular orbital results. It has a higher electron density between the two atoms, thusminimising nuclear repulsion and permitting the nuclei to be closer to eachother then in the un bonded state. It has llower energy then the individual separated atomic orbitals. Atraction force (between protons of one atome and electrons of the other atom) would be greater than the repulsive force in this case.

(4)When orbitals with unlike signs (out of the phase overlapping, subtraction) overlap an antibonding molecular orbital results. It has a node(no electron density) in the region between the nuclei. The repulsion of its nuclei is higher and it has a higher energy than the individual separated atomic orbitals. Antibonding molecular orbital contains no electrons in the ground state of the molecule. Repulsive force(between the two nuclei and between the electrons of the two atoms)would be greatr than the attraction force.

An energy diagram for the molecular orbital for the hydrogen molecule is shown in fig. given below. Notice that electron are placed in molecular orbitals in the same way that they were in the atomic orbitals (i.e,molecular orbitals follow Auffbau principle, and Hund's rule). Two electrons (with their opposite spin) occupy the BMO, where their total energy is less than theseparate atomic orbitals. This is the lowest electronic state or ground state of the hydrogen molecule.

Number of electrons pairs tell us the type of hybridization as fallows:

ep	hybridization
2	sp
3	sp^2
4	sp^3
5	sp^3d
6	sp^3d^2

Examples:

(i) $CH_3 - \overset{\oplus}{CH_2}$

bp = 3

lp = 0

ep = 3, sp^2

(ii) $CH_2 = \overset{\oplus}{CH}$

bp = 2

lp = 0+0=0

ep = 2, sp

(iii) $CH_3 - \overset{\ominus}{CH} - CH$

bp = 3

lp = 1

ep = 4, sp^3

(iv) $CH_2 = \overset{\ominus}{CH}$

bp = 2

lp = 0 + 1 = 1

ep = 3, sp^2

(v) $CH \equiv \overset{\ominus}{C}$

bp = 1

lp = 0 + 1 = 1

ep = 2, sp

(Vi) $CH - \overset{\bullet}{C} - CH_3$, CH_3

bp = 3

lp = 0

ep = 3, sp^2

(vii) $\underset{Sp^3}{CH_3} - \underset{sp^3}{CH_2} - \underset{sp^2}{CH} = \underset{sp}{C} = \underset{sp^2}{CH} - \overset{\oplus}{\underset{sp^2}{CH_2}}$

REACTION INTERMEDIATES

Reaction intermediates are generated by the breaking of covalent bond of the substrate. They are short lived species and are highly reactive. There are six important types of reaction – intermediates.

(1) Carbocation (2) Carbanion (3) Free redical (4) Carbene (5) Benzyne and (6) Nitrene

Carbocations

(1) An organic species which has a carbon atom bearing six electrons in its outermost orbit and has a positive charge is called a carbocation.

(2) carbocation can be classified into the following groups:

(A) **Alkly carbocation :** (i) When positive charge is present on the alkyl on the carbon. carbocation Is known as alkly carbocation .

(ii) Alkly carbocation is of four types :

Methyl carbocation $CH_3^{\oplus}$

Primary alkly carbocation R —— CH2

Secondary alkly carbocation R— C — HR

Tertiary alkly carbocation R — CH — R (with R below CH)

(iii) Stability of can be explained by

(i) Inductive effect and

(ii)Hyperconjugation

(iv) Accoriding to these two effect the stability orde is as follows :

R — CH — R (with R below CH) → R — C — HR → R — CH2 → $CH_3^{\oplus}$

Stability in decreasing order

(3) stability of different types of carbocations in decreasing order :

$(C_6H_5)_3C$ > $(C_6H_5)_2CH$ > $C_6H_5\text{-}CH_2$ ≥ $CH_2\text{=}CH\text{-}CH_2$ ≥ R-C(-R)-R > R-CH- R > $R\text{-}CH_2$ > CH_3 > $CH_2\text{=}CH$

(4) Characteristics of carbocations(except vinyl carbocation) :

(i) It has three bond pair with empty *p*-orbital.Its hybridisationis sp^2.

(ii) Shape of carocation is trigonal planer.

Note : Triphenyl methyl carbocation has proprller shape.

(iii) There are six electrons in the outermost orbite of carbocationic carbon hance its octet is incomplete. All the six electrons are paired.

(iv) It is charged electrophile.

(v) It is diamagnetic in character.

(vi) It is formed by hetrolytic bond fission

(Vii) It reacts with nucleophiles.

Carbanions

Anions of carbon is known as cabanion . cabanion carries three bond pair and one lone pair ,thus making the carbon atom negatively charged. So carbanion may be represented as

(1) Characteristic of Carbanions : (i)

Hybridisation and geometry : alkly carbocation has three bond pair and one lone pair. Thus hybridization is sp^3 and geometry is pyramidal.

Note : geometry of allyl and benzyl carbanion is almost planar and hybridization in sp^2.

(ii) There are eight electron in the outer most orbit of carbanion carbon hence its octet is complete.

(iii) It behaves as charged nucleophile.

(iv) It is diamagnetic in character because all eight electrons are paired.

(v) It formed by hetrolytic bond fission.

(vi) It reacts with electrophiles.

Stability of Carbanions: The stability of Carbanions may be explained by

(A) Electronegativity of Carbanionic carbon : Stability ∝ Electronegativity of Carbanionic carbon

∝ **%** s-character of Carbanionic carbon

(I) **%** s-character in increasing order

(ii) stability in increasing order

(B) Inductive effect: stability of carbanions depends on the+I or –I group as follows:

(i) Stability ∝ $\frac{1}{+I \text{ powerof the group}}$

(i) +I power in increasing order

(ii) stability in decreasing order

(ii) Stability of Carbanions ∝ -I power of the group

For example :

$I \leftarrow CH_2^{\oplus}$ $Br \leftarrow CH_2^{\oplus}$ $Cl \leftarrow CH_2^{\oplus}$ $F \leftarrow CH_2^{\oplus}$

(i) -I popwer of halo group is in increasing order

. (ii) stability in increasing order

(C) Delocalisation or Resoance: Allyl and benzyl Carbanions are stabilized by delocalization of negative charge.

$CH_2{=}CH{-}CH_2^{\oplus}$ $C_6H_5{-}CH_2^{\oplus}$ $(C_6H_5)_2CH^{\oplus}$ $(C_6H_5)_3C^{\oplus}$

(i) Number of resonating structures is in increasing order

(ii) stability in increasing order

QUESTIONS

Q1. What ype of defect can arise when a solid is heated?

Q2. Write two application of adsorption.

Q3. What is the basic principle of zone refining of metals?

Q4. Why is ICl more reactive than I_2.

Q5. Write down the formula of Tetraamineaquachloridocobalt(III)chloride.

Q6. Arrange the following in increasing order of boling point:

(i) $CH_3CH_2CH_2CH_2Br$
(ii) $(CH_3)_3C.Br$
(iii) $(CH_3)_2.CH.CH_2.Br$

Q7. Write the IUPAC name of the following:

Q8. Aldehydes and Ketones have lower boling points than corresponding alcohols. Why?

Q9. Why do gases nearly always tend to be less soluble in liquid as the temperature is raised?

Q10. Write down the structures and names of the products formed when D-glucose is treated with

(i) Brimine water

(ii) Hydrogen Iodide (Prolonged heating)

Q11. How is the stability of a co-ordination compound in solution decided? How is the dissociation constant of a complex defined?

Q12. Illestrate the following reactions :

(a) Sandmeyer's reaction

(b) Coupling reaction

Q13. (a) Name the only vitamin which can be synthesized in our body. Name the disease that is casued due to the deficiency of this vitamin.

(b).State two functions of carbohydrates.

Q14. The extraction of gold by leaching with NaCN involves both oxidation and reduction. Justify giving chemical equations.

Q15. (a) Which form of sulphur shows paramagnetic behavior and why?

(b). Fluorine exhibits only -1oxidation state whereas other halogens exhibit +1,+3,+5 and +7 oxidation state also. Explain as to why.

Q16. What is ment by rate of a reaction ? Differentiate between average rate and instantaneous rate of a reaction.

Q17. How would you account for the following :

(a) Aniline is a weaker base than cyclohexylamine.

(b) Methylamine in aqueous medium gives reddish- brown precipitate with $FeCl_3$.

OR

How would you account for the following :

(a) Electrophilic substitution in case of aromatic amines takes place more readily then benzene.

(b) Ethanamide is a weaker base than ethanamine.

Q18. Write the reaction taking place at cathode and anode in lead strage battery when the battry is in use. What happenes on charging the battery?

Q19. (a) What are intrinsic semi-conductors ? Give an example.

(b) What is the distance between $Na^+$and Cl^- ionsin NaCl crystal if its density is 2.165gcm^{-3} ? [Atomic Mass of Na =23u,Cl=35.5u;Avogadro's number =6.023x10^{23}]

Q20. (a)How many coulombs are requiredto reduce 1 mole $Cr_2O_7^{2-}$ to Cr^{3+}?

(b)The conductivity of 0.001M acetic is 4x10^{-5}S/m.Calculate the dissociation constantof acetic acid if Λ^0_m for acetic acid is 390 S cm^2 mol^{-1}

Q21. What are the following substances? Give one example of each.

(i) Broad spectrum antibiotics

(ii) Narcotic analgesics

(iii) Synthetic detergents

Q22. Explain the term co-polymerization and give two examples copolymers and the reactions for their preparations.

Q23. (a) How would you obtain the following:

(i) 2-methylpentan-2-ol from 2-methyl-1-pentene

(ii)Acetophenone from phenol

(b) Write IUPAC name of the following:

Q24. In general it is observed that the rate of a chemical reaction doubles with every 10 degree rise in temperature.If the generalization holds good for the reaction in the temperature range 295 K to 305 K, what would be the value of activation energy for this reaction ? [R=8.314 mol^{-1}K^{-1}]

Q25. How are the two types of emulsions different from one another ? Give suitable examples to justify the difference. State two applications of emulision.

Q26. Account for the following :

(a) The dipole moment of chlorobenzene is lower than that of cyclohexyl chloride.

(b) Alkyl halides ,though polar, are immiscible with water.

(c) Grignard's reagents should be prepared under anhydrous conditions.

Q27. If N_2 gas is bubbled through water at 293 K, how many millimoles of N2 gas would dissolve in 1 litter of water? Assums that N_2 exert a partial pressure of 0.987 bar. Given that Henry's law constant for N_2 at 293 K is 76.48.

OR

The partial pressure of ethane over a saturated solution containing 6.56×10^{-2} g of ethane is 1 bar . if the solution contains 5.0×10^{-2} g of ethane , then what will be the partial pressure of the gas?

Q28. (a) Give chemical tests to distinguish between the following pairs of compounds:

(i) Benzene amide and 4-aminobenzoic acid

(ii) Methyl acetate and Ethyl acetate

(b) An organic compound with molecular formula $C_9H_{10}O$ forms 2,4-DNPderivative and reduces Tollen's reagent and undergoes Cannizzaro's reaction. On vigorous oxidation, it gives 1,2-benzenedicarboxylic acid. Identify the compound and write chemical equations for the reactions.

OR

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

(i) Benzoic acid and Phenol

(ii) Benzaldehyde and Acetophenone

(b) An organic compound with molecular formula $C_5H_{10}O$ does not reduces Tollen's reagent but forms an addition compound with sodium hydrogen sulphaite and gives a positive idoform test.. On vigorous oxidation, it givesethanoic acid and propanoic acid. Identify the compound and write all chemical equations for the reactions

Q29. Account for the following :

(i) Chlorine water loses its yellow colour on standing.

(ii) $BrCl_2$ is more stable then $BrCl_5$.

(iii) Fluorine does not form oxoacids.

(iv) PCl_5 acts as an oxidizing agent.

(v) SO_2 is an air pollutant.

OR

(a) With help of chemical equations the principle of contact process in brief for the manufacture of sulphuric acid. (No diagram)

(b) Account for the following :

(i) Bond dissociation energy of F_2 is less than that of Cl_2.

(ii) Nitric oxide (NO) becomes brown when released in air.

Q30. (a) Describe the preparation of potassium dichromate from chromite ore. What is the effect of change of pH on dichromate ion?

(b) How is the variability in oxidation state of transition elements of different from that of non-transition elements? Illustrate with examples.

OR

(a) Describe the preparation of potassium permanganate from pyrolusite ore . What happens when acidified potassium permanganate solution reacts with ferrous sulphate solution? Write balanced chemical equations.

(b) Account for the following :

(i) Mn^{2+} compounds are more stable than Fe^{2+} compounds towards oxidation to their +3 state.

(ii) Cr^{2+} is reducing and Mn^{3+} oxidizing when both have d^4 configuration.

ANSWERS

1. Metal excess defect

2. (a) In chromatography for the separation of mixtures .
(b) Adsorption toxic gases by activated charcoal or gas masks.(or any other correct application)

3. this method is based on the principle that the impurities are more soluble in the melt than the solid of the metal.

4. Because of low bond dissociation enthalpy.

5. $[Co(NH_3)_4(H_2O)Cl]Cl_2$

6. $(CH_3)_3CBr$ > $(CH_3)_2CHCH_2Br$ > $CH_3CH_2CH_2CH_2Br$

7. 2-methyllcyclohexanone

8. Because of the adsence of hydrogen bonding in aldehydes and ketones.

9. As the temperature rises the value of Henry's law constant.K_H increases Solubility of gas in liquids decreasas with increase in K_H.10..

10. (i)

Gluconic acid

(ii) CH3-(CH2)-CH3

n-hexane

11. Stability of a coordination compound in solution is decided by its stability constant K. Larger is the stability constant, higher will be the stability of complex formed. The reciprocal of the formation constsnt is known as the *dissociation constant*.(or any other correct answer)

12. Sadmeyer's reaction

(any one)

(i) **Coupling reaction**

13. (a) Vitamin D,Rickets

(b) (i) Carbohydrates act as a structural material for plant cell walls.

(ii) They as a reserve food material . (or any other correct function)

14. Oxidation

$4Au(s) + 8CN^-(aq) + 2H_2O + O_2(g) \longrightarrow 4[Au(Cu)_2]- + 4OH^-$

Reduction

$2[Au(Cu)_2]^- + Zn \quad [Zn(CN)_4]^{2-} + 2Au$

Note: Molecular equation can be accepted.

15. (a) In vapour phase sulphur shows paramagnetic behavior due to the presence of 2 unpaired electrons.

b) Because fluorine is most electronegative and does not have vacant d-orbitals.

16. Decrase or increase (change) in the concentration of reaction with time is known as the rate of reaction.

Avarage rate is measured in larger time intervals whereas instantaneous rate is measured in shortest time intervals (at a particular instant of time).

17. (ii) It is because in aniline the $-NH_2$ group is attached directly to the benzene ring . It results in the unshared electron pair on nitrogen atom to be in conjugation with the benzene ring and thus making it less available for protonation. (or any other suitable reason)

(iii) Methyl amine in water gives OH- ions which react with $FeCl_3$ to give precipitate of ferric hydroxide

or

$$CH_3NH_2 + H_2O \longrightarrow CH_3NH_3^+OH^- \longrightarrow CH_3NH_3^+ + OH^-$$

$$Fe^{3+} + 3OH^- \longrightarrow Fe(OH)_3$$

OR

(a) because $-NH^2$ is a very strong activating group due to the presence of lone pair of electrons on nitrogen/ or due to resonance in atomatic ammines.

(b) Because NH^2 of ethanamide involves in resonance with carbonyl group (-CO-) which leads to positive charge on N and less basic.

18. Anode Reaction :- $Pb + SO_4^{2-} \longrightarrow PbSO_4(s) + 2e^-$

Cathode Reaction :- $PbO_2 + 4H^+ + SO_4^{2-} + 2e^- \longrightarrow PbSO_4 + 2H_2O$

On charging the battery the reaction is reversed.

19. (a) The pure substances in which electrical conductivity is due to the thermal promotion of valence electrons to the conduction band are called intrinsicsemi-conductors. Eg Si / Ge (any one correct example)

(b) $d = z \times M$

$a^3 \times N_A$ For fcc lattice z=4

$$2.165\ g\ cm^{-3} = \frac{4 \times 58.5 g\ mol^{-1}}{a^3 \times 6.023 \times 10^{23} mol^{-1}}$$

$$a^3 = \frac{4 \times 58.5\ g\ mol^{-1}}{2.165\ g\ cm^{-3} \times 6.023 \times 10^{23} Mol^{-1}}$$

$a = 5.64 \times 10^{-8}$ cm or 564pm

There fore the distance between Na^+ and Cl^- ions is 564/2=282pm

20. (a) 6F -= 6 x 96500 C = 5.76 x 10^5C

(b) $\Lambda m = K/c = \dfrac{4 \times 10^{-7}\ cm^{-1} \times 1000\ cm^3\ L^{-1}}{0.001\ molL^{-1}} = 0.4\ Scm^2\ mol^{-1}$

$$\alpha = \frac{\Lambda m}{\Lambda m^0} = \frac{0.4\ Scm^2\ mol^{-1}}{390\ Scm^2\ mol^{-1}} = 0.00103$$

$$K = \frac{C\alpha^2}{C(1-\alpha)} = C\alpha^2 = 0.001 \times (0.00103)^2 = 1.06 \times 10^{-9}$$

21. (i) Broad Spectrom Antibiotics; which killer inhibit a wide range of Gram +ve and Gram –ve are called broad spectrum antibiotics. Eg. Chloramphenicol (or any one correct example)

(ii) Narcotic Analgesics : The medicines which when administered relieve pain and produce sleep are called narcotic analgesics.
eg. Morphine (or any one correct example)

(iii)Synthetic Detegents : are cleansing agents which have all the properties of soap but which actually do not contain any soap
eg. Sodium Lauryl sulphate (or any one correct example)

22. (i) The polymer made by addition polymerization from two different monomers are termed as co-polymers and the process is called co-polymerization.
Eg. Bune-S , Buna-N (or any one correct example)

<u>Bune-S</u>

$$^{n}CH_2{=}CH{-}CH{=}CH_2 + C_6H_5CH{=}CH_2 \longrightarrow (CH_2{-}CH{=}CH{-}CH_2{-}CH_2{-}\underset{}{\overset{C_6H_5}{\overset{|}{CH}}})_n$$

<u>Buna-N</u>

$$^{n}CH_2 = CH - CH = CH_2 + {}^{n}CH_2 = \overset{CN}{\overset{|}{CH}}$$

$$\downarrow$$

$$-(CH_2 - CH = CH - CH_2 - CH_2 - \overset{CN}{\overset{|}{CH}})- n$$

23. (a) (i) $CH_2 = C - CH_2 - CH_2 - CH_3 \xrightarrow{H_2O/H^+} CH_3-C(OH)(CH_3)-CH_2-CH_2-CH_3$

(ii)

(b) 1 - ethoxy – 2 –nitrocyclohexane

24. (b) $\log \frac{k_2}{k_1} = \frac{Ea}{2.303\ R} \left(\frac{T_2-T_1}{T_1-T_2} \right)$

$\log 2 = \frac{Ea}{2.303 \times 8.314\ jk^{-1}\ mol^{-1}} \left(\frac{305 - 295}{305 \times 295} \right) K^{-1}$

$0.30010 = \frac{Ea}{2.303 \times 8.314\ jk^{-1}\ mol^{-1}} \frac{10K^{-1}}{305 \times 295}$

$Ea = 51855.2\ j\ mol^{-1}$ or $51.86\ k\ j\ mol^{-1}$

25. (i) **<u>Oil in water :</u>** The emulsion in which oil is dispersed phase and water is dispersion medium eg. Milk is an emulsion of fats in water

(ii) **<u>Water in oil:</u>** the emulsion in which water is dispersed phase and oil is dispersion medium . eg. Butter , cod liver oil

<u>Applications:</u> (i) Cleansing action of soaps and detergents

(ii) concentration of sulphide ones by Froth Floatation Process. (or any one correct applic

26. (a)Due to –I and effect of Cl group , the net dipole reduces to a large extent in chlorobenzene . (or diagrammatic explanation)

(b) Because alkyl halides can not form hydrogen bond with water.

(c) Because in the presence of moisture it change to alkane .(or chemical reaction)

27. x (Nitrogen) $= \frac{p \text{ (nitrogen)}}{K_H} = \frac{0.987 \text{bar}}{76{,}480 \text{ bar}} = 1.29 \times 10^{-5}$

As 1 litre of water contains 55.5 mol of it, therefore if n represents number of moles of N2 in solution,

x (Nitrogen) $= \frac{n \text{ mol}}{n \text{ mol} + 55.5 \text{ mol}} = \frac{n}{55.5} = 1.29 \times 10^{-5}$

(n in denominator is neglected as it is < < 55.5)

Thus $n = 1.29 \times 10^{-5} \times 55.5$ mol $= 7.16 \times 10^{-4}$ mol10^{-4}

$$= \frac{7.16 \times 10^{-4} \text{ mol} \times 1000 \text{ mol}}{1 \text{ mol}} = 0.716 \text{ m mol}$$

OR

Applying henry's law

$m = k_H \times p$, 6.56×10^{-2} g $= k_H \times 1$ bar

$k_H = 6.56 \times 10^{-2}$ g bar^{-1}

put the value of k_H in the second case

$5 \times 10^{-2} = 6.56 \times 10^{-2}$ g bar$^{-1} \times p$

$$P = \frac{5 \times 10^{-2} \text{ g}}{6.56 \times 10^{-2} \text{ g bar}^{-1}} = 0.765 \text{ bar}$$

28. (a) (i) Add $NaHCO_3$ to both the compounds, 4- aminobenzoic acid will give brisk effervescence wheres Benzene amide will not give this test. (or any other correct suitable test)

(ii) Warm both the esters with NaOh and then heat them with I2 and NaOH. Ethyl acetate gives yellow ppt of Iodoform. (or any other correct suitable test)

(b)

OR

(a) (i) **<u>Phenol and Benzoic acid:</u>** Add neutral $FeCl^3$ to both of them .phenol gives violet colour. (Other relevant test can be acceptedaa)

(b) As the compound does not reduce Tollen's reagent but forms an addition compound with $NaHSO_3$ there for compound gives positive contains a ketone group. Since compound gives positive iodoform test therefore compound contains CH_3CO group.
On vigorous oxidation compound gives ethanoic acid and propanoic acid which shows the compound $C_5H_{10}O$ is $CH_3CH_2CH_2COCH_3$(pentan – 2-one

$$CH_3CH_2CH_2COCH_3 \xrightarrow{\text{Oxidation}} CH_3CH_2COOH + CH_3COOH$$

(or the given reaction can be explained by the equation)

29. (i) Because of the formation of HOCl / or due to its oxidation.

(ii) Because of inert pair effect.

(iii) Because of high electronegativity of florine.

(iv) Because +3 oxidation state of P is more stable than +5.

(v) Because in air SO_2 gets oxidized to H_2SO which is very corrosive and poisonous

CONTACT PROCESS

i) burning of sulphur or sulphide ores in air to generate SO_2.

(ii) conversion of SO_2 to SO_3 by the reaction with oxygen in the presence of a catalyst (V_2O_5), and

(iii) absorption of SO_3 in H_2SO_4 to give *Oleum* ($H_2S_2O_7$).

A flow diagram for the manufacture of sulphuric acid is shown in
The SO_2 produced is purified by removing dust and other impurities such as arsenic compounds.

The key step in the manufacture of H_2SO_4 is the catalytic oxidation of SO_2 with O_2 to give SO_3 in the presence of V_2O_5 (catalyst).

$$2SO_2g + O_2g \xrightarrow{V_2O_5} 2SO_3g \quad \Delta_r H^0 = -196.6\ kJmol^{-1}$$

The reaction is exothermic, reversible and the forward reaction leads to a decrease in volume. Therefore, low temperature and high pressure are the favourable conditions for maximum yield. But the temperature should not be very low otherwise rate of reaction will become slow.

(b) (i) Because of large electron – electron pair repulsion among the lone pair in F_2 molecule.
(ii) because of the formation of NO_2 gas.

30. (a) it is prepared from one called chromate or ferro chrome iron , FeOCr2O3.The various steps involved are

(i) preparation of sodium chromate

$$4FeO.Cr_2O_3 + O_2 \longrightarrow Fe_2O_3 + 4Cr_2O_3$$

$$4Na_2CO_3 + 2Cr_2O_3 + 3O_2 \longrightarrow 4Na_2CrO_4 + 4CO_2$$

(ii) Conversion of sodium chromate in to sodium dichromate.

$$2NaCrO_4 + H_2SO_4 \longrightarrow Na_2Cr_2O_7 + Na_2SO_4 + H_2O$$

(iii) Conversion of sodium dichromate in to potassium dichromate

$$Na_2Cr_2O_7 + 2KCl \longrightarrow K_2Cr_2O_7 + 2NaCl$$

Dichromate ion (Cr2O72-) converts to chromate ion (CrO42-) in the presence of alkali (i.e. pH> 7) or ionic equation.

(b) In transition elements oxidation state differ from each other by unity eg. V^{2+} ,V^{3+} , V^{4+} , V^{5+}

Whereas in non- transition elements oxidation state normally differ by a unit of two eg. Cl^-, Cl^+ , Cl^{3+} , Cl^{5+} (or any one correct example)

OR

(a) $2MnO_2 + 4KOH + O_2 \longrightarrow 2K2MnO_4 + 2H_2O$

$$2MnO_4^{2-} + Cl_2 \longrightarrow 2MnO_4^- + 2Cl^-$$

HALOALKANES , HALOARENES

1- Important terms and concept

$R\text{-}H + X_2 \longrightarrow R\text{-}X + H\text{-}X$

(i) Halogen derivative of alkenes called halo alkenes e.g. R- CH_3

(ii)Halogen derivative of arenes called halo arenes e.g. R- C_6H_5

2. (a) Vicinal di halides – where the two halogens are attached on the adjacent carbon atom.
e.g.CH2Cl
|
CH2Cl

(b) geminal dihalide- where two halogen atoms are attached to the same carbon atom eg CH3CHBr2

2- Important mechanism

(i) Nucleophilic substitution
(ii) Electrophilic substitution
(iii) Elimination reaction
(iv) Carbylamine reaction
(v) Reimer Tiemann reaction
(vi) Wurtz reaction
(vii) Wurtz fittig reaction

Nucleophillic substitution it involves the replacement of an atom or group by another atom or group

$A - B + C \rightarrow A - C + B$

It must be remembered that A – B and A – C both are covalent compounds.

(i) In aliphatic system

$R - X + OH^- \rightarrow R - OH + X^-$

$R - X + O^-C_2H_5 \rightarrow R\text{-}O\text{-}C_2H_5 + X^-$

Decreasing order of Basicity $CH_3 > NH_2 > O^-R > OH^- > I^- > Br^- > Cl^-$

In general

$R - X + :B^- \rightarrow R - B + X^-$

$: B^- \rightarrow OH^-, RO^-, CN^-, RCOO^-, NO_3^-, SH^-, RS^-$

Bimolecular Nuclephilic substitution SN^2

(i) It takes place in one step.
(ii) Most of the SN^2 reaction are second order but some time when Nucleophillic reagent is present in excess quantity the reaction is of I_{ts} order but still proceeds by SN^2

(iii) It is bimolecular

(iv) It leads to inversion of configuration attack of Nucleophillic occur from direction opposite to the leaving group.

SN1 ⟶ (i) It takes place in two steps.

(ii) All are Ist order.

(iii) Unimolecular

(iv) It leads racemisation Retenation

(v) Retention of configuration

The preservation of spatial arrangement of bonds at an asymmetric centre during the chemical reaction.

<u>Stereochemistry of SN1 reaction</u>

It an alkyl halide is optically active then the product is racemic mixture, here the attack of Nucleophiles from the both side [50:50 mix of the two enantiomers.

R Mg- X
H2O
RH + Mg (OH) X
R'OH
RH + Mg (OR') X
(i)CO2
R COOH + Mg (OH) X
(II)H2O/H+
H CHO— RCH2OH
H+/H2O
R —CHO
R
R
CH—OH
H+/H2O
R2CO
R3COH
H+/H20
H+/H2O
HCN
R— C=N MgXR
RCHO
R—CN
R2 C=N—MgX
H2O/H+
R2 C=O

R—X

- HOH or NaOH/HOH → R OH, Reaction is known as hydrolysis
- R' O- Na → R—O—R', Ethers
- Na^+S^-H → R—S—H Thio Alcohols
- Na_2S → R—S—R Thio ethers
- $R'S^-Na^+$ → R—S—R' Thio ethers
- ●● R_2S → R—S(R)—R Sulphonium ions
- NaCN → R—C≡N Alkyl cyanides
- $Na^+N_3^-$ → $R—N_3$ Azides
- R'—C≡C^-Na^+ → R'—C≡C—R Non terminal akyne
- $C—O(=O)—O^-$ → R'—C(=O)—O—R Ester
- ●● R'_3N → $R—N^-R'_3X^+$ Quaternary ammonium halide
- H^- From $LiAlH_4$ → R—H Hydrocarbons
- $O^- – N = O$ → R –O-N = O + R Alkyl nitrites
  From Na^+O^--N=O
- $AgNO_3$ → R – O – N = O +R –N(=O)=O
  (Minor) (major)
  Nitro alkanes
- ●● Ag –C≡N → $R – N^+≡C^-$ Isocyanides
- R'Mgx → R—R' Hydrocarbons
- R'Li → R—R' Hydrocarbons
- R'_2CuLi → R—R' Hydrocarbons
- Moist Ag_2O → R—OH
- Dry Ag_2O → R—O—R

Electrophillic s ubstitution sees in aromatic compound mech.

E.g. Nitration – how Electrophiles produce.

$HNO_3 + 2H_2SO_4 \rightarrow NO^+_2\ H_3O^+ + 2HSO^-_4$

OR

$BF_3 + HNO_3 \rightarrow NO_2^+ + HO\text{-}BF_3^-$

Y^+ →

- → N+O2
- → Cl^+ [Cl-Cl +$FeCl_3$ → $Cl^+ + Cl^-$ $FeCl_3$]
- → SO_3 [$2H_2SO_4$ $SO_3+H_3O^++HSO_4^-$

  Sometime

  $SO_3+H_2SO_4 \rightleftharpoons HSO_4^- + HSO_3^+$
- → CH_3^+ [$CH_3Cl+AlCl_3 \rightleftharpoons CH_3^+ - Cl^- - AlCl_3$]
- → CH_3CO^+ [$CH_3COCl+AlCl_3 \rightarrow CH_3CO^+ - AlCl_4^-$]

Elimination reaction

Two groups or atoms attached to two adjacent carbon atom and simultaneous formation of multiple bonds between these carbon atom.[Reverse of addition]

Two types (i) β. Elimination -

- $E_1 \rightarrow$ Two step eliminate
- $E_2 \rightarrow$ One step eliminate

(ii) α- elimination

Saytzaff's Rule

(i)

$CH_3 - CH_2 - CH(Br) - CH_3 \xrightarrow{\text{Aloc.KOH}} CH_3 - CH = CH - CH_3$

81% More highly substituted Alkenes, More stable

Some important name reaction

1. Carbylamines reaction.

$R - NH_2 + CHCl_3 + 3\ KOH \longrightarrow R.NC + 3KCl + 3H_2O$

$C_6H_5NH_2 + CHCl_3 + 3\ KOH \rightarrow C_6H_5NC + 3KCl + 3H_2O$

2. Reimer Tiemann Reaction x

3. **Haloform reaction**

$CH_3CH_2OH \rightarrow 4I_2 + 6\ Na\ OH \rightarrow CHI_3 + HCOONa + 5NaI + 5H_2O$

$CH_3CHOH\ CH_3 + 4I_2 + 6\ Na\ OH \rightarrow CHI_3 + CH_3COONa + 5NaI + 5H_2O$

$CH_3COC_6H_5 + 3I_2 + 4NaOH \rightarrow CHI_3 + C_6H_5COONa + 3NaI + 3H_2O$

4. Wurtz reaction

$R - X + 2Na + xr \xrightarrow{ether} R - R + 2\,NaX$

WurtzFITTIG REACTION

$C_6H_5Br + 2Na + Br + C_2H_5 \xrightarrow{ether} C_6H_5\,C_2H_5 + 2\,NaBr$

Coupling reac.

Diazonium Salt

CONCEPTUAL QUESTIONS

Q1. Why haloalkanes are more reactive than haloarenes.

Ans. In haloarenes, there is double bond character b/w carbon and halogen due to resonance effect which makes him less reactive.

(ii) In benzene, carbon being sp^2 hybridised which is smaller in size than sp^3 present in haloalkanes . So C-Cl bond in aryl halides is shorter and stronger.

Q2. Why do haloalkenes under go nucleophillic substitution whereas haloarenes under go electophillic substitution .

Ans. Due to more electro negative nature of halide atom in haloalkanes carbon atom becomes slightly positive and is easily attacked by nucleophillic reagents.

While in haloarenes due to resonance, carbon atom becomes slightly negative and attacked by electrophillic reagents.

Q3. When an alkyl halide is treated with ethanolic solution of KCN, the major product is alkyl cyanide where as if alkyl halide is treated with AgCN,the major product is alkyl isocyanide.

Ans. KCN is ionic they can attach through C or N but C-C bond is strong than C-N bond. So alkyl cyanide is the major product but AgCN is covalent so more electronegative N can attach to C and forms isocyanides.

Q4. How do 1^0 2^0 3^0 alcohols differ in terms of dehydrogenation?

Ans. 1^0alcohol $\xrightarrow{Cu,300^0c}$ aldehyde

2^0alcohol $\xrightarrow{Cu,300^0c}$ ketone

3^0alcohol $\xrightarrow{Cu,300^0C}$ alkene

Q5. Why are the reaction of alcohol /phenol with acid chloride in the presence of pyridine ?

Ans. Because esterification reaction is reversible and presence of base (pyridine) nuetralises HCl produced during reaction thus promoting forward reaction .

Q6. Explain why o-nitrophenol is more acidic than o-methoxy phenol ?

Ans. $-NO_2$ group is electron with - drawing group, e^- density on O decreases and loss of H^+ is easy whereas $-OCH_3$ group is electron releasing group , which increases e^- density on O , which makes difficult to the loss of H^+, hence are less acidic .

Q7. Aryl halides cannot be prepared by the action of sodium halide in the presence H_2SO_4 .Why?

Ans. Due to resonance the carbon- oxygen bond in phenols has partial double bond and it is stronger than carbon oxygen single bond.

Q8. Why Grignard reagent should be prepared under an hydrous conditions.?

Ans. Grignard reagent react with H_2O to form alkanes , therefore they are prepared under anhydrous condition.

Q9. Why is Sulphuric acid not used during the reaction of alcohols with KI ?

Ans. It is because HI formed will get oxidized to I_2 by concentrated Sulphuric acid which is an oxidizing agent.

Q10. p- dichlorobenzene has highest m.p. than those of ortho and m-isomers.?

Ans. p- dichlorobenzene is symmetrical, fits into crystal lattice more readily and has higher melting point.

Q11. Although chlorine is an electron- withdrawing group, yet it is ortho and para directing in electrophillic aromatic substitution reactions.Why

Ans. Chlorobenzene is resonance hybrid, there is –ve charge at 0 and para positions, electrophillic substitution reaction will take place at 0 and para position due to +R effect. +R effect is dominating over – I effect. .

Q12. The treatment of alkyl chlorides with aqueous KOH lead to the formation of alcohols but in presence of alcoholic KOH alkenes are major products. Explain?

Ans. In aqueous KOH,OH^- is nucleophile which replaces another nucleophile.

$$R\text{-}X + KOH \longrightarrow R\text{-}OH + KX$$

Where as in alcoholic KOH

$$C_2H_5OH + KOH \longrightarrow C_2H_5O^- + K^+$$

$$CH_3CH_2\text{-}Cl + \text{alcoholic KOH} \longrightarrow CH_2 = CH_2 + C_2H_5OH$$

$$(C_2H_5O^-)$$

Q13. Explain why vinyl chloride is unreactive in nucleophillic substitution reaction?

Ans. Vinyl chloride is unreactive in nucleophillic substitution reaction because of double bond character between C=CL bond which is difficult to break.

$$CH_2 = CH - Cl \longrightarrow CH_2^- - CH = Cl^+$$

Q14. Arrange the following compounds according to reactivity towards nucleophillic substitution reaction with reagents mentioned :-

(i) 4- nitro chloro benzene, 2,4 di nitro chloro bemzene, 2,4,6, trinitrochlorobenzene with CH_3ONa

Ans- 2,4,6, trinitrochlorobenzene > 2,4 dinitrochlorobemzene > 4- nitrochlorobenzene

Q15. Which compound will react faster in SN_2 reaction with OH^-?

Ans- (a) CH_3Br and CH_3I (SN_2)

CH_3I will react faster than CH_3Br

(b) $(CH_3)_3C\text{-}Cl$ or CH_3Cl (SN_2)

CH_3Cl will react faster than 3^0 halide

Q16. Arrange in order of boiling points.

(a) Bromobenzene, Bromoform, chloromethane,Dibromo-methane
(b) 1-chloropropane, Isopropyle chloride, 1-Chlorobutane.

Ans. (a) chloromethane < Bromobenzene < Dibromo-methane < , Bromoform

(b) , Isopropyle chloride <1-chloropropane <1-Chlorobutane

(As Branching increases , boiling point decreases)

Q 17. Predict the reactivity in SN_1

(a) $C_6H_5CH_2Br$, $C_6H_5CH(C_6H_5)Br$, $C_6H_5CH(CH_3)Br$, $C_6H_5C(CH_3)(C_6H_5)Br$

Ans. $3^0 > 2^0 > 1^0$ (SN_1)

$C_6H_5C(CH_3)(C_6H_5)Br > C_6H_5(C_6H_5)Br > C_6H_5CH(CH_3)Br > C_6H_5CH_2Br$

(3^0) (2^0) (2^0) (1^0)

Q18. Which compound undergoes SN_1 reaction first ?

(a)

(a) Ans. $3^0 > 2^0 > 1^0$(SN_1)

(b) (2^0)

VERY SHORT ANSWER TYPE QUESTION

[1 MARKS]

Q.1. Write the formula & chemical name of DDT?

Q.2. An alkyl halide having molecular formula C_4H_9Cl is optically active. what is its structure?

Q.3. Why is vinyl chloride less reactive than ethyl chloride?

Q.4. Write the structural isomers of $C_3H_6Cl_2$ which can exihibit enantiomerism ?

Q.5. Write down the structure of the following compounds;

(a) 1- chloro-4-ethyl cyclohexane

(b)1,4-dibrone but-2-ene

(c) 4-tert,butyl-3-iodoheptane

(d)1-bromo-4-secbutyl-2-methylbenzene

Q.6. Which compound $(CH_3)_3$- C-Cl or ; CH_3Cl will react faster in s_n^2 reactionwith –OH?

Q.7. A hydrocarbon C_5H_{10} does not react with chlorine in dark but it gives a single monobromo compound in bright sunlight.identify the compound.

Q.8. Why is sulphuric acid not used during the reaction of alcohols with KI?

Q.9. Out of $C_6H_5CH_2Cl$ & $C_6H_5CH_2Cl$ $_6H_5$ which is more easily hydrolysed with aq. KOH & why ?

Q.10. Chloroform is stored in dark coloured & sealed bottle. why?

Short answer type questions

Q,1. Give the IUPAC names of the following compounds?

A)$ClCH_2C = CCH_2Br$ b) $(CCl_3)_3CCl$

C)$CH_3CH(Cl)CH(Br)CH_3$

Q.2. Starting from methyl iodine, how will you prepare :

A) nitromethane B)methyl nitrite

Q.3. How can iodoform be prepared from ethanol ?

Q.4.predict the product of the following reactions;

Q.5.write the reaction involved in :

A) the isocyanide test

B) iodoform test

Q.6. Rearranging the following in order of increasing case of dehydro halogenations $CH_3CH_2CH_2Cl$, $CH_3CHClCH_3$, $CH_3 - C- Cl(CH_3)^{2.}$

Q.7.how will you distinguish between

(i) CH_3NH_2 and $(CH_3)_2NH$

(ii) ethanol & 1-propanol

Q.8. Give the uses of (a) CCl_4 (b) iodoform

Q.9. Propose the mechanism of the following reaction :

$CH_3\text{-}CH_2\text{-}Br + CH_3O \longrightarrow CH_3\text{-}CH_2\text{-}OCH_3 + Br$

Q.10. Which will have a higher boiling point 1-chloropentane or 2-chloro-2-methylbutane?

Q.11.How will you bring the following conversion?

(a) Propene to Propyne

(b) Toluene to Benzyle Alcohol

(c) Aniline to Phenylisocyanide

Q.12.What happen when;

(a) n-butyl chloride is treated with alc.KOH.

(b) ethyl chloride is treated with aq.KOH.

(c) methyl chloride is treated with KCN.

Q.13Complete the following reaction;

(a)$Cl_2CH\text{-}CH\text{-}Cl_2 + Zn \xrightarrow{\triangle}$

(b)$(CH_3)_2\text{-}CH\text{-}CH\text{-}CH_2\text{-}CH_3$ (Cl) Ethanol $\xrightarrow{C_2H_5ONa}$

(c)$C_6H_5ONa + C_2H_5Cl \longrightarrow$

<u>3 MARKS QUESTIONS</u>

Q1. How can we produce nitro benzene from phenol?

Ans. (I) First convert phenol to benzene by heating with Zn dust.

(II) Nitration of benzene with conc. nitric acid in presence of conc. sulphuric acid.

Q 2. Alcohols reacts with halogen acids to form haloalkenes but phenol does not form halobenzene. Explain

. Ans. The C-O bond in phenol acquires partial double bond character due to resonance and hence be cleared by X^- ions to form halobenzenes. But in alcohols a pure C — O bond is maintained and can be cleared by X^- ions.

Q 3. Explain why o-nitrophenol is more acidic than o-methoxy phenol?

Ans . Due to — R and — I effect of — NO_2 group, e– density on ‗O′ if O — H bond decreases and loss of H+ is easy.– I effect In contrast, in o-methoxy phenol due to + R effect, – OCH_3 increases. e– density on O^2 of O—H group, and hence loss of H+ is difficult.(both –ve charge repel each other)

Q4. Of benzene and phenol, which is more easily nitrated and why?

Ans. Nitration is an electrophilic substitution. The –OH group in phenol increases the electron density at ortho and para position as follows Since phenol has higher electron density due to electron releasing nature of -OH group , compared to benzene , therefore nitration is easy in phenol than benzene.

Q5. How will you account for the following? Ethers possess a net dipole moment even if they are symmetrical in structure?

A. Because of greater electronegativity of o- atom than carbon C – O bonds are polar.
C – O bond are inclined to each other at an angle of 110° (or more), two dipoles do not cancel out each other.

Q 6. How do 1°, 2° and 3° alcohols differ in terms of their oxidation reaction and dehydrogenation ?

Ans. (I) Oxidation reaction : (O) (O)
1° alcohol → aldehyde → carboxylic acid (O) (O)
2° alcohol→ ketone → carboxylic acid (acid with loss of 1 carbon atom) (O)
3° alcohol→ resistant to oxidation
(II) Hydrogenation reaction : give
1° alcohol → aldehyde
2° alcohol → ketone
3° alcohol → alkene 3° alcohols prefer to undergo dehydration and form alken

Q7. (i)How is diethyl ether prepared from ethyl alcohol?

Ans. Ethyl alcohol is first treated with sodium to form sodium ethoxide
C_2H_5OH + Na C_2H_5O– Na+ + H_2
Sodium ethoxide is then treated with ethyl halide to form di ethyl ether. SN^2
C_2H_5O Na + — C_2H_5X → C_2H_5O C_2H_5 + NaX (Williamson synthesis)
(II) Complete the reaction:
(a) CH_3OCH_3 + PCl_5 ?
(b) $C_2H_5OCH_3$ + HCl ?
(c) $(C_2H_5)_2$ O + HCl
A. (a) 2 CH_3Cl (b) CH_3Cl + C_2H_5OH (c) C_2H_5Cl + C_2H_5OH

Q8. Why are reactions of alcohol/phenol and with acid chloride in the presence of pyridine?

Ans. Because esterification reaction is reversible and presence of base (pyridine) neutralises HCl produced during reaction thus promoting forward reaction.

LONG ANSWER TYPE QUESTIONS

Q1) How the following conversions can be carried out?

(i) Propene to propan-1-ol
(ii) 1-Bromopropane to 2-bromopropane
(iii) Toluene to benzyl alcohol
(iv) Benzene to 4-bromonitrobenzene
(v) Benzyl alcohol to 2-phenylethanoic acid

1

2

3

4

5

Q2) How the following conversions can be carried out?

(i) Ethanol to propanenitrile
(ii) Aniline to chlorobenzene
(iii) 2-Chlorobutane to 3, 4-dimethylhexane
(iv) 2-Methyl-1-propene to 2-chloro-2-methylpropane
(v) Ethyl chloride to propanoic acid

6

7

9

10

Q3) How the following conversions can be carried out?

(i) But-1-ene to n-butyliodide
(ii)2-Chloropropane to 1-propanol
(iii) Isopropyl alcohol to iodoform
(iv) Chlorobenzene to p-nitrophenol
(v) 2-Bromopropane to 1-bromopropane

11

12

13

Cl
HNO_3 / H_2SO_4
(Nitration)
Chlorobenzene
NO_2
+
p – Chloronitrobenzene
(Major product)
m – Chloronitrobenzene
o – Chloronitrobenzene

Cl
(i) NaOH, 433 K
(ii) dil HCl
OH
NO_2
p – Chloronitrobenzene
p – Nitrophenol

14

Br
$CH_3 — CH — CH_3$
2 – Bromopropane
KOH (alc) / Δ
Dehydrohalogenation
$CH_3 — CH = CH_2$ + HBr
Propene
(Anti–Markovnikov addition)
HBr / Peroxide
$CH_3 — CH_2 — CH_2 — Br$
1 – Bromopropane

15

Q4) How the following conversions can be carried out?

(i) Chloro ethane to butane

(ii) Benzene to diphenyl

(iii) tert-Butyl bromide to isobutyl bromide

(iv) Aniline to phenylisocyanide

16

17

18

19

ALCOHOLS PHENOLS AND ETHERS

Family	Functional group	Example
Alcohol	R – O – H	CH_3OH methanol
Phenol	Ar – O – H	C_6H_5OH Phenol
Ether		methyletherCH$_3$ OCH$_3$
Aldehyde	- CHO	Acetaldehyde CH_3CHO
Ketone		Acetone CH_3COCH_3
Carboxylic acid		Acetic acid CH_3COOH
Ester		Ester CH_3 – $COOCH_3$ Methyl / acetate
Amide		acetamide CH_3CONH_2
Acid Anhydride		$CH_3COOCOCH_3$ acetic anhydride
Acid chloride		acetyl chloride

IUPAC Name

$CH_3 – O – CH_2 – CH_2 – CH_3$ —— 1- Methoxypropane

$C_6H_5OCH_3$ Methoxy benzene

[Anisole]

$C_6H_5O(CH_2)_6 – CH_3$ 1- Phenoxy heptanes

$CH_3 – O – CH(CH_3) – CH_3$ 2- Methoxy propane

2- ethoxy – 1, 1- dimethyl cyclohexane

Benzene – 1,2 – diol

2,5 – Dimethyl phenol

CH_3-OH	Methanol
$CH_3-CH_2-CH_2-OH$	Propan-1-ol
$CH_3-CH(OH)-CH_3$	Propan-2-ol
$CH_3-CH_2-CH_2-CH_2-OH$	Butan-1-ol
$CH_3-CH(OH)-CH_2-CH_3$	Butan-2-ol
$CH_3-CH(OH)-CH_2-CH_3$	2-Methylpropan-1-ol
$CH_3-C(CH_3)_2-OH$	2-Methylpropan-2-ol
$CH_2(OH)-CH(OH)-CH_2(OH)$	Propane -1, 2, 3-triol

(i)

2,2,4-Trimethylpentan-3-ol

(ii)

5-Ethylheptane-2,4-diol

IUPAC names of phenols

Phenol

2-Methylphenol

3-Methylphenol

4-Methylphenol

Benzene-1,2-diol

Benzene-1,3-diol

Benzene-1,4-diol

2,5-Dimethylphenol

IUPAC names of some ethers

Compound	IUPAC name
CH_3OCH_3	Methoxymethane
$C_2H_5OC_2H_5$	Ethoxyethane
$CH_3OCH_2CH_2CH_3$	1-Methoxypropane
$C_6H_5OCH_3$	Methoxybenzene (Anisole)
$C_6H_5OCH_2CH_3$	Ethoxybenzene
$C_6H_5O(CH_2)_6-CH_3$	1-Phenoxyheptane
$CH_3O-CH(CH_3)-CH_3$	2-Methoxypropane
$C_6H_5-O-CH_2-CH_2-CH(CH_3)-CH_3$	3- Methylbutoxybenzene
$CH_3-O-CH_2-CH_2-OCH_3$	1,2-Dimethoxyethane
	2-Ethoxy- -1,1-dimethylcyclohexane

Name reaction

(1) Reimer Tiemann. Reaction – [See in haloalkanes]
(2) Transesterification
(3) Williamson synthesis
(4) Kolbe reaction
(5) Friedel craft

Transesterification : When an ester treated with excess of another alcohol [other than the one from which ester has been derived] in presence of corresponding sod. Or pot. Alkoxide or an acid H_2SO_4 / HCl as catalyst i.e. also cleavage by analcohol calcolysis

$$R-\overset{\overset{\displaystyle O}{\|}}{C}-OR' + R'-O-H \underset{}{\overset{H^+}{\rightleftharpoons}} R-\overset{\overset{\displaystyle O}{\|}}{C}-OR' + R'-OH$$

Williamson synthesis:- Reaction with alkyl halide with sodium alkoxide or sod. Phenoxide called Williamson synthesis.

$$R-X + R^1-O-Na \longrightarrow R-O-R' + NaX$$

$$H_3I + CH_3CH_2ONa \longrightarrow CH_3O.CH_2-CH_3 + NaI$$

$CH_3CH_2-I +$

$+ NaI$

Both simple and mixed ether can be produced.

Depending upon structure and cleavage of unsymmetrical ethers by halogen acid may occur either by SN^2 or SN^1 mechanism.

e.g. (i) $CH_3 - CH(CH_3) - O - CH_3 + HI \xrightarrow[Sn^2]{373k} CH_3 - I + CH_3 - CH(CH_3) - OH$

(3) $CH_3 - C(CH_3)_2 - O - CH_3 + HI \rightarrow (CH_3)_3 - C - I + CH_3 - OH$

LIMITATIONS OF WILLIAMSON SYNTHESIS

(i) $CH_3 - C(CH_3)_2 - C - O^- Na^+ + CH_3 - CH_2 - Br \longrightarrow CH_3 - C(CH_3)_2 - O - CH_2 - CH_3 + NaBr$

(ii) $CH_3 - C(CH_2-H) - Br + Na^+ - O^- C_2H_5^- \rightarrow CH_3 - C = CH + C_2H_5OH + NaBr$

(iii) $CH_3 - CH(CH_3) - Br + CH_3 - CH_2 - O^- - Na^+$

$CH_3 - CH = CH_2$ $\qquad$ $CH_3 - CH(CH_3) - OCH_2 - CH_3$

79% 21%

Kolbe reaction

2-Hydroxybenzoic acid
(Salicylic acid)

Friedel craft reaction

2-Methoxy-toluene (Minor) 4-Methoxy-toluene (Major)

Ethanoyl chloride 2-Methoxy-acetophenone (Minor) 4-Methoxy-acetophenone (Major)

DISTINCTION BETWEEN PAIR OF COMPOUNDS

When 1^0,2^0, and 3^0 alcohol treated with lucas reagent [con, HCL + an hydrous $ZnCl_2$] at room temp

(i) If turbidity appears immediately alcohol is 3^0.

(ii) If turbidity appears in five minutes alcohol is2^0.

(iii) 1^0 alcohol does not react with L.R. at room temp.

(II) All those compound like alcohol, aldehyde Ketones which on oxidation giving CH_3 - CO^- Group undergoes odoform test.

e.g. (i) CH_3CH_2-OH

(II) CH_3-CHO

(III) $(CH_3) - CH - OH$

(IV) $CH_3 - COCH_3$

(V) $C_6H_5 - CO-CH_3$

(VI) $CH_3 - \underset{\underset{OH}{|}}{CH} - CH_2 - CH_2 - CH_3$

(VII) $CH_3 - \underset{\underset{O}{||}}{C} - CH_2 - CH_2 - CH_3$

Important mechanism

(i) Hydration of alkenes

(i) $H_2SO_4 \rightleftharpoons H^+ + HSO_4^-$

(ii)

(iii)

(iv)

Mechanism

The mechanism of the reaction involves the following three steps:

Step 1: Protonation of alkene to form carbocation by electrophilic attack of H_3O^+.

$H_2O + H^+ \rightarrow H_3O^+$

Step 2: Nucleophilic attack of water on carbocation.

Step 3: Deprotonation to form an alcohol.

Important reaction

(2) Preparation of phenol from Cumene

(3) Preparation of aspirin and salol

Explain phenol is acidic?

Phenpxide ion is resonance stabilised

:- If electron with drawing group are attached into the benzene ring it enchance acidic character and vice versa.

2,4,6 trinitrophenol > 2,4, dinitrophenol > 4-nitrophenol > phenol

Phenol > m- cresol > P cresol > O cresol

m-methoxyphenol > phenol > O methoxy phenol > P methoxy phenol.

O chloro phenol > O bromophenol > O iodo phenol > O fluoro phenol

FORMATION OF PICRIC ACID

(I)

2,4,6 tribromo phenol (white plot)

(I)Phenol gives violet colour with $fecl_3$ solution .

PREPARATION OF $1^0, 2^0, 3^0$ ALCOHOLS

$HCHO + R\ Mg\ x$ → $R\text{-}CH_2OH$ 1^0 alc

$CH_3CHO + R\ Mg\ x$ → $(R)(R)(CH_3)CHOH$ 2^0 alc

$(CH_3)(CH_3)C{=}0 + CH_3\ Mg\ Br$ → $(R)(R)(R)C\text{-}OH$ 3^0 alc

$\{R \rightarrow CH_3\}$

CONCEPTUAL QUESTIONS

Q1) Preparation of ethers by acid dehydration of secondry or 3^0 alcohols is not a suitable method?

Ans:- The formation of ethers by dehydration of alcohol is a bimolecular reaction (SN_2) group is hindered. as a result elimination dominates substitution as 3^0 carbocation is more stable. Hence in place of others , alkenes are formed.

$(CH_3)(CH_3)(CH_3)C - OH \xrightarrow[\text{CON.}]{H_2SO_4} (CH_3)(CH_3)C = CH_2$

Q2) Phenols do not give protonation reactions readily. Why?

Ans:- The lone pair on oxygen of O-H in phenol is being shared with benzene ring through resonance.Thus,lone pair is not fully present on oxygen and hence phenols do not undergo protonatian reactions.

Q3) Ortho- nitrophenol is more acidic than ortho –methoxy phenol ? why?

Ans:- NO_2 group is electron with drawing which increases acidic charcter due to easily ease

REASONING QUESTIONS

Q1. Explain why propanol has higher boiling point than that of the hydrocarbon, butane?

Ans . The molecules of Butane are held together by weak van der Waal's Forces of attraction while those of propanol are held together by stronger intermolecular hydrogen bonding.

Q2. Alcohols are comparatively more soluble in water than hydrocarbons of comparable molecular masses. Explain this fact.

Ans. Alcohols can form hydrogen bonds with water and break the hydrogen bonds already existing between water molecules Therefore they are soluble in water. Whereas hydrocarbons cannot form hydrogen bonds with water and hence are insoluble in water.

Q3 . While separating a mixture of ortho and para nitrophenols by steam distillation, name the isomer which will be steam volatile. Give reason.

ANS. O-nitrophenol is steam volatile due to intramolecular hydrogen bonding and hence can be separated by steam distillation from p-nitrophenol which is not steam volatile because of inter-molecular hydrogen bonding.

Q4. Explain why is ortho nitrophenol more acidic than ortho methoxyphenol?

o – Nitrophenol

o – Methoxyphenol

ANS. The nitro-group is an electron-withdrawing group. The presence of this group in the ortho position decreases the electron density in the O-H bond . As a result, it is easier to lose a proton. Also,the o-nitrophenoxide ion formed after the loss of proton is stabilized by resonance. Hence,ortho-nitrophenol is stronger acid.On the other hand, methoxy group is an electron-releasing group. Thus ,it increases the electron density in the O-H bond and hence, the proton cannot be given out easily. Therefor ortho-nitrophenol is more acidic than ortho- methoxyphenol.

Q5. Preparation of ethers by acid dehydration of secondary or tertiary alcohols is not a suitable method. Give reason.

ANS. The formation of ethers by dehydration of alcohol is a bimolecular reaction $(SN)_2$
involving the attack of an alcohol molecule on a protonated alcohol molecule. In the method, the alkyl group should be unhindered. In case of secondary or tertiary alcohols, the alkyl group is hindered. As a result, elimination dominates substitution.

Q6. What is meant by hydroboration-oxidation reaction? Illustrate it with an example .

ANS. Diborane $(BH_3)_2$ reacts with alkenes to give trialkyl boranes as addition product. This is oxidised to alcohol by hydrogen peroxide in the presence

of aqueous sodium hydroxide.

Q7. Give the equations of reactions for the preparation of phenol from cumene.

Ans.

Q8. Write chemical reaction for the preparation of phenol from chlorobenzene.

Ans. Chlorobenzene is fused with NaOH at 623K and 320 atmospheric pressure. Phenol is obtained by acidification of sodium phenoxide so produced.

Q9. How is aspirin (Acetylsalicylic acid) prepared from salicylic acid? Ans. Acetylation of salicylic acid produces aspirin.

Q10. Which out of propan-1-ol and propan-2-ol is stronger acid?

Ans. Propan-1-ol is stronger acid than propan-2-ol. The acidic strength of alcohols is in the order $1^0 > 2^0 > 3^0$.

Q11. What is denaturation of an alcohol?

Ans. The commercial alcohol is made unfit for drinking by mixing in it some copper sulphate (to give it a colour) and pyridine (a foul smelling liquid). It is known as denaturation of alcohol.

Q12. Give IUPAC name of $CH_3OCH_2OCH_3$

ANS. Dimethoxymethane

Q13. Diethyl ether does not react with sodium. Explain.

ANS. Diethyl ether does not contain any active hydrogen.

2 MARKS QUESTIONS

Q1. Give two reactions that show the acidic nature of phenol. Compare acidity of phenol with that of ethanol.

ANS. The acidic nature of phenol can be represented by the following two reactions: (i) Phenol reacts with sodium to give sodium phenoxide, liberating H_2.

(ii) Phenol reacts with sodium hydroxide to give sodium phenoxide and water as by-products

The acidity of phenol is more than that of ethanol. This is because after losing a proton, the phenoxide ion undergoes resonance and gets stabilized whereas ethoxide ion does not.

Q2. How does phenol react with dilute and conc. HNO_3 ?

ANS. (i) With dilute nitric acid at low temperature (298 K), phenol yields a mixture of ortho

and para nitrophenols. (ii) With concentrated nitric acid, phenol is converted to 2,4,6-trinitrophenol. The product is commonly known as picric acid.

Q3. How does phenol react with Br_2 in CS_2 and Bromine water?

ANS. (i) When the reaction is carried out in solvents of low polarity such as $CHCl_3$ or CS_2 and at low temperature, monobromophenols are formed.

(iii) When phenol is treated with bromine water, 2,4,6-tribromophenol is formed as white precipitate.

2,4,6-Tribromophenol

Q4. How do you account for the fact that unlike phenol, 2, 4-dinitrophenol and 2, 4, 6-trinitrophenol are soluble in aqueous solution of sodium carbonate?

ANS. 2, 4-Dinitrophenol and 2, 4, 6-trinitrophenol are stronger acids then carbonic acid (H_2CO_3) due to the presence of electron withdrawing – NO_2 groups. Hence, they react with Na_2CO_3 to form their corresponding salts and dissolve in aq. Na_2CO_3 solution.

Q5 . (i) Why is the Dipole moment of methanol higher than that of phenol? (ii) . Explain why phenols do not undergo substitution of the –OH group like alcohols.

ANS. (i) Due to electron withdrawing effect of phenyl group, the C—O bond in phenol is less polar, whereas in case of methanol the methyl group has electron releasing effect and hence C—O bond in it is more polar.

(ii) C—O bond in phenols has partial double bond character due to resonance and hence is difficult to cleave.

Q6. Account for the following

a. Boiling point of the C_2H_5OH is more than that of C_2H_5Cl

b. The solubility of alcohols in water decreases with increase in molecular mass.

ANS. a. Because of hydrogen bonding.

b. With increase in molecular mass the non-polar alkyl group becomes more predominant.

Q7. Answer the following

a. What is the order of reactivity of 10, 20 and 30 alcohols with sodium metal?

b. How will you account for the solubility of lower alcohols in water?

ANS: a. 10>20>30.

b. Here—OH group is predominant and the alcohol molecules can form hydrogen bonds with water molecules.

Q8. Give reasons:

i)Nitration of phenol gives ortho- and para- products only.

ii)Why do alcohols have higher boiling points than the haloalkanes of the same molecular mass?

ANS (1) -OH group increases the electron density more at ortho and para positions through its electron releasing resonance effect.

(2) Alcohols are capable of forming intermolecular H-bonds.

Q9. Account for the following:

i) Phenols has a smaller dipole moment than methanol

ii) Phenols do not give protonation reactions readily.

ANS. (a). In phenol the electron withdrawing inductive effect of –OH group is opposed by electron releasing the resonance effect of –OH.

(b). The lone pair on oxygen of –OH in phenol is being shared with benzene ring through resonance. Thus, lone pair is not fully present on oxygen and hence phenols do not undergo protonation reactions.

Q10. Explain the fact that in aryl alkyl ethers
(i) The alkoxy group activates the benzene ring towards electrophilic substitution and
(ii) It directs the incoming substituents to ortho and para positions in benzene ring.

Aryl alkyl ether

ANS. (i)
In aryl alkyl ethers, due to the +R effect of the alkoxy group, the electron density in the benzene ring increases as shown in the following resonance structure.

Thus, benzene is activated towards electrophilic substitution by the alkoxy group.

(ii) It can also be observed from the resonance structures that the electron density increases more at the ortho and para positions than at the meta position. As a result, the incoming substituents are directed to the ortho and para positions in the benzene .

3 MARKS QUESTIONS

Q1. How are primary, secondary and tertiary alcohols prepared from Grignard Reagents?

ANS.

.

The reaction produces a primary alcohol with methanal, a secondary alcohol with other aldehydes and tertiary alcohol with ketones.

Q2. Give the equations of oxidation of primary, secondary and tertiary alcohols by Cu at 573 K.

ANS.

Q3. Give equations of the following reactions:
(i) Oxidation of propan-1-ol with alkaline $KMnO_4$ solution.
(ii) Bromine in CS_2 with phenol.
(iii) Dilute HNO_3 with phenol.

ANS. (i)

$$CH_3CH_2CH_2OH \xrightarrow{\text{alk } KMnO_4} CH_3CH_2COOH$$

Propan-1-ol Propanoic acid

Q4. Show how will you synthesize:

(i) 1-phenylethanol from a suitable alkene.

(ii) (ii) cyclohexylmethanol using an alkyl halide by an SN_2 reaction.

(iii) (iii) pentan-1-ol using a suitable alkyl halide?

ANS. (i) By acid-catalyzed hydration of ethylbenzene (styrene), 1-phenylethanol can be synthesized.

(ii) When chloromethylcyclohexane is treated with sodium hydroxide, cyclohexylmethanol is obtained.

(iv) When 1-chloropentane is treated with NaOH, pentan-1-ol is produced.

$$\underset{\text{1-Chloropentane}}{CH_3CH_2CH_2CH_2CH_2Cl} + NaOH \longrightarrow \underset{\text{Pantan-1-ol}}{CH_3CH_2CH_2CH_2CH_2OH} + NaCl$$

Q5. How are the following conversions carried out?

(i)Propene → Propan-2-ol

(ii) Benzyl chloride → Benzyl alcohol

(iii) Ethyl magnesium chloride → Propan-1-ol.

ANS. (i)If propene is allowed to react with water in the presence of an acid as a catalyst, then propan-2-ol is obtained.

(ii) If benzyl chloride is treated with NaOH (followed by acidification) then benzyl alcohol is produced.

(iii)When ethyl magnesium chioride is treated with methanol, an adduct is the produced which gives propan -1-ol on hydrolysis.

Q6. Name the reagents used in the following reactions:

(i) Oxidation of a primary alcohol to carboxylic acid.

(ii) (ii) Oxidation of a primary alcohol to aldehyde.

(iii) Bromination of phenol to 2,4,6-tribromophenol.

ANS. (i) Acidified potassium permanganate

(ii) Pyridinium chlorochromate (PCC)

(iii) Bromine water

Q7. How is 1-propoxypropane synthesised from propan-1-ol? Write mechanism of this reaction.

ANS. 1-propoxypropane can be synthesized from propan-1-ol by dehydration. Propan-1-ol undergoes dehydration in the presence of protic acids (such as H_2SO_4, H_3PO_4) to give 1-propoxypropane.

$$2CH_3CH_2CH_2-OH \xrightarrow{H^+} CH_3CH_2CH_2-O-CH_2CH_2CH_3$$

Propane-1-ol 1-Propoxypropane

The mechanism of this reaction involves the following three steps:

Step 1: Protonation

Step 2: Nucleophilic attack

Step 3: Deprotonation

Q8. Write the equation of the reaction of hydrogen iodide with:

(i) 1-propoxypropane (ii) Methoxybenzene and (iii) Benzyl ethyl ether

ANS. (i)

$$C_2H_5CH_2-O-CH_2C_2H_5 + HI \xrightarrow{373K} CH_3CH_2CH_2-OH + CH_3CH_2CH_2-I$$

1-Propoxypropane Propan-1-ol 1 – Iodopropane

(ii)

(iii)

5 MARKS QUESTIONS

Q1. Write equations of the following reactions:

(i) Friedel-Crafts reaction−alkylation of anisole.

(ii) Nitration of anisole.

(iii) Bromination of anisole in ethanoic acid medium.

(iv) Friedel-Craft's acetylation of anisole.

(v)Reaction of phenol with Zn dust.

ANS. (i)

(ii)

OCH3
H2SO4
HNO3
NO2
Anisole
2 – Nitroanisole
(Minor)
4 – Nitroanisole
(Major)

(iii)

OCH3
Br2 in
Ethanoic acid
Br
Anisole
p – Bromoanisole
(Major)
o – Nitroanisole
(Minor)

(iv)

OCH3
CH3COCl
Anhyd.AlCl3
COCH3
Anisole
Ethanoyl chloride
2 – Methoxy –
acetophenone
(Minor)
4 – Methoxy –
acetophenone
(Major)

(v)

OH
Zn
ZnO

Na
$C_2H_5ONa + H_2$
NaH
$C_2H_5ONa + H_2$
$HCl_{(g)}$
C_2H_5Cl
$HBr_{(g)}$
C_2H_5X
(PCl_5, PCl_3, I_2)
$SOCl_2$
C_2H_5Cl
CH_3-C-OH/H^+
$CH_3-COC_2H_5$
CH_3-C-Cl
$CH_3-C-OC_2H_5$
$K_2Cr_2O_7/H^+$
CH_3-C-OH
Cu/575 K
CH_3-C-H

CHCl3
NaOH
CHO
NaOH
H
Na2Cr2O7
H2SO4

ALDEHYDES, KETONES AND CARBOXYLIC ACIDS

The π Electron cloud of >C=O is unsymmetrical .On the other hand, due to same electonegativity of the two carbon atoms, the π-electron of the >C=C< bond is symmetrical.

Nature of carbonyl group:- The Pi electron cloud of >C=O is unsymmetrical therefore, partial positive charge develop over carbon of carbonyl group while negative charge develop over oxygen of carbonyl group and dipole moment is approximate 2.6D.

FORMULA	NAME OF THE CORRESPONDING ACID	COMMON NAME	IUPAC NAME
HCHO	HCOOH(formic acid)	Formaldehyde	Methanal
CH_3CHO	CH_3COOH(Acetic acid)	Acetaldehyde	Ethanal
CH_3CH_2CHO	CH_3CH_2COOH(Propanoic acid)	Propionaldehyde	Propanal
$CH_3CH_2CH_2CHO$	$CH_3CH_2CH_2COOH$(Butyric acid)	Butyraldehyde	Butanal
$CH_3CH(CH_3)CHO$	$CH_3CH(CH_3)COOH$(Isobutyric acid)	Isobutyraldehyde	2-Methylpropanal
$CH_3CH_2CH(CH_3)CHO$	$CH_3CH_2CH(CH_3)COOH$(α-Methylbutyic acid)	α-Methylbutyraldehyde	2-Methylbutanal
$CH_3CH(CH_3)CH_2CHO$	$CH_3CH(CH_3)CH_2COOH$ (β-Methylbutyric acid)	B-Methylbutyraldehyde	3-Methylbutanal
			2-Phenylethanal

FORMULA	COMMON NAME	IUPAC NAME
CH_3COCH_3	Dimethyl Ketone or acetone	Propanone
$CH_3COCH_2CH_3$ 1 2	Ethyl methyl Ketone	Butan-2-one or Butanone
$CH_3COCH_2CH_2CH_3$ 1 2 3	Methyl n-propyl Ketone	Pentan-2-one
$CH_3CH_2COCH_2CH_3$	Diethyl Ketone	Pentan-3-one

Addition to C=O bonds

The structure of the carbonyl group in aldehydes and Ketones is , not entirely adequately represented by >C=O, nor by the alternative $>C^{+}-O^{-}$. The real structure or resonance hybrid lies somewhere between the following structure:

$$>C=O \longleftrightarrow >C^{+}=O^{-}$$

For Mechanism

Second Mechanism

As we know that anion is more stable than the cation, thus the addition to carbonyl groups should take place via mechanism second which has been further proved in the addition of HCN to carbonyl group.

Reactivity of aldehyde and Ketones is as
HCHO>RCHO>RCOR>RCOOR>$RCONH_2$.

POINTS TO REMEMBER

:-Aldehydes, Ketones and Carboxylic acids are important classes of organic compounds containing carbonyl groups.
:-They are highly polar molecules.
:-They boil at higher temperatures than the corresponding hydrocarbons and weakly polar compounds such as ethers.
:-Lower members are soluble in water because they can form H-bond with water.
:-Higher members are insoluble in water due to large size of their hydrophobic group.
:-Aldehydes are prepared by-

a. Dehydrogenation of primary alcohols
b. Controlled oxidation of primary alcohols.
c. Controlled and selective reduction of acyl halides
Aromatic aldehydes can be prepared by-
a. Oxidation of toluene with chromyl chloride or CrO_3 in the presence of acetic anhydride
b. Formylation of arenes with carbon monoxide and Hydrochloric acid in the
presence of anhydrous aluminiumchloride / Cuprous chloride
c. Hydrolysis of benzal chloride

Ketones are prepared by-
a. oxidation of secondary alcohols
b. Hydration of alkenes
c. Reaction acyl chlorides with dialkylcadmium
d. By friedel crafts reaction

Carboxylic acids are prepared by –
a. oxidation of primary alcohols, aldehydes and alkenes
b. hydrolysis of nitriles
c. Treatment of grignard reagent with carbondioxide.

NAME REACTIONS

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ROSENMUND REDUCTION:

. **ROSENMUND REDUCTION**:

Acyl chlorides when hydrogenated over catalyst, palladium on barium

sulphate yield aldehydes

Benzoyl chloride Benzaldehyde 2

2. **STEPHEN REACTION**

Nitriles are reduced to corresponding imines with stannous chloride in the presence of Hydrochloric acid, which on hydrolysis give corresponding aldehyde.

$$RCN + SnCl_2 + HCl \longrightarrow RCH{=}NH \xrightarrow{H_3O} RCHO$$ 3.

ETARD REACTION

On treating toluene with chromyl chlorideCrO_2Cl_2, the methyl group is oxidized to a chromium complex, which on hydrolysis gives corresponding benzaldehyde.

OR

Toluene Chromium complex Benzaldehyde

This reaction is called **Etard reaction**.

CLEMMENSEN REDUCTION

The carbonyl group of aldehydes and ketone is reduced to $-CH_2$ group on treatment with zinc amalgam and conc. Hydrochloric acid.

$$>C=O \xrightarrow[HCl]{Zn\text{-}Hg} >CH_2 + H_2O$$

Alkanes –

WOLFF- KISHNER REDUCTION

On treatment with hydrazine followed by heating with sodium or potassium hydroxide in high boiling solvent like ethylene glycol

$$>C=O \xrightarrow[-H_2O]{NH_2NH_2} >C=NNH_2 \xrightarrow[\text{Heat}]{\text{KOH/ethylene glycol}} >CH_2 + N_2$$

ALDOL CONDENSATION

Aldehydes and ketones having at least one α-hydrogen condense in the presence of dilute alkali as catalyst to form β-hydroxy alddil ehydes (aldol) or β-hydroxy ketones (ketol).

$$\underset{\text{ethanal}}{2CH_3\text{-}CHO} \underset{}{\overset{NaOH}{\rightleftharpoons}} \underset{\underset{OH\ (Aldol)}{|}}{CH_3\text{-}CH\text{-}CH_2\text{-}CHO} \xrightarrow[-H_2O]{} \underset{\text{But-2-enal}}{CH_3\text{-}CH=CH\text{-}CHO}$$

$$\underset{\text{Propanone}}{2CH_3\text{-}CO\text{-}CH_3} \underset{}{\overset{Ba(OH)_2}{\rightleftharpoons}} \underset{\underset{OH\ (Ketal)}{|}}{CH_3\text{-}\overset{\overset{CH3}{|}}{C}\text{-}CH_2\text{-}CO\text{-}CH_3} \xrightarrow[-H_2O]{\text{Heat}} \underset{\text{4-Metylpent-3-en2-one}}{CH_3\text{-}\overset{\overset{CH_3}{|}}{C}=CH\text{-}CO\text{-}CH_3}$$

CROSS- ALDOL CONDENSATION

When aldol condensation is carried out between two different aldehydes and / or ketones,a mixture of self and cross-aldol products are obtained.

$$\underset{+\ CH_3\text{-}CH_2\text{-}CHO}{CH_3CHO} \xrightarrow[2\ \triangle]{1\ NaOH} \underset{\text{But-2-enal}}{CH_3CH=CH\text{-}CHO} + \underset{\text{2-Methylpent-2-ena}}{CH_3CH_2CH=\underset{\underset{CH_3}{|}}{C}\text{-}CHO}$$

$$CH_3\text{-}CH=C\text{-}CHO + CH_3CH_2\text{-}CH=CHCHO$$

CH_3 CH_3

2 -Methylbut-2-enal Pent-2-enal

CANNIZARO REACTION

Aldehydes which do not have an α-hydrogen atom, undergo self oxidation and reduction (dispropotionation) reaction on treatment with concentrated alkali ,to yield carboxylioc acid salt and an alcohol respectively.

H-CHO + H-CHO + Conc.KOH $\longrightarrow$ CH_3OH + HCOOK

Formaldehyde

-CHO + NaOH (con.) $\xrightarrow{\text{Methanol}}$ Pot. Formate $C_6H_5CH_2OH$ + C_6H_5COONa

Benzaldehyde Benzyl alcohol Sodium benzoate

CARBOXYLIC ACID

1. **HELL-VOLHARD-ZELINSKY REACTION (HVZ)**

Carboxylic acids having an α – hydrogen are halogenated at the α –position on treatment with chlorine or bromine in the presence of small amount of red phosphorus to give α –halocarboxylic acids.

$$RCH_2\text{-}COOH \xrightarrow[\text{ii } H_2O]{\text{i } X_2/\text{ Red phosphorus}} R\text{-}\underset{\underset{X}{|}}{CH}\text{-}COOH$$

X= Cl ,Br

α –halocarboxylic acids

2. **ESTERIFICATION**

Carboxylic acids react with alcohols or phenols in the presence of a mineral acid such as conc.H_2SO_4 as catalyst to form esters.

H^+

$$\underset{\text{Carboxylic acid}}{RCOOH} + \underset{\text{alcohol}}{R'OH} \rightleftharpoons \underset{\text{Ester}}{RCOOR'} + H_2O$$

3. **DECARBOXYLATION**:

4. Carboxylic acids lose carbondioxide to form hydrocarbons when their sodium salts are heated with sodalime NaOH and CaO in the ratio 3: 1 .

