KENDRIYA VIDYALAYA SANGTHAN

RANCHI REGION

तत् त्वं पूषन् अपावृणु
केन्द्रीय विद्यालय संगठन

XII

STUDENT STUDY MATERIAL

CHEMISTRY

SESSION
2023-24

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CLASS XII (2023-24) (THEORY)

Time: 3 Hours **70 Marks**

S.No.	Title	No. of Periods	Marks
1.	Solutions	10	7
2.	Electrochemistry	12	9
3.	Chemical Kinetics	10	7
4.	d -and f -Block Elements	12	7
5.	Coordination Compounds	12	7
6.	Haloalkanes and Haloarenes	10	6
7.	Alcohols, Phenols and Ethers	10	6
8.	Aldehydes, Ketones and Carboxylic Acids	10	8
9.	Amines	10	6
10.	Biomolecules	12	7
	Total		**70**

SYLLABUS

Unit I: Solutions (10 Periods)

Types of solutions, expression of concentration of solutions of solids in liquids, solubility of gases in liquids, solid solutions, Raoult's law, colligative properties - relative lowering of vapour pressure, elevation of boiling point, depression of freezing point, osmotic pressure, determination of molecular masses using colligative properties, abnormal molecular mass, Van't Hoff factor.

Unit II: Electrochemistry (12 Periods)

Redox reactions, EMF of a cell, standard electrode potential, Nernst equation and its application to chemical cells, Relation between Gibbs energy change and EMF of a cell, conductance in electrolytic solutions, specific and molar conductivity, variations of conductivity with concentration, Kohlrausch's Law, electrolysis and law of electrolysis (elementary idea), dry cell-electrolytic cells and Galvanic cells, lead accumulator, fuel cells, corrosion.

Unit III: Chemical Kinetics (10 Periods)

Rate of a reaction (Average and instantaneous), factors affecting rate of reaction: concentration, temperature, catalyst; order and molecularity of a reaction, rate law and specific rate constant, integrated rate equations and half-life (only for zero and first order reactions), concept of collision theory (elementary idea, no mathematical treatment), activation energy, Arrhenius equation.

Unit IV: d and f Block Elements (12 Periods)

General introduction, electronic configuration, occurrence and characteristics of transition metals, general trends in properties of the first-row transition metals – metallic character, ionization enthalpy, oxidation states, ionic radii, colour, catalytic property, magnetic properties, interstitial compounds, alloy formation, preparation and properties of $K_2Cr_2O_7$ and $KMnO_4$. Lanthanoids - Electronic configuration, oxidation states, chemical reactivity and lanthanoid contraction and its consequences. Actinoids - Electronic configuration, oxidation states and comparison with lanthanoids.

Unit V: Coordination Compounds (12 Periods)

Coordination compounds - Introduction, ligands, coordination number, colour, magnetic properties and shapes, IUPAC nomenclature of mononuclear coordination compounds. Bonding, Werner's theory, VBT, and CFT; structure and stereoisomerism, importance of coordination compounds (in qualitative analysis, extraction of metals and biological system).

Unit VI: Haloalkanes and Haloarenes. (10 Periods)

Haloalkanes: Nomenclature, nature of C–X bond, physical and chemical properties, optical rotation mechanism of substitution reactions. Haloarenes: Nature of C–X bond, substitution reactions (Directive influence of halogen in monosubstituted compounds only). Uses and environmental effects of - dichloromethane, trichloromethane, tetrachloromethane, iodoform, freons, DDT.

Unit VII: Alcohols, Phenols and Ethers (10 Periods)

Alcohols: Nomenclature, methods of preparation, physical and chemical properties (of primary alcohols only), identification of primary, secondary and tertiary alcohols, mechanism of dehydration, uses with special reference to methanol and ethanol. Phenols: Nomenclature, methods of preparation, physical and chemical properties, acidic nature of phenol, electrophillic substitution reactions, uses of phenols. Ethers: Nomenclature, methods of preparation, physical and chemical properties, uses.

Unit VIII: Aldehydes, Ketones and Carboxylic Acids (10 Periods)

Aldehydes and Ketones: Nomenclature, nature of carbonyl group, methods of preparation, physical and chemical properties, mechanism of nucleophilic addition, reactivity of alpha hydrogen in aldehydes, uses. Carboxylic Acids: Nomenclature, acidic nature, methods of preparation, physical and chemical properties; uses.