5. $$RCOONa \xrightarrow{NaOH \text{ and } CaO \,/\, \Delta} R\text{-}H + Na_2CO_3$$

MECHANISMS

.

1. $$CH_3CH_2OH \xrightarrow[443\ K]{Con\ H_2SO_4} CH_2 = CH_2 + H_2O$$

Mechanism:

(i) $H_2SO_4 \rightleftharpoons H^+ + HSO_4^+$

(ii) $CH_3CH_2 - O - H + H^+ \longrightarrow CH_3 - CH_2 - O^+ - H$
$\qquad\qquad\qquad

Mechanism:-

i) $H_2SO_4 \longrightarrow H^+ + HSO_{-4}^{\ -}$

+

ii) $CH_3\ CH_2\ OH + H^+ \longrightarrow CH_3 - CH_2 - O - H$

$$\begin{array}{c} | \\ H \end{array}$$

(iii) $CH_3CH_2 - \underset{\underset{H}{|}}{O^+} - H \longrightarrow CH_3\ CH_2^{\ +} + H_2O$

iv) $CH_3\ CH_2 - O - H + CH_3\ CH_2^{\ +} \longrightarrow CH_3 - CH_2 - \underset{\underset{CH_2CH_3}{|}}{O^+} - H$

v) $CH_3CH_2 - \underset{\underset{CH_2CH_3}{|}}{O^+} - H \longrightarrow CH_3CH_2 - O - CH_2CH_3 + H^+$

vi) $HSO_4^- + H^+ \longrightarrow H_2SO_4$

NOMENCLATURE

a. $CH_3CH\ CH_3\ CH_2CH_2CHO$
   4-Methylpentanal

b. $CH_3CH_2COCH\ C_2H_5\ CH_2CH_2Cl$
   6-chloro-4-ethylhexan-3-one

c. $CH_3CH{=}CHCHO$
   But-2- enal

d. $CH_3COCH_2COCH_3$
   Pentane. 2,4-dione .

e. $OHCC_6H_4CHO$-p
   Benzene-1,4-di carbaldehyde

f. $CH_3CH_2CHC_6H_5CHO$
   2-Phenylbutanal

2. Draw the structures of the following compounds;

(i) p-Methylbenzaldehyde

Ans. OHC - - CH_3

(ii) 4-Methypent-3-en-2-one

Ans. CH_3-C(=O)-CH=C(CH_3)-CH_3

iii) 3-Bromo-4-phenylpentanoic acid

Ans. CH_3-CH(C_6H_5) -CH(Br)-CH_2-COOH

iv)Hex-2-en-4-ynoic acid

Ans. CH_3-C□C-CH=CH-COOH

DISTINGUISH

Q1:-Distinguish between the following:-

(a) Phenol and alcohol

(b) Benzaldehyde and Propanal

(c) Acetic acid and formic acid

(d) Benzophenone and acetophenone

(e) Ethanal and propanal

(f) Propanol and ethanol

(g) Pentanone-2 and pentanone-3

(h) 2 Alcohol and 3 alcohol

(i) 1,2,3 amine

(j) Benzoic acid and benzene

(k) Phenol and benzoic acid

(l) Aniline and ethyl amine

(m) Aniline and nitrobenzene

(n) Benzaldehyde and acetophenone

(o) Methanol and benzaldehyde

(p) Chloro benzene and benzyl chloride

ANSWERS

(a) Phenol
It gives $FeCl_3$ test
(voilet colour)

Alcohol
It doesn't give this test

(b) Benzaldehyde
It gives tollen's

It doesn't give fehling solution test

Propanal
It also give tollen's reagent test
It gives fehling solution test

(c) Acetic acid
It doesn't gives tollen's reagent
It doesn't give fehling's test

Formic acid
It gives tollen's test
It gives fehling test

(d) Benzophenone
It doesn't give iodoform test

Acetophenone
It gives iodoform test

(e) Ethanal
It gives iodoform test

Propanal
It doesn't gives iodoform test

(f) Propanol
It doesn't give iodoform test

Ethanol
It gives iodoform test

(g) pentanone-2
It gives iodoform test

pentanone-3
It doesn't gives iodoform test

(h) 2 alcohol

It takes 5 minutes

3 alcohol

turbility is formed within no seconds

(i) 1 amine

$C_2H_5NH_2 + C_6H_5SO_2Cl \longrightarrow C_6H_5NH\text{-}SO_2\text{-}C_6H_5$

(benzene sulphonyl chloride) soluble in alkali

2 amine

$C_2H_5\text{-}NH(C_2H_5) + C_6H_5SO_2Cl \longrightarrow C_2H_5\text{-}N(C_2H_5)\text{-}SO_2C6H_5$

Insoluble in KOH

3 amine

$C_2H_5\text{-}N(C_2H_5)\text{-}C_2H_5 + C_6H_5SO_2Cl \longrightarrow X$ (No reaction)

(J)

Benzoic acid	Benzene
add $NaHCO_3$	no effervescence
Effervescence obtained(CO_2)	obtained

(k)

Phenol	Benzoic acid
It gives voilet colour with $FeCl_3$ test	It doesn't give voilet colour with $FeCl_3$
It doesn't give effervescenes of CO_2	Effervescence of CO_2 evolve when $NaHCO_3$ is added

(l)

Aniline	Ethyl amine
It gives azo-dye test (orange dye)	It doesn't give azo-dye

(m)

Aniline	Nitrobenzene
It gives azo-dye test	It doesn't

(n)

Benzaldehyde	Acetophenone
It gives tollen's test	It doesn't
It doesn't give iodoform test	It gives iodoform test

(o)

Methanal	Benzaldehyde
It gives fehling solution test	It doesn't

(p)

Chloro benzene	Benzyl choride

CONCEPTUAL QUESTIONS

Q1) Although phenoxide ion has more no. of resonating structures than carboxylate ion , even though carboxylic acid is a stronger acid why ?

Ans:- The phenoxide ion has non equivalent resonance structures in which –ve charge is at less electronegative C atom and +ve charge as at more electronegative O-atom.

In carboxylate ion –ve charge is delocalized on two electronegative O-atoms hence resonance is more effective and a stronger acid.

Q.2 Why Corboxylic acid have higher boiling point than alcohols as alcohol forms strongest inter molecular hydrogen bonding?

Ans. As Corboxylic acid forms a dimer due to which their surface area increses and forms strong intermolecular H-bonding

- It having more boiling point than alcohols.

Q.3 There are two-NH_2 group in semicarbazide . However only one is involved in formation of semicarbazones. Why?

Ans.

Due to resonance one NH_2 group undergoes or involved in resonance and hence can't participate in the formation of semicarhazone.

Long pair of NH_2 group is not involved in resonance and is available for nucleophillic attack

Q.4 Why does solubility decreases with increasing molecular mass in carboxytic acid?

Ans. Because of increase in alkyl chain length which is hydrophobic in nature.

Hence solubility decreases.

Q.5 Why are aldehydes are more reactive than ketones when undergo nucleophillic addition reaction?

Ans (a) + I effect:- The alkyl group in Ketones due to their e-releasing character decrease the +ve charge on C-Atom and thus reduce its reactivity.

(b) Steric hinderance:- Due to steric hinderance in ketones they are less reactive.

Q.6 Why PCC cannot oxidise methanol to methanoic acid and while $KMNO_4$ can?

Ans. This is because PCC is a mild oxidising agent and can oxide methanol to methanal only.

While $KMNO_4$ being strong oxidising agent oxidises it to methanoic acid.

Q.7 During preparation of esters from a carboxylic acid and an alcohol in the presence of acid catalyst water or ester formed should be removed as soon as it is formed.

Ans. The formation of esters from a carboxylic acid and an alcohol in the presence of acid catelyst in a reversible reaction.

$$R - COOH + R'OH \xrightleftharpoons{H_2SO_4} R - COOR' + H_2O$$

To shift the equilibrium in forward direction, the water or ester formed should be removed as fast as it is formed.

Q.8 Why HCOOH does not give HVZ reaction while CH_3COOH does?

Ans. CH_3COOH contains α-hydrogens and hence give HVZ reaction but HCOOH does not contain α-hydrogen and hence does not give HVZ reaction.

Q.9 Suggest a reason for the large difference in the boling point of butanol and butanal although they have same solubility in water.

Ans. Because Butanol has strong intermolacular H-bonding while butanal has weak dipole-dipole interaction.

However both of them form H-bonds with water and hence are soluble.

Q.10 Would you expect benzaldehyde to be more reactive or less reactive in nuderophillic addition reaction than propanol. Explain.

Ans. C-atom of Carbonyl group of benzaldehyde is less electrophilic than C-atom of Carbonyl group in propanol.

Polarity of Carbonyl group is in bonzaldehyde reduced due to resonance making it less reactive in nucleophillic addition reactions.

Q.11 Why does methanal not give aldol condensation while ethanol gives?

Ans. This is because only those compounds which have α-hydrogen atoms can undergo aldol reaction ethanol pessess α-hydrogen and undergoes aldol condensation Methanal has no alpha hydrogen atoms hence does not undergo aldol condensation.

Q.12 Why does methanal undergo cannizaro's reaction?

Ans. because it does not possesses α-hydrogen atom.

Q.13 Which acid is stronger and why?

$F_3C\text{-}C_6H_4COOH$ and $CH_3C_6H_4COOH$

Ans . CF_3^- has strong (-I)effect
Whereas, CH_3^- has strong (+I)effect
Due to greater stability of $F_3CC_6H_4COO$ ion over $CH_3\text{-}C_6H_4COO$ ion
$CF_3\ C_6H_4COOH$ is much stronger acis than $CH_3\text{-}C_6H_4COOH$.

Q.14 Explain why O-hydroxy benzaldehyde is a liquid at room temperature while p- hydroxy benzaldehyde is a high melting solid.

Ans. Due to intramolecular H-bonding in O-hydroxy benzaldehyde exists as discrete molecule whereas due to intermolecular H-bonding p-hydroxy benzaldehyde exist as associated molecules.

To break this intermolecular H-bonds a large amount of energy is needed. Consequently P-isomer has a much higher m.p. and b.p. than that of O-isomer. As a result O-hydroxy benzaldehyde is liquid.

Q.15 Why is the boiling point of an acid anhydride higher than the acid from which it is derived?

Ans . Acid anhydrides are bigger in size than corresponding acids have more surface area more van der Waals. Force of attraction hence have higher boiling point.

Q.16 Why do Carboxylic acids not give the characteristic reactions of a carbonyl group?

Ans. Due to resonance, It doesn't give the characteristics reactions of carbonyl group. It does not have free

$>C=O$ group

Q.17 Cyclohexanone forms cyanohydrin in good yield but 2,2,6 trimethyle cyclo-hexanone does not. Why?

Ans . In 2,2,6 trimethyl cyclohexaunone there is strearic hinderance of 3 methyl groups, It does not form cynohydrin in good yield.

Q.18 Why is carboxyl group in benzoic acid meta directing?

Ans. In benzoic acid the Carboxyl group is meta directing because it is electron-withdrawing

There is +ve charge on ortho acid para positions

Electrophillic substitution takes place at meta-position.

Q.19 Treatment of Benzaldehyde with HCN gives a mixture of two isomers which cannot be separated even by careful fractional distillation. Explain why?

Ans. It is because we get two optical isomers which have same physical properties

Cannot be Separated by Fractional distillation.

Q.20 Sodium Bisulphite is used for the purification of aldehydes and Ketones. Explain.

Ans. Aldehydes and Ketones form addition compounds with $NaHSO_3$ whereas impurities do not.

On hydrolysis we get pure aldehydes and Ketones back.

(PURE)

Q.21 Why pH of reaction should be carefully controlled while preparing ammonia derivatives of carbonyl compound?

Ans. In strongly acidic medium ammonia derivatives being basic will react with acids and will not react with carbonyl compound. In basic mesium, OH^- will attack carbonyl group.

pH of a reaction should be carefully controlled.

Q.22 Why formic acid is stronger acid than acetic acid?

Ans. Due to +I effect, CH_3^- group in acetic acid increases e^- density on carbon atom which makes it. Weak acid.

While in formic acid no such pushing group is present, hence is more stronger acid than acetic acid.

Q.23 Why is oxidation of alcohals to get aldehydes carried out under controlled conditions?

Ans . It is because aldehydes get further oxidised to acids, oxidation of alcohals to aldehydes needs to be controlled.

Q.24 Why the oxidation of toluene to benzaldehyde with CrO3 is carried out in the presence of acetic anhydride.

Ans. If acetic anhydride is not used we will get benzoic acid.

Acetic anhydride used to prevent oxidation of benzaldehyde to benzoic acid.

Q.25 Melting point of an acid with even no. of carbon atoms is higher than those of its neighbour with odd no. of carbon atoms.

Ans . They fit into crystal lattice more readily than odd ones that is why they have higher lattice energy and higher melting point.

Q.26 Why do aldehydes have lower boiling point than corresponding alcohals?

Ans. alcohals have lower boiling point as they are not associated with intermolecular whereas alcohals are associated with intermoleculer H-bonding

Aldehydes have lower B.p.

Q.27 Why do aldehydes behave like polar compounds?

Ans. Due to presence of $>$C=O group whoch is polar

Q.28 Most aromatic acids are solids while acetic acid and others of this series are liquids. Explain why?

Ans. Aromatic acids have higher molecular weight,

More van-der waals force of attracrtion as compared to aliphalic acids They are solids.

Q.29 ethers possess a dipole moment ever if the alkyl radicals in the molecule are identical. Why?

Ans. It is because ethers are bent molecles, dipole do not get cancelled.

Q.**30 Why does acyl chorides have lower boling point than corresponding acids?**

Ans. Acyl chlorides are not associated with intermolecular H-bonding

They have lower boiling point.

Q.31 Why ethers are stored in coloured bottles?

Ans. They are stored in coloured bottles. In presence of sunlight they react with oxygen to form peroxides which may cause explosion.

Q.32 Why formaldehyde cannot be prepared by Rosenmund's reduction?

Ans. Because the formyl chloride thus formed is unstable at room temperature.

Cannot be prepared by Rosenmund reduction.

-Q1. An organic compound (A) {$C_8H_{16}O_2$} was hydrolysed with dilute sulphuric acid to give a carboxylic acid (B)and an alcohol (C). Oxidation of (C)with chromic acid produced (B).(C) on dehyration gives but-1-ene .Identity A,B,C

Ans-: $CH_3CH_2CH_2COOCH_2CH_2CH_2CH_3 + H_2O \xrightarrow{H_2SO_4}$

(A) Butyl Butanoate

$CH_3CH_2CH_2COOH$

(B)

+

$CH_3CH_2CH_2\ CH_2OH$

(C)

$CH_3CH_2CH_2\ CH_2OH \xrightarrow{K_2Cr_2O_7} CH_3CH_2CH_2COOH$

(c) (B)

$CH_3CH_2CH_2\ CH_2OH \xrightarrow[H_2SO_4]{Conc.} CH_3CH_2CH = CH_2$ (bute – 1-ene)

Q2 -: An organic compound with the molecular formula $C_9H_{10}O$ forms 2,4 DNP derivative reduces tollens reagent and undergoes cannizaro reaction . on vigorous oxidation ,it gives 1,2 benzenecarboxylic acid . identify the compound .

Ans:-

Q3. An organic compound (A) with molecular formula C_8H_8O forms an orange-red precipitate with 2,4 DNP reagent and gives yellow precipitate on heating with iodine in the presence of sodium hydroxide. It neither reduces tollen's or fetiling's reagent , nor does it decolourise bromine water or baeyer's reagents .On drastic oxidation with chromic acid .it gives a carboxylic acid (B) having molecular formula $C_7H_6O_2$. Identify the compounds (A) and (B).

Q4. Two moles of organic compound A on treatment with a strong base gives two compounds B and C. Compound B on dehydration with cu gives A while acidification of C yields carboxylic acid D having molecular formula of CH_2O_2 .Identify the compoundsA,B,C,D

Ans:- $2HCHO \xrightarrow[KOH]{Conc.} HCOOK + CH_3OH$

(A) (C) (B)

$CH_3OH \xrightarrow[573\ K]{Cu} HCHO$

(B) (A)

$HCOOK + HCL \longrightarrow HCOOH + KCL$

(c) (D)

Q5. An aliphatic compound ‘A’with a molecular formula of C_3H_6O reacts with phenylhydrazine to give compound ‘B’ . Reaction of ‘A’ with I_2 in alkalene medium on warming gives a yellow precipitate ‘C’. Identify the component A,B,C

Ans:- $CH_3COCH_3 + C_6H_5NH - NH_2 \longrightarrow CH_3C(=N - HN - C_6H_5)$

O (A) CH_3 (B)

$CH_3\overset{O}{\overset{\|}{C}} - CH_3 + 3I_2 + NaOH \longrightarrow CHI_3$

(A) (Iodoform)

(c)

Q6 . A compnent ‘A’ with molecular formula $C_5H_{10}O$ gave a positive 2,4 DNP test but a negative tollen’s reagents test . It was oxidised to carboboxylic acid ‘B’ with molecular formula $C_3H_60_2$ when treated with alkalines KMnO4 under vigrous condition . sodium salt of ‘B’ gave hydrocarbon ‘C’ on kolbe eletrolysis reduction . Identify A,B,C and D.

Ans:- $CH_3 - CH_2 - \underset{\underset{O}{\|}}{C} - CH_2 - CH_3 \xrightarrow[KOH]{KMnO_4} CH_3CH_2COOH$

(A) (B)

⇨

⇨ $CH_3CH_2COONa \xrightarrow{\text{electrolysis}} CH_3CH_2CH_2CH_3$ (c) + $2CO_2$

Sodium propanoate

2

Q7 An organic compound ‘A’ has the molecular formula $C_5H_{10}O$ .It does not reduse fehling’s solution but forms a bisulphite compound .It also gives positive Iodoform test. What are possible structure of ‘A’ ?Explain your reasoning.

Ans-: It does not reduce fehling’s solution but forms bisulpphite compound so it is a ketone therefore it gives positive iodoform test therefore it is methyl ketone .

The possible structure are-:

Q8. An organic compound ‘A’ which has characterstic odour , on treatment with NaOH forms two compounds ‘B’ and ‘C’. Compound ‘B’ has the molecular formula C_7H_8O which on oxidation gives back compound ‘A’. Compound ‘C’ is the sodium salt of an acid which when heated with soda lime yields an aromatic hydrocarbon ‘D’. Deduce A,B,C,D

Ans.

Q9. An organic compound ‘A’ is resistant to oxidation forms an oxidation forms a compound 'B’(C_3H_80) on reduction .‘B'reacts with HBr to form a bromide ‘C’ which on treatment with alkoholic KOH forms an alkene ‘D’ (C_3H_6). Deduce A,B,C,D.

Ans:- $CH_3 - \underset{\underset{O}{\|}}{C} - CH_3 \xrightarrow{LiAlH_4} CH_3\underset{\underset{OH}{|}}{CH} - CH_3$

(A) (B)

$CH_3\text{-}\underset{\underset{OH}{|}}{CH} - CH_3 + HBr \longrightarrow CH_3\underset{\underset{Br}{|}}{CH} - CH_3$

(B) (C)

$CH_3\text{-}\underset{\underset{Br}{|}}{CH} - CH_3$ alc KOH $\longrightarrow CH_3 - CH = CH_2 + KBr$

Br (D)

Q10. Eherial solution of an organic compound 'A’ when heated with magnesium gave 'B’ on treatment with ethanal followed by acid hydrolysis gave 2-propanol .Identify the compound 'A’ . What is 'B' known as?

Ans:- $CH_3\ Br + Mg$ $CH_3\ MgBr$

(a) (b)

$CH_3CHO + CH_3MgBr$ $CH_3 - \underset{\underset{OH}{|}}{CH} - CH_3 + Mg\ (OH)Br$

Q11. Identify A,B,C,D

ANS.

A = CH_3CH_2CHO

B = $CH_3CH = CH – CH_3$

C = $CH_3 – CH(Br) – CH(Br) – CH_3$

D = $CH_3 –C \equiv C –CH_3$

Q12. Primary alkyl halide C_4H_9Br (A) reacted with alcoholic KOH to give compound (B) is reacted with HBr to give (C) which is an isomer of (A). When (A) is reacted with sodium metal it gives compound (D) C_8H_{18} that was different from the compound formed when n-butyl bromide is reacted with sodium . Give the formula of (A) and write equations.

Ans:-

C is the isomer of A

Q13 . An organic compound 'A' having molecular formula C_4H_8 on treatment with dil.H_2SO_4 gives 'B . B on treatment with conc. HCL and anhydrous $ZnCl_2$ gives C and on treatment with sodium ethoxide gives back A.Identify A,B,C.

Ans:- $CH_3CH = CH – CH_3 + H_20 \xrightarrow{H_2SO_4}$ (B)

(A)

$CH_3 – CH – CH_2 – CH_3$

OH

$CH_3 – CH – CH_2 – CH_3 \xrightarrow[ZNCl_2]{HCL} CH_3 – CH – CH_2 – CH_3$

Cl (c)

$\xrightarrow{C_2H_5OH\text{-}KOH}$

$CH_3 – CH = CH – CH_3$ (A)

Q14. An aromatic compound A on treatment with aqueous ammonia and heating forms compound B which on heating with Br_2 and KOH forms a compound C of molecular formula C_6H_7N .Identify A,B,C .

Ans:- COOH

$\xrightarrow[\Delta]{NH_3}$

$CONH_2$

$\xrightarrow[Br_2]{KOH}$

NH_2

(Benzoic acid) (Benzamide) (Aniline)

Q15 . Two isomeric compound A and B having molecular formula $C_{15}H_{11}N$, both lose N_2 on treatment with HNO_2 and gives compound C and D. C is resistant to oxidation but immediately responds to oxidation to lucas reagent after 5 minutes and gives a positive Iodoform test. Identify A and B .

Ans:- $CH_3 - \underset{\underset{NH_2}{|}}{CH} - CH_2 - CH_3 + HNO_2 \longrightarrow CH_3 - \underset{\underset{OH}{|}}{CH} - CH_2 - CH_3$ (B) (D) + N_2

$$CH_3 - \overset{\overset{CH_3}{|}}{\underset{\underset{NH_2}{|}}{C}} - CH_3 + HNO_2 \longrightarrow CH_3 - \overset{\overset{CH_3}{|}}{\underset{\underset{OH}{|}}{C}} - CH_3 \text{ (c)} + N_2$$

$$CH_3 - \overset{\overset{CH_2CH_3}{|}}{\underset{\underset{OH}{|}}{C}} - CH_3 \xrightarrow[ZNCl_2 \Delta]{CONC.\ HCl} CH_3 - \overset{\overset{C_2H_5}{|}}{\underset{\underset{Cl}{|}}{C}} - CH_3 \quad (3^0)$$

©

But 'D' respond to lucas reagent in 5 minutes.

$$.. \quad CH_3 - \underset{\underset{OH}{|}}{CH} - CH_2 - CH_3 + HCL \xrightarrow{\Delta} CH_3 - \underset{\underset{Cl}{|}}{CH} - CH_2 - CH_3 \text{ (D)}$$

$$CH_3 - CH(OH) - CH_2 - CH_3 + I_2 + NaOH \longrightarrow CHI_3 + CH_3 - CH_2\ COONa$$

Q16. An organic compound ‘A’ having molecular formula $C_2H_5O_2N$ reacts with HNO_2 and gives $C_2H_4O_3N_2$. On reduction ‘A’ gives a compound ‘B’ with molecular formula C_2H_7N.‘C’ on treatment with HNO_2 gives ‘C’ which givespositive idoform test . Identify A,B,C.

Ans:- $CH_3CH_2NO_2 + HNO_2 \longrightarrow CH_3 - CH(NO_2) - NO_2$

(A) NO_2 (B)

$CH_3 - CH_2NO_2 +$ SN/HCL $\longrightarrow CH_3 - CH_2NH_2$ (B)

$\downarrow HNO_2$

CH_3CH_2OH

(C) $\downarrow I_2/NaOH$

CHI_3 (IODOFORM)

Q17. An organic compound ‘A’ having molecular formula C_3H_5N on reduction gave another compound ‘B’. The compound B on treatment with HNO_2 gave propyl alcohol . B on warming with $CHCl_3$ and alcohalic caustic potash give the offensive smelling C .Identify A,B,C

Ans:- $C_2H_5CN + 2H_2 \longrightarrow CH_3CH_2CH_2NH_2 \xrightarrow{HNO_2} CH_3CH_2CH_2OH$

(A) (B)

$CH_3CH_2CH_2NH_2 + CHCl_3 + 3KOH \longrightarrow \rightarrow CH_3CH_2NC$

(B) (C)

Q18 . Idomethane reacts with KCN to form a major product A .Compound ‘A’ on reduction in presence of $LiAlH_4$ forms a higher amine 'B’. Compound B on treatment with $CuCl_2$ forms a blue colur complex C . Identify A,B,C

Ans .M $CH_3I + KCN \longrightarrow CH_3 - CN \longrightarrow CH_3CH_2NH_2$ (B)

$$CH_3CH_2NH_2 \xrightarrow{CuCl_2} [Cu(CH_3CH_2NH_2)_4]Cl_2$$

Bluecomplex

Q19. An aliphatic compound A with molecular formula C_2H_3Cl on treatment with AgCN gives two isomeric compounds of unequal amount with the molecular formula C_3H_3N .The minor of these two products on complete reduction with H_2 in the presence of Ni gives a compound ‘B’ with molecular formula C_3H_9N.Identify the compounds.

Ans:- $CH_2 = CH - Cl + AgCN \longrightarrow CH_2 = CH - CN + CH_2 = CH - N - C$

(A) (MINOR) (MAJOR)

$$CH_2 = CH - C = N \xrightarrow[H_2]{Ni} CH_3 - CH_2 - CH_2 - NH_2$$

B

Q20. A compound 'X' having molecular formula C_3H_7NO reacts with Br_2 in presence of KOH to give another compound Y. the compound Y reacts with HNO_2 to form ethanol N_2 gas. Identify X,Y,

Ans:- $CH_3CH_2CONH_2 + Br_2 + 4\ KOH \longrightarrow CH_3CH_2NH_2$

(X) (Y)

$\downarrow HNO_2$

$CH_3CH_2OH + N_2\ (g)$

Q21. A compound ⍰A' of molecular formula $C_3H_7O_2N$ reaction with Fe and conc, HCl gives a compound ⍰B' OF molecular formula C_3H_9N. Compound ⍰B' on treatment with $NaNO_2$ and HCl gives another compound ⍰C' of molecular formula C_3H_8o.The compound ⍰C'gives effervescences with Na on oxidation with CrO_3.The compound ⍰C' gives a saturated aldehyde containing three carbon atom deduce A,B,C.

Ans:- $CH_3CH_2CH_2NO_2 \longrightarrow CH_3CH_2CH_2NH_2$ (B)

$\downarrow NaNO_2/HCL$

$CH_3CH_2CH_2OH$ (C)

$\downarrow Na$

$CH_3CH_2CH_2ONa$

Sodium propoxide

$CH_3CH_2CH_2OH \xrightarrow[CrO_3]{} CH_3CH_2CHO$

(C)

Q22. A Chloro compound ‘A’ on reduction with Zn – Cu and alcohol gives the hydro carbon (B) with five carbon atom.When ‘A’ is dissolved in ether and treated with sodium 2,2,5,5 tetramethyl hexhane is formed structure of A and B?

Ans.

IDENTIFY A,B,C

Q1. $CH_3COOH \xrightarrow[NH_3]{\Delta} A \xrightarrow[NaOBr]{} B \xrightarrow[NaNO_2]{HCl} C$

Q2. $C_6H_5NO_2 \xrightarrow{Fe/HCl} A \xrightarrow{NaNO_2/HCl} B \xrightarrow{H_2O/H} C^+$

Q3. $C_6H_5NO_2 \xrightarrow{Fe/HCl} A \xrightarrow{NaNO_2} B \xrightarrow{C_6H_5OH} C$

Q4. $CH_3CH_2Br \xrightarrow[CuCN]{KCN} A \xrightarrow[H_2O/H^+]{LiAlH_4} B \xrightarrow[NH_3]{HNO_2} C$

Q5. $C_6H_5N^+{}_2Cl^- \longrightarrow A \longrightarrow B \longrightarrow C$

Q6. $CH_3CH_2I \xrightarrow{NaCN} A \xrightarrow{OH^-} B \xrightarrow{NaOH} C$

Q7. $C_6H_5NH_2 + (CH_3C0_2)_2O \longrightarrow A$

Q8. $C_6H_5N_2^+Cl^- \xrightarrow[HBF_4]{NaNO_2/Cu\ \Delta} A$

Q9. $A \xrightarrow[Br_2]{NaOH} B \xrightarrow[Dil\ HNO_3]{HNO_2} C \xrightarrow[Sn/HCl]{Red\ p\ I_2} D\ (CH_3I)$

$NaNO_2 + HCl$

Q10. $A \longrightarrow B \longrightarrow C \longrightarrow C_6H_5N_2Cl$

Q11. $A \xrightarrow[KOH]{\Delta} B \xrightarrow[HNO_2]{Br_2} C \xrightarrow[CH3I]{} C_2H_5NH_2$

Q12. $A \xrightarrow{AgCN} B \xrightarrow[H^+/H_2O]{Sn/HCl} C \xrightarrow[LiAlH_4]{} CH_3 – CH2 - N\ H – CH_3$

Q13. $CH_3CN \longrightarrow A \longrightarrow B$

Q14. $R_2CO \xrightarrow{NH_2} A \xrightarrow{LI/H_2} B$

Q15.

$\xrightarrow{CN} A \xrightarrow{LiAlH_4} B$

Q16.

$\xrightarrow[O^0C]{NaNO_2/HCl} A \xrightarrow[CuCl]{} B$

Q17.

ANSWERS

1.A= CH_3CONH_2 , B = CH_3NH_2 , C = CH_3OH

2.A = $C_6H_5NH_2$, B =$C_6H_5N_2^+Cl^-$, C =

3.A = CH_3CH_2CN , B =CH_3CH_2-CH_2NH_2 , C = $CH_3CH_2CH_2OH$

4.A= $C_6H_5NH_2$, B= $C_6H_5N_2^+Cl^-$, C= $CH_3CH_2CH_2OH$

5.A = C_6H_5CN , B = C_6H_5COOH , C= $C_6H_5CONH_2$

6.A= CH_3CH_2CN, B = $CH_3CH_2CONH_2$, C = $CH_2CH_2NH_2$

7.A)

8. $C_6H_5NO_2$ = A

9. A = CH_3CONH_2 , B = CH_3NH_2 , C = CH_3OH

10.A)

11.A= $CH_3CH_2COONH_4$, B= $CH_3CH_2CONH_2$, C= $CH_3CH_2NH_2$

12.A = CH_3Cl , B = CH_3NC , C= CH_3-CH2-NH-CH_3

13.A = CH_3COOH , B = CH_3CH_2OH

14.A = $R-\underset{\underset{R}{|}}{C}=NH$, B = $R-\underset{\underset{R}{|}}{CH}-NH_2$

15)

(A)

(B)

16)

17) A =

, B =

1 MARK QUESTIONS

Q1. Name the reaction and the reagent used for the conversion of acid chlorides to the corresponding aldehydes.

A. Name : Rosenmund's reaction Reagent : H_2 in the presence of Pd (supported over $BaSO_4$) and partially poisoned by addition of Sulphur or quinoline.

$$R-\overset{\overset{\displaystyle O}{||}}{C}-Cl + H \xrightarrow[+\ S \text{ or quinoline}]{Pd/BaSO_4} R-\overset{\overset{\displaystyle O}{||}}{C}-H + HCl$$

Q 2. Suggest a reason for the large difference in the boiling points of butanol and butanal, although they have same solubility in water

. A. The b.p. of butanol is higher than that of butanal because butanol has strong intermolecular H-bonding while butanal has weak dipole-dipole interaction. However both of them form H-bonds with water and hence are soluble.

Q 3. What type of aldehydes undergo Cannizaro reaction ?

A. Aromatic and aliphatic aldehydes which do not contain α- hydrogens.

Q 4. Out of acetophenone and benzophenone, which gives iodoform test ? Write the reaction involved. (The compound should have CH_3CO-group to show the iodoform test.)

A. Acetophenone ($C_6H_5COCH_3$) contains the grouping (CH_3CO attached to carbon) and hence given iodoform test while benzophenone does not contain this group and hence does not give iodoform test.

$$\underset{\text{Acetophenane}}{C_6H_5COCH_3} + 3\ I_2 + 4\ NaOH \longrightarrow \underset{\text{Iodoform}}{CHI_3} + C_6H_5COONa + 3\ NaI + 3\ H_2O$$

$$C_6H_5COC_6H_5 \xrightarrow[I_2/NaOH]{} \text{No reaction}$$

Q5. Give Fehling solution test for identification of aldehyde gp (only equations). Name thealdehyde which does not give Fehling's soln. test.

A. $R-CHO - 2\ Cu^{2+} + 5\ OH^- \longrightarrow RCOO^- + Cu_2O + 3\ H_2O$

Benzaldehyde does not give Fehling soln. test. (Aromatic aldehydes do not give this test.)

Q6. What makes acetic acid a stronger acid than phenol ?

A. Greater resonance stabilization of acetate ion over phenoxide ion.

Q7. Why HCOOH does not give HVZ (Hell Volhard Zelinsky) reaction but CH_3COOH does?

A. CH_3COOH contains α- hydrogens and hence give HVZ reaction but HCOOH does not contain α-hydrogen and hence does not give HVZ reaction

Q8. During preparation of esters from a carboxylic acid and an alcohol in the presence of an acid catalyst, water or the ester formed should be removed as soon as it is formed.

A. The formation of esters from a carboxylic acid and an alcohol in the presence of acid catalyst in a reversible reaction.

$$\underset{\text{Carboxylic acid}}{RCOOH} + \underset{\text{alcohol}}{R'OH} \underset{}{\overset{H_2SO_4}{\rightleftharpoons}} \underset{\text{Ester}}{RCOOR'} + H_2O$$

To shift the equilibrium in the forward direction, the water or ester formed should be removed as fast as it is formed

Q 9. **Arrange the following compounds in increasing order of their acid strength. Benzoic acid, 4-Nitrobenzoic acid, 3, 4-dinitrobenzoic acid, 4-methoxy benzoic acid.**

A. 4-methoxybenzoic acid < benzoic acid < 4-nitrobenzoic acid <4, dinitrobenzoic acid.

Q 10. **How is tert-butyl alcohol obtained from acetone? A.**

2 / 3 MARKS QUESTIONS

1. Arrange the following compounds in increasing order of their boiling points. Explain by giving reasons.

CH_3CHO, CH_3CH_2OH, CH_3OCH_3, $CH_3CH_2CH_3$.

A. The molecular masses of all these compounds are comparable :

CH_3CHO (44), CH_3CH_2OH (46), CH_3COCH_3 (46), $CH_3CH_2CH_3$ (44).

CH_3CH_2OH exists as associated molecule due to extensive intermolecular hydrogen bonding and hence its boiling point is the highest (351 K). Since dipole-dipole interaction are stronger in CH_3CHO than in CH_3OCH_3, hence boiling point of CH_3CHO (293 K) is much higher than that of CH_3OCH_3 (249 K). Further, molecules of $CH_3CH_2CH_3$ have only weak Vander Waals forces while the molecules of CH_3OCH_3 have little stronger dipole-dipole interactions and hence the boiling point of CH_3OCH_3 is higher (249 K) than that of $CH_3CH_2CH_3$ (231 K). Thus the overall increasing order of boiling points is :

$$CH_3CH_2CH_3 < CH_3OCH_3 < CH_3CHO < CH_3CH_2O$$

2. Which acid of each pair shown here would you expect to be stronger? CH_3CO_2H or FCH_2CO_2H

Thus due to lesser electron density in the O — H bond and greater stability of FCH_2COO^- ion over CH_3COO^- ion FCH_2COOH is a stronger acid than CH_3COOH.

3. Which acid is stronger and why?

$F_3C — C_6H_4 — COO H$, $CH_3 — C_6H_4 — COOH$

A. CF3 has a strong(– I) effect. It stabilises the carboxylate ion by dispersing the – ve charge.

CH3 has a weak (+ I) effect. It stabilises the carboxylate ion by intensifying the – ve charge.

Therefore due to greater stability of $F_3C — C_6H_4 — COO^-$ (p) ion over $CH_3 — C_6H_4COO^-$ (p) ion, $F_3C — C_6H_4 — COOH$ is a much stronger acid than $CH_3 — C_6H_4 — COOH$.

4. Arrange the following compounds in increasing order of their reactivity towards HCN. Explain it with proper reasoning.

Acetaldehyde, Acetone, Di-tert-butyl ketone, Methyl tert-butyl ketone.

ANS. Addition of HCN to the carboxyl compounds is a nucleophilic addition reaction.

The reactivity towards HCN addition decreases as the + I effect of the alkyl groups increases and/or the steric hindrance to the nucleophilic attack by CN– at the carboxyl carbon increases. Thus the reactivity decreases in the order.

———————— + I effect increases————————

———————— Steric hindrance increases————————

 ———————— Reactivity towards HCN addition decreases ————————

In other words, reactivity increases in the reverse order, i. e.

Ditert-butyl Ketone < tert-Butyl methyl Ketone < Acetone < Acetaldehyde

5. Explain why o-hydroxybenzaldehyde is a liquid at room temperature while p-hydroxybenzaldehyde is a high melting solid.

ANS.

Due to interamolecular H-bonding ortho-hydroxy benzaldehyde exists as discrete molecule whereas due to intermolecular H-bonding, p-hydroxybenzaldehyde exists as associated molecules. To break these intermolecular H-bonds, a large amount of energy is needed. Consequently, p-hydroxybenzaldehyde has a much higher m.p. and b.p. than that of o-hydroxy benzaldehyde. As a result, o-hydroxy benzaldehyde is a liquid at room temperature while p-hydroxy benzaldehyde is a high melting solid.

5 MARKS QUESTIONS

1. **Arrange the following compounds in order ot their property as indicated-**

   i) Acetaldehyde,Acetone, di-tert-butyl ketone, Methyl tert-butyl ketonereactivity towards HCN

   - di-tert-butyl ketone < Methyl tert-butyl ketone <Acetone <Acetaldehyde

   -aldehydes are more reactive towards nucleophilic addition across the >C=O due to steric and electronic reasons.

   -Sterically the presence of two relatively large substituents inketones hinders the approach of nucleophile to carbonyl carbon than in aldehydes having only one such substituent.

   –Electronically , the presence of two alkyl groups reduces the electrophilicity of the carbonyl carbon in ketones.

   ii) $CH_3CH_2CHBrCOOH$, $CH_3CHBrCH_2COOH$, $(CH_3)_2CHCOOH$, $CH_3CH_2CH_2COOH$ acid strength

   -$(CH_3)_2CHCOOH < CH_3CH_2CH_2COOH < CH_3CHBrCH_2COOH < CH_3CH_2CHBrCOOH$

-Electron withdrawing groups like –Br increases the acidity of carboxylic aids by stabilizing the conjugate base through delocalisation of negative charge by negative inductive effect. The closer the electron withdrawing group to the –COOH group, greater is the stabilising effect.

-Electron donating groups decrease the acidity by destabilizing the conjugate base.greater the number of –CH3 groups, greater the destabilizing effect and lower the acidity.

iii) Benzoic acid, 4-Nitrobenzoic acid, 3,4-Dinitrobenzoic acid, 4- Methoxybenzoic acid (acid strength)

4- Methoxybenzoic acid< Benzoic acid <4-Nitrobenzoic acid < 3,4-Dinitrobenzoic acid

- Benzoic acid is a stronger acid than aliphatic carboxylic acid due to stabilization of the conjugate base due to resonance.
- Presence of electron withdrawing group-NO_2 on the phenyl ring of aromatic carboxylic acid increases their acidity while electron donating groups-OCH_3 decreases their acidity.

UNIT 9: CO-ORDINATION COMPOUNDS

1	CO-ORDINATION COMPOUND	1. Nomenclature of co-ordination compounds
		2. Hybridisation co-ordination complexes
		3. Isomerization
		4. crystal field theory in octahedral complexes

POINTS TO REMEMBER:

1. **Coordination compounds**

Coordination compounds are compounds in which a central metal atom or ion is linked to a number of ions or neutral molecules by coordinate bonds or which contain complex ions.
Examples- $K_4[Fe(CN)_6]$; $[Cu(NH_3)_4]SO_4$; $Ni(CO)_4$

2. **ThemainpostulatesofWerner'stheoryofcoordinationcompounds**

i) In coordination compounds metals show two types of linkages or valencies- Primary and Secondary.
ii) The primary valencies are ionisable and are satisfied by negative ions.
iii) The secondary valencies are non- ionisable and are satisfied by neutral molecules or negative ions. The secondary valence is equal to the C.N and is fixed for a metal.
iv) The ions or groups bound by secondary linkages to the metal have characteristic spatial arrangements corresponding to different coordination nos.

3.Difference between a double salt and a complex

Both double salts as well as complexes are formed by the combination of two or more stable compounds in stoichiometric ratio. However, double salts such as carnallite, $KCl.MgCl_2.6H_2O$, Mohr's salt, $FeSO_4.(NH_4)_2SO_4.6H_2O$, potash alum, $KAl(SO_4)_2.12H_2O$, etc. dissociate into simple ions completely when dissolved in water. However, complex ions such as $[Fe(CN)^6]^{4-}$ of $K4[Fe(CN)_6]$, do not dissociate into Fe^{2+} and CN^- ions

IMPOTANT TERMINOLOGY

(i) Coordination entity: It constitutes the central metal ion or atom bonded to a fixed number of ions or molecules represented within a square bracket.

(ii) Central atom/ ion: In a coordination entity, the atom/ion to which a fixed number of ions/groups are bound in a definite geometrical arrangement around it, is called the central atom or ion.

iii) **Ligands**: The neutral or negative ions bound to the central metal or

ion in the coordination entity. These donate a pair/s of electrons to the central metal atom /ion. Ligands may be classified as-

a) **Monodentate/Unidentate**: Ligands bound to the central metal atom/ion through a single donor atom. Ex- Cl^- ; H_2O ; NH_3 ; NO_2^-.
b) **Didentate**: Ligates through two donor atoms. Ex- $C_2O_4^{2-}$ (ox); $H_2NCH_2CH_2NH_2$(en)
c) **Polydentate**: which ligates through two or more donor atoms present in a single ligand. Ex- $(EDTA)^{4-}$
d) **Chelating ligands**: Di- or polydentate ligands that uses two or more donor atoms to bind to a single metal ion to form ring- like complexes. (Ox); (edta)
e) **Ambidentate ligand**: A ligand that can ligate through two different atoms, one at a time. Ex-NO_2^- ; SCN^-
v) **Coordination number**: The no. of ligand donor atoms to which the metal is directly bonded through sigma bonds only. It is commonly 4 or 6.
vi) **Counter ions**: The ionisable groups written outside the square bracket. Ex- K+ in $K_4[Fe(CN)_6]$ OR $3Cl^-$ in $[Co(NH_3)_6]Cl_3$
vii) **Coordination Polyhedron**: The spatial arrangement of the ligand atoms which are directly attached to the central metal atom/ion. They are commonly Octahedral, Square-planar or Tetrahedral

Oxidation number: The charge that the central atom would carry if all the ligands are removed along with their pairs of electrons shared with the central atom. It is represented in parenthesis.

viii) **Homoleptic complexes**: Complexes in which a metal is bonded to only one kind of donor groups. Ex- $[Co(NH_3)_6]^{3+}$

ix) **Heteroleptic complexes**: Complexes in which a metal is bonded to more than one kind of donor groups. Ex- $[Co(NH_3)_4\ Cl_2]^+$

5. NAMING OF MONONUCLEAR COORDINATION COMPOUNDS

The principle of additive nomenclature is followed while naming the coordination compounds. The following rules are used-

i The cation is named first in both positively and negatively charged coordination entities.

ii The ligands are named in an alphabetical order before the name of the central atom/ion

iii The name of the anionic ligands end in –o, those of neutral and cationic ligands are the same except aqua for H_2O, ammine for NH_3, carbonyl for CO and nitrosyl for NO. these are placed within enclosing marks .

iv When the prefixes mono, di, tri, etc., are used to indicate the number of the individual ligands in the coordination entity. When the names of the ligands include a numerical prefix, then the terms, bis, tris , tetrakis are used, the ligand to which they refer being placed in parenthesis.

v Oxidation state of the metal in cation, anion, or neutral coordination entity is indicated by roman numeral in parenthesis.

vi If the complex ion is a cation , the metal is same as the element.

vii The neutral complex molecule is named similar to that of the complex cation.

6.NAMES OF SOME COMMON LIGANDS

NEGATIVE LIGANDS		CHARGE	NEUTRAL LIGANDS		CHARGE
CN-	Cyano	-1	NH_3	Ammine	0
Cl-	Chlorido	-1	H_2O	Aqua/aquo	0
Br-	Bromido	-1	NO	Nitrosyl	0
F-	Fluoride	-1	CO	Carbonyl	0
SO_4^{2-}	Sulphato	-2	PH_3	Phosphine	0
$C_2O_4^{2-}$	Oxalato	-4	CH_2-NH_2 CH_2NH_2	(1,2-Ethane diamine)	0
NH_2^-	Amido	-1	POSITIVE LIGANDS		
NH^{2-}	Imido	-2	NH_2-$NH3^+$	Hydrazinium	+1
ONO^-	Nitrito-O	-1	NO^+	Nitrosonium	+1
NO_2^-	Nitro	-1	NO_2^+	Nitronium	+1

NO_3^-	Nitrato	-1			
SCN^-	Thiocyanato	-1			
NCS^-	Isothiocyanato	-1			
$CH_2(NH_2)COO^-$	Glycinato	-1			
-OH	Hydroxo	-1			

7. ISOMERISM IN COORDINATION COMPOUNDS

Two or more substances having the same molecular formula but different spatial arrangements are called isomers and the phenomenon is called isomerism. Coordination compounds show two main types of isomerism-

A) Structural Isomerism B) Stereoisomerism

STRUCTURAL ISOMERISM:- It arises due to the difference in structures of coordination compounds. It is further subdivided into the following types-

1) **Ionisation isomerism :** This form of isomerism arises when the counter ion in a complex salt is itself a potential ligand and can displace a ligand which can then become the counter ion. An example is provided by the ionization isomers $[Co(NH_3)_5SO_4]Br$ and $[Co(NH_3)_5Br]SO_4$.

2) **Hydrate or solvate isomerism**: This form of isomerism is known as ‗hydrate isomerism' in case where water is involved as a solvent. This is similar to ionisation isomerism. Solvate isomers differ by whether or not a solvent molecule is directly bonded to the metal ion or merely present as free solvent molecules in the crystal lattice. An example is provided by the aqua complex $[Cr(H_2O)_6]Cl_3$ (violet) and its solvate isomer $[Cr(H_2O)_5Cl]Cl_2.H_2O$ (grey-green).

3) **Linkage Isomerism**: Linkage isomerism arises in a coordination compound containing ambidentate ligand. A simple example is provided by complexes containing the thiocyanate ligand, NCS^-, which may bind through the nitrogen to give M–NCS or through sulphur to give M–SCN.

4) **Coordination isomerism:** It arises from the interchange of ligands between cationic and anionic entities of different metal ions present in a complex .
Example $[Co(NH_3)_6][Cr(CN)_6]$ & $[Cr(NH_3)_6][Co(CN)_6]$

STEREOISOMERISM: Stereo isomers have the same chemical formula and chemical bonds but they have different spatial arrangement. They are of two kinds

A. Geometrical isomerism

B. Optical isomerism

GEOMETRICAL ISOMERISM- This type of isomerism arises in heteroleptic complexes due to different possible geometric arrangements of the ligands. Important examples of this behaviour are found with coordination numbers 4 and 6. In a square planar complex of formula $[MX_2L_2]$ (X and L are unidentate), the two ligands X may be arranged adjacent to each other in a cis isomer, or opposite to each other in a trans isomer [MABXL]-Where A,B,X,L are unidentates Two cis- and one trans- isomers are possible

cis

trans

cis

trans

Another type of geometrical isomerism occurs in octahedral coordination entities of the type $[Ma_3b_3]$ like $[Co(NH_3)_3(NO_2)_3]$. If three donor atoms of the same ligands occupy adjacent positions at the corners of an octahedral face, we have the facial (fac) isomer. When the positions are around the meridian of the octahedron, we get the meridional (mer) isomer.

fac–

mer–

b) **OPTICAL ISOMERISM:** Optical isomers are mirror images that cannot be superimposed on one another. These are called as enantiomers. The molecules or ions that cannot be superimposed are called chiral. The two forms are called dextro (d) and laevo (l) depending upon the direction they rotate the plane of polarised light in a polarimeter (d rotates to the right, l to the left). Optical isomerism is common in octahedral complexes involving didentate ligands. In a coordination entity of the type $[CoCl_2(en)_2]^{2+}$, only the cis-isomer shows optical activity

Trans $[CoCl_2(en)_2]^+$ isomer-optically inactive
(Superimposable mirror images)

Cis $[CoCl_2(en)_2]^+$ isomer-optically active
(Non-superimposable mirror images)

TYPES OF HYBRIDISATION

Coordination number	Type of hybridisation	Acquired geometry
4	sp^3	Tetrahedral
4	dsp^2	Square planar
5	sp^3d	Trigonal bipyramidal
6	sp^3d^2	Octahedral
6	d^2sp^3	Octahedral

8.CRYSTAL FIELD THEORY:

1. The metal-ligand bond is ionic arising purely from electrostatic interactions between the metal ion and the ligand.
2. Ligands are treated as point charges or dipoles in case of anions and neutral molecules.
3. In an isolated gaseous metal atom or ion the five d-orbitals are degenerate.
4. Degeneracy is maintained if a spherically symmetrical field of negative charges surrounds the metal /ion.
5. In a complex the negative field becomes asymmetrical and results in splitting of the d-orbitals.

A) **CRYSTAL FIELD SPLLITING IN OCTAHEDRAL COORDINATION ENTITIES**

d orbital splitting in an octahedral crystal field

1. For d^4 ions, two possible patterns of electron distribution arise:

(i) If $\Delta_o < P$, the fourth electron enters one of the e_g orbitals giving the

configuration $t^3_{2g}\, e^1_g$. Ligands for which $\Delta_o < P$ are known as weak

field ligands and form high spin complexes.

(ii) If $\Delta o > P$, it becomes more energetically favourable for the fourth electron to occupy a t_{2g} orbital with configuration $t^4_{2g}\, e^0_g$. Ligands which produce this effect are known as strong field ligands and form low spin complexes.

B) **CRYSTAL FIELD SPLLITING IN TETRAHEDRAL COORDINATION ENTITIES**

1. The four surrounding ligands approach the central metal atom/ion along the planes between the axes.
2. The t_{2g} orbitals are raised in energy (2/5) $_t$.
3. The two e_g orbitals are lowered in energy (3/5) $_t$
4. The splitting is smaller as compared to octahedral field splitting, $_t$=(4/9) $_0$.

5. Pairing of electrons is rare and thus complexes have generally high spin configurations.

BONDING IN METAL CARBONYLS

The metal-carbon bond in metal carbonyls possess both σ and π character. The M–C σ bond

is formed by the donation of lone pair of electrons on the carbonyl carbon into a vacant orbital of the metal. The M–C π bond is formed by the donation of a pair of electrons from a filled d orbital of metal into the vacant antibonding π* orbital of carbon monoxide. The metal to ligand bonding creates a synergic effect which strengthens the bond between CO and the metal .

SOLVED QUESTIONS

1 MARK QUESTIONS

1. What are ambidentate ligands? Give two examples for each.

ANS. Ambidentate ligands are ligands that can attach themselves to the central metal atom through two different atoms. For example:

(a)

(The donor atom is N)

(The donor atom is oxygen)

(b)

(The donor atom is S) (The donor atom is N)

Q2. Using IUPAC norms write the formula for the following: Tetrahydroxozincate(II)
ANS. $[Zn(OH)_4]^{2-}$

Q3. Using IUPAC norms write the formula for the following: Hexaamminecobalt(III) sulphate
ANS. $[Co(NH_3)_6]_2\ (SO_4)_3$

Q4. Using IUPAC norms write the formula for the following: Pentaamminenitrito-O-cobalt(III)
ANS. $[Co(ONO)\ (NH_3)_5]^{2+}$

Q5. Using IUPAC norms write the systematic name of the following: [Co(NH3)6]Cl3

ANS. Hexaamminecobalt(III) chloride

Q6. Using IUPAC norms write the systematic name of the following: [Pt(NH3)2Cl(NH2CH3)]Cl

ANS. Diamminechlorido(methylamine) platinum(II) chloride

Q7. Using IUPAC norms write the systematic name of the following: $[Co(en)_3]^{3+}$

ANS. Tris(ethane-1, 2-diammine) cobalt(III) ion

Q8. Draw the structures of optical isomers of: c$[Cr(C_2O_4)_3]^{3-}$

ANS .

Q9. What is meant by the chelate effect? Give an example.
ANS. When a ligand attaches to the metal ion in a manner that forms a ring, then the metal-ligand association is found to be more stable.

2 / 3 MARK QUESTIONS

Q1. What is spectrochemical series? Explain the difference between a weak field ligand and a strong field ligand.

ANS. A spectrochemical series is the arrangement of common ligands in the increasing order of their crystal-field splitting energy (CFSE) values.

$I^- < Br^- < S^{2-} < SCN^- < Cl^- < N_3 < F^- < OH^- < C_2O_4^{2-} \sim H_2O < NCS^- \sim H^- < CN^- < NH_3 < en \sim SO_3^{2-} < NO_2^- < phen < CO$

Q2. $[Cr(NH_3)_6]^{3+}$ is paramagnetic while $[Ni(CN)_4]^{2-}$ is diamagnetic. Explain why?

ANS. Cr is in the +3 oxidation state i.e., d^3 configuration. Also, NH_3 is a weak field ligand that does not cause the pairing of the electrons in the 3d orbital.

Cr^{3+} :

Therefore, it undergoes d^2sp^3 hybridization and the electrons in the 3d orbitals remain unpaired. Hence, it is paramagnetic in nature.
In $[Ni(CN)_4]^{2-}$, Ni exists in the +2 oxidation state i.e., d^8 configuration.

Ni^{2+}:

CN^- is a strong field ligand. It causes the pairing of the 3d orbital electrons. Then, Ni^{2+} undergoes dsp^2 hybridization.

Q3. A solution of $[Ni(H_2O)_6]^{2+}$ is green but a solution of $[Ni(CN)_4]^{2-}$ is colourless. Explain.

ANS. In $[Ni(H_2O)_6]^{2+}$, $H_2\ddot{O}$ is a weak field ligand. Therefore, there are unpaired electrons in Ni^{2+}. In this complex, the d electrons from the lower energy level can be excited to the higher energy level i.e., the possibility of d−d transition is present. Hence, $Ni(H_2O)_6]^{2+}$ is coloured.

In $[Ni(CN)_4]^{2-}$, the electrons are all paired as CN^- is a strong field ligand. Therefore, d-d transition is not possible in $[Ni(CN)_4]^{2-}$. Hence, it is colourless. As there are no unpaired electrons, it is diamagnetic.

Q2. Draw all the isomers (geometrical and optical) of:

(i) $[CoCl_2(en)_2]^+$
(ii) $[Co(NH_3)Cl(en)_2]^{2+}$
(iii) $[Co(NH_3)_2Cl_2(en)]^+$

<u>ANS.</u> **(i)** $[CoCl_2(en)_2]^+$

In total, three isomers are possible.

Trans-isomers are optically inactive.

Cis-isomers are optically active.

(iii) $[Co(NH_3)_2Cl_2(en)]^+$

Q3. Write all the geometrical isomers of $[Pt(NH_3)(Br)(Cl)(py)]$ and how many of these will exhibit optical isomers?

<u>**ANS.**</u> $[Pt(NH_3)(Br)(Cl)(py)$

From the above isomers, none will exhibit optical isomers. Tetrahedral complexes rarely show optical isomerization. They do so only in the presence of unsymmetrical chelating agents.

Q4. What is meant by stability of a coordination compound in solution? State the factors which govern stability of complexes.

<u>**ANS.**</u> The stability of a complex in a solution refers to the degree of association between the two species involved in a state of equilibrium. Stability can be expressed quantitatively in terms of stability constant or formation constant.

$$M + 3L \longleftrightarrow ML_3$$

$$\text{Stability constant, } \beta = \frac{[ML_3]}{[M]\,[L]^3}$$

For this reaction, the greater the value of the stability constant, the greater is the proportion of ML_3 in the solution.

5 MARKS QUESTIONS

Q1. (a) Discuss the nature of bonding in the following coordination entities on the basisof valence bond theory:

(i) $[Fe(CN)_6]^{4-}$ (ii) $[FeF_6]^{3-}$ (iii) $[Co(C_2O_4)3]^{3-}$ (iv) $[CoF_6]^{3-}$

ANS. (i) $[Fe(CN)_6]^{4-}$In the above coordination complex, iron exists in the +II oxidation state.Fe^{2+} : Electronic configuration is $3d^6$ Orbitals of Fe^{2+} ion:

As CN^- is a strong field ligand, it causes the pairing of the unpaired 3d electrons.Since there are six ligands around the central metal ion, the most feasible hybridization is d^2sp^3. d^2sp^3 hybridized orbitals of Fe^{2+} are:

6 electron pairs from CN^- ions occupy the six hybrid d^2sp^3orbitals.Then,

Hence, the geometry of the complex is octahedral and the complex is diamagnetic (as there are no unpaired electrons).

(ii) $[FeF_6]^{3-}$

In this complex, the oxidation state of Fe is +3.

Orbitals of Fe^{+3} ion:

There are 6 F^- ions. Thus, it will undergo d^2sp^3 or sp^3d^2 hybridization. As F^- is a weak field ligand, it does not cause the pairing of the electrons in the 3d orbital. Hence, the most feasible hybridization is sp^3d^2.sp^3d^2 hybridized orbitals of Fe are:

Hence, the geometry of the complex is found to be octahedral.

(iii) $[Co(C_2O_4)_3]^{3-}$

Cobalt exists in the +3 oxidation state in the given complex.Orbitals of Co^{3+} ion:Oxalate is a weak field ligand. Therefore, it cannot cause the pairing of the 3d orbital electrons. As there are 6 ligands, hybridization has to be either sp^3d^2 or d^2sp^3 hybridization.sp^3d^2 hybridization of Co^{3+}:

The 6 electron pairs from the 3 oxalate ions (oxalate anion is a bidentate ligand) occupy these sp^3d^2 orbitals.

Hence, the geometry of the complex is found to be octahedral.

(iv) $[CoF_6]^{3-}$Cobalt exists in the +3 oxidation state.

Orbitals of Co^{3+} ion:

Again, fluoride ion is a weak field ligand. It cannot cause the pairing of the 3d electrons. As a result, the Co^{3+} ion will undergo sp^3d^2 hybridization.sp^3d^2 hybridized orbitals of Co^{3+} ion are:

Hence, the geometry of the complex is octahedral and paramagnetic.

Q3. Write down the IUPAC name for each of the following complexes and indicate the oxidation state, electronic configuration and coordination number. Also give stereochemistry and magnetic moment of the complex:

(i) $K[Cr(H_2O)_2(C_2O_4)_2].3H_2O$ (ii) $[Co(NH_3)_5Cl]Cl_2$ <u>**ANS.**</u> **(i)** Potassium diaquadioxalatochromate (III) trihydrate.

Oxidation state of chromium = 3 Electronic configuration: $3d^3$: t_{2g}^3
Coordination number = 6 Shape: octahedral

Stereochemistry:

Trans

Cis

Trans is optically inactive

Cis is optically active

Magnetic moment, μ $= \sqrt{n(n+2)}$

$= \sqrt{3(3+2)}$

$= \sqrt{15}$

~ 4BM

(ii) $[Co(NH_3)_5Cl]Cl_2$

IUPAC name: Pentaamminechloridocobalt(III) chloride
Oxidation state of Co = +3
Coordination number = 6
Shape: octahedral.

Electronic configuration: d^6: t_{2g}^6.

Stereochemistry:

2 isomers

Magnetic Moment = 0

LEVEL 1

1.Why do tetrahedral complex not show geometrical isomerism?

2. Why does the colour changes on heating $[Ti(H_2O)_6]^{3+}$.

3. $[Fe(H_2O)_6]^{3+}$ is strongly paramagnetic whereas $[Fe(CN)_6]^{3-}$ is weakly paramagnetic. Explain.

4. What happens when potassium ferrocyanide solution is added to a ferric salt solution?

LEVEL 2

5. A coordination compound has a formula ($CoCl_3$. $4NH_3$). It does not liberate NH_3but precipitates chloride ion as AgCl. Give the IUPAC name of the complex and write its structural formula.

6. Write the correct formula for the following co-ordination compounds. $CrCl_3$. $6H_2O$ (Violet, with 3 Chloride ions/ Unit formula) $CrCl_3$. $6H_2O$ (Light green colour with 2 Chloride ions/ unit formula)

7. Give the electronic configuration of the d-orbitals of Ti in $[Ti(H_2O)_6]^{3+}$ ion in anoctahedral crystal field.

8. Co(II) is stable in aqueous solution but in the presence of strong ligands and air, it can get oxidized to Co(III). (Atomic Number of cobalt is 27). Explain.

9. Give a chemical test to distinguish between $[Co(NH_3)_5Br]SO_4$ and $[Co(NH_3)_5Br]SO_4Br$. Name the type of isomerism exhibited by these compounds.

10. What is the coordination entity formed when excess of aqueous KCN is added to an aqueous solution of copper sulphate? Why is that no precipitate of copper sulphate is obtained when H_2S (g) is passed through this solution?

LEVEL 3

11. Aqueous copper sulphate solution (blue in colour) gives a green precipitate with aqueous potassium fluoride, a bright green solution with aqueous potassium chloride. Explain these experimental results.

12. A metal complex having the composition $Cr(NH)_4Cl_2Br$ has been isolated in two forms, A and B. The form A reacts with $AgNO_3$ solution to give a white precipitate readily soluble in dilute aqueous ammonia whereas B give a pale yellow precipitate soluble in concentrated ammonia solution. Write the formulae of A and B and write their IUPAC names.

13. Explain the following

i. All octahedral complexes of Ni^{2+}must be outer orbital complexes. ii.

NH_4^+ ion does not form any complex.

iii. $(SCN)^{-1}$ ion is involved in linkage isomerism in co-ordination compounds.

14. A metal ion Mn^+ having d^4 valence electronic configuration combines with three didentate ligands to form complexes. Assuming $\Delta_o > P$ Draw the diagram showing d orbital splitting during this complex formation. Write the electronic configuration of the valence electrons of the metal Mn^+ ion in terms of t_{2g} and e_g. What type of the hybridization will Mn^+ ion have? Name the type of isomerism exhibited by this complex.

15. The coordination no. of Ni^{2+} is 4.

$NiCl_2$ + KCN(excess) → A(a cyano complex)

A + Conc HCl(excess) → B (a chloro complex)

i) Write IUPAC name of A and B

ii) Predict the magnetic nature of A and B

iii) Write hybridization of Ni in A and B

16. Explain the following
i. $Cu(OH)_2$ is soluble in ammonium hydroxide but not in sodium hydroxide solution. ii.

EDTA is used to cure lead poisoning

iii. Blue coloured solution of $[CoCl_4]^{2-}$ changes to pink on reaction with $HgCl_2$.

1 MARK QUESTIONS

Q1. Write the formula for the following coordination compound:
Tetraamineaquachloridocobalt(III) chloride

Q2. Write the IUPAC name of the following coordination compound:

$[CoCl_2(en)_2]Cl$

Q3. Why is geometrical isomerism not possible in tetrahedral complexes having two different types of unidentate ligands coordinated with the central metal ion ?

Q4. Out of the following two coordination entities which is chiral (optically active)?

(a) *cis*-$[CrCl_2 (ox)_2]^{3-}$ (b) *trans*-$[CrCl_2 (ox)_2]^{3-}$

Q5. The spin only magnetic moment of $[MnBr_4]^{2-}$ is 5.9 BM. Predict the geometry of the complex ion?

Q6. $[NiCl_4]^{2-}$ is paramagnetic while $[Ni(CO)_4]$ is diamagnetic though both are tetrahedral. Why?

2 MARKS QUESTIONS

Q1. Draw structures of geometrical isomers of $[Fe(NH_3)_2(CN)_4]^-$

Q2. Indicate the type of isomerism exhibited by the following complex and draw the structures for these isomers:

$[Co(en)_3]Cl_3$

Q3. Give evidence that $[Co(NH_3)_5 Cl]SO_4$ and $[Co(NH_3)_5 SO_4]Cl$ are ionization isomers.

Q4. Calculate the overall complex dissociation equilibrium constant for the $[Cu(NH_3)_4]^{2+}$ ion, given that β_4 for this complex is 2.1×10^{13}.

Q5. What is meant by unidentate ligand? Give two examples.

Q6. What is meant by didentate ligand? Give two examples.

Q7. What is meant by ambidentate ligands? Give two examples.

Q8. Draw the structures of optical isomers of:

$[Cr(C_2O_4)_3]^{3-}$

Q9. Discuss the nature of bonding in metal carbonyls.

Q10. What is meant by the *chelate effect*? Give an example.

Q11. Draw the structures of:

(i) $Ni(CO)_4$ (ii) $Fe(CO)_5$

3 MARKS QUESTIONS

Q1. Discuss the nature of bonding in the following coordination entities on the basis of valence bond theory:

(i)$[Fe(CN)_6]^{4-}$ (ii) $[FeF_6]^{3-}$ (iii) $[Co(C_2O_4)_3]^{3-}$

Also predict their magnetic behaviour.

Q2. What is crystal field splitting energy? Draw figure to show the splitting of *d* orbitals in an octahedral crystal field. How does the magnitude of Δ_o decide the actual configuration of *d* orbitals in a coordination entity?

Q3. Discuss briefly giving an example in each case the role of coordination compounds in:

(i) biological systems (iii) analytical chemistry

(ii) medicinal chemistry .

UNIT 13:
AMINES

2.	Amines	1. Ammonolysis of alkylholids, Gabriel Phthalimide synthesis, Hoffmann Bromamide Degradation. 2. Basic character of Amines(pK_b) and comparisons in gaseous and aqueous phase. 3. Carbylomine Reaction ,Hinsberg's Test. 4. Electrophilic substitution. 5. Diazonium salts –reactions

IUPAC NOMENCLATURE

IUPAC NOMENCLATURE

Amine	IUPAC name
$CH_3-CH_2-NH_2$	Ethanamine
$CH_3-CH_2-CH_2-NH_2$	Propan-1-amine
$CH_3-CH(NH_2)-CH_3$	Propan-2-amine
$CH_3-N(H)-CH_2-CH_3$	N-Methylethanamine
$CH_3-N(CH_3)-CH_3$	N,N-Dimethylmethanamine
$C_2H_5-N(C_2H_5)-\overset{1}{C}H_2-\overset{2}{C}H_2-\overset{3}{C}H_2-\overset{4}{C}H_3$	N,N-Diethylbutan-1-amine
$NH_2-\overset{1}{C}H_2-\overset{2}{C}H=\overset{3}{C}H_2$	Prop-2-en-1-amine
$NH_2-(CH_2)_6-NH_2$	Hexane-1,6-diamine
	Aniline or Benzenamine
	2-Aminotoluene
	4-Bromobenzenamine or 4-Bromoaniline
	N,N-Dimethylbenzenamine

NAME REACTIONS

1. Gabriel phthalimide synthesis

Gabriel synthesis is used for the preparation of primary amines. Phthalimide on treatment with ethanolic potassium hydroxide forms potassium salt of phthalimide which on heating with alkyl halide followed by alkaline hydrolysis produces the corresponding primary amine. Aromatic primary amines cannot be prepared by this method because aryl halides do not undergo nucleophilic substitution with the anion formed by phthalimide.

2. Hoffmann bromamide degradation reaction

Hoffmann developed a method for preparation of primary amines by treating an amide with bromine in an aqueous or ethanolic solution of sodium hydroxide. The amine so formed contains one carbon less than that present in the amide.

$$R-\overset{\overset{\displaystyle O}{\|}}{C}-NH_2 + Br_2 + 4NaOH \longrightarrow R-NH_2 + Na_2CO_3 + 2NaBr + 2H_2O$$

3. Carbylamine reaction

Aliphatic and aromatic primary amines on heating with chloroform and ethanolic potassium hydroxide form isocyanides or carbylamines which are foul smelling substances. Secondary and tertiary amines do not show this reaction. This reaction is known as carbylamine reaction or isocyanide test and is used as a test for primary amines.

$$R-NH_2 + CHCl_3 + 3KOH \xrightarrow{Heat} R-NC + 3KCl + 3H_2O$$

4. Hinsberg Test:

Benzenesulphonyl chloride ($C_6H_5SO_2Cl$), which is also known as Hinsberg's reagent, reacts with primary and secondary amines to form sulphonamides.

(a) The reaction of benzenesulphonyl chloride with primary amine

yields N-ethylbenzenesulphonyl amide.

N-Ethylbenzenesulphonamide
(soluble in alkali)

The hydrogen attached to nitrogen in sulphonamide is strongly acidic due to the presence of strong electron withdrawing sulphonyl group. Hence, it is soluble in alkali.

(b) In the reaction with secondary amine, N,N-diethylbenzenesulphonamide

is formed.

N,N-Diethylbenzenesulphonamide

Since N, N-diethylbenzene sulphonamide does not contain any hydrogen atom attached to nitrogen atom, it is not acidic and hence insoluble in alkali.

(c) Tertiary amines do not react with benzenesulphonyl chloride. This property of amines reacting with benzenesulphonyl chloride in a different manner is used for the distinction of primary, secondary and tertiary amines and also for the separation of a mixture of amines.

5. Sandmeyer Reaction

The Cl–, Br– and CN– nucleophiles can easily be introduced in the benzene ring of diazonium salts in the presence of Cu(I) ion.

6. Gatterman Reaction

Chlorine or bromine can be introduced in the benzene ring by treating the diazonium salt solution with corresponding halogen acid in the presence of copper powder.

7. Coupling reactions

The azo products obtained have an extended conjugate system having both the aromatic rings joined through the –N=N– bond. These compounds are often coloured and are used as dyes. Benzene diazonium chloride reacts with phenol in which the phenol molecule at its para position is coupled with the diazonium salt to form p-hydroxyazobenzene. This type of reaction is known as coupling reaction.

Similarly the reaction of diazonium salt with aniline yields p-aminoazobenzene.

DISTINCTION BETWEEN PAIRS OF COMPOUNDS

Give one chemical test to distinguish between the following pairs of compounds.

(i) Methylamine and dimethylamine
(ii) Secondary and tertiary amines
(iii) Ethylamine and aniline

(iv) Aniline and benzylamine
(v) Aniline and N-methylaniline.

ANS. (i) Methylamine and dimethylamine can be distinguished by the carbylamine test. Carbylamine test: Aliphatic and aromatic primary amines on heating with chloroform and ethanolic potassium hydroxide form foul-smelling isocyanides or carbylamines. Methylamine (being an aliphatic primary amine) gives a positive carbylamine test, but dimethylamine does not.

$$\underset{\text{Methylamine}(1^0)}{CH_3-NH_2} + CHCl_3 + 3KOH \xrightarrow{\Delta} \underset{\text{Methyl isocyanide (foul smell)}}{CH_3-NC} + 3KCl + 3H_2$$

$$(CH_3)_2NH + CHCl_3 + 3KOH \xrightarrow{\Delta} \text{No reaction}$$

(ii) Secondary and tertiary amines can be distinguished by allowing them to react with Hinsberg's reagent (benzenesulphonyl chloride, $C_6H_5SO_2Cl$).Secondary amines react with Hinsberg's reagent to form a product that is insoluble in an alkali. For example, N, N−diethylamine reacts with Hinsberg's reagent to form N, N−diethylbenzenesulphonamide, which is insoluble in an alkali. Tertiary amines, however, do not react with Hinsberg's reagent.

(iii) Ethylamine and aniline can be distinguished using the azo-dye test. A dye is obtained when aromatic amines react with HNO_2 ($NaNO_2$ + dil.HCl) at 0-5°C, followed by a reaction with the alkaline solution of 2-naphthol. The dye is usually yellow, red, or orange in colour. Aliphatic amines give a brisk effervescence due (to the evolution of N_2 gas) under similar conditions.

$$CH_3CH_2-NH_2 + HONO \xrightarrow{0\text{-}5^\circ C} C_2H_5OH + N_2\uparrow + H_2O$$

(iv) Aniline and benzylamine can be distinguished by their reactions with the help of nitrous acid, which is prepared in situ from a mineral acid and sodium nitrite.

Benzylamine reacts with nitrous acid to form unstable diazonium salt, which in turn gives alcohol with the evolution of nitrogen gas.

On the other hand, aniline reacts with HNO_2 at a low temperature to form stable diazonium salt. Thus, nitrogen gas is not evolved.

(v) Aniline and N-methylaniline can be distinguished using the Carbylamine test. Primary amines, on heating with chloroform and ethanolic potassium hydroxide, form foul-smelling isocyanides or carbylamines. Aniline, being an aromatic primary amine, gives positive carbylamine test. However, N-methylaniline, being a secondary amine does not.

REASONING QUESTIONS

Q1. Account for the following:

(i) pKb of aniline is more than that of methylamine.

(ii) Ethylamine is soluble in water whereas aniline is not.

(iii) Methylamine in water reacts with ferric chloride to precipitate hydrated ferric oxide.

(iv) Although amino group is o– and p– directing in aromatic electrophilic substitution reactions, aniline on nitration gives a substantial amount of m-nitroaniline.

(v) Aniline does not undergo Friedel-Crafts reaction.

(vi) Diazonium salts of aromatic amines are more stable than those of aliphatic amines.

(vii) Gabriel phthalimide synthesis is preferred for synthesising primary amines.

ANS. (i) pK_b of aniline is more than that of methylamine:

Aniline Methylamine

Aniline undergoes resonance and as a result, the electrons on the N-atom are delocalized over the benzene ring. Therefore, the electrons on the N-atom are less available to donate.

On the other hand, in case of methylamine (due to the +I effect of methyl group), the electron density on the N-atom is increased. As a result, aniline is less basic than methylamine. Thus, pK_b of aniline is more than that of methylamine.

(ii) Ethylamine is soluble in water whereas aniline is not:

Ethylamine when added to water forms intermolecular H−bonds with water. Hence, it is soluble in water.

Ethylamine

But aniline does not undergo H−bonding with water to a very large extent due to the presence of a large hydrophobic $-C_6H_5$ group. Hence, aniline is insoluble in water.

(iii) Methylamine in water reacts with ferric chloride to precipitate hydrated ferric oxide:

Methylamine Water

Due to the +I effect of $-CH_3$ group, methylamine is more basic than water. Therefore, in water, methylamine produces OH^- ions by accepting H^+ ions from water.

$$CH_3-NH_2 + H-OH \longrightarrow CH_3-\overset{+}{N}H_3 + OH^-$$

Ferric chloride ($FeCl_3$) dissociates in water to form Fe^{3+} and Cl^- ions.

$$FeCl_3 \longrightarrow Fe^{3+} + 3Cl^-$$

Then, OH^- ion reacts with Fe^{3+} ion to form a precipitate of hydrated ferric oxide.

$$2Fe^{3+} + 6OH^- \longrightarrow \underset{\text{Hydrated ferric oxide}}{Fe_2O_3 \cdot 3H_2O}$$

(iv) Although amino group is o,p− directing in aromatic electrophilic substitution reactions, aniline on nitration gives a substantial amount of m-nitroaniline:

Nitration is carried out in an acidic medium. In an acidic medium, aniline is protonated to give anilinium ion (which is meta-directing).

For this reason, aniline on nitration gives a substantial amount of m-nitroaniline.

(v) Aniline does not undergo Friedel-Crafts reaction:

A Friedel-Crafts reaction is carried out in the presence of $AlCl_3$. But $AlCl_3$ is acidic in nature, while aniline is a strong base. Thus, aniline reacts with $AlCl_3$ to form a salt (as shown in the following equation).

Due to the positive charge on the N-atom, electrophilic substitution in the benzene ring is deactivated. Hence, aniline does not undergo the Friedel-Crafts reaction.