Unit IX: Amines (10 Periods)

Amines: Nomenclature, classification, structure, methods of preparation, physical and chemical properties, uses, identification of primary, secondary and tertiary amines. Diazonium salts: Preparation, chemical reactions and importance in synthetic organic chemistry.

Unit X: Biomolecules (12 Periods)

Carbohydrates - Classification (aldoses and ketoses), monosaccharides (glucose and fructose), D-L configuration oligosaccharides (sucrose, lactose, maltose), polysaccharides (starch, cellulose, glycogen); Importance of carbohydrates. Proteins -Elementary idea of - amino acids, peptide bond, polypeptides, proteins, structure of proteins - primary, secondary, tertiary structure and quaternary structures (qualitative idea only), denaturation of proteins; enzymes. Hormones - Elementary idea excluding structure. Vitamins - Classification and functions. Nucleic Acids: DNA and RNA.

UNIT I: SOLUTIONS

A **solution** is a homogeneous mixture of two or more chemically non-reacting substances. Solutions are the homogeneous mixtures of two or more than two components. A solution havingtwo components is called a **binary solution.** It includes **solute and solvent**.

A solution may be classified as **solid, liquid or a gaseous solution**.

Concentration: It is the amount of solute in given amount of solution.

1. **Mass by mass percentage (w/w):** Mass of the solute dissolved in 100 g of solution.

$$\text{Mass \% of component} = \frac{\text{Mass of the component in the solution}}{\text{Total mass of the solution}} \times 100$$

2. **Molarity** (M): It is the number of moles of solute present in 1L of solution.

$$\text{Molarity (M)} = \frac{\text{Mass of solute (w)}}{\text{Molar mass of solute x Volume of solution (ml)}} \times 1000$$

3. **Molality** (m): It is the number of moles of solute present in 1kg of solvent.

$$\text{Molality (m)} = \frac{\text{Mass of solute (w)}}{\text{Molar mass of solute x Mass of solvent (g)}} \times 1000$$

Saturated solution: It is a solution in which no more solute can be dissolved at the same temperature and pressure.

In endothermic process, solubility increases with increase in temperature.

In exothermic process, solubility increases with decrease in temperature.

Solubility is defined as the amount of solute in a saturated solution per 100g of a solvent. The **solubility of a gas in a liquid** depends upon:

(a) the nature of the gas and the nature of the liquid,
(b) the temperature of the system, and
(c) the pressure of the gas is governed by **Henry's Law.** $\mathbf{p = K_H x}$

Raoult's Law, the vapour pressure of a solution containing a non-volatile solute is directly proportional to the mole fraction of the solvent (X_A). The proportionality constant being the vapour pressure of the pure solvent,

$$P_A \alpha X_A$$
$$P_A = P_A^\circ X_A$$

Liquid solutions can be classified into two types; ideal and non-ideal solutions.

Ideal Solution: When a solution obey Raoult's law for all the concentration and temperature ranges it is known as an ideal solution. Here

(i) $\Delta H_{mix} = 0$ (ii) $\Delta V_{mix} = 0$ (iii) $P_A = P_A^\circ X_A$ (iv) $P_A = P_A^\circ X_A$ (v) $P_B = P_B^\circ X_B$

Examples -- Benzene and toluene, hexane and heptane, Bromoethane and Chloroethane etc.

Non-ideal Solution:

(i) When a solution does not obey Raoult's law for all the concentration and temperature ranges it is known as a non-ideal solution. A non-ideal solution may show positive or negative deviation from Raoult's law.

(ii) $\Delta H_{mix} \neq 0$

(iii) $\Delta V_{mix} \neq 0$

E.g. acetone and benzene, carbon disulphide and acetone etc.

Colligative properties of solutions are those properties which depend only upon the number of solute particles in the solution and not on their nature.

Such properties are:

(a) Relative lowering in vapour pressure,
(b) Elevation of boiling point,
(c) Depression of freezing point and
(d) Osmotic pressure.

(a) Relative lowering in vapour pressure: According to Raoult's Law, the relative lowering of vapour pressure of a solution is equal to the mole fraction of the solute.

$$\frac{P_A^\circ - P_A}{P_A^\circ} = X_B$$

$$M_B = \frac{w_B\, M_A}{w_A\,(P_A^0 - P_A)/P_A^0}$$

(b) Elevation of boiling point: Boiling point of a liquid is the temperature at which its vapour pressure becomes equal to the atmospheric pressure. $\Delta T_b = T_b - T_b^0$

The **elevation in boiling point** is found to be proportional to the molality of the solution.

$\Delta T_b \,\alpha\, m$

$\Delta T_b = K_b\, m$,

$\Delta T_b = K_b\, m = (K_b \times w_B \times 1000)/M_B \times w_A$

$$M_B = \frac{(K_b \times w_B \times 1000)}{\Delta T_b \times w_A}$$

(c) Depression of freezing point: Freezing point is the temperature at which the solid and the liquid states of the substance have the same vapour pressure. $\Delta T_f = T_f^{\,0} - T_f$

The **depression in freezing point** (ΔT_f) is proportional to the molality of the solution.

$\Delta T_f \,\alpha\, m$

$\Delta T_f = K_f\, m$ Where K_f is molal depression constant)..

$\Delta T_f = K_f\, m = (K_f \times w_B \times 1000)/M_B \times w_A$

$$M_B = \frac{(K_f \times w_B \times 1000)}{\Delta T_f \times w_A}$$

(d) Osmosis: The flow of solvent molecules from a lower concentration into a higher concentration solution when the two are separated by a semipermeable membrane.

Osmotic pressure (π) is the pressure which must be applied to the solution side (more concentrated solution) to just prevent the passage of pure solvent into it through a semipermeable membrane.

$\pi = cRT$

$$M_B = \frac{w_B\, RT}{\pi\, V}$$

where π is the osmotic pressure of the solution, C is the concentration of solution, n_B is the number of moles of solute, M_B is the molar mass of the solute, V is the volume of the solution in liters,
R is the gas constant, and T is the temperature on the Kelvin scale.

Reverse Osmosis: The direction of osmosis can be reversed if a pressure larger than the osmotic pressure is applied to the solution side. That is, now the pure solvent flows out of the solution through the semi permeable membrane. This phenomenon is called reverse osmosis

Isotonic solutions - same osmotic pressure. $\pi_1 = \pi_2$ Also, $C_1 = C_2$

Hypertonic solutions - more osmotic pressure than other solutions.

Hypotonic solutions - less osmotic pressure than other solutions

Abnormal molecular mass: A molar mass that is either lower or higher than the expected or normal value is called as abnormal molar mass.

Van't Hoff factor: In 1880 Van't Hoff introduced a factor *i*, known as the Van't Hoff factor, to account for the extent of dissociation or association. This factor *i* is defined as:

i = Normal molar mass / Abnormal molar mass

= Observed colligative property / Calculated colligative property

$$i = \frac{\text{Total number of moles of particles after association/dissociation}}{\text{Number of moles of particles before association/dissociation}}$$

Due to Van't Hoff factor modifies the equations for colligative properties as follows:

Relative lowering of vapour pressure of solvent, $\frac{P_A^\circ - P_A}{P_A^\circ} = iX_B$

Elevation of Boiling point, $\Delta T_b = i\,K_b\,m$

Depression of Freezing point, $\Delta T_f = i\,K_f\,m$

Osmotic pressure of solution, $\pi = i\,n_B R\,T / V$

Values of *i* for KCl-- 2, NaCl --2, $MgSO_4$ --3 and K_2SO_4 --- 3

MCQ

1. Low concentration of oxygen in the blood and tissues of people living at high altitude is due to ____________.

(i) low temperature
(ii) low atmospheric pressure
(iii) high atmospheric pressure
(iv) both low temperature and high atmospheric pressure

Ans. (ii)

Explanation: At high altitude, due to low atmospheric pressure the solubility of oxygen in blood get decreased.

2. Considering the formation, breaking and strength of hydrogen bond, predict which of the following mixtures will show a positive deviation from Raoult's law?

(i) Methanol and acetone. (ii) Chloroform and acetone.
(iii) Nitric acid and water. (iv) Phenol and aniline.

Ans. (i)

Explanation: A-A interaction is greater than the A-B interaction. Intermolecular hydrogen bonding in methanol is more than methanol and acetone. So, methanol and acetone mixtures will show a positive deviation from Raoult's law.