(vi) Diazonium salts of aromatic amines are more stable than those of aliphatic amines:

The diazonium ion undergoes resonance as shown below:

This resonance accounts for the stability of the diazonium ion. Hence, diazonium salts of aromatic amines are more stable than those of aliphatic amines.

(vii) Gabriel phthalimide synthesis is preferred for synthesising primary amines:

Gabriel phthalimide synthesis results in the formation of 1° amine only. 2° or 3° amines are not formed in this synthesis. Thus, a pure 1° amine can be obtained. Therefore, Gabriel phthalimide synthesis is preferred for synthesizing primary amines.

Q2. Why cannot aromatic primary amines be prepared by Gabriel phthalimide

synthesis?

ANS. Gabriel phthalimide synthesis is used for the preparation of aliphatic primary amines. It involves nucleophilic substitution (S_N2) of alkyl halides by the anion formed by the phthalimide.

But aryl halides do not undergo nucleophilic substitution with the anion formed by the phthalimide.

Hence, aromatic primary amines cannot be prepared by this process.

Q3. Give plausible explanation for each of the following:

(i) Why are amines less acidic than alcohols of comparable molecular masses?

(ii) Why do primary amines have higher boiling point than tertiary amines?

(iii) Why are aliphatic amines stronger bases than aromatic amines?

ANS. (i) Amines undergo protonation to give amide ion.

$$R-NH_2 \longrightarrow R-\bar{N}H + H^+$$

Amide ion

Similarly, alcohol loses a proton to give alkoxide ion.

$$\underset{\text{Alcohol}}{R-OH} \longrightarrow \underset{\text{Alkoxide ion}}{R-\bar{O}} + H^+$$

In an amide ion, the negative charge is on the N-atom whereas in alkoxide ion, the negative charge is on the O-atom. Since O is more electronegative than N, O can accommodate the negative charge more easily than N. As a result, the amide ion is less stable than the alkoxide ion. Hence, amines are less acidic than alcohols of comparable molecular masses.

(ii) In a molecule of tertiary amine, there are no H−atoms whereas in primary amines, two hydrogen atoms are present. Due to the presence of H−atoms, primary amines undergo extensive intermolecular H−bonding.

As a result, extra energy is required to separate the molecules of primary amines. Hence, primary amines have higher boiling points than tertiary amines.

(iii) Due to the −R effect of the benzene ring, the electrons on the N- atom are less available in case of aromatic amines. Therefore, the electrons on the N-atom in aromatic amines cannot be donated easily. This explains why aliphatic amines are stronger bases than aromatic amines.

SOLVED QUESTIONS

1 MARK QUESTIONS

Q1. Give the IUPAC name of the compound and classify into primary, secondary or tertiary amines.

$(CH_3)_2CHNH_2$ 1-Methylethanamine (1^0 amine)

Q2. Give the IUPAC name of the compound and classify into primary, secondary or tertiary amines.

$CH_3(CH_2)_2NH_2$ Propan-1-amine (1^0 amine)

Q3. Give the IUPAC name of the compound and classify into primary, secondary or tertiary amines.

$CH_3NHCH(CH_3)_2$ N−Methyl-2-methylethanamine (2^0 amine)

Q4. Give the IUPAC name of the compound and classify into primary, secondary or tertiary amines.

$(CH_3)_3CNH_2$ 2-Methylpropan-2-amine (1^0 amine)

Q5. Give the IUPAC name of the compound and classify into primary, secondary or tertiary amines.

$C_6H_5NHCH_3$ N−Methylbenzamine or N-methylaniline (2^0 amine)

Q6. Write short notes on diazotization

Aromatic primary amines react with nitrous acid (prepared in situ from $NaNO_2$ and a mineral acid such as HCl) at low temperatures (273-278 K) to form diazonium salts. This conversion of aromatic primary amines into diazonium salts is known as diazotization. For example, on treatment with $NaNO_2$ and HCl at 273−278 K, aniline produces benzenediazonium chloride, with NaCl and H_2O as by-products.

Q7. Write short notes on ammonolysis

When an alkyl or benzyl halide is allowed to react with an ethanolic solution of ammonia, it undergoes nucleophilic substitution reaction in which the halogen atom is replaced by an amino ($-NH_2$) group. This process of cleavage of the carbon-halogen bond is known as ammonolysis.

When this substituted ammonium salt is treated with a strong base such as sodium hydroxide, amine is obtained.

Though primary amine is produced as the major product, this process produces a mixture of primary, secondary and tertiary amines, and also a quaternary ammonium salt

$$\underset{(1^\circ)}{RNH_2} \xrightarrow{RX} \underset{(2^\circ)}{R_2NH} \xrightarrow{RX} \underset{(3^\circ)}{R_3N} \xrightarrow{RX} \underset{\text{Quaternary ammonium salt}}{R_4\overset{+}{N}\overset{-}{X}}$$

Q8. Write short notes on acetylation.

Acetylation (or ethanoylation) is the process of introducing an acetyl group into a molecule. Aliphatic and aromatic primary and secondary amines undergo acetylation reaction by nucleophilic substitution when treated with acid chlorides, anhydrides or esters. This reaction involves the replacement of the hydrogen atom of $-NH_2$ or > NH group by the acetyl group, which in turn leads to the production of amides. To shift the equilibrium to the right hand side, the HCl formed during the reaction is removed as soon as it is formed. This reaction is carried out in the presence of a base (such as pyridine) which is stronger than the amine.

$$C_2H_5NH_2 + CH_3COCl \xrightarrow{\text{pyridine}} C_2H_5NHCOCH_3 + HCl$$

Q9.Why are amines basic in character?

<u>ANS</u>. Like ammonia, the nitrogen atom in amines RNH_2 is trivalent and bears an unshared pair of electrons. Thus it acts like a Lewis base and donates the pair of electrons to electron-deficient species which further increases due to +I effect of alkyl radical.

Q10. Arrange the following in decreasing order of their basic strength:

$C_6H_5NH_2$, $C_2H_5NH_2$, $(C_2H_5)_2NH$, NH_3

The decreasing order of basic strength of the above amines and ammonia

follows the following order:

$(C_2H_5)_2NH$ > $C_2H_5NH_2$ > NH_3 > $C_6H_5NH_2$

<u>SOLVED EXAMPLES</u> (2 Marks)

Q1. Write chemical equations for the following reactions:

(i) Reaction of ethanolic NH_3 with C_2H_5Cl.

(ii) Ammonolysis of benzyl chloride and reaction of amine so formed

with two moles of CH_3Cl

ANS.

(i) $C_2H_5–Cl \xrightarrow{NH_3} C_2H_5–NH_2 \xrightarrow{C_2H_5-Cl} C_2H_5–\overset{\overset{H}{|}}{N}–C_2H_5 \xrightarrow{C_2H_5-Cl} C_2H_5–\underset{\underset{C_2H_5}{|}}{N}–C_2H_5$

Chloroethane Ethanamine N-Ethylethanamine N,N-Diethylethanamine

(ii) $C_6H_5–CH_2–Cl \xrightarrow{NH_3} C_6H_5–CH_2NH_2 \xrightarrow{2CH_3Cl} C_6H_5–CH_2–\underset{\underset{CH_3}{|}}{N}–CH_3$

Benzylchloride Benzylamine N,N-Dimethylphenylmethanamine

Q2. Write chemical equations for the following conversions:

(i) CH_3 –CH_2 –Cl into CH_3 –CH_2 –CH_2 –NH_2

(ii) C_6H_5–CH_5 –Cl into C_6H_5 –CH_2 –CH_2 –NH_2

(i) $CH_3–CH_2–Cl \xrightarrow{\text{Ethanolic NaCN}} CH_3–CH_2–C\equiv N \xrightarrow{\text{reduction}} CH_3–CH_2–CH_2–NH_2$

Chloroethane Propanenitrile Propan-1-amine

(ii) $C_6H_5–CH_2–Cl \xrightarrow{\text{Ethanolic NaCN}} C_6H_5–CH_2–C\equiv N \xrightarrow{H_2/Ni} C_6H_5–CH_2–CH_2–NH_2$

Chlorophenylmethane (Benzyl chloride) Phenylethanenitrile (Benzyl cyanide) 2-Phenylethanamine

Q3.Write structures and IUPAC names of

(i) the amide which gives propanamine by Hoffmann bromamide

reaction.

(ii) the amine produced by the Hoffmann degradation of benzamide.

ANS. (i) Propanamine contains three carbons. Hence, the amide molecule must contain four carbon atoms. Structure and IUPAC name of the starting amide with four carbon atoms are given below:

$CH_3–CH_2–CH_2–\underset{\underset{O}{||}}{C}–NH_2$ (Butanamide)

(ii) Benzamide is an aromatic amide containing seven carbon atoms. Hence, the amine formed from benzamide is aromatic primary amine containing six carbon atoms.

(Aniline or benzenamine)

Q4. How will you convert 4-nitrotoluene to 2-bromobenzoic acid?

ANS.

Q5. Write the reactions of (i) aromatic and (ii) aliphatic primary amines with nitrous acid.

ANS. (i) Aromatic amines react with nitrous acid (prepared in situ from $NaNO_2$ and a mineral acid such as HCl) at 273 − 278 K to form stable aromatic diazonium salts i.e., NaCl and H_2O.

(ii) Aliphatic primary amines react with nitrous acid (prepared in situ from $NaNO_2$ and a mineral acid such as HCl) to form unstable aliphatic diazonium salts, which further produce alcohol and HCl with the evolution of N_2 gas.

Q6. How will you convert:

(i) Ethanoic acid into methanamine

(ii) Hexanenitrile into 1-aminopentane

ANS. (i)

(ii)

Q7. How will you convert:

(i) Methanol to ethanoic acid

(ii) Ethanamine into methanamine

ANS. (i)

(ii)

Q8. How will you convert

(i) Ethanoic acid into propanoic acid

(ii) Methanamine into ethanamine

<u>ANS.</u> (i)

(ii)

Q9. How will you convert

(i) Nitromethane into dimethylamine

(ii) Propanoic acid into ethanoic acid?

(i)

(ii)

Q10. An aromatic compound ‗A' on treatment with aqueous ammonia and heating forms compound ‗B' which on heating with Br_2 and KOH forms a compound ‗C' of molecular formula C_6H_7N. Write the structures and IUPAC names of compounds A, B and C.

ANS. It is given that compound ‗C' having the molecular formula, C_6H_7N is formed by heating compound ‗B' with Br_2 and KOH. This is a Hoffmann bromamide degradation reaction. Therefore, compound ‗B' is an amide and compound ‗C' is an amine. The only amine having the molecular formula, C_6H_7N is aniline, ($C_6H_5NH_2$).The given reactions can be explained with the help of the following equations:

3 MARKS QUESTIONS

Q1. Arrange the following:

(i) In decreasing order of the pKb values:
$C_2H_5NH_2$, $C_6H_5NHCH_3$, $(C_2H_5)_2NH$ and $C_6H_5NH_2$

(ii) In increasing order of basic strength:

$C_6H_5NH_2$, $C_6H_5N(CH_3)_2$, $(C_2H_5)_2$ NH and CH_3NH_2

(iii) In increasing order of basic strength:

Aniline, p-nitroaniline and p-toluidine

ANS. (i) The order of increasing basicity of the given compounds is as follows:
$C_6H_5NH_2 < C_6H_5NHCH_3 < C_2H_5NH_2 < (C_2H_5)_2NH$
We know that the higher the basic strength, the lower is the pK_b values.
$C_6H_5NH_2 > C_6H_5NHCH_3 > C_2H_5NH_2 > (C_2H_5)_2NH$
(ii)The increasing order of the basic strengths of the given compounds is as follows:
$C_6H_5NH_2 < C_6H_5N(CH_3)_2 < CH_3NH_2 < (C_2H_5)_2NH$
(iii) The increasing order of the basic strengths of the given compounds is :
p-Nitroaniline < Aniline < p-Toluidine

Q2. Arrange the following
(i) In decreasing order of basic strength in gas phase:
$C_2H_5NH_2$, $(C_2H_5)_2NH$, $(C_2H_5)_3N$ and NH_3
(ii) In increasing order of boiling point:
C_2H_5OH, $(CH_3)_2NH$, $C_2H_5NH_2$
(iii) In increasing order of solubility in water:
$C_6H_5NH_2$, $(C_2H_5)_2NH$, $C_2H_5NH_2$.

ANS. (i) The given compounds can be arranged in the decreasing order of their basic strengths in the gas phase as follows:
$(C_2H_5)_3N > (C_2H_5)_2NH > C_2H_5NH_2 > NH_3$
(ii) The given compounds can be arranged in the increasing order of their boiling points as follows:
$(CH_3)_2NH < C_2H_5NH_2 < C_2H_5OH$
(iii) The more extensive the H−bonding, the higher is the solubility. $C_2H_5NH_2$ contains two H-atoms whereas $(C_2H_5)_2NH$ contains only one H-atom. Thus, $C_2H_5NH_2$ undergoes more extensive H−bonding than $(C_2H_5)_2NH$. Hence, the solubility in water of $C_2H_5NH_2$ is more than that of $(C_2H_5)_2NH$.

Q3. Accomplish the following conversions:
(i) Nitrobenzene to benzoic acid
(ii) Benzene to m-bromophenol
(iii) Benzoic acid to aniline

ANS. (i)

(ii)

(iii)

Q4. Accomplish the following conversions:
(i) Aniline to 2,4,6-tribromofluorobenzene
(ii) Benzyl chloride to 2-phenylethanamine
(iii) Chlorobenzene to p-chloroaniline

ANS. (i)

NH2
Br2/H2O
Aniline
NH2
Br
Br
Br
2, 4, 6-Tribromoaniline
NaNO2/HCl
273–278 K
N2Cl
Br
Br
Br
2, 4, 6-Tribromobenzene diazonium chloride
HBF4
N2BF4
Br
Br
Br
Δ
–N2, –BF3
F
Br
Br
Br
2, 4, 6-Tribromofluorobenzene

(ii)

CH2Cl
Ethanolic NaCN
–NaCl
CH2CN
H2/Ni
CH2CH2NH2
Benzyl chloride
Phenylethanenitrile
2-Phenylethanamine

(iii)

Q5. Accomplish the following conversions:
(i) Aniline to p-bromoaniline
(ii) Benzamide to toluene
(iii) Aniline to benzyl alcohol.

<u>ANS.</u> (i)

(ii)

(iii)

5 MARKS QUESTIONS

Q1. Give the structures of A, B and C in the following reactions:

(i) $CH_3CH_2I \xrightarrow{NaCN} A \xrightarrow[\text{Partial hydrolysis}]{OH^-} B \xrightarrow{NaOH + Br_2} C$

(ii) $C_6H_5N_2Cl \xrightarrow{CuCN} A \xrightarrow{H_2O/H^+} B \xrightarrow[\Delta]{NH_3} C$

(iii) $CH_3CH_2Br \xrightarrow{KCN} A \xrightarrow{LiAlH_4} B \xrightarrow[0^0C]{HNO_2} C$

(iv) $C_6H_5NO_2 \xrightarrow{Fe/HCl} A \xrightarrow[273K]{NaNO_2 + HCl} B \xrightarrow[\Delta]{H_2O/H^+} C$

(v) $CH_3COOH \xrightarrow[\Delta]{NH_3} A \xrightarrow{NaOBr} B \xrightarrow{NaNO_2/HCl} C$

ANS. (i)

(ii)

(iii)

(iv)

(v)

Q2. Complete the following reactions:

(i) $C_6H_5NH_2 + CHCl_3 + alc.KOH \rightarrow$

(ii) $C_6H_5N_2Cl + H_3PO_2 + H_2O \rightarrow$

(iii) $C_6H_5NH_2 + H_2SO_4(conc.) \rightarrow$

(iv) $C_6H_5N_2Cl + C_2H_5OH \rightarrow$

(v) $C_6H_5NH_2 + Br_2(aq) \rightarrow$

<u>ANS.</u> (i)

(ii)

$$C_6H_5N_2Cl + H_3PO_2 + H_2O \rightarrow C_6H_6 + N_2 + H_3PO_3 + HCl$$

Benzenediazonium chloride — Benzene

(iii)

$$C_6H_5NH_2 + conc.H_2SO_4 \rightarrow C_6H_5\overset{+}{N}H_3\overset{-}{HSO_4}$$

Aniline — Anilinium hydrogen sulphate

(iv)

$$C_6H_5N_2Cl + C_2H_5OH \rightarrow C_6H_6 + CH_3CHO + N_2 + HCl$$

Benzenediazonium chloride — Ethanol — Benzene — Ethanal

(v)

Assignments

Level 1

1. Write IUPAC Name of $C_6H_5N(CH_3)_3Br$?
2. Which reaction is used for preparation of pure aliphatic & aralkyl primary amine ?
3. Name one reagent used for the separation of primary, secondary & tertiary amine ?
4. What amine salts are used for determing their molecular masses ?
5. What is the directive influence of amino group in arylamines?
6. Why are benzene diazonium salts soluble in water ?
7. Which is more basic: CH_3NH_2 & $(CH_3)_3N$?
8. Which is more acidic, aniline or ammonia ?
9. Write the IUPAC name of $C_6H_5NHCH_3$?
10. Mention two uses of sulphanilic acid?

Level 2

1. What for are quaternary ammonium salts widely used ?
2. What product is formed when aniline is first diazotized and then treated with Phenol in alkaline medium ?
3. How is phenyl hydrazine prepared from aniline ?
4. What is the IUPAC name of a tertiary amine containing one methyl, one ethyl And one n-propyl group ?
5. Explain why silver chloride is soluble in aqueous solution of methylamine ?
6. Write the IUPAC name of $C_6H_5N(CH_3)_3$ Br ?
7. Primary amines have higher boiling points then tertiary amines why ?

8. Why is it necessary to maintain the temperature between 273 K & 278 K during diazotization?
9. Arrange the following in order of decreasing basic strength : Ethyl amine, Ammonia, Triethylamine ?
10. Why aniline is acetylated first to prepare mono bromo derivative?

LEVEL 3

1. Arrange the following in decreasing order of their basic strength.

   $C_6H_5NH_2$, C2H5NH2, $(C_2H_5)_2NH$, NH_3

2. Write chemical equation for the conversion

   CH_3-CH_2-Cl into CH_3 –CH_2-CH_3-NH_2

3. Write the equation involved in Carbylamines reactions?

4. How will you distinguish the following pairs? (i) Methanamine and N-methyl methane amine (ii) Aniline and ethyl amine

5. Write chemical sections involved in following name reactions. (i) Hoffmann Bromoamide reaction. (ii) Diazotisation reaction.

COMMON ERRORS

Basic character of amines in aqueous and in gaseous state, p_{ka} and p_{kb} values

1 MARK QUESTIONS

Q1. Arrange the following in decreasing order of their basic strength:

$C_6H_5NH_2$, $C_2H_5NH_2$, $(C_2H_5)_2NH$, NH_3
Q2. Arrange the following in decreasing order of the p*Kb* values:
$C_2H_5NH_2$, $C_6H_5NHCH_3$, $(C_2H_5)_2NH$ and $C_6H_5NH_2$
Q3. p*Kb* of aniline is more than that of methylamine. Why?
Q4. Ethylamine is soluble in water whereas aniline is not. Give reason.
Q5. Methylamine in water reacts with ferric chloride to precipitate hydrated ferric oxide. Why?
Q6. Although amino group is *o*– and *p*– directing in aromatic electrophilic substitution reactions, aniline on nitration gives a substantial amount of
m-nitroaniline. Give reason.
Q7. Aniline does not undergo Friedel-Crafts reaction. Why?
Q8. Diazonium salts of aromatic amines are more stable than those of aliphatic amines. Why?
Q9. Gabriel phthalimide synthesis is preferred for synthesising primary amines. Give reason
Q10. Why cannot aromatic primary amines be prepared by Gabriel phthalimide synthesis?
Q11. Why do primary amines have higher boiling point than tertiary amines?
Q12. Why are aliphatic amines stronger bases than aromatic amines?
Q13. Direct nitration of aniline is not carried out. Give reason.
Q14. The presence of base is needed in the ammonolysis of alkyl halides. Why?

<u>2 MARKS QUESTIONS</u>

Q1. Write structures and IUPAC names of
(i) the amide which gives propanamine by Hoffmann bromamide reaction.
(ii) the amine produced by the Hoffmann degradation of benzamide.
Q2. Give one chemical test to distinguish between the following pairs of compounds.
(i) Methylamine and dimethylamine (ii) Ethylamine and aniline
Q3. Write short notes on the following:
(i) Carbylamine reaction (ii) Diazotisation
Q4. Explain the following with the help of an example.
(i) Hofmann's bromamide reaction (ii) Coupling reaction
Q5. Explain the following with the help of an example.
(i) Ammonolysis (ii) Gabriel phthalimide synthesis
Q6. How can you convert an amide into an amine having one carbon less than the starting compound? Name the reaction.
Q7. Give a chemical test to distinguish between:
(a) $C_6H_5NH_2$ & CH_3NH_2
(b) CH_3NHCH_3 & $(CH_3)_3N$
Q8. Give the IUPAC names of:
(a) $(CH_3)_2CHNH_2$
(b) $(CH_3CH_2)_2NCH_3$
Q9. Write the structures of:
(a) 3-Bromobenzenamine

(b) 3-Chlorobutanamide

3 MARKS QUESTIONS

Q1. How will you convert
(i) Benzene into aniline (ii) Benzene into N, N-dimethylaniline
(iii) Aniline to Sulphanilic acid

Q2. An aromatic compound 'A' on treatment with aqueous ammonia and heatingforms compound 'B' which on heating with Br_2 and KOH forms a compound 'C'of molecular formula C_6H_7N. Write the structures and IUPAC names of compounds A, B and C.

Q3. How will you carry out the following conversions (Write Chemical equations and reaction conditions):
(a) Aniline to Phenol
(b)Acetamide to Ethylamine
(c) Aniline to *p*-nitroaniline

Chapter:-6 General Principles & Process of Isolation of Elements

Important Points :

1. The chemical substances in the earth's crust obtained by mining are called Minerals.
2. Minerals, which act as source for metal, are called Ore.
3. The unwanted impurities present in ore are called Gangue.
4. The entire process of extraction of metal from its ore is called Metallurgy.
5. Removal of gangue from ore is called Concentration, Dressing or Benefaction of ore.
6. Concentration by Hydraulic washing is based on the difference in gravities of ore and gangue particles.
7. Concentration by Magnetic separation is based on differences in magnetic properties of ore components. If either of ore or gangue is capable of attracted by a magnet field, then such separation is carried out.
8. Concentration by Froth Flotation Process is based on the facts that sulphide ore is wetted by oil & gangue particles are wetted by water.
9. Concentration by Leaching is based on the facts that ore is soluble in some suitable reagent & gangue is insoluble in same reagent. e.g. Bauxite ore contains impurities of silica, iron oxide & TiO_2 .The powdered ore is treated with NaOH which dissolve Al & impurities remains insoluble in it.

$$Al_2O_3 + 2NaOH + 3\,H_2O \longrightarrow 2\,Na\,[Al(OH)_4].$$

10. Calcination involves heating of ore in absence of air below melting point of metal. In this process volatile impurities escapes leaving behind metal oxide.

$$Fe_2O_3.xH_2O \longrightarrow Fe_2O_3 + xH_2O$$

$$ZnCO_3 \longrightarrow ZnO + CO_2$$

$$CaCO_3.MgCO_3 \longrightarrow CaO + MgO + 2CO_2$$

11. Roasting involves heating of ore in presence of air below melting point of metal in reverberatory furnace. In this process volatile impurities escapes leaving behind metal oxide and metal sulphide converts to metal oxide.

$$2\,ZnS + 3\,O_2 \longrightarrow 2ZnO + 2SO_2$$

$$2PbS + 3\,O_2 \longrightarrow 2\,PbO + 2\,SO_2$$

$$2\,Cu_2S + 3\,O_2 \longrightarrow 2Cu_2O + 2\,SO_2$$

12. Reduction of metal oxide involves heating of metal in presence of suitable reagent Coke or CO_2.

13. Reactions taking place at different zones of blast furnace in extraction of iron:-

(i) Zone of reduction:- Temperature range 250^oC-700^oC

$$3Fe_2O_3+CO \longrightarrow 2Fe_3O_4+CO_2$$

$$Fe_3O_4+CO \longrightarrow 3FeO+ CO_2$$

$$FeO +CO \longrightarrow Fe+ CO_2$$

(ii) Zone of slag formation:- Temperature range 800^oC-1000^oC

$$CaCO_3 \longrightarrow CaO+CO_2$$

$$CaO+SiO_2 \longrightarrow CaSiO_3, \qquad P_4O_{10}+10C \longrightarrow 4P+10CO,$$

$$SiO_2+2C \longrightarrow Si+2CO, \qquad MnO_2+2C \longrightarrow Mn+2CO$$

(iii) Zone of fusion: - Temperature range 1150^oC-1350^oC

$$CO_2 + C \longrightarrow 2CO$$

(iv) Zone of fusion: - Temperature range 1450^oC-1950^oC

$$C +O_2 \longrightarrow CO_2$$

14. **FLOW SHEET FOR EXTRACTION OF IRON:-**

Iron ore(Magnetite Fe_3O_4)

↓

Concentration is done by Gravity separation followed by magnetic separation

↓

Calcination &Roasting i.e. Ore + Air +Heat→Moisture,CO_2,SO_2, As_2O_3 removed And FeO oxidized to Fe_2O_3

↓

Smelting of charge i.e. mixture of ore, coke & $CaCO_3$ takes place in long BLAST FURNACE. Following reaction take place at different zones:-

(refer to point 13)

↓

Pig iron is obtained, which is remelted and cooled then cast iron is obtained

15. Pig Iron: - It contains Fe 93-95%, Carbon 2.5-5%, and Impurities 3%.

16. Cast Iron: - It contains Fe 99.5-99.8%, Carbon 0.1-0.2% Impurities 0.3%.

17. Spongy iron: - Iron formed in the zone of reduction of blast furnace is called spongy iron. It contains impurities of C, Mn , Si, etc.

18. FLOW SHEET FOR EXTRACTION OF COPPER:-

Copper Pyrites $CuFeS_2$

↓

Concentration is done by Froth floatation process

Powdered ore + water +pine oil +air→ Sulphide ore in the froth

↓

Roasting is presence of air. following reactions take place:-

$S + O2 \rightarrow SO_2$, $4As+3O_2 \rightarrow 2As_2O_3$, $2CuFeS_2+O_2 \rightarrow Cu_2S+2FeS+SO_2$

↓

Smelting in small blast furnace of a mixture of Roasted ore, coke, and silica.

$2FeS + 3O_2 \rightarrow 2FeO + 2SO_2$, $FeO + SiO_2 \rightarrow FeSiO_3$(slag)

↓

A mixture of Cu_2S, FeS & silica is obtained from blast furnace known as Copper matte

↓

Bessemerisation of copper matte is done in Bessemer converter in presence of air. Following reactions take place:-

$2FeS + 3O_2 \rightarrow 2FeO + 2SO_2$, $FeO + SiO_2 \rightarrow FeSiO_3$ (slag),

$2Cu_2S + 3O_2 \rightarrow 2Cu_2O + 2SO_2$, $2Cu_2O + 2Cu_2S \rightarrow 6Cu + SO_2$

↓

Melted copper is cooled, and then SO_2 is evolved. such copper is known as BLISTER COPPER(98%Cu+2% impurities)

19. **FLOW SHEET FOR EXTRACTION OF ALUMINIUM:-**

Bauxite $Al_2O_3.2H_2O$

↓

Concentration of ore is done by leaching .Bauxite is treated with NaOH .Following reaction takes place:-

$Al_2O_3 + 2NaOH + 3H_2O \longrightarrow 2Na[Al(OH)_4]$ and impurities of Fe_2O_3, TiO2 &SiO_2 are removed.

↓

$Na[Al(OH)_4]$,then reacts with CO_2 then pure Alumina is obtained.

$Na[Al(OH)_4] + 2CO_2 \rightarrow Al_2O_3.xH_2O + 2NaHCO_3$

↓

Electrolytic reduction of pure alumina takes place in iron box (cathode) with cryolite (Na_3AlF_6) & fluorspar CaF_2.Graphide rods act as anode. Following reactions take place:-

At cathode:- $Al^{3+} + 3e \rightarrow Al$, At Anode:- $2O^{2-} \rightarrow O_2 + 4e$

↓

By this process 98.8% pure Aluminum is obtained.

20. Vapour phase refining is used for extraction of Nickel (MOND PROCESS) and Zirconium &Titanium (VAN ARKEL PROCESS).

21. Zone refining is used for extraction of Si, Ge, Ga, etc.

22. Chromatography method is based on selective distribution of various constituents of a mixture between two phases, a stationary phase and a moving phase. The stationary phase can be either solid or liquid on solid support.

22. Column chromatography is based on adsorption phenomenon. This method is useful for those elements, which are available in small amounts and the impurities are not much different in chemical properties from the element to be purified.

VERY SHORT ANSWER TYPE QUESTION

(1 marks)

Q.1- What is slag?

A.1- It is easily fusible material fusible material, which is formed when gangue still present in roasted ore combines with the flux.

e.g. CaO (flux) + SiO2 (gangue) $\rightarrow CaSiO_3$ (slag)

Q.2- Which is better reducing agent at 983K, carbon or CO?

A.2- CO, (above 983K CO being more stable & does not act as a good reducing agent but carbon does.)

Q.3- At which temperature carbon can be used as a reducing agent for Foe ?

A.3- Above 1123K, carbon can reduce FeO to Fe.

Q.4- What is the role of graphite rods in electrometallurgy of aluminium ?

A.4- Graphite rods act as anode, are attacked by oxygen to form CO_2 and so to be replace time to time.

Q.5- What is the role of cryolite in electrometallurgy of aluminium?

A.5- alumina cannot be fused easily because of high melting point. Dissolving of alumina in cryolite furnishes Al^{3+} ions, which can be electrolyzed easily.

Q.6- What are depressants?

A.6- It is possible to separate two sulphide ore by adjusting proportion of oil to water in froth flotation process by using a substance known as depressant.

e.g. NaCN is used to separate ZnS and PbS.

Q.7- Copper can be extracted by hydrometallurgy but not Zn. Why?

A.7- The E^0 of Zn is lower than that of Cu thus Zn can displace Cu^{2+} ion from its solution. On other hand side to displace Zn from Zn^{2+} ion, we need a more reactive metal than it.

Q.8- Give name and formula of important ore of iron .

A.8- Haematite – Fe_2O_3, Magnetite –Fe_3O_4, Iron pyrites FeS_2.

Q.9- Give name and formula of important ore of Copper .

A.9- Copper pyrites $CuFeS_2$, Malachite $CuCO_3 . Cu(OH)_2$, Cuprite Cu_2O.

Q.10- Give name and formula of important ore of Zinc .

A.10- Zinc blende - ZnS, Calamine- $ZnCO_3$, Zincite – ZnO .

SHORT ANSWER TYPE QUESTION

(2 marks)

Q.1 Describe the method of refining of nickel.

A.1- In the Mond Process, Ni is heated in a stream of CO forming a volatile complex, which then decomposes at higher temperature to give Ni.

At 330-350K: - $Ni + 4CO \rightarrow Ni(CO)_4$

At 450-470K $Ni(CO)_4 \rightarrow Ni + 4CO$

Q.2- What is Zone Refining? Explain with example.

A.2- Zone refining is a method of obtaining a metal in very pure state. It is based on the principal that impurities are more soluble in molten state of metal than solidified state.

In this method, a rod of impure metal is moved slowly over circular heater. The portion of the metal being heated melts & forms the molten zone. As this portion of the rod moves out of heater, it solidified while the impurities pass into molten zone. The process is repeated to obtain ultrapure metal and end of rod containing impure metal cutoff.

Q.3 Write the principal of electro-refining.

A.3- In this method of purification impure metal is made Anode and pure metal is made the cathode. On passing electricity, pure metal is deposited at the cathode while the impurities dissolve dissolve in solution as anode mud. E.g. electro-refining of copper:-

At Cathode: - $Cu^{2+} + 2e \rightarrow Cu$

At Anode: - $Cu \rightarrow Cu^{2+} + 2e$

Q.4- Write difference between calcinations and roasting .

A.4- Refer points no 10 &11.

Q.5- Describe the method of refining of Zirconium and Titanium.

A.5- Van Arkel process is used for obtaining ultrapure metal. The impure metal is converted into volatile compound, which then decomposes electrically to get pure metal.

At 850K: - Zr impure) + 2 I_2 → ZnI_4

At 2075K:- ZnI_4 → Zr (pure) + 2 I_2

Q.6- Out of C & CO, which is better reducing agent for ZnO?

A.6- Since free energy of formation of CO from C is lower at temperature above 1120K while that of CO_2 from carbon is lower above 1323K than free energy of formation 0f ZnO. However, the free energy of formation of CO_2 from CO is always higher than that of ZnO. Hence, C is better reducing agent of ZnO.

Q.7- The value of $\Delta_f G^0$ for Cr_2O_3 is -540kJ/mole & that of Al_2O_3 is -827kJ/mole. Is the reduction of Cr_2O_3 possible with aluminium?

A.7- The desired conversion is

$$4\,Al + 2Cr_2O_3 \rightarrow 2Al_2O_3 + 4Cr$$

It is obtained by addition of following two reactions:-

$4Al + 3O_2 \rightarrow 2\,Al_2O_3$ $\Delta_f G^0$=-827kJ/mole

$2Cr_2O_3 \rightarrow 4Cr + 3O_2$ $\Delta_f G^0$==+ 540 kJ/mole

Therefore, ΔG^0 for desired reaction is -827+540=-287, as a result reduction is possible.

Q.8:- Why copper matte is put in silica lined converter?

A.8:- Copper matte consists of Cu_2S and FeS. When blast of air is passed through molten matte in silica-lined converter, FeS present in matte is oxidized to FeO, which combines with silica to form slag.

(i) $2FeS + 3O_2 \rightarrow 2FeO + 2\,SO_2$, (ii) $FeO + SiO_2 \rightarrow FeSiO_3$ (slag),

(III) $2Cu_2S + 3O_2 \rightarrow 2Cu_2O + 2SO_2$, (IV) $2Cu_2O + 2Cu_2S \rightarrow 6Cu + SO_2$

Q.9- What is meant by term chromatography?

A.9-Chromato means Colour and graphy means writing because the method was first used for separation of coloured substance. It is based on selective distribution of various constituents of a mixture between two phases, a stationary phase and a moving phase. The stationary phase can be either solid or liquid on solid support.

Q.10-Why is reduction of metal oxide easier if metal formed is in liquid state at temperature of reduction.

A.10- The entropy of a substance is higher in liquid state than solid state. In the reduction of metal oxide, the entropy change will be positive if metal formed is in liquid state. Thus, the value of ΔG^0 becomes negative and reduction occurs easily.

SHORT ANSWER TYPE QUESTION

(3 marks)

Q.1- Explain the following:-

(i) Zinc but not copper is used for recovery of Ag from the complex $[Ag(CN)_2]^-$.

(ii) Partial roasting of sulphide ore is done in the metallurgy of copper.

(iii) Extraction of Cu from pyrites is difficult than that from its oxide ore through reduction.

A.1- (i) Zn is more powerful reducing agent in comparison to copper.Zn is also cheaper than Cu.

(ii) Partial roasting of sulphide ore forms some oxide. This oxide then reacts with remaining sulphide ore to give copper i.e. self-reduction occurs.

$$2Cu_2S + 3O_2 \rightarrow 2Cu_2O + 2SO_2,$$

$$2Cu_2O + 2Cu_2S \rightarrow 6Cu + SO_2.$$

(iii) Though carbon is good reducing agent for oxide but it is poor reducing agent for sulphides. The reduction of metal sulphide does not have large negative value.

Q.2- Explain the method for obtaining pig iron from magnetite.

A.2- Extraction of iron from Magnetite takes place in following steps:-

(i) Concentration of ore: - It is done by Gravity separation followed by magnetic separation process.

(ii) Calcination: - It involve heating when the volatile matter escapes leaving behind metal oxide.

$$Fe_2O_3.xH_2O \rightarrow Fe_2O_3 + xH_2O.$$

(iii) Roasting: - It involves heating of ore in presence of air, thus moisture,CO_2,SO_2, As_2O_3 removed And FeO oxidized to Fe_2O_3.

(iv) Smelting of roasted ore: - A mixture of ore, coke & $CaCO_3$ is smelted in long BLAST FURNACE. Following reaction takes place at different temperature zones:-

(i) Zone of reduction: - Temperature range 250^oC-700^oC

$$3Fe_2O_3 + CO \longrightarrow 2Fe_3O_4 + CO_2$$

$$Fe_3O_4 + CO \longrightarrow 3FeO + CO_2$$

$$FeO + CO \longrightarrow Fe + CO_2$$

(ii) Zone of slag formation:- Temperature range 800^oC-1000^oC

$$CaCO3 \longrightarrow CaO + CO2$$

$$CaO + SiO_2 \longrightarrow CaSiO_3, \qquad P_4O_{10} + 10C \longrightarrow 4P + 10CO,$$

$$SiO_2 + 2C \longrightarrow Si + 2CO, \qquad MnO_2 + 2C \longrightarrow Mn + 2CO$$

(iii) Zone of fusion:- Temperature range 1150^oC-1350^oC

$$CO_2 + C \longrightarrow 2CO$$

(iv) Zone of fusion:- Temperature range 1450^oC-1950^oC

$$C + O_2 \longrightarrow CO_2$$

Thus, Pig iron is obtained from Blast Furnace.

Q.3- Describe the principles of extraction of copper from its ore .

A.3- Refer points no 18. For steps, involve in the extraction.

Q.4- Name the principal ore of aluminium and describe how Al is extracted from its ore.

A.4- Important ores -(i) Bauxite $Al_2O_3.xH_20$ (ii) Corrundum Al_2O_3. Bauxite is commercially important ore Al.

Extraction from Bauxite ore involves the following two stages:-

(i) Purification of bauxite to get pure alumina (Al_2O_3)
(ii) Electrolysis of pure alumina in molten cryolite

Step:-1 Bauxite is treated with NaOH .Following reaction takes place:-

$Al_2O_3 + 2NaOH + 3\ H_2O \longrightarrow 2\ Na\ [Al(OH)_4]$ and impurities of Fe_2O_3,TiO_2 &SiO_2 are removed . Na $[Al(OH)_4]$,then reacts with CO_2 then pure Alumina is obtained.

$$Na\ [Al(OH)_4] + 2CO_2 \rightarrow Al_2O_3.xH_2O + 2NaHCO_3$$

Step:-2 Electrolytic reduction of pure alumina takes place in iron box (cathode) with cryolite (Na_3AlF_6) & fluorspar CaF_2.Graphide rods act as anode. Following reactions take place:-

At cathode:- $Al^{3+} + 3e \rightarrow Al$, At Anode:- $2O^{2-} \rightarrow O_2 +$ By this process 98.8% pure Aluminum is obtained.

Q.5- Describe the principles of extraction of Zinc from zinc blende .

A.5- Important ores of Zn:-Zinc blende - ZnS, Calamine- $ZnCO_3$, and Zincite – ZnO. ZnS is commercially important ore of Zn.Various stages involved in the extraction of Zn from ZnS are as following:-

(i) Concentration of ore:-It is concentrated by Froth flotation process followed by gravity separation process.

(ii) Roasting:- The concentrated ore is roasted in presence of air. Following reactions take place:-

$$2ZnS + 3O_2 \rightarrow 2ZnO + 2SO_2$$

The mass obtained during roasting is porous and is called porous clinker.

(iii) Reduction of ZnO to Zn: - ZnO is made into bricketts with coke and clay and heated ai1163K.Zn formed distills off and is collected by rapid cooling of zinc vapours.

$$ZnO + C \rightarrow Zn + CO$$

----------END----------

Bio molecule

Gist Of The Chapter

1.Carbohydrates- These are optically active polyhydroxy aldehydes or ketones due to presence of chiral `C' or the compounds which produce these on hydrolysis except dihydroxy acetone is not optically active.

2. Classification-

(i) Monosaccharide's – Those carbohydrates which cannot get hydrolysed e.g. glucose ,fructose, galactose etc.

(ii) Oligosaccharides- Those carbohydrates which give to or more monosaccharide's on hydrolysis e.g. sucrose on hydrolysis gives glucose and fructose. Raffinose on hydrolysis gives glucose, fructose and galactose.

(iii) Polysaccharides- Those carbohydrates which on hydrolysis give large number of monosaccharide's hydrolysis.eg starch, cellulose, glycogen.

3. Sugar-

(i)Reducing Sugars- Those which reduce Fehling's or Tollen's reagent. They have free aldehydic groups, eg , glucose, fructose , galactose

(ii)Non Reducing Sugars- Those which do not reduce Fehling's or Tollen's reagent. They do not have free functional group ,e.g., sucrose

4. Glucose- It is a monosaccharide's with molecular formula $C_6H_{12}O_6$

5. Preparation

(i)From Sucrose

$C_{12}H_{22}O_{11} + H_2O$ -------> $C_6H_{12}O_6 + C_6H_{12}O_6$ (Only from sucrose)

(ii)From Starch

$(C_6H_{10}O_5)_n + nH_2O$ -------> $C_{12}H_{22}0_{11} + H_20$ ------> $2C_6H_{12}O_6$

6.Structure

(i)Fischer structure –

$CHO — (CHOH)_4 — CH_2OH$

(+) Glucose has `D' configuration as shown

`D' means —OH group on first chiral `C' from the bottom is on right hand and + means it is dextro rotator, i.e, it rotates plane polarized light towards right.

(ii) Cyclic Structure OF Glucose: the straight chain is unable to explain the following reactions.

(a) It does not give the 2, 4-DNP test, Schiff's Test and does not form the hydrogensulphide product with $NaHSO_3$.

(b) The pentacetate of glucose does not react with NH_2OH, indicating the absence of free aldehydic group.

(iii) Glucose exist in 2 different crystalline forms α and β forms. These are called anomers. They differ in optical rotation, they also differ in melting point.

Anomers are isomers which have a different configuration across C-1 (first chiral 'C' atom).

7. Glycosidic Linkage: The linkage between two monosaccharide units through oxygen is called the glycosidic linkage.

8. Proteins: These are micro molecules made up of amino acids joined via a peptide link (-(-CONH-)- is the peptide linkage). These are required for growth and development of the body.

9. Amino Acids: These contain an amino ($-NH_2$) and an acidic (-COOH) group and are therefore amphoteric in nature. In solution they exist in the form of zwitter ion.

10. Classification

Fibrous Protein	**Globular Protein**
(i) Polypeptide chains run parallel or anti-parallel and held together by hydrogen and disulphide bonds.	(i) Chains of Polypeptide coil around to give a spherical shape.
(ii) Generally insoluble in water. e.g. Keratin, collagen,myosin,fibroin.	(ii) Usually soluble in water. e.g., insulin, thyroglobin,albumin, haemoglobin and fibrinogen gets converted into fibrous protein fibroin on clotting of blood.

11. Structure And Shape of Protein

Primary Strutcure	**Secondary Structure**	**Tertiary Structure**	**Quaternary Structure**
The specific sequence of amino acids in the polypeptide chain. Change in amino acids sequence changes the protein. They have covalent	It is the shape in which the long polypeptide chain can exist. It is of two types : α- helix and β- pleated. These structures arise due to regular folding of the backbone of the polypeptide chain	Represents overall folding of the polypeptide chain. It gives rise to the fibrous or globular molecular shapes. Forces stabilizing the 2° and 3° structures are	Protein can be composed of two or more polypeptide chains called sub units. The spatial arrangement of these sub units with respect to each other

bonds.	due to H-bonding between the C=o and –NH- groups of the peptide bond.	hydrogen bonds, disulphide linkages, van der waal's and electrostatic forces of attraction.	quaternary structure of the protein.

12. Denaturaion of Protein: The protein in native state, when subjected to a physical change like temperature, pH etc undergoes uncoiling and looses it's biological activity. The 2° and 3° structures are destroyed, only 1° structure is retained.

Renaturation of Protein:

Some proteins regain their biological activity by reversible process it is called Renaturation of Proteins. In such a cases, when temperature in pH of a denatured proteins is brought back to conditions in which the native protein is stable, secondary and tertiary structures of proteins are restored to which leads to recovery of biological activity.

13. Enzymes: These are biocatalyst and generally globular proteins e.g., invertase,zymase,phenyl, alaninehydroxylase, urease etc.

14. Vitamins: They are organic compounds required in the diet in small amounts to perform specific biological functions for maintenance of optimum growth and health of the organism. They are classified as follows

(i) Fat Soluble Vitamins: Vitamin A,D,E and K. They are stored in liver and adipose tissues.

(ii) Water Soluble Vitamins: B group vitamins and vitamin C. They need to supplied regularly in diet as they are excreted in urine and cannot be stored(except vitamin B_{12}) in our body.

Their deficiency causes diseases.

Biotin (Vit H) is however neither fat nor water soluble. It's deficiency leads to loss of hair.

15. Nucleic Acids: These are biomolecules which are long chain polymers of nucleotides. They are:

(i) Deoxyribonucleic acid (DNA)

(ii) Ribonucleic acid (RNA)

They are responsible for protein synthesis and transfer of genetic characteristics to offspring's.

16. Composition of Nucleic Acid:

They are made up of pentose sugar(β-D-2-deoxyribose in DNA and β-D-ribose in RNA), phosphoric acid and a nitrogen containing heterocyclic compound(base).

DNA- Bases present are Adenine(A), Thymine(T),Guanine(G) and Cytosine(C).

RNA- contains Adenine(A), Guanine(G), Cytosine(C) and Uracil(U).

17. Nucleoside: The unit formed by the attachment of a base to n1'-position of sugar (Base+Sugar).

18. Nucleotide: Nucleoside and phosphoric acid at 5'-position. Nucleotides are bonded by phosphodiester linkages between 5' and 3' carbon atoms of pentose sugar (Base+ Sugar+ Phosphoric Acid).

19.DNA : has a double helical structure with AT and GC linked together through 2 and 3 hydrogen bonds respectively. It is responsible for transfer of genetic characteristics.

20. RNA: is of three types- messenger RNA(m-RNA), ribosomal RNA(r-RNA) and transfer RNA (t-RNA). RNA helps in protein synthesis.

21. Biological Functions of Nuclei Acid: DNA is chemical basis of hereditary and have the coded message for proteins to be synthesized in the cell. RNA carry out the protein synthesis in the cell.

Biomolecules

VSA Type Questions – (1 Mark)

Q1 – Which functional groups are present in monosaccharides?

Ans - —OH and —CHO or —OH and >CO

Q2 – Name an aldopentone, aldohexone and ketohexone.

Ans – Ribose,glucose and fructose respectively.

Q3 – What is animal starch?

Ans – Glycogen.

Q4 – Which types of bonds are present in a protein molecule?

Ans – Peptide bonds, hydrogen bonds, sulphide bonds, ionic bonds etc.

Q5 – Which α-helix or β-helix is more stable?

Ans – α-helix is right handed and is more stable due to intermolecular H bonding between first and fourth amino acid.

Q6 – The sequence of bases in one strand of DNA is TACGGACA. What is the sequence of bases of complementary strand of DNA.

Ans – ATGCCTGT.

Q7 – Name the vitamin whose deficiency causes rickets?

Ans – Vitamin D.

Q8 – Name the pwines present in DNA.

Ans – Adenine and guanine.

Q9 – Give an example of

(a)water soluble (b)fat soluble is

Ans – (a)Vitamin C (b)Vitamin D.

Q10 – Name a protein which is insoluble in water.

Ans – Veratin.

SAI Type Questions

Q1 – Name polysaccharides that make up starch and what is the difference between them.

Ans – Amylose which is linear polymer of α-glucose and amytopectin which is branched polymer of α-glucose. Amylose is water soluble where as amylopectine is water insoluble.

Q2 – What are anomers?

Ans – Monosaccharides which differ only in the orientation of the —OH group at C-1.e.g, α-glucose and β-glucose.

Q3 – Where does the water present in the egg go after boiling the egg?

Ans – On boiling during denaturation process water gets adsorbed/absorbed in the denatured proteins.

Q4 – Write two main functions of carbohydrates in plants.

Ans – (i)structural material (ii)reserved food material.

Q5 – What do you understand by glycosidic linkage?

Ans – During condensation of two monosaccharides, a water molecule given out and two monosaccharides get linked together by an oxide or ethereal linkage (—O—) called as glycosidic linkage.

Q6 – What are essential and non essential amino acid? Give two examples of each type.

Ans – Essential amino acids are those which are not produced in our body.e.g.,valine,leucine.

Non-essential amino acids are those which are produced by our body.e.g.glycine and alanine.

Q7 – How do you explain the amphoteric behavior of amino acids?

Ans – Amino acids have both acidic as well as basic group and they react both with acids as well as bases,therefore they are amphoteric in nature.

Q8 – What is the difference between a nucleoside and a nucleotide?

Ans - Nucleoside = sugar + base

Nucleotide = sugar + base + phosphoric acid

Q9 – Define (a)Enzymes (b)Antibody

Ans – (a)Enzymes – they are biological catalyst which catalyse biochemical reactions.e.g.,

$C_{12}H_{22}0_{11} + H_20$ ----------> $C_6H_{12}0_6 + C_6H_{12}0_6$

sucrose glucose fructose

This reaction is catalysed by the enzyme investase.

(b)Antibody – they are chemical substances which destroy antigens that cause infections.e.g.,vaccination for typhoid produces antibodies in our body to prevent typhoid.

Q10 – What is invert sugar?

Ans – An equimolar aqueous solution of glucose and fructose is called invert sugar.

SA II Type Questions –

Q1 – Give three differences between DNA and RNA.

Ans –

DNA	RNA
1. it has deoxyribose as sugar.	1.it contains ribose as sugar.
2. it contains thymine along with adenine, cytosine and guanine as bases.	2.it contains uracil in place of thymine with other bases.
3. it is responsible for maintaining heredity traits from generation to generation.	3. it is responsible for protein synthesis.

Q2 – Difference between globular protein and fibrous protein.

Ans –

Globular Protein	Fibrous Protein
1. they form α-helix structure. 2. they are water soluble. 3. they involve H bonding.	1. they have β-pleated structure. 2. they are water insoluble. 3. they have strong intermolecular forces of attraction.

Q3 – Give reactions with support cyclic structure of glucose.

Ans – (a)Glucose does not give 2,4-DNP test, Schiff`s test and sodium hydrogen suphide test.

(b)The pentaacetate of glucose does not react with NH_2OH indicating absence of free —CHO group.

(c)Glucose exists in two crystalline form α and β.

Q4 – Define with example

(a)Isoelectric point (b)Mutarotation (c)Transcription

Ans –

(a)Isoelctric point – the pH at which there is no net migration of any ion towards electrode.e.g,amino acids have isoelectric point at pH = 5.5-6.3

(b)Mutarotation - it is spontaneous change in optical rotation when an optically active substance is dissolved in water.e.g, α-glucose when dissolved in water changes its optical rotation from 111° to $52.5^{o.}$

(c)Transcription – it is process by which m—RNA is generated from DNA.e.g,if DNA has base sequence ATACA then m—RNA has base sequence TATCGT.

Q5 – What happens when glucose reacts with

(a)HI (b) HNO_3 (c)Br_2 water

Ans –

(a)$C_6H_{12}0_6$ + HI ------> n-hexane C_6H_{14}
(b) $C_6H_{12}0_6$ + HNO_3 -------> saccharic acid
(c) $C_6H_{12}0_6$ +Br_2 water --------> gluconic acid

Q6 – Differentiate primary , secondary and tertiary structure of protein.

Ans – -In <u>primary structure</u> specific sequence of amino acid are present joined by covalent bonds.

-<u>secondary structure</u> is responsible for the shape of a protein. α-helix and β-pleated in which polypeptide chains have peptide bonds.

-<u>tertiary structure</u> represents overall folding of polypeptide chain and give rise to the fibrous or globular molecular shape.

Q7. Discuss the specificity and mechanism of enzyme action.

Ans. In case of enzymatic reaction the enzyme is so built that it binds to the substrate in a specific manner. Enzymatic reaction involves following steps (Lock and Key Model)-

Step (i): Binding of substrate(S) to enzyme (E) to form complex

E + S → [ES] (Enzyme substrate complex)

Step (ii): Product formation in complex

[ES] → EP (Enzyme product complex)

Step (iii): Dissociation of enzyme product complex, leaving enzyme unchanged

EP → E + P

The specificity of enzyme is due to presence of some specific regions called active site on their surface.

Q8. Mention structural differences between amylopectin and cellulose.

Ans.

Amylopectin	Cellulose
1. It is linear polymer of α-glucose. 2. It consists of branched chains of α-glucose.	1. It is linear polymer of β-glucose. 2. In cellulose, the chains are arranged to form bundles and held together by hydrogen bond between glucose and adjacent strands.

Q9. What deficiency diseases are caused due to lack of vitamins B_1, B_6 and K in human diet.

Ans.

Vitamins	Deficiency Disease
B_1	Beri beri (loss of appetite)
B_6	Convulsions
K	Increased blood clotting time

Q10. Glucose or Sucrose are soluble in water but cyclohexane and benzene are insoluble in water. Explain.

Ans. Glucose contains five-OH groups and Sucrose contains eight-OH groups, because of this they form intermolecular hydrogen bonding, so they are soluble in water. But benzene and cyclohexane does not contain –OH groups, hence does not form intermolecular hydrogen bonding, so they are not soluble in water.

HOTS Questions

VSA (1 Mark)

Q1. How many atoms are present in the ring of pyranose structure of glucose?

Ans. 5 Carbon atoms and one Oxygen atom.

Q2. Write the formula of Zwitter ion for Glycine.

Ans.

R-CH-COO^-	CH_2-COO^-
|	|
NH_3^+	NH_3^+
General Formula	Zwitter ion of glycine

Q3. Which proteins possess α-Helix structure?

Ans. Keratin and myosin possess α-Helix structure.

Q4. What is the native state of protein?

Ans. The energetically most stable shape of the protein at normal pH and temperature is called native state.

Q5. Fresh tomatoes are a better source of Vitamin C that which have been stored for some time. Explain.

Ans. Vitamin C is destroyed on prolonged exposure to air due to its oxidation.

Q6. Why are carbohydrates generally active?

Ans. It is due to the presence of Chiral Carbon atoms in their molecules.

Q7. What type of linkages hold together monomers in DNA?

Ans. Monomers in DNA are linked by phosphate linkages.

Q8. Why is cellulose not digested in human body?

Ans. It is due to the fact that human beings do not have enzymeto digest cellulose.

Q9. Name the enzyme that is used to dissolve blood clots?

Ans. Streptokinase.

Q10. Name two diseases caused due to deficiency of enzymes.

Ans. Albinism and phenylketonuria.

SA Type I (2 Marks)

Q1. Give reasons for the following-

(i) On electrolysis in acidic solution amino acids migrate towards cathode, while in alkaline solution these migrate towards anode.

(ii) The monoamino monocarboxylic acids have two pK_a values.

Ans. (i) In acidic solution, the carboxylate anion accept a proton and gets converted into carboxylic group resulting in the formation of positive ion.

$$\underset{\text{(Zwitter ion)}}{\begin{array}{c} H_3N^{+}-CH-COO^{-} \\ | \\ R \end{array}} \xrightarrow[\text{(acid)}]{H^{+}} \underset{\text{(Positive ion)}}{\begin{array}{c} H_3N^{-}-CH-COOH \\ | \\ R \end{array}}$$

In presence of a base the $N^{+}H_3$ ion changes to $—NH_2$ group by losing a proton and this gives a negative ion.

(Zwitter ion) (Negative ion)

This means that in acidic medium, the amino acid migrates towards the cathode while in alkaline solution it migrates towards anode on electrolysis.

(ii) In aqueous solution, monoamino monocarboxylic amino acid behave like salt at isoelectric point. At a pH lower than isoelectric point (i.e. in acidic medium) it shows one pK_a value which corresponds to structure

and at a pH higher than isoelectric point, it shows a pK_a value which corresponds to another,

Q2. Which forces are responsible for the stability of α-helix? Why is it named as 3.6_{13} helix?

Ans. Hydorgen bonds between – N-H and —C=O groups of peptide bonds give stability to the structure.

It is known as 3.6_{13} helix, since each turn of helix has approximately 3.6 amino acid residue and a 13 member ring is formed by hydrogen bonding.

Q3. Write about the following protein synthesis-

(i) Name the location where the protein synthesis occurs?

Ans. Protein synthesis occurs at the ribosome in cytoplasm.

(ii) How do 64 codones code for only 20 amino acids?

Ans. The 64 codones for 20 amino acids; more than one codon can code for same amino acids, e.g., CUU and CUU both can code leucine. Proline is encoded by CCU, CCA, CCG, and CCC.

Q4. Describe the mechanism of replication of DNA.

Ans. Replication of DNA:- The process by which a DNA molecule produces two identical copies of itself is called replication of DNA. In the DNA double helix the sequence of bases in one chain is incomplemanty to the sequence in the other chain, therefore one controls the other. During all division the two strands of the DNA double helix partly unwind and each serves as the template for the synthesis of a new DNA molecule. DNA replication follows the base pairing rules by which A pairs with T and G pairs with C. Therefore, each daughter molecule is an exact replication of the parent molecule. DNA replication is semi conservative i.e. only half of the parental DNA is conserved and only one strand is synthesised. DNA replication takes place only in 5'→3' direction.

Q5. Answer the following queries about proteins-

(i) How are proteins related to amino acids?

Ans. Proteins consist of large number of amino acids linked to each other by peptide linkage, having 3- dimensional structure. Thus, proteins are biopolymers of amino acids.

(ii) When is protein said to be denatured?

Ans. When nature proteins are subjected to the action of heat, acids or alkalies, they are coagulated or precipitated. The protein in this state is said to be denatured. During

denaturation process the water soluble form of globular protein change to water insoluble fibrous protein.

SA(II) 3 Marks

Q6. Draw simple Fishcha projections of D and L- glucose. Are these enantiomers?

D-Glucose

L-Glucose

Yes these two fischer projections are called enatiomers.

Q7. A tripeptide on complete hydolysis gives glycine, alanine and phynylalanine using three letter symbols write down the possible sequence of tripeptide.

Ans. Each amino acid may be present at the N-terminal as well as C-terminal.

(i) Gly-Ala-Gly

(ii) Gly-Phe-Ala

(iii) Ala-Gly-Phe

(iv) Ala- Phe-Gly

(v) Phe-Ala-Gly

(vi) Phe-Gly-Ala

Q8. Glycine exists as a Zwitter ion but 0-and p-amino benzoic acids do not. Explain.

Ans. The lone pair of N-atom in O- and p-aminobenzoic acid is involved in resonance. The lone pair of N-atom in transferred towards benzene ring. This decreases the acidic character of $-NH_2$ group. Therefore these groups do not transfer and accept H^+ ions, respectively.

Q9. Write short notes on-

(i) Co-enzymes

(ii) Prosthetic groups

Ans. (i) Co-enzymes:- These are usually derived from vitamins such as thaimine ,riboflamin, niacin etc. They are loosely held to the protein and can be easily separated by dialysis.

(ii) Prosthetic groups:- They are also derived from vitamins such as biotin but are tightly held to the protein molecule by covalent bonds. They can be separated only by careful hydrolysis.

Q10. The melting points and solubility in water of amino acids are generally higher than that of the corresponding halo acids. Explain.

Ans. The amino acids exists as zwitter ion ($H_3N—CHR—COO^-$). They have salt like structure. There are strong dipole-dipole and electrostatic attractions. Therefore, amino acids have high melting points. Amino acids strongly interact with water molecules and are soluble in it. The halo-acids do not have salt like structure and have low melting points. Halo-acids do not interact as strongly with water molecules as do amino acids. Therefore, solubility of amino acids in water is more than those of halo-acids.

POLYMERS

GIST

1. Polymer:

It is a very large molecule having molecular mass 10^3 - 10^7 g mol^{-1}. They are formed by joining together repeating structural units.

2. Classification of Polymers:

(a) Based On Source:

(i) Natural: Found in plants and animals, e.g. Proteins, cellulose, natural rubber, silk, wool.

(ii) Synthetic: Man-made e.g. Nylon, polyster, neoprene, Bakelite, Teflon, PVC, polystyrene.

(b) Based On Structure:

(i) Linear Polymers: this consist of long and straight chain repeating units e.g. Polythene (HDPE), PVC, nylon, polyester.

(ii) Branched Polymers: This contain linear chains having some branches e.g. amylopectin, glycogen etc.

(iii) Cross Linked Polymers: Strong covalent bonds are present between various linear polymer chains. E.g. Bakelite, urea- formaldehyde polymer, melamine, formaldehyde polymer etc.

(c) Based On Mode Of Polymerization:

(i) Addition Polymers: These are formed by the repeated addition of monomer molecules possessing multiple bonds, e.g., polythene, polypropene, polystyrene, PMMA (polymethyl metha crylate)

(ii) Condensation Polymers: These are formed by the repeated condensation reaction of different bifunctional or trifunctional monomers, with the elimination of small molecules like water,HCL,NH_3, alcohol etc. e.g. Bakelite,nylon,polyster,urea- formaldehyde resin.

(d) Based On Molecular Forces:

(i) Elastomers: Forces of interaction between polymer chains is weakest, e.g. natural rubber, neoprene, vulcanized rubber.

(ii) Fibers: Strong hydrogen bonds are present between the polymer chains. They have high tensile strength e.g., nylon.polyster, silk, wool, orlon, rayon etc.

(iii) Thermoplastics: They are linear/slightly branched chains molecules capable of repeated softening on heating and hardening on cooling,e.g., polythene,PVC, polystrene, polypropene.

(iv) Thermosetting Plastics: They are cross-linked or heavily branched molecules, which on heating undergo extensive cross-linkages and become infusible, e.g., bakelite,urea formaldehyde resin.

(e) Based On Growth Of Polymerization: Depending upon the mechanism of Polymerization, polymers are classified as

(i) Addition Polymers Or Chain Growth Polymers:

They follow mostly free radical mechanism.

(ii) Condensation Polymers or Step Growth Polymers

because they are formed in gradual steps.

Polymer	Monomer	Uses
(i) Polyethene	Ethene	Insulation of wires, toys, manufacture of dustbins etc.
(ii) Polytetra Fluroethene(Teflon)	Tetrafluoroethene	Oil seal and Gasket and non Stick kitchen wares
(iii) Polyarcylonitrile	Acrylonitrile	Substitute for wool
(iv) Terylene or Decron	Glycol + Terephthalic Acid	Ropes, safety belts, tyre -cord , sails of boats, saree and dress material
(v) Nylon-6,6	Hexamethylenediamine + Adipic acid	Stocking, socks, ropes, Parachutes, fabrics, bristles of tooth brush
(vi) Nylon-6	Caprolactum	Tyre-cords, Ropes, fabrics
(vii) Novolac	Phenol + Formaldehyde	Used for binding glue, laminated wooden planks
(viii) Phenol Formaldehyde resin	Formaldehyde + Phenol	Combs,records, switches boards
(ix) Melamine polymers	Melamine + Formaldehyde	Manufacture of unbreakable crockery
(x) Buna-S Copolymer	1,3-Butadiene + Styrene	Autotyres floor, tiles foot-wear components
(xi) Natural rubber	2-methyl-1,3-butadiene	Used for tyres
(xii) Neoprene	2-chloro-1,3-butadiene	Conveyor belts, gasket , hoses
(xiii) Buma-N	1,3-butadiene + acrylonitrile	Resistance to action of petrol. Make oil seals,tank linings etc.
(xiv) (PHBV) poly-β hydroxybutyrateco-β- hydroxyl valerate (biodegradable)	3-hydroxybutanoic acid + 3-hydroxypantanoic acid	Packaging orthopaedic devices
(xv) Nylon-2-nylon-6	Glycine + aminocaproic acid	It is biodegradable step growth Polymer
(xvi)Poly(glycolicacid Poly(lactic acid) (dexton) (biodegradable)	Glycolic acid + lactic acid	Sutures ,ie,for stitching wounds after operation. Biodegradables

VSA (1 marks)

1.Name a natural elastomer.

Ans . Natural rubber.

2. Write name of a synthetic polymer which is an ester.

Ans. Nylon 6 or Nylon 6,6.

3. Name of monomer of Nylon 6.

Ans. €- Aminocaproic acid

4. Write the monomer units of Bakelite.

Ans. Phenol and formaldehyde.

5. Define a copolymer.

Ans.The polymers made by addition polymerisation from two different
monomers are termed as **copolymers**, *e.g.*, Buna-S, Buna-N, etc.

6. Write one use of PVC.

Ans: In manufacture of rain coats& vinyl flooring.

7. Define Polymer.

Ans: Polymer is defined as very large molecules having molecular mass (103-107u). These are also referred to as **macromolecules,**

8. Give an example of thermoplastics.

Ans: Thermoplastics are polythene, polystyrene, polyvinyls, etc.

9. To which class of polymers does Nylon-66 belong?

Ans: ***Polyamides***

10. Name the type of monomers in terylene?

Ans: Ethylene glycol and terephthalic acid.

SA-1 (2 marks)

1.Arrange the following polymers in increasing order of their intermolecular forces.

(i) Nylon 6,6, Buna-S, Polythene.

(ii) Nylon 6, Neoprene, Polyvinyl chloride.

Ans. (i) Buna-S< Polythene<Nylon 6,6

(ii)Neoprene < Polyvinyl chloride< Nylon 6.

2. Classify the following as addition and condensation polymers: Terylene, Bakelite,
Polyvinyl chloride, Polythene.

Ans. (i) addition polymers :Polyvinyl chloride, Polythene.

(ii) condensation polymers: Terylene , Bakelite.

3. What is a biodegradable polymer ? Give an example of a biodegradable aliphatic polyester.
Ans. Polymers which disintegrate by themselves over a period of time due to environmental degradation by bacteria,etc.are called biodegradable polymers. e.g. PHBV

4.How can you differentiate between addition and condensation polymerization

Ans. In addition polymerization the molecules of the same monomer or diferent monomers add together on a large scale to form a polymer. The monomers used are unsaturated compounds, *e.g.*, alkenes, alkadienes and their derivatives.

Condensation polymerisation generally involves a repetitive condensation
reaction between two bi-functional monomers. These polycondensation
reactions may result in the loss of some simple molecules as water, alcohol, etc., and lead to the formation of high molecular mass condensation polymers. *e.g.* , Nylon 6,6.

5.What is meant by PTFE ?Give its popular name.

Ans.Polytetrafluoroethylene.it is called Teflon.

6.Write chemical name of (Ziegler-Natta catalyst).

Ans: Triethylaluminium and titanium tetrachloride

7.Write down the two differences between thermoplastic and thermosetting plastic and examples.

Ans: Thermoplastic are the linear or slightly branched long chain molecules

capable of repeatedly softening on heating and hardening on cooling.
These polymers possess intermolecular forces of attraction intermediate between elastomers and fibres. Some common thermoplastics are polythene, polystyrene, polyvinyls, etc.

Thermosetting plastic polymers are cross linked or heavily branched molecules,
which on heating undergo extensive cross linking in moulds and again become infusible. These cannot be reused. Some common examples are bakelite, urea-formaldelyde resins, etc.

8.Differentiate Novolac and Bakelite on the basis of structure.

Ans: A linear product of ***Phenol - formaldehyde polymer*** is **Novolac,**
used in paints.

Novolac on heating with formaldehyde undergoes cross linking to form an infusible solid mass called **bakelite**. It is used for making combs, phonograph records, electrical switches and handles of various utensils.

9. Distinguish between the terms homopolymer and copolymer and give an
example of each.

Ans: the addition polymers formed by the polymerisation of a single monomeric species are known as **homopolymers**, *e.g.*, polythene.

The polymers made by addition polymerisation from two different monomers are termed as **copolymers**, *e.g.*, Buna-S, Buna-N, etc.

10. How will you differentiate between LDP and HDP?

Ans: ***Low density polythene*:** It is obtained by the polymerisation of ethene under high pressure of 1000 to 2000 atmospheres
at a temperature of 350 K to 570 K in the presence of traces

of dioxygen or a peroxide initiator (catalyst).

Low density polythene is chemically inert and tough but flexible and a poor conductor of electricity.e.g., squeeze bottles, toys and flexible pipes.

High density polythene: It is formed when addition polymerisation of ethene takes place in a hydrocarbon solvent in the presence of a catalyst Ziegler-Natta catalyst at a temperature of 333 K to 343 K and under a pressure of 6-7 atmospheres.

HDP consists of linear molecules and has a high density due to close packing. It is more tougher and harder. It is used for manufacturing buckets, dustbins, bottles, pipes, etc.

SA-II (3 marks)

1. Write the names of monomers of the following polymers:
   (i) Nylon 6,6 (ii) Neoprene(iii) Buna –N

Ans. (i) hexamethylenediamine and adipic acid.

(ii) chloroprene.

(iii)1, 3 – butadiene and acrylonitrile.

3.How are polymers classified on the basis of structure?

Ans.On the basis of structure, the polymers are classified as below:

(i) Linear polymers such as polythene, polyvinyl chloride,HDP etc.

(ii) Branched chain polymers such as low density polythene,LDP,etc.

(iii) Cross linked polymers such as bakelite, melamine, etc.

4. Write the monomers of the following polymers:
   (i) Buna-N (ii) Teflon(iii) Neoprene.

Ans.(i) 1, 3 – butadiene and acrylonitrile (ii) ***tetrafluoroethene (iii)*** chloroprene.

6. Write use of each orion and Nylon-6.

Ans: use of orion is clothing as a substitute for wool& for Nylon-6. use of Nylon-6 is as fibrics

8. Explain elastomeric polymers & Fibres

Ans: These are rubber – like solids with elastic properties. In these elastomeric polymers, the polymer chains are held together by the weakest intermolecular forces. These weak binding forces permit the
polymer to be stretched. A few 'crosslinks' are introduced in between
the chains, which help the polymer to retract to its original position after the force is released as in vulcanised rubber. The examples are buna-S, buna-N, neoprene, etc.
Fibres are the thread forming solids which possess high tensile strength and high modulus. These characteristics can be attributed to the strong intermolecular forces like hydrogen bonding. These strong forces also lead to close packing of chains and thus impart crystalline nature. The examples are polyamides (nylon 6, 6), polyesters (terylene), etc.

9 . What is the function of sulphur in vulcanisation of rubber?
Ans: Sulphur introduces sulphur bridges.So it is become more tensile strength,elasticity and resistance to abrasion etc.

10. Write **Commercially Importants of following Polymers**
(1) Polypropene (2) Polystyrene (3) Glyptal
Ans: (1) Manufacture of ropes, toys, pipes, fibres, etc.
(2)As insulator, wrapping material, manufacture of toys, radio and television cabinets.
(3) Manufacture of paints and lacquers.

HOTS QUESTIONS
VSA (1mark)

1.What is the main constituent of bubble gum?
Ans - Styrene - butadiene copolymer (SBR).
2.What is a plasticizer?
Ans; The substances which are added to increase the softness of hard polymers.

3.Draw the structures of the monomer of PAN.

Ans: $CH_2=CH-CN$

4.Give the name of polymer which is used for making non- stick utensils.

Ans: Teflon($CF_2=CF_2$)

5.What is the % of sulphur using during in vulcanization of rubber ?

Ans: 3% to 5%

SA-I(2 marks)

1.Give the common and the IUPAC name of the monomer of natural rubber.

Ans: cis-Isoprene & 2-methyl-1,3-butadiene

2.Discuss the two main purpose of vulcanization of rubber.

Ans: (i)It makes the rubber hard.

(ii)It is more elastic.

(iii)It has more wear and tear resistance.

3.Explain the term ***Thermosetting polymers*** and give one example.

Ans: ***Thermosetting polymers:***These polymers are cross linked or heavily branched molecules,
which on heating undergo extensive cross linking in moulds and again become infusible. These cannot be reused. Some common examples are bakelite, urea-formaldelyde resins, etc.

4. Why should one always use purest monomer in free radical polymerisation?

Ans: Impurities of other substances if present,may inhibit or hinder the chain propagation.

5.How is dacron obtained from ethylene glycol and terephthalic acid?

Ans: It is the condensation product of ethylene glycol and terephthalic acid

Carried out at 420 to 460K in the presence of catalyst mixture of zinc acetate and antimony trioxide.

SA-II(3 marks)

1.What does the following polymers stand for ?
(i)PVC (ii) DOP(iii) PAN

Ans: (1) Polyvinylchloride

(2)Dioctylphthalate

(3) Polyacrylonitrile

2. Why is Bakelite a thermosetting polymer?

Ans: It is a cross-linked polymer. On heating it sets permanently into a solid.It can not be remoulded by heating again.

3.A regular copolymer of ethylene and vinyl chloride contains alternate monomers of each type.What is the weight percent of ethylene in this copolymer?

Ans: the weight percent of ethylene in this copolymer

[28/(28+62.5)]*100

30.93%

4.C_6H_{10}=NOH $\xrightarrow{\text{Acid}}$ A $\xrightarrow{\text{polymerisation}}$ B Give the products A& B.

A=€- Aminocaproic acid

B=nylon-6

5.(i) Give an example of a synthetic rubber.

(ii) Mention main advantage of synthetic rubber.

(iii)Arrange the polymers in the increasing order of tensile strength,

Nylon-6, Buna-S,Polythene.

Ans: (i) synthetic rubber is Buna-S

(ii) It is used for making oil seals, tank linings.

(iii) Buna-S<Polythene< Nylon-6

Unit-16 CHEMISTRY IN EVERYDAY LIFE

POINTS TO BE REMEMBERED

1. **DRUGS – Drugs are chemical of low molecular masses, which interact with macromolecular targets and produce a biological response.**
2. **CHEMOTHERAPY- The use of chemicals for therapeutic effect is called chemotherapy.**
3. **CLASSIFICATION OF DRUGS –**

(a) ***ON THE BASIS OF PHARMACOLOGICAL EFFECT*-drugs for a particular type of problem as analgesics-----for pain relieving.**

(b) ***ON THE BASIS OF DRUG ACTION*-Action of drug on a particular biochemical process.**

(c) ***ON THE BASIS OF CHEMICAL ACTION*-Drugs having similar structure .eg-sulpha drugs.**

(d) ***ON THE BASIS OF MOLECULAR TARGETS*- Drugs interacting with biomolecules as lipids, proteins.**

4. **ENZYMES AS DRUG TARGETS**

(i) ***CATALYTIC ACTION OF EN ZYMES*-**

(a) Enzymes have active sites which hold the substrate molecule .it can be attracted by reacting molecules.

(b) Substrate is bonded to active sites through hydrogen bonds, ionic bonds, Vander Waal or dipole –dipole interactions.

(ii) ***DRUG- ENZYME INTERACTIONS*-**

(a)Drug complete with natural substrate for their attachments on the active sites of enzymes .They are called competitive inhibitors.

(b)Some drugs binds to a different site of the enzyme called allosteric sites which changes the shape of active sites.

5. **ANTAGONISTS- The drugs that bind to the receptor site and inhibit its natural function.**
6. **AGONISTS-Drugs mimic the natural messenger by switching on the receptor.**
7. **ANTACIDS-These are compounds which neutralize excess acid of stomach.eg-Aluminium hydroxide, Magnesium hydroxide.**
8. **ANTI HISTAMINES-The drugs which interfare with the natural action of histamines and prevent the allergic reaction. eg- rantidine,tegarnet, avil.**
9. **TRANQULIZERS-The class of chemical compounds used for the treatment of stress,mild or even severe mental diseases. Eg-idardil, iproniagid, luminal, second equaqnil .**
10. **ANALGESICS-They reduce pain without causing impairment of consciousness, mental confusion or some other disturbance of the nervous system.**

Eg - aspirin, seridon , phenacetin.

11. **ANTIMICROBIALS-They tend to prevent/destroy or inhibit the pathogenic action of microbes as bacteria ,virus ,fungi etc .They are classified as**

(i)*ANTIBIOTICS*-Those are the chemicals substances which are produced by micro-organisms.

Eg- Pencillin , ofloxacin .

***NARROW SPECTRUM ANTI-BIOTICS*-These are effective mainly against gram positive or gram negative bacteria. Eg- Penicillin , streptomycin.**

***BROAD SPECTRUM ANTI-BIOTICS*-They kill or inhibit a wide range of micro-organisms.**

eg- chloramphenicol , tetracydine .

(ii)*ANTISEPTICS OR DISINFECTANT*-These are which either kill/inhibit the growth of micro-organisms

Antiseptics are applied to the living tissuses such as wounds, cuts, ulcers etc. eg- furacine,chloroxylenol & terpinol(dettol) .Disinfectant are applied to inanimate objects such as floors , drainage , system.

Eg- 0.2% solution of phenol is an antiseptic while 1% solution is an disinfectant.

12. ANTIFERTILITY DRUGS- These is the chemical substances used to control the pregnancy. They are also called oral contraceptives or birth control pills.

Eg-Mifepristone, norethindrone.

13. ARTIFICIAL SWEETNING AGENTS-These are the chemical compounds which give sweetening effect to the food without adding calorie.

They are good for diabatic people eg- aspartame, saccharin, alitame , sucrolose.

14. FOOD PRESERVATIVES- They prevents spoilage of food to microbial growth.eg-salt, sugar, and sodium benzoate.

15. CLEANSING AGENTS-

(i) *SOAPS*- They is sodium or potassium salts of long chain fatty acids.They are obtained by the soapnification reaction, when fatty acids are heated with aqueous sodium hydroxide.

They do not work well in hard water.

(iii) *TOILETS SOAP*-That are prepared by using better grade of fatty acids and excess of alkali needs to be removed .colour & perfumes are added to make them attractive.

(iv) *MEDICATED SOAPS*- Substances of medicinal value are added.eg- Buthional , dettol.

16. SYNTHETIC DETERGENTS-They are cleaning agents having properties of soaps, but actually contain no soap .They can used in both soft and hard water .They are-

(i)*ANIONIC DETERGENTS*-They are sodium salts of sulphonated long chain alcohols or hydrocarbons.eg-sodium lauryl sulphonate . They are effective in acidic solution.

$CH_3\ (CH_2)\ CH2OH \rightarrow CH_3\ (CH_2)_{10}CH_2OSO_3H$

(laurylalchol)

$\rightarrow CH_3\ (CH_2)_{10}CH_2SO_3^-Na^+$

(Sodium lauryl sulphonate)

(ii)*CATIONIC DETERGENTS*- They are quarternary ammonium salts of amines with acetates , chlorides, or bromides.They are expensive used tolimited extent.eg- cytyltrimethylammoniumbromide

(iii)*NON-IONIC DETERGENTS*- They does not contain any ions. Some liquid dishwashing detergents which are of non-ionic type .

17. BIODEGREDABLE DETERGENTS- The detergents which are linear and can be attacked by micro-organisms are biodegradable.
Eg -sodium 4-(1-dodecyl) benzene \ sulphonate.
18. NON-BIODEGREDABLE DETERGENTS- The detergents which are branched and cannot be decomposed by micro-organisms are called non-biodegdradable.eg-sodium 4-(1,3,5,7 tetramethyloctl)-benzene sulphonate .It creates water pollution.

VERY SHORT ANSWER TYPE QUESTION

(1 marks)

Q-1 Define the term chemotherapy?
Ans-1 Treatment of diseases using chemicals is called chemotherapy.
Q-2 why do we require artificial sweetening agents?
Ans-2 To reduce calorie intake.
Q-3 what are main constiuent of Dettol?
Ans-3 Choloroxylenol & Terpinol .
Q-4 what type drug phenaticinis?
Ans-4 It is antipyretics.
Q-5 Name the drug that are used to control allergy?
Ans-5 Antihistamines.
Q-6Why is the use of aspartame limited to cold food and drinks?
Ans-6 It is unstable at cooking temperature and decompose.
Q-7What is tranquilizers? Give an example?
Ans-7 They is the drug used in stress, mild severe mental disease.
Q-8 what type of drug chloramphenicol?
Ans-8 It is broad spectrum antibiotic.
Q-9Why is biothional is added to the toilet soap?
Ans-9It acts as antiseptics.
Q-10 what are food preservatives?
Ans-10 The substances that prevent spoilage of food due to microbial growth. eg- sodium benzonate.

SHORT ANSWER TYPE QUESTION

(2 marks)

Q-1 Mention one important use of the following-
(i) Equanil (ii)Sucrolose
Ans-1 (i) Equanil- It is a tranquilizer.
(ii) Sucrolose-It is an artificial sweetener.
Q-2 Define the following and give one example-
(i)Antipyretics (ii) Antibiotics
Ans-2 (i) Antipyretics- Those drugs which reduce the temperature of feveral body are called Antipyretics.
Eg - Paracetamol

(ii) Antibiotics-The drugs which prevent the growth of other micro-organisms. Eg- Pencillin.

Q-3 Name the medicines used for the treatment of the following-

(i) Tuberculosis (ii) Typhoid Tuberculosis- Sterptomycin

Typhoid- Cholororophenicol

Q-4 what are tincture of iodine?

Ans-4 2-3% iodine solution of alcohol water is called tincture of Iodine. It is a powerful antiseptics and is applied on wounds.

Q- 5 What is artificial sweetening agent? Give two examples?

Ans-5 The substances which give sweetening to food but don't add calorie to our body .

Eg- Saccharin, alitame.

Q-6 How is synthetic detergents better than soaps?

Ans- 6 (i) Detergents can be used in hard water but soaps cannot be used.

(ii) Detergents have a stronger cleansing action than soaps.

Q-7 what are sulpha drugs? Give two examples?

Ans-7 a group of drugs which are derivatives of sulphanilamide and are used in place of antibiotics is called sulpha drugs.

Eg- sulphadizine, sulphanilamide.

Q-8 what forces are involved in holding the active sites of the enzymes?

Ans-8 The forces are involved in holding the active sites of the enzymes are hydrogen bonding , ionic bonding , dipole-dipole attractions or Vander waals force of attractions.

Q-9 Describe the following giving an example in each case- (i) Edible colours

(ii) Antifertility drugs

(i) Edible colours- They are used for dying food.
Eg- saffron is used to colour rice.

(ii) Antifertility drugs- Those drugs which control the birth of the child are called antifertility drugs.

Q-10 Give two examples of organic compounds used as antiseptics?

Ans-10 Phenol (0.2%), iodoform

SHORT ANSWER TYPE QUESTION

(3 marks)

Q-1 what are Biodegredable and non-biodegdredable detergents? Give one example of each.

Ans-1 Detergents having straight hydrocarbon chain and are easily decomposed by micro-organisms are called Biodegredable detergents.The detergents having branched hydrocarbon chain and are not easily decomposed by micro-organisms are called Non-Biodegredable detergents.

Q-2 what are barbiturates? To which class of drugs do they belong? Give two examples.

Ans-2 Derivatives of barbituric acid are called barbiturates.They are tranquilizers. They also act as hypnotics. eg- luminal , seconal.

Q-3 what is the use of –

(i) Benadryl (ii) sodium benzoate (iii) Progesterone

Ans-3 (i) Antihistamines
(ii) Preservatives
(iii) Antifertility drug
Q-4 Identify the type of drug-
(i) Ofloxacin (ii) Aspirin (iii) Cimetidine
Ans- 4 (i) Antibiotic (ii) Analgesics & Antipyretics
(iii) Antihistamines & antacid
Q-5 Describe the following with suitable example-
(i) Disinfectant (ii) Analgesics
(iii) Broad spectrum antibiotics

(i) <u>Disinfectant</u>- chemicals used to kill the micro-organisms can applied on non living articles.

(ii) <u>Analgesics</u>- They are the drugs which are used to relieve pain . eg – Aspirin , Ibuprofen.

(iii) <u>Broad spectrum antibiotics</u>- They kill the wide range of gram positive and gram negative bacteria.
Eg- Chloramphenicol , ofloxacin.

BRILLIANT PUBLIC SCHOOL, SITAMARHI

(Affiliated up to +2 level to C.B.S.E., New Delhi)

Class-XII

IIT-JEE Advanced Chemistry

Study Package

Session: 2014-15

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STUDY PACKAGE

Target: IIT-JEE (Advanced)

SUBJECT: CHEMISTRY-XII

Chapters:

1. **Solid State**
2. **Solutions**
3. **Surface Chemistry**
4. **Chemical Kinetics**
5. **Thermochemistry**
6. **Electrochemistry**

STUDY PACKAGE

Target: IIT-JEE (Advanced)

SUBJECT: CHEMISTRY-XII

TOPIC: 13. Solid State

Index:

1. Key Concepts

2. Exercise I

3. Exercise II

4. Exercise III

5. Exercise IV

6. Answer Key

7. 34 Yrs. Que. from IIT-JEE

8. 10 Yrs. Que. from AIEEE

THE KEY

Crystalline solids:

Crystalline solids are those whose atom, molecules or ions have an ordered arrangement extending over a **Long Range.** example-(Rock salt, NaCl).

Amorphous solids:

Amorphous solids are those whose constitutent particles are randomly arrange and have no ordered long range structure. example: Rubber, Glass ect.

TYPES OF CRYSTALLINE SOLIDS:

Type of Solid	Intermolecular forces	Properties	Examples
Ionic	Ion-Ion forces	Brittle, hard high Melting	NaCl, KCl, $MgCl_2$
Molecular	Dispersion forces/Dipole-Dipole /H-bond	Soft, low melting non-conducting	H_2O, Br_2, CO_2, CH_4
Covalent network	Covalent bonds	Hard: High melting	C-Diamond SiO_2
Metallic	Metallic bonds	Variable hardness and melting point conducting	Na, Zn, Cu, Fe

TYPES OF UNIT CELL:

Collection of lattice points, whose repetition produce whole lattice is called a unit cell. The whole lattice can be considered to be made by repetion of unit cell.

1. Unit Cell:

Crystal Systems		Bravais Lattice	Unit Cell Parameters	
			Intercepts	Crystal Angles
1	Cubic	Primitive, Face Centered, Body Centered	$a = b = c$	$\alpha = \beta = \gamma = 90°$
2	Orthorhombic	Primitive, Face Centered, Body Centered, End Centered	$a \neq b \neq c$	$\alpha = \beta = \gamma = 90°$
3	Rhombohedral	Primitive	$a = b = c$	$\alpha = \beta = \gamma \neq 90°$
4	Monoclinic	Primitive, End Centered	$a \neq b \neq c$	$\alpha = \gamma = 90°, \beta \neq 90°$
5	Triclinic	Primitive	$a \neq b \neq c$	$\alpha \neq \beta \neq \gamma \neq 90°$
6	Tetragonal	Primitive, Body Centered	$a = b \neq c$	$\alpha = \beta = \gamma = 90°$
7	Hexagonal	Primitive	$a = b \neq c$	$\alpha = \beta = 90°, \gamma = 120°$

Simple Cubic
$a = b = c$
$\alpha = \beta = \gamma = 90°$

Tetragonal
$a = b \neq c$
$\alpha = \beta = \gamma = 90°$

Orthorhombic
$a \neq b \neq c$
$\alpha = \beta = \gamma = 90°$

Monoclinic
$a \neq b \neq c$
$\alpha = \gamma = 90°, \beta \neq 90°$

Triclinic
$a \neq b \neq c$
$\alpha \neq \beta \neq \gamma \neq 90°$

Hexagonal Primitive
$a = b \neq c$
$\alpha = \beta = 90°, \gamma = 120°$

1.1 Primitive or simple cubic (PS/SC) unit cell: Spheres in one layer sitting directly on top of those in previous layer, so that all layers are identical. Each sphere is touched by six other, hence coordination number is 6. 52% of available space occupied by spheres.
Example: Polonium crystallises in simple cubic arrangement.

Z = 1 ; C.N. = 6

1.2 Body Centered cubic (BCC) unit cell: Spheres in one layer sit in the depression made by first layer in a-b-a-b manner. Coordination number is 8, and 68% of available space is occupied by atoms.
Example: Iron, sodium and 14 other metal crystallises in this manner.

Z = 2 ; C.N. = 8

1.3 Face centered cubic (FCC) unit cell:
Examples : Al, Ni, Fe, Pd all solid noble gases etc.

Z = 4 ; C.N. = 12

2. Density of cubic crystals:

TYPE OF PACKING:

3. Closest packing of atoms: This is the most efficient way of packing 74% of available space is occupied by spheres and coordination number is 12.

(i) ***Hexagonal close pack (A-B-A-B) type packing :*** Each layer has hexagonal arrangement of touching sphere and 3rd layer is similar (exactly on top) of first layer.

(ii) ***Cubic close pack (A-B-C-A-B-C):*** AB layers are similar to HCP arrangement but third layer is offset from both A and B layers. The fourth layer is exactly on top of first layer.

Hexagonal primitive unit cell

4. Types of voids

4.1 Tetrahedral void

Number of tetrahedral voids per FCC unit cell

4.2 Octahedral void

An octahedral void at the centre of an edge in a FCC unit cell.

An octahedral void at the body centered position in FCC unit cell

5. Radius ratio

5.1 Radius ratio for co-ordination number 3

(Triangular Arrangement): $r^+ + r^- = \frac{2}{3}\sqrt{3}\, r^-$; $\frac{r^+}{r^-} = \frac{2-\sqrt{3}}{\sqrt{3}} = 0.155$

5.2 Radius ratio for coordination number 4

(Tetrahedral arrangement): $r^+ + r^- = \frac{\sqrt{3}a}{4}$; $4r^- = \sqrt{2}\,a = \frac{\sqrt{3}}{\sqrt{2}}r^-$

$$\frac{r^+}{r^-} = \frac{\sqrt{3}-\sqrt{2}}{\sqrt{2}} = 0.225$$

5.3 Radius ratio for coordination number 6: $r^+ + r^- = \sqrt{2}\ r^-$

(Octahedral Arrangement) or $\frac{r^+}{r^-} = \sqrt{2} - 1 = 0.414$

Radius ratio for coordination number 4
(Square plannar arrangement)

Top view of octahedral arrangement

5.4 Radius ratio for coordination number 8 : $r^+ + r^- = \frac{\sqrt{3}}{2}\ a$

(Body centered cubic crystal) $r^+ + r^- = \sqrt{3}\ r^-$

$$\frac{r^+}{r^-} = \sqrt{3} - 1 = 0.732$$

6. Types of ionic structures

6.1 Rock salt structure:(NaCl) Larger atom formic ccp arrangement and smaller atom filling all octahedral voids.

Rock salt structure

6.2 Zinc blende (sphalerite) structure:(ZnS) Larger atom formic ccp arrangement and smaller atom filling half of alternate tetrahedral voids

Zinc blende structure

6.3 Fluorite structure:(CaF_2) Ca^{2+} forming ccp arrangement and F^- filling all tetrahedral voids.

Fluorite structure

6.4 Antifluorite structure :(Li_2O) O^{2-} ion forming ccp and Li^+ taking all tetrahedral voids.

Antifluorite structure

6.5 Cesium halide structure: ($CsCl$) Cl^- at the corners of cube and Cs^+ in the center.

Cesium chloride structure

6.6 Corundum Structure: (Al_2O_3) O^{2-} forming hcp and Al^{3+} filling 2/3 octahedral voids.

6.7 Rutile structure: (TiO_2) O^{2-} forming hcp while Ti^{4+} ions occupy half of the octahedral voids.

6.8 Pervoskite structure:($CaTiO_3$) Ca^{2+} in the corner of cube O^{2-} at the face center and Ti^{4+} at the centre of cube.

Pervoskite structure

6.9 Spinel and inverse spinel structure: ($MgAl_2O_4$)O^{2-} forming fcc, Mg^{2+} filling 1/8 of tetrahedral voids and Al^{3+} taking half of octahedral voids.In an inverse spinel structure, O^{2-} ion form FCC lattice, A^{2+} ions occupy 1/8 of the tetrahedral voids and trivalent cation occupies 1/8 of the tetrahedral voids and 1/4 of the octahedral voids.

7. Crystal defects:

Point defects: When ions or atoms do not hold the theoretical position, this is called point defect. Point defects are of two types:

(I) ***Stoichiometric defects***:

(a) **Schottky defect:** Due to missing of ions from lattice point in pairs.

(b) **Frenkel defect:** It is caused due to the creation of lattice vacancy as a result of misplaced ion in interstitial site.

✶ Schottky defect common in ionic solid with high coordination number. NaCl, KCl, KBr

✶ Frenkel defect :- Solid with low coordination number ZnS, AgBr.

(II) ***Non-Stoichiometric defects***: Ratio of positive and negative ion differ from that indicated by chemical formula.

✶ **Metal-excess defect :**

(a) A negative ion replaced by electron. (F-centre)

(b) Extra metal ion present in lattice and electron also present in interstitial site.

✶ **Metal-deficiency defect caused by :** Cation missing from lattice point, electroneutrality maintained by metal ions with higher oxidation state as $Fe_{0.94}{}^{\circ}O$.

THE ATLAS

TYPES OF SOLIDS

Crystalline Solids

Crystalline solids have long range order i.e. the constituent particles are arranged in a regular fashion and this symmetrical arrangement extends throughout the crystal length.

Amorphous Solids

Lattice - Unit Cells

(i) A unit cell is the smallest repeating structural unit the crystalline solid. Bravais has predicted that there are only 14 unit cells that exists in nature.

(ii)The relation between the edge length (a) and the radius of atom (r) forming lattice are as follows. PC :a=2r, BCC: $\sqrt{3}a=4$;FCC:$\sqrt{2}a=4r$& HP:a=2r height(c) $=4r\sqrt{\frac{2}{3}}$

Packing fraction and density determination

(i) The ratio of volume occupied by the effective atoms to the volume of the unit cell is called packing fraction. Its values for various unit cells are PC = 0.52, BCC = 0.68, FCC & HP = 0.74.

(ii)Density (ρ) of cubic crystal is calculated using the relation $\rho = \frac{n \times M}{N_{AV} \times a^3}$ where

n=number of effective atoms, M=Atomic mass,N_{AV}=Avogadro's number and a= Edge length.

Type of void and radius ratio rule

(i) Tetrahedral & octahedral voids are present only inclosest packed structures. The effective number of octahedral voids in a unit cell is equal to the effective number of atoms in the unit cell & effective number of tetrahedral voids is equal to double the number of effective atoms in the unit cell.

(ii)The sum of radius of the atom of host lattice (r_h) and the radius of atom occupying void($r_{f(t)}$or $r_{f(o)}$) is given by

For octahedral void, $r_h+r_{f(o)}= \frac{a}{2}$& for tetrahedral void,$r_h+r_{f(t)}= \frac{\sqrt{3}a}{4}$

(iii)Limiting radius is defined as the minimum ratio of cation to anion radius. It is defined when cation is in contact with anions and anions are also in contact with each other.

(iv)Radius ratio depends on the co-ordination number. The limiting radius ratio for the various co-ordination numbers are

C.N.3 : 0.155, C.N.4 (Tetrahedral) : 0.225, C.N.4(Square planar) : 0.414, C.N.6 (Octahedral) : 0.414, C.N.8 (BCC) : 0.732, C.N.12 (Ideal FCC) : 1

Defects in Solids

Ionic lattice has 2 major defects. Schottky defect occurs due to the cation-anion pair vacancy, which decreases the density of crystal. Frenkel defect occurs when an ion leaves its lattice site and fits into an interstitial space. Due to Frenkel defect, density of crystal remains unaffected.

EXERCISE I

Formula of ionic solid from unit cell description

Q.1 A cubic solid is made up of two elements A and B. Atoms B are at the corners of the cube and A at the body centre. What is the formula of compound.

Q.2 A compound alloy of gold and copper crystallizes in a cubic lattice in which gold occupy that lattice point at corners of the cube and copper atom occupy the centres of each of the cube faces. What is the formula of this compound.

Q.3 A cubic solid is made by atoms A forming close pack arrangement, B occupying one. Fourth of tetrahedral void and C occupying half of the octahedral voids. What is the formula of compound.

Q.4 What is the percent by mass of titanium in rutile, a mineral that contain Titanium and oxygen, if structure can be described as a closet packed array of oxide ions, with titanium in one half of the octahedral holes. What is the oxidation number of titanium?

Q.5 Spinel is a important class of oxides consisting of two types of metal ions with the oxide ions arranged in CCP pattern. The normal spinel has one-eight of the tetrahedral holes occupied by one type of metal ion and one half of the octahedral hole occupied by another type of metal ion. Such a spinel is formed by Zn^{2+}, Al^{3+} and O^{2-}, with Zn^{2+} in the tetrahedral holes. Give the formulae of spinel.

Edge length, density and number of atoms per unit cell

Q.6 KF crystallizes in the NaCl type structure. If the radius of K^+ ions 132 pm and that of F^- ion is 135 pm, what is the shortest K–F distance? What is the edge length of the unit cell? What is the closet K–K distance?

Q.7 A closed packed structure of uniform spheres has the edge length of 534 pm. Calculate the radius of sphere, if it exist in
(a) simple cubic lattice (b) BCC lattice (c) FCC lattice

Q.8 Calculate the density of diamond from the fact that it has face centered cubic structure with two atoms per lattice point and unit cell edge length of 3.569 Å.

Q.9 An element crystallizes into a structure which may be described by a cubic type of unit cell having one atom on each corner of the cube and two atoms on one of its body diagonals. If the volume of this unit cell is 24×10^{-24} cm^3 and density of element is 7.2 g cm^{-3}, calculate the number of atoms present in 200 g of element.

Q.10 Silver has an atomic radius of 144 pm and the density of silver is 10.6 g cm^{-3}. To which type of cubic crystal, silver belongs?

Q.11 AgCl has the same structure as that of NaCl. The edge length of unit cell of AgCl is found to be 555 pm and the density of AgCl is 5.561 g cm^{-3}. Find the percentage of sites that are unoccupied.

Q.12 Xenon crystallises in the face-centred cubic lattice and the edge of the unit cell is 620 pm. What is the nearest neighbour distance and what is the radius of xenon atom?

Q.13 The two ions A^+ and B^- have radii 88 and 200 pm respectively. In the closed packed crystal of compound AB, predict the co-ordination number of A^+.

Q.14 CsCl has the bcc arrangement and its unit cell edge length is 400 pm. Calculate the interionic distance in CsCl.

Q.15 Gold crystallizes in a face centered cubic lattice. If the length of the edge of the unit cell is 407 pm, calculate the density of gold as well as its atomic radius assuming it to be spherical. Atomic mass of gold = 197 amu.

Q.16 The density of KBr is 2.75 g cm^{-3} . The length of the edge of the unit cell is 654 pm. Show that KBr has face centered cubic structure.
($N = 6.023 \times 10^{23}$ mol^{-1} , At. mass : K = 39, Br = 80)

Q.17 An element crystallizes in a structure having FCC unit cell of an edge 200 pm. Calculate the density, if 200 g of this element contains 24×10^{23} atoms.

Q.18 The effective radius of the iron atom is 1.42 Å. It has FCC structure. Calculate its density (Fe = 56 amu)

Q.19 A crystal of lead(II) sulphide has NaCl structure. In this crystal the shortest distance between Pb^{+2} ion and S^{2-} ion is 297 pm. What is the length of the edge of the unit cell in lead sulphide? Also calculate the unit cell volume.

Q.20 If the length of the body diagonal for CsCl which crystallises into a cubic structure with Cl^- ions at the corners and Cs^+ ions at the centre of the unit cells is 7 Å and the radius of the Cs^+ ion is 1.69 Å, what is the radii of Cl^- ion?

PROFICIENCY TEST

1. Crystalline solids are isotropic.

2. Rhombohedral, triclinic and hexagonal are the unit cells, which have only primitive arrangement possible.

3. Packing fraction of FCC and HP units cells are same.

4. The minimum void fraction for any unit cell in any shape having only one type of atom and all voids unfilled is 0.26.

5. Packing fraction of a lattice structure depends on the radius of the atom crystallizing in it.

6. The location of tetrahedral voids in FCC unit cell are the centers of 8 minicubes forming a large cube.

7. Effective number of octahedral voids in a unit cell is equal to the effective number of atoms in the unit cell.

8. Radius ratio for co-ordination number 4 having tetrahedral and square planar geometry is same.

9. The radius ratio value for co-ordination number 4 having square planar geometry and co-ordination number 6 having octahedral geometry is same.

10. A metallic element crystallises into a lattice containing a sequence of layers of AB AB AB ..... . Any packing of spheres leaves out voids in the lattice 26% percent by volume of this lattice is empty space.

11. The relation between edge length (a) and radius of atom (r) for BCC lattice is_____.

12. The relation between edge length (a) and radius of atom (r) for FCC lattice is_____.

13. ABCABC.....layering pattern is called _____ packing, found in _____ lattice.

14. ABABAB.....layering pattern is called _____packing , found in _____ lattice.

15. Height (c) of the hexagonal primitive unit cell in terms of radius of atom (r) is_____.

16. Anions would be in contact with each other only if the cation to anion radius for a given co-ordination number is_____.

17. The number of tetrahedral voids in hexagonal primitive unit cell is_____.

18. The limiting radius for co-ordination number 8 is_____.

19. For cesium chloride structure, the interionic distance (in terms of edge length, a) is equal to _____.

20. Density of a crystal ___due to Schottky defect and _____due to Frankel defect.

EXERCISE II

Q.1 Iron has body centered cubic lattice structure. The edge length of the unit cell is found to be 286 pm. What is the radius of an iron atom?

Q.2 Cesium chloride forms a body centered cubic lattice. Cesium and chloride ions are in contact along the body diagonal of the unit cell. The length of the side of the unit cell is 412 pm and Cl^- ion has a radius of 181 pm. Calculate the radius of Cs^+ ion.

Q.3 In a cubic closed packed structure of mixed oxides the lattice is made up of oxide ions, one eighth of tetrahedral voids are occupied by divalent ions (A^{2+}) while one half of the octahedral voids occupied trivalent ions (B^{3+}). What is the formula of the oxide?

Q.4 A solid A^+ and B^- had NaCl type closed packed structure. If the anion has a radius of 250 pm, what should be the ideal radius of the cation? Can a cation C^+ having a radius of 180 pm be slipped into the tetrahedral site of the crystal of A^+B^- ? Give reasons for your answer.

Q.5 Calculate the value of Avogadro's number from the following data:
Density of NaCl = 2.165 cm^{-3}
Distance between Na^+ and Cl^- in NaCl = 281 pm.

Q.6 If the radius of Mg^{2+} ion, Cs^+ ion, O^{2-} ion, S^{2-} ion and Cl^- ion are 0.65 Å , 1.69 Å, 1.40 Å, 1.84 Å, and 1.81 Å respectively. Calculate the co-ordination numbers of the cations in the crystals of MgS, MgO and CsCl.

Q.7 Iron occurs as bcc as well as fcc unit cell. If the effective radius of an atom of iron is 124 pm. Compute the density of iron in both these structures.

Q.8 KCl crystallizes in the same type of lattice as does NaCl. Given that $\frac{r_{Na^+}}{r_{Cl^-}}=0.5$ and $\frac{r_{Na^+}}{r_{K^+}}=0.7$ Calculate:
(a) The ratio of the sides of unit cell for KCl to that for NaCl and
(b) The ratio of densities of NaCl to that for KCl.

Q.9 An element A (Atomic weight = 100) having bcc structure has unit cell edge length 400 pm. Calculate the density of A and number of unit cells and number of atoms in 10 gm of A.

Q.10 Prove that the void space percentage in zinc blende structure is 25%.

Q.11 A unit cell of sodium chloride has four formula units. The edge of length of the unit cell is 0.564 nm. What is the density of sodium chloride.

Q.12 In a cubic crystal of CsCl (density = 3.97 gm/cm^3) the eight corners are occupied by Cl^- ions with Cs^+ ions at the centre. Calculate the distance between the neighbouring Cs^+ and Cl^- ions.

Q.13 KF has NaCl structure. What is the distance between K^+ and F^- in KF if density of KF is 2.48 gm/cm^3.

Q.14 The composition of a sample of wustite is $Fe_{0.93}O_{1.0}$. What percentage of iron is present in the form of Fe(III)?

Q.15 $BaTiO_3$ crystallizes in the prevoskite structure. This structure may be described as a cubic lattice with barium ions occupying the corner of the unit cell, oxide ions occupying the face-centers and titanium ion occupying the center of the unit cell.

(a) If titanium is described as occupying holes in BaO lattice, what type of holes does it occupy?

(b) What fraction of this type hole does it occupy?

Q.16 Rbl crystallizes in bcc structure in which each Rb^+ is surrounded by eight iodide ions each of radius 2.17 Å. Find the length of one side of RbI unit cell.

Q.17 If NaCl is dopped with 10^{-3} mol % $SrCl_2$, what is the numbers of cation vacancies?

Q.18 Find the size of largest sphere that will fit in octahedral void in an ideal FCC crystal as a function of atomic radius 'r'. The insertion of this sphere into void does not distort the FCC lattice. Calculate the packing fraction of FCC lattice when all the octahedral voids are filled by this sphere.

Q.19 A cubic unit cell contains manganese ions at the corners and fluoride ions at the center of each edge.

(a) What is the empirical formula of the compound?

(b) What is the co-ordination number of the Mn ion?

(c) Calculate the edge length of the unit cell, if the radius of Mn ion is 0.65 Å and that of F^- ion is 1.36 Å.

Q.20 NaH crystallizes in the same structure as that of NaCl. The edge length of the cubic unit cell of NaH is 4.88 Å.

(a) Calculate the ionic radius of H^-, provided the ionic radius of Na^+ is 0.95 Å.

(b) Calculate the density of NaH.

Q.21 Metallic gold crystallises in fcc lattice. The length of the cubic unit cell is a = 4.07 Å.

(a) What is the closest distance between gold atoms.

(b) How many "nearest neighbours" does each gold atom have at the distance calculated in (a).

(c) What is the density of gold?

(d) Prove that the packing fraction of gold is 0.74.

Q.22 Ice crystallizes in a hexagonal lattice. At the low temperature at which the structure was determined, the lattice constants were a = 4.53 Å, and b = 7.60 Å(see figure). How many molecules are contained in a given unit cell? [density (ice) = 0.92 gm/cm^3)]

Q.23 Using the data given below, find the type of cubic lattice to which the crystal belongs.

	Fe	V	Pd
a in pm	286	301	388
ρ in gm cm^{-3}	7.86	5.96	12.16

Q.24 Potassium crystallizes in a body-centered cubic lattice with edge length, a = 5.2 Å.

(a) What is the distance between nearest neighbours?

(b) What is the distance between next-nearest neighbours?

(c) How many nearest neighbours does each K atom have?

(d) How many next-nearest neighbours does each K atom have?

(e) What is the calculated density of crystalline potassium?

Q.25 Prove that void space in fluorite structure per unit volume of unit cell is 0.243.

Q.26 A compound formed by elements X & Y, Crystallizes in a cubic structure, where X is at the corners of the cube and Y is at six face centers. What is the formula of the compound? If side length is 5Å, estimate the density of the solid assuming atomic weight of X and Y as 60 and 90 respectively.

Q.27 The metal nickel crystallizes in a face centred cubic structure. Its density is 8.9 gm/cm^3. Calculate
(a) the length of the edge of the unit cell.
(b) the radius of the nickel atom. [Atomic weight of Ni = 58.89]

Q.28 The olivine series of minerals consists of crystals in which Fe and Mg ions may substitute for each other causing substitutional impurity defect without changing the volume of the unit cell. In olivine series of minerals, oxide ion exist as FCC with Si^{4+} occupying $\frac{1}{4}$ th of octahedral voids and divalent ions occupying $\frac{1}{4}$ th of tetrahedral voids. The density of forsterite (magnesium silicate) is 3.21 g/cc and that of fayalite (ferrous silicate)is 4.34 g/cc. Find the formula of forsterite and fayalite minerals and the percentage of fayalite in an olivine with a density of 3.88 g/cc.

Q.29 The mineral hawleyite, one form of CdS, crystallizes in one of the cubic lattices, with edge length 5.87Å. The density of hawleyite is 4.63 g cm^{-3}.
(i) In which cubic lattice does hawleyite crystallize?
(ii) Find the Schottky defect in g cm^{-3}.

Q.30 A strong current of trivalent gaseous boron passed through a germanium crystal decreases the density of the crystal due to part replacement of germanium by boron and due to interstitial vacancies created by missing Ge atoms. In one such experiment, one gram of germanium is taken and the boron atoms are found to be 150 ppm by weight, when the density of the Ge crystal decreases by 4%. Calculate the percentage of missing vacancies due to germanium, which are filled up by boron atoms.
Atomic wt. Ge = 72.6, B = 11

EXERCISE III

Q.1 A solid has a structure in which W atoms are located at the corners of a cubic lattice, O atom at the centre of the edges and Na atom at centre of the cubic. The formula for the compound is
(A) $NaWO_2$ (B) $NaWO_3$ (C) Na_2WO_3 (D) $NaWO_4$

Q.2 The density of CaF_2 (fluorite structure) is 3.18 g/cm^3. The length of the side of the unit cell is
(A) 253 pm (B) 344 pm (C) 546 pm (D) 273 pm

Q.3 Which of the following statements is correct in the rock-salt structure of an ionic compounds?
(A) coordination number of cation is four whereas that of anion is six.
(B) coordination number of cation is six whereas that of anion is four.
(C) coordination number of each cation and anion is four.
(D) coordination number of each cation and anion is six.

Q.4 The coordination number of cation and anion in Fluorite CaF_2 and CsCl are respectively
(A) 8:4 and 6:3 (B) 6:3 and 4:4 (C) 8:4 and 8:8 (D) 4:2 and 2:4

Q.5 The interstitial hole is called tetrahedral because
(A) It is formed by four spheres.
(B) Partly same and partly different.
(C) It is formed by four spheres the centres of which form a regular tetrahedron.
(D) None of the above three.

Q.6 The tetrahedral voids formed by ccp arrangement of Cl^- ions in rock salt structure are
(A) Occupied by Na^+ ions (B) Occupied by Cl^- ions
(C) Occupied by either Na^+ or Cl^- ions (D) Vacant

Q.7 The number of nearest neighbours around each particle in a face-centred cubic lattice is
(A) 4 (B) 6 (C) 8 (D) 12

Q.8 If the anions (A) form hexagonal closest packing and cations (C) occupy only 2/3 octahedral voids in it, then the general formula of the compound is
(A) CA (B) CA_2 (C) C_2A_3 (D) C_3A_2

Q.9 A solid is formed and it has three types of atoms X, Y, Z. X forms a FCC lattice with Y atoms occupying all the tetrahedral voids and Z atoms occupying half the octrahedral voids. The formula of the solid is:
(A) X_2Y_4Z (B) XY_2Z_4 (C) X_4Y_2Z (D) X_4YZ_2

Q.10 The intermetallic compound LiAg crystallizes in cubic lattice in which both lithium and silver have coordination number of eight. The crystal class is
(A) Simple cubic (B) Body centred cubic (C) Face centred cubic (D) None

Q.11 A compound XY crystallizes in BCC lattice with unit cell edge lenght of 480 pm. If the radius of Y^- is 225 pm, then the radius of X^+ is
(A) 127.5 pm (B) 190.68 pm (C) 225 pm (D) 255 pm

Q.12 The mass of a unit cell of CsCl corresponds to
(A) 1 Cs^+ and 1 Cl^- (B) 1 Cs^+ and 6 Cl^- (C) 4 Cs^+ and 4 Cl^- (D) 8 Cs^+ and 1 Cl^-

Q.13 In the closest packing of atoms A (radius : r_a), the radius of atom B that can be fitted into tetrahedral voids is

(A) 0.155 r_a (B) 0.225 r_a (C) 0.414 r_a (D) 0.732 r_a

Q.14 Which one of the following schemes of ordering closed packed sheets of equal sized spheres do not generate close packed lattice.

(A) ABCABC (B) ABACABAC (C) ABBAABBA (D) ABCBCABCBC

Q.15 An ionic compound AB has ZnS type structure. If the radius A^+ is 22.5 pm, then the ideal radius of B^- would be

(A) 54.35 pm (B) 100 pm (C) 145.16 pm (D) none of these

Q.16 NH_4Cl crystallizes in a body-centered cubic type lattice with a unit cell edge length of 387 pm. The distance between the oppositively charged ions in the lattice is

(A) 335.1 pm (B) 83.77 pm (C) 274.46 pm (D) 137.23 pm

Q.17 r_{Na^+} = 95 pm and r_{Cl^-} =181 pm in NaCl (rock salt) structure. What is the shortest distance between Na^+ ions?

(A) 778.3 pm (B) 276 pm (C) 195.7 pm (D) 390.3 pm

Q.18 In diamond, carbon atom occupy FCC lattice points as well as alternate tetrahedral voids. If edge length of the unit cell is 356 pm, then radius of carbon atom is

(A) 77.07 pm (B) 154.14 pm (C) 251.7 pm (D) 89 pm

Q.19 Which of the following will show schottky defect

(A) CaF_2 (B) ZnS (C) AgCl (D) CsCl

Q.20 Give the correct order of initials **T** (true) or **F** (false) for following statements.

I. In an anti-fluorite structure anions form FCC lattice and cations occupy all tetrahedral voids.

II. If the radius of cations and anions are 0.2 Å and 0.95 Å then coordinate number of cation in the crystal is 4.

III An atom/ion is transferred from a lattice site to an interstitial position in Frenkel defect.

IV. Density of crystal always increases due to substitutinal impurity defect.

(A) TFFF (B) FTTF (C) TFFT (D) TFTF

EXERCISE IV

Q.1 The edge length of unit cell of a metal having atomic weight 75 g/mol is 5 Å which crystallizes in cubic lattice. If the density is 2 g/cc then find the radius of metal atom. ($N_A = 6 \times 10^{23}$). Give the answer in pm. **[JEE 2006]**

Q.2 An element crystallises in FCC lattice having edge length 400 pm. Calculate the maximum diameter which can be placed in interstital sites without disturbing the structure. **[JEE 2005]**

Q.3 Which of the following FCC structure contains cations in alternate tetrahedral voids?
(A) NaCl (B) ZnS (C) Na_2O (D) CaF_2 **[JEE 2005]**

Q.4(i) AB crystallizes in a rock salt structure with A : B = 1 : 1. The shortest distance between A and B is $Y^{1/3}$ nm. The formula mass of AB is 6.023 Y amu where Y is any arbitrary constant. Find the density in kg m^{-3}.

(ii) If measured density is 20 kg m^{-3}. Identify the type of point defect. **[JEE–2004]**

Q.5 Marbles of diameter 10 mm each are to be arranged on a flat surface so that their centres lie within the area enclosed by four lines of length each 40 mm. Sketch the arrangement that will give the maximum number of marbles per unit area, that can be enclosed in this manner and deduce the expression to calculate it. **[JEE–2003]**

Q.6 A substance A_xB_y crystallises in a FCC lattice in which atoms "A" occupy each corner of the cube and atoms "B" occupy the centres of each face of the cube. Identify the correct composition of the substance A_xB_y.
(A) AB_3 (B) A_4B_3
(C) A_3B (D) composition cannot be specified **[JEE-2002]**

Q.7 The figures given below show the location of atoms in three crystallographic planes in FCC lattice. Draw the unit cell for the corresponding structure and identify these planes in your diagram. **[JEE-2000]**

Q.8 In a solid "AB" having NaCl structure "A" atoms occupy the corners of the cubic unit cell. If all the face-centred atoms along one of the axes are removed, then the resultant stoichiometry of the solid is
(A) AB_2 (B) A_2B (C) A_4B_3 (D) A_3B_4 **[JEE-2000]**

Q.9 In any ionic solid [MX] with schottky defects , the number of positive and negative ions are same.**[T/F]** **[JEE-2000]**

Q.10 The coordination number of a metal crystallising in a hcp structure is **[JEE-2000]**
(A) 12 (B) 4 (C) 8 (D) 6

Q.11 A metal cryatallises into two cubic phases, FCC and BCC whose unit cell lengths are 3.5 and 3.0 Å respectively. Calculate the ratio of densities of FCC and BCC. **[JEE-1999]**

Q.12 Which of the following statements are correct :
(A) The coordination number of each type of ion in CsCl is 8.
(B) A metal that crystallises in BCC structure has a coordination number 12.
(C) A unit cell of an ionic crystal shares some of its ions with other unit cells
(D) The length of the unit cell in NaCl is 552 pm.
[r_{Na^+} = 95 pm ; r_{Cl^-} = 181 pm] **[JEE-1998]**

Q.13 In the sodium chloride structure, each Na^+ ion is surrounded by six Cl^- nearest neighbours and _____ Na^+ ions next nearest neighbours. **[JEE-1997]**

Q.14 A unit cell of sodium chloride has four formula units. The edge length of the unit cell is 0.564 nm. What is the density of sod. chloride. **[JEE-1997]**

Q.15 Chromium crystallises with bcc lattice. The unit cell length is 287 pm. Calculate atomic rad. What would be the density of chromium. **[JEE-1997]**

ANSWER KEY

EXERCISE I

Q.1	A-B	Q.2	$AuCu_3$	Q.3	$A_4B_2C_2$	Q.4	59.95%, +4
Q.5	$ZnAl_2O_4$	Q.6	267 pm, 534 pm, 378 pm			Q.7	267 pm, 231.2 pm, 188.8 pm
Q.8	3.5 g cm^{-3}	Q.9	3.472×10^{24} atoms			Q.10	FCC
Q.11	0.24%	Q.12	438.5 pm, 219.25 pm			Q.13	6
Q.14	346.4 pm	Q.15	19.4g/cm^3 , 143.9 pm			Q.17	41.67 g cm^{-3}
Q.18	5.74 g cm^{-3}	Q.19	a =5.94×10^{-8}cm, V=2.096×10^{-22} cm^{-3}			Q.20	1.81Å

PROFICIENCY TEST

1.	F	2.	T	3.	T	4.	T
5.	F	6.	T	7.	T	8.	F
9.	T	10.	T	11.	$\sqrt{3}$ a = 4r	12.	$\sqrt{2}$ a = 4r]
13.	cubic close, FCC			14.	hexagonal close, HP		
15.	$c = 4r\sqrt{\frac{2}{3}}$	16.	least or minimum			17.	12
18.	0.732	19.	$\frac{\sqrt{3}a}{2}$	20.	decreases, remains constant		

EXERCISE II

Q.1	123.84 pm	Q.2	175.8 pm	Q.3	AB_2O_4	Q.4	103.4 pm, No
Q.5	6.01×10^{23}	Q.6	4, 6, 8	Q.7	7.887 g/cc , 8.59 gm/cm^3		

Q.8 **(a)** 1.143, **(b)** 1.172

Q.9 5.188 gm/cm^3, 6.023×10^{22} atoms of A, 3.0115×10^{22} unit cells

Q.11	2.16 gm/cm^3	Q.12	3.57 Å	Q.13	2.685 Å	Q.14	15.053

Q.15	**(a)** octahedral, **(b)** 1/4	Q.16	4.34 Å
Q.17	6.02×10^{18} mol^{-1}	Q.18	0.414 r, 79.3%
Q.19	(a) MnF_3, (b) 6, (c) 4.02Å	Q.20	(a) 1.49 Å, (b) 1.37 g/cm^3

Q.21 **(a)** 2.88 Å, **(b)** 12 , **(c)** 19.4 g/cc

Q.22 4 molecules of H_2O

Q.23 for Fe is bcc, for V is bcc, for Pd is face centered

Q.24 (a) 4.5 Å, (b) 5.2 Å, (c) 8, (d) 6, (e) 0.92 g/cm^3

Q.26 XY_3, 4.38 g/cm^3

Q.27 **(a)** 3.52 Å,**(b)** 1.24 Å

Q.28 Mg_2SiO_4, Fe_2SiO_4, 59%

Q.29 (i) 3.90, (ii) 0.120 g/cc

Q.30 2.376%

EXERCISE III

Q.1	B	Q.2	C	Q.3	D	Q.4	C	Q.5	C	Q.6	D	Q.7	D
Q.8	C	Q.9	A	Q.10	B	Q.11	B	Q.12	A	Q.13	B	Q.14	C
Q.15	B	Q.16	A	Q.17	D	Q.18	A	Q.19	D	Q.20	D		

EXERCISE IV

Q.1 216.5 pm

Q.2 117.1 pm

Q.3 B

Q.4 (i) = 5 kg m^{-3}
(ii) There is huge difference in theoretically calculated density and observed density. It is only possible if some foreign species occupies interstitial space i.e. substitution defect.

Q.5 Discuss

Q.6	A	Q.7	Discuss	Q.8	D	Q.9	True	Q.10	A
Q.11	1.259	Q.12	A, C, D	Q.13	12	Q.14	2.165 g/cm^3		

Q.15 (i)124.27 pm, (ii) 7.30 g/cm^3

STUDY PACKAGE

Target: IIT-JEE (Advanced)

SUBJECT: CHEMISTRY-XII

TOPIC: 14. Solutions

Index:

1. Key Concepts

2. Exercise I

3. Exercise II

4. Exercise III

5. Exercise IV

6. Answer Key

7. 34 Yrs. Que. from IIT-JEE

8. 10 Yrs. Que. from AIEEE

KEY CONCEPTS

Vapor Pressure. The pressure exerted by the vapors of a liquid which are in equilibrium with it at a given temperature.

Note: It depends only on temperature and on nature of the liquid. It does NOT depend on the surface area

Raoult's Law. The equilibrium vapor pressure of a volatile component is linearly proportional to the mole fraction of that compoent in liquid phase.

For non-volatile solutes : $P(\text{solution}) = x_{solvent} P^o$

or relative lowering of vapor pressure, $(P^o - P)/P^o = x_{solute}$.

A more useful form is $(P^o - P)/P = n/N$

where n = total number of moles of *all the free solute species* in the solution *finally* (i.e. at equilibrium).

Three cases arise.

(i) **Non-electrolyte** is dissolved e.g. glucose or urea. These molecules do not dissociate into ions. If 0.1 mol of urea is dissolved in 50 moles of water, then n/N = 0.1/50 simply.

(ii) **Strong electrolyte** is dissolved e.g. NaCl, $Ca(NO_3)_2$etc. These dissociate nearly completely into ions. If 0.1 mol of NaCl is dissolved in 50 moles of water, then n/N = 0.2/50 since NaCl dissociates completely in 0.1 mol Na^+ ions and 0.1 mol Cl^- ions. Similarly, for $Ca(NO_3)_2$, n/N = 0.3/50 if 0.1 mol of it dissociates completely into ions.

(iii) **Weak electrolyte** is dissolved e.g. HCOOH, CH_3NH_2 etc. In such cases, we should determine the *total* number of moles of all the solute species at equilibrium. e.g. i f n_o moles of formic acid considered non-volatile here) are dissolved in N moles of solvent then,

$$HCOOH \Leftrightarrow H^+ + COOH^-$$

$$n_o(1-\alpha) \qquad n_o\alpha \qquad n_o\alpha$$

Total number of moles at equilibrium $= n_o(1+\alpha)$. Hence, $n/N = n_o(1+\alpha)/N$.

Note : This factor, n (at equilibrium)/n(original) is referred to as **van't Hoff factor**.

Ideal Solutions. The solutions which obey Raoult's Law are called ideal solution. For ideality :

(i) $\Delta H_{mix} = 0$, (ii) $\Delta V_{mix} = 0$ as well for liquid-liquid solutions.

Non ideal solution (Deviations From Raoult's Law)

Positive deviation. When the observed vapor pressure is *more than* that expected by Raoult's law.

This is observed when $\Delta H_{mix} > 0$ i.e. energy is absorbed on mixing. Usually obtained by mixing of polar liquids with non-polar ones. e.g. cyclohexane and ethanol.

Negative deviation. When the observed vapor pressure is *less than* that expected by Raoult's law. This is observed when $\Delta H_{mix} < 0$ i.e. energy is released on mixing. Attractive forces between unlike molecules are greater than the forces of attraction between like molecules. e.g. chloroform and acetone. (Curve 3 in Fig. 1 and 2).

x is mole fraction of more volatile component (2)

Fig. 1

x is mole fraction of more volatile component (2)

Fig. 2

Azeotropic Solutions. During distillation, the mole fraction of more volatile component in vapor state is higher than that in liquid state. This makes distillation possible. However, there exist some solutions for particular compositions of which the mole fraction of components in liquis and vapor state is same. Thus, no advantage is derived by distilling such a mixture and it is termed as **azeotropic.**

Completely Immiscible Liquids : When they are distilled, they distil in the ratio of their vapor pressure at that temperature. e.g. When A and B are distilled wt ratio $\frac{w_B}{w_A}$ is given as $\frac{w_B}{w_A} = \frac{P_B^\circ \cdot M_B}{P_A^\circ \cdot M_A}$

Completely Miscibile Liquids. They can be handled by Raoult's Law i.e.

$$\mathbf{y_i P = x_i P_i^o}$$

where P = Total pressure of vapors in equilibrium with the liquid solution,
P_i^o = vapor pressure of component *i* in pure state
y_i = mole fraction of ith component *in vapor state,* x_i = mole fraction of ith component *in liquid state*
This most fundamental expression may be arranged in many useful forms. e.g. for binary solutions :

$$\mathbf{P = x_1(P_1^0 - P_2^0) + P_2^0}$$

or

$$\mathbf{1/P = 1/P_2^0 + y_1(1/P_1^0 - 1/P_2^0)}$$

Note : Vapor pressure of an ideal solution is always between P_1^0 and P_2^0 (Curve1 in Fig. 1 and 2)

Bubble Point. When the first bubble of vapor appears in liquid solution.

Dew Point. When the first drop of liquid condenses from a mixture of vapors. OR when the last drop of liquid remains and rest of the liquid is completely vaporised.

Colligative Properties. The properties which depend only on the number of moles of solute (and not on their molecular weights or sizes) are referred to as colligative properties.
e.g. Lowring of vapor pressure, depression of freezing point, elevation of boiling point, osmotic pressure etc.

1. **Relative lowering of vapour Pressure.** $\frac{P^0 - P}{P^0} = \frac{n}{n+N} = \frac{w/m}{w/m + W/M} = x_{solute}$

2. **Elevation in Boiling Point, ΔT_b.** For dilute solutions, $\mathbf{\Delta T_b = K_b m}$
where *m* is molality of the solution (i.e. total number of moles of all the solute particles per kg of solvent).
K_b is ebullioscopic or boiling point elevation constant which is given by

$$K_b = \frac{R(T_b^0)^2 M_{solvent}}{1000\Delta H_{vap}}$$

ΔH_{vap} is the enthalpy of vaporisation of solvent.

3. **Depression in freezing Point (ΔT_f).** For dilute solutions, $\mathbf{\Delta T_f = K_f m}$

where, $$K_f = \frac{R(T_f^0)^2 M_{solvent}}{1000\Delta H_{fusion}}$$

Osmosis. Spontaneous flow of solvent molecules through a semipermeable membrane from a pure solvent to the solution (or from a dilute solution to a concentrated solution) is termed as osmosis.

Reverse Osmosis. If a pressure greater than the osmotic pressure is applied on the concentrated solution, the solvent starts to flow from concentrated solution to dilute solution (or pure solvent). This is reverse osmosis.One of its chief uses is desalination of sea water to get pure drinking water.

4. **Osmotic Pressure (π).** The hydrostatic pressure built up on the solution which just stops osmosis. Alternately, it may be defined as the pressure which must be applied to the concentrated solution in order to stop osmosis.

For dilute solutions $\mathbf{\pi = cRT = h\rho g}$

where *c* is the total molar concentration of all the free species present in the solution, h is the height developed by the column of the concentrated solution and $\boldsymbol{\rho}$ is the density of the solution in the column. On the basis of osmotic pressure, the solutions can be classified in three classes.

Isotonic solutions. Two solutions having same osmotic pressures at same temperature. (This implies $c_1 = c_2$).

Hypertonic solution. When two solutions are being compared, then the solution with higher osmotic pressure is termed as hypertonic. The solution with lower osmotic pressure is termed as **hypotonic.**

Important. Osmotic pressures can be determined quite accurately, hence it is used in the determination of molecular weights of large proteins and similar substances.

Van't Hoff Factor (i)

Since colligative properties depends upon the number of particles of the solute, in some cases where the solute associates or dissociates in solution, abnormal results for molecules masses are obtained.

$$i = \frac{Observed\ colligative\ property(actual)}{Theoretical\ colligative\ property}$$

THE ATLAS

Liquid Solutions

1. Vapour Pressure

2. Raoult's law

(i) When volatile solute is added
(a) When solute and solvent; both are miscible
(b) When both are immiscible

(ii) When non-volatile solute is added.

3. Condensation of vapours of solution

4. Ideal and non-ideal solutions

5. Azeotropic mixtures

Colligative properties (C.P.)

1. Introduction

2. The various C.P.

(i) Lowering of V.P.

(a) Determination of molar masses

(b) It's measurement

(ii) Boiling point elevation

(iii) Depression in freezing point

(iv) Osmotic pressure

(a) Osmosis
(b) Reverse osmosis
(c) Isotonic solution

3.Van't Haff factor; Where the solute associates or dissociates in solution.

EXERCISE I

Raoult's law

Q.1 At 25°C, the vapour pressure of methyl alcohol is 96.0 torr. What is the mole fraction of CH_3OH in a solution in which the (partial) vapor pressure of CH_3OH is 23.0 torr at 25°C?

Q.2 The vapour pressure of pure liquid solvent A is 0.80 atm. When a nonvolatile substance B is added to the solvent its vapour pressure drops to 0.60 atm. What is the mole fraction of component B in the solution?

Q.3 The vapour pressure of pure water at 26°C is 25.21 torr. What is the vapour pressure of a solution which contains 20.0 glucose, $C_6H_{12}O_6$, in 70 g water?

Q.4 The vapour pressure of pure water at 25°C is 23.76 torr. The vapour pressure of a solution containing 5.40 g of a nonvolatile substance in 90.0 g water is 23.32 torr. Compute the molecular weight of the solute.

Raoult's law in combinaton with Dalton's law of P.P. and V.P. lowering

Q.5 The vapour pressure of ethanol and methanol are 44.5 mm and 88.7 mm Hg respectively. An ideal solution is prepared at the same temperature by mixing 60 g of ethanol with 40 g of methanol. Calculate total vapour pressure of the solution.

Q.6 Calculate the mole fraction of toluene in the vapour phase which is in equilibrium with a solution of benzene and toluene having a mole fraction of toluene 0.50. The vapour pressure of pure benzene is 119 torr; that of toluene is 37 torr at the same temperature.

Q.7 What is the composition of the vapour which is in equilibrium at 30°C with a benzene-toluene solution with a mole fraction of benzene of 0.40? With a mole fraction of benzene of 0.60?

$P_b^\circ = 119$ torr and $P_t^\circ = 37$ torr

Q.8 At 90°C, the vapour pressure of toluene is 400 torr and that of σ-xylene is 150 torr. What is the composition of the liquid mixture that boils at 90°C, when the pressure is 0.50 atm? What is the composition of vapour produced?

Q.9 Two liquids A and B form an ideal solution at temperature T. When the total vapour pressure above the solution is 400 torr, the mole fraction of A in the vapour phase is 0.40 and in the liquid phase 0.75. What are the vapour pressure of pure A and pure B at temperature T?

Q.10 Calculate the relative lowering in vapour pressure if 100 g of a nonvolatile solute (mol.wt.100) are dissolved in 432 g water.

Q.11 What weight of the non–volatile solute, urea needs to be dissolved in 100 g of water, in order to decrease the vapour pressure of water by 25%? What will be the molality of the solution?

Q.12 The vapour pressure of an aqueous solution of glucose is 750 mm Hg at 373 K. Calculate molality and mole fraction of solute.

Q.13 The vapour pressure of pure benzene at 25° C is 639.7 mm of Hg and the vapour pressure of a solution of a solute in C_6H_6 at the same temperature is 631.7 mm of Hg. Calculate molality of solution.

Q.14 The vapour pressure of pure benzene at a certain temperature is 640 mm of Hg. A nonvolatile nonelectrolyte solid weighing 2.175 g is added to 39.0 of benzene. The vapour pressure of the solution is 600 mm of Hg. What is molecular weight of solid substance?

Q.15 The vapour pressure of water is 17.54 mm Hg at 293 K. Calculate vapour pressure of 0.5 molal solution of a solute in it.

Q.16 Benzene and toluene form two ideal solution A and B at 313 K. Solution A (total pressure P_A) contains equal mole of toluene and benzene. Solution B contains equal masses of both (total pressure P_B). The vapour pressure of benzene and toluene are 160 and 60 mm Hg respectively at 313 K. Calculate the value of P_A/P_B.

Boiling point elevation and freezing point depression

Q.17 When 10.6 g of a nonvolatile substance is dissolved in 740 g of ether, its boiling point is raised 0.284°C. What is the molecular weight of the substance? Molal boiling point constant for ether is 2.11°C·kg/mol.

Q.18 A solution containing 3.24 of a nonvolatile nonelectrolyte and 200 g of water boils at 100.130°C at 1atm. What is the molecular weight of the solute? (K_b for water 0.513°C/m)

Q.19 The molecular weight of an organic compound is 58.0 g/mol. Compute the boiling point of a solution containing 24.0 g of the solute and 600 g of water, when the barometric pressure is such that pure water boils at 99.725°C.

Q.20 An aqueous solution of a nonvolatile solute boils at 100.17°C. At what temperature will this solution freeze? [K_f for water 1.86°C/m]

Q.21 Pure benzene freeze at 5.45°C. A solution containing 7.24 g of $C_2H_2Cl_4$ in 115.3 g of benzene was observed to freeze at 3.55°C. What is the molal freezing point constant of benzene?

Q.22 A solution containing 6.35 g of a nonelectrolyte dissolved in 500 g of water freezes at – 0.465°C. Determine the molecular weight of the solute.

Q.23 The freezing point of a solution containing 2.40 g of a compound in 60.0 g of benzene is 0.10°C lower than that of pure benzene. What is the molecular weight of the compound? (K_f is 5.12°C/m for benzene)

Q.24 The elements X and Y form compounds having molecular formula XY_2 and XY_4. When dissolved in 20 gm of benzene, 1 gm XY_2 lowers the freezing point by 2.3°, whereas 1 gm of XY_4 lowers the freezing point by 1.3°C. The molal depression constant for benzene is 5.1. Calculate the atomic masses of X and Y.

Q.25 Calculate the molal elevation constant, K_b for water and the boiling of 0.1 molal urea solution. Latent heat of vaporisation of water is 9.72 kcal mol^{-1} at 373.15 K.

Q.26 Calculate the amount of ice that will separate out of cooling a solution containing 50g of ethylene glycol in 200 g water to –9.3°C. (K_f for water = 1.86 K mol^{-1} kg)

Q.27 A solution of 0.643 g of an organic compound in 50ml of benzene (density ; 0.879 g/ml) lowers its freezing point from 5.51°C to 5.03°C. If K_f for benzene is 5.12 K, calculate the molecular weight of the compound.

Q.28 The cryoscopic constant for acetic acid is 3.6 K kg/mol. A solution of 1 g of a hydrocarbon in 100 g of acetic acid freezes at 16.14°C instead of the usual 16.60°C. The hydrocarbon contains 92.3% carbon. What is the molecular formula?

Osmotic pressure

Q.29 Find the freezing point of a glucose solution whose osmotic pressure at 25°C is found to be 30 atm. K_f(water) = 1.86kg.mol^{-1}.K.

Q.30 At 300 K, two solutions of glucose in water of concentration 0.01 M and 0.001 M are separated by semipermeable membrane. Pressure needs to be applied on which solution, to prevent osmosis? Calculate the magnitude of this applied pressure.

Q.31 At 10°C, the osmotic pressure of urea solution is 500 mm. The solution is diluted and the temperature is raised to 25°C, when the osmotic pressure is found to be105.3 mm. Determine extent of dilution.

Q.32 The osmotic pressure of blood is 7.65 atm at 37°C. How much glucose should be used per L for an intravenous injection that is to have the same osmotic pressure as blood?

Q.33 What would be the osmotic pressure at 17°C of an aqueous solution containing 1.75 g of sucrose ($C_{12}H_{22}O_{11}$) per 150 cm^3 of solution?

Q.34 A 250 mL water solution containing 48.0 g of sucrose, $C_{12}H_{22}O_{11}$, at 300 K is separated from pure water by means of a semipermeable membrane. What pressure must be applied above the solution in order to just prevent osmosis?

Q.35 A solution of crab hemocyanin, a pigmented protein extracted from crabs, was prepared by dissolving 0.750 g in 125 cm^3 of an aqueous medium. At 4°C an osmotic pressure rise of 2.6 mm of the solution was observed. The solution had a density of 1.00 g/cm^3. Determine the molecular weight of the protein.

Q.36 The osmotic pressure of a solution of a synthetic polyisobutylene in benzene was determined at 25°C. A sample containing 0.20 g of solute/100 cm^3 of solution developed a rise of 2.4 mm at osmotic equilibrium. The density of the solution was 0.88 g/cm^3. What is the molecular weight of the polyisobutylene?

Q.37 A 5% solution (w/v) of cane-sugar (Mol. weight = 342) is isotonic with 0.877%(w/v) of urea solution. Find molecular weight of urea.

Q.38 10 gm of solute A and 20 gm of solute B are both dissolved in 500 ml water. The solution has the same osmotic pressure as 6.67 gm of A and 30 gm of B dissolved in the same amount of water at the same temperature. What is the ratio of molar masses of A and B?

Van't Hoff factor & colligative properties

Q.39 A storage battery contains a solution of H_2SO_4 38% by weight. What will be the Van't Hoff factor if the $\Delta T_{f(experiment)}$ in 29.08. [Given K_f = 1.86 mol^{-1} Kg]

Q.40 A certain mass of a substance, when dissolved in 100 g C_6H_6, lowers the freezing point by 1.28°C. The same mass of solute dissolved in 100g water lowers the freezing point by 1.40°C. If the substance has normal molecular weight in benzene and is completely ionized in water, into how many ions does it dissociate in water? K_f for H_2O and C_6H_6 are 1.86 and 5.12K kg mol^{-1}.

Q.41 2.0 g of benzoic acid dissolved in 25.0g of benzene shows a depression in freezing point equal to 1.62K. Molal depression constant (K_f) of benzene is 4.9 K.kg.mol^{-1}. What is the percentage association of the acid?

Q.42 A decimolar solution of potassium ferrocyanide is 50% dissociated at 300K. Calculate the osmotic pressure of the solution. (R=8.314 JK^{-1} mol^{-1})

Q.43 The freezing point of a solution containing 0.2 g of acetic acid in 20.0g of benzene is lowered by 0.45°C. Calculate the degree of association of acetic acid in benzene. (K_f for benzene = 5.12 K mol^{-1} kg)

Q.44 0.85 % aqueous solution of $NaNO_3$ is apparently 90% dissociated at 27°C. Calculate its osmotic pressure. (R= 0.082 *l* atm K^{-1} mol^{-1})

Q.45 A 1.2% solution (w/v) of NaCl is isotonic with 7.2% solution (w/v) of glucose. Calculate degree of ionization and Van't Hoff factor of NaCl.

PROFICIENCY TEST

Q.1 ***Fill in the blanks with appropriate items :***

1. Lowering of vapour pressure is _____ to the mole fraction of the solute.
2. The ratio of the value of any colligative property for NaCl solution to that of equimolal solution of sugar is nearly_____.
3. Semipermeable membrane allows the passage of _____through it.
4. A binary solution which has same composition in liquid as well as vapour phase is called_____.
5. The molal elevation constant of solvent is also called _____.
6. The 0.1 M aqueous solution of acetic acid has boiling point _____ than that of 0.1 M aqueous solution of KCl.
7. For ideal solutions, the plot of total vapour pressure v/s composition is _____.
8. A solution of $CHCl_3$ and acetone shows_____deviation.
9. Gases which react with water are generally _____ soluble in it.
10. Assuming complete dissociation, Van't Hoff's factor for Na_2SO_4 is equal to _____.
11. The osmotic pressure of a solution _____ with increase in temperature.
12. Water will boil at 101.5°C at pressure of _____76 cm of Hg.
13. Vant's Hoff's factor 'i' for dimerisation of CH_3COOH in benzene is_____.
14. $\pi = \frac{n_B}{V} RT$ is known as_____.
15. The molal elevation constant is the ratio of the elevation in boiling point to _____.

Q.2 ***True or False Statements :***

16. Relative lowering of vapour pressure is a colligative property.
17. Lowering of vapour pressure of a solution is equal to the mole fraction of the non-volatile solute present in it.
18. The components of an azeotropic solution can be separated by simple distillation.
19. Vapour pressure of a liquid depends on the size of the vessel.
20. Addition of non-volatile solute to water always lowers it vapour pressure.
21. Reverse osmosis is generally used to make saline water fit for domestic use.
22. A 6% solution of NaCl should be isotonic with 6% solution of sucrose.
23. A real solution obeys Raoult's law.
24. Boiling point is a characteristic temperature at which vapour pressure of the liquid becomes higher than the atmospheric pressure.
25. Molal depression constant is independent of the nature of solute as well as that of solvent.
26. The real solutions can exhibit ideal behaviour at high concentrations.
27. The osmotic pressure decreases on addition of solvent to the solution.
28. For urea the value of Vant's Hoff's factor 'i' is equal to 1.
29. The unit of k_b is kg K^{-1} mol^{-1}.
30. 0.1 M solution of urea would be hypotonic with 0.1 M solution of NaCl.

EXERCISE II

Q.1 An aqueous solution containing 288 gm of a non-volatile compound having the stoichiometric composition $C_xH_{2x}O_x$ in 90 gm water boils at 101.24°C at 1.00 atmospheric pressure. What is the molecular formula?

$K_b(H_2O) = 0.512$ K mol^{-1} kg

$T_b(H_2O) = 100°C$

Q.2 The degree of dissociation of $Ca(NO_3)_2$ in a dilute aqueous solution containing 7 gm of the salt per 100 gm of water at 100°C is 70%. If the vapour pressure of water at 100°C is 760 mm. Calculate the vapour pressure of the solution.

Q.3 The addition of 3 gm of substance to 100 gm CCl_4(M = 154 gm mol^{-1}) raises the boiling point of CCl_4 by 0.60°C of K_b (CCl_4) is 5.03 kg mol^{-1} K. Calculate

(a) the freezing point depression

(b) the relative lowering of vapour pressure

(c) the osmotic pressure at 298 K

(d) the molar mass of the substance

Given $K_f(CCl_4) = 31.8$ kg mol^{-1}K and ρ (density) of solution = 1.64 gm/cm^3

Q.4 A 10% solution of cane sugar has undergone partial inversion according to the reaction:
Sucrose + Water ⟶ Glucose + Fructose. If the boiling point of solution is 100.27°C.

(a) What is the average mass of the dissolved materials?

(b) What fraction of the sugar has inverted? $K_b(H_2O) = 0.512$ K mol^{-1} kg

Q.5 If 20 ml of ethanol (density = 0.7893 gm/ml) is mixed with 40 ml water (density = 0.9971 gms) at 25°C, the final solution has density of 0.9571 gm/ml. Calculate the percentage change in total volume of mixing. Also calculate the molality of alcohol in the final solution.

Q.6 Mixture of two liquids A and B is placed in cylinder containing piston. Piston is pulled out isothermally so that volume of liquid decreases but that of vapour increases. When negligibly small amount of liquid was remaining, the mole fraction of A in vapour is 0.4. Given P_A° =0.4 atm and P_B° = 1.2 atm at the experimental temperature. Calculate the total pressure at which the liquid has almost evaporated. (Assume ideal behaviour).

Q.7 1.5 g of a monobasic acid when dissolved in 150g of water lowers the freezing point by 0.165°C. 0.5 g of the same acid when titrated, after dissolution in water, requires 37.5 ml of N/10 alkali. Calculate the degree of dissociation of the acid (K_f for water = 1.86°C mol^{-1}).

Q.8 Sea water is found to contain 5.85% NaCl and 9.50% $MgCl_2$ by weight of solution. Calculate its normal boiling point assuming 80% ionisation for NaCl and 50% ionisation of $MgCl_2$ [$K_b(H_2O) = 0.51$kgmol^{-1}K].

Q.9 The latent heat of fusion of ice is 80 calories per gram at 0°C. What is the freezing point of a solution of KCl in water containing 7.45 grams of solute in 500 grams of water, assuming that the salt is dissociated to the extent of 95%?

Q.10 A complex is represented as $CoCl_3 \cdot x\,NH_3$. It's 0.1 molal solution in aq. solution shows $\Delta T_f = 0.558°C$. K_f for H_2O is 1.86 K mol^{-1}kg . Assuming 100% ionisation of complex and coordination no. of Co is six, calculate formula of complex.

Q.11 The molar volume of liquid benzene (density = 0.877 g ml^{-1}) increases by a factor of 2750 as it vaporizes at 20°C and that of liquid toluene (density = 0.867gml^{-1}) increases by a factor of 7720 at 20°C has a vapour pressure of 46.0 torr. Find the mole fraction of benzene in the vapour above the solution.

Q.12 At 100°C, benzene & toluene have vapour pressure of 1375 & 558 Torr respectively. Assuming these two form an ideal binary solution, calculate the composition of the solution that boils at 1 atm & 100°C. What is the composition of vapour issuing at these conditions?

Q.13 Calculate the boiling point of a solution containing 0.61g of benzoic acid in 50g of carbon disulphide assuming 84% dimerization of the acid. The boiling point and K_b of CS_2 are 46.2°C and 2.3 K kg mol^{-1}, respectively.

Q.14 At 25°C, 1 mol of A having a vapor pressure of 100torr and 1 mol of B having a vapor pressure of 300 torr were mixed. The vapor at equilibrium is removed, condensed and the condensate is heated back to 25°C. The vapors now formed are again removed, recondensed and analyzed. What is the mole fraction of A in this condensate?

Q.15 Phenol associates in benzene to a certain extent to form a dimer. A solution containing 20×10^{-3} kg phenol in 1 kg of benzene has its freezing point depressed by 0.69 K. Calculate the fraction of phenol that has dimerised. K_f for benzene = 5.12 kg mol^{-1}K.

Q.16 30 ml of CH_3OH (d = 0.7980 gm cm^{-3}) and 70 ml of H_2O (d=0.9984 gm cm^{-3}) are mixed at 25°C to form a solution of density 0.9575 gm cm^{-3}. Calculate the freezing point of the solution. $K_f(H_2O)$ is 1.86 kg mol^{-1} K. Also calculate its molarity.

Q.17 Dry air was drawn thorugh bulbs containing a solution of 40 grams of urea in 300 grams of water, then through bulbs containing pure water at the same temperature and finally through a tube in which pumice moistened with strong H_2SO_4 was kept. The water bulbs lost 0.0870 grams and the sulphuric acid tube gained 2.036 grams. Calculate the molecular weight of urea.

Q.18 Vapour pressure of C_6H_6 and C_7H_8 mixture at 50°C is given by **P (mm Hg) = 180 X_B + 90**, where X_B is the mole fraction of C_6H_6. A solution is prepared by mixing 936g benzene and 736g toluene and if the vapours over this solution are removed and condensed into liquid and again brought to the temperature of 50°C, what would be mole fraction of C_6H_6 in the vapour state?

Q.19 When the mixture of two immicible liquids (water and nitrobenzene) boils at 372 K and the vapour pressure at this temperature are 97.7 kPa (H_2O) and 3.6 kPa ($C_6H_5NO_2$). Calculate the weight % of nitrobenzene in the vapour.

Q.20 The vapour pressure of a certain liquid is given by the equation:

$\text{Log}_{10}P = 3.54595 - \dfrac{313.7}{T} + 1.40655 \log_{10} T$ where P is the vapour pressure in mm and T = Kelvin Temperature. Determine the molar latent heat of vaporisation as a function of temperature. Calculate the its value at 80 K.

Q.21 A very dilute saturated solution of a sparingly soluble salt A_3B_4 has a vapour pressure of 20 mm of Hg at temperature T, while pure water exerts a pressure of 20.0126 mm Hg at the same temperature. Calculate the solubility product constant of A_3B_4 at the same temperature.

Q.22 The molar volume of liquid benzene (density = 0.877g ml^{-1}) increases by a factor of 2750 as it vaporises at 20°C while in equilibrium with liquid benzene. At 27°C when a non-volatile solute (that does not dissociate) is dissolved in 54.6 cm^3 of benzene vapour pressure of this solution, is found to be 98.88 mm Hg.Calculate the freezing point of the solution.
Given *: Enthalpy of vaporization of benzene(l) = 394.57 J/gm*
Molal depression constant for benzene = 5.0 K kg. mol^{-1} .
Freezing point of benzene = 278.5 K.

Q.23 If the apparent degree of ionization of KCl (KCl = 74.5 gm mol^{-1}) in water at 290 K is 0.86. Calculate the mass of KCl which must be made up to 1 dm^3 of aqueous solution to the same osmotic pressure as the 4.0% solution of glucose at that temperature.

Q.24 An ideal solution was prepared by dissolving some amount of cane sugar (non–volatile) in 0.9 moles of water. The solution was then cooled just below its freezing temperature (271 K), where some ice get separated out. The remaining aqueous solution registered a vapour pressure of 700 torr at 373 K. Calculate the mass of ice separated out, if the molar heat of fusion of water is 6 kJ.

Q.25 The freezing point depression of a 0.109 M aq. solution of formic acid is –0.21°C. Calculate the equilibrium constant for the reaction,

$$HCOOH\ (aq) \rightleftharpoons H^+(aq) + HCOOH^-\ (aq)$$

K_f for water = 1.86 kg mol^{-1} K

Q.26 10 gm of NH_4Cl (mol. weight = 53.5) when dissolved in 1000 gm of water lowered the freezing point by 0.637°C. Calculate the degree of hydrolysis of the salt if its degree of dissociation of 0.75. The molal depression constant of water is 1.86 kg mol^{-1} K.

Q.27 The freezing point of 0.02 mol fraction solution of acetic acid (A) in benzene (B) is 277.4K. Acetic acid exists partly as a dimer $2A = A_2$. Calculate equilibrium constant for the dimerisation. Freezing point of benzene is 278.4 K and its heat of fusion ΔH_f is 10.042 kJ mol^{-1}.

Q.28 A saturated solution of a sparingly soluble salt, MCl_2 has a vapour pressure of 31.78 mm of Hg at 30°C, while pure water exerts a pressure of 31.82 mm of Hg at the same temperature. Calculate the solubility product of the compound at this temperature.

Q.29 The vapour pressure of two pure liquids, A and B that form an ideal solution are 300 and 800 torr respectively, at temperature T. A mixture of the vapour of A and B for which the mole fraction of A is 0.25 is slowly compressed at temperature T. Calculate
(a) the composition of the first drop of the condensate,
(b) the total pressure when this drop is formed,
(c) the composition of the solution whose normal boiling point is T,
(d) the pressure when only the last bubble of vapour remains, and
(e) the composition of the last bubble.

Q.30 Tritium, T (an isotope of H) combines with fluorine to form weak acid TF, which ionizes to give T^+. Tritium is radioactive and is a β–emitter. A freshly prepared aqueous solution of TF has pT (equivalent of pH) of 1.5 and freezes at –0.372°C. If 600ml of freshly prepared solution were allowed to stand for 24.8 years. Calculate (i) ionization constant of TF. (ii) Number of β–particles emitted.
(Given K_f for water = 1.86 kg mol K^{-1}, $t_{1/2}$ for tritium = 12.4 years)

EXERCISE III

Q.1 For an ideal binary liquid solution with $P_A^\circ > P_B^\circ$, which relation between X_A (mole fraction of A in liquid phase) and Y_A (mole fraction of A in vapour phase) is correct?