3. Colligative properties depend on ____________.

(i) the nature of the solute particles dissolved in solution.
(ii) the number of solute particles in solution.
(iii) the physical properties of the solute particles dissolved in solution.
(iv) the nature of solvent particles.

Ans. (ii)

4. Which of the following aqueous solutions should have the highest boiling point?

(i) 1.0 M NaOH (ii) 1.0 M Na2SO4
(iii) 1.0 M NH4NO3 (iv) 1.0 M KNO3

Ans. (ii)

Explanation: In 1.0 N Na2SO4 solution i> 1. So, the no. of ions dissociated will be more.

5. The unit of ebulioscopic constant is _______________.
(i) K kg mol–1 or K(molality)-1 (ii) mol kg K–1 or K–1(molality)
(iii) kg mol–1 K–1 or K–1(molality)–1 (iv) K mol kg–1 or K(molality)
Ans. (i)

6. In comparison to a 0.01 M solution of glucose, the depression in freezing point of a 0.01 M MgCl2 solution is _____________.
(i) the same (ii) about twice (iii) about three times (iv) about six times
Ans. (iii)

Explanation: van't. Hoff factor of $MgCl_2$=3 that is why depression in freezing point will be three times.

7. An unripe mango placed in a concentrated salt solution to prepare pickle, shrivels because _____________.
(i) it gains water due to osmosis. (ii) it loses water due to reverse osmosis.
(iii) it gains water due to reverse osmosis. (iv) it loses water due to osmosis.
Ans. (iv)

8. At a given temperature, osmotic pressure of a concentrated solution of a substance _____________.
(i) is higher than that at a dilute solution. (ii) is lower than that of a dilute solution.
(iii) is same as that of a dilute solution. (iv) cannot be compared with osmotic pressure of dilute solution.
Ans. (i)

9. A plant cell shrinks when it is kept in a
(a) hypotonic solution (b) hypertonic solution (c) isotonic solution (d) pure water
Ans. (b) hypertonic solution

10. The values of van't Hoff factors for KCl, NaCl and K2SO4, respectively, are _____________.
(i) 2, 2 and 2 (ii) 2, 2 and 3 (iii) 1, 1 and 2 (iv) 1, 1 and 1
Ans. (ii)

Q11 Determine the osmotic pressure of a solution prepared by dissolving 25 mg of K_2SO_4 in 2 litres of water at 25° C, assuming that it is completely dissociated.

Ans. If K_2SO_4 is completely dissociated, then i = 3
Molar mass of K_2SO_4 = 174
$\pi = i\ cRT = i\ (n_B/V)\ RT = i\ (w_B\ RT/M_BV)$
$= 3 \times 25 \times 10^{-3} \times 0.082 \times 298 / 174 \times 2$
$\pi = 5.27 \times 10^{-3}$ atm.

Q12. a) Molal elevation constant for benzene is 2.52 K/m. A solution of some organic substance in benzene boils at 0.126oC higher than benzene. What is the molality of the solution?
b) What are the values of van't Hoff factor for NaCl and K2SO4, respectively?
Ans: a) ΔTb= Kb m , molality=0.05m
b) 2 and 3

Q13. a) State Henry's law.
b) Which cold drink you prefer one chilled or other one at room temperature and why?
c)At the same temperature hydrogen is more soluble in water than Helium. Which of them will have higher value of K_H and why?
Ans: a) Mole fraction of gas in the solution is directly proportional to partial pressure of gas in the vapour phase
b) Chilled as solubility of CO2 is more at low temp.
c) Helium as greater the KH value lower the solubility

Q14.Calculate Henry's law constant when the solubility of H_2S(a toxic gas with rotten egg like smell)in water at STP is 0.195 m
Answer: Moles of H_2S=0.195,Moles of water = 55.55, Mole fraction =0.0035p =K_Hx, K_H=p/x=0.987 bar/0.0035 =282 bar

Q15.Find the vapour pressure of water and its relative lowering in the solution which is 50 g of urea(NH_2CONH_2) dissolved in 850 gof water. (Vapour pressure of pure water at 298 K is 23.8mmHg)

Answer: Mole of urea= 50/600.833,

Moles of water=850/18=47.222 Mole fraction of urea=0.0173

P^0_A– P_A)/P^0_A= x_B, P_A=23.39

23.39 mm of Hg, the vapour pressure of water in the given solution is 23.39 mm of Hg and its relative lowering is 0.0173.