(A) $Y_A < Y_B$ (B) $X_A > X_B$ (C) $\frac{Y_A}{Y_B} > \frac{X_A}{X_B}$ (D) $\frac{Y_A}{Y_B} < \frac{X_A}{X_B}$

Q.2 Mole fraction of A vapours above the solution in mixture of A and B ($X_A = 0.4$) will be
[Given : $P_A^\circ = 100$ mm Hg and $P_B^\circ = 200$ mm Hg]
(A) 0.4 (B) 0.8 (C) 0.25 (D) none of these

Q.3 The exact mathematical expression of Raoult's law is

(A) $\frac{P^0 - P_s}{P^0} = \frac{n}{N}$ (B) $\frac{P^0 - P_s}{P^0} = \frac{N}{n}$ (C) $\frac{P^0 - P_s}{P_s} = \frac{n}{N}$ (D) $\frac{P^0 - P_s}{P^0} = n \times N$

Q.4 A mixture contains 1 mole of volatile liquid A (P_A° =100 mm Hg) and 3 moles of volatille liquid B (P_B° = 80 mm Hg). If solution behaves ideally, the total vapour pressure of the distillate is
(A) 85 mm Hg (B) 85.88 mm Hg (C) 90 mm Hg (D) 92 mm Hg

Q.5 Which of the following aqueous solution will show maximum vapour pressure at 300 K?
(A) 1 M NaCl (B) 1 M $CaCl_2$ (C) 1 M $AlCl_3$ (D) 1 M $C_{12}H_{22}O_{11}$

Q.6 The Van't Hoff factor for a dilute aqueous solution of glucose is
(A) zero (B) 1.0 (C) 1.5 (D) 2.0

Q.7 The correct relationship between the boiling points of very dilute solution oif $AlCl_3$ (T_1K) and $CaCl_2$ (T_2K) having the same molar concentration is
(A) $T_1 = T_2$ (B) $T_1 > T_2$ (C) $T_2 > T_1$ (D) $T_2 \le T_1$

Q.8 A 0.001 molal solution of a complex $[MA_8]$ in water has the freezing point of –0.0054°C. Assuming 100% ionization of the complex salt and K_f for H_2O = 1.86 km^{-1}, write the correct representation for the complex
(A) $[MA_8]$ (B) $[MA_7]A$ (C) $[MA_6]A_2$ (D) $[MA_5]A_3$

Q.9 The vapour pressure of a solution of a non-volatile electrolyte B in a solvent A is 95% of the vapour pressure of the solvent at the same temperature. If the molecular weight of the solvent is 0.3 times the molecular weight of solute, the weight ratio of the solvent and solute are
(A) 0.15 (B) 5.7 (C) 0.2 (D) 4.0

Q.10 At a given temperature, total vapour pressure in Torr of a mixture of volatile components A and B is given by

$$P_{Total} = 120 - 75\ X_B$$

hence, vapour pressure of pure A and B respectively (in Torr) are
(A) 120, 75 (B) 120, 195 (C) 120, 45 (D) 75, 45

Q.11 Assuming each salt to be 90 % dissociated, which of the following will have highest boiling point?
(A) Decimolar $Al_2(SO_4)_3$
(B) Decimolar $BaCl_2$
(C) Decimolar Na_2SO_4
(D) A solution obtained by mixing equal volumes of (B) and (C)

Q.12 The vapour pressure of a solvent decreased by 10 mm of Hg when a non-volatile solute was added to the solvent. The mole fraction of solute in solution is 0.2, what would be mole fraction of the solvent if decrease in vapour pressure is 20 mm of Hg
(A) 0.2 (B) 0.4 (C) 0.6 (D) 0.8

Q.13 Elevation of boiling point of 1 molar aqueous glucose solution (density = 1.2 g/ml) is
(A) K_b (B) 1.20 K_b (C) 1.02 K_b (D) 0.98 K_b

Q.14 What will be the molecular weight of $CaCl_2$ determined in its aq. solution experimentally from depression of freezing point?
(A) 111 (B) < 111 (C) > 111 (D) data insufficient

Q.15 1.0 molal aqueous solution of an electrolyte A_2B_3 is 60% ionised. The boiling point of the solution at 1 atm is ($K_{b(H_2O)} = 0.52$ K kg mol^{-1})
(A) 274.76 K (B) 377 K (C) 376.4 K (D) 374.76 K

Q.16 Which of the following plots represents an ideal binary mixture?
(A) Plot of P_{total} v/s $1/X_B$ is linear (X_B = mole fraction of 'B' in liquid phase).
(B) Plot of P_{total} v/s Y_A is linear (Y_B = mole fraction of 'A' in vapour phase)
(C) Plot of $\frac{1}{P_{total}}$ v/s Y_A is linear
(D) Plot of $\frac{1}{P_{total}}$ v/s Y_B is non linear

Q.17 Pressure over ideal binary liquid mixture containing 10 moles each of liquid A and B is gradually decreased isothermally. If P_A^o =200 mm Hg and P_B^o =100 mm Hg, find the pressure at which half of the liquid is converted into vapour.
(A) 150 mm Hg (B) 166.5 mm Hg (C) 133 mm Hg (D) 141.4 mm Hg

Q.18 The lowering of vapour pressure in a saturated aq. solution of salt AB is found to be 0.108 torr. If vapour pressure of pure solvent at the same temperature is 300 torr. Find the solubility product of salt AB
(A) 10^{-8} (B) 10^{-6} (C) 10^{-4} (D) 10^{-5}

Q.19 Which of the following represents correctly the changes in thermodynamic properties during the formation of 1 mol of an ideal binary solution.

(A)

(B)

(C)

(D)

Q.20 $FeCl_3$ on reaction with $K_4[Fe(CN)_6]$ in aqueous solution gives blue colour. These are separated by a semipermeable membrane AB as shown. Due to osmosis there is

(A) blue colour formation in side X.
(B) blue colour formation in side Y.
(C) blue colour formation in both of the sides X and Y.
(D) no blue colour formation.

EXERCISE IV

OBJECTIVE

Q.1 The van't Hoff factor for 0.1 M $Ba(NO_3)_2$ solution is 2.74. The degree of dissociation is
(A) 91.3% (B) 87% (C) 100% (D) 74% **[JEE 1999]**

Q.2 In the depression of freezing point experiment, it is found that
(I) The vapour pressure of the solution is less than that of pure solvent.
(II) The vapour pressure of the solution is more than that of pure solvent.
(III) Only solute molecules solidify at the freezing point.
(IV) Only solvent molecules solidify at the freezing point.
(A) I, II (B) II, III (C) I, IV (D) I, II, III **[JEE 1999]**

Q.3 During depression of freezing point in a solution, the following are in equilibrium
(A) liquid solvent-solid solvent (B) liquid solvent-solid solute
(C) liquid solute-solid solute (D) liquid solute-solid solvent **[JEE 2003]**

Q.4 A 0.004 M solution of Na_2SO_4 is isotonic with a 0.010 M solution of glucose at same temperature. The apparent degree of dissociation of Na_2SO_4 is
(A) 25% (B) 50% (C) 75% (D) 85% **[JEE 2004]**

Q.5 The elevation in boiling point, when 13.44 g of freshly prepared $CuCl_2$ are added to one kilogram of water, is [Some useful data, K_b (H_2O) = 0.52 kg K mol^{-1}, mol. wt. of $CuCl_2$ = 134.4 gm]
(A) 0.05 (B) 0.1 (C) 0.16 (D) 0.21 **[JEE 2005]**

SUBJECTIVE

Q.6 A very small amount of a nonvolatile solute (that does not dissociate) is dissolved in 56.8 cm^3 of benzene (density 0.889 g cm^{-3}), At room temperature, vapour pressure of this solution is 98.88 mm Hg while that of benzene is 100 mm Hg. Find the molality of this solution. If the freezing temperature of this solution is 0.73 degree lower than that of benzene. What is the value of molal freezing point depression constant of benzene? **[JEE 1997]**

Q.7 A solution of a nonvolatile solute in water freezes at –0.30°C. The vapor pressure of pure water at 298K is 23.51mmHg and K_f for water is 1.86 degree/molal. Calculate the vapor pressure of this solution at 298K. **[JEE 1998]**

Q.8 To 500 cm^3 of water, 3×10^{-3} kg of acetic acid is added. If 23% of acetic acid is dissociated, what will be the depression in freezing point ? K_f and density of water are 1.86 K kg^{-1} mol^{-1} and 0.997 g cm^{-3} respectively. **[JEE 2000]**

Q.9 The vapour pressure of two miscible liquids (A) and (B) are 300 and 500 mm of Hg respectively. In a flask 10 mole of (A) is mixed with 12 mole of (B). However, as soon as (B) is added, (A) starts polymerising into a completely insoluble solid. The polymerisation follows first-order kinetics. After 100 minute, 0.525 mole of a solute is dissolved which arrests the polymerisation completely. The final vapour pressure of the solution is 400 mm of Hg. Estimate the rate constant of the polymerisation reaction. Assume negligible volume change on mixing and polymerisation and ideal behaviour for the final solution. **[JEE 2001]**

Q.10 Match the boiling point with K_b for x, y and z, if molecular weight of x, y and z are same. **[JEE 2003]**

	b.pt.	K_b
x	100	0.68
y	27	0.53
z	253	0.98

Q.11 1.22 g of benzoic acid is dissolved in (i) 100 g acetone (K_b for acetone = 1.7) and (ii)100 g benzene (K_b for benzene = 2.6). The elevation in boiling points T_b is 0.17°C and 0.13°C respectively.

(a) What are the molecular weights of benzoic acid in both the solutions?

(b) What do you deduce out of it in terms of structure of benzoic acid? **[JEE 2004]**

Q.12 72.5 g of phenol is dissolved in 1 kg of a solvent (k_f = 14) which leads to dimerization of phenol and freezing point is lowered by 7 kelvin. What percent of total phenol is present in dimeric form? **[JEE 2006]**

ANSWER

EXERCISE I

Q.1	0.24	Q.2	0.25	Q.3	24.5 torr	Q.4	57.24 g/mol
Q.5	66.13 mm Hg	Q.6	0.237	Q.7	0.682, 0.318; 0.829, 0.171		
Q.8	92 mol% toluene; 96.8 mol % toluene			Q.9	$P_A^\circ = 213.33$ torr, $P_B^\circ = 960.0$ torr		
Q.10	0.04	Q.11	111.1g, 18.52 molal			Q.12	0.741 m, 0.013
Q.13	0.162 m	Q.14	65.25	Q.15	17.38	Q.16	0.964
Q.17	106 g/mol	Q.18	64.0 g/mol	Q.19	100.079°C	Q.20	– 0.62°C
Q.21	5.08°C/m	Q.22	50.8 g/mol	Q.23	2050 g/mol	Q.24	x = 25.6, y = 42.6
Q.25	$K_b = 0.512$ kg mol K^{-1}, $T_b = 373.20$ K			Q.26	38.71 g	Q.27	156.06
Q.28	C_6H_6	Q.29	$T_f = -2.28°C$	Q.30	P = 0.2217 atm should be applied		
Q.31	($V_{final} = 5.V_{original}$)	Q.32	54.2 g	Q.33	0.81 atm	Q.34	13.8 atm
Q.35	5.4×10^5 g/mol	Q.36	2.4×10^5 g/mol			Q.37	59.99
Q.38	$M_A/M_B = 0.33$	Q.39	i = 2.5	Q.40	3 ions	Q.41	$\alpha = 99.2\%$
Q.42	7.482×10^5 Nm^{-2}	Q.43	94.5 %	Q.44	4.64 atm	Q.45	0.95; 1.95

PROFICIENCY TEST

1. proportional	2. 2 : 1	3. solvent molecules	4. azeotropic mixture
5. Ebullioscopic constant	6. lesser	7. straight line with slope $\neq 0$	
8. negative	9. more	10. 3	11. increases
12. greater than	13. less than 1		
14. Van't Hoff's solution equation		15. molality	16. T

17.	F	18.	F	19.	F	20.	T
21.	T	22.	F	23.	F	24.	F
25.	F	26.	F	27.	T	28.	T
29.	F	30.	T				

EXERCISE II

Q.1 $C_{44}H_{88}O_{44}$ Q.2 746.24 mm/Hg

Q.3 (a) 3.79°C, (b) 0.018, (c) 4.65 atm, (d) 251.5 Q.4 (a) 210, (b) 64.1%

Q.5 % change in volume = 3.05, 8.604 m Q.6 0.66 atm Q.7 18.34%

Q.8 $T_b = 102.3^oC$ Q.9 $T_f = -0.73^oC$ Q.10 $[Co(NH_3)_5Cl]Cl_2$ Q.11 0.73

Q.12 $x_b = 0.2472$, $Y_b = 0.4473$ Q.13 46.33°C Q.14 $x_a'' = 0.1$

Q.15 $\alpha = 0.7333$ Q.16 –19.91°C, 7.63 M Q.17 M = 53.8

Q.18 0.93 Q.19 20.11 %

Q.20 ΔH_v at 80 K is 1659.1 calorie; $\Delta H_v = R\ [2.303 \times 313.7 + 1.40655T$

Q.21 5.4×10^{-13} Q.22 $T_f = 277.5$ K Q.23 8.9 gm

Q.24 12.54 Q.25 $K_a = 1.46\times10^{-4}$` Q.26 h = 0.082 Q.27 K = 3.36

Q.28 $4.9 \times 10^{-5}\ M^3$

Q.29 (a)0.47, (b) 565 torr, (c) x_A=0.08, x_B= 0.92, (d) 675 torr, (e) x'_A= 0.11, x'_B= 0.89

Q.30 (i) $K_a = 7.3 \times 10^{-3}$ (ii) 4.55×10^{22}

EXERCISE III

Q.1	C	Q.2	C	Q.3	C	Q.4	B	Q.5	D	Q.6	B	Q.7	B
Q.8	C	Q.9	B	Q.10	C	Q.11	A	Q.12	C	Q.13	D	Q.14	B
Q.15	D	Q.16	C	Q.17	D	Q.18	C	Q.19	C	Q.20	D		

EXERCISE IV

Q.1 B Q.2 C Q.3 A Q.4 C

Q.5 C Q.6 0.1452, 5.028 K m^{-1}

Q.7 23.44 mm Hg Q.8 0.229 Q.9 1.0×10^{-4}

Q.10 $K_b(x) = 0.68$, $K_b(y) = 0.53$, $K_b(z) = 0.98$

Q.11 (a)122, (b) It means that benzoic acid remains as it is in acetone while it dimerises in benzene as

Q.12 35% phenol is present in dimeric form

STUDY PACKAGE

Target: IIT-JEE (Advanced)

SUBJECT: CHEMISTRY-XII

TOPIC: 15. Surface Chemistry

Index:

1. Key Concepts

2. Exercise I

3. Exercise II

4. Exercise III

5. Exercise IV

6. Answer Key

7. 34 Yrs. Que. from IIT-JEE

8. 10 Yrs. Que. from AIEEE

SURFACE CHEMISTRY

PHASE OF COLLOIDS :

A colloidal system is heterogeneous in character. It consists of two phases, namely a dispersed phase and a dispersion medium.

(a) ***Dispersed Phase :*** It is the component present in small proportion and is just like a solute in a true solution. For example, in the colloidal state of sulphur in water, the formeracts as a dispersed phase.

(b) ***Dispersion Medium :*** It is normally the component present in excess and is just like a solvent in a solution.

The particles of the dispersed phase are scattered in the dispersion medium in a colloidal system.

CLASSIFICATION OF COLLOIDS :

Colloids can be can be classified in a number of ways based upon some of their important characteristics.

(1) ***Physical state of Dispersed Phase & Dispersion Medium:***

Depending upon whether the dispersed phase and the dispersion medium are solids, liquids or gaseous, eight types of colloidal system are possible. A gas mixed with another gas forms a homogeneous mixture and not a colloidal system. Typical examples of various type alongwith their characteristic names are given in table.

Common Colloidal System

Dispersed Phase	*Dispersion medium*	*Colloidal system*	*Examples*
Gas	Liquid	Foam or froth	Soap sols, lemonade froth, whipped cream.
Gas	Solid	Solid foam	Pumice stone, styrene, foam, foam rubber.
Liquid	Gas	Aerosols of Liquids	Fog, clouds, fine insecticide sprays.
Liquid	Liquid	Emulsions	Milk
Liquid	Solid	Gels	Cheese, butter, boot polish, table jellies.
Solid	Gas	Aerosols of Solid	Smoke, dust
Solid	Liquid	Sols	Must paint, starch dispersed in water, gold sol, muddy water, inks.
Solid	Solid	Solid sols	Ruby glass, some gem stones.

* A colloidal system in which the dispersion medium is a liquid or gas are called sols. They are called hydrosols or aqua sols, if the dispersion medium is water. When the dispersion medium is alcohol or benzene , they are accordingly called alcosols or benzosol.
* Colloidal systems in which the dispersion medium is a gas are called aerosols.
* Colloids in which the dispersion medium is a solid are called gels, e.g. cheese etc. They have a more rigid structure. Some colloids, such as gelatin, can behave both as a sol and a gel. At high temperature and low concentration of gelatin, the colloid is a hydrosol. But at low temperature and high gelatin concentration, the hydrosol can change into a gel.

(2) ***Based on interaction or affinity of phases :*** On the basis of the affinity or interaction between the dispersed phase and the dispersion medium, the colloids may be classified into two types :

(i) ***Lyophilic Colloids :*** The colloidal system in which the particle of dispersed phase have great affinity for the dispersion medium, are called lyophilic (solvent-loving) colloids. In such colloids, the dispersed phase does not get easily precipitated and the sols are more stable. Such colloidal systems, even if precipitated, may be reconverted to the colloidal state by simply agitating them with the dispersion medium. Hence lyophilic colloids are reversible. When the dispersion medium is water, these are called hydrophilic colloids. Some common examples of lyophilic colloids are gum, gelatin, starch, rubber, proteins, etc.

(ii) ***Lyophobic colloids :*** The colloidal system in which the dispersed phase have no affinity for the dispersion medium are called lyophobic (solvent hating) colloids. They are easily precipitated (or coagulated) on the addition of small amounts of the electrolyte, by heating or by shaking. They are less stable and irreversible. When the dispersion medium is water, these are known as hydrophobic colloids. Examples of lyophobic colloids include sols of metals and their insoluble compounds like sulphides and oxides.

The essential differences between the lyophilic and lyophobic colloids are summarised in table.

Difference between Lyophilic and Lyophobic sols

Property	***Lyophilic sols***	***Lyophobic sols***
1. Nature	Reversible	Irreversible
2. Preparation	They are prepared very easily by shaking or warming the substance with dispersion medium. They do not required any electrolyte for stabilization.	They are difficult to prepare, Special methods are used. Addition of stabiliser is essential for their stability.
3. Stability	They are very stable and are not easily coagulated by electrolytes.	They are generally unstable and get easily coagulated on addition of electrolytes.
4. Charge	Particles carry no or very little charge depending upon the pH of the medium.	Colloidal particles have characteristic charge (positive or negative)
5. Viscosity	Viscosity is much higher than that of the medium.	Viscosity is nearly the same as that of the medium
6. Surface Tension	Surface tension is usually less than that of the medium.	Surface tension is nearly the same as that of the medium.
7. Migration in electric field	The particles may or may not migrate in an electric field.	The colloidal particles migrate either towards cathode or anode in an electric field.
8. Solvation	Particles are heavily solvated.	Particles are not solvated.
9. Visibility	The particles cannot be seen under ultra microscope.	The particles though invisible, can be seen under ultra microscope.
10. Tyndall effect	Less distinct.	More distinct.
11. Action of electrolyte	Large amount of electrolyte is required to cause coagulation.	Small amount of electrolyte is sufficient to cause cogulation.
12. Examples	Mostly organic substances e.g. starch, gums, proteins, gelatin etc.	Generally inorganic substance e.g., metal sols, sulphides and oxides sols.

* ***PROTECTIVE COLLOIDS :***

Lyophilic sols are more stable than the lyophobic sols. This is because, lyophilic colloids are extensively hydrated and these hydrated particles do not combine to form large aggregates.

Lyophobic sols are more easily coagulated by the addition of suitable electrolyte. To avoid the precipitation of lyohobic sol. by the addition of electrolyte, some lyophilic colloid is added to it. Such lyophilic colloid is called protective colloid and the action of lyophilic colloid by the electrolytes is known as protective anion. The substances commonly used as protective colloids are gelating, albumin, gum arabic, casein, starch, glue etc. A gold sol. containing a little gelatin as protective colloid needs a very large amount of sodium chloride to coagulate the sol.

Explanation : The particles of the protective colloid get adsorbed on the particles of the lyophobic colloid, thereby forming a protective layer around it (figure). The protective layer prevents the precipitating ions from coming in contact with the colloidal particles.

According to a recent view, the increase in stability of the lyophobic colloid is due to the mutual adsorption of the lyophilic and lyophobic colloids. It is immaterial which is adsorbed on which. In fact the smaller particles, whether of the protective colloid or the lyophobic colloid, are adsorbed on the bigger particles.

(3) ***Based on type of particles of the dispersed phase :*** Depending upon the molecular size, the colloidal system has been classified into three classes :

(i) ***Multimolecular colloids :*** The multimolecular colloidal particles consists of aggregate of atoms of small molecules with diameters less than 10^{-9} m or 1 nm.

For example, a sol. of gold contains particles of various sizes having several atoms. A sol. of sulphur consists of particles containing a thousand or so S_2 molecules. These particles are held together by vander Waal's forces. These are usually lyophobic sols.

(ii) ***Macromolecular colloids :*** The macromolecular colloidal particles themselves are large molecules. They have very high molecular weights varrying from thousands to millions. These substances are generally polymers. Naturally occurring macromolecules are such as starch, cellulose and proteins. Artificial macromolecules are such as polyethylene, nylon, polysyrene, dacron, synthetic rubber, plastics, etc. The size of these molecules are comparable to those of colloidal particles and therefore, their dispersion known as macromolecular colloids. Their dispersion also resemble true solutions in some respects.

(iii) ***The associated colloids or miscelles :*** These colloids behave as normal electrolytes at low concentrations but colloids at higher concentrations. This is because at higher concentrations, they form aggregated (associated) particles called miscelles. Soap and synthetic detergents are examples of associated colloids. They furnish ions which may have colloidal dimensions.

$$\underset{\text{Sod. Stearate soap}}{RCOONa} \rightleftharpoons \underset{(R = C_{17}H_{35})}{RCOO^- + Na^+}$$

The long-chain $RCOO^-$ ions associates or aggregate at higher concentrations and form miscelles and behave as colloids. They may contain 100 or more molecules.

Sodium stearate $C_{17}H_{35}COONa$ is an example of an associated colloid. In water it gives Na^+ and sterate, $C_{17}H_{35}COO^-$ ions. These ions associate to form miscelles of colloidal size.

Colloids which behave as normal electrolytes at low concentration, but exhibit colloidal properties at higher concentration due to the formation of aggregated particles called micelles are referred to as associated colloids. The micelles are formed by the association of dispersed particles above a certain concentration and certain minimum concentration is required for the process of aggregation to take place. The minimum concentration required for micelle formation is called micellisation concentration (CMC) and its value depends upon the nature of the dispersed phase. For soaps CMC is 10^{-3} mole L^{-1}.

Mechanism of Micelle Formation :

Micelles are formed by surface active molecules called surfactants such as soaps and detergents. These molecules have lyophilic group at one end and a lyphobic group at the other end. Let us take the example of a soap (say sodium oleate, $C_{17}H_{33}COO^{-}Na^{+}$). The long hydrocarbon part of oleate radical ($C_{17}H_{33}$–) is lyophobic end while COO^{-} part is lyophilic end. When the concentration of the solution is below its CMC, sodium oleate behaves as a normal electrolyte and ionises to give $C_{17}H_{33}COO^{-}$ and Na^{+} ions. When the concentration exceeds CMC, the lyophobic part starts receding away from the solvent and tends to approach each other. However, the polar COO^{-} ends tends to interact with the solvent (water). This finally leads to the formation of bigger molecules having the dimensions of colloidal particles. Thus 100 or more oleate ions are grouped together in a spherical way keeping their hydrocarbon parts inside and the –COO^{-} part remains projected in water.

PROPERTIES OF COLLOIDAL SOLUTIONS :

(1) ***Physical properties :***

(i) ***Heterogeneity :*** Colloidal solutions are heterogeneous in nature consisting of two phases viz, the dispersed phase and the dispersion medium. Experiments like dialysis and ultra filteration clearly indicate the heterogeneous character of colloidal system. Recent investigations however, shown that colloidal solutions are neither obviously homogeneous nor obviously heterogeneous.

(ii) ***Filterability :*** Colloidal particles readily pass through orginary filter papers. It is because the size of the pores of the filter paper is larger than that of the colloidal particles.

(iii) ***Non-settling nature :*** Colloidal solutions are quite stable as the colloidal particles remain suspended in the dispersion medium indefinitely. Thus there is no effect of gravity on the colloidal particles.

(iv) ***Colour :*** The colour of the colloidal solution is not always the same as the colour of the substances in the bulk. The colour of the colloidal solution depends upon the following factors :

(a) Size and shape of colloidal particles.
(b) Wavelength of the source of light.
(c) Method of preparation of the colloidal solution.
(d) Nature of the colloidal solution.
(e) The way an observer receives the light, i.e., whether by reflection or by transmission.
(f) ***Stability :*** Colloidal solutions are quite stable. Only a few solutions of larger particles may settle but very slowly.

Examples :

(i) Finest gold is red in colour. As the size of particles increases, it becomes purple.
(ii) Dilute milk gives a bluish tinge in reflected light whereas reddish tinge in transmitted light.

(2) ***Mechanical Properties :***

(a) ***Brownian movement :*** Colloids particles exhibit a ceaseless random and swarming motion. This kinetic activity of particles suspended in the liquid is called Brownina movement.
Robert Brown first observed this motion with pollen grains suspended in water.

Cause of movement : Brownian movement is due to bombardment of the dispersed particles by molecules of the medium. The Brownian movement (figure) depends upon the size of sol. particles. With the increase in the size of the particle, the chance of unequal bombardment decrease, and the Brownial movement too disappears. It is due to the fact that the suspension fails to exhibit this phe-nomenon.
It should be noted that Brownian movement does not change with time but changes with temperatures.

Importance :

(i) Brownian movement is a direct demonstration of the assumption that the molecules in a gas or solution are in a state of constant ceaseless motion. Thus it confirms kinetic theory.

(ii) Brownian movement does not allow the colloidal particles to settle down due to gravity and thus is responsible for their stability.

(iii) Brownian movement helps to calculate the Avogadro's number (Detail beyond the scope of the book).

(b) ***Sedimentation :*** Heavier sol. particle tend to settle down very slowly under the influence of gravity. This phenomenon is called sedimentation.

(3) ***Optical Properties (Tyndal Effect) :***

When a strong and converging beam of light is passed through a colloidal solution, its path becomes visible (bluish light) when viewed at right angles to the beam of light (figure). This effect is called Tyndall effect. The light is observed as a bluish cone which is called Tyndall cone.

The Tyndall effect is due to scattering of light by the colloidal particles. The scattering of light cannot be due to simple reflection, because the size of the particles is smaller than the wave, length of the visible light and they are unable to reflect light waves. In fact, colloidal particles first absorb light and then a part of the absorbed light is scattered from the surface of the colloidal particles as a light of shorter wavelength. Since maximum scattering of light takes place at right angles to the place of incident light, it becomes visible when seen from that direction.

The Tyndall effect is observed under the following conditions :

(i) The diameter of the dispersed particles must not be much smaller than the wavelength of light employed.

(ii) The refractive indices of the dispersed phase and the dispersion medium must differ widely. This condition is fulfilled by lyophobic colloids.

It is important to note that Tyndall effect is not shown by true solutions as their particles are too small to cause scattering. Tyndall effect has been used in devising ultramicroscope and in determining the number of colloidal particles in a colloidal solution.

(4) ***Electrical Properties :***

The two electrical properties of colloidal solutions are :

(a) ***Electrophoresis or Cataphoresis*** and (b) ***Electro-osmosis***

(a) ***Electrophoresis or Cataphoresis :*** In a colloidal solution, the colloidal particles are electrically charged and the dispersion medium has equal but opposite charge. Thus colloidal solution on the whole is electrically neutral. When an electric current is passed through a colloidal solution, the charged particles move towards the oppositely charged electrode where coagulate due to loss of charge.

The phenomenon involving the migration of colloidal particles under the influence of electric field towards the oppositively charged electrode, is called electrophoresis or cataphoresis.

This phenomenon is used to determine the charge on the colloidal particles. For example, when a sol. of ferric hydroxide is taken in a U-tube and subjected to electric field, the ferric hydroxide (sol.) particles get accumulated near the cathode (figure). This shows that ferric hydroxide sol. particles are positively charged.

The sol. particles of metals and their sulphides are found to be negatively charged while those of metal hydroxides are positively charged. Basic dyes such as methylene blue haemoglobin are positively charged while acid dyes like are negatively charged.

Origin of charge : Various reasons have been given regarding the original of charge on the colloidal particles. These are given below :

(i) ***Frictional electrification :*** It is believed to be frictional due to the rubbing of the dispersed phase particles with medium molecules.

(ii) ***Dissociation of the surface molecules :*** It leads to electric charge on colloidal particles. For example, an aqueous solution of a soap (sodium palmitate) dissociates into ions.

$$\underset{\text{sod. palmitate}}{C_{15}H_{31}COONa} \rightleftharpoons C_{15}H_{31}COO^{-} + Na^{+}$$

The Na^+ ions pass into the solution while $C_{15}H_{31}COO^-$ ions have a tendency to form aggregates due to weak attractive forces present in the hydrocarbon chains. Thus, the anions which are of colloidal size bear negative charge.

(iii) ***Preferential adsorption of ions from solution :*** The charge on the colloidal particles is generally acquired by preferentially adsorbing positive or negative ions from the electrolyte. Thus AgCl particles can adsorb Cl^- ions from chloride solutions and Ag^+ ions; the sol. will be negatively charged in the first case and positively charged in the second case.

(iv) ***Capture of electron :*** It is from air during preparation of sol. by Bredig's arc method.

(v) ***Dissociation of molecular electrolytes on the surface of particles :*** H_2S molecules get adsorbed on sulphides during precipitation. By dissociation of H_2S, H^+ ions are lost and colloidal particles become negatively charged.

Electrical charged sols.

Positively charged sols	***Negatively charged sols***
1. Ferric hydroxide, aluminium hydroxide	Metals such as Pt, Au, Ag, Metals sulphides, e.g. arsenius sulphide.
2. Basic dyes such as methylene blue	Starch, clay, silicic acid.
3. Haemoglobin	Acid dyes, such as eosin.

(b) ***Electro-osmosis :*** The phenomenon involving the migration of the dispersion medium and not the colloidal particles under the influence of an electric field is electro-osmosis.
Take the pure solvent (dispersion medium) in two limbs of U-tube. In the lower middle portion of U-tube, a porous diaphragm containing the colloidal system is present which divides the U-tube in two sections. In each section of U-tube, an electrode is present, as shown in figure. When the electrode potential is applied to the electrodes, the solid phase of sol. (colloidal system) cannot move but the solvent (dispersion medium) moves through the porous diaphragm towards one of the electrodes. The direction of migration of dispersion medium due to electro-osmosis determines the charge on sol. particles e.g., if the dispersion medium moves towards the cathode (negative electrode), the sol. particles are also negatively charged because the dispersion medium is positively charged as on the whole colloidal solution is neutral.

<u>Electric double layer :</u>
The surface of a colloidal particle acquires a positive or a negative charge by selective adsorption of ions carrying +ve or – ve charges respectively. The charged layer attracts counter ions from the medium which forms a second layer. Thus, an electrical double layer is formed on the surface of the particles i.e., one due to absorbed ions and the other due to oppositely charged ions forming a diffused layer. This layer consists of ion of both the signs, but its net charge is equal and opposite to those absorbed by the colloidal particles. The existence of charges of opposite signs on the fixed and diffused parts of the double layer creates a potential between these layers. This potential difference between the fixed charge layer and diffused layer of opposite change is called electrokinetic potential or zeta potential.

(c) ***Coagulation :*** the colloidal sols are stable due to the presence of electric charges on the colloidal particles. Because of the electrical repulsion, the particles do not come close to one another to form precipitates. The removal of charge by any means will lead to the aggregation of particles and hence precipitation will occur immediately.
This process by means of which the particles of the dispersed phase in a sol. are pecipitated is known as *coagulation*.
If the coagulated particles instead of settling at the bottom of the container, float on the surface of the dispersion medium, the coagulation is called *flocculation*.
Most of the sols are coagulated by adding an electrolyte of opposite sign. This is due to the fact that the colloidal particles take up the ions of electrolyte whose charges are opposite to that on colloidal particles with the result that charge on the colloidal particles is neutralized. Thus coagulation takes place. For example, arsenius sulphide sol. (negatively charged) precipitated by adding barium chloride solution. It is due to the fact that the negatively charged particles of the sol. take up barium ions and get neutralized which lower the stability. As a result precipitation takes place.

It is observed that different amounts of different electrolytes is required to bring coagulation of a particular solution.

The minimum amount of an electrolyte required to cause precipitation of one litre of a colloidal solution is called coagulation value or flocculation value of the electrolyte for the sol.

The reciprocal of coagulation value is regarded as the *coagulating power*.

For example, the coagulation values of NaCl, $BaCl_2$ and $AlCl_3$ for arsenic sulphide sol. are 51, 0.69 and 0.093 millimoles/litre respectively. Thus their coagulating powers are $\frac{1}{51}$, $\frac{1}{0.69}$ and $\frac{1}{0.093}$ i.e., 0.0196, 1.449 and 10.75 respectively.

The coagulation values of a few electrolytes for negatively charged arsenic sulphide and positively charged ferric hydroxide sol. are given in table given below. The valency of the coagulation ion (the ion whose charge is opposite to that of the colloidal particles) is also give.

Coagulation values of different electrolytes

Arsenic sulphide sol.			***Ferric hydroxide sol.***		
Electrolyte	Valency of coagulating cation	coagulation value (millimoles/litre)	Electrolyte	Valency of coagulating cation	coagulation value (millimoles/litre)
K_2SO_4	1	63	KBr	1	138
NaCl	1	51	KNO_3	1	132
KNO_3	1	50	KCl	1	103
$MgSO_4$	2	0.81	K_2CrO_4	2	0.320
$BaCl_2$	2	0.69	K_2SO_4	2	0.215
$AlCl_3$	3	0.093	$K_3Fe(Cn)_6$	3	0.096

From the above table, it is clear that the coagulating power of Al^{3+} ions in precipitating the arsenic sulphide sol. is approximately 550 times more than that of sodium (Na^+) or potassium (K^+) ions. Again, it is observed that the negatively charged arsenic sulphide sol. is coagulated by cations while positively charged ferric hydroxide sol. is coagulated by anions.

Hardy-Schulz rules : H. Schulze (1882) and W.B. Hardy (1900) suggested the following rules to discuss the effect of electrolytes of the coagulation of the sol.

(1) Only the ions carrying charge opposite to the one present on the sol. particles are effective to cause coagulation, e.g., the negative charged sol. is best coagulated by cations and a positive sol. is coagulated by anions.

(2) The charge on coagulating ion influences the coagulation of sol.
In general, the coagulating power of the active ion increases with the valency of the active ion. After observing the regularities concerning the sing and valency of the active ion, a law was proposed by Hardy and Schulz which is termed as Hardy-Schulze law which is stated as follows: "*Higher is the valency of the active ion, greater will be its power to precipitate the sol.*"

Thus, coagulating power of cations is in the order of $Al^{3+} > Ba^{2+}$ or $Mg^{2+} > Na^+$ or K^+.
Similarly, to coagulating the positively charged sol. the coagulating power of anion is in the order of $[Fe(CN)_6]^{4-} > PO_4^{3-} > SO_4^{2-} > Cl^-$

Some other methods of coagulation :
Apart from the addition of electrolyte, coagulation can also be carried out by following methods:

(i) ***By persistent dialysis :*** It has been observed that traces of electrolytes are associated with the solution due to which it is stable. If the solution is subjected to prolonged dialysis, the traces of electrolytes are removed and coagulation takes place.

(ii) ***By mutual coagulation of colloids :*** When two sols of oppositively charges are mixed together in a suitable proportion, the coagulation takes place. The charge of one is neutralized by the other. For example, when negatively charged arsenic sulphide sol. is added to positively charged ferric hydroxide sol., the precipitation of both occurs simultaneously.

(iii) ***By electrical method :*** If the electrical charge of lyophobic sol. is removed by applying any electric field such as in electrophoresis, they also precipitate out.

(iv) By excessive cooling or by excessive heating.

(5) ***Colligative properties :*** Colloidal solutions too exhibit colligative properties such as osmotic pressure, lowering of vapour pressure, depression in freezing point and elevation in boiling point. But the effect of colloidal particles on colligative properties except osmotic pressure is very small. This is due to the large size of colloidal particles. The number of colloidal particles produced by a given mass of colloid is much less than the number produced in a molecular solution, containing the same mass of solute. Hence the colligative effect in colloidal solutions is too less.

Isoelectric Point of Colloid :

The hydrogen ion concentration at which the colloidal particles are neither positively charged nor negatively charged (i.e. uncharged) is known as isoelectric point of the colloid. At this point lyophilic colloid is expected to have minimum stability because at this point particles have no charge. The isoelectric point of gelatin is 4.7. This indicates that at pH = 4.7, gelating has no electrophoretic motion. Below 4.7, it moves towards the cathode and above 4.7 it moves forwards the anode. It is not always true, e.g., silicic acid has been found to have maximum stability at the isoelectric point.

EMULSIONS :

An emulsion is a colloidal solution of a liquid. It may be defined as a heterogeneous system consisting of more than one immiscible liquids dispersed in one another in the form of droplets whose diameter, in general, exceeds 0.1 μ.

For example, milk is an emulsion in which small drops of liquid fat are dispersed in aqueous medium. Cod liver oil is an emulsion in which the water drops are dispersed in the oil. This means in most of the emulsions one of the liquid is water and the other liquid is oil. Here the term 'oil' is used to represent all organic substances which are soluble in water.

The emulsion are classified as :

(1) ***Oil in water type emulsion (O/W):*** In this emulsion, oil is the dispersed phase and water is the dispersion medium. It is denoted by O/W or O in W. For example, milk (liquid fat dispersed in water), vanishing cream, etc.

(2) ***Water in oil type :*** In this emulsion, water is the dispersed phase and oil is the dispersion medium. It is denoted by W/O or W in O. For example, butter, cod liver oil, cold cream, etc.

The type of emulsion obtained by agitating two immiscible liquids depends upon the relative amounts of two components liquids. The liquid that is in excess forms the dispersion medium. Thus, the two types of emulsions can be interconverted into each other by changing the concentration of one of the liquids.

Distinction between two types of emulsions : the two types of emulsions may be distinguished from each other in a number of ways.

(1) ***Dye test :*** It involves the addition of oil soluble dye to the emulsion under experiment. If the emulsion acquires the colour of the dye readily, it is water-in-oil type emulsion and it the emulsion remains colourless, it is oil-in-water type emulsion.

(2) ***Conductivity test :*** It involves the addition of electrolyte to the emulsion under experiment. If the conductivity of the emulsion increases appreciably with the addition of electrolyte, it is oil-in-water type emulsion and it conductivity is very small, it is water-in-oil type emulsion.

(3) ***Dilution test :*** As a general rule, an emulsion can be diluted with the dispersion medium while the addition of the dispersed phase forms a separate layer. Thus, if an emulsion can be diluted with oil, it is water-in-oil type.

Preparation of emulsion (Emulsification) : Emulsification is the process which involves the preparation of emulsion. Generally, an emulsion is prepared by subjecting a mixture of the immiscible liquid to a distinct layers upon standing. The oil globules rise to form an upper layer while aqueous medium forms lower layers. To prevent the separation of layers and to get the stable emulsion, a small quantity of the third substance is added. This substance which stabilizes the emulsion is called *emulsifier* or *emulsifying agent*. The commonly used emulsifying agents are soaps, detergents and lyophilic colloids. Casein, a lyophilic colloid present in milk, acts as an emulsifier as it forms a protective layer around fat molecules dispersed in water. Hence milk is a fairly stable emulsion.

Function of emulsifier : The main function of emulsifier or emulsifying agents is to lower the interfacial tension between oil and water and thus helps the intermixing of two liquids. For example, a molecule of a soap or detergent (emulsifier) gets concentrated at the interface between oil and water. The polar end of the emulsifier is in water and non-polar end is in oil as shown in figure.
In a soap, RCOONa, R is the non-polar end, whereas COO^{-} Na^{+} is the polar end.

Properties of emulsion :

(i) The size of particles of the dispersed phase of an emulsion is usually larger than in sols.

(ii) Like colloidal particles, emulsions exhibit properties such as Tyndall effect, Brownian movement (provided the particles are not too large), electrophoresis, coagulation, etc.

Demulsification : The process which involves the breaking of an emulsion into two separate liquid layers is called demulsification. The following methods may be used to bring demulsification:

(1) ***Chemical Methods :*** An emulsion may be demulsified by adding a chemical substance whose action on the dispersed phase and the dispersion medium is opposite to that of the original emulsifying agent used to produce the stable emulsion.

(2) ***Centrifugation :*** Cream is separated from milk by the centrifugal method.

(3) ***Cooling :*** Fat can be removed from milk by keeping it in a refrigerator for a few hours.

Demulsification :

Besides the above noted methods of demulsification, the following methods have also been developed :

(i) Suitable centrifugal action-milk cream is separated from milk by centrifugation.
(ii) Application of electric field-electrophoresis.
(iii) Addition of an electrolyte having multivalent opposite charge than that on the dispersed phase.
(iv) Chemical destruction of stabiliser.
(v) Distilling off of one of the components, usually water.
(vi) Addition of demulsifiers like alcohol, phenol etc.

Oil in water type emulsion (O/W) ***Use of emulsion :***

(1) Many pharmaceutical preparations-medicines, ointments, creams and various lotions are emulsions. It is believed that medicines are more effective and easily assimilated by the body tissues when they are in colloidal form i.e., emulsion.

(2) All paints are emulsions.

(3) The digestion of fat in the intestines is helped by emulsification. A little of the fat forms a medium soap (emulsifier) with the alkaline solution of the intestine and this soap emulsifier the rest of the fats, thus making it easier for the digestive enzymes to do their metabolic functions.

(4) Soaps and detergents remove dust and dirt from the dirty piece of cloth by making an oil in water emulsion.

(5) Milk is an emulsion of liquid fats in water.

(6) In the process of metallurgy, one of the important steps is the concentration of ore which is usually done by froth floatation process in which an oil is added to the finely-divided ore taken in water. The particles of ore go on the surface due to formation of foams while the other impurities are left at the bottom of the vessel.

(7) The emulsion of asphalt in water is used in road making and building.

GELS :

Colloidal system in which liquids are the dispersed phase and solid act as the dispersion medium are called gels. The common examples are : boot polishes, jelly, gum arabic, agar agar, processed cheese and silicic acid.

When the gels are allowed to stand for a long time, they give out small quantities of trapped liquids with accumulate on its surface. This action of gels is known as Synresis or Weeping. Some gels such as silica, gelatin and ferric hydroxide liquify on shaking and reset on allowing to stand. This phenomenon of Sol-gel transformation is called thixotropy.

Gels are divided into two categories i.e. elastic gels and non elastic gels. The two categories differ from their behaviour towards dehydration and rehydration as under.

Elastic gels	***Non-elastic gels***
1. They change to solid mass on dehydration which can be changed back to original form by addition of water followed by warming.	1. They change to solid mass on dehydration which cannot be changed back to original form with water.
2. They absorb water when placed in it with simultaneous swelling. This phenomenon is called imbibation.	2. They do not exhibit imbibation.

USES OF COLLOIDS :

(1) ***Medicines :*** The medicines containing gold, silver or calcium etc. in colloidal form are more effective and easily assimilated by the human systems.

(2) ***Dyes :*** In dyeing, mordants colloidal substances are used in textile dyeing industry to fasten dyes.

(3) ***Rubber industry :*** Latex is a colloidal solution of negatively charged particles. The article to be rubber plated is made the anode. Under the influence of electric field the rubber particles get deposited on the anode and the article gets rubber plated.

(4) ***Smoke screens :*** Smoke screens which consist of titanium dioxide dispersed in air are used in warfare for the purpose of concealment and camouflage.

(5) ***Formation of delta :*** The river waver carries with it charged clay particles and many other substances in the form of colloidal solution. When the sea water comes in contact with these particles, the colloidal particles in river water are coagulated by the electrolytes present in sea water to form deltas.

(6) ***Purification of water :*** The turbidity in water is due to the presence of negatively charged clay particles. The addition of potash alum, i.e., Al^{3+} ions neutralizes the negative charge on the colloidal particles and thus causes their coagulation. The coagulated matter settles down and thus becomes clear.

(7) ***Artificial rain :*** Artificial rain can be caused by throwing electrified sand on clouds which are colloidal solutions or charged particles of water in air.

(8) ***Smoke precipitation :*** Smoke coming out of the chimney is industrial area is a nuisance and health hazard. It is a colloidal particles are charged particles and thus they are removed from fuel gases by electrical precipitation (Cottrell Precipitator).

In cottrell precipitator, the smoke is made to pass through chambers fitted with highly electrically charged plates which precipitate the carbon and dust particles leaving in the gases to escape through chimney (figure).

(9) ***Sewage disposal :*** Sewage water consists of particles of dirt, rubbish, mud, etc., which are of colloidal dimensions and carry an electric charge and thus do not settle down easily. These particles can thus be removed by cataphoresis. A system of two tanks fitted with metallic electrodes is used for this purpose. When electric field is created, then the dust particles are coagulated on he oppositely charged electrodes. The deposit may be utilized as a manure.

(10) ***Cleansing action of soap and detergent :*** Soap solution may be used to wash off the dirt sticking to the fabric, in the presence

(i) If forms a collodial solution in water forms (miscelles), removes dirt by simple adsorption of oily substance and thus washes away.

(ii) It decreases the interfacial tension between water and grease, and it causes the emulsification of grease in water. By mechanical action such as rubbing, the dirt particles are also detached alongwith the only material.

(11) ***In Photography :*** Various colloidal system are used in photographic process. In the preparation of photographic plates, the silver bromide in gelatin is coated on thin glass plates. In developing and fixation, various colloidal substances are used. In different kinds of colour printing, gelatin and other colloidal mixtures are used.

(12) ***Blue colour of the sky :*** Colloidal particles scatter only blue light and the rest of is absorbed. In sky there are a number of dust and water particles. They scatter blue light and, therefore, sky looks bluish. If there were no scattering, the sky would have appeared totally dark.

SUMMARY OF COLLOIDAL STATE :

(1) Thomas Grahm classified the substances into two categories on the basis of their diffusion through parchment membrane namely (i) Colloids (ii) Crystalloids.

(2) It has been realised that colloid is not a substance but it is a state of a substance which depends upon the molecular size.

(3) When the size of the particles is between 10^{-9} m (1nm) 10^{-7} m (100 nm), it behaves like colloid.

(4) In true solutions, the particle size is less than 1 nm and in suspensions, the particle size is more than 100 nm.

(5) The colloidal solutions in which there is no affinity between particles of the dispersed phase and the dispersion medium are called Iyopholic colloids or irreversible colloids.

(6) Associated colloids are the substances which behave as normal electrolytes at low concentration but behave as colloidal particles at higher concentration. For example, soap i.e. sod. stearate.

(7) Lyophobic colloids are prepared by mainly three types of method
(i) Condensation methods
(ii) Dispersions method
(iii) Peptisation

(8) The process of converting a freshly prepared precipitate into colloidal form by the addition of a suitable electrolyte is called peptisation.

(9) The process of separating the particles of colloids from those of crystalloids by means of diffusion through a suitable membrane is called dialysis.

(10) The process of dialysis i.e. , separation of crystalloids from colloids is quickened by passing electric current through two electrodes suspended around the parchment bag. This process is called electrodialysis.

(11) Ultra filtration is a process of removing the impurities from the colloidal solution by passing it through graded filter papers called ultra-filter papers.

(12) The continuous zig-zag movement of the colloidal particles in a colloidal solutions is called Brownian movement. It is due to the collisions of dispersion medium particles with dispersed phase particles.

(13) The process of scattering of light by the colloidal particles as a result of which the path of the beam becomes visible is called Tyndall effect.

(14) The presence of electric charge either (positive or negative) on colloidal particles is responsible for the stability of colloidal solutions.

(15) The phenomenon of movement of colloidal particles under the influence of electric field is called electrophoresis or cataphoresis.

(16) A phenomenon in which the molecules of the dispersion medium are allowed to move under the influence of an electric current, whereas colloidal particles are not allowed to move, is called Electro-osmosis.

(17) The phenomenon of precipitation of a colloidal solution by the addition of excess of an electrolyte is called coagulation or flocculation.

(18) According to Hardy Schulze rule :
(i) The ions carrying the charge opposite to that of sol particles are effective in causing coagulation of the sol.
(ii) Coagulation power of an electrolyte is directly proportional to the valency of the active ions (ions causing coagulation).

(19) The minimum concentration of an electrolyte which is required to cause the coagulation or flocculation of a sol. is known as flocculation value. It is usually expressed as millimoles per litre. The coagulating power of an electrolyte is inversely related to its coagulating value.

(20) Gold number of a protective colloid is a minimum weight of it in milligrams which must be added to 10 ml of a standard red gold sol so that no coagulation of the gold sol. (i.e. change of colour from red to blue) takes place when 1 ml of 10 % sodium chloride solution is rapidly added to it. Obviously, smaller the gold number of a protective colloid, the greater is the protective action.

ADSORPTION :

(1) Molecules at the surface of a solid, a metal, or a liquid experience in net inward force of attraction with free valencies.

(2) The phenomenon of attracting and retaining the molecules of a substance on the surface of a solid or a liquid resulting in the higher concentration of the molecules on the surface is called adsorption.

(3) The substance adsorbed on the surface is called adsorbate and the substance on which it is adsorbed is called adsorbent.

(4) The reverse process i.e. removal of adsorbed substance from the surface is called desorption.

(5) The adsorption of gases on the surface of metals is called occlusion.

(6) The term sorption is employed when adsoption as well as absorption take place simultaneously.

(7) Adsorption is a surface phenomenon, whereas absorption is a bull phenomenon. Adsorption occurs only at the surface of adsorbent, whereas absorption occurs throughout the body of the material.

(8) When the concentration of the adsorbate is more on the surface of the adsorbent than in the bulk, it is called positive adsorption.

(9) When the concentration of the adsorbate is less relative to its concentration in the bulk, it is called negative adsorption.

(10) When a gas is adsorbed at the surface of a solid by week forces (Vander Waal's forces), it is called physical adsorption.

(11) When a gas is held on the surface of a solid by forces similar to those of a chemical bond, it is called chemical adsorption or chemiosorption.

(12) Adsorption is accompanied by evolution of heat. The amount of heat evolved when one mole of a gas is adsorbed on a solid, is known as molar heat of adsorption. Its magnitude depends upon the nature of the gas.

(13) The magnitude of gaseous adsorption depends upon temperature, pressure, nature of the gas and the nature of the adsorbent.

(14) Adsorption decreases with increase in temperature, since it is accompanied by evolution of heat.

(15) The adsorption increases with increase in pressure, since adsorption of gas leads to decrease in pressure.

(16) The variation of adsorption with pressure at a constant temperature is called isotherm.

(17) At low pressure, the amount of the gas adsorbed per unit quantity of adsorbent is proportional to the pressure. At high pressure, the amount of adsorbed gas is independent of pressure. At intermediate pressures, Freundlich adsorption isotherm is expected to hold

(18) More readily soluble and easily liquefiable gases HCl, Cl_2 , SO_2 and NH_3 are adsorbed more than the so called permanent gases such as H_2 , O_2 , N_2 etc. because Vander Waal's forces involved in adsorption are much predominant in the former gases than the latter category of gases.

PROFICIENCY TEST

Q.1 Fill in the blanks with appropriate items:

1. The substance on whose surface adsorption takes place is called an _____.
2. Removal of adsorbate from the surface of adsorbent is called _____.
3. Migration of colloidal particles under the effect of electric field is called _____.
4. The heat of adsorption in case of physisorption is approximately _____.
5. The phenomenon of zig-zag motion of colloidal particles is known as _____.
6. Lyophilic sols are _____ stable than lyophobic sols.
7. Electrical properties of a colloidal solution are demonstrated by _____.
8. Tyndall effect takes place due to _____ of light by collloidal particles.
9. The liquid-liquid colloidal dispersions are called _____.
10. The movement of dispersion medium under the influence of an electric field is called _____.
11. Smoke is a colloidal solution of _____ in _____.
12. The adhering of the molecules of a gas on the surface of a solid is called _____.
13. The protective action of different colloids is compared in terms of _____.
14. The colloidal dispersion of a liquid in a liquid is called _____.
15. The colloidal dispersions of liquids in solid media are called _____.

Q.2 True/False statements

1. Physisorption is non-specific.
2. Chemisorption needs activation energy.
3. A graph of x/m vs temperature at constant pressure is called adsorption isotherm.
4. Suspensions have solute particles with size less than 1 nm.
5. $Fe(OH)_3$ sol contains positively charged colloidal particles.
6. Chemisorption is irreversible.
7. Adsorption isobars of chemisorption and physisorption are of the same type.
8. Milk is an example of water in oil emulsions.
9. Gold sol can be prepared by Bredig's arc method.
10. Gel is a system in which liquid is the dispersed phase and solid is the dispersion medium.

Select the correct alternative. (Only one is correct)

Q.1 Which gas will be adsorbed on a solid to greater extent.
(A) A gas having non polar molecule
(B) A gas having highest critical temperature (T_c)
(C) A gas having lowest critical temperature.
(D) A gas having highest critical pressure.

Q.2 Which of the following factors affects the adsorption of a gas on solid?
(A) T_c(critical temp.) (B) Temperature of gas (C) Pressure of gas (D) All of them

Q.3 The volume of gases NH_3, CO_2 and CH_4 adsorbed by one gram of charcoal at 298 K are in
(A) $CH_4 > CO_2 > NH_3$ (B) $NH_3 > CH_4 > CO_2$
(C) $NH_3 > CO_2 > CH_4$ (D) $CO_2 > NH_3 > CH_4$

Q.4 The heat of physisorption lie in the range of
(A) 1 – 10 kJ mol^{-1} (B) 20 to 40 kJ mol^{-1} (C) 40 to 200 kJ mol^{-1} (D) 200 to 400 kJ mol^{-1}

Q.5 Which of the following is not a gel?
(A) Cheese (B) Jellies (C) Curd (D) Milk

Q.6 Which of the following is used to adsorb water
(A) Silica gel (B) Calcium acetate (C) Hair gel (D) Cheese

Q.7 An emulsion is a colloidal system of
(A) two solids (B) two liquids
(C) one gas and one solid (D) one gas and one liquid

Q.8 Which of the following is a lyophobic colloid?
(A) Gelatin (B) Sulphur (C) Starch (D) Gum arabic

Q.9 The nature of bonding forces in adsorption are
(A) purely physical such as Van Der Waal's forces
(B) purely chemical
(C) both chemical and physical
(D) sometimes physical and sometimes chemical

Q.10 The Tyndall effect associated with colloidal particles is due to
(A) presence of electrical charges (B) scattering of light
(C) absorption of light (D) reflection of light

Q.11 Which one of the following is not applicable to chemisorption?
(A) Its heat of adsorption is high (B) It takes place at high temperature
(C) It is reversible (D) It forms mono-molecular layers

Q.12 In the colloidal state the particle size ranges
(A) below 1 nm (B) between 1 nm to 100 nm
(C) more than 100 nm (D) none of the above

Q.13 All colloids
(A) are suspensions of one phase in another
(B) are two-phase systems
(C) contain only water-soluble particles
(D) are true solutions

Q.14 Colloids can be purified by
(A) condensation (B) peptization (C) coagulation (D) dialysis

Q.15 Milk is an example of
(A) emulsion (B) suspension (C) foam (D) sol.

Q.16 Colloidal particles in a sol. can be coagulated by
(A) heating (B) adding an electrolyte
(C) adding oppositely charged sol (D) any of the above methods

Q.17 Emulsifier is an agent which
(A) accelerates the dispersion (B) homogenizes an emulsion
(C) stabilizes an emulsion (D) aids the flocculation of an emulsion

Q.18 Fog is a colloidal system of
(A) gas in liquid (B) liquid in gas (C) gas in gas (D) gas in solid

Q.19 Given below are a few electrolytes, indicate which one among them will bring about the coagulation of a gold sol. quickest and in the least of concentration?
(A) NaCl (B) $MgSO_4$ (C) $Al_2(SO_4)_3$ (D) $K_4[Fe(CN)_6]$

Q.20 When a colloidal solution is observed under ultramicroscope, we can see
(A) light scattered by colloidal particle
(B) size of the colloidal particle
(C) shape of the colloidal particle
(D) relative size of the colloidal particle

Q.21 Colloidal solutions are classified on the basis of
(A) molecular size (B) orgainc or inorganic
(C) surface tension value (D) pH value

Q.22 The electrical charge on a colloidal particle is indicated by
(A) Brownian movement (B) electrophoresis
(C) ultra microscope (D) molecular sieves

Q.23 The minimum concentration of an electrolyte required to cause coagulation of a sol is called
(A) flocculation value (B) gold number (C) protective value (D) none of these

Q.24 Smoke precipitator works on the principle of
(A) distribution law (B) neutralization of charge on colloids
(C) Le-Chaterlier's principle (D) addition of electrolytes

Q.25 Which one of following statements is not correct in respect of lyophilic sols?
(A) There is a considerable interaction between the dispersed phase and dispersion medium
(B) These are quite stable and are not easily coagulated
(C) They carry charge
(D) The particle are hydrated

Q.26 As_2S_3 sol is
(A) positive colloid (B) negative colloid (C) neutral colloid (D) none of the above

Q.27 Crystalloids differ from colloids mainly in respect of
(A) electrical behaviour (B) particle nature
(C) particle size (D) solubility

Q.28 Which of the following electrolyte will be most effective in coagulation of gold sol.?
(A) $NaNO_3$ (B) $K_4[Fe(CN)_6]$ (C) Na_3PO_4 (D) $MgCl_2$

Q.29 At the critical micelle concentration (CMC) the surfactant molecules
(A) decompose (B) dissociate
(C) associate (D) become completely soluble

Q.30 Alums purify muddy water by
(A) dialysis (B) absorption (C) coagulation (D) forming true solution

Q.31 Solute dispersed in ethanol is called
(A) emulsion (B) micelle (C) hydrophilic sol. (D) alcosols

Q.32 Which one of the following is lyophillic colloid?
(A) Milk (B) Gum (C) Fog (D) Blood

Q.33 Small liquid droplets dispersed in another liquid is called
(A) suspension (B) emulsion (C) gel (D) true solution

Q.34 The process which is catalysed by one of the product is called
(A) acid-base catalysis (B) autocatalysis
(C) negative catalysis (D) homogeneous catalysis

Q.35 Tyndall effect would be observed in a
(A) solution (B) solvent (C) precipitate (D) colloidal sol.

Q.36 Adsorption is multilayer in case of
(A) physical adsorption (B) chemisorption
(C) in both (D) none of the these

Q.37 Crystalloids differ from colloids mainly in respect of
(A) electrical behaviour (B) particle size
(C) particle nature (D) solubility

Q.38 A liquid is found to scatter a beam of light out leaves no residue when passed through the filter paper. The liquid can be described as
(A) a suspension (B) oil (C) a colloidal sol. (D) a true solution

Q.39 The ability of an ion to bring about coagulation of a given colloid depends upon
(A) its charge (B) the sign of the charge alone
(C) the magnitude of the charge (D) both magnitude and sign of charge

Q.40 An arsenious sulphide sol. carries a negative charge. The maximum precipitating power of this sol. is possessed by
(A) K_2SO_4 (B) $CaCl_2$ (C) Na_3PO_4 (D) $AlCl_3$

Q.41 Reversible adsorption is
(A) chemical adsorption (B) physical adsorption
(C) both (D) none

Q.42 The function of gum arabic in the preparation of Indian ink is
(A) coagulation (B) peptisation (C) protective action (D) absorption

Q.43 Which of the following is an example of associated colloid?
(A) Protein + water (B) Soap + water (C) Rubber + benzene (D) $As_2O_3 + Fe(OH)_3$

Q.44 Adsorption of gases on solid surface is generally exothermic because
(A) enthalpy is positive (B) entropy decreases
(C) entropy increases (D) free energy increases

Q.45 An emulsifier is a substance
(A) which stabilises an emulsion
(B) which breaks the emulsion into its constituent liquids
(C) which can convert liquid into an emulsion
(D) which brings about coagulation of an emulsion

Question No. 46 to 50 (5 questions)

Whenever a mixture of gases is allowed to come in contact with a particular adsorbent under the same conditions, the more strong adsorbate is adsorbed to greater extent irrespective of its amount present, e.g. H_2O is adsorbed to more extent on silica gel than N_2 and O_2. This shows that some adsorbates are preferentially adsorbed. It is also observed that preferentially adsorbable adsorbents can displace a weakly adsorbed substance from the surface of an adsorbent.

Q.46 Which of the following gases is adsorbed to maximum extent:
(A) He (B) Ne (C) Ar (D) Xe

Q.47 Which of the gas can displace remaining all the gases
(A) O_2 (B) N_2 (C) CO (D) H_2

Q.48 When temperature is increased
(A) extent of adsorption increases
(B) extent of adsorption decreases
(C) no effect on adsorption
(D) extent of adsorption first decreases, then increases

Q.49 Chromatogarphic separations are based on
(A) differential solubility (B) differential adsorption
(C) differential absorption (D) None of these

Q.50 Activated charcoal is prepared by
(A) heated charcoal with steam so that it becomes more porous
(B) adding $Ca_3(PO_4)_2$ to charcoal
(C) adding impurity to charcoal
(D) reacted with conc. HNO_3

Question No. 51 to 54 (4 questions)

The clouds consist of charged particles of water dispersed in air. Some of them are + vely charged, others are negatively charged. When + vely charged clouds come closer they have cause lightening and thundering whereas when + ve and –ve charged colloids come closer they cause heavy rain by aggregation of minute particles. It is possible to cause artificial rain by throwing electrified sand or silver iodide from an aeroplane and thus coagulation the mist hanging in air.

Q.51 When excess of $AgNO_3$ is treated with KI solution, AgI forms
(A) +ve charged sol (B) –vely charged sol (C) neutral sol (D) true solution

Q.52 Clouds are colloidol solution of
(A) liquid in gas (B) gas in liquid (C) liquid in liquid (D) solid in liquid

Q.53 AgI helps in artificial rain because
(A) It helps in coagulation (B) It helps in dispersion process
(C) Both (D) None

Q.54 Electrical chimneys are made on the principle of
(A) Electroosmosis (B) Electrophoresis (C) Coagulation (D) All of these

Question No. 55 to 58 (4 questions)

In macromolecular type of colloids, the dispersed particles are themselves large molecules (usually polymers). Since these molecules have dimensions comparable to those of colloidal particles, their dispersions are called macromolecular colloids. Most lyophilic sols belong to this category. There are certain colloids which behave as normal strong electrolytes at low concentrations, but exhibit colloidal properties at higher concentrations due to the formation of aggregated particles. These are known as micelles or associated colloids. Surface active agents like soaps and synthetic detergents belong to this class.

- Critical micelle concentration (CMC) is the lowest concentration at which micelle formation appears. CMC increases with the total surfactant concentration. At concentration higher than CMC, they form extended parallel sheets known as **lamellar micelles** which resemble biological membranes. With two molecules thick, the individual molecule is perpendicular to the sheets such that hydrophilic groups are on the outside in aqueous solution and on the inside is a non-polar medium.
- In concentrated solutions, micelles take the form of long cylinders packed in hexagonal arrays and are called lytotropic mesomorphs.
- In an aqueous solution (polar medium), the polar group points towards the periphery and the hydrophobic hydrocarbon chains point towards the centre forming the core of the micelle.
- Micelles from the ionic surfactants can be formed only above a certain temperature called the **Kraft temperature**.
- They are capable of forming ions
- Molecules of soaps and detergents consist of lyophilic as well as lyophilic parts which associate together to form micelles.
- Micelles may contain as many as 100 molecules or more.

Q.55 Select incorrect statement(s):

(A) Surface active agent like soaps and synthetic detergents are micelles

(B) Soaps are emulsifying agents

(C) $C_{17}H_{35}$ (hydrocarbon part) and $-COO^-$ (carboxylate) part of stearate ion ($C_{17}H_{35}COO^-$) both are hydrophobic

(D) All are incorrect statements

Q.56 Which part of the soap ($RCOO^-$) dissolves grease and forms micelle?

(A) R part (called tail of the anion) (B) $-COO^-$ part (called head of the anion)

(C) both (A) and (B) (D) none of these

Q.57 In multimolecular colloidal sols, atoms or molecules are held together by:

(A) H-bonding (B) van der Waals forces

(C) ionic bonding (D) polar covalent bonding

Q.58 Cleansing action of soap occurs because:

(A) oil and grease can be absorbed into the hydrophobic centres of soap micelles and washed away

(B) oil and grease can be absorbed into hydrophilic centres of soap micelles acid washed away

(C) oil and grease can be absorbed into both hydrophilic and hydrophobic centres but not washed away

(D) cleansing action is not related to micelles

Question No.59 to 61 (3 questions)

The protective power of the lyophilic colloids is expressed in terms of gold number a term introduced by Zsigmondy.Gold number is the number of milligram of the protective colloid which prevent the coagulation of 10 ml of red gold sol. when 1 ml of a 10 percent solution of sodium chloride is added to it. Thus, smaller the gold number of lyophilic colloid, the greater is the protective power.

Q.59 On addition of one mL of solution of 10% NaCl to 10 mL of red gold sol in presence of 0.025 g of starch, the coagulation is just prevented. The gold number of starch is

(A) 0.025 (B) 0.25 (C) 2.5 (D) 25

Q.60 Which of the following statement(s) is/are correct
(A) Higher the gold number, more protective power of colloid
(B) Lower the gold number, more the protective power
(C) Higher the coagulation value, more the coagulation power
(D) Lower the coagulation value, higher the coagulation power

Q.61 Gold number gives an indication of
(A) protective nature of colloids
(B) purity of gold in suspension
(C) the charge on a colloidal solution of gold
(D) g-mole of gold per litre

Question No. 62 & 65 (4 questions)
These questions consist of two statements each, printed as assertion and reason, while answering these questions you are required to choose any one of the following responses.
(A) If assertion is true but the reason is false.
(B) If assertion is false but the reason is true.
(C) If both assertion and reason are true and the reason is a correct explanation of assertion.
(D) If both assertion and reason are true but reason is not a correct explanation of assertion.

Q.62 **Assertion :** Isoelectric point is pH at which colloidal can move towards either of electrode
Reason : At isoelectric point, colloidal particles become electrically neutral.

Q.63 **Assertion :** When $AgNO_3$ is treated with excess of potassium iodide, colloidal particles gets attracted towards anode.
Reason : Colloidal particles adsorb common ions and thus become charged.

Q.64 **Assertion :** For adsorption ΔG, ΔH, ΔS all have –ve values
Reason : Adsorption is a spontaneous exothermic process in which randomness decreases due to force of attraction between adsorbent and adsorbate.

Q.65 **Assertion :** A gas with higher critical temperature gets adsorbed to more extent than a gas with lower critical temperature.
Reason : The easily liquifiable gases get adsorbed to more extent.

<u>Select the correct alternative</u>. (More than one are correct)

Q.66 Which of the following is/are correct statements
(A) Hardy Schulz rule is related to coagulation
(B) Brownian movement and Tyndall effect are shown by colloids
(C) When liquid is dispersed in liquid, it is called gel.
(D) Gold number is a measure of protective power of lyophillic colloid.

Q.67 Which statements is/are correct?
(A) Physical adsorption is multilayer non-directional and non specific
(B) Chemical adsorption takes more time to attain equilibrium
(C) Physical adsorption is due to free valence of atoms
(D) Chemical adsorption is stronger than physical adsorption

Q.68 Which of the following is/are correct for lyophillic sols?
(A) Its surface tension is lower than that of H_2O
(B) Its viscosity is higher than that of water
(C) Its surface tension is higher than that of water
(D) Its viscosity is equal to that of water

Q.69 Which statement/s is/are correct
(A) A solution is prepared by addition of excess of $AgNO_3$ solution in KI solution. The charge likely to develop on colloidal particle is positive.
(B) The effects of pressure on physical adsorption is high if temperature is low.
(C) Ultracentrifugation process is used for preparation of lyophobic colloids.
(D) Gold number is the index for extent of gold plating done.

Q.70 Colloidal solution can be purified by
(A) Dialysis (B) Electrodialysis (C) Electrophoresis (D) Ultrafiltration

Q.71 Coagulation of colloids can be achieved by
(A) Centrifugation (B) Adding electrolyte (C) Change in pH (D) Adding water

Q.72 When –vely charged colloid like As_2S_3 sol is added to + vely charged $Fe(OH)_3$ sol in suitable amounts
(A) Both the sols are precipitated simultaneously
(B) This process is called mutual coagulation
(C) They becomes + vely charged colloid
(D) They become – vely charged colloid

Q.73 Which of the following is not lyophillic
(A) Gelatin sol (B) Silver sol (C) Sulphur sol (D) As_2S_3 sol

Q.74 Which of the following are multimolecular colloids
(A) Sulphur sol (B) Egg albumin in water
(C) Gold sol (D) Soap solution

Q.75 Colloidal Gold can be prepared by
(A) Bredig's are method (B) Reduction of $AuCl_3$
(C) Hydrolysis (D) Peptization

Q.76 The coagulation of sol particles may be brought about by
(A) heating (B) adding oppositely charged sol.
(C) adding electrolyte (D) persistent dialysis

Q.77 Which one is not lyophobic in nature?
(A) Gelatine (B) Sulphur (C) Starch (D) Protein

Q.78 Which of the following are colloids?
(A) Milk (B) Ice cream (C) Urea solution (D) Blood

Q.79 Which are the properties of sols?
(A) Adsorption (B) Tyndall effect (C) Flocculation (D) Paramagnetism

Q.80 The migration of colloidal particles under the influence of an electrical field is known as
(A) electro osmosis (B) electrophoresis (C) electrodialysis (D) None

ANSWER KEY

PROFICIENCY TEST

Q.1

1. adsorbent	2. desorption	3. electrophoresis	4. 20–40 kJ-mol^{-1}
5. Brownian movement		6. more	7. elecrophoresis
8. scattering	9. emulsions	10. electro-osmosis	11. solid in gas
12. adsorption	13. gold number	14. emulsion	15. gel

Q.2

1.	T	2.	T	3.	F	4.	F
5.	T	6.	T	7.	F	8.	F
9.	T	10.	T				

Select the correct alternative. (Only one is correct)

Q.1	B	Q.2	D	Q.3	C	Q.4	B	Q.5	D	Q.6	A	Q.7	B
Q.8	B	Q.9	C	Q.10	B	Q.11	C	Q.12	B	Q.13	B	Q.14	D
Q.15	A	Q.16	D	Q.17	C	Q.18	B	Q.19	C	Q.20	A	Q.21	A
Q.22	B	Q.23	A	Q.24	B	Q.25	C	Q.26	B	Q.27	C	Q.28	D
Q.29	C	Q.30	C	Q.31	D	Q.32	B	Q.33	B	Q.34	B	Q.35	D
Q.36	A	Q.37	C	Q.38	D	Q.39	D	Q.40	D	Q.41	B	Q.42	C
Q.43	B	Q.44	B	Q.45	A	Q.46	D	Q.47	C	Q.48	B	Q.49	B
Q.50	A	Q.51	A	Q.52	A	Q.53	C	Q.54	B	Q.55	C,D	Q.56	C
Q.57	B	Q.58	A	Q.59	D	Q.60	B,D	Q.61	A	Q.62	B	Q.63	D
Q.64	C	Q.65	C										

Select the correct alternative. (More than one are correct)

Q.66	A,C,D	Q.67	B	Q.68	A,B	Q.69	A,B
Q.70	A,B,D	Q.71	A,B,C	Q.72	A,B	Q.73	B,C,D
Q.74	A,C	Q.75	A,B	Q.76	B,C	Q.77	B,C
Q.78	A,B,D	Q.79	A,B,C	Q.80	B		

STUDY PACKAGE

Target: IIT-JEE (Advanced)

SUBJECT: CHEMISTRY-XII

TOPIC: 9. Chemical Kinetics

Index:

1. Key Concepts

2. Exercise I

3. Exercise II

4. Exercise III

5. Exercise IV

6. Answer Key

7. 34 Yrs. Que. from IIT-JEE

8. 10 Yrs. Que. from AIEEE

THE KEY

CHEMICAL KINETICS :

It is a branch of physical chemistry deals with the "Rate of Chemical Reactions" including the effect of temperature, pressure, concentration, etc., on the rates, and the mechanism by which the reaction takes place.

RATE OF CHEMICAL REACTION is defined as the change in concentration of a reactant (or a product) in a particular time interval. Average rate of reaction, Instantaneous rate of reaction.

Units of Reaction Rate are unit of concentration divided by the unit of time (mol $L^{-1}s^{-1}$ or mol $L^{-1}min^{-1}$ or so on).

FACTORS AFFECTING REACTION RATES :

(i) Concentration of reactants and

(ii) Reaction temperature

Besides these, presence of catalyst and surface area (if a reactant or a catalyst is a solid) exposure to radiation also affect the reaction rates.

EXPRESSIONS OR THE RATE :

For a general reaction : $aA + bB \longrightarrow cC + dD$,

The rate of disappearance of A = $-\dfrac{d[A]}{dt}$; Rate of disappearance of B = $-\dfrac{d[B]}{dt}$;

Rate of appearance of C = $\dfrac{d[C]}{dt}$ & Rate of appearance of D = $\dfrac{d[D]}{dt}$.

The positive sign shows that concentrations of C and D increases with time and the negative sign indicating that concentrations of A and B decrease with time. Thus the rate of general reaction.

rate : $-\dfrac{1}{a}\dfrac{d[A]}{dt} = -\dfrac{1}{b}\dfrac{d[B]}{dt} = \dfrac{1}{c}\dfrac{d[C]}{dt} = \dfrac{1}{d}\dfrac{d[D]}{dt}$.

RATE EQUATION AND RATE CONSTANT :

An expression which relates the rate of a reaction to the concentration of the reactants is called the ***Rate Equation*** **or** ***Rate Law***. Rate $\propto [A]^a \cdot [B]^b$ or Rate = $k\,[A]^a\,[B]^b$. The constant of proportionality, k is known as the ***Rate Constant*** (specific reaction rate) and may be defined as the rate at unit concentrations of the reactants. k depends on the temperature and is independent of the initial concentrations of the reactants. At a fixed temperature, k is constant characteristic of the reaction. Larger value of k indicates fast reaction and small k indicates slow reactions.

MOLECULARITY :

Molecularity of a reaction is defined as the numbers of particles (atoms, ions, groups or molecules) of reactants actually taking part in a single step chemical reaction.

Molecularity of a reaction is :

(i) Always a whole number (not zero) and never a fraction.

(ii) The value of molecularity of a simple or one step reaction does not exceed 3.

ORDER OF REACTION :

It is defined as the sum of the exponents (powers) of the molar concentrations of the reactants in the experimentally determined rate equations.

If rate of reaction $\alpha\,[A]^p\,[B]^q\,[C]^r$ or Rate of reaction = $k\,[A]^p\,[B]^q\,[C]^r$

order of reaction = p + q + r & the order w.r.t. A, B & C are p, q & r respectively.

For a "Reaction of nth order", the order of the reaction is n and the rate equation (or Rate law) is rate $\propto [A]^n = k\,[A]^n$.

The order of a reaction is obtained from the experimentally determined rate (and not from the stoichiometric equation) and may be zero, an integer or a fraction and never exceeds 3. In a multi-step complex reaction, the order of the reaction depends on the slowest step.

ZERO ORDER REACTION :

A reaction is said to be of zero order if the rate is independent of the concentration of the reactants.

$A \longrightarrow$ products ; Rate α k $[A]^\circ$ = k mol L^{-1} s^{-1}

EXAMPLES :

(i) $H_2(g) + Cl_2(g) \xrightarrow{h\nu} 2HCl(g)$

(ii) $N_2O(g) \xrightarrow[\text{Surface}]{\text{hot Pt.}} N_2(g) + \frac{1}{2} O_2(g)$

(iii) $2NH_3(g) \xrightarrow[\text{surface}]{\text{Mo or W}} N_2 + 3H_2$

(iv) $2HI(g) \xrightarrow[\text{surface}]{\text{Au}} H_2(g) + I_2(g)$

CHARACTERISTICS OF ZERO ORDER REACTION :

(1) Concentration of reactant decreases lineraly with time. $[A]_t = [A]_0 - kt$.

(2) Units of k are, mol l^{-1} $time^{-1}$.

(3) Time required for the completion of reaction $t = \frac{[A]_0}{k}$ & $t_{1/2} = \frac{0.5\,[A]_0}{k}$

FIRST ORDER REACTION :

A reaction is said to be of first order if its rate is proportinal to the concentration of one reactant only.

	$A \longrightarrow$	Products.
at time t = 0	a (or C_0)	0
at time t = t	a – x (or C_t)	x

Rate α $[A] = k_1 [A]$ or $\frac{dx}{dt} = k_1(a - x)$ (1 st order differntial equation)

Integrated 1 st order rate equation is $k_1 = \frac{2.303}{t} \log \frac{a}{a - x}$.

Exponential form of 1 st order equation is $C_t = C_0 e^{-k_1 t}$

Characteristics Of First Order Reaction :

(1) Unit of rate constant is $time^{-1}$.

(2) Change in concentration unit will not change the numerical value of k_1.

(3) $t_{1/2} = \frac{0.693}{k_1}$ (Half-life); Average life = $\frac{1}{k}$;

(4) log (a – x) v/s t is a straight line with slope $-\frac{k_1}{2.303}$.

EXAMPLES :

(i) Radioactive disintegration is a first order reaction.

(ii) $C_{12}H_{22}O_{11} + H_2O \xrightarrow[\text{Inversion}]{H^+ \text{ catalysed hydrolysis}} \underset{\text{(glucose)}}{C_6H_{12}O_6} + \underset{\text{(fructose)}}{C_6H_{12}O_6}$.

(iii) Mineral acid catalyzed hydrolysis of esters.

(iv) Decomposition of H_2O_2 in aqueous solution.

SECOND ORDER REACTION :

(i) When two molecules of the same reactant are involved or the concentrations of the both reactants are equal reactions $2A \longrightarrow$ products or $A + B \longrightarrow$ products.

Differential rate equation $\frac{dx}{dt} = k_2(a - x)^2$

Integrated rate equation $k_2 = \frac{1}{t} \cdot \frac{x}{a(a - x)}$ or $k_2 t = \frac{1}{a - x} - \frac{1}{a}$.

(ii) When the initial concentrations of the two reactants are different;

$A + B \longrightarrow$ products

a b

differential rate equation $\frac{dx}{dt} = k_2 (a-x)(b-x)$.

Integrated rate equation $k_2 = \frac{2.303}{t(a-b)} \log_{10} \frac{b(a-x)}{a(b-x)}$

CHARACTERISTICS OF SECOND ORDER REACTION :

(i) Unit of rate constant L mol^{-1} $time^{-1}$.

(ii) Numerical value of k will depend upon unit of concentration.

(iii) $t_{1/2} \propto a^{-1}$ (In general $t_{1/2} \propto a^{(1-n)}$; n = order of reactions).

(iv) 2nd order reaction conforms to first order when one of the reactant in excess.

EXAMPLES :

(i) Saponification (hydrolysis of esters catalysed with alkali).

$CH_3COOC_2H_5 + NaOH \longrightarrow CH_3COONa + C_2H_5OH$

(ii) Hydrogenation of ethane $C_2H_4 + H_2 \xrightarrow{100°C} C_2H_6$.

(iii) $2\ O_3 \longrightarrow 3\ O_2$.

n^{th} ORDER REACTION.

$A \rightarrow$ Product

$$k_n t = \frac{1}{n-1}\left\{\frac{1}{(a-x)^{n-1}} - \frac{1}{a^{n-1}}\right\} \qquad [n \neq 1,\ n = \text{order}]$$

$$t_{1/2} = \frac{1}{k_n (n-1)} \cdot \left[\frac{2^{n-1}-1}{a^{n-1}}\right]$$

SIDE OR CONCURENT REACTION :

; $\ln \frac{[A]_0}{[A]_t} = (k_1 + k_2)\, t$; $\frac{[B]}{[C]} = \frac{k_1}{k_2}$

CONSECUTIVE REACTION :

$$A \xrightarrow{k_1} B \xrightarrow{k_2} C\ ;\ t_{max} = \frac{1}{(k_1 - k_2)} \ln\left(\frac{k_1}{k_2}\right); \quad [B]_{max} = [A]_0 \left(\frac{k_2}{k_1}\right)^{\frac{k_2}{k_1 - k_2}}$$

THRESHOLD ENERGY AND ACTIVATION ENERGY :

For a reaction to take place the reacting molecules must colloid together, but only those collisions, in which colliding molecules possess certain minimum energy is called threshold energy (E_T).

ACTIVATION ENERGY (E_a) :

The extra energy needed for the reactant molecules to be able to react chemically is known as Activation energy.

E_T = Threshold energy

E_a = Activation energy of forward reaction

E'_a = activation energy of backward reaction

P_1 = Potential energy of reactants

P_2 = Potential energy of products

INFLUENCE OF TEMPERATURE ON REACTION RATES :

TEMPERATURE COEFFICIENT :

The temperature coefficient of a chemical reaction is defined as the ratio of the reaction rates at two temperatures differing by 10°C. Its value usually lies between 2 & 3.

Temperature coefficient = $\frac{k_{t+10}}{k_t}$.

ARRHENIUS EQUATION :

A quantitative relationship was proposed by Arrhenius $k = A.\ e^{-Ea/RT}$ Where,

k = rate constant ; A = frequency factor (or pre – exponential factor);

R = gas constant ; T = Temperature (kelvin) ; E_a =Activation energy.

The Logarithmic expressions are $\log_{10}\frac{k_2}{k_1} = \frac{E_a}{2.303R}\left[\frac{1}{T_1} - \frac{1}{T_2}\right]$;Vant Hoff 's Isochore $\frac{d}{dt} ln\, k = \frac{E_a}{RT^2}$

GRAPHICAL REPRESENTATIONS ARE :

METHODS OF DETERMINATION OF ORDER OF REACTIONS :

A few methods commonly used are given below :

1. **Hit & Trial Method** : It is method of using integrated rate equations, where the experimental values of a, x & t are put into these equations. One which gives a constant value of k for different sets of a, x & t correspond to the order of the reaction.

2. **Graphical Method** :

(i) A plot of log (a – x) versus 't' gives a straight lines for the First order reaction.

(ii) A plot of $(a - x)^{-(n-1)}$ versus 't' gives a straight line any reaction of the order n (except n = 1).

3. **Half Life Method** : The half life of different order of reactions is given by $a_n = \left(\frac{1}{2}\right)^n a_0$.

   By experimental observation of the dependence of half life on initial concentration we can determine n, the order of reaction. $n = 1 + \frac{\log t_2 - \log t_1}{\log a_1 - \log a_2}$.

4. **Initial rate method.** Initial rate method is used to determine the order or reaction in cases where more than one reactant is used. It involves the determination of the order of different reactants separately. A series of experiments are performed in which concentration of one particular reactant is varied whereas conc. of other reactants are kept constant. In each experiment the initial rate is determined from the plot of conc. vs. time, e.g., if conc. of A is doubled, and initial rate of reaction is also doubled, order of reaction is l.

MECHANISM OF REACTIONS :

The path way which reactants are converted into the products is called the reaction mechanism. It should be clear that experimentally determined rate expression cannot be predicted from the stiochiometry of the reaction. For example for the reaction ;

$NO_2(g) + CO\ (g) \longrightarrow CO_2(g) + NO(g)$, the rate expression is ; rate = $-\frac{d}{dt}[NO_2] = k[NO_2]^2$, i.e. the expression has no dependence of CO (g) concentration.

The reason is that the reaction occurs by a series of elementary steps.
The sequence of elementary processes leading to the overall stiochiometry is known as the "Mechanism of the reaction". A_n in a sequence of reactions leading to the formation of products from reactants, the slowest step is the rate determining step.
The mechanism proposed for the above reaction is a two step one.

$NO_2 + NO_2 \longrightarrow NO + NO_3$ (step 1 : slow)

$NO_3 + CO \longrightarrow CO_2 + NO_2$ (step 2 : fast)

The sum of the two gives the stiochiometry & the slow step decided the rate expression.

Nuclear Chemistry

Neutron / proton ratio and stability

- For atomic number < 20, most stable nuclei have n: p ratio nearly 1 : 1 (except H & Ar).
- For n/p ratio > 1.5, nucleus is unstable. Largest stable nucleus is $^{209}_{83}Bi$ for which n/p ratio is 1.52.
- For atomic number > 83, there are no stable nuclei.

Magic numbers and nuclear stability

Nuclei with 2, 8, 20, 28, 50, 82 or 126 protons or neutrons are unusually stable and have a larger number of stable isotopes than neighboring nuclei in the periodic table. These numbers are called magic numbers. They are supposed to represent completely filled nuclear shells of energy levels.

- Nuclei with magic number of protons as well as neutrons have notably high stabilities. [eg. $^{4}_{2}He$, $^{16}_{8}O$, $^{40}_{20}Ca$ and $^{208}_{82}Pb$]. 165 such stable nuclei are known.
- There exist 55 known nuclei with even number of protons and odd number of neutrons, and 50 known stable nuclei with odd number of protons and even number of neutrons. On the other hand, the number of known stable nuclei having odd numbers of both neutrons and protons is only 4.

Expected emissions from unstable nucleus

1. ***n/p ratio above stability belt:*** electron (β^-) or neutron.
2. ***n/p ratio below stability belt:*** positron (β^+) or K capture.
3. ***Atomic number > 83,*** various particles, including α–particles.

Radioactive decay

- Radioactive decay is a first order process. Hence $-\frac{dN}{dt} = \lambda N$ or $N = N_0 e^{-\lambda t}$

  where N = number of radioactive nuclei at any time t ; N_0 = number of radioactive nuclei at $t = 0$; λ = decay constant.

- **Activity** activity (a) = $-\frac{dN}{dt} = \lambda N$

  S.I. units : disintegration per second (symbol s^{-1} or dps). This unit is also called *becquerel* (symbol Bq)
  Other units: Curie (Ci) 1Ci = 3.7×10^{10}dps.

- **Half life ($t_{½}$)** The time taken by half the nuclei (originally present) to decay. $t_{½} = 0.693/\lambda$

  Note : After *n* half–lives have passed, activity is reduced to $\frac{1}{2^n}$ of its initial value.

- **Average life (t_{av})** $t_{av} = 1/\lambda = 1.44\ t_{½}$

  Isotopes : Nuclei with same atomic number but different atomic mass number.
  Isobars : Nuclei with different atomic number but same atomic mass number.
  Isotones : Nuclei with same number of neutrons but different number of protons.

THE ATLAS

Some basic concept

1.Rate of reaction.
2.Rate of reaction in terms of extent of reaction.
3.Average and instantaneous rate of reaction.
4.Dependence of rate of reaction on concentration, pressure, temperature and catalyst.
5.Rate law expression.
6.Order and molecularity of reaction.

CHEMICAL KINETICS

Experimental Aspects

1.Determination of order of reaction.
(a) Graphical Method.
(b) Initial rate method.
(c) Oswald's isolation method.
(d) Half life meyhod.
2. Differential and integerated expressions for
(a) Zero order
(b) First order
(c) nth order reaction
(d) $t_{1/2}$ and $t_{p/q}$ of a reaction.
(e) Rate constant expression in which conc. terms is replaced by other variables litre pressure, volume of reagent, obsorbance etc..
(f) Brancing Decay
(g) Conseqative or sequential Decay
(h) Mechanism of reaction
3. Radioactivity.

Theoretical Aspects

1.Collision theory of rate of reaction
2. Temperature depedence of rate of reaction
3. Transition state theory for rate of reaction
4. Mechanism of reaction and steady state approximation

GLOSSARY

IMPORTANT TERMS AND DEFINITIONS

1. **Rate of reaction.** It is defined as the change in concentration of reactant (or product) in a particular time interval. Its unit is mol $L^{-1}s^{-1}$. If time is in minutes, then units are mol L^{-1} min^{-1} and so on.
2. **Average rate.** The rate of reaction measured over a long time interval is called average rate of reaction. It is equal to $\Delta x/\Delta t$ as shown in fig.(a) and (b).

Instantaneous and average rate of reaction

3. **Instantaneous rate.** It is the rate of reaction when the average rate is taken over a very small interval of time. It is equal to dx / dt as shown in fig. (a) and (b).
4. **Rate law or rate equation.** It is the expression which relates the rate of reaction with concentration of the reactants. The constant of proportionality 'k' is known as rate constant.
5. **Rate constant.** When concentration of both reactants are unity, then the rate of reaction is known as rate constant. It is also called specific reaction rate.
6. **Molecularity.** Total number of molecules of the reactants involved in the reaction is termed as its molecularity. It is always in whole number, It is never more than three. It cannot be zero.
7. **Order of a reaction.** The sum of the powers of the concentration of reactants in the rate law is termed as order of the reaction. It can be in fraction. It can be zero also.
8. **Zero order reaction.** The rate of reaction does not change with the concentration of the reactants, i.e., $\text{rate} = k[A]^{\circ}$
9. **First order reaction.** The reaction in which the rate of reaction is directly proportional to the concentration of reacting substance. Rate constant of first order reaction is

$$k = \frac{2.303}{t}\log\frac{a}{a-x} \text{ or } k = \frac{2.303}{t}\log\frac{[A_0]}{[A]}$$

where 'a' is initial concentration, (a–x) is the conc. of reactants after time 't'. The unit of 'k' is s^{-1} or min^{-1}. A plot between *l*n [A] vs. t is a straight line with slope equal to –k. [A] is concentration of reactants after time t.

10. **Half–life of a reaction.** The time taken for a reaction when half of the starting material has reacted is called half–life of a reaction. For first order reaction

$$t_{1/2} = \frac{0.693}{k}, \text{ where k is rate constant.}$$

11. **Second order reaction**. The reaction in which sum of powers of concentration terms in rate law or rate equation is equal to 2, e.g.,

$$\frac{dx}{dt} = k[A]^1[B]^1$$

12. **Third order reaction.** The reaction in which sum of powers of concentration terms in rate law or rate equation is equal to 3, e.g.,

$$\frac{dx}{dt} = k[A]^x[B]^y \text{ where } x + y = 3$$

13. **Specific rate constant (k).** It is defined as equal to rate of reaction when molar concentration of reactant is unity.
14. **Activation energy.** It is extra energy which must be possessed by reactant molecules so that collision between reactant molecules is effective and leads to formation of product molecules.
15. **Initial rate.** The rate at the beginning of the reaction when the concentrations have not changed appreciably is called in initial rate of reaction.
16. **Arrhenius equation of reaction rate.** It gives the relation between rate of reaction and temperature.

$$K = Ae^{-E_a/RT}$$

where k = rate constant A = frequency factor, E_a = energy of activation
R = gas constant, T = temperature in kelvin.

$$\ln k = \ln A - E_a/RT$$

$$\log k = \log A - \frac{E_a}{2.303\,RT}$$

17. **Photochemical reactions.** Those reactions which take place in the presence of light are called photochemical reactions. Photosynthesis is an example of photochemical reaction.
18. **Photosensitization.** The process in which a molecule that absorbs light transfers its extra energy to another molecule which may undergo a reaction. This process is called photosensitization.
19. **Chain reaction.** The sequence of reactions, where a reactive species produces more reactive species is called chain reaction. It involves free radicals.
20. **Elementary processes.** Some reactions occur by a series of elementary steps and such simple steps are called elementary processes.
21. **Mechanism of reaction.** The sequence of elementary processes leading to the overall stiochiometry of a chemical reaction is known as mechanism of a reaction.
22. **Slow reaction.** Those reactions which take place very slowly are called slow reactions, e.g., rusting of iron and reaction of oxalic acid with acidified $KMnO_4$ at room temperature are slow reactions.
23. **Life time.** The time in which 98% of the reaction is complete is called lifetime.
24. **Threshold energy.** The minimum energy that reacting species must possess in order to undergo effective collision to form product molecules is called threshold energy.
25. **Effective collision (f).** Those collisions which lead to the formation of product molecules are called effective collisions. Rate of reaction = f × z where 'z' is collision frequency and 'f' is fraction of collisions, which are effective.
26. **Collision frequency (z).** It is defined as total number of collisions per unit volume per unit time.
27. **Activated complex.** It is defined as unstable intermediate formed between reacting molecules which is highly unstable and readily changes into product.
28. **Thermodynamic stability.** A mixture of substances may not undergo reaction although thermodynamic predict the reaction to be spontaneous. Such substances are thermodynamically unstable at ordinary temperature but may not be kinetically unstable.
29. **Kinetic stability.** The reaction occurs only when the reactant crosses energy–barrier. Once it occurs, it becomes kinetically unstable because the reaction is spontaneous. The energy evolved helps the other reactants to cross energy–barrier. Thus, reactants should be thermodynamically as well as kinetically unstable so as to change into products at a particular temperature.

30. **Rate determining step.** The slowest step in the reaction mechanism is called rate determining step.

31. **Temperature coefficient.** It is the ratio of rate constant at temperature 308 K to the rate constant at temperature 298 K.

$$\text{Temperature coefficient} = \frac{\textit{Rate constant } \text{'k' at 308 K}}{\textit{Rate constant } \text{'k' at 298 K}}$$

It lies between 2 and 3.

32. **Pseudo first order reaction.** The reaction in which one reacted is in excess so order is one is called Pseudo first order reaction, e.g., acidic hydrolysis of ester.

$$CH_3COOC_2H_5 + H_2O\ (\text{excess}) \overset{H^+}{\rightleftharpoons} CH_3COOH + C_2H_5OH$$

33. **Einstein's law of photochemical equivalence.** Each atom or molecule is activated by 1 photon (quantum of light).
34. **Chain initiation step.** The step in which neutral molecule changes into free radicals by absorbing photons is called chain initiation step.
35. **Chain propagation step.** The step in which free radical reacts with neutral molecule to form a neutral molecule and a free radical is called chain propagation step.
36. **Chain termination step.** The step in which radicals combine to form neutral molecules.
37. **Fast reactions.** Those reactions which occur instantaneously and is complete in fraction of seconds are called fast reactions, e.g., $AgNO_3(aq) + HCl(aq) \longrightarrow AgCl\downarrow + HNO_3$, takes place in 10^{-12} seconds.
38. **Thermochemical reactions.** Those reactions initiated by heat energy are called thermochemical reactions. They can occur in dark. Temperature coefficient is generally high because rate of reaction increases with increase in temperature. ΔG is – ve for such reactions.

EXERCISE-I

RATE OF REACTION AND STOICHIOMETRIC COEFFICIENT

Q.1 In a catalytic experiment involving the Haber process, $N_2 + 3H_2 \longrightarrow 2NH_3$, the rate of reaction was measured as

$$\text{Rate} = \frac{\Delta[NH_3]}{\Delta t} = 2 \times 10^{-4} \text{ mol L}^{-1} \text{ s}^{-1}.$$

If there were no sides reactions, what was the rate of reaction expressed in terms of (a) N_2, (b) H_2?

Q.2 For the reaction $3BrO^- \rightarrow BrO_3^- + 2Br^-$ in an alkaline aquesous solution, the value of the second order (in BrO^-) rate constant at 80°C in the rate law for $-\frac{\Delta[BrO^-]}{\Delta t}$ was found to be 0.056L $mol^{-1}s^{-1}$.

What is the rate of constant when the rate law is written for (a) $\frac{\Delta[BrO_3^-]}{\Delta t}$, (b) $\frac{\Delta[Br^-]}{\Delta t}$?

Q.3 Dinitropentaoxide decomposes as follows :

$$N_2O_5(g) \longrightarrow 2NO_2(g) + \frac{1}{2} O_2(g)$$

Given that $-d\,[N_2O_5] / dt = k_1[N_2O_5]$

$d\,[NO_2] / dt = k_2[N_2O_5]$

$d\,[O_2] / dt = k_3[N_2O_5]$

What is the relation between k_1, k_2 and k_3?

Q.4 The reaction $2A + B + C \rightarrow D + E$ is found to be first order in A second order in B and zero order in C.

(i) Give the rate law for the reaction in the form of differential equation.

(ii) What is the effect in rate of increasing concentrations of A, B, and C two times?

Q.5 For the elementary reaction $2A + B_2 \longrightarrow 2AB$. Calculate how much the rate of reaction will change if the volume of the vessel is reduced to one third of its original volume?

Q.6 Ammonia and oxygen reacts at higher temperatures as

$4NH_3(g) + 5O_2(g) \longrightarrow 4NO(g) + 6H_2O(g)$

In an experiment, the concentration of NO increases by 1.08×10^{-2} mol $litre^{-1}$ in 3 seconds. Calculate.

(i) rate of reaction.

(ii) rate of disappearance of ammonia

(iii) rate of formation of water

Q.7 In the following reaction $2H_2O_2 \longrightarrow 2H_2O + O_2$

rate of formation of O_2 is 3.6 M min^{-1}.

(a) What is rate of formation of H_2O?

(b) What is rate of disappearance of H_2O_2?

Q.8 The reaction $A(g) + 2B(g) \longrightarrow C(g) + D(g)$ is an elementary process. In an experiment, the initial partial pressure of A & B are $P_A = 0.6$ and $P_B = 0.8$ atm, if $P_C = 0.2$ atm then calculate the ratio of rate of reaction relative to initial rate.

ZERO ORDER

Q.9 In the following reaction, rate constant is 1.2×10^{-2} M s^{-1} $A \longrightarrow B$. What is concentration of B after 10 and 20 min., if we start with 10 M of A.

Q.10 For the following data for the reaction $A \longrightarrow$ products. Calculate the value of k.

Time (min.)	[A]
0.0	0.10 M
1.0	0.09 M
2.0	0.08 M

Q.11 The rate constant for a zero order reaction is 2×10^{-2} mol $L^{-1}sec^{-1}$, if the concentration of the reactant after 25 sec is 0.25 M, calculate the initial concentration.

Q.12 A drop of solution (volume 0.10 ml) contains 6×10^{-6} mole of H^+, if the rate constant of disappearance of H^+ is 1×10^7 mole $litre^{-1}$ sec^{-1}. How long would it take for H^+ in drop to disappear?

Q.13 A certain substance A is mixed with an equimolar quantity of substance B. At the end of an hour A is 75% reacted. Calculate the time when A is 10% unreacted. (Given: order of reaction is zero)

FIRST ORDER

Q.14 A first order reaction is 75% completed in 72 min.. How long time will it take for
(i) 50% completion (ii) 87.5% completion

Q.15 A first order reaction is 20% complete in 10 min. calculate (i) the specific rate constant , (ii) the time taken for the reactions to go to 75% completion.

Q.16 Show that in case of unimolecular reaction, the time required for 99.9% of the reaction to take place in ten times that required for half of the reaction.

Q.17 A first order reaction has a rate constant is 1.5×10^{-3} sec^{-1}. How long will 5.0 g of this reactant take to reduce to 1.25 g.

Q.18 A drug is known to be ineffective after it has decomposed 30%. The original concentration of a sample was 500 units/ml. When analyzed 20 months later, the concentration was found to be 420 units/ml. Assuming that decomposition is of I order, what will be the expiry time of the drug?

Q.19 A viral preparation was inactivated in a chemical bath. The inactivation process was found to be first order in virus concentration. At the beginning of the experiment 2.0 % of the virus was found to be inactivated per minute . Evaluate k for inactivation process.

Q.20 If a reaction $A \longrightarrow$ Products, the concentrations of reactant A are C_0, aC_0, a^2C_0, a^3C_0, ... after time interval 0, t, 2t, 3t, ... where a is a constant. Given $0 < a < 1$. Show that the reaction is of first order. Also calculate the relation in k, a and t.

Q.21 The reaction $SO_2Cl_2(g) \longrightarrow SO_2(g) + Cl_2(g)$ is a first order gas reaction with $k = 2.2 \times 10^{-5}$ sec^{-1} at 320°C. What % of SO_2Cl_2 is decomposed on heating this gas for 90 min.

ORDER OF REACTION & RATE LAW

Q.22 At 800° C the rate of reaction

$$2\,NO + H_2 \longrightarrow N_2 + H_2O$$

Changes with the concentration of NO and H_2 are

	[NO] in M	$[H_2]$ in M	$-\frac{1}{2}\frac{d[NO]}{dt}$ in M sec^{-1}
(i)	1.5×10^{-4}	4×10^{-3}	4.4×10^{-4}
(ii)	1.5×10^{-4}	2×10^{-3}	2.2×10^{-4}
(iii)	3.0×10^{-4}	2×10^{-3}	8.8×10^{-4}

(a) What is the order of this reaction?
(b) What is the rate equation for the reaction?
(c) What is the rate when
$[H_2] = 1.5 \times 10^{-3}$ M and $[NO] = 1.1 \times 10^{-3}$M?

Q.23 The data below are for the reaction if NO and Cl_2 to form NOCl at 295 K

Concentration of Cl_2 [M]	Concentration of NO	Initial Rate ($M\ s^{-1}$)
0.05	0.05	1×10^{-3}
0.15	0.05	3×10^{-3}
0.05	0.15	9×10^{-3}

(a) What is the order w.r.t NO and Cl_2 in the reaction.
(b) Write the rate expression
(c) Calculate the rate constant
(d) Determine the reaction rate when concentration of Cl_2 and NO are 0.2 M & 0.4 M respectively.

Q.24 The catalytic decomposition of N_2O by gold at 900°C and at an initial pressure of 200mm is 50% complete in 53 minutes and 73% complete in 100 minutes.
(i) What is the order of the reaction?
(ii) Calculate the velocity constant.
(iii) How much of N_2O will decompose in 100 min. at the same temperature but at initial pressure of 600 mm?

Q.25 The following data are for the reaction A + B → products:

Conc. A (M)	**Conc. B (M)**	**Initial Rate (mol L^{-1} s^{-1})**
0.1	0.1	4.0×10^{-4}
0.2	0.2	1.6×10^{-3}
0.5	0.1	2.0×10^{-3}
0.5	0.5	1.0×10^{-2}

(i) What is the order with respect to A and B for the reaction?
(ii) Calculate the rate constant.
(iii) Determine the reaction rate when the concentrations of A and B are 0.2M and 0.35M, respectively.

Q.26 The pressure of a gas decomposing at the surface of a solid catalyst has been measured at different times and the results are given below

t (sec)	0	100	200	300
Pr. (Pascal)	4×10^3	3.5×10^3	3×10^3	2.5×10^3

Determine the order of reaction, its rate constant.

Q.27 The half life period of decomposition of a compound is 50 minutes. If the initial concentration is halved, the half life period is reduced to 25 minutes. What is the order of reaction?

Q.28 At 600°C, acetone (CH_3COCH_3) decomposes to ketene ($CH_2 = C = O$) and various hydrocarbons. Given the initial rate data in the table:
(a) What is the order?
(b) Write rate law
(c) Calculate rate constant
(d) Calculate the rate of decomposition when the acetone concentartion is 1.8×10^{-3} M

Experiment	Initial [CH_3COCH_3]	Rate $M\ s^{-1}$
1.	6.0×10^{-3} M	5.2×10^{-5}
2.	9.0×10^{-3} M	7.8×10^{-5}
3.	1.8×10^{-3} M	?

HALF LIFE

Q.29 The half life period of a first order reaction is 50 min. In what time will it go to 90% completion?

Q.30 A first order reaction has $k = 1.5 \times 10^{-6}$ per second at 200°C. If the reaction is allowed to run for 10 hrs., what percentage of the initial concentration would have changed into the product? What is the half life of this reaction?

Q.31 Show that in case of a first order reaction, the time required for 93.75% of the reaction to take place is four times that required for half of the reaction.

Q.32 The half time of the first order decomposition of nitramide is 2.1 hour at 15°C.

$$NH_2NO_2\ (aq.) \longrightarrow N_2O\ (g) + H_2O\ (l)$$

If 6.2 g of NH_2NO_2 is allowed to deompose, calculate (i) time taken for NH_2NO_2 to decompose 99%, and (ii) volume of dry N_2O produced at this point, measured at STP.

Q.33 A flask contains a mixture of compounds A and B. Both compounds decompose by first-order kinetics. The half-lives are 54.0 min for A and 18.0 min. for B. If the concentartions of A and B are equal initially, how long will it take for the concentration of A to be four times that of B?

Q.34 Two substances A ($t_{1/2}$= 5 mins) and B ($t_{1/2}$ = 15 mins) follow first order kinetics are taken in such a way that initially [A]= 4[B]. Calculate the time after which the concentration of both the substance will be equal.

CONCENTRATION REPLACED BY OTHER QUANTITIES IN FIRST ORDER INTEGRATED RATE LAW

Q.35 In this case we have

$A \longrightarrow B + C$

Time	t	∞
Total pressure of A + B+C	P_2	P_3

Find k.

Q.36 $A \longrightarrow B + C$

Time	t	∞
Total pressure of (B+C)	P_2	P_3

Find k.

Q.37 $A \longrightarrow B + C$

Time	0	t
Volume of reagent	V_1	V_2

The reagent reacts with A, B and C. Find k.

Q.38 $A \longrightarrow 2B + 3C$

Time	t	∞
Volume of reagent	V_2	V_3

Reagent reacts with all A, B and C. Find k.

Q.39 $S \longrightarrow G + F$

Time	t	∞
Rotation of Glucose & Fructose	r_t	r_∞

Find k.

Q.40 At 27°C it was observed during a reaction of hydrogenation that the pressure of hydrogen gas decreases from 2 atmosphere to 1.1 atmosphere in 75 minutes. Calculate the rate of reaction (in M sec^{-1}) and rate of reaction in terms of pressure.

Q.41 At 100°C the gaseous reaction $A \longrightarrow 2B + C$ was observed to be of first order. On starting with pure A it is found that at the end of 10 minutes the total pressure of system is 176 mm. Hg and after a long time 270 mm Hg. From these data find (a) initial pressure of A (b) the pressure of A at the end of 10 minutes (c) the specific rate of reaction and (d) the half life period of the reaction?

Q.42 The reaction $AsH_3(g) \longrightarrow As(s) + \frac{3}{2} H_2(g)$ was followed at constant volume at 310°C by measuring the gas pressure at intervals Show from the following figures that reaction is of first order.

Time (in hrs)	0	5	7.5	10
Total pressure (in mm)	758	827	856	882

Q.43 The decomposition of N_2O_5 according to the equation $2\,N_2O_5(g) \longrightarrow 4\,NO_2(g) + O_2(g)$ is a first order reaction. After 30 min. from start of decomposition in a closed vessel the total pressure developed is found to be 284.5 mm Hg. On complete decomposition, the total pressure is 584.5 mm Hg. Calculate the rate constant of the reaction.

Q.44 The thermal decomposition of dimethyl ether as measured by finding the increase in pressure of the reaction

$$(CH_3)_2O(g) \longrightarrow CH_4(g) + H_2(g) + CO(g)$$

at 500°C is as follows:

Time (sec.)	390	1195	3155	∞
Pressure increase (mm Hg)	96	250	467	619

the initial pressure of ether was 312 mm Hg. Write the rate equation for this reaction and determine the rate constant of reaction.

Q.45 From the following data show that decomposition of H_2O_2 in aqueous solution is first order.

Time (in minutes)	0	10	20
Volume (in c.c. of $KMnO_4$)	22.8	13.3	8.25

Q.46 A definite volume of H_2O_2 under going spontaneous decomposition required 22.8 c.c. of standard permanganate solution for titration. After 10 and 20 minutes respectively the volumes of permanganate required were 13.8 and 8.25 c.c.

(a) Find order of reaction. How may the result be explained?

(b) Calculate the time required for the decomposition to be half completed.

(c) Calculate the fraction of H_2O_2 decomposed after 25 minutes.

Q.47 The following data were obtained in experiment on inversion of cane sugar.

Time (minutes)	0	60	120	180	360	∞
Angle of rotation (degree)	+13.1	+ 11.6	+ 10.2	+9.0	+5.87	–3.8

Show that the reaction is of first order. After what time would you expect a zero reading in polarimeter?

Q.48 In the hydrolysis of propyl acetate in the presence of dilute hydrochloric acid in dilute aqueous solution the following data were recorded :

Time from start in minutes	60	350
Percentage of ester decomposed	18.17	69.12

Calculate the time in which half the ester was decomposed.

Q.49 Hydrogen peroxide solution was stored in a mild steel vessel. It was found, however, that the hydrogen peroxide decomposed on the walls of the vessel (a first order reaction). An experiment with 100 ml of a solution gave 10.31 ml oxygen (corrected to N.T.P.) after 5.1 days under similar storage conditions. Find how long the peroxide can be stored before the loss of 20.00 ml oxygen occurs (per 100 ml solution) if complete decomposition of the sample to H_2O_2 gave 46.34 ml oxygen.

Q.50 The reaction given below, rate constant for disappearance of A is 7.48×10^{-3} sec^{-1}. Calculate the time required for the total pressure in a system containing A at an initial pressure of 0.1 atm to rise to 0.145 atm and also find the total pressure after 100 sec.

$$2A(g) \longrightarrow 4B(g) + C(g)$$

PARALLEL AND SEQUENTIAL REACTION

Q.51 For a reaction $x \xrightarrow{k_1} y$, $x \xrightarrow{k_2} z$, calculate value of ratio, $\dfrac{[x]_t}{[y]+[z]}$ at any given instant t.

Q.52 $A \xrightarrow{k_1} B$, $A \xrightarrow{k_2} C$ $k_1 = x\ hr^{-1}$; $k_1 : k_2 = 1 : 10$. Calculate $\frac{[C]}{[A]}$ after one hour from the start of the reaction. Assuming only A was present in the beginning.

Q.53 A substance undergoes first order decomposition. The decomposition follows two parallel first order reactions as $A \xrightarrow{k_1} B$, $A \xrightarrow{k_2} C$; $k_1 = 1.26 \times 10^{-4}\ sec^{-1}$ and $k_2 = 3.6 \times 10^{-5}\ sec^{-1}$. Calculate the % distribution of B & C.

Q.54 For a reaction $A \longrightarrow B \longrightarrow C$ $t_{1/2}$ for A & B are 4 and 2 minutes respectively. How much time would be required for the B to reach maximum concentration.

TEMPERATURE DEPENDENCE OF RATE (ACTIVATION ENERGY)

Q.55 In gaseous reactions important for understanding the upper atmosphere, H_2O and O react bimolecularly to form two OH radicals. ΔH for this reaction is 72 kJ at 500 K and $E_a = 77\ kJ\ mol^{-1}$, then calculate E_a for the biolecular recombination of 2OH radicals to form H_2O & O at 500 K

Q.56 The energy of activation of a first order reaction is 104.5 kJ $mole^{-1}$ and pre – exponential factor (A) is $5 \times 10^{13}\ sec^{-1}$. At what temperature, will the reaction have a half life of 1 minute?

Q.57 The specific rate constant for a reaction increases by a factor of 4, if the temperature is changed from 27°C to 47°C. Find the activation energy for the reaction.

Q.58 The energy of activation and specific rate constant for a first order reaction at 25°C are 100 kJ/ mole and $3.46 \times 10^{-5}\ sec^{-1}$ respectively. Determine the temperature at which half life of the reaction is 2 hours.

$$2N_2O_5(g) \longrightarrow 2N_2O_4(g) + O_2\ (g)$$

Q.59 A first order reaction is 50% complete in 30 minutes at 27°C and in 10 minutes at 47°C. Calculate the

(a) rate constant for the reaction at 27°C & 47°C and

(b) energy of activatioin for the reaction.

Q.60 A catalyst lowers the activation energy for a certain reaction from 75 kJ to 25 kJ mol^{-1}. What will be the effect on the rate of reaction at 25°C, after things being equal.

Q.61 Given that the temperature coefficient for the saponification of ethyl acetate by NaOH is 1.75. Calculate activation energy for the saponification of ethyl acetate.

MECHANISM OF REACTION

Q.62 The reaction $2NO + Br_2 \longrightarrow 2NOBr$, is supposed to follow the following mechanism

(i) $NO + Br_2 \overset{fast}{\rightleftharpoons} NOBr_2$

(ii) $NOBr_2 + NO \xrightarrow{slow} 2NOBr$

Suggest the rate of law expression.

Q.63 For the reaction $2H_2 + 2NO \longrightarrow N_2 + 2H_2O$, the following mechanism has been suggested:

$2NO \rfloor N_2O_2$ equilibrium constant K_1 (fast)

$N_2O_2 + H_2 \xrightarrow{K_2} N_2O + H_2O$ (slow)

$N_2O + H_2 \xrightarrow{K_3} N_2 + H_2O$ (fast)

Establish the rate law for given reaction.

Q.64 Write a stoichiometric equation for the reaction whose mechanism is detailed below. Determine the value of the equilibrium constant for the first step. Write a rate law equation for the overall reaction in terms of its initial reactants.

$A_2 \rfloor 2A$ $\quad k_1 = 10^{10} s^{-1}$ (forward)

$\quad k_{-1} = 10^{10} M^{-1} s^{-1}$ (reverse)

$A + C \longrightarrow AC$ $\quad k_2 = 10^{-4} M^{-1} s^{-1}$ (slow)

Q.65 Reaction between NO and O_2 to form NO_2 is $2NO + O_2 \longrightarrow 2NO_2$ follows the following mechanism

$NO + NO \underset{K_{-1}}{\overset{K_1}{\rightleftharpoons}} N_2O_2$ (in rapid equilibrium)

$N_2O_2 + O_2 \xrightarrow{K_2} 2NO_2$ (slow)

Show that the rate of reaction is given by $\frac{1}{2}\left(\frac{d[NO_2]}{dt}\right) = K[NO]^2[O_2]$

Q.66 Deduce rate law expressions for the conversion of H_2 and I_2 to HI at 400°C corresponding to each of the following mechanisms:

(a) $H_2 + I_2 \longrightarrow 2HI$ (one step)

(b) $I_2 \rightleftharpoons 2I$
$2I + H_2 \longrightarrow 2HI$ (slow)

(c) $I_2 \rightleftharpoons 2I$
$I + H_2 \rightleftharpoons IH_2$
$IH_2 + I \longrightarrow 2HI$ (slow)

(d) Can the observed rate law expression rate = $k[H_2][I_2]$ distinguish among these mechanisms?

(e) If it is known that ultraviolet light causes the reaction of H_2 and I_2 to proceed at 200°C with the same rate law expression, which of these mechanisms becomes most improbable? Are any of these mechanisms proved?

RADIOACTIVITY

Q.67 Classify each of the following nuclides as "beta emitter", or "positron emitter":
${}^{49}_{20}Ca$ ${}^{195}_{80}Hg$ ${}^{8}_{5}B$ ${}^{150}_{67}Ho$ ${}^{30}_{13}Al$ ${}^{94}_{36}Kr$. Note: ${}^{200}_{80}Hg$ and ${}^{165}_{67}Ho$ are stable

Q.68 Of the three isobars ${}^{114}_{48}Cd$ ${}^{114}_{49}In$ and ${}^{114}_{50}Sn$, which is likely to be radioactive? Explain your choice.

Q.69 Complete the following nuclear equations:

(a) ${}^{14}_{7}N + {}^{4}_{2}He \rightarrow {}^{17}_{8}O + ...$

(b) ${}^{9}_{4}Be + {}^{4}_{2}He \rightarrow {}^{12}_{6}C + ...$

(c) ${}^{9}_{4}Be\ (p, \alpha).....$

(d) ${}^{30}_{15}P \rightarrow {}^{30}_{14}S + ...$

(e) ${}^{3}_{1}H \rightarrow {}^{3}_{2}He + ...$

(f) ${}^{43}_{20}Ca(\alpha,....) \rightarrow {}^{46}_{21}Sc$

Q.70 What symbol is needed to complete the nuclear equation ${}^{63}_{29}Cu(p,.....){}^{62}_{29}Cu$?

Q.71 Complete the following equations.

(a) ${}^{23}_{11}Na + {}^{4}_{2}He \rightarrow {}^{26}_{12}Mg + ?$

(b) ${}^{64}_{29}Cu \rightarrow \beta^+ + ?$

(c) ${}^{106}Ag \rightarrow {}^{106}Cd + ?$

(d) ${}^{10}_{5}B + {}^{4}_{2}He \rightarrow {}^{13}_{7}N + ?$

Q.72 How many α and β particle will be emitted when ${}^{a}_{c}X$ changes to ${}^{b}_{d}Y$?

Q.73 What is the α-activity in disintigration per minute 1 gm sample of ${}^{226}Ra$. ($t_{1/2}$ = 1620 year)

Q.74 The half life of the nuclide Rn^{220} is 54.5 sec. What mass of radon is equivalent to 1 millicurie.

Q.75 The activity of the radioactive sample drops to $\left(\frac{1}{64}\right)^{th}$ of its original value in 2 hr find the decay constant (λ).

Q.76 ${}_{84}Po^{210}$ decays with α to ${}^{206}_{82}Pb$ with a half life of 138.4 days. If 1.0 gm of Po^{210} is placed in a closed tube, how much helium accumlate in 69.2 days at STP.

Q.77 The half life period of ${}_{53}I^{125}$ is 60 days. What % of radioactivity would be present after 240 days.

Q.78 At a certain instant a piece of radioactive material contains 10^{12} atoms. The half life of material is 30 days. Calculate the no. of disintegrations in one second.

Q.79 Calculate the age of a vegetarian beverage whose tritium content is only 15% of the level in living plants. Given $t_{1/2}$ for ${}_{1}H^{3}$ = 12.3 years.

Q.80 A radioactive substance decays 20% in 10 min if at start there are 5×10^{20} atoms present, after what time will the number of atoms be reduced to 10^{18} atoms?

PROFICIENCY TEST

Q.1 ***Fill in the blanks with appropriate items :***

1. 1 Curie = _____ Bq.
2. $^{14}_{6}C$ decays by emission of _____.
3. Emission of a β-particle by a nuclide results in the formation _____ of the element.
4. The number of α and β-particles emitted, when the following nuclear transformation takes place are _____ and _____ respectively.

   $^{238}_{92}X \longrightarrow ^{206}_{82}Y$
5. The nuclides with same difference of number of neutrons and number of protons are called _____.
6. When $^{30}_{15}P$ emits a position, the daughter nuclide formed is _____.
7. A nuclide which lies above the zone of stability is likely to emit _____.
8. $^{3}_{1}H$ and $^{4}_{2}He$ are _____.
9. The half-life period of radioactive element if 87.5% of it disintegrates in 40 min is _____.
10. For collision to be effective the energy possessed by the colliding molecules should be equal to or greater than the _____.
11. In the reaction, $H_2 + I_2 \longrightarrow 2HI$, the rate of disappearance of H_2 is _____ the rate of appearance of HI.
12. For an endothermic process, the minimum value of activation energy can be _____.
13. The rate of a reaction is _____ to the collision frequency.
14. The rate constant for the zero order reaction has the dimensions_____.
15. The reactions with molecularity more than three are _____.
16. A catalyst increases the rate of the reaction by_____ activation energy of reactants.
17. If activation energy of reaction is low, it proceeds at _____ rate.
18. In a multistep reaction, the _____ step is rate determining.
19. Rate constant of a reaction, generally _____ with increase in temperature.
20. The ratio $t_{7/8} / t_{1/2}$ for a first order reaction would be equal to _____.
21. For a zero order reaction, the rate of the reaction is equal to the _____ of the reaction.
22. The value of temperature coefficient is generally between _____.
23. For a certain reaction, $xM \longrightarrow yL$, the rate of reaction increases by 4 times when the concentration of M is doubled. The rate law is _____.
24. The rate equation $r = k\,[A][B]^{1/2}$ suggests that order of overall reaction is _____.
25. A plot of [A] vs t for a certain reaction $A \longrightarrow B$ with $r = k\,[A]^0$ will be a straight line with slope equal to _____.

26. $[E_{activated\ complex} - E_{reactants}]$ = _____.

27. Among similar reactions, the endothermic reaction has _____ activation energy than exothermic reaction.

28. For a _____ order reaction the half-life ($t_{1/2}$) is independent of the initial conc. of the reactants.

29. For a first order reaction a graph of log [A] vs t has a slope equal to _____.

30. Average lifetime of a nuclei, T_{av} = _____ $t_{1/2}$.

Q.2 ***True or False Statements :***

1. Order of a reaction can be written from the balanced chemical equation.
2. For a reaction having order equal to 3/2, the units for rate constant are sec^{-1}.
3. In a complex reaction the rate of overall reaction is governed by the slowest step.
4. $t_{1/2}$ for a first order reaction is 6.93 s, the value of rate constant for the reaction would be $10s^{-1}$.
5. The ratio $t_{1/2} / t_{7/8}$ for a first order reaction is equal to 1/3.
6. The rate of an exothermic reaction increases with the rise in temperature.
7. Molecularity of a reaction is always whole number.
8. The reactants which are thermodynamically unstable are always kinetically unstable also.
9. Order and molecularity of a single step reaction may or may not be same.
10. The activation energy of a catalysed reaction is more than the activation energy of the uncatalysed reaction.
11. For a zero order reaction $t_{3/4}$ is related to $t_{1/2}$ as $t_{3/4} = 1.5\ t_{1/2}$
12. A nuclide having one proton and one neutron is represented as ${}^{1}_{1}H$.
13. A radioactive element decays by emitting one α and two β-particles. The daughter element formed is an isotope of the parent element.
14. The daughter product formed by the emission of α-particle has mass number less by 4 units than the parent nuclide.
15. ${}^{27}_{13}Al$ is a stable isotope while ${}^{29}_{13}Al$ is expected to disintegrate by β-emission.
16. Half-life period of a radioactive substance can be changed by using some suitable catalyst.
17. Emission of a β-particle by a radioactive nuclide results in decrease in N / P ratio.
18. Positron has same mass as that of an electron.
19. ${}^{14}_{9}N$ and ${}^{16}_{8}O$ are isotones.
20. The S.I.unit of activity is Curie (Ci).

EXERCISE -II

Q.1 To investigate the decomposition of oxalic acid in concentrated H_2SO_4 at 50°C, a scientist prepared a 1/40 M solution of oxalic acid in 99.5 percent H_2SO_4, then removed aliquots at various reaction times t, and then determined the volumes υ of a potassium permanganate solution required to react with a 10 ml portion. The results are given below :

t, *min*	0	120	240	420	600	900	1440
υ,*mL*	11.45	9.63	8.11	6.22	4.79	2.97	1.44

Determine the reaction order with respect to oxalic acid and evaluate the specific rate constant.

Q.2 A solution of A is mixed with an equal volume of a solution of B containing the same number of moles, and the reaction A+B=C occurs. At the end of 1h, A is 75 % reacted. How much of A will be left unreacted at the end of 2 h if the reaction is (a) first order in A and zero order in B; (b) first order in both A and B ; and (c) zero order in both A and B ?

Q.3 The approach to the following equilibrium was observed kinetically from both directions:
$PtCl_4^{2-} + H_2O \rightleftharpoons [Pt(H_2O)Cl_3^-] + Cl^-$ at 25°C, it was found that

$$-\frac{\Delta}{\Delta t}[PtCl_4^{2-}] = [3.9\times10^{-5}\ sec^{-1}][PtCl_4^{2-}] - [2.1\times10^{-3}\ L.mol^{-1}\ sec^{-1}]\times[Pt(H_2O)Cl_3]^-[Cl^-]$$

What is the value of equilibrium constant for the complexation of the fourth Cl^- by Pt(II)?

Q.4 The oxidation of certain metals is found to obey the equation $\tau^2 = \alpha t + \beta$ where τ is the thickness of the oxide film at time t, α and β are contants. What is the order of this reaction?

Q.5 The complex $[Co(NH_3)_5F]^{2+}$ reacts with water according to the equation.
$[Co(NH_3)_5F]^{2+} + H_2O \rightarrow [Co(NH_3)_5(H_2O)]^{3+} + F^-$
The rate of the reaction = rate const. x$[complex]^a$x$[H^+]^b$. The reaction is acid catalysed i.e. $[H^+]$ does not change during the reaction. Thus rate = $k'[Complex]^a$ where $k' = k[H^+]^b$, calculate 'a' and 'b' given the following data at 25^0C.

[Complex]M	$[H^+]$M	$T_{1/2}$hr	$T_{3/4}$hr
0.1	0.01	1	2
0.2	0.02	0.5	1

Q.6 The reaction $CH_3{-}CH_2{-}NO_2 + OH^- \longrightarrow CH_3{-}CH{-}NO_2 + H_2O$ obeys the rate law for pseudo first order kinetics in the presence of a large excess of hydroxide ion. If 1% of nitro ethane undergoes reaction in half a minute when the reactant concentration is 0.002 M, What is the pseudo first order rate constant?

Q.7 A flask containing a solution a solution of N_2O_5 in CCl_4 was placed in a thermostat at 40°C. The N_2O_5 began to decompose by a first–order reaction, forming NO_2 and N_2O_4, which remained in the solution, and oxygen, which defined pressure. The measurements were started (t = 0) when 10.75ml gas had collected. At t = 2400 sec., 29.65ml was measured. After a very long time, (t = ∞)45.50ml was measured. Find the (a) rate constant, (b) half–life time for reaction at 40°C in CCl_4 solution. (c) What volume of gas should have collected after 4800 sec?

Q.8 At room temperature (20°C) orange juice gets spoilt in about 64 hours. In a referigerator at 3°C juice can be stored three times as long before it gets spoilt. Estimate (a) the activation energy of the reaction that causes the spoiling of juice. (b) How long should it take for juice to get spoilt at 40°C?

Q.9 A first order reaction, A → B, requires activation energy of 70 kJ mol^{-1}. When a 20% solution of A was kept at 25°C for 20 minutes, 25% decomposition took place. What will be the percent decomposition in the same time in a 30% solution maintianed at 40°C? Assume that activation energy remains constant in this range of temperature.

Q.10 Two reations (i) A → products (ii) B → products, follow first order kinetics. The rate of the reaction (i) is doubled when the temperature is raised from 300 K to 310K. The half life for this reaction at 310K is 30 minutes. At the same temperature B decomposes twice as fast as A. If the energy of activation for the reaction (ii) is half that of reaction (i), calculate the rate constant of the reaction (ii) at 300K.

Q.11 Choose the correct set of identifications.

	(1)	(2)	(3)	(4)
(A)	ΔE for $E + S \rightarrow ES$	E_a for $ES \rightarrow EP$	$\Delta E_{overall}$ for $S \rightarrow P$	E_a for $EP \rightarrow E + P$
(B)	E_a for $E + S \rightarrow ES$	ΔE for $E + S \rightarrow ES$	E_a for $ES \rightarrow EP$	$\Delta E_{overall}$ for $S \rightarrow P$
(C)	E_a for $ES \rightarrow EP$	E_a for $EP \rightarrow E + P$	$\Delta E_{overall}$ for $S \rightarrow P$	ΔE for $EP \rightarrow E + P$
(D)	E_a for $E + S \rightarrow ES$	E_a for $ES \rightarrow EP$	E_a for $EP \rightarrow E + P$	$\Delta E_{overall}$ for $S \rightarrow P$
(E)	ΔE for $E + S \rightarrow ES$	$\Delta E_{overall}$ for $S \rightarrow P$	ΔE for $_1$ $EP \rightarrow E + P$	E_a for $EP \rightarrow E + P$

Q.12 A certain organic compound A decomposes by two parallel first order mechanism

If $k_1 : k_2 = 1 : 9$ and $k_1 = 1.3 \times 10^{-5}\ s^{-1}$.

Calculate the concentration ratio of C to A, if an experiment is started with only A and allowed to run for one hour.

Q.13 Decomposition of H_2O_2 is a first order reaction. A solution of H_2O_2 labelled as 20 volumes was left open. Due to this, some H_2O_2 decomposed. To determine the new volume strength after 6 hours, 10 mL of this solution was diluted to 100mL. 10mL of this diluted solution was titrated against 25mL of 0.025M $KMnO_4$ solution under acidic conditions. Calculate the rate constant for decomposition of H_2O_2.

Q.14 The reaction

$$\text{cis–Cr(en)}_2\text{(OH)}^+_2 \underset{k_2}{\overset{k_1}{\rightleftharpoons}} \text{trans–Cr(en)}_2\text{(OH)}^+_2$$

is first order in both directions. At 25°C the equilibrium constant is 0.16 and the rate constant k_1 is $3.3 \times 10^{-4} s^{-1}$. In an experiment starting with the pure *cis* form, how long would it take for half the equilibrium amount of the *trans* isomer to be formed ?

Q.15 A metal slowly forms an oxide film which completely protects the metal when the film thickness is 3.956 thousand ths of an inch. If the film thickness is 1.281 thou. in 6 weeks, how much longer will it be before it is 2.481 thou.? The rate of film formation follows first order kinetics.

Q.16 An optically active compound A upon acid catalysed hydrolysis yield two optically active compound B and C by pseudo first order kinetics. The observed rotation of the mixture after 20 min was 5° while after completion of the reaction it was – 20°. If optical rotation per mole of A, B & C are 60°, 40° & – 80°. Calculate half life and average life of the reaction.

Q.17 A bacterial preparation was inactivated in a chemical bath. The inactivation process was found to be first order in bacterial concentration having rate constant $1.7\times10^{-2}\ sec^{-1}$. Meanwhile the multiplication of bacteria (1bacterium $\rightarrow$ 2 bacteria) which also follows first order kinetics with rate constant $1.5\times10^{-3}\ sec^{-1}$ also continued. Calculate the number of bacteria left after 2 minutes if the initial number of bacteria is 10^3.

Q.18 The formation in water of *d*–potassium chromo–oxalate from its *l*–form is reversible reaction which is first order in both directions, the racemate being the equilibrium product. A polarimeter experiment at 22°C showed that, after 506 sec, 12 mole % of the *l*–isomer was converted to the *d*–form. Find the rate constant for the forward and the reverse reactions.

Q.19 For a reversible first–order reaction $A \underset{k_2}{\overset{k_1}{\rightleftharpoons}} B$

$k_1 = 10^{-2}\ s^{-1}$ and $[B]_{eq}/[A]_{eq} = 4$. If $[A]_0 = 0.01$ mole L^{-1} and $[B]_0 = 0$, what will be the concentration of B after 30 s ?

Q.20 For the reaction $A \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} P$. Following data is produced:

Time / Hr.	0	1	2	3	4	∞
% A	100	72.5	56.8	45.6	39.5	30

Find k_1 , k_{-1} and K_{eq}.

Q.21 For the system $\underset{(g)}{A} \rightleftharpoons \underset{(g)}{B}$, ΔH for the forward reaction is –33 kJ/mol (Note : ΔH = ΔE in this case).

Show that equilibrium constant $K = \frac{[B]}{[A]} = 5.572 \times 10^5$ at 300 K. If the activation energies E_f & E_b are in the ratio 20 : 31, calculate E_f and E_b at this temperature. Assume that the pre-exponential factor is the same for the forward and backward reactions.

Q.22 The conversion of A into B is an autocatalytic reaction $A \rightarrow B$ where B catalyzes the reaction. The rate equation is –dx/dt = Kxy where x and y are concentrations of A and B at time t. Integrate this equation for initial concentrations x_0 and y_0 for A and B. Show that : $kt = \frac{2.303}{x_0 + y_0} \log \frac{x_0 y}{x y_0}$.

Q.23 A vessel contains dimethyl ether at a pressure of 0.4 atm. Dimethyl ether decomposes as $CH_3OCH_3(g) \longrightarrow CH_4(g) + CO(g) + H_2(g)$. The rate constant of decomposition is $4.78 \times 10^{-3}\ min^{-1}$. Calculate the ratio of initial rate of diffusion to rate of diffusion after 4.5 hours of initiation of decomposition. Assume the composition of gas present and composition of gas diffusing to be same.

Q.24(a) The reaction A proceeds in parallel channels $A \begin{matrix} \nearrow B \\ \searrow C \end{matrix}$ Although the $A \rightarrow C$ branch is thermodynamically more favorable than the branch $A \rightarrow B$, the product B may dominate in quantity over C. Why may this be so?

(b) In the above problem, suppose the half life values for the two branches are 60minutes and 90 minutes, what is the overall half-life value?

Q.25 For the two parallel reactions $A \xrightarrow{k_1} B$ and $A \xrightarrow{k_2} C$, show that the activation energy E′ for the disappearance of A is given in terms of activation energies E_1 and E_2 for the two paths by

$$E' = \frac{k_1 E_1 + k_2 E_2}{k_1 + k_2}$$

Q.26 For the mechanism $A + B \underset{K_2}{\overset{K_1}{\rightleftharpoons}} C$ $\quad C \xrightarrow{k_3} D$

(a) Derive the rate law using the steady-state approximation to eliminate the concentration of C.

(b) Assuming that $k_3 << k_2$, express the pre-exponential factor A and E_a for the apparent second-order rate constant in terms of A_1, A_2 and A_3 and E_{a1}, E_{a2} and E_{a3} for the three steps.

Q.27 The reaction of formation of phosgene from CO and Cl_2 is $CO + Cl_2 \longrightarrow COCl_2$

The proposed mechanism is

(i) $Cl_2 \underset{K-1}{\overset{K_1}{\rightleftharpoons}} 2Cl$ (fast equilibrium) (ii) $Cl + CO \underset{K-2}{\overset{K_2}{\rightleftharpoons}} COCl$ (fast equilibrium)

(iii) $COCl + Cl_2 \xrightarrow{K_3} COCl_2 + Cl$ (slow)

Show that the above mechanism leads to the following rate law $\frac{d[COCl_2]}{dt} = K[CO][Cl_2]^{3/2}$.

Where $K = k_3 . \frac{k_2}{k_{-2}} \left(\frac{k_1}{k-1}\right)^{1/2}$.

Q.28 The following kinetic data have been obtained at 250 °C, for the reaction

$$CO\,(g) + Cl_2\,(g) \longrightarrow COCl_2(g)$$

SET – 1		**SET – 2**	
Initial Pressure CO = 400 Pa		Initial Pressure CO = 1600×10^3 Pa	
$Cl_2 = 800 \times 10^3$ Pa		Cl_2 = 400 Pa	
Time(sec)	Pressure of $COCl_2$ (Pa)	Time(sec)	Pressure of $COCl_2$ (Pa)
0	0	0	0
2072	200	2070	300
4140	300	4140	375
10280	375	infinity	400
infinity	400		

(i) Determine the order of reaction with respect to CO and Cl_2.

(ii) Calculate the rate constant, when pressure in pascal and time in seconds.

Q.29 The decomposition of a compound P, at temperature T according to the equation

$$2P_{(g)} \longrightarrow 4Q_{(g)} + R_{(g)} + S_{(l)}$$

is the first order reaction. After 30 minutres from the start of decomposition in a closed vessel, the total pressure developed is found to be 317 mm Hg and after a long period of time the total pressure observed to be 617 mm Hg. Calculate the total pressure of the vessel after 75 mintute, if volume of liquid S is supposed to be negligible. Also calculate the time fraction $t_{7/8}$.

Given : Vapour pressure of S (*l*) at temperature T = 32.5 mm Hg.

Q.30 A certain reactant B^{n+} is getting converted to $B^{(n+4)+}$ in solution. The rate constant of this reaction is measured by titrating a volume of the solution with a reducing reagent which only reacts with B^{n+} and $B^{(n+4)+}$. In this process, it converts B^{n+} to$B^{(n-2)+}$ and $B^{(n+4)+}$ to$B^{(n-1)+}$. At *t=0*, the volume of the reagent consumed is 25 ml and at t = 10 min, the volume used up is 32 ml. Calculate the rate constant of the conversion of B^{n+} to $B^{(n+4)+}$ assuming it to be a first order reaction.

Q.31 The catalytic decomposition of formic acid may take place in two ways :

(a) $HCOOH = H_2O + CO$ (b) $HCOOH = H_2 + CO_2$.

The rate constant and activation energy for reaction (a) are 2.79×10^{-3} min^{-1} at 236°C and 12.0 kcal $mole^{-1}$ respectively and for reaction (b) are 1.52×10^{-4} min^{-1} at 237°C and 24.5 kcal $mole^{-1}$ respectively. Find the temperature which will give a product made up of equimolar quantities of water vapour, carbon monoxide, hydrogen and carbon dioxide.

Q.32 The rate constant for the forward reaction A → Product is given by

$$\log k\,(sec^{-1}) = 14.34 - \frac{1.25\times10^4 K}{T}$$

and the rate constant for the reverse reaction is 1.2×10^{-4} sec^{-1} at 50°C. Calculate the value of maximum rate constant possible for the backward reaction. Given : Enthalpy of the reaction = – 478 kJ/mol.

Q.33(a) The equilibrium between two isomers 'A' and 'B' can be represented as follow .

$$A \underset{k_2}{\overset{k_1}{\rightleftharpoons}} B$$

Where k_1 and k_2 are first order rate constants for forward and reverse reactions respectively. Starting with a non equilibrium mixture of conc. $[A]_0$ = a and $[B]_0$ = b, it was found that 'x' mole of 'A' has reacted after time 't'. Give an expression for rate, $\frac{dx}{dt}$, and hence show that integerated rate expression is $\ln\left(\frac{P}{P-x}\right) = (k_1 + k_2)\,t$ where $P = \left(\frac{k_1a - k_2b}{k_1 + k_2}\right)$

(b) After 69.3 minute $x = \frac{P}{2}$. Calculate k_1 and k_2 if equilibrium constant K = 4.

(Given : log2 = 0.3010)

Q.34 The gaseous reaction : $n_1A(g) \rightarrow n_2B(g)$ is first order with respect to A. It is studied at a constant pressure, with a_0 as the initial amount of A. Show that the volume of system at the concentration of A at time 't' are given by the expressions

$$V = V_0\left[\left(\frac{n_2}{n_1}\right)-\left(\frac{n_2}{n_1}-1\right)\exp(-n_1kt)\right] \quad ; \quad [A]_t = [A]_0\left[\frac{\exp(-n_1kt)}{(n_2/n_1)-\{(n_2/n_1)-1\}\exp(-n_1kt)}\right]$$

Q.35 For the following first order gaseous reaction

$$A(g) \begin{cases} \xrightarrow{k_1} 2B(g) \\ \xrightarrow{k_2} C(g) \end{cases}$$

The initial pressure in a container of capacity V litres is 1 atm. Pressure at time t = 10 sec is 1.4 atm and after infinite time it becomes 1.5 atmosphere. Find the rate constant k_1 and k_2 for the appropriate reactions.

RADIOACTIVITY

Q.36 In a nature decay chain series starts with $_{90}Th^{232}$ and finally terminates at $_{82}Pb^{208}$. A thorium ore sample was found to contain 8×10^{-5} ml of helium at STP and 5×10^{-7} gm of Th^{232}. Find the age of ore sample assuming that source of He to be only due to decay of Th^{232}. Also assume complete retention of helium within the ore. (Half–life of $Th^{232} = 1.39 \times 10^{10}$Y)

Q.37 A 0.20 mL sample of a solution containing 1.0×10^{-7}Ci of ^3_1H is injected into the blood stream of a laboratory animal. After sfficient time for circulatory equilibrium to be established, 0.10 mL blood is found to have an activity of 20 dis/min. Calculate the blood volume of the animal.

Q.38 A sample of $^{131}_{53}I$, as iodine ion, was administered to a patient in a carrier consisting of 0.10 mg of stable iodide ion. After 4.00 days, 67.7% of the initial radioactivity was detected in the thyroid gland of the patient. What mass of the stable iodide ion had migrated to the thyroid gland? ($t_{½}$ = 8 days.)

Q.39 Potassium having atomic mass=39.1u contains 93.10 atom % ^{39}K, having atomic mass 38.96371 u; 0.0118 atom % ^{40}K, which has mass of 40.0 u and is radioactive with $t_{½} = 1.3 \times 10^9$y and 6.88 atom % ^{41}K having a mass of 40.96184 u. Calculate the specific activity of naturally occurring potassium.

Q.40 A mixture of ^{239}Pu and ^{240}Pu has a specific activity of 6×10^9 dis/s/g. The half lives of the isotopes are 2.44×10^4 y and 6.08×10^3 y respectively. calculate the isotopic composition of this sample.

Q.41 $_{92}U^{238}$ by successive radioactive decays changes to $_{82}Pb^{206}$. A sample of uranium ore was analyzed and found to contain 1.0g of U^{238} and 0.1g of Pb^{206}. Assuming that all the Pb^{206} had accumulated due to decay of U^{238}, find out the age of the ore. (Half life of $U^{238} = 4.5 \times 10^9$ years).

Q.42 Fallout from nuclear explosions contains ^{131}I and ^{90}Sr. Calculate the time required for the activity of each of these isotopes to fall to 1.0 % of its initial value. Radioiodine and radiostrontium tend to concentrate in the thyroid and the bones, respectively, of mammals which ingest them. Which isotope is likely to produce the more serious long-term effects? Half-life of ^{131}I = 8 days, ^{90}Sr = 19.9 yrs.

Q.43 $_{84}Po^{218}$ ($t_{/12}$ = 3.05 min) decay to $_{82}Pb^{214}$ ($t_{1/2}$ = 2.68 min) by α-emission, while Pb^{214} is a β-emitter. In an experiment starting with 1 gm atom of Pure Po^{218}, how much time would be required for the number of nuclei of $_{82}Pb^{214}$ to reach maximum.

Q.44 A sample pitch blende is found to contain 50% Uranium and 2.425% Lead. Of this Lead only 93% was Pb^{206} isotope, if the disintegration contant is 1.52×10^{-10} yr^{-1}. How old could be the pitch blende deposit.

Q.45 A sample of Uraninite, a Uranium containing mineral was found on analysis to contain 0.214 gm of Pb^{206} for every gram of Uranium. Assuming that the lead all resulted from the radioactive disintegration of the Uranium since the geological formation of the Uraninite and all isotopes of Uranium other than ^{238}U can be neglected. Estimate the day when the mineral was formed in the Earth's crust. [$t_{1/2}$ of $^{238}U = 4.5 \times 10^9$ years]

EXERCISE -III

Q.1 The rate of a reaction is expressed in different ways as follows :

$$+\frac{1}{2}\frac{d[C]}{dt} = -\frac{1}{3}\frac{d[D]}{dt} = +\frac{1}{4}\frac{d[A]}{dt} = -\frac{d[B]}{dt}$$

The reaction is:

(A) $4A + B \longrightarrow 2C + 3D$ (B) $B + 3D \longrightarrow 4A + 2C$

(C) $A + B \longrightarrow C + D$ (D) $B + D \longrightarrow A + C$

Q.2 Units of rate constant for first and zero order reactions in terms of molarity M unit are respectively

(A) sec^{-1}, $M\ sec^{-1}$ (B) sec^{-1}, M (C) $M\ sec^{-1}$, sec^{-1} (D) M, sec^{-1}

Q.3 The rate constant for the forward reaction $A(g) \rightleftharpoons 2B(g)$ is $1.5 \times 10^{-3}\ s^{-1}$ at 100 K. If 10^{-5} moles of A and 100 moles of B are present in a 10 litre vessel at equilibrium then rate constant for the backward reaction at this temperature is

(A) $1.50 \times 10^{4}\ L\ mol^{-1}\ s^{-1}$ (B) $1.5 \times 10^{11}\ L\ mol^{-1}\ s^{-1}$

(C) $1.5 \times 10^{10}\ L\ mol^{-1}\ s^{-1}$ (D) 1.5×10^{-11}

Q.4 Reaction $A + B \longrightarrow C + D$ follow's following rate law : rate = $k = [A]^{+\frac{1}{2}}[B]^{\frac{1}{2}}$. Starting with initial conc. of one mole of A and B each, what is the time taken for amount of A of become 0.25 mole. Given $k = 2.31 \times 10^{-3}\ sec^{-1}$.

(A) 300 sec. (B) 600 sec. (C) 900 sec. (D) none of these

Q.5 Consider the following first order competing reactions:

$X \xrightarrow{k_1} A + B$ and $Y \xrightarrow{k_2} C + D$

if 50% of the reaction of X was completed when 96% of the reaction of Y was completed, the ratio of their rate constants (k_2/k_1) is

(A) 4.06 (B) 0.215 (C) 1.1 (D) 4.65

Q.6 A first order reaction is 50% completed in 20 minutes at 27°C and in 5 min at 47°C. The energy of activation of the reaction is

(A) 43.85 kJ/mol (B) 55.14 kJ/mol (C) 11.97 kJ/mol (D) 6.65 kJ/mol

Q.7 For the first order reaction $A \longrightarrow B + C$, carried out at 27 ºC if 3.8×10^{-16} % of the reactant molecules exists in the activated state, the E_a (activation energy) of the reaction is

(A) 12 kJ/mole (B) 831.4 kJ/mole (C) 100 kJ/mole (D) 88.57 kJ/mole

Q.8 The reactions of higher order are rare because

(A) many body collisions involve very high activation energy

(B) many body collisions have a very low probability

(C) many body collisions are not energetically favoured.

(D) many body collisions can take place only in the gaseous phase.

Q.9 The following mechanism has been proposed for the exothermic catalyzed complex reaction.

$$A + B \underset{}{\overset{fast}{\rightleftharpoons}} IAB \xrightarrow{k_1} AB + I \xrightarrow{k_2} P + A$$

If k_1 is much smaller than k_2. The most suitable qualitative plot of potential energy (P.E.) versus reaction coordinate for the above reaction.

(A)

(B)

(C)

(D)

Question No. 10 to 11 (2 questions)

Oxidation of metals is generally a slow electrochemical reaction involving many steps. These steps involve electron transfer reactions. A particular type of oxidation involve overall first order kinetics with respect to fraction of unoxidised metal **(1–*f*)** surface thickness relative to maximum thickness **(T)** of oxidised surface, when metal surface is exposed to air for considerable period of time

Rate law : $\frac{df}{dt}$ **= k(1 – *f*), where *f* = x/T,**

x = thickness of oxide film at time 't'

& T = thickness of oxide film at t = ∞

A graph of ln(1 – *f*) vs t is shown in the adjacent figure.

Q.10 The time taken for thickness to grow 50% of 'T' is

(A) 23.1 hrs (B) 46.2 hrs (C) 100 hrs (D) 92.4 hrs

Q.11 The exponential variation of '*f*' with t(hrs) is given by

(A) $[1 - e^{-3t/200}]$ (B) $e^{-3t/200} - 1$ (C) $e^{-3t/200}$ (D) $e^{3t/200}$

Question No. 12 to 13 (2 questions)

For a hypothetical elementary reaction $A \xrightarrow{k_1} 2B$, $A \xrightarrow{k_2} 2C$ where $\frac{k_1}{k_2} = \frac{1}{2}$

Initially only 2 moles of A are present.

Q.12 The total number of moles of A, B & C at the end of 50% reaction are

(A) 2 (B) 3 (C) 5 (D) None

Q.13 Number of moles of B are

(A) 2 (B) 1 (C) 0.666 (D) 0.333

Q.14 Two radioactive nuclides A and B have half lives of 50 min and 10 min respectively. A fresh sample contains the nuclides of B to be eight time that of A. How much time should elapse so that the number of nuclides of A becomes double of B

(A) 30 (B) 40 (C) 50 (D) None

Q.15 Give the correct order of initials **T** (true) or **F** (false) for following statements.

(i) On bombarding $_7N^{14}$ Nuclei with α-particle, the nuclei of the product formed after release of proton would be $_8O^{17}$.

(ii) $_{89}Ac^{228}$ and $_{90}Th^{229}$ belong respectively to Actinium and Neptunium series.

(iii) Nuclide and it's decay product after α-emission are called isodiaphers.

(iv) Half life of radium is 1580 years. Its average life will be 1097.22 years.

(A) TFTF (B) TTTF (C) FFTT (D) TFFF

EXERCISE-IV

OBJECTIVE PROBLEM

Q.1 For a first order reaction
(A) the degree of dissociation is equal to $(1 - e^{-kt})$
(B) a plot of reciprocal concentration of the reactent vs time gives a straight line.
(C) the time taken for completeion of 75% of reaction is thrice the $t_{1/2}$ of the reaction
(D) the pre-exponential factor in the Arrhenius equation has the dimensionof time, T^{-1}. **[JEE 1998]**

Q.2 The rate law for the reaction
RCl + NaOH (aq) $\longrightarrow$ ROH + NaCl is given by Rate = k[RCl]. The rate of the reaction will be
(A) Doubled on doubling the concentration of sodium hydroxide
(B) Halved on reducing the concentration of alkyl halide to one half
(C) Decreased on increasing the temperature of reaction
(D) Unaffected by increasing the temperature of the reaction. **[JEE 1998]**

Q.3 Which of the following statement(s) is (are) correct
(A) A plot of log K_p versus 1/T is linear
(B) A plot of log [X] versus time is linear for a first order reaction, X $\longrightarrow$ P
(C) A plot of log P versus 1/T is linear at constant volume.
(D) A plot of P versus 1/V is linear at constant temperature. **[JEE 1999]**

Q.4 The rate constnat for the reaction **[JEE SCR 2000]**

$$2N_2O_5 \longrightarrow 4NO_2 + O_2$$

is 3.0×10^{-5} sec^{-1}. if the rate is 2.4×10^{-5} mol $litre^{-1}$ sec^{-1}, then the concentration of N_2O_5 (in mol $litre^{-1}$) is
(A) 1.4 (B) 1.2 (C) 0.004 (D) 0.8

Q.5 If I is the intensity of absorbed light and C is the concentration of AB for the photochemical proces AB + hv $\longrightarrow$ AB*, the rate of formation of AB* is directly proportional to **[JEE SCR 2001]**
(A) C (B) I (C) I^2 (D) CI

Q.6 Consider the chemical reaction, $N_2(g) + 3H_2(g) \longrightarrow 2NH_3(g)$. The rate of this reaction can be expressed in term of time derivative of concentration of $N_2(g)$, $H_2(g)$ or NH_3 (g). Identify the correct relationshiop amongst the rate expressions. **[JEE SCR 2002]**
(A) Rate = $-d[N_2]/dt = -1/3\, d[H_2]/dt = 1/2 d[NH_3]/dt$
(B) Rate = $-d[N_2]/dt = -3\, d[H_2]/dt = 2d[NH_3]/dt$
(C) Rate = $d[N_2]/dt = 1/3\, d[H_2]/dt = 1/2 d[NH_3]/dt$
(D) Rate = $-d[N_2]/dt = -d[H_2]/dt = d[NH_3]/dt$

Q.7 In a first order reaction the concentration of reactant decreases from 800 mol/dm^3 to 50 mol/dm^3 in 2×10^4 sec. The rate constant of reaction in sec^{-1} is **[JEE SCR 2003]**
(A) 2×10^4 (B) 3.45×10^{-5} (C) 1.3486×10^{-4} (D) 2×10^{-4}

Q.8 The reaction, X $\longrightarrow$ Product follows first order kinetics. In 40 minutes the concentration of X changes from 0.1 M to 0.025 M. Then the rate of reaction when concentration of X is 0.01 M
(A) 1.73×10^{-4} M min^{-1} (B) 3.47×10^{-5} M min^{-1}
(C) 3.47×10^{-4} M min^{-1} (D) 1.73×10^{-5} M min^{-1} **[JEE SCR 2004]**

Q.9 Which of the following statement is incorrect about order of reaction? **[JEE 2005]**
(A) Order of reaction is determined experimentally
(B) It is the sum of power of concentration terms in the rate law expression
(C) It does not necessarily depend on stoichiometric coefficients
(D) Order of the reaction can not have fractional value.

Q.10 Loss of a β – particle is equivalent to **[JEE 1998]**
(A) Increase of one proton only (B) Decrease of one neutron only
(C) Both (A) and (B) (D) None of these.

Q.11 Decrease in atomic number is observed during **[JEE 1998]**
(A) α – emission (B) β – emission (C) Positron emission (D) Electron capture.

Q.12 The number of neutrons accompanying the formation of ${}_{54}X^{139}$ and ${}_{38}Sr^{94}$ from the absorption of slow neutron by ${}_{92}U^{235}$ followed by nuclear fision is **[JEE 1999]**
(A) 0 (B) 2 (C) 1 (D) 3

Question No. 13 to 15 (3 questions)

Carbon 14 is used to determine the age of orgainc material. The procedure is based on the formation of ${}^{14}C$ by neutron capture in the upper atmosphere.

$$ {}_{7}N^{14} + {}_{0}n^{1} \longrightarrow {}_{6}C^{14} + {}_{1}H^{1} $$

${}^{14}C$ is absorbed by living organisms during photosynthesis. The ${}^{14}C$ content is constant in living organism once the plant or animal dies, the uptake of carbon dioxide by it ceases and the level of ${}^{14}C$ in the dead being falls due to the decay which C^{14} undergoes.

$$ {}_{6}C^{14} \longrightarrow {}_{7}N^{14} + {}_{-1}e^{\circ} $$

The half life period of ${}^{14}C$ is 5770 years. The decay constant (λ) can be calculated by using the following formula $\lambda = \dfrac{0.693}{t_{1/2}}$

The comparison of the β^{-} activity of the dead matter with that of carbon still in circulation enables measurement of the period of the isolation of the material from the living cycle. The method however, ceases to be accurate over periods longer than 30,000 years. The proportion of ${}^{14}C$ to ${}^{12}C$ in living matter is $1 : 10^{12}$ **[JEE 2006]**

Q.13 Which of the following option is correct?
(A) In living organisms, circulation of ${}^{14}C$ from atmosphere is high so the carbon content is constant in organism
(B) Carbon dating can be used to find out the age of earth crust and rocks
(C) Radioactive absorption due to cosmic radiation is equal to the rate of radioactive decay, hence the carbon content remains constant in living organism
(D) Carbon dating cannot be used to determine concentration of ${}^{14}C$ in dead beings.

Q.14 What should be the age of fossil for meaningful determination of its age?
(A) 6 years (B) 6000 years
(C) 60000 years (D) it can be used to calculate any age

Q.15 A nuclear explosion has taken place leading to increase in concentration of C^{14} in nearby areas. C^{14} concentration is C_1 in nearby areas and C_2 in areas far away. If the age of the fossil is determined to be t_1 and t_2 at the places respectively, then

(A) The age of the fossil will increase at the place where explosion has taken place and $t_1 - t_2 = \dfrac{1}{\lambda}\ln\dfrac{C_1}{C_2}$

(B) The age of the fossil will decrease at the place where explosion has taken place and $t_1 - t_2 = \dfrac{1}{\lambda}\ln\dfrac{C_1}{C_2}$

(C) The age of fossil will be determined to be the same

(D) $\dfrac{t_1}{t_2} = \dfrac{C_1}{C_2}$

SUBJECTIVE PROBLEM

Q.1(a) In the Arrhenius equation k = Aexp (–E/RT), A may be termed as the rate constant at _____. **[JEE 1997]**

(b) The rate constant for the first order decomposition of a certain reaction is discribed by the equation

$$\ln k\ (s^{-1}) = 14.34 - \frac{1.25\times10^4 K}{T}$$

(i) What is the energy of activation for this reaction?

(ii) The rate constant at 500 K.

(iii) At what temperature will its half life period be 256 minutes? **[JEE 1997]**

(c) The time required for 10% completion of a first order reaction at 298 K is equal to that required for its 25% completion at 308 K. If the pre exponential factor for the reaction is $3.56 \times 10^9\ s^{-1}$, calculate the rate constant at 318 K and also the energy of activation. **[JEE 1997]**

(d) The rate constant for an isomerisation reaction $A \rightarrow B$ is $4.5 \times 10^{-3}\ min^{-1}$. If the initial concentration of A is 1 M. Calculate the rate of the reaction after 1 h. **[JEE 1999]**

Q.2 A hydrogenation reaction is carried out at 500 K. If the same reaction is carried out in the presence of a catalyst at the same rate, the temperature required is 400 K. Calculate the activation energy of the reaction if the catalyst lowers the activation barrier by 20 $kJmol^{-1}$. **[JEE 2000]**

Q.3 The rate of a first order reaction is 0.04 mole $litre^{-1}\ s^{-1}$ at 10 minutrs and 0.03 mol $litre^{-1}\ s^{-1}$ at 20 minutes after initiation. Find the half life of the reaction. **[JEE 2001]**

Q.4 $2X(g) \longrightarrow 3Y(g) + 2Z(g)$

Time (in Min)	0	100	200
Partial pressure of X (in mm of Hg)	800	400	200

Assuming ideal gas condition. Calculate

(a) Order of reaction (b) Rate constant

(c) Time taken for 75% completion of reaction (d) Total pressure when $P_X = 700$ mm. **[JEE 2005]**

RADIOACTIVITY

Q.5 ^{64}Cu (half-life = 12.8 hr) decays by β^- emission (38%), β^+ emission (19%) and electron capture (43%). Write the decay product and calculate partial half-lives for each of the decay processes. **[JEE'2002]**

Q.6 Fill in the blanks

(a) $^{235}_{92}U + ^{1}_{0}n \longrightarrow ^{137}_{52}A + ^{97}_{40}B +$ _____.

(b) $^{82}_{34}Se \longrightarrow 2\ ^{0}_{-1}e +$ _____. **[JEE 2005]**

ANSWER KEY

EXERCISE-I

RATE OF REACTION AND STOICHIOMETRIC COEFFICIENT

Q.1 (a) 1×10^{-4} mol L^{-1} s^{-1} , (b) 3×10^{-4} mol L^{-1} s^{-1}

Q.2 (a) 0.019 mol L^{-1} s^{-1}, (b) 0.037 mol L^{-1} s^{-1}

Q.3 $2k_1 = k_2 = 4k_3$ Q.4 (i) $\frac{dx}{dt} = k[A][B]^2$, (ii) rate increases by 8 times

Q.5 rate increase by 27 times

Q.6 (i) $r = \frac{1}{4}\frac{d[NO]}{dt} = 9 \times 10^{-4}$mol litre^{-1} sec^{-1}, (ii) 36×10^{-4}mol litre^{-1}sec^{-1}, (iii) 54×10^{-4} mol litre^{-1}sec^{-1}

Q.7 (i) 7.2 mol litre^{-1}min^{-1}, (ii) 7.2 mol litre^{-1} min^{-1} Q.8 1/6

ZERO ORDER

Q.9 (i) 7.2 M, (ii) Think Q.10 K = 0.01 M min^{-1}

Q.11 0.75 M Q.12 6×10^{-9} sec Q.13 1.2 hr

FIRST ORDER

Q.14 (i) 36 min., (ii) 108 min. Q.15 (i) 0.0223 min^{-1}, (ii) 62.17 min Q.17 924.362 sec

Q.18 expiry time = 41 months Q.19 $3.3 \times 10^{-4}s^{-1}$ Q.20 $k = \frac{2.303}{t}\log\frac{1}{a}$ Q.21 11.2%

ORDER OF REACTION & RATE LAW

Q.22 (a) Third order, (b) $r = k[NO]^2[H_2]$, (c) 8.85×10^{-3} M sec^{-1}.

Q.23 (a) order w.r.t NO = 2 and w.r.t Cl_2 = 1, (b) $r = K[NO]^2[Cl_2]$, (c) K = 8 $L^2mol^{-2}s^{-1}$, (d) rate = 0.256 mole $L^{-1}s^1$]

Q.24 (i) first order (ii) $k = 1.308 \times 10^{-2}$ min^{-1} (iii) 73%

Q.25 (i) rate=[A] [B] ; (ii) $k = 4 \times 10^{-2}M^{-1}s^{-1}$; (iii) rate = $2.8 \times 10^{-3}M \cdot s^{-1}$

Q.26 (i) Zero order, (ii) K = 5 Pa/s

Q.27 Zero order Q.28 (a) n =1, (b) $\frac{dx}{dt} = k[CH_3COCH_3]$, (c) 8.67×10^{-3} s^{-1}, (d) 1.56×10^{-5} M s^{-1}

HALF LIFE

Q.29 166.6 min Q.30 4.62×10^5 sec Q.32 (i) t = 13.96 hrs, (ii) 2.2176 litre

Q.33 54 min Q.34 15 min

CONCENTRATION REPLACED BY OTHER QUANTITIES IN FIRST ORDER INTEGRATED RATE LAW

Q.35 $k = \frac{1}{t} ln \frac{P_3}{2(P_3 - P_2)}$ Q.36 $k = \frac{1}{t} ln \frac{P_3}{(P_3 - P_2)}$

Q.37 $k = \frac{1}{t} ln \frac{V_1}{(2V_1 - V_2)}$ Q.38 $k = \frac{1}{t} ln \frac{4V_3}{5(V_3 - V_2)}$ Q.39 $k = \frac{1}{t} ln \frac{r_\infty}{(r_\infty - r_t)}$

Q.40 8.12×10^{-6} Ms^{-1}, 0.012 atm min^{-1}

Q.41 (a) 90 mm, (b) 47 mm, (c) 6.49×10^{-2} per minutes, (d) 10.677 min.
Q.42 First order Q.43 $k_1 = 2.605 \times 10^{-3}$ min^{-1}
Q.44 (i) $r = K[(CH_3)_2O]$, 0.000428 sec^{-1} Q.45 First order
Q.46 (a) first order, (b) 13.75 minutes, (c) 0.716
Q.47 966 min Q.48 206.9 min Q.49 11.45 days
Q.50 0.180 atm, 47.69 sec

PARALLEL AND SEQUENTIAL REACTION

Q.51 $\frac{1}{e^{(K_1+K_2)}t-1}$ Q.52 $\frac{[C]}{[A]} = \frac{10}{11}(e^{11x} - 1)$ Q.53 72.7, 22.3 Q.54 t = 4 min

TEMPERATURE DEPENDENCE OF RATE (ACTIVATION ENERGY)

Q.55 5 kJ mol^{-1} Q.56 349.1 k Q.57 55.33 kJ mole^{-1} Q.58 306 k
Q.59 (a) 2.31×10^{-12} min^{-1}, 6.93×10^{-2} min^{-1}, (b) 43.85 kJ mole^{-1}
Q.60 rate of reaction increases 5.81×10^8 times
Q.61 10.757 k cal mol^{-1}

MECHANISM OF REACTION

Q.62 $r = K'[NO]^2[Br_2]$ Q.63 $r = K[NO]^2[H_2]$, where $K = k_2 \times K_1$
Q.64 $k_{eq} = 1$, rate $= k_2 (C)(A_2)^{1/2}$ Q.66 (d) No, (e) mechanism (a) is incorrect

RADIOACTIVITY

Q.67 beta emitter : ^{49}Ca, ^{30}Al, 94 Kr, positron emitter : ^{195}Hg, ^{8}B, ^{150}Ho
Q.68 $^{114}_{49}In$, odd number of nucleons Q.69 (a) $^{1}_{1}H$, (b) $^{1}_{0}n$, (c) $^{6}_{3}Li$, (d) $^{0}_{+1}e$, (e) $^{0}_{-1}e$, (f) p (proton)
Q.70 d, deuteron Q.71 (a) $^{1}_{1}H$ (b) $^{64}_{28}Ni$ (c) $^{0}_{-1}\beta$ (d) $^{1}_{0}n$
Q.72 $\alpha = \frac{a-b}{4}$; $\beta = d + \frac{(a-b)}{2} - c$ Q.73 2.16×10^{12} events / min
Q.74 1.06×10^{-15} kg Q.75 $\lambda = 5.77 \times 10^{-4}$ sec^{-1} Q.76 32 ml
Q.77 6.25 % Q.78 2.674×10^5 dps Q.79 33.67 years Q.80 4.65 hour

PROFICIENCY TEST

Q.1

1.	3.7×10^{10}	2.	β-rays	3.	isobar	4.	8, 6
5.	isodiaphers	6.	$^{30}_{14}Si$	7.	β-particles	8.	isotones
9.	10 min.	10.	threshold energy	11.	half	12.	equal to ΔH
13.	directly proportional			14.	mol L^{-1}s^{-1}	15.	rare
16.	lowering	17.	faster	18.	slowest	19.	increases
20.	3	21.	rate constant	22.	2 and 3	23.	rate = k[M]^2
24.	$1\frac{1}{2}$	25.	– k	26.	Activation energy		
27.	higher	28.	first	29.	$-\frac{k}{2.303}$	30.	1.44

Q.2

1.	False	2.	False	3.	True	4.	False
5.	True	6.	True	7.	True	8.	False
9.	False	10.	False	11.	True	12.	False
13.	True	14.	True	15.	True	16.	False
17.	True	18.	True	19.	False	20.	False

EXERCISE-II

Q.1 First order, k= 0.00144, 0.00144, 0.00145, 0.00145, 0.00150, 0.00140, average 0.00145min $^{-1}$

Q.2 (a) 6.25 ; (b) 14.3 ; (c) 0% Q.3 53.84 Q.4 $(d\tau/dt) = \alpha/2\tau$, –1 order

Q.5 a = b = 1 Q.6 2×10^{-2} min^{-1}

Q.7 (a) $3.27 \cdot 10^{-4}$sec^{-1}; (b) 2120 sec; (c) 38.27 (measured : 55.00ml)

Q.8 (a) 43.46kJmol^{-1}, (b) 20.47 hour Q.9 % decomposition = 67.21%

Q.10 k = 0.0327 min^{-1} Q.11 B Q.12 0.537 Q.13 k = 0.022 hr^{-1}

Q.14 4.83 mins Q.15 15.13 week Q.16 20 min, 28.66 min

Q.17 156 Q.18 $K_f = K_b =$ 0.00027 sec^{-1} Q.19 0.0025 m

Q.20 k=9.74×10^{-5} sec^{-1},k_{-1} = 4.18×10^{-5}sec^{-1} Q.21 $E_f = 6 \times 10^4$J; $E_b = 9.3 \times 10^4$J

Q.23 0.26 : 1 Q.24 (b)$t_{1/2}$ = 36min

Q.26 (a) $\frac{d(D)}{dt} = \frac{k_1 k_3 (A)(B)}{k_2 + k_3}$; (b) $E_a = E_{a1} + E_{a3} - E_{a2}$. $A = \frac{A_1 A_3}{A_2}$

Q.28 Set – I : 3.5×10^{-4}S^{-1}; Set – II : 6.7×10^{-4}S^{-1}

Q.29 P_t = 379.55 mm Hg, $t_{7/8}$ = 399.96 min Q.30 0.0207 min^{-1}

Q.31 399^0C ; R = 1.987Kcal.mol^{-1}K^{-1} Q.33 $k_2 = 2 \times 10^{-3}$ sec^{-1} ,$k_1 = 8 \times 10^{-3}$ sec^{-1}

Q.35 0.805

RADIOACTIVITY

Q.36 t = 4.89×10^9 years Q.37 V = 1.1 L Q.38 0.0958 mg

Q.39 Specific activity = 30.69 dis. g^{-1}s^{-1} Q.40 ^{239}Pu = 45.1%, ^{240}Pu = 54.9%

Q.41 t = 7.1×10^8 years Q.42 53.1 days, 132 yrs, ^{90}Sr is likely to be serious, the iodine will soon be gone

Q.43 4.125 min Q.44 3.3×10^8 years Q.45 1.4×10^9 yrs

EXERCISE-III

Q.1	B	Q.2	A	Q.3	D	Q.4	B	Q.5	D	Q.6	B	Q.7	C
Q.8	B	Q.9	A	Q.10	B	Q.11	A	Q.12	B	Q.13	C	Q.14	C
Q.15	A												

EXERCISE-IV

OBJECTIVE PROBLEM

Q.1	A, D	Q.2	B	Q.3	A, B, D	Q.4	D	Q.5	B
Q.6	A	Q.7	C	Q.8	C	Q.9	D		

RADIOACTIVITY

Q.10	C	Q.11	C, D	Q.12	D	Q.13	C	Q.14	B
Q.15	A								

SUBJECTIVE PROBLEM

Q.1 (a) infinte temperature ; (b) (i) 2.50×10^4 cal mol^{-1}, (ii) 2.35×10^{-5} sec^{-1}, (iii) 513 ;
(c) $K_{318} = 9.2 \times10^{-4}$ sec^{-1}, E_a =18.33 K cal mol^{-1} ; (d) A = 5.40×10^{10} sec^{-1},E_a=2.199×10^4 Jmol^{-1}

Q.2 100 kJmol^{-1} Q.3 $t_{1/2}$ = 24.14 min Q.4 (a) 1, (b) 6.93×10^{-3} min^{-1} , (c) 200, (d) 950 mm

RADIOACTIVITY

Q.5 $^{64}_{30}$Zn , $^{64}_{28}$Ni , $(t_{1/2})_1$ = 33.68 hr, $(t_{1/2})_2$ = 67.36 hr, $(t_{1/2})_3$ = 29.76 hr Q.6 (a) $2\,^1_0$n , (b) $^{82}_{36}$Kr

STUDY PACKAGE

Target: IIT-JEE (Advanced)

SUBJECT: CHEMISTRY-XI

TOPIC: 10. Thermochemistry

Index:

1. Key Concepts
2. Exercise I
3. Exercise II
4. Exercise III
5. Exercise IV
6. Answer Key
7. 34 Yrs. Que. from IIT-JEE
8. 10 Yrs. Que. from AIEEE

EXERCISE I

Heat of reaction & it's type

Q.1 When 2 moles of C_2H_6 are completely burnt 3120 kJ of heat is liberated . Calculate the heat of formation, ΔH_f^o for C_2H_6 . Given ΔH_f^o for $CO_2(g)$ & $H_2O(l)$ are – 395 & – 286 kJ respectively.

Q.2 The standard heats of formation of CH_4 (g) , CO_2 (g) and H_2O (*l*) are – 76.2 , – 398.8 , – 241.6 kJ mol^{-1} . Calculate amount of heat evolved by burning 1 m^3 of methane measured under normal (STP) conditions.

Q.3 Calculate the enthalpy change when infinitely dilute solution of $CaCl_2$ and Na_2CO_3 mixed ΔH_f° for Ca^{2+}(aq), CO_3^{2-} (aq) and $CaCO_3$ (s) are – 129.80, – 161.65, – 288.5 kcal mol^{-1} repectively.

Q.4 The enthalpies of neutralization of NaOH & NH_4OH by HCl are – 13680 calories and – 12270 cal respectively . What would be the enthalpy change if one gram equivalent of NaOH is added to one gram equivalent of NH_4Cl in solution ? Assume that NH_4OH and NaCl are quantitatively obtained.

Q.5 The heat of solution of anhydrous $CuSO_4$ is – 15.9 kcal and that of $CuSO_4.5H_2O$ is 2.8 kcal. Calculate the heat of hydration of $CuSO_4$.

Q.6 The heat of reaction $\frac{1}{2}H_2(g) + \frac{1}{2}Cl_2(g) \longrightarrow HCl(g)$ at 27°C is – 22.1 k cal . Calculate the heat of reaction at 77° C . The molar heat capacities at constant pressure at 27°C for hydrogen , chlorine & HCl are 6.82, 7.70 & 6.80 cal mol^{-1} respectively.

Q.7 Calculate standard heats of formation of carbon–di–sulphide (*l*) . Given the standard heat of combustion of carbon (s) , sulphur (s) & carbon–di–sulphide (*l*) are : – 393.3, – 293.72 and – 1108.76 kJ mol^{-1} respectively.

Q.8 A cylinder of gas supplied by a company contains 14 kg of butane . The heat of combustion of butane is 2658 kJ/mol . A normal family requires 20 MJ of energy per day of cooking. If the cylinder lasts for 26 days, what percentage of gas is wasted due to inefficient combustion.

Q.9 The enthalpy change for the reaction $C_3H_8 + H_2(g) \longrightarrow C_2H_6(g) + CH_4(g)$ at 25° C is – 55.7 kJ/mol. Calculate the heat of combustion of $C_2H_6(g)$. The heats of combustion of H_2, CH_4 & $C_{graphite}$ are – 285.8, – 890.0 & – 393.5 kJ/mole respectively. Heat of combustion of propane is –2220 kJ mol^{-1}.

Q.10 The standard enthalpy of neutralization of KOH with (a) HCN (b) HCl in dilute solution is – 2480 cal . g eq^{-1} and – 13.68 kcal . g eq^{-1} respectively . Find the enthalpy of dissociation of HCN at the same temperature.

Q.11 At 300 K, the standard enthalpies of formation of C_6H_5COOH(s), CO_2 (g) & H_2O (*l*) are ; – 408, – 393 & –286 KJ mol^{-1} respectively . Calculate the heat of combustion of benzoic acid at:(i) constant pressure & (ii) constant volume.

Q.12 The heat liberated on complete combustion of 7.8 g of benzene is 327 kJ . This heat has been measured at constant volume & at 27° C . Calculate the heat of combustion of benzene at constant pressure.

Q.13 A cylinder of gas is assumed to contains 11.2 kg of butane. If a normal family needs 20,000 kJ of energy per day for cooking, how long will the cylinder last if the enthalpy of combustion, $\Delta H = -2658$ kJ/mole for butane.

Q.14 The molar enthalpy of vaporization of benzene at its boiling point (353 K) is 30.84 $kJmol^{-1}$ What is the molar internal energy change? For how long would a 12 volt source need to supply a 0.5 A current in order to vaporise 7.8 g of the sample at its boiling point ?

Q.15 When 12.0 g of carbon reacted with oxygen to form CO & CO_2 at 25° C & constant pressure, 75.0 kcal of heat was liberated and no carbon remained . Calculate the mass of oxygen which reacted. $\Delta H_f^o (CO_2) = -95$ kcal mol^{-1}, $\Delta H_f^o (CO) = -24$kcal mol^{-1}.

Q.16 If the enthalpy of formation of HCl (g) and Cl^- (aq) are –92.3 kJ/mole and – 167.44 kJ/mol, find the enthalpy of solution of hydrogen chloride gas.

Calorimeter

Q.17 0.16 g of methane was subjected to combustion at 27° C in a bomb calorimeter . The temperature of calorimeter system (including water) was found to rise by 0.5°C . Calculate the heat of combustion of methane at (i) constant volume (ii) constant pressure .
The thermal capacity of calorimeter system is 17.7 kJ K^{-1} . (R = 8.313 mol^{-1} K^{-1})

Q.18 1.00 *l* sample of a mixture of CH_4(g) & O_2(g) measured at 25° C & 740 torr was allowed to react at constant pressure in a calorimeter which together with its contents had a heat capacity of 1260 cal/K. The complete combustion of the methane to CO_2 & H_2O caused a temperature rise in the calorimeter of 0.667 K. What was the mole percent of CH_4 in the original mixture?
$\Delta H^o_{comb} (CH_4) = -215$ k cal mol^{-1} .

Q.19 Two solutions initially at 25°C were mixed in a adiabatic constant pressure calorimeter. One contains 400 ml of 0.2 M weak monoprotic acid solution. The other contain 100 ml of 0.80 M NaOH. After mixing temperature increased to 26.2 °C. How much heat is evolved in the neutralization of 1 mole of acid? Assume density of solution 1.0 g/cm^3, and specific heat of solution 4.2 J/g-K. Neglect heat capacity of the calorimeter.

Q.20 When 1.0 g of fructose $C_6H_{12}O_6$(s) is burned in oxygen in a bomb calorimeter, the temperature of the calorimeter water increases by 1.56 °C. If the heat capacity of the calorimeter and its contents is 10.0 kJ/°C. Calculate the enthalpy of combustion of fructose at 298 K.

Q.21 A quantity of 1.92 g of methanol was burnt in a constant pressure calorimeter. The temperature of water increased by 4.2 °C. If the quantity of water surrounding the inner vessel was 2000 ml and the heat capacity of the inner vessel was 2.02 kJ/°C. Calculate the heat of combustion of methanol. [Specific heat of capacity of H_2O = 4.18 J/g°C]

Bond energy

Q.22 The enthalpy of dissociation of PH_3 is 954 kJ/mol and that of P_2H_4 is 1.485 M J mol^{-1}. What is the bond enthalpy of the P–P bond?

Q.23 Using the bond enthalpy data given below, calculate the enthalpy change for the reaction.
$C_2H_4(g) + H_2(g) \rightarrow C_2H_6\ (g)$
Data:

Bond	C–C	C = C	C–H	H–H
Bond Enthalpy	336.81 KJ/mol	606.68 KJ/mol	410.87 KJ/mol	431.79 KJ/mol

Q.24 The enthalpy change for the following process at 25°C and under constant pressure at 1 atm are as follows:
$CH_4(g) \longrightarrow C(g) + 4H(g) \quad \Delta_r H = 396$ kcal/mole
$C_2H_6(g) \longrightarrow 2C(g) + 6H(g) \quad \Delta_r H = 676$ kcal/mole
Calculate C–C bond energy in C_2H_6 & heat of formation of $C_2H_6(g)$
Given: Δ_{sub} C(s) = 171.8 kcal/mole
B.E. (H–H) = 104.1 kcal/mole

Q.25 The polymerisation of ethylene to linear polyethylene is represented by the reaction $n\,CH_2 = CH_2 \rightarrow (-CH_2-CH_2)_n$ where n has a large integral value. Given that the average enthalpies of bond dissociation for C=C & C–C at 298 K are +590 & +331 KJ mol^{-1} respectively. Calculate the enthalpy of polymerisation per mole of ethylene at 298 K.

Q.26 From the following data :
Enthalpy of formation of CH_3CN = 87.86 KJ/mol ,Enthalpy of formation of C_2H_6 = – 83.68 KJ/mol
Enthalpy of sublimation of graphite = 719.65 KJ/mol
Enthalpy of dissociation of nitrogen = 945.58 KJ/mol ; Enthalpy of dissociation of H_2 = 435.14 KJ/mol
C–H bond enthalpy = 414.22 KJ/mol
Calculate the (i) $\in_{C-C}$; (ii) $\in_{C\equiv N}$

Q.27 The heat of combustion of acetylene is 312 kcal. If heat of formation of CO_2 & H_2O are –94.38 & –68.38 kcal respectively, calculate C ≡ C bond energy. Given that heat of atomisation of C & H are 150.0 & 51.5 k cal respectively and C — H bond energy is 93.64 k cal.

Q.28 Using the given data calculate enthalpy of formation of acetone (g). [All values in kJ mol^{-1}]
binding energy of : C — H = 413.4 ; C — C = 347.0 ; C = O = 728.0 ;
O = O = 495.0 ; H — H = 435.8 ; ΔH_{sub} of C = 718.4.

Q.29 Find the enthalpy of S–S bond from the following data.

(i) $C_2H_5 - S - C_2H_5\ (g)$ $\Delta H_f^\circ = -147.2$ kJ/mol

(ii) $C_2H_5 - S - S - C_2H_5\ (g)$ $\Delta H_f^\circ = -201.9$ kJ/mol

(iii) S (g) $\Delta H_f^\circ = 222.8$ kJ/mol

Born Haber cycle

Q.30 Calculate the electron affinity of fluorine atom using the following data. Make Born – Haber's cycle. All the values are in kJ mol^{-1} at 25° C. ΔH_{diss} (F_2) = 160, ΔH_f° (NaF(s)) = – 571, I.E. [Na(g)] = 494, ΔH_{vap} [Na(s)] = 101. Lattice energy of NaF(s) = – 894.

Q.31 Cesium chloride is formed according to the following equation
$Cs(s) + 0.5Cl_2(g) \longrightarrow CsCl(s)$.
The enthalpy of sublimation of Cs, enthalpy of dissociation of chlorine, ionization energy of Cs & electron affinity of chlorine are 81.2, 243.0, 375.7 and – 348.3 kJ mol^{-1}. The energy change involved in the formation of CsCl is – 388.6 kJ mol^{-1}. Calculate the lattice energy of CsCl.

Q.32 The Born–Haber cycle for rubidium chloride (RbCl) is given below (the energies are in k cal mol^{-1})

Find out the electron affinity of chlorine in kJ mol^{-1} .

Resonance Energy

Q.33 The enthalpy of formation of ethane, ethylene and benzene from the gaseous atoms are –2839.2, –2275.2 and –5506 KJmol^{-1} respectively. Calculate the resonance energy of benzene. The bond enthalpy of C–H bond is given as equal to + 410.87 KJ/mol.

Q.34 Calculate the heat of combustion of methyl alcohol at 298 K from the following data

Bond	C – H	C – O	O – H	O = O	C = O
Energy kJ mol^{-1}	414	351.5	464.5	494	711

Resonance energy of CO_2 = – 143 kJ mol^{-1}

Latent heat of vaporisation of methyl alcohol = 35.5 kJ mol^{-1}.

Latent heat of vaporisation of water = 40.6 kJ mol^{-1}.

Q.35 Calculate the enthalpy of combustion of benzene (*l*) on the basis of the following data :

(i) Resonance energy of benzene(*l*) = – 152 kJ/mol

(ii) Enthalpy of hydrogenation of cyclohexene(*l*) = – 119 kJ/mol

(iii) ΔH^o_f of $C_6H_{12}(l)$ = – 156 kJ/mol

(iv) ΔH^o_f of $H_2O(l)$ = – 285.8 kJ/mol

(v) ΔH^o_f of $CO_2(g)$ = – 393.5 kJ/mol

PROFICIENCY TEST

Q.1 Fill in the blanks with appropriate items:

1. The combustion of a substance is always_____.
2. If heat content of X is smaller than that of Y then the process X $\longrightarrow$ Y is _____.
3. C (Diamond) $\longrightarrow$ C (Graphite) + x kJ. The heat change in this process is called_____.
4. For any reaction, ΔH° = _____.
5. As per reaction, $N_2(g) + 2O_2(g) \rightarrow 2NO_2(g) - 66$ kJ the value of ΔH_f of NO_2 is _____.
6. Heats of combustion of methane, carbon and hydrogen are –212, –94, –68 kcal mol^{-1}. The heat of formation of CH_4 is _____.
7. The heat of neutralisation of 1 mole of $HClO_4$ with 1 gm-equivalent of NaOH in aqueous solutions is _____kJ mol^{-1}.
8. The heat of combustion of graphite and carbon monoxide respectively are – 393.5 kJ mol^{-1} and – 283 kJ mol^{-1}. Thus, heat of formation of carbon monoxide in kJ mol^{-1} is_____.
9. At 298 K, the bond energies of C–H, C–C, C = C and H–H bonds are respectively 414, 347, 615 and 435 kJ mol^{-1}. The value of enthalpy change for the reactions
   $H_2C = CH_2(g) + H_2(g) \longrightarrow H_3C - CH_3(g)$ at 298 K will be_____.
10. For the reaction,
    $C_3H_8\,(g) + 5O_2(g) \longrightarrow 3CO_2(g) + 4H_2O\,(l)$
    at constant temperature, $\Delta H - \Delta U$ is_____.

Q.2 Mark the following statements as True or False:

1. The ΔH of a reaction is independent of temperature.
2. The enthalpies of elements are always taken to be zero.
3. Integral heat of solution is same as heat of hydration of substance.
4. Heat of neutralisation of weak acid-strong base is not constant.
5. Combustion reactions are always exothermic.
6. Resonance energy is always negative.
7. $\Delta E = 0$ Combustion of benzene in a sealed container that is immersed in a water bath at 25°C and has rigid, thermally conducting walls.
8. For reaction $2A(g) + B(g) \longrightarrow 3\,C(g)$ $\Delta H = -x$ kJ
   then for reactiion $\frac{3}{2}C\,(g) \longrightarrow A(g) + \frac{B}{2}(g)$ $\Delta H = \frac{x}{2}$ kJ.
9. ΔH_f° (C, diamond) $\neq 0$.
10. For a particular reaction $\Delta E = \Delta H + P.\,\Delta V$

EXERCISE II

Q.1 Calculate the mass of mercury which can be liberated from HgO at 25° C by the treatment of excess HgO with 41.84 kJ of heat at
(a) constant pressure (b) constant volume conditions .
Given : ΔH_f^o (HgO, s) = – 90.8 kJ mol^{-1} & M (Hg) = 200.6 g mol^{-1} .

Q.2 For reduction of ferric oxide by hydrogen, $Fe_2O_3(s) + 3\,H_2(g) \longrightarrow 2\,Fe(s) + 3\,H_2O(l)$;
$\Delta H^o_{298} = -35.1$ kJ . The reaction was found to be too exothermic to be convenient . It is desirable that ΔH^o should be at the most – 26 kJ . At what temperature is it possible ?
$C_P[Fe_2O_3] = 104.5$, $C_P[Fe(s)] = 25.5$, $C_P[H_2O(l)] = 75.3$, $C_P[H_2(g)] = 28.9$ (all in J/mol)

Q.3 From the following data of ΔH of the following reactions
$C(s) + 1/2O_2(g) \longrightarrow CO(g)$; $\Delta H = -110$ KJ
and $C(s) + H_2O(g) \longrightarrow CO(g) + H_2(g)$; $\Delta H = 132$ KJ
Calculate the mole composition of the mixture of steam and oxygen on being passed over coke at 1273 K, keeping the reaction temperature constant.

Q.4 Although C_P is usually assumed to be constant, for more accurate calculations we must consider its variation with temperature as well . This relation is given by ;
$C_P = a + bT + cT^2 + dT^3$ cal mol^{-1} K^{-1}.
(a) Find the expression for the amount of heat required to raise the temperature of 1 mole of gas from T_1K to T_2K, while
(i) keeping the first term [i.e. $C_P = a$] (ii) keeping the first two terms .
(iii) keeping all the terms . of the above expression . Note that each successive term introduces higher accuracy.
(b) For CO_2, a = 5.0 , b = 15 x 10^{-5} . Find the heat required to raise its temperature from 300 K to 500 K in case (i) and case (ii) . (number of moles = 1) . Case (ii) gives a more accurate value . Find the percent error in case (i) .

Q.5 An intimate mix of ferric oxide & Al is used as solid rocket fuel . Calculate the fuel value per gm & fuel value per CC of the mix . Heats of formation & densities are :
ΔH_f^o (Al_2O_3) = – 399 k cal/mole ; ΔH_f^o (Fe_2O_3) = – 199 kcal / mole,
density of Fe_2O_3 = 5.2 g/cc ; density of Al = 2.7 g/cc.

Q.6 A person takes 15 breaths per minute . The volume of air inhaled in each breath is 448 ml and contains 21% of oxygen by volume . The exhaled air contains 16% of oxygen by volume . If all the oxygen is used in the combustion of sucrose, how much of the latter is burnt in the body per day & how much heat is evolved . ΔH_{com} of sucrose is = – 6000 kJ mol^{-1} . Take temperature to be 300 K throughout.

Q.7 The enthalpies of neutralization of a strong acid HA & a weaker acid HB by NaOH are – 13680 cal/equivalent & – 2900 cal/equivalent respectively . When one equivalent of NaOH is added to a solution containing one equivalent of HA & one equivalent of HB, the enthalpy change was – 6900 calories . In what ratio is the base distributed between HA & HB ?

Q.8 Calculate the heat produced when 3.785 litre of octane (C_8H_{18}) reacts with oxygen to form CO & water vapour at 25° C. The density of octane is 0.7025 gm/ml. Heat of combustion of C_8H_{18} is – 1302.7 k cal/mol .
ΔH_f^o $CO_2(g)$ = – 94.05 k cal mol^{-1} ; ΔH_f^o CO(g) = – 26.41 k cal mol^{-1} ;
ΔH_f^o $H_2O(l)$ = – 68.32 k cal mol^{-1} ; ΔH_f^o $H_2O(g)$ = – 57.79 k cal mol^{-1}

Q.9 Using the data (all values are in kJ/mol at 25°C) given below :

$\Delta H^o_{combustion}$ (ethane) = – 1559.8 ; $\Delta H^o_{combustion}$ (ethene) = – 1410.9

$\Delta H^o_{combustion}$ (acetylene) = – 1299.7 ; $\Delta H^o_{combustion}$ (acetaldehyde) = – 1192.3

ΔH^o_f $CO_2(g)$ = – 393.5 ; ΔH^o_f of $H_2O(l)$ = – 285.8

ΔH^o for $C_{(s)}$ (graphite) $\rightarrow C_{(g)}$ = + 716.68 ; Bond energy of H – H = 435.94

Bond energy of O = O = 498.94

Calculate the following bond energies :

(i) C – C (ii) C – H (iii) C = O (iv) C = C (v) C ≡ C

Q.10 Using bond energy data, calculate heat of formation of isoprene .

$$5\,C(s) + 4\,H_2(g) \longrightarrow H_2C = \underset{\underset{CH_3}{|}}{C} - \underset{\underset{H}{|}}{C} = CH_2(g)$$

Given : C — H = 98.8 k cal ; H — H = 104 k cal ;

C — C = 83 k cal ; C = C = 147 k cal &

C(s) → C(g) = 171 k cal .

Q.11 Use the following data to calculate the enthalpy of formation of As_2O_3 .

(i) $As_2O_3(s) + [(3\,H_2O + aq)] \rightarrow 2\,H_3AsO_3\,(aq)$; $\Delta H = +\,7550$ cal

(ii) $As(s) + \frac{3}{2}Cl_2(g) \rightarrow AsCl_3\,(l)$; $\Delta H = -\,71390$ cal

(iii) $AsCl_3(l) + (3\,H_2O + aq) \rightarrow H_3AsO_3\,(aq) + 3\,HCl(aq)$; $\Delta H = -\,17580$ cal

(iv) $HCl(g) + aq \rightarrow HCl\,(aq)$; $\Delta H = -\,17315$ cal

(v) $\frac{1}{2}H_2(g) + \frac{1}{2}Cl_2(g) \rightarrow HCl(g)$; $\Delta H = -\,22000$ cal

(vi) $H_2(g) + \frac{1}{2}O_2(g) \rightarrow H_2O\,(l)$; $\Delta H = -\,68360$ cal

Q.12 Calculate the enthalpy change for the reaction $XeF_4 \longrightarrow Xe^+ + F^- + F_2 + F$.
The average Xe–F bond energy is 34 kcal/mol, first I.E. of Xe is 279 kcal/mol, electron affinity of F is 85 kcal/mol & bond dissociation energy of F_2 is 38 kcal/mol.

Q.13 By using the following data draw an appropriate energy cycle & calculate the enthalpy change of hydration of (i) the chloride ion ; (ii) the iodide ion.
Comment on the difference in their values.

* enthalpy change of solution of NaCl(s) = – 2 kJ/mol.
* enthalpy change of solution of NaI(s) = + 2 kJ/mol.
* enthalpy change of hydration of $Na^+(g)$ = – 390 kJ/mol.
* lattice energy of NaCl = – 772 kJ/mol.
* lattice energy of NaI = – 699 kJ/mol.

Q.14 The standard enthalpy of combustion of sucrose is – 5645 kJ mol^{-1} . What is the advantage (in kJ mol^{-1} of energy released as heat) of complete aerobic oxidation compared to anaerobic hydrolysis of sucrose to lactic acid ? ΔH_f^o for lactic acid, CO_2 and H_2O is –694, –395.0 and –286.0 respectively.

Q.15 In the combustion of solid naphthalene ($C_{10}H_8$) at 298 K and atmospheric pressure 5157 kJ/mol of heat are evolved. Calculate resonance energy of naphthalene.Given
Latent heat of sublimation of naphthalene = 72.0 kJ/mol
Enthalpy of formation of H_2O = –286.0 kJ mol^{-1}
Enthalpy of formation of CO_2 = –393.5 kJ mol^{-1}
Enthalpy of atomization of C = 715.5 kJ mol^{-1}
B.E. for C– C bond = 345.5 kJ mol^{-1}
C = C bond = 617.0 kJ mol^{-1}
C – H bond = 413.0 kJ mol^{-1}
H–H bond = 436 kJ/mol

Q.16 Calculate the proton affinity of $NH_3(g)$ from the following data (in kJ/mole)

$\Delta H^\circ_{dissociation} : H_2(g) = 218$; $\Delta H^\circ_{dissociation} : Cl_2(g) = 124$

$\Delta H^\circ_{formation} : NH_3(g) = -46$; $\Delta H^\circ_f : NH_4Cl(s) = -314$

Lattice energy of NH_4Cl (s) = – 683
Ionization energy of H = 1310
Electron affinity of Cl = 348

Q.17 The standard enthalpy of formation of FeO & Fe_2O_3 is – 65 kcal mol^{-1} and –197kcalmol^{-1} respectively. A mixture of two oxides contains FeO & Fe_2O_3 in the mole ratio 2 : 1 . If by oxidation, it is changed into a 1 : 2 mole ratio mixture, how much of thermal energy will be released per mole of the initial mixture ?

Q.18 The enthalpy of formation of $C_2H_5OH(l)$ is – 66 k cal/mol . The enthalpy of combustion of CH_3–O–CH_3 is – 348 k cal/mol . Given that the enthalpies of formation of $CO_2(g)$ and $H_2O(l)$ are –94 k cal/mol & – 68 k cal/mol respectively, calculate ΔH for the isomerisation of ethanol to methoxymethane. All data are at 25° C.

Q.19 During one of his adventures, Chacha Chaudhary got trapped in an underground cave which was sealed two hundred years back. The air inside was poisonous, having some amount of carbon monoxide in addition to O_2 and N_2. Sabu, being huge, could not enter the cave. So, in order to save Chacha Chaudhary, he started sucking the poisonous air out of the cave by mouth. Each time he used to fill his lungs with cave air and exhale it out in the surroundings. In the meantime, fresh air from the surroundings effused into the cave till the pressure was again one atmosphere. Each time Sabu sucked out some air, the pressure in the cave dropped to half its initial value of one atmosphere.
An initial sample of air taken from the cave measured 11.2 mL at STP and gave 7J on complete combustion at constant pressure.

(i) If the safe level of CO in the atmosphere is less than 0.001% by volume, how many times does Sabu need to suck out air in order to save Chacha Chaudhary?

(ii) Sabu should rescue Chacha Chaudhary within 6 minutes else he will die. Precious 80 seconds are wasted in thinking of a way to rescue him. At maximum, how much time should each cycle of inhaling–exhaling take?

$\Delta H_{comb}(CO) = -280 kJ.mol^{-1}$. Neglect any use of Graham's Law.

Q.20 Fe_xO_4 a mixed oxide of iron consists of only Fe^{+2} & Fe^{+3} ions, with the ratio of Fe^{+2} : Fe^{+3} = 1:2 in the mixed oxide. From the data given below,

Enthalpy of formation, $\Delta H_f(Fe_xO_4) = -1092$ kJ/mol.

Enthalpy of sublimation, ΔH_{sub} (Fe) = 390 kJ/mol.

B.D.E of O_2 = 490 kJ/mol.

$I.E_1$ of Fe = 760 kJ/ mol.

$I.E_2$ of Fe = 1560 kJ/mol.

$I.E_3$ of Fe = 2960 kJ/mol.

$I.E_1$ of O^{2-} = –844 kJ/mol.

$I.E_2$ of O^{2-} = 142 kJ/mol.

Lattice Energy of Fe_xO_4 = 18930 kJ/mol.

Prove that value of x is 3 with the help of given data.

EXERCISE III

Q.1 For which of the following change $\Delta H \neq \Delta E$?
(A) $H_2(g) + I_2(g) \longrightarrow 2HI(g)$
(B) $HCl(aq) + NaOH(aq) \longrightarrow NaCl(aq) + H_2O(l)$
(C) $C(s) + O_2(g) \longrightarrow CO_2(g)$
(D) $N_2(g) + 3H_2(g) \longrightarrow 2NH_3(g)$

Q.2 $\Delta_r H$ of which of the following reactions is zero?
(A) $H_2(g) \longrightarrow 2H^+(g) + 2e^-$
(B) $2H(g) + aq \longrightarrow 2H^+(aq) + 2e^-$
(C) $2H(g) \longrightarrow 2H^+(g) + 2e^-$
(D) $H_2(g) + aq \longrightarrow 2H^+(aq) + 2e^-$

Q.3 ΔH_f^0 of water is -285.8 kJ mol^{-1}. If enthalpy of neutralisation of monoacid strong base is -57.3 kJ mol^{-1}, ΔH_f^0 of OH^- ion will be
(A) -228.5 kJ mol^{-1}
(B) 228.5 kJ mol^{-1}
(C) 114.25 kJ mol^{-1}
(D) -114.25 kJ mol^{-1}

Q.4 50.0 mL of 0.10 M HCl is mixed with 50.0 mL of 0.10 M NaOH. The solution temperature rises by 3.0°C. Calculate the enthalpy of neutralization per mole of HCl.
(A) -2.5×10^2 kJ
(B) -1.3×10^2 kJ
(C) -8.4×10^1 kJ
(D) -6.3×10^1 kJ

Q.5 The enthalpy of neutralisation of a weak acid in 1 M solution with a strong base is -56.1 kJ mol^{-1}. If the enthalpy of ionization of the acid is 1.5 kJ mol^{-1} and enthalpy of neutralization of the strong acid with a strong base is -57.3 kJ equiv^{-1}, what is the % ionization of the weak acid in molar solution (assume the acid to be monobasic)?
(A) 10
(B) 15
(C) 20
(D) 25

Q.6 For the allotropic change represented by the equation C (graphite) $\longrightarrow$ C (diamond), $\Delta H = 1.9$ kJ. If 6 g of diamond and 6 g of graphite are separately burnt to yield CO_2, the heat liberated in first case is
(A) less than in the second case by 1.9 kJ
(B) more than in the second case by 11.4 kJ
(C) more than in the second case by 0.95 kJ
(D) less than in the second case by 11.4 kJ

Q.7 If x_1, x_2 and x_3 are enthalpies of H–H, O=O and O–H bonds respectively, and x_4 is the enthalpy of vaporisation of water, estimate the standard enthalpy of combustion of hydrogen
(A) $x_1 + \frac{x_2}{2} - 2x_3 + x_4$
(B) $x_1 + \frac{x_2}{2} - 2x_3 - x_4$
(C) $x_1 + \frac{x_2}{2} - x_3 + x_4$
(D) $2x_3 - x_1 - \frac{x_2}{2} - x_4$

Q.8 $NH_3(g) + 3Cl_2(g)$ l $NCl_3(g) + 3HCl(g)$; $-\Delta H_1$
$N_2(g) + 3H_2(g)$ l $2NH_3(g)$; ΔH_2
$H_2(g) + Cl_2(g)$ l $2HCl(g)$; ΔH_3
The heat of formation of $NCl_3(g)$ in the terms of ΔH_1, ΔH_2 and ΔH_3 is
(A) $\Delta H_f = -\Delta H_1 + \frac{\Delta H_2}{2} - \frac{3}{2}\Delta H_3$
(B) $\Delta H_f = \Delta H_1 + \frac{\Delta H_2}{2} - \frac{3}{2}\Delta H_3$
(C) $\Delta H_f = \Delta H_1 - \frac{\Delta H_2}{2} - \frac{3}{2}\Delta H_3$
(D) None

Q.9 Ethanol can undergoes decomposition to form two sets of products

$$C_2H_5OH\,(g) \longrightarrow \begin{cases} \xrightarrow{1} C_2H_4(g) + H_2O\,(g) & \Delta H^\circ = 45.54 \text{ kJ} \\ \xrightarrow{2} CH_3CHO(g) + H_2\,(g) & \Delta H^\circ = 68.91 \text{ kJ} \end{cases}$$

if the molar ratio of C_2H_4 to CH_3CHO is 8 : 1 in a set of product gases, then the energy involved in the decomposition of 1 mole of ethanol is

(A) 65.98 kJ (B) 48.137 kJ (C) 48.46 kJ (D) 57.22 kJ

Q.10 Reactions involving gold have been of particular interest to a chemist . Consider the following reactions,

$Au(OH)_3 + 4\,HCl \longrightarrow HAuCl_4 + 3\,H_2O$, $\Delta H = -28$ kcal

$Au(OH)_3 + 4\,HBr \longrightarrow HAuBr_4 + 3\,H_2O$, $\Delta H = -36.8$ kcal

In an experiment there was an absorption of 0.44 kcal when one mole of $HAuBr_4$ was mixed with 4 moles of HCl . What is the percentage conversion of $HAuBr_4$ into $HAuCl_4$?

(A) 0.5 % (B) 0.6 % (C) 5 % (D) 50 %

Q.11 (i) Cis–2 – butene $\rightarrow$ trans – 2 – butene, ΔH_1

(ii) Cis – 2– butene $\rightarrow$ 1 – butene, ΔH_2

(iii) Trans – 2 – butene is more stable than cis – 2 – butene.

(iv) Enthalpy of combustion of 1–butene, $\Delta H = -649.8$ kcal/mol

(v) $9\Delta H_1 + 5\,\Delta H_2 = 0$

(vi) Enthalpy of combustion of trans 2 – butene, $\Delta H = -647.0$ kcal/mol.

The value of ΔH_1 & ΔH_2 in Kcal/mole are

(A) –1.0 , 1.8 (B) 1.8, -1.0 (C) –5, 9 (D) –2, 3.6

Q.12 The reaction $CH_4(g) + Cl_2(g) \longrightarrow CH_3Cl(g) + HCl(g)$ has $\Delta H = -25$ kCal.

Bond	Bond Energy kCal
$\varepsilon_{C—Cl}$	84
$\varepsilon_{H—Cl}$	103
$\varepsilon_{C—H}$	x
$\varepsilon_{Cl—Cl}$	y
x : y = 9 : 5	

From the given data, what is the bond energy of Cl—Cl bond

(A) 70 kCal (B) 80 kCal (C) 67.75 kCal (D) 57.75 kCal

Q.13 From the following data at 25°C

Reaction	$\Delta_r H°$ kJ/mol
$\frac{1}{2}H_2(g) + \frac{1}{2}O_2(g) \longrightarrow OH(g)$	42
$H_2(g) + \frac{1}{2}O_2(g) \longrightarrow H_2O(g)$	–242
$H_2(g) \longrightarrow 2H(g)$	436
$O_2(g) \longrightarrow 2O(g)$	495

Which of the following statement(s) is/are correct:

Statement (a) : $\Delta_r H°$ for the reaction $H_2O(g) \longrightarrow 2H(g) + O(g)$ is 925.5 kJ/mol

Statement (b) : $\Delta_r H°$ for the reaction $OH(g) \longrightarrow H(g) + O(g)$ is 502 kJ/mol

Statement (c) : Enthalpy of formation of H(g) is –218 kJ/mol

Statement (d) : Enthalpy of formation of OH(g) is 42 kJ/mol

(A) Statement c (B) Statement a, b, d (C) Statement b, c (D) Statement a, d

Q.14 A mixture of hydrogen gas and the theoretical amount of air at 25°C and a total pressure of 1 atm, is exploded in a **closed rigid vessel**. If the process occurs under **adiabatic condition** then using the given datas answer the questions that follow :

Given (i) $C_P = 8.3$ cal deg^{-1} mol^{-1}; (ii) $C_P = 11.3$ cal deg^{-1} mol^{-1} ; ΔH_f [$H_2O(g)$] = –57.8 Kcal

[Take air as 80% N_2, 20% O_2 by volume]

(i) The value of C_P of N_2 & H_2O in the order N_2, H_2O will be (in cal. deg.$^{-1}$ mol^{-1})

(A) 8.3, 8.3 (B) 8.3, 11.3 (C) 11.3, 11.3 (D) 11.3, 8.3

(ii) What will be the maximum temperature attained if the process occurs in adiabatic container.

(A) ≅ 2940 K (B) ≅ 2665 K (C) ≅ 1900 K (D) ≅ 298 K

(iii) What will be the final pressure in atm.

(A) ≅ 8.5 (B) ≅ 7.6 (C) ≅ 5.46 (D) ≅ 0.85

(iv) If at initial temperature T_1E_1 is initial internal energy & at higher final temperature. T_2E_2 is the final internal energy, then which option is true

(A) $E_1 > E_2$ (B) $E_2 > E_1$

(C) $E_1 = E_2$ (D) can't be compared from the given data

Q.15 The commerical production of "Water gas" utilises the endothermic reaction $C(s) + H_2O(g) \longrightarrow H_2(g) + CO(g)$. The heat required for this reaction is generated by combustion of coal to CO_2 using stoichiometric amount of air.(79% N_2 by volume and 21% O_2 by volume). The superheated steam undergoes 75% conversion. Using the following data, answer the question that follows :

ΔH_f [CO(g)] = –110.53 kJ/mol ; ΔH_f [$H_2O(g)$] = –241.81 kJ/mol ; ΔH_f [$CO_2(g)$]=–314.0 kJ/mol

(i) The amount of heat liberated when one litre of product gases are burnt at 373 K and one atm is

(A) ≅ 3.6 kJ (B) ≅ 3.9 kJ (C) ≅ 4.43 kJ (D) ≅ 5.34 kJ

(ii) Match the gas and percentage of each gas in one litre product gases.

	Gas		Percentage
(I)	N_2	(a)	≈ 23.1
(II)	CO_2	(b)	≈ 36.4
(III)	H_2	(c)	≈ 7.7
(IV)	H_2O	(d)	≈ 9.7

(A) (I-a), (II-b), (III-c), (IV-d) (B) (I-b), (II-a), (III-d), (IV-c)

(C) (I-c), (II-d), (III-a), (IV-c) (D) (I-b), (II-d), (III-a), (IV-c)

EXERCISE IV

OBJECTIVE

Q.1 Which of the following reactions defines ΔH°_f ?

(A) $C_{(diamond)} + C_2(g) \longrightarrow CO_2(g)$ (B) $1/2\ H_2(g) + 1/2\ F_2(g) \longrightarrow HF(g)$

(C) $N_2(g) + 3H_2(g) \longrightarrow 2NH_3$ (D) $CO(g) + 1/2O_2(g) \longrightarrow CO_2(g)$ **[JEE 2003]**

Q.2 ΔH°_f for $CO_2(g)$, $CO(g)$ and $H_2O(g)$ are – 393.5, –110.5 and –241.8 kJ mol^{-1} respectively. The standard enthalpy change (in kJ) for the reaction

$CO_2(g) + H_2(g) \longrightarrow CO(g) + H_2O\ (g)$ is

(A) 524.1 (B) 41.2 (C) –262.5 (D) – 41.2 **[JEE 2000]**

Q.3 Which of the following is not an endothermic reaction?

(A) Combustion of methane

(B) Decomposition of water

(C) Dehydrogenation of ethene to ethylene

(D) Conversion of graphite to diamond **[JEE 1999]**

Q.4 Standard molar enthalpy of formation of CO_2 is equal to

(A) zero

(B) standard molar enthalpy of combustion of carbon (graphite)

(C) standard molar enthalpy of combustion of gaseous carbon

(D) sum of molar enthalpies of formation of CO and O_2 **[JEE 1997]**

SUBJECTIVE

Q.5 Diborane is a potential rocket fuel which undergoes combustion according to the reaction,

$B_2H_6(g) + 3O_2(g) \longrightarrow B_2O_3(s) + 3H_2O(g)$

From the following data, calculate the enthalpy change for the combustion of diborane :

$2B(s) + \frac{3}{2}O_2(g) \longrightarrow B_2O_3(s)$; $\Delta H = -1273$ kJ

$H_2(g) + \frac{1}{2}O_2(g) \longrightarrow H_2O(l)$; $\Delta H = -286$ kJ

$H_2O(l) \longrightarrow H_2O(g)$; $\Delta H = 44$ kJ

$2B(s) + 3H_2(g) \longrightarrow B_2H_6(g)$; $\Delta H = 36$ kJ **[JEE 2000]**

Q.6 Estimate the average S–F bond energy in SF_6. The ΔH_f° values of SF_6 (g), S(g), and F (g) are – 1100 , 275 and 80 kJ/mol respectively. **[JEE 99, 5]**

Q.7 From the following data, calculate the enthalpy change for the combustion of cyclopropane at 298 k. The enthalpy of formation of CO_2 (g), H_2O (*l*) and propene (g) are – 393.5, – 285.8 & 20.42 kJ/mol respectively. The enthalpy of isomerisation of cyclopropane to propene is – 33.0 kJ/mol. **[JEE '98, 5]**

Q.8 Compute the heat of formation of liquid methyl alcohol in kJ mol^{-1}, using the following data. Heat of vaporisation of liquid CH_3OH = 38 kJ/ mol . Heat of formation of gaseous atoms from the elements in their standard states ; H , 218 KJ / mol ; C, 715 KJ / mol ; O, 249 KJ / mol.

Average Bond energies C – H, 415 KJ / mol ;

C – O , 356 KJ / mol ; O – H , 463 KJ / mol **[JEE '97, 5]**

Q.9 The Enthalpy change involved in the oxidation of glucose is -2880 KJ mol^{-1} . 25% of this energy is availbale for muscular work . If 100 kJ of muscular work is needed to walk one km. What is the maximum distance a person will be able to walk after eating 120 g of glucose. **[JEE '97, 2]**

ANSWER KEY

EXERCISE I

Q.1 –88kJ/mol Q.2 35.973 MJ Q.3 2.95 kcal Q.4 – 1410 cal

Q.5 – 18.7 kcal Q.6 –22.123 k cal Q.7 128.02 kJ Q.8 18.95 %

Q.9 –1560.1 $kJmol^{-1}$ Q.10 11.2Kcal.

Q.11 **(i)** – 3201 kJ/mol **; (ii)** – 3199.75 kJ/mol Q.12 – 3273.77 kJ/mol Q.13 25.66 days

Q.14 ΔE= 27.91 KJ mol^{-1}, t= 514 sec.

Q.15 27.43 g O_2 Q.16 – 75.14 kJ/mole Q.17 **(i)** – 885 kJ/mol **(ii)** – 889.980 kJ/mol

Q.18 10.0 mol % CH_4 Q.19 –31.5 kJ/mole Q.20 –2808 kJ/mole Q.21 –726.6 kJ/mole

Q.22 213 kJ / mol Q.23 – 120.08 J/ml

Q.24 B.E. (C–C) = 82 kcal/mole; $\Delta_f H[C_2H_6(g)]$ = –20.1 kcal/mole

Q.25 – 72 kJ mol^{-1}

Q.26 (i) 343.08 ; (ii) 891.2 Q.27 $E_{C \equiv C}$ = 160.86 k cal

Q.28 – 192.3 kJ mol^{-1} Q.29 277.5 kJ/mol Q.30 E.A. = – 352 kJ mol^{-1}

Q.31 – 618.7 kJ mol^{-1} Q.32 – 90.75 kcal mol^{-1}

Q.33 – 23.68 KJ/mol Q.34 – 669.7 kJ mol^{-1}

Q.35 H_f^o(benzene) = 49 kJ mol^{-1}, H_C^o(benzene) = – 3267.4 kJ mol^{-1}

PROFICIENCY TEST

Q.1 1. exothermic 2. endothermic 3. Heat of transition 4. $\sum \nu_p \Delta H^\circ_{(P)} - \sum \nu_r \Delta H^\circ_{(R)}$

5.+33 kJ mol^{-1} 6. –18 kcal mol^{-1} 7. –57.2 kJ 8.–110.5

9. –125.0 kJ 10. – 3RT

Q.2 1.False 2. False 3. False 4. True 5. True

6. True 7. False 8. True 9. True 10. False

EXERCISE II

Q.1 (a) 92.435 g (b) 93.72 g Q.2 404 K Q.3 mole % $O_2(g) = 37.5$, $H_2O(g) = 62.5$

Q.4 **(a) (i)** $a\Delta T$ **(ii)** $a\Delta T + \frac{b}{2}(T_2^2 - T_1^2)$ **(b)** 1000 cal, 1012 cal, 1.1858 % error

Q.5 0.9346 k cal g^{-1}, 3.94 kcal cm^{-3} Q.6 9.822 MJ/day evolved

Q.7 0.371 : 0.629 Q.8 -666.81 k cal mol^{-1}, 15.55 Mcal

Q.9 C – C = 97.81 kJ, C – H = 454.64 kJ, C= O = 804.26 kJ, C = C = 434.3 kJ, C ≡ C = 733.48 kJ

Q.10 + 20.6 k cal Q.11 – 154.68 k cal

Q.12 292 kcal/mol Q.13 for Cl^- – 384 kJ mol^{-1}, for I^- – 307 kJ mol^{-1}

Q.14 advantage = 5396 kJ.mol^{-1} Q.15 –287.0 kJ mol^{-1} Q.16 – 718 kJ/mol

Q.17 Heat released= 13.4 kcal. per mol of initial mixture Q.18 22 kcal mol^{-1}

Q.19 (i) 13 times, (ii) 21.53 sec

EXERCISE III

Q.1 D Q.2 D Q.3 A Q.4 A Q.5 C Q.6 C Q.7 B

Q.8 A Q.9 B Q.10 C Q.11 A Q.12 D Q.13 D

Q.14 (i) B (ii) A (iii) A (iv) C Q.15 (i) A (ii) D

EXERCISE IV

Q.1 B Q.2 B Q.3 A Q.4 B Q.5 –2035kJ mol^{-1}

Q.6 309.6 kJ/mol Q.7 – 2091.32 kJ mol^{-1} Q.8 – 266 kJ mol^{-1}

Q.9 4.82 km

STUDY PACKAGE

Target: IIT-JEE (Advanced)

SUBJECT: CHEMISTRY-XII

TOPIC: 11. Electrochemistry

Index:

1. Key Concepts

2. Exercise I

3. Exercise II

4. Exercise III

5. Exercise IV

6. Answer Key

7. 34 Yrs. Que. from IIT-JEE

8. 10 Yrs. Que. from AIEEE

KEY CONCEPTS

ELECTROCHEMICAL CELLS

An electrochemical cell consists of two electrodes (metallic conductors) in contact with an electrolyte (an ionic conductor).
An electrode and its electrolyte comprise an **Electrode Compartment.**

Electrochemical Cells can be classified as:

(i) **Electrolytic Cells** in which a non–spontaneous reaction is driven by an external source of current.

(ii) **Galvanic Cells** which produce electricity as a result of a spontaneous cell reaction

Note: In a **galvanic cell**, cathode is positive with respect to anode.
In a **electrolytic cell**, anode is made positive with respect to cathode.

ELECTROLYSIS

The decomposition of electrolyte solution by passage of electric current, resulting into deposition of metals or liberation of gases at electrodes is known as electrolysis.

ELECTROLYTIC CELL

This cell converts electrical energy into chemical energy. The entire assembly except that of the external battery is known as the electrolytic cell

ELECTRODES

The metal strip at which positive current enters is called ***anode***; anode is positively charged in electrolytic cell. On the other hand, the electrode at which current leaves is called **cathode**. Cathodes are negatively charged.

Anode	Positive	Loss of electron or oxidation takes place	Positive current enters
Cathode	Negative	Gain of electron or reduction takes place	Current leaves

ELECTROLYSIS OF MOLTEN SODIUM CHLORIDE

$NaCl(molten) \longrightarrow Na^+ + Cl^-$

Reactions at anode (oxidation) : cathode (reduction)

$2Cl^- \longrightarrow Cl_2(g) + 2e^-$: $2Na^+ + 2e^- \longrightarrow 2Na(l)$

There are two types of electrodes used in the electroytic cell, namely attackable and non - attackable. The attackable elecrodes participitate in the electrode reaction. They are made up of reactive metals like Zn, Cu, Ag etc. In such electrodes, atom of the metal gets oxidised into the corresponding cation, which is passed into the solution. Thus, such anodes get dissolved and their mass decreases. On the other hand, non-attackable electrodes do not participiate in the electrode reaction as they made up of unreactive elements like Pt, graphite etc. Such electrodes do not dissolve and their mass remain same.

FARADAY'S LAWS OF ELECTROLYSIS:

(i) *First law of electrolysis :*

Amount of substance deposited or liberated at an electrode is directly proportional to amount of charge passed (utilized) through the solution.

$$w \propto Q$$

W = weight liberated, Q = charge in coulomb

$$w = ZQ$$

Z = electrochemical equivalent

when Q = 1 coulomb, then w = Z

Thus, weight deposited by 1 coulomb charge is called electrochemical equivalent.

Let 1 ampere current is passed till 't' seconds .

Then, $Q = It$ $\therefore$ $w = ZIt$

1 Faraday = 96500 coulomb = Charge of one mole electrons

One faraday is the charge required to liberate or deposit one gm equivalent of a substance at corresponding electrode.

Let 'E' is equivalent weight then 'E' gm will be liberated by 96500 coulomb.

$\therefore$ 1 Coulomb will liberate $\frac{E}{96500}$ gm ; By definition, $Z = \frac{E}{96500}$

$\therefore$ $W = \frac{ItE}{96500}$

When a gas is evolved at an electrode, then above formula changes as,

$$V = \frac{ItV_e}{96500}$$

where V = volume of liberated gas, V_e = equivalent volume of gas.

Equivalent volume may be defined as:

The volume of gas liberated by 96500 coulomb at STP.

(ii) *Second law of electrolysis :*

When same amount of charge is passed through different electrolyte solutions connected in series then weight of substances deposited or dissolved at anode or cathode are in ratio of their equivalent weights. i.e. $w_1/w_2 = E_1/E_2$

QUALITATIVE ASPECTS OF ELECTROLYSIS

In the electrolysis process we have discussed above, we have taken molten salt as electrolyte, which contains only one cation and anion. Now, if the electrolyte taken contains more than one cation and anion (for example, aqueous solution of the ionic electrolyte), then the cation and anion that will get discharged depends on the ability of cation to get reduced and the ability of anion to get oxidised.

The ability of an ion to get oxidised or reduced depends upon the size, mass, positive charge, negative charge etc. Thus, it is not possible to predict qualitatively that which ion would be discharged first, as one factor might enhance the ability to discharge while the other factor may hamper it. This can only be predicted on the basis of quantitative value assigned based on the cumulative effect of all the factors reponsible for an ion's ability to discharge. The value is referred as standard potential, which is determined by keeping the concentration of ion as 1 M, pressure of gas at 1 atm, and the measurement done at 25°C. For a cation, the standard reduction potential (SRP) values are compared. The cation having higher standard reduction potential value is discharged in preference to cation with lower SRP value provided the ions are at 1 M concentration. For an anion, the standard oxidation potential (SOP) values are compared and anion having higher SOP is preferentially discharged, if the concentration is 1 M for each of the ion. The SRP values at 25°C for some of the reduction half reactions are given in the table below.

S.NO.	Reduction half cell reaction	E° in volts at 25°C
1.	$F_2 + 2e^- \rightleftharpoons 2F^-$	+ 2.65
2.	$S_2O_8^{2-} + 2e^- \rightleftharpoons 2SO_4^{2-}$	+ 2.01
3.	$Co^{3+} + e^- \rightleftharpoons Co^{2+}$	+ 1.82
4.	$PbO_2 + 4H^+ + SO_4^{2-} + 2e^- \rightleftharpoons PbSO_4 + 2H_2O$	+ 1.65
5.	$MnO_4^- + 8H^+ + 5e^- \rightleftharpoons Mn^{2+} + 4H_2O$	+ 1.52
6.	$Au^{3+} + 3e^- \rightleftharpoons Au$	+ 1.50
7.	$Cl_2 + 2e^- \rightleftharpoons 2Cl^-$	+ 1.36
8.	$Cr_2O_7^{2-} + 14H^+ + 6e^- \rightleftharpoons 2Cr^{3+} + 7H_2O$	+ 1.33
9.	$O_2 + 4H^+ + 4e^- \rightleftharpoons 2H_2O$	+ 1.229
10.	$Br_2 + 2e^- \rightleftharpoons 2Br^-$	+ 1.07
11.	$NO_3^- + 4H^+ + 3e \rightleftharpoons NO + 2H_2O$	+ 0.96
12.	$2Hg^{2+} + 2e^- \rightleftharpoons Hg_2^{2+}$	+ 0.92
13.	$Cu^{2+} + I^- + e^- \rightleftharpoons CuI$	+ 0.86
14.	$Ag^+ + e^- \rightleftharpoons Ag$	+ 0.799
15.	$Hg_2^{2+} + 2e^- \rightleftharpoons 2\,Hg$	+ 0.79
16.	$Fe^{3+} + e^- \rightleftharpoons Fe^{2+}$	+ 0.77
17.	$I_2 + 2e^- \rightleftharpoons 2I^-$	+ 0.535
18.	$Cu^+ + e^- \rightleftharpoons Cu$	+ 0.53
19.	$Cu^{2+} + 2e^- \rightleftharpoons Cu$	+ 0.34
20.	$Hg_2Cl_2 + 2e^- \rightleftharpoons 2Hg + 2Cl^-$	+ 0.27
21.	$AgCl + e^- \rightleftharpoons Ag + Cl^-$	+ 0.222
22.	$Cu^{2+} + e^- \rightleftharpoons Cu^+$	+ 0.15
23.	$Sn^{4+} + 2e^- \rightleftharpoons Sn^{2+}$	+ 0.13
24.	$2H^+ + 2e^- \rightleftharpoons H_2$	0.00
25.	$Fe^{3+} + 3e^- \rightleftharpoons Fe$	– 0.036
26.	$Pb^{2+} + 2e^- \rightleftharpoons Pb$	– 0.126
27.	$Sn^{2+} + 2e^- \rightleftharpoons Sn$	– 0.14
28.	$AgI + e^- \rightleftharpoons Ag + I^-$	– 0.151
29.	$Ni^{2+} + 2e^- \rightleftharpoons Ni$	– 0.25
30.	$Co^{2+} + 2e^- \rightleftharpoons Co$	– 0.28
31.	$Cd^{2+} + 2e^- \rightleftharpoons Cd$	– 0.403
32.	$Cr^{3+} + e^- \rightleftharpoons Cr^{2+}$	– 0.41
33.	$Fe^{2+} + 2e^- \rightleftharpoons Fe$	– 0.44
34.	$Cr^{3+} + 3e^- \rightleftharpoons Cr$	– 0.74
35.	$Zn^{2+} + 2e^- \rightleftharpoons Zn$	– 0.762
36.	$2H_2O + 2e^- \rightleftharpoons H_2 + 2OH^-$	– 0.828
37.	$Mn^{2+} + 2e^- \rightleftharpoons Mn$	– 1.18
38.	$Al^{3+} + 3e^- \rightleftharpoons Al$	– 1.66
39.	$H_2 + 2e^- \rightleftharpoons 2H^-$	– 2.25
40.	$Mg^{2+} + 2e^- \rightleftharpoons Mg$	– 2.37
41.	$Na^+ + e^- \rightleftharpoons Na$	– 2.71
42.	$Ca^{2+} + e^- \rightleftharpoons Ca$	– 2.87
43.	$Ba^{2+} + 2e^- \rightleftharpoons Ba$	– 2.90
44.	$Cs^+ + e^- \rightleftharpoons Cs$	– 2.92
45.	$K^+ + e^- \rightleftharpoons K$	– 2.93
46.	$Li^+ + e^- \rightleftharpoons Li$	– 3.03

When solution of an electroyte contains more than one type of cations and anions at concentrations different than 1 M, the discharge of an ion does not depend solely on standard potentials but also depends on the concentration of ion in the solution. This value is refered as potential, called as reduction potential for cation and oxidation potential for anion. The relation between reduction potential and standard reduction potential is given by Nernst equation, as

$$E_{RP} = E^\circ_{RP} - \frac{RT}{nF} \ln \frac{[\text{concentration of product}]}{[\text{concentration of reactant}]}$$

where E_{RP} = Reduction potential of cation and E°_{RP} = Standard reduction potential of cation.
Thus, it is possible that a cation (A^+) with lower standard reduction potential getting discharged in preference to cation (B^+) having higher standard reduction potential because their concentration might be such that the reduction potential of A^+ is higher than that of B^+.
When two metal ions in the solution have identical values of their reduction potentials, the simultaneous deposition of both the metals will occur in the form of an alloy.

GALVANIC CELL

This cell converts chemical energy into electrical energy.

Galvanic cell is made up of two half cells i.e., anodic and cathodic. The cell reaction is of redox kind. Oxidation takes place at anode and reduction at cathode. It is also known as ***voltaic cell***. It may be represented as shown in Fig. Zinc rod immersed in $ZnSO_4$ behaves as anode and copper rod immersed in $CuSO_4$ behaves as cathode.

Oxidation takes place at anode:

$Zn \rightleftharpoons Zn^{2+} + 2e^-$ (loss of electron : oxidation)

Reduction takes place at cathode:

$Cu^{2+} + 2e^- \rightleftharpoons Cu$ (gain of electron ; reduction)

Over all process:

$Zn(s) + Cu^{2+} \rightleftharpoons Cu(s) + Zn^{2+}$

In galvanic cell like Daniell cell; electrons flow from anode (zinc rod) to the cathode (copper rod) through external circuit; zinc dissolves as Zn^{2+} ; Cu^{2+} ion in the cathode cell picks up two electron and become deposited at cathode.

SALT BRIDGE

Two electrolyte solutions in galvanic cells are seperated using salt bridge as represented in the Fig. salt bridge is a device to minimize or eliminate the liquid junction potential. Saturated solution of salt like KCI, KNO_3, NH_4Cl and NH_4NO_3 etc. in agar-agar gel is used in salt bridge. Salt bridge contains high concentration of ions viz. K^+ and NO_3^- at the junction with electrolyte solution. Thus, salt bridge carries whole of the current across the boundary ; more over the $K^+$and NO_3^- ions have same speed. Hence, salt bridge with uniform and same mobility of cations and anions minimize the liquid junction potential & completes the electrical circuit & permits the ions to migrate.

Representation of a cell (IUPAC conventions): Let us illustrate the convention taking the example of Daniel cell.

(i) Anodic half cell is written on left and cathodic half cell on right hand side.

$Zn(s) \mid ZnSO_4(sol) \parallel CuSO_4(sol) \mid Cu(s)$

(ii) Two half cells are separated by double vertical lines: Double vertical lines indicate salt bridge or any type of porous partition.

(iii) EMF (electromotive force) may be written on the right hand side of the cell.

(iv) Single vertical lines indicate the phase separation between electrode and electrolyte solution.

$Zn \mid Zn^{2+} \parallel Cu^{2+} \mid Cu$

(Illustration of Phase boundary)

(v) Inert electrodes are reprsented in the bracket

$Zn \mid ZnSO_4 \parallel H^+ \mid H_2, Pt$

CONCEPT OF ELECTROMOTIVE FORCE (EMF) OF A CELL

Electron flows from anode to cathode in external circuit due to a pushing effect called or electromotic force (e.m.f.). E.m.f. is some times called as *cell potential*. Unit of e.m.f. of cell is volt.

EMF of cell may be calculated as :

E_{cell} = reduction potential of cathode − Reduction potential of anode

Similarly, standard e.m.f. of the cell (E°) may be calculated as

$E°_{cell}$ = Standard reduction potential of cathode − Standard reduction potential of anode

SIGN CONVENTION OF EMF

EMF of cell should be positive other wise it will not be feasible in the given direction .

$Zn \mid ZnSO_4 \parallel CuSO_4 \mid Cu$ E = +1.10 volt (Feasible)

$Cu \mid CuSO_4 \parallel ZnSO_4 \mid Zn$ E = −1.10 volt (Not Feasible)

NERNST EQUATION

Walter Nernst derived a relation between cell potential and concentration or Reaction quotient.

$$\Delta G = \Delta G° + RT \ln Q \qquad ..(1)$$

where ΔG and ΔG° are free energy and standard free energy change; 'Q' is reaction quotient.

Let n, Faraday charge is taken out from a cell of e.m.f. (E) then electrical work done by the cell may be calculated as,

Work done = Charge x Potential = nFE

From thermodynamics we know that decrease in Gibbs free energy of a system is a measure of reversible or maximum obtainable work by the system if there is no work due to volume expansion

$\therefore\ -\Delta G = nFE$ and $-\Delta G° = nFE°$

Thus from Eq. (i),we get $-nFE = -nFE° + RT \ln Q$

At 25°C, above equation may be written as $\mathbf{E = E^0 - \frac{0.0591}{n} \log Q}$

Where 'n' represents number of moles of electrons involved in process.

E, E° are e.m.f. and standard e.m.f. of the cell respectively.

In general , for a redox cell reaction involving the transference of n electrons

$aA + bB \longrightarrow cC + dD$, the EMF can be calculated as:

$$E_{Cell} = E^{\circ}_{Cell} - \frac{0.0591}{n}\log\frac{[C]^c[D]^d}{[A]^a[B]^b}$$

Prediction and feasibility of spontaniety of a cell reaction.

Work done by the cell = nFE;

It is equivalent to decrease in free energy $\Delta G = -nFE$

Under standard state $\Delta G^0 = -nFE^0$ (i)

(i) From thermodynamics we know, ΔG = negative for spontaneous process. Thus from eq.(i) it is clear that the EMF should be +ve for a cell process to be feasible or spontaneous.

(ii) When ΔG = positive, E = negative and the cell process will be non spontaneous.

(iii) When G = 0 , E = 0 and the cell will attain the equilibrium.

Reactions	**ΔG**	**E**
Spontaneous	(–)	(+)
Non- spontaneous	(+)	(–)
Equilibrium	0	0

Standard free energy change of a cell may be calculated by electrode potential data.

Substituting the value of E^0 (i.e., standard reduction potentialof cathode- standard reduction potential of anode) in eq. (i) we may get ΔG^0.

Let us see whether the cell (Daniell) is feasible or not: i.e. whether Zinc will displace copper or not.

$Zn \mid (s) \mid ZnSO_4\ (sol) \parallel CuSO_4\ (sol) \mid Cu(s)$

$$E^0_{Zn^{2+}/Zn} = -0.76\text{volt}\ ;\ E^0_{Cu^{2+}/Cu} = +0.34\text{volt}$$

$$E^0_{cell} = E^0_{Cu^{2+}/Cu} - E^0_{zn^{2+}/Zn}$$

$$= 0.34 - (-0.76) = +1.10 \text{ volt}$$

Since E^0 = +ve , hence the cell will be feasible and zinc will displace copper from its salt solution. In the other words zinc will reduce copper.

THERMODYNAMIC TREATMENT OF NERNST EQUATION

Determination of equilibrium constant : We know, that

$$E = E^0 - \frac{0.0591}{n}\log Q \qquad ..(i)$$

At equilibrium, the cell potential is zero because cell reactions are balanced, i.e. E = 0

∴ From Eq. (i), we have

$$0 = E^0 - \frac{0.0591}{n}\log K_{eq} \quad \text{or} \quad K_{eq} = \text{anti}\log\left[\frac{nE^0}{0.0591}\right]$$

Heat of Reaction inside the cell: Let n Faraday charge flows out of a cell of e.m.f. E, then

$$-\Delta G = nFE \qquad (i)$$

Gibbs Helmholtz equation (from thermodynamics) may be given as,

$$\Delta G = \Delta H + T\left[\frac{\partial \Delta G}{\partial T}\right]_p \qquad (ii)$$

From Eqs. (i) and (ii), we have

$$-nFE = \Delta H + T\left[\frac{\partial(-nFE)}{\partial T}\right]_p = \Delta H - nFT\left[\frac{\partial E}{\partial T}\right]_p$$

$$\therefore \qquad \Delta H = -nFE + nFT\left[\frac{\partial E}{\partial T}\right]_p$$

Entropy change inside the cell : We know that G = H - TS or $\Delta G = \Delta H - T\Delta S$ ...(i)

where ΔG = Free energy change ; ΔH = Enthalpy change and ΔS = entropy change.

According to Gibbs Helmoholtz equation,

$$\Delta G = \Delta H + T\left[\frac{\partial \Delta G}{\partial T}\right]_p$$

$$\Delta G = \Delta H = T\left[\frac{\partial \Delta G}{\partial T}\right]_p$$

From Eqs. (i) and (ii), we have

$$-T\Delta S = T\left[\frac{\partial \Delta G}{\partial T}\right]_p \qquad \text{or} \qquad \Delta S = -\left[\frac{\partial \Delta G}{\partial T}\right]_p$$

or $$\Delta S = nF\left[\frac{\partial E}{\partial T}\right]_p$$

where $\left[\frac{\partial E}{\partial T}\right]_p$ is called temperature coefficient of cell e.m.f.

DIFFERENT TYPES OF HALF-CELLS AND THEIR REDUCTION POTENTIAL

(1) Gas-Ion Half Cell:

In such a half cell, an inert collector of electrons, platinum or graphite is in contact with gas and a solution containing a specified ion. One of the most important gas-ion half cell is the hydrogen-gas-hydrogen ion half cell. In this half cell, purified H_2gas at a constant pressure is passed over a platinum electrode which is in contact with an acid solution.

$$H^+(aq) + e^- \rightleftharpoons 1/2\ H_2$$

$$E_{H^+/H_2} = E^0_{H^+/H_2} - \frac{0.0591}{1}\log\frac{(pH_2)^{1/2}}{[H^+]}$$

(2) Metal-Metal Ion Half Cell:

This type of cell consist of a metal M in contact with a solution containing M^{n+} ions.

$$M^{n+}(aq) + ne^- \rightleftharpoons M(s)$$

$$E_{M^{n+}/M} = E^0_{M^{n+}/M} - \frac{0.0591}{n}\log\frac{1}{[M^{n+}]}$$

(3) Metal-Insoluble Salt - Anion Half Cell:

In this half cell, a metal coated with its insoluble salt is in contact with a solution containing the anion of the insoluble salt. eg. Silver-Silver Chloride Half Cell:

This half cell is represented as $Cl^-/AgCl/Ag$. The equilibrium reaction that occurs at the electrode is

$$AgCl(s) + e^- \rightleftharpoons Ag(s) + Cl^-(aq)$$

$$E_{Cl^- / AgCl / Ag} = E^0_{Cl^- / AgCl / Ag} - \frac{0.0591}{1}\log\left[Cl^-\right]$$

potential of such cells depends upon the concentration of anions. Such cells can be used as **Reference Electrode**.

(4) Oxidation-reduction Half Cell:

This type of half cell is made by using an inert metal collector, usually platinum, immersed in a solution which contains two ions of the same element in different states of oxidation. eg. Fe^{2+} - Fe^{3+} half cell.

$Fe^{3+}(aq) + e^- \rightleftharpoons Fe^{2+}(aq)$

$$E_{Fe^{3+} / Fe^{2+}} = E^0_{Fe^{3+} / Fe^{2+}} - \frac{0.0591}{1}\log\frac{\left[Fe^{2+}\right]}{\left[Fe^{3+}\right]}$$

CONCENTRATION CELL

The cells in which electrical current is produced due to transport of a substance from higher to lower concentration. Concentration gradient may arise either in electrode material or in electrolyte. Thus there are two types of concentration cell .

(i) Electrode concentration cell

(ii) Electrolyte concentration cell

Electrode Gas concentration cell :

$Pt, H_2(P_1) \mid H^+(C) \mid H_2(P_2), Pt$

Here, hydrogen gas is bubbled at two different partial pressures at electrode dipped in the solution of same electrolyte.

Cell process : $1/2H_2(p_1) \rightarrow H^+(c) + e^-$ (Anode process)

$$\frac{H^+(c) + e^- \rightarrow 1/2H_2(p_2)}{1/2H_2(p_1) \Leftrightarrow 1/2H_2(p_2)}$$

$$\therefore \quad E = -\frac{2.303RT}{F}\log\left[\frac{p_2}{p_1}\right]^{1/2}$$

or $$E = \left[\frac{2.303RT}{2F}\right]\log\left[\frac{p_2}{p_1}\right]$$, At 25^0C , $$E = \frac{0.059}{2F}\log\left[\frac{p_1}{p_2}\right]$$

For spontanity of such cell reaction, $p_1 > p_2$

Electrolyte concentration cells:

$Zn(s) \mid ZnSO_4\ (C_1) \parallel ZnSO_4\ (C_2) \mid Zn(s)$

In such cells, concentration gradient arise in electrolyte solutions. Cell process may be givewn as,

$Zn(s) \rightarrow Zn^{2+}(C_1) + 2e$ (Anodic process)

$$\frac{Zn^{2+}(C_2) + 2e \longrightarrow Zn(s)}{Zn^{2+}(C_2) \bullet Zn^{2+}(C_1)}$$ (Over all process)

$\therefore$ From Nernst equation, we have

$$E = 0 - \frac{2.303RT}{2F}\log\left[\frac{C_1}{C_2}\right] \quad \text{or} \quad E = \frac{2.303RT}{2F}\log\left[\frac{C_2}{C_1}\right]$$

For spontanity of such cell reaction, $C_2 > C_1$

CONDUCTANCE

Introduction:

Both metallic and electrolytic conductors obey Ohm's law

i.e. $V = IR$

where V = Potential difference in volt; I = Current in ampere ; R = resistance in Ohm

We know, resistance is directly proportional to length of conductor and inversely proportional to cross sectional area of the conductor.

$$R \propto \frac{l}{A} \quad \text{or} \quad R = \rho\frac{l}{A} \qquad (\rho = \text{Specific resistance})$$

Specific resistance is the resistance of a conductor having lengths of 1 cm and corss sectional area of 1 cm^2.

Unit of R is ohm and unit of specific resistance is ohm cm

Reciprocal of resistance is called as *conductance* and reciprocal of specific resistance is called as *specific conductance*.

$$\frac{1}{R} = \frac{1}{\rho}\frac{A}{l} \quad \text{or} \quad C = K\frac{A}{l}$$

where C = conductance ohm^{-1} ; K = specific conductance $ohm^{-1}cm^{-1}$.

Mho and siemens are other units of conductance

$$K = \frac{l}{A}C$$

Specific conductance= Cell constant x Conductance

SPECIFIC CONDUCTANCE IS CONDUCTANCE OF 1 CM^3 OF AN ELECTROLYTE SOLUTION.

In case of electrolytic solution, the specific conductance is defined as the conductance of a solsution of definite concentration enclosed in a cell having two electrodes sof unit area separated by 1 cm apart.

1. Equivalent Conductance

Equivalent conductance is the conductance of an electrolyte solution containing 1 gm equivalent of electrolyte. It is densoted by $\wedge$.

$$\wedge = K \times V$$

$(\wedge = ohm^{-1}\ cm^{-1} \times cm^3 = ohm^{-1}\ cm^2)$

Usually concen ration of electrolyte solution is expressed as C gm equivalent per litre.

Thus, $V = \frac{1000}{C}$

{Volumehavinglgmequivalentelectrolyteinthesolution} Thus, $\wedge = K \times \frac{1000}{C}$

2. Molar Conductance

Molar conductance may be defined as conductance of an electrolyte solution having 1 gm mole electrolyte in a litre. It is denoted by $\wedge_m$.

$$\wedge_m = K \times V$$

Usually concentration of electrolyte solution is expressed as 'M' gm mole elecrtrolyte per litre.

Thus, $V=\frac{1000}{M}$

Hence, $\wedge_m = K x \frac{1000}{M}$

Relation between $\wedge$ and $\wedge_m$: $\wedge_m = n \times \wedge$

DETERMINATION OF $\wedge_m^0$ OR $\wedge^0$

A plot of $\wedge_m$ vs $\sqrt{C}$ as found experimentally is as shown below graphically.

The $\wedge_m$ vs $\sqrt{C}$ plot of strong electrolyte being linear it can be extrapolated to zero concentration. Thus, $\wedge_m$ values of the solution of the test electrolyte are determined at various concentrations the concentrations should be as low as good.

$\wedge_m$ values are then plotted against $\sqrt{C}$ when a straight line is obtained. This is the extrapolated to zero concentration. The point where the straight line intersects $\wedge_m$ axis is $\wedge_m^0$ of the strong electrolyte. However, the plot in the case weak electrolyte being non linear, shooting up suddenly at some low concentration and assuming the shape of a straight line parallel to $\wedge_m$ axis. Hence extrapolation in this case is not possible. Thus, $\wedge_0$ of a weak electrolyte cannot be determined experimentally. It can, however, be done with the help of Kohlrausch's law to be discussed later.

Kohlrausch's Law of Independent Migration of Ions

Kohlrausch determined $\wedge_0$ values of pairs of some strong electrolytes containing same cation say KF and KCl, NaF and NaCl etc., and found that the difference in $\wedge_0$ values in each case remains the same:

$$\wedge_m^0 (KCl) - \wedge_m^0 (KF) = \wedge_m^0 (NaCl) - \wedge_m^0 (NaF)$$

He also detemined $\wedge_0$ values of pairs of strong electrolytes containing same anion say KF and NaF, KCl and NaCl etc.and found that the difference in $\wedge_0$ values in each case remains the same.

$$\wedge_m^0 (KF) - \wedge_m^0 (NaF) = \wedge_m^0 (KCl) - \wedge_m^0 (NaCl)$$

This experimental data led him to formulate the following law called Kohlrausch's law of independent migration of ions.

At infinite dilution when dissociation is complete, every ion makes some definite contribution towards molar conductance of the electrolyte irrespective of the nature of the other ion which with it is associated and that the molar conductance at infinite dilution for any electrolyte is given by the sum of the contribution of the two ions. Thus,

$$\wedge_m^0 = \lambda_+^0 + \lambda_-^0$$

Where λ_+^0 is the contribution of the cation and λ_-^0 is the contribution of the anion towards the molar conductance at infinite dilution. These contributions are called molar ionic conductances at infinite dilution. Thus, λ_+^0 is the molar ionic conductance of cation and λ_-^0 is the molar ionic conductnace of anion, at infinite dilution. The above equation is, however, correct only for binary electrolyte like NaCl, $MgSO_4$ etc.

Application of Kohlrausch's law :

(1) Determination of $\wedge_m^0$ of a weak electrolyte:

In order to calculate $\wedge_m^0$ of a weak electrolyte say CH_3COOH, we determine experimentally $\wedge_m^0$ values of the following three strong electrolytes:

(a) A strong electrolyte containing same cation as in the test electrolyte, say HCl

(b) A strong electrolyte containing same anion as in the test electrolyte, say CH_3COONa

(c) A strong electrolyte containing same anion of (a) and cation of (b) i.e. NaCl.

$\wedge_m^0$ of CH_3COOH is then given as:

$$\wedge_m^0 (CH_3COOH) = \wedge_m^0 (HCl) + \wedge_m^0 (CH_3COONa) - \wedge_m^0 (NaCl)$$

Proof:

$$\wedge_m^0 (HCl) = \lambda_H^0 + \lambda_{Cl^-} \quad \text{.....(i)}$$

$$\wedge_m^0 (CH_3COONa) = \lambda^0_{CH_3COO^-} + \lambda_{Na^+} \quad \text{.....(ii)}$$

$$\wedge_m^0 (NaCl) = \lambda^0_{Na^+} + \lambda^0_{Cl^-} \quad \text{.....(iii)}$$

Adding equation (i) and equation (ii) and subtracting (iii) from them:

$$\wedge_m^0 (HCl) + \wedge^0_{(CH_3COONa)} - \wedge^0_{(NaCl)} = \lambda^0_{(H^+)} + \lambda^0_{(CH_3COO^0)} = \wedge_{0(CH_3COOH)}$$

(2) Determination of degree of dissociation (α) :

$$\alpha = \frac{\text{No. of moleculesionised}}{\text{total number of moleculesdissolved}} = \frac{\wedge_m}{\wedge_m^0}$$

(3) Determination of solubility of sparingly soluble salt

The specific conductivity of a saturated solution of the test electrolyte (sparingly soluble) made in conductivity water is determined by the method as described above. From this the specific conductivity of conductivity water is deducted. The molar conductance of the saturated solution is taken to be equal to $\wedge_m^0$ as the saturated solution of a sparingly soluble salt is extremely dilute. Hence from equation (4).

$$\wedge_m^0 = \frac{1000\kappa}{C},$$

where C is the molarity of solution and hence the solubility.

ATLAS

Some Basic Concept

(1) Electrolytes,

(2) Electrolysis,

(3) Conductance

- Electrochemical Cells
  - Electrolytic Cell
    - 1. Set up of cell
    - 2.Types of electrodes
    - 3. Faraday's laws of electrolysis
    - 4. Qualitative aspects of electrolysis
  - Galvanic Cell
    - 1.(a) Set up of cell
      (b) Cell Notations
      (c) Cell potential & Nearest equation
      (d) Relationship between standard free energy & equlibrium constant
    - 2. Types of half cells / electrodes
    - 3. Concentration cells
      (a) Electrode concentrations cells
      (b) Electrolyte concentration cells
    - 4. Type of batteries
- Electrolytic conductance
  - 1. Conductance of solutions
  - 2. Equivalent and molar conductivity & relationship between them
  - 3. Variation of molar conductivity with concentration
  - 4. Kohlrausch's law & it's application

EASY RIDE

ELECTROLYTIC CELL :

Q.1 Calculate the no. of electrons lost or gained during electrolysis of
(a) 3.55 gm of Cl^- ions (b) 1 gm Cu^{2+} ions (c) 2.7 gm of Al^{3+} ions

Q.2 How many faradays of electricity are involved in each of the case
(a) 0.25 mole Al^{3+} is converted to Al.
(b) 27.6 gm of SO_3 is convered to SO_3^{2-}
(c) The Cu^{2+} in 1100 ml of 0.5 M Cu^{2+} is converted to Cu.

Q.3 0.5 mole of electron is passed through two electrolytic cells in series. One contains silver ions, and the other zinc ions. Assume that only cathode reaction in each cell is the reduction of the ion to the metal. How many gm of each metals will be deposited.

Q.4 The electrosynthesis of MnO_2 is carried out from a solution of $MnSO_4$ in H_2SO_4 (aq). If a current of 25.5 ampere is used with a current efficiency of 85%, how long would it take to produce 1 kg of MnO_2?

Q.5 A constant current of 30 A is passed through an aqueous solution of NaCl for a time of 1.0 hr. How many grams of NaOH are produced? What is volume of Cl_2 gas at S.T.P. produced?

Q.6 If 0.224 litre of H_2 gas is formed at the cathode, how much O_2 gas is formed at the anode under identical conditions?

Q.7 If 0.224 litre of H_2 gas is formed at the cathode of one cell at S.T.P., how much of Mg is formed at the cathode of the other electrolytic cell.

Q.8 Assume 96500 C as one unit of electricity. If cost of electricity of producing x gm Al is Rs x, what is the cost of electricity of producing x gm Mg?

Q.9 Chromium metal can be plated out from an acidic solution containing CrO_3 according to following equation:
$CrO_3(aq) + 6H^+ (aq) + 6e^- \rightarrow Cr(s) + 3H_2O$
Calculate :
(i) How many grams of chromium will be plated out by 24000 coulombs and
(ii) How long will it take to plate out 1.5 gm of chromium by using 12.5 ampere current

Q.10 Calculate the quantity of electricity that would be required to reduce 12.3 g of nitrobenzene to aniline, if the current efficiency for the process is 50 percent. If the potential drop across the cell is 3.0 volts, how much energy will be consumed?

Q.11 How long a current of 2A has to be passed through a solution of $AgNO_3$ to coat a metal surface of $80cm^2$ with 5μm thick layer? Density of silver = $10.8g/cm^3$.

Q.12 3A current was passed through an aqueous solution of an unknown salt of Pd for 1Hr. 2.977g of Pd^{+n} was deposited at cathode. Find n.

Q.13 50mL of 0.1M $CuSO_4$ solution is electrolyzed with a current of 0.965 A for a period of 200 sec. The reactions at electrodes are:
Cathode : $Cu^{2+} + 2e^- \rightarrow Cu(s)$ Anode : $2H_2O \rightarrow O_2 + 4H^+ + 4e$.
Assuming no change in volume during electrolysis, calculate the molar concentration of Cu^{2+}, H^+ and SO_4^{2-} at the end of electrolysis.

Q.14 A metal is known to form fluoride MF_2. When 10A of electricity is passed through a molten salt for 330 sec., 1.95g of metal is deposited. Find the atomic weight of M. What will be the quantity of electricity required to deposit the same mass of Cu from $CuSO_4$?

Q.15 10g fairly concentrated solution of $CuSO_4$ is electrolyzed using 0.01F of electricity. Calculate:
(a)The weight of resulting solution (b)Equivalents of acid or alkali in the solution.

Q.16 An electric current is passed through electrolytic cells in series one containing $Ag(NO_3)$(aq.) and other H_2SO_4(aq). What volume of O_2 measured at 25^0C and 750mm Hg pressure would be liberated from H_2SO_4 if
(a) one mole of Ag^+ is deposited from $AgNO_3$ solution
(b) 8×10^{22} ions of Ag^+ are deposited from $AgNO_3$ solution.

Q.17 Cadmium amalgam is prepared by electrolysis of a solution of $CdCl_2$ using a mercury cathode. How long should a current of 5A be passed in order to prepare 12% Cd–Hg amalgam on a cathode of 2gm Hg (Cd=112.4)

Q.18 After electrolysis of NaCl solution with inert electrodes for a certain period of time. 600 mL of the solution was left. Which was found to be 1N in NaOH. During the same time, 31.75 g of Cu was deposited in the copper voltameter in series with the electrolytic cell. Calculate the percentage yield of NaOH obtained.

Q.19 Three electrolytic cells A, B, C containing solution of $ZnSO_4$, $AgNO_3$ and $CuSO_4$, respectively are connected in series. A steady current of 2 ampere was passed through them until 1.08 g of silver deposited at the cathode of cell B. How long did the current flow? What mass of copper and of zinc were deposited?

Q.20 Copper sulphate solution (250 mL) was electrolysed using a platinum anode and a copper cathode. A constant current of 2 mA was passed for 16 minutes. It was found that after electrolysis the concentration of the solution was reduced to 50% of its original value. Calculate the concentration of copper sulphate in the original solution.

Q.21 A solution of $Ni(NO_3)_2$ is electrolysed between platinum electrodes using a current of 5 ampere for 20 mintue. What mass of Ni is deposited at the cathode?

Q.22 A current of 3.7A is passed for 6hrs. between Ni electrodes in 0.5L of 2M solution of $Ni(NO_3)_2$. What will be the molarity of solution at the end of electrolysis?

GALVANIC CELL :

Representation of Cell diagrams, complete and half cell reactions :

Q.23 Make complete cell diagrams of the following cell reactions :

(a) $Cd^{2+}(aq) + Zn(s) \rightleftharpoons Zn^{2+}(aq) + Cd(s)$

(b) $2Ag^+(aq) + H_2(g) \rightleftharpoons 2H^+(aq) + 2Ag(s)$

(c) $Hg_2Cl_2(s) + Cu(s) \rightleftharpoons Cu^{2+}(aq) + 2Cl^-(aq) + 2Hg(l)$

(d) $Cr_2O_7^{2-}(aq.) + 14H^+(aq) + 6Fe^{2+}(aq) \rightleftharpoons 6Fe^{3+}(aq) + 2Cr^{3+}(aq) + 7H_2O(l)$

Q.24 Write cell reaction of the following cells :

(a) $Ag \mid Ag^+(aq) \mid\mid Cu^{2+}(aq) \mid Cu$

(b) $Pt \mid Fe^{2+}, Fe^{3+} \mid\mid MnO_4^-, Mn^{2+}, H^+ \mid Pt$

(c) $Pt, Cl_2 \mid Cl^-(aq) \mid\mid Ag^+(aq) \mid Ag$

(d) $Pt, H_2 \mid H^+(aq) \mid\mid Cd^{2+}(aq) \mid Cd$

Q.25 Write half cells of each cell with following cell reactions :

(a) $Zn\ (s) + 2H^+\ (aq) \rightleftharpoons Zn^{2+}\ (aq) + H_2\ (g)$

(b) $2Fe^{3+}\ (aq) + Sn^{2+}\ (aq) \rightleftharpoons 2Fe^{2+}\ (aq) + Sn^{4+}\ (aq)$

(c) $MnO_4^-\ (aq) + 8H^+\ (aq) + 5Fe^{2+}\ (aq) \rightleftharpoons 2Fe^{3+}\ (aq) + Mn^{2+}\ (aq) + 4H_2O\ (l)$

(d) $Pb\ (s) + Br_2\ (l) \rightleftharpoons Pb^{2+}\ (aq) + 2Br^-\ (aq)$

Electrode potential and standard electrode potential :

Q.26 For the cell reaction $2Ce^{4+} + Co \rightleftharpoons 2Ce^{3+} + Co^{2+}$

E^o_{cell} is 1.89 V. If $E^o_{Co^{2+}|Co}$ is – 0.28 V, what is the value of $E^o_{Ce^{4+}|Ce^{3+}}$?

Q.27 Determine the standard reduction potential for the half reaction :

$Cl_2 + 2e^- \rightleftharpoons 2Cl^-$

Given $Pt^{2+} + 2Cl^- \rightleftharpoons Pt + Cl_2$, $E^o_{Cell} = -0.15$ V

$Pt^{2+} + 2e^- \rightleftharpoons Pt$ $E° = 1.20$ V

Q.28 What is E^o_{Cell} if

$2Cr + 3H_2O + 3OCl^- \rightleftharpoons 2Cr^{3+} + 3Cl^- + 6OH^-$

$2Cr^{3+} + 3e^- \rightleftharpoons Cr$, $E° = -0.74$ V

$OCl^- + H_2O + 2e^- \rightleftharpoons Cl^- + 2OH^-$, $E° = 0.94$ V

ΔG°, E^o_{Cell} and K_{eq} :

Q.29 Is 1.0 M H^+ solution under H_2SO_4 at 1.0 atm capable of oxidising silver metal in the presence of 1.0 M Ag^+ ion?

$E^o_{Ag^+|Ag} = 0.80$ V, $E^o_{H^+|H_2(Pt)} = 0.0$ V

Q.30 If for the half cell reactions $Cu^{2+} + e^- \rightleftharpoons Cu^+$ $E° = 0.15$ V

$Cu^{2+} + 2e^- \rightleftharpoons Cu$ $E° = 0.34$ V

Calculate E° of the half cell reaction

$Cu^+ + e^- \rightleftharpoons Cu$

also predict whether Cu^+ undergoes disproportionation or not.

Q.31 If $E^o_{Fe^{2+}|Fe} = -0.44$ V, $E^o_{Fe^{3+}|Fe^{2+}} = 0.77$ V. Calculate $E^o_{Fe^{3+}|Fe}$.

Q.32 If $E^o_{Cu^+|Cu} = 0.52$ V, $E^o_{Cu^{2+}|Cu} = 0.34$ V, what is E^o_{Cell} of the cell reaction

$Cu + Cu^{2+} \rightleftharpoons 2Cu^+$?

is cell reaction spontaneous?

Q.33 Calculate the EMF of a Daniel cell when the concentration of $ZnSO_4$ and $CuSO_4$ are 0.001 M and 0.1M respectively. The standard potential of the cell is 1.1V.

Q.34 Calculate the equilibrium constant for the reaction $Fe + CuSO_4 \rightleftharpoons FeSO_4 + Cu$ at 25^0C.
Given $E^0\ (Fe/Fe^{2+}) = 0.44$V, $E^0\ (Cu/Cu^{2+}) = -0.337$V.

Q.35 For a cell $Mg(s) \mid Mg^{2+}(aq) \parallel Ag^{+}(aq) \mid Ag$, Calculate the equilibrium constant at 25^0C. Also find the maximum work that can be obtained by operating the cell.
$E^0 (Mg^{2+}/Mg) = -2.37V$, $E^0 (Ag^{+}/Ag) = 0.8$ V.

Q.36 The standard reduction potential at 25^0C for the reduction of water
$2H_2O + 2e^- \rightleftharpoons H_2 + 2OH^-$ is -0.8277 volt. Calculate the equilibrium constant for the reaction
$2H_2O \rightleftharpoons H_3O^+ + OH^-$ at 25^0C.

Q.37 At 25^0C the value of K for the equilibrium $Fe^{3+} + Ag \rightleftharpoons Fe^{2+} + Ag^+$ is 0.531mol/litre. The standard electrode potential for $Ag^+ + e^- \rightleftharpoons Ag$ is 0.799V. What is the standard potential for $Fe^{3+} + e^- \rightleftharpoons Fe^{2+}$?

Q.38 The EMF of the cell $M \mid M^{n+} (0.02M) \parallel H^+ (1M) \mid H_2(g)$ (1 atm), Pt at 25^0C is 0.81V. Calculate the valency of the metal if the standard oxidation of the metal is 0.76V.

Q.39 Equinormal Solutions of two weak acids, HA ($pK_a = 3$) and HB ($pK_a = 5$) are each placed in contact with standard hydrogen electrode at 25^0C. When a cell is constructed by interconnecting them through a salt bridge, find the emf of the cell.

Q.40 In two vessels each containing 500ml water, 0.5m mol of aniline ($K_b = 10^{-9}$) and 25mmol of HCl are added separately. Two hydrogen electrodes are constructed using these solutions. Calculate the emf of cell made by connecting them appropriately.

Q.41 Calculate E^0 and E for the cell $Sn \mid Sn^{2+} (1M) \parallel Pb^{2+} \mid Pb(10^{-3}M)$, $E^0 (Sn^{2+} \mid Sn) = -0.14V$, $E^0 (Pb^{2+} \mid Pb) = -0.13V$. Is cell representation is correct?

Q.42 At what concentration of Cu^{2+} in a solution of $CuSO_4$ will the electrode potential be zero at 25^0C?
Given : $E^0 (Cu \mid Cu^{2+}) = -0.34$ V.

Q.43 A zinc electrode is placed in a 0.1M solution at 25^0C. Assuming that the salt is 20% dissociated at this dilutions calculate the electrode potential. $E^0 (Zn^{2+} \mid Zn) = -0.76V$.

Q.44 From the standard potentials shown in the following diagram, calculate the potentials E_1° and E_2°.

Q.45 For the reaction, $4Al(s) + 3O_2(g) + 6H_2O + 40H^- \rightleftharpoons 4 [Al(OH)_4^-]$; $E^\circ_{cell} = 2.73$ V. If $\Delta G_f^\circ (OH^-) = -157$ kJ mol^{-1} and $\Delta G_f^\circ (H_2O) = -237.2$ kJ mol^{-1}, determine $\Delta G_f^\circ [Al(OH)_4^-]$.

Concentration cells :

Q.46 Calculate the EMF of the following cell

$Zn \mid Zn^{2+}$ (0.01M) $\parallel Zn^{2+}$ (0.1 M) $\mid Zn$

at 298 K.

Q.47 Calculate the EMF of the cell,

$Zn - Hg(c_1M) \mid Zn^{2+}$ (aq) $\mid Hg - Zn(c_2M)$

at 25°C, if the concentrations of the zinc amalgam are: c_1 = 10g per 100g of mercury and c_2 = 1g per100 g of mercury.

Q.48 Calculate pH using the following cell :

Pt (H_2) | H^+ (x M) | | H^+ (1 M) | Pt (H_2) if E_{cell} = 0.2364 V.

1 atm 1 atm

Q.49 Calculate the EMF of following cells at 25^0C.

(i) $Fe \mid Fe^{2+}$ (a_1 = 0.3) $\parallel Sn^{2+}$ (a_2 = 0.1) $\mid Sn$ E^0 (Fe^{2+}/Fe) = –0.44 V

(ii) Pt, H_2 (2atm) | HCl |H_2 (10 atm), Pt. E^0 (Sn^{2+}/Sn) = –0.14 V

Q.50 EMF of the cell $Zn \mid ZnSO_4$ (a_1= 0.2) $\parallel ZnSO_4$(a_2) | Zn is –0.0088V at 25^0C. Calculate the value of a_2.

CONDUCTANCE

Conductivities and cell constant:

Q.51 The resistance of a conductivity cell filled with 0.01N solution of NaCl is 210 ohm a t 1 8 °C . Calculate the equivalent conductivity of the solution. The cell constant of the conductivity cell is 0.88 cm^{-1}.

Q.52 The molar conductivity of 0.1 M CH_3COOH solution is 4.6 S cm^2 $mole^{-1}$. What is the specific conductivity and resistivity of the solution ?

Q.53 The conductivity of pure water in a conductivity cell with electrodes of cross sectional area 4 cm^2 and 2 cm apart is 8 x 10^{-7} S cm^{-1}.

(i) What is resistance of conductivity cell ?

(ii) What current would flow through the cell under an applied potential difference of 1 volt?

Q.54 Resistivity of 0.1M KCl solution is 213 ohm cm in a conductivity cell. Calculate the cell constant if its resistance is 330 ohm.

Q.55 Resistance of a 0.1M KCl solution in a conductance cell is 300 ohm and specific conductance of 0.1M KCl is 1.29 x 10^{-2} ohm^{-1} cm^{-1}. The resistance of 0.1M NaCl solution in the same cell is 380 ohm. Calculate the equivalent conductance of the 0.1M NaCl solution.

Q.56 For 0.01N KCl, the resistivity 709.22 mho cm. Calculate the conductivity and equivalent conductance.

Q.57 A solution containing 2.08 g of anhydrous barium chloride is 400 CC of water has a specific conductivity 0.0058 $ohm^{-1}cm^{-1}$. What are molar and equivalent conductivities of this solution.

Application of Kohlrausch's law:

Q.58 Equivalent conductance of 0.01 N Na_2SO_4 solution is 112.4 $ohm^{-1}\ cm^2\ eq^{-1}$. The equivalent conductance at infinite dilution is 129.9 $ohm^{-1}\ cm^2$. What is the degree of dissociation in 0.01 N Na_2SO_4 solution?

Q.59 Specific conductance of a saturated solution of AgBr is $8.486\times10^{-7}\ ohm^{-1}cm^{-1}$ at 25^0C. Specific conductance of pure water at 25^0C is $0.75\times10^{-6}\ ohm^{-1}\ cm^{-2}$. Λ_m^∞ for KBr , $AgNO_3$ and KNO_3 are 137.4 , 133 , 131 ($S\ cm^2\ mol^{-1}$) respectively. Calculate the solubility of AgBr in gm/litre.

Q.60 Saturated solution of AgCl at 25^0C has specific conductance of $1.12\times10^{-6}\ ohm^{-1}\ cm^{-1}$. The $\lambda_\infty Ag^+$ and $\lambda_\infty Cl^-$ are 54.3 and 65.5 $ohm^{-1}\ cm^2$ / equi. respectively. Calculate the solubility product of AgCl at 25^0C.

Q.61 Hydrofluoric acid is weak acid. At 25^0C, the molar conductivity of 0.002M HF is 176.2 $ohm^{-1}\ cm^2\ mole^{-1}$. If its Λ_m^∞ = 405.2 $ohm^{-1}\ cm^2\ mole^{-1}$, calculate its degree of dissociation and equilibrium constant at the given concentration.

Q.62 The value of Λ_m^∞ for HCl, NaCl and CH_3CO_2Na are 426.1, 126.5 and 91 $S\ cm^2\ mol^{-1}$ respectively. Calculate the value of Λ_m^∞ for acetic acid. If the equivalent conductivity of the given acetic acid is 48.15 at 25° C, calculate its degree of dissociation.

Q.63 Calculate the specific conductance of a 0.1 M aqueous solution of NaCl at room temperature, given that the mobilities of Na^+ and Cl^- ions at this temperature are 4.26×10^{-8} and $6.80\times10^{-8}\ m^2\ v^{-1}\ s^{-1}$, respectively.

Q.64 For the strong electroytes NaOH, NaCl and $BaCl_2$ the molar ionic conductivities at infinite dilution are 248.1×10^{-4}, 126.5×10^{-4} and 280.0×10^{-4} mho $cm^2\ mol^{-1}$ respectively. Calculate the molar conductivity of $Ba(OH)_2$ at infinite dilution.

Q.65 At 25°C, $\lambda_\infty(H^+) = 3.4982\times10^{-2}\ S\ m^2\ mol^{-1}$ and $\lambda_\infty(OH^-) = 1.98\times10^{-2}\ S\ m^2mol^{-1}$.
Given: Sp. conductnace = $5.1\times10^{-6}\ S\ m^{-1}$ for H_2O, determine pH and K_w.

PROFICIENCY TEST

1. In highly alkaline medium, the anodic process during the electrolytic process is
$$4OH^- \longrightarrow O_2 + 2H_2O + 4e^-.$$

2. Compounds of active metals (Zn, Na, Mg) are reducible by H_2 whereas those of noble metals (Cu, Ag, Au) are not reducible.

3. The mass of a substance deposited on the cathode or anode during electrolysis is given by $w = \frac{EIt}{F}$.

4. Faraday's second law of electrolysis is related to the equivalent, mass of the electrolyte.

5. Equivalent conductance at infinite dilution of salt AB is equal to the sum of equivalent conductances of ions, A^+ and B^- at infinite dilution.

6. The standard reduction potential of $Cl^- | AgCl | Ag$ half-cell is related to that of $Ag^+ | Ag$ half-cell through the expression $E^\circ_{Ag^+|Ag} = E^\circ_{Cl^-|AgCl|Ag} + \frac{RT}{F} \text{ In } K_{SP}(AgCl)$.

7. The cell potential is given by $E_{cell} = E_{RP(cathode)} - E_{RP(anode)}$.

8. A half-cell reaction is $A^{(x+n)} + ne^- \longrightarrow A^{x+}$. It is possible to determine the value of n from the measurements of cell potential.

9. In a galvanic cell, the half-cell with higher reduction potential acts as a reducing agent.

10. In an electrode concentration cell, the cel reaction $Zn(c_1) \longrightarrow Zn(c_2)$ will be spontaneous if $c_1 > c_2$.

11. The absolute value of electrode potential cannot be determined.

12. All chemical reactions used in galvanic cells are redox reactions.

13. The amount of the product formed by the passage of 1 coulomb of electricity through electrolyte is called electrochemical equivalent of the substance.

14. The redox reaction involved in galvanic cell is a non- spontaneous process.

15. In galvanic cell, the cathode is a – ve terminal of the cell.

16. The specific conductance of a 0.1 N KCl solution at 23°C is 0.012 $ohm^{-1}\ cm^{-1}$. The resistance of the cell containing the solution at the same temperature was found to be 55 ohms. The cell constant is ____.

17. Dilute sulphuric acid on electrolysis liberates_____ at the anode.

18. The electrical conductivity of a solution of acetic acid will _____ if a solution of sodium hydroxide is added.

19. A cation having a _____reduction potential is preferentially reduced at the cathode.

20. When an aqueous solution of sodium sulphate is electrolysed, the gases liberated at the anode & cathode are _____ and _____, respectively.

21. A cell in which two electrodes of the same metal are dipped in solutions of metal ion of different concentrations in called_____.

22. The half-cell involving the reaction,

$$Cr_2O_7^{2-}(aq.) + 14H^+(aq.) + 6e^- \longrightarrow 2Cr^{3+}(aq.) + 7H_2O$$

is represented as _____.

23. During discharge of lead storage battery, the overall reaction is_____.

24. In the calomel half-cell, the reduction reaction is _____.

25. Temperature coefficient and change in enthalpy are related by the expression_____.

26. In salt bridge, the electrolyte used should be _____.

27. In electrochemical cell, the electrical neutrality in two half cells is maintained by _____.

28. The E° value for $H_2 \longrightarrow 2H^+ + 2e^-$ is _____.

29. $E°_{cell}$ of $E°_{oxi.}$(anode) + _____.

30. Coulomb refers to _____ of electricity while ampere refers to _____ at which it flows.

31. The cathodic reactions always involve_____.

32. During electrolysis of aqueous solution of $CuSO_4$ using Pt electrodes the product at anode is _____.

33. The quantity of electricity required for complete reduction of 0.5 mole MnO_4^- to Mn^{2+} is _____C.

34. During electrolysis process _____energy is converted into _____.

35. $\wedge_{eq} \times$ normality = _____.

MIDDLE GAME

Q.1 Same quantity of electricity is being used to liberate iodine (at anode) and a metal x (at cathode). The mass of x deposited is 0.617g and the iodine is completely reduced by 46.3 cc of 0.124M sodium thiosulphate. Find the equivalent mass of x.

Q.2 The standard reduction potential values, $E^0(Bi^{3+}|Bi)$ and $E^0(Cu^{2+}|Cu)$ are 0.226V and 0.344V respectively. A mixture of salts of bismuth and copper at unit concentration each is electrolysed at 25^0C. to what value can $[Cu^{2+}]$ be brought down before bismuth starts to deposit, in electrolysis.

Q.3 In a fuel cell, H_2 & O_2 react to produce electricity. In the process, H_2 gas is oxidized at the anode & O_2 at the cathode . If 67.2 litre of H_2 at STP react in 15 minutes, what is the average current produced ? If the entire current is used for electrode deposition of Cu from Cu (II) solution, how many grams of Cu will be deposited?

Anode : $H_2 + 2OH^- \longrightarrow 2H_2O + 2e^-$ Cathode : $O_2 + 2H_2O + 4e^- \longrightarrow 4OH^-$

Q.4 One of the methods of preparation of per disulphuric acid, $H_2S_2O_8$, involve electrolytic oxidation of H_2SO_4 at anode ($2H_2SO_4 \rightarrow H_2S_2O_8 + 2H^+ + 2e^-$) with oxygen and hydrogen as by–products. In such an electrolysis, 9.722 L of H_2 and 2.35 L of O_2 were generated at STP. What is the weight of $H_2S_2O_8$ formed?

Q.5 During the discharge of a lead storage battery the density of sulphuric acid fell from 1.294 to 1.139 $g.ml^{-1}$. H_2SO_4 of density 1.294 g mL^{-1} is 39% and that of density 1.39 g mL^{-1} is 20% by weight. The battery holds 3.5L of acid and the volume practically remains constant during the discharge. Calculate the number of ampere hours for which the battery must have been used. The discharging reactions are:

$Pb + SO_4^{2-} \rightleftharpoons PbSO_4 + 2e^-$ (anode)

$PbO_2 + 4H^+ + SO_4^{2-} + 2e^- \rightleftharpoons PbSO_4 + 2H_2O$ (cathode)

Q.6 The emf of the cells obtained by combining Zn and Cu electrode of a Daniel cell with N calomel electrode in two different arrangements are 1.083V and 0.018V respectively at 25^0C. If the standard reduction potential of N calomel electrode is –0.28V and that of Zn is –0.76 V, find the emf of Daniel cell.

Q.7 Given the standard reduction potentials $Tl^+ + e^- \rightleftharpoons TI$, $E^0 = -0.34V$ and $TI^{3+} + 2e^- \rightleftharpoons TI^+$, $E^0 = 1.25V$. Examine the spontaneity of the reaction, $3TI^+ \rightleftharpoons 2TI + TI^{3+}$. Also find E^0 for this disproportionation.

Q.8 The emf of the cell $Ag|AgI|KI(0.05M) \| AgNO_3(0.05M)|Ag$ is 0.788V. Calculate the solubility product of AgI.

Q.9 The cell Pt, H_2(1 atm) | H^+(pH=x) || Normal calomel Electrode has an EMF of 0.67V at 25^0C. Calculate the pH of the solution. The oxidation potential of the calomel electrode on hydrogen scale is –0.28 V.

Q.10 Estimate the cell potential of a Daniel cell having 1 M Zn^{++} & originally having 1 M Cu^{++} after sufficient NH_3 has been added to the cathode compartment to make NH_3 concentration 2 M.
K_f for $[Cu(NH_3)_4]^{2+} = 1 \times 10^{12}$, E^0 for the reaction,
$Zn + Cu^{2+} \rightleftharpoons Zn^{2+} + Cu$ is 1.1 V.

Q.11 Consider the cell $Ag|AgBr(s)|Br^-\|AgCl(s), Ag|Cl^-$ at 25° C . The solubility product constants of AgBr & AgCl are respectively 5×10^{-13} & 1×10^{-10} . For what ratio of the concentrations of Br^- & Cl^- ions would the emf of the cell be zero ?

Q.12 The pK_{sp} of AgI is 16.07 . If the E° value for $Ag^+|Ag$ is 0.7991 V . Find the E° for the half cell reaction $AgI(s) + e^- \rightleftharpoons Ag + I^-$.

Q.13 Voltage of the cell Pt, H_2 (1 atm)|HOCN (1.3×10^{-3} M)||Ag^+ (0.8 M)|Ag(s) is 0.982 V . Calculate the K_a for HOCN . Neglect $[H^+]$ because of oxidation of $H_2(g)$.
$Ag^+ + e \rightleftharpoons Ag(s) = 0.8$ V.

Q.14 The normal potential of Zn referred to SHE is 0.76V and that of Cu is –0.34V at 25^0C. When excess of Zn is added to $CuSO_4$, Zn displaces Cu^{2+} till equilibrium is reached. What is the ratio of Zn^{2+} to Cu^{2+} ions at equilibrium?

Q.15 Calculate the potential of an indicator electrode versus the standard hydrogen electrode, which originally contained 0.1M MnO_4^- and 0.8M H^+ and which was treated with 90% of the Fe^{2+} necessary to reduce all the MnO_4^- to Mn^{+2}.
$MnO_4^- + 8H^+ + 5e \rightleftharpoons Mn^{2+} + 4H_2O$, $E^0 = 1.51$V

Q.16 K_d for complete dissociation of $[Ag(NH_3)_2]^+$ into Ag^+ and $2NH_3$ is 6×10^{-8}. Calculate E^0 for the following half reaction; $Ag(NH_3)_2^+ + e^- \rightleftharpoons Ag + 2NH_3$
$Ag^+ + e^- \rightleftharpoons Ag$, $E^0 = 0.799$ V

Q.17 The overall formation constant for the reaction of 6 mol of CN^- with cobalt (II) is 1×10^{19}. The standard reduction potential for the reaction
$[Co(CN)_6]^{3-} + e^- \rightleftharpoons Co(CN)_6^{4-}$ is –0.83 V. Calculate the formation constant of $[Co(CN)_6]^{3-}$
Given $Co^{3+} + e^- \rightleftharpoons Co^{2+}$; $E^0 = 1.82$ V

Q.18 Calculate the emf of the cell
Pt, H_2(1.0 atm) | CH_3COOH (0.1M) || NH_3(aq, 0.01M) | H_2 (1.0 atm),
Pt $K_a(CH_3COOH) = 1.8 \times 10^{-5}$, $K_b(NH_3) = 1.8 \times 10^{-5}$.

Q.19 A current of 3 amp was passed for 2 hour through a solution of $CuSO_4$,3 g of Cu^{2+} ions were deposited as Cu at cathode. Calculate percentage current efficiency of the process.

Q.20 The Edison storage cell is represented as Fe(s) | FeO(s) | KOH(aq) | Ni_2O_3 (s) | Ni(s) The half–cell reaction are
$Ni_2O_3(s) + H_2O(i) + 2e^- \rightleftharpoons 2NiO(s) + 2OH^-$, $E^0 = +0.40$V
$FeO(s) + H_2O(l) + 2e^- \rightleftharpoons Fe(s) + 2OH^-$, $E^0 = -0.87$V

(i) What is the cell reaction?
(ii) What is the cell e.m.f.? How does it depend on the concentration of KOH?
(iii) What is the maximum amount of electrical energy that can be obtained from one mole of Ni_2O_3?

Q.21 For the galvanic cell : Ag|AgCl(s)| KCl (0.2M) || K Br (0.001 M)| AgBr(s) | Ag,
Calculate the EMF generated and assign correct polarity to each electrode for a spontaneous process after taking into account the cell reaction at 25^0C.
$[K_{sp(AgCl)} = 2.8 \times 10^{-10}; K_{sp(AgBr)} = 3.3 \times 10^{-13}]$

Q.22 An aqueous solution of NaCl on electrolysis gives $H_{2(g)}$, $Cl_{2(g)}$ and NaOH according to the reaction:
$$2Cl^-_{(aq)} + 2H_2O \rightleftharpoons 2OH^-_{(aq)} + H_{2(g)} + Cl_{2(g)}$$
A direct current of 25 amperes with a current efficiency of 62% is passed through 20 liters of NaCl solution (20% by weight). Write down the reactions taking place at the anode and the cathode. How long will it take to produce 1Kg of Cl_2? What will be the molarity of the solution with respect to hydroxide ion? (Assume no loss due to evaporation).

Q.23 An acidic solution of Cu^{2+} salt containing 0.4 g of Cu^{2+} is electrolyzed until all the copper is deposited. The electrolysis is continued for seven more minutes with the volume of solution kept at 100 ml and the current at 1.2 amp. Calculate the volume of gases evolved at NTP during the entire electrolysis.

Q.24 In the refining of silver by electrolytic method what will be the weight of 100 gm Ag anode if 5 ampere current is passed for 2 hours? Purity of silver is 95% by weight.

Q.25 Hydrogen peroxide can be prepared by successive reactions:

$2NH_4HSO_4 \rightarrow H_2 + (NH_4)_2S_2O_8$

$(NH_4)_2S_2O_8 + 2H_2O \rightarrow 2NH_4HSO_4 + H_2O_2$

The first reaction is an electrolytic reaction the second is steam distillation. What amount of current would have to be used in first reaction to produce enough intermediate to yield 100 gm pure H_2O_2 per hour? Assume 50% anode current efficiency.

Q.26 Dal lake has water 8.2×10^{12} litre approximately. A power reactor produces electricity at the rate of 1.5×10^{6}coulomb per second at an appropriate voltage.How many years would it take to electrolyse the lake?

Q.27 Calculate the potential at 25°C for the cell

$Cd \mid Cd^{2+}$ (2.00 M) $\parallel Pb^{2}$ (0.0010 M) $\mid Pb$

Given $E^\circ_{cell} = 0.277$ V.

Q.28 Calculate E° for the following reactions at 298 K,

$$Ag(NH_3)_2^+ + e^- \rightleftharpoons Ag + 2NH_3$$

$$Ag(CN)_2^- + e^- \rightleftharpoons Ag + 2CN^-$$

Given: $E^\circ_{Ag^+|Ag} = 0.7991\,V, K_{Ins}[Ag(NH_3)_2^+] = 6.02 \times 10^{-8}$ and $K_{Ins}[Ag(CN)_2^-] = 1.995 \times 10^{-19}$

Q.29 Determine the degree of hydrolysis and hydrolysis constant of aniline hydrochloride in M/32 solution of salt at 298 K from the following cell data at 298 K.

$Pt \mid H_2$ (1 atm) $\mid H^+$(1M) $\parallel$ M/32 $C_6H_5NH_3Cl \mid H_2$ (1 atm) $\mid Pt$; $E_{cell} = -0.188$ V.

Q.30 The emf of the cell, $Pt \mid H_2$ (1 atm), $\mid H^+$ (0.1 M, 30 ml) $\parallel Ag^+$ (0.8 M) $\mid Ag$ is 0.9 V. Calculate the emf when 40 ml of 0.05 M NaOH is added.

Q.31 Given, E° = –0.268 V for the $Cl^- \mid PbCl_2 \mid Pb$ couple and – 0.126 V for the $Pb^{2+} \mid Pb$ couple, determine K_{sp} for $PbCl_2$ at 25°C?

Q.32 The equivalent conductance of 0.10 N solution of $MgCl_2$ is 97.1 mho cm^2 $equi^{-1}$ at 25^0C. a cell with electrode that are 1.5 cm^2 in surface area and 0.5 cm apart is filled with 0.1 N $MgCl_2$ solution. How much current will flow when potential difference between the electrodes is 5 volt.

Q.33 A dilute aqueous solution of KCl was placed between two electrodes 10 cm apart, across which a potential of 6 volt was applied. How far would the K^+ ion move in 2 hours at 25^0C? Ionic conductance of K^+ ion at infinite dilution at 25^0C is 73.52 ohm^{-1} cm^2 $mole^{-1}$?

Q.34 When a solution of specific conductance 1.342 ohm^{-1} $metre^{-1}$ was placed in a conductivity cell with parallel electrodes, the resistance was found to be 170.5 ohm. Area of electrodes is 1.86×10^{-4} m^2. Calculate separation of electrodes.

Q.35 The specific conductance at 25^0C of a saturated solution of $SrSO_4$ is 1.482×10^{-4} ohm^{-1} cm^{-1}while that of water used is 1.5×10^{-6} mho cm^{-1}. Determine at 25^0C the solubility in gm per litre of $SrSO_4$ in water. Molar ionic conductance of Sr^{2+} and SO_4^{2-} ions at infinite dilution are 59.46 and 79.8 ohm^{-1} cm^2 $mole^{-1}$ respectively. [Sr = 87.6 , S = 32 , O = 16]

ZENITH

Q.1 A lead storage cell is discharged which causes the H_2SO_4 electrolyte to change from a concentration of 34.6 % by weight (density 1.261g ml^{-1} at 25°C) to 27 % by weight. The original volume of electrolyte is one litre. Calculate the total charge released at anode of the battery. Note that the water is produced by the cell reaction as H_2SO_4 is used up. Over all reaction is

$$Pb(s) + PbO_2(s) + 2H_2SO_4(l) \longrightarrow 2PbSO_4(s) + 2H_2O(l)$$

Q.2 Assume that impure copper contains only iron, silver and a gold as impurities. After passage of 140 A, for 482.5s of the mass of the anode decreased by 22.260g and the cathode increased in mass by 22.011 g. Estimate the % iron and % copper originally present.

Q.3 100ml $CuSO_4$(aq) was electrolyzed using inert electrodes by passing 0.965 A till the pH of the resulting solution was 1. The solution after electrolysis was neutralized, treated with excess KI and titrated with 0.04M $Na_2S_2O_3$. Volume of $Na_2S_2O_3$ required was 35 ml. Assuming no volume change during electrolysis, calculate:
(a) duration of electrolysis if current efficiency is 80% (b) initial concentration (M) of $CuSO_4$.

Q.4 Calculate the equilibrium constant for the reaction:

$$3Sn(s) + 2Cr_2O_7^{2-} + 28H^+ \longrightarrow 3Sn^{4+} + 4Cr^{3+} + 14H_2O$$

E^0 for Sn/Sn^{2+} =0.136 V E^0 for Sn^{2+}/Sn^{4+} = – 0.154 V
E^0 for $Cr_2O_7^{2-}/Cr^{3+}$ = 1.33 V

Q.5 Calculate the equlibrium concentrations of all ions in an ideal solution prepared by mixing 25.00 mL of 0.100M Tl^+ with 25.00mL of 0.200M Co^{3+}.
E^0 (Tl^+/Tl^{3+})= –1.25 V ; E^0 (Co^{3+}/Co^{2+}) = 1.84 V

Q.6 Calculate the voltage, E, of the cell at 25^0 C

$$Mn(s) \mid Mn(OH)_2(s) \mid Mn^{2+}(x\ M), OH^-(1.00 \times 10^{-4}M) \parallel Cu^{2+}(0.675M) \mid Cu(s)$$

given that $K_{sp} = 1.9 \times 10^{-13}$ for $Mn(OH)_2(s)$ E^0 (Mn^{2+}/Mn) = –1.18 V

Q.7 Calculate the voltage, E, of the cell

$$Ag(s) \mid AgIO_3(s) \mid Ag^+(x\ M), HIO_3\ (0.300M) \parallel Zn^{2+}\ (0.175M) \mid Zn(s)$$

if K_{sp} = 3.02×10^{-8} for $AgIO_3(s)$ and K_a = 0.162 for HIO_3.

Q.8 The voltage of the cell

$$Pb(s) \mid PbSO_4(s) \mid NaHSO_4(0.600M) \parallel Pb^{2+}(2.50 \times 10^{-5}M) \mid Pb(s)$$

is E = +0.061 V. Calculate $K_2 = [H^+]\ [SO_4^{2-}] / [HSO_4^-]$, the dissociation constant for HSO_4^-.
Given : $Pb\ (s) + SO_4^{2-}(aq) \rightleftharpoons PbSO_4\ (s) + 2e^-$ (E^0 = 0.356) $E^0(Pb^{2+}/Pb)$ = –0.126 V

Q.9 The voltage of the cell

$$Zn(s) \mid Zn(CN)_4^{2-}(0.450M), CN^-(2.65 \times 10^{-3}M) \parallel Zn^{2+}(3.84 \times 10^{-4}M) \mid Zn(s)$$

is E = +0.099 V. Calculate the constant K_f for $Zn^{2+} + 4CN^- \rightleftharpoons Zn(CN)_4^{2-}$, the only $Zn^{2+} + CN^-$ complexation reaction of importance.

Q.10 An external current source giving a current of 5.0 A was joined with Daniel cell and removed after 10 hrs. Before passing the current the LHE and RHE contained 1L each of 1M Zn^{2+} and Cu^{2+} respectively. Find the EMF supplied by the Daniel cell after removal of the external current source. E^0 of Zn^{2+}/Zn and Cu^{2+}/Cu at 25°C is –0.76 and +0.34V respectively.

Q.11 Determine at 298 for cell

$Pt \mid Q, QH_2, H^+ \parallel 1M\ KCl \mid Hg_2Cl_2(s) \mid Hg(l) \mid Pt$

(a) it's emf when pH = 5.0

(b) the pH when $E_{cell} = 0$

(c) the positive electrode when pH = 7.5

given $E^0_{RP(RHS)} = 0.28$, $E^0_{RP(LHS)} = 0.699$

Q.12 At 25°C, $\Delta H_f(H_2O,l) = -56700$ cal / mol and energy of ionization of $H_2O\ (l) = 19050$ cal/mol. What will be the reversible EMF at 25°C of the cell,

$Pt \mid H_2(g)\ (1\ atm) \mid H^+ \parallel OH^- \mid O_2(g)\ (1\ atm) \mid Pt$, if at 26°C the emf increas by 0.001158 V.

Q.13 Calculate the cell potential of a cell having reaction: $Ag_2S + 2e^- \rightleftharpoons 2Ag + S^{2-}$ in a solution buffered at pH = 3 and which is also saturated with 0.1 M H_2S.

For H_2S : $K_1 = 10^{-8}$ and $K_2 = 1.1 \times 10^{-13}$, $K_{sp}(Ag_2S) = 2 \times 10^{-49}$, $E^\circ_{Ag^+/Ag} = 0.8$.

Q.14 Calculate the solubility and solubility product of $Co_2\ [Fe(CN)_6]$ in water at 25^0C from the following data:

Conductivity of a saturated solution of $Co_2[Fe(CN)_6]$ is $2.06 \times 10^{-6}\Omega^{-1}\ cm^{-1}$ and that of water used $4.1 \times 10^{-7}\Omega^{-1}\ cm^{-1}$. The ionic molar conductivities of Co^{2+} and $Fe(CN)_6^{4-}$ are 86.0 $\Omega^{-1}\ cm^2\ mol^{-1}$ and 444.0 $\Omega^{-1}\ cm^{-1} mol^{-1}$.

Q.15 A sample of water from a large swimming pool has a resistance of 9200 Ω at 25°C when placed in a certain conductance cell. When filled with 0.02 M KCl solution, the cell has a resistance of 85 Ω at 25°C. 500 gm of NaCl were dissolved in the pool, which was throughly stirred. A sample of this solution gave a resistance of 7600 Ω. Calculate the volume of water in the pool.

Given : Molar conductance of NaCl at that concentration is 126.5 $\Omega^{-1}\ cm^2\ mol^{-1}$ and molar conductivity of KCl at 0.02 M is 138 $\Omega^{-1}\ cm^2\ mol^{-1}$.

SUHANA SAFAR

OBJECTIVE

Q.1 A dilute aqueous solution at Na_2SO_4 is electrolysed using platinum electrodes.The products at the anode and cathode are

(A) O_2, H_2 (B) $S_2O_8^{2-}$, Na (C) O_2, Na (D) $S_2O_8^{2-}$, H_2 **[JEE 1996]**

Q.2 The standard reduction potentials of Cu^{2+}/ Cu and Cu^{2+} / Cu^{+} are 0.337 and 0.153 V respectively. The standard electrode potential of Cu^{+} / Cu half cell is

(A) 0.184 V (B) 0.827 V (C) 0.521 V (D) 0.490 V **[JEE 1997]**

Q.3 A standard hydrogen electrons has zero electrode potential because

(A) hydrogen is easier to oxidise

(B) this electrode potential is assumed to be zero

(C) hydrogen atom has only one electron

(D) hydrogen is the lighest element. **[JEE 1997]**

Q.4 The standard reduction potential values of the three metallic cations X, Y, Z are 0.52, –3.03, and –1.18 V respectively. The order of reducing power of the corresponding metals is

(A) Y > Z > X (B) X > Y > Z (C) Z > Y > X (D) Z > X > Y **[JEE 1998]**

Q.5 A gas X at 1 atm is bubbled through a solution containing a mixture of 1 M Y^- and 1 M Z^- at 25°C. If the reduction potential of Z > Y > X, then

(A) Y will oxidise X and not Z (B) Y will oxidise Z and X

(C) Y will oxidise both X and Z (D) Y will reduce both X and Z. **[JEE 1999]**

Q.6 For the electrochemical cell, $M \mid M^+ \parallel X^- \mid X$, $E^\circ (M^+/M) = 0.44$ V and $E^\circ (X/X^-) = 0.33$V. From this data , one can deduce that

(A) $M + X \longrightarrow M^+ + X^-$ is the spontaneous reaction

(B) $M^+ + X^- \longrightarrow M + X$ is the spontaneous reaction

(C) $E_{cell} = 0.77$ V

(D) $E_{cell} = -0.77$ V **[JEE 2000]**

Q.7 The reaction,

$3ClO^-(aq) \longrightarrow ClO_3^-(aq) + 2Cl^-(aq)$

is an example of

(A) Oxidation reaction (B) Reduction reaction

(C) Disproportionation reaction (D) Decomposition reaction **[JEE 2001]**

Q.8 The correct order of equivalent conductance at infinite dilution of LiCl, NaCl and KCl is

(A) LiCl > NaCl > KCl (B) KCl > NaCl > LiCl

(C) NaCl > KCl > LiCl (D) LiCl > KCl > NaCl **[JEE 2001]**

Q.9 Saturated solution of KNO_3 is used to make salt bridge because

(A) velocity of K^+ is greater than that of NO_3^-

(B) velocity of NO_3^- is greater than that of K^+

(C) velocities of both K^+ and NO_3^- are nearly the same

(D) KNO_3 is highly soluble in water **[JEE 2001]**

Q.10 Standard electrode potential data are useful for understanding the suitablilty of an oxidant in a redox titration. Some half cell reactions and their standard potentials are given below:

$$MnO_4^- (aq) + 8H^+(aq) + 5e^- \rightleftharpoons Mn^{2+} (aq) + 4H_2O (l); E° = 1.51 V$$

$$Cr_2O_7^{2-} (aq) + 14 H^+ (aq) + 6e^- \rightleftharpoons 2Cr^{3+} (aq) + 7H_2O (l); E° = 1.38 V$$

$$Fe^{3+} (aq) + e^- \rightleftharpoons Fe^{2+} (aq); E° = 0.77 V$$

$$Cl_2 (g) + 2e^- \rightleftharpoons 2Cl^- (aq); E° = 1.40 V$$

Identify the only incorrect statement regarding quantitative estimation of aqueous $Fe(NO_3)_2$

(A) MnO_4^- can be used in aqueous HCl

(B) $Cr_2O_7^{2-}$ can be used in aqueous HCl

(C) MnO_4^- can be used in aqueous H_2SO_4

(D) $Cr_2O_7^{2-}$ can be used in aqueous H_2SO_4 **[JEE 2002]**

Q.11 In the electrolytic cell, flow of electrons is from:

(A) Cathode to anode in solution (B) Cathode to anode through external supply

(C) Cathode to anode through internal supply (D) Anode to cathode through internal supply.

[JEE 2003]

Q.12 $Zn | Zn^{2+} (a = 0.1M) || Fe^{2+} (a = 0.01M) | Fe$. The emf of the above cell is 0.2905 V. Equilibrium constant for the cell reaction is

(A) $10^{0.32/0.0591}$ (B) $10^{0.32/0.0295}$

(C) $10^{0.26/0.0295}$ (D) $e^{0.32/0.295}$ **[JEE 2004]**

Q.13 The half cell reactions for rusting of iron are: **[JEE 2005]**

$$2H^+ + \frac{1}{2}O_2 + 2e^- \rightleftharpoons H_2O; E^0 = + 1.23 V, Fe^{2+} + 2e^- \rightleftharpoons Fe; E^0 = -0.44 V$$

ΔG^0 (in kJ) for the reaction is:

(A) –76 (B) –322

(C) –122 (D) –176

SUBJECTIVE

Q.14 The standard reduction potential for Cu^{2+} / Cu is 0.34 V. Calculate the reduction potential at pH = 14 for the above couple. K_{sp} of $Cu(OH)_2$ is 1×10^{-19}. **[JEE 1996]**

Q.15 Electrolysis of a solution of $MnSO_4$ in aqueous sulphuric acid is a method for the preparation of MnO_2 as per the reaction, $Mn^{2+}_{aq} + 2H_2O \rightarrow MnO_2(s) + 2H^+_{aq} + H_2(g)$

Passing a current of 27A for 24 hours gives one kg of MnO_2. What is the value of current efficiency? Write the reaction taking place at the cathode and at the anode. **[JEE 1997]**

Q.16 How many grams of silver could be plated out on a serving tray by electrolysis of a solution containing silver in +1 oxidation state for a period of 8.0 hours at a current of 8.46 Amperes? What is the area of the tray if the thickness of the silver plating is 0.00254 cm? Density of silver is 10.5 g/cm^3. **[JEE 1997]**

Q.17 Calculate the equilibrium constant for the reaction

$Fe^{2+} + Ce^{4+} \rightleftharpoons Fe^{3+} + Ce^{3+}$, [given : $E^0_{Ce^{4+}/Ce^{3+}} = 1.44V; E^0_{Fe^{3+}/Fe^{2+}} = 0.68V$] **[JEE 1997]**

Q.18 Calculate the equilibrium constant for the reaction, $2Fe^{3+} + 3I^- \rightleftharpoons 2Fe^{2+} + I_3^-$. The standard reduction potentials in acidic conditions are 0.77 and 0.54 V respectively for Fe^{3+}/Fe^{2+} and I_3^-/I^- couples. **[JEE 1998]**

Q.19 Find the solubility product of a saturated solution of Ag_2CrO_4 in water at 298 K if the emf of the cell $Ag|Ag^+$ (satd.Ag_2CrO_4 soln.) $\| Ag^+(0.1\ M) | Ag$ is 0.164 V at 298K. **[JEE 1998]**

Q.20 Copper sulphate solution (250 mL) was electrolysed using a platinum anode and a copper cathode. A constant current of 2 mA was passed for 16 mintue. It was founf that agfter electrolysis, the absorbance of the solution was reduced to 50% of its original value. Calculate the concentration of copper sulphate in the solution to begin with. **[JEE 2000]**

Q.21 The following electrochemical cell has been set up

$$Pt_{(I)} | Fe^{3+}, Fe^{2+}(a=1) \| Ce^{4+}, Ce^{3+}(a=1) | Pt_{(II)}$$

$$E^\circ_{Fe^{3+}/Fe^{2+}} = 0.77\ V \text{ and } E^\circ_{Ce^{4+}/Ce^{3+}} = 1.61\ V$$

If an ammetter is connected between the two platinum electrodes. predict the direction of flow of current. Will the current increase or decrease with time? **[JEE 2000]**

Q.22 The standard potential of the following cell is 0.23 V at 15^0 C & 0.21 V at 35^0 C

$Pt | H_2(g) | HCl\ (aq) | AgCl(s) | Ag(s)$

(i) Write the cell reaction.

(ii) Calculate ΔH^0, ΔS^0 for the cell reaction by assuming that these quantities remain unchanged in the range 15^0C to 35^0C.

(iii) Calculate the solubility of AgCl in water at 25^0C. Given standard reduction potential of the Ag^+/Ag couple is 0.80 V at 25^0C. **[JEE 2001]**

Q.23 Two students use same stock solution of $ZnSO_4$ and a solution of $CuSO_4$. The e.m.f of one cell is 0.3 V higher than the other. The conc. of $CuSO_4$ in the cell with higher e.m.f value is 0.5 M. Find out the conc. of $CuSO_4$ in the other cell $\left(\frac{2.303RT}{F} = 0.06\right)$. **[JEE 2003]**

Q.24 Find the equilibrium constant at 298 K for the reaction,

$$Cu^{2+}(aq) + In^{2+}(aq) \rightleftharpoons Cu^+(aq) + In^{3+}(aq)$$

Given that $E^\circ_{Cu^{2+}|Cu^+} = 0.15V$, $E^\circ_{In^{3+}|In^+} = -0.42V$, $E^\circ_{In^{2+}|In^+} = -0.40V$ **[JEE 2004]**

Q.25(a)Calculate ΔG^0_f of the following reaction

$$Ag^+(aq) + Cl^-(aq) \rightleftharpoons AgCl(s)$$

Given: ΔG^0_f (AgCl) = –109 kJ/mole, ΔG^0_f (Cl^-) = –129 kJ/mole, ΔG^0_f (Ag^+) = 77 kJ/mole

Represent the above reaction in form of a cell

Calculate E^0 of the cell. Find $\log_{10}K_{SP}$ of AgCl

(b) 6.593×10^{-2} g of metallic Zn (amu = 65.39) was added to 100 ml of saturated solution of AgCl. Calculate $\log_{10}\frac{[Zn^{2+}]}{[Ag^+]^2}$, given that

$Ag^+ + e^- \rightleftharpoons Ag \quad E^0 = 0.80\ V$

$Zn^{2+} + 2e^- \rightleftharpoons Zn \quad E^0 = -0.76V$

Also find how many moles of Ag will be formed? **[JEE 2005]**

ANSWER KEY
EASY RIDE

Q.1 (a) 6.02×10^{22} electrons lost, (b) 1.89×10^{22} electrons gained, (c) (b) 1.80×10^{23} electrons gained

Q.2 (a) 0.75 F, (b) 0.69 F, (c)1.1 F

Q.3 (i) 54 gm, (ii) 16.35 gm

Q.4 1.023×10^5 sec

Q.5 1.12 mol, 12.535 litre

Q.6 0.112 litre

Q.7 0.24 gms

Q.8 Rs. 0.75x

Q.9 (i) 2.1554 gm ; (ii) 1336. 15 sec

Q.10 115800C, 347.4 kJ

Q.11 t = 193 sec

Q.12 n = 4

Q.13 Cu^{2+} = 0.08M, H^+ = 0.04M, SO^{2-}_4 = 0.1M

Q.14 A = 114, Q = 5926.8C

Q.15 Final weight = 9.6g,0.01Eq of acid

Q.16 (a) $V(O_2)$=6.2L, (b)$V(O_2)$ = 0.824L

Q.17 t = 93.65 sec.

Q.18 60 %

Q.19 (i) 482.5 sec (ii) 0.3175 gm (iii) 0.327 gm

Q.20 7.958×10^{-5}M

Q.21 1.825 g

Q.22 2M

Q.23 (a) $Zn \mid Zn^{2+} \mid\mid Cd^{2+} \mid Cd$, (b) $Pt, H_2 \mid H^+ \mid\mid Ag^+ \mid Ag$, (c) $Cu \mid Cu^{2+} \mid\mid Cl^- \mid Hg_2Cl_2 \mid Hg$

(d) $Pt \mid Fe^{2+}, Fe^{3+} \mid\mid Cr_2O_7^{2-}$, $Cr^{3+} \mid Pt$

Q.24 (a) $2Ag + Cu^{2+} \longrightarrow 2Ag^+ + Cu$, (b) $MnO_4^- + 5Fe^{2+} + 8H^+ \longrightarrow Mn^{2+} + 5Fe^{3+} + 4H_2O$

(c) $2Cl^- + 2Ag^+ \longrightarrow 2Ag + Cl_2$, (d) $H_2 + Cd^{2+} \longrightarrow Cd + 2H^+$

Q.25

Anode	Cathode
(a) $Zn \mid Zn^{2+}$	$H^+, H_2 \mid Pt$
(b) $Pt \mid Sn^{2+}, Sn^{4+}$	$Fe^{3+}, Fe^{2+} \mid Pt$
(c) $Pt \mid Fe^{2+}, Fe^{3+}$	MnO_4^- , $Mn^{2+} \mid Pt$
(d) $Pb \mid Pb^{2+}$	$Br_2, Br^- \mid Pt$]

Q.26 1.61 V

Q.27 1.35 V

Q.28 1.68 V

Q.29 – 0.80 V, NO

Q.30 0.53 V, disproportionation

Q.31 – 0.0367 V

Q.32 E^o_{Cell} = – 0.36 V, not spontaneous

Q.33 E =1.159V

Q.34 $K_c = 2.18 \times 10^{26}$

Q.35 $K_c = 1.864 \times 10^{107}$, ΔG^0 = – 611.8 kJ

Q.36 $K_w \approx 10^{-14}$

Q.37 E^0 = 0.7826 V

Q.38 n = 2

Q.39 E = 0.059

Q.40 E = 0.395 V

Q.41 E^0_{cell} = +0.01V, E_{cell} = –0.0785V, correct representation is $Pb|Pb^{2+}(10^{-3}M)||Sn^{2+}(1M)|Sn$

Q.42 $[Cu^{2+}] = 2.97 \times 10^{-12}$M for E =0

Q.43 E = –0.81eV

Q.44 0.52 V, 0.61 V

Q.45 -1.30×10^3 kJ mol^{-1}

Q.46 0.0295 V

Q.47 0.0295 V

Q.48 pH = 4

Q.49 (i) E = 0.286V; (ii) E = –0.0206V

Q.50 a_2 = 0.1006 M

Q.51 419 S cm^2 $equivalent^{-1}$

Q.52 0.00046 S cm^{-1} ; 2174 ohm cm

Q.53 (i) 6.25×10^5 ohm, (ii) 1.6×10^{-6} amp

Q.54 1.549 cm^{-1}

Q.55 101.8 ohm^{-1} cm^2 / gm equivalent

Q.56 0.0141 mho g $equiv^{-1}$ m^2, 0.141 mho m^{-1}

Q.57 (i) 232 Mho $cm^2 mol^{-1}$, (ii) 116 Mho cm^2 $equivalent^{-1}$

Q.58 0.865

Q.59 1.33×10^{-4} gm/litre

Q.60 8.74×10^{-11} $mole^2$ /$litre^2$

Q.61 α = 0.435 , k = 6.7×10^{-4}

Q.62 (i) 390.6 S cm^2 mol^{-1} (ii) 12.32%

Q.63 1.067 S m^{-1}

Q.64 523.2×10^{-4} mho cm^2 mol^{-1}

Q.65 (i) 6.98 (ii) 1.08×10^{-14}

PROFICIENCY TEST

1.	T	2.	F	3.	T	4.	T	5.	T
6.	F	7.	T	8.	T	9.	F	10.	T
11.	T	12.	T	13.	T	14.	F	15.	F
16.	0.66 cm^{-1}	17.	O_2	18.	increase	19.	higher		
20.	O_2 & H_2	21.	Electrolyte concentration cell						

22. $Cr_2O_7^{2-}$ (aq.), Cr^{3+}(aq.), H^+ | Pt

23. $Pb(s) + PbO_2(s) + 2H_2SO_4 \rightarrow 2PbSO_4(s) + 2H_2O\ (l)$

24. $Hg_2Cl_2(s) + 2e^- \rightarrow 2Hg(l) + 2Cl^-(aq.)$

25. $\Delta H = nF\left[T\left(\frac{dE}{dT}\right) - E\right]$ 26. inert, i.e., should not interfere with net cell reaction

27.	Salt bridge or porous partition	28.	zero	29.	E°_{red} cathode
30.	Amount, rate	31.	reduction process	32.	Oxygen
33.	2.5 × 96500 C				

MIDDLE GAME

Q.1	Eq. wt. = 107.3	Q.2	$[Cu^{2+}] = 10^{-4}M$	Q.3	643.33amp,190.5g
Q.4	43.456g	Q.5	265 Amp. hr.	Q.6	E = 1.1 V
Q.7	$E^\circ = -1.59V$, non-spontaneous			Q.8	$K_{sp} = 1.1 \times 10^{-16}$
Q.9	pH = 6.61	Q.10	$E^0 = 0.71V$	Q.11	$[Br^-] : [Cl^-] = 1 : 200$
Q.12	$E^0 = {}^-0.1511V$	Q.13	$K_a = 6.74 \times 10^{-4}$	Q.14	$[Zn^{2+}]/[Cu^{2+}] = 1.941 \times 10^{37}$
Q.15	1.39V	Q.16	0.373V	Q.17	$K_f = 8.227 \times 10^{63}$
Q.18	–0.46 V	Q.19	42.2 %	Q.20	(ii). 1.2V, (iii) 245.1 kJ
Q.21	–0.037 V	Q.22	A48.71 hour, $[OH^-] = 1.41$ M		
Q.23	$V(O_2) = 99.68$ mL, $V(H_2) = 58.46$ mL, Total vol. = 158.1 mL				
Q.24	57.5894 gm	Q.25	315.36 A	Q.26	1.9 million year
Q.27	0.179 V				
Q.28	0.372 V , – 0.307 V	Q.29	$h = 2.12 \times 10^{-2}$, $K_h = 1.43 \times 10^{-5}$ M		
Q.30	0.95 V	Q.31	$1.536 \times 10^{-5}\ M^3$	Q.32	0.1456 ampere
Q.33	3.29 cm	Q.34	4.25×10^{-2} metre	Q.35	0.1934 gm/litre

ZENITH

Q.1	1.21×10^5 coulomb	Q.2	Cu = 98.88%, Fe = 0.85%	Q.3	1250 s, 0.064 M
Q.4	$K = 10^{268}$	Q.5	$Tl^+ = 10^{-8}$; $Co^{3+} = 2 \times 10^{-8}$	Q.6	1.66V
Q.7	–1.188V	Q.8	10^{-2}	Q.9	5.24×10^{16}
Q.10	1.143V	Q.11	(a) –0.124 V, (b) 7.1, (c) calomel electrode		
Q.12	0.4414 V	Q.13	– 0.167 V	Q.14	$K_{SP} = 7.682 \times 10^{-17}$
Q.15	$2 \times 10^5\ dm^3$				

SUHANA SAFAR

OBJECTIVE

Q.1	A	Q.2	C	Q.3	B	Q.4	A	Q.5	A
Q.6	B	Q.7	C	Q.8	B	Q.9	C	Q.10	A
Q.11	C	Q12	B	Q.13	B				

SUBJECTIVE

Q.14 $E^0 = -0.22N$

Q.15 $\eta = 94.8\%$; Cathode : $2H^+ + 2e^- \rightarrow H_2$, Anode : $Mn^{2+} \rightarrow Mn^{4+} + 2e^-$

Q.16 $W_{Ag} = 272.2g$, area $= 1.02 \times 10^4\ cm^2$ Q.17 $K_c = 7.6 \times 10^{12}$ Q.18 $K_C = 6.26 \times 10^7$

Q.19 $K_{sp} = 2.287 \times 10^{-12}\ M^{-3}$ Q.20 $7.95 \times 10^{-5} M$

Q.21 decrease with time

Q.22 $\Delta H^0 = -49987\ Jmol^{-1}$, $\Delta S^0 = -96.5\ J\ mol^{-1}\ K^{-1}$, $s = 1.47 \times 10^{-5}\ M$

Q.23 0.05 M Q.24 $K_C = 10^{10}$

Q.25 (a) $E^0 = 0.59$ V, $\log_{10} K_{SP} = -10$
(b) 52.8, 10^{-6} moles