Q16. What is meant by positive deviations from Raoult's law? Give an example. What is the sign of □mix*H* for positive deviation?

Ans :Positive deviation : For non-ideal solutions,if the vapour pressure is higher, then it is said to exhibit positive deviation. *A B* interactions are weaker than *A A* or *B B* interactions. Due to this,vapour pressure increases which results in positive deviation. In positive deviation, intermolecular force decreases, volume increases, vapour pressures increases. enthalpy increases. _therefore, □*Hmix* = +ve,□*Vmix* = + ve. *e.g.*, ethanol + acetone and carbon disulphide + acetone show positive deviation.

Q17. Define azeotropes. What type of azeotrope is formed by positive deviation from Raoult's law? Give an example.

Ans: Azeotropes are the binary mixtures of solutions that have the same composition in liquid and vapour phases and that have constant boiling points. It is not possible to separate the components of azeotropes by fractional distillation. showing a large positive deviation from Raoult's law at a speci_c composition. For example an ethanolwater mixture containing approximately 95%

ethanol by volume

Q18 If 1.202 g mL^{-1} is the density of 20% aqueous KI, determine the following:

(a) Molality of KI (b) Molarity of KI (c)Mole fraction of KI

Ans. 20% solution of KI means 20g of KI are present in 100g of solution or 80g of water.

(a) Molar mass of KI = 166

Moles of KI = 20/166 = 0.120 Molality =0.120 x 1000 /80 = 1.5 m

(b) Volume of solution = 100/1.202 = 83.19 ml Molarity = 0.120 x 1000 / 83.19 = 1.44 M

(c) Moles of KI = 20/166 = 0.120 Moles of water = 80/18 = 4.44

Mole fraction of KI 0.120/(4.44+0.120) = 0.0263

Q19. List any four factors on which the colligative properties of a solution depend.

Ans: (i) Number of particles of solute

(ii) Association or dissociation of solute

(iii) Concentration of solute

(iv) Temperature

Q20. Outer hard shells of two eggs are removed.One of the egg is placed in pure water and the other is placed in saturated solution of sodium chloride. What will be observed and why?

Ans: The egg placed in pure water will swell because the concentration of proteins is high inside the egg as compared to water. Theerefore, endosmosis occurs and water diffuses through the semipermeable membrane. The egg which is placed in sodium chloride solution will shrink due to osmosis of water out of the egg.

Q21. 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. Molal depression constant for benzene is 4.9 K kg mol–1. What is the percentage association of acid I fit forms dimer in solution?

Answer: M_B = 241.98 g mol^{-1}, Molecular mass of C_6H_5COOH = 122 g mol^{-1} $2C_6H_5COOH \rightleftharpoons (C_6H_5COOH)_2$,

Degree of association of benzoic acid in benzene=99.2%

Q22. 0.6 mL of acetic acid (CH_3COOH), having density 1.06 g mL^{-1}, is dissolved in 1 litre of water. The depression in freezing point observed for this strength of acid was 0.0205°C. Calculate the Van't Hoff factor and the dissociation constant of acid.

Answer: Molality=0.0106molkg^{-1}, ΔT_f=0.0197K Van't Hoff factor (i)=1.041

Dissociation constant of acid Ka =1.86 x10^{-5}

Q23.Determine the amount of $CaCl_2$ (*i*= 2.47) dissolved in 2.5 litre of water such that its osmotic pressure is 0.75atm at 27° C.

Answer: *i*= 2.47, $\pi = i\ c\ RT = i\ (n_B/V)\ RTn_B$

=0.0308 mol

Amount of $CaCl_2$ dissolved=0.0308x111=3.42g.

Q24.Determine the osmotic pressure of a solution prepared by dissolving 25 mg of K_2SO_4 in 2 litre of water at 25° C, assuming that it is completely dissociated.

Answer: If $K_2SO_4$is completely dissociated, Here *i*= 3

$\pi = i\ c\ RT = i\ (n_B/V)RT = i(w_B/\ M_B\ V)RT$=5.27 x10^{-3}atm.

Q25. How much of sucrose is to be added to 500 g of water such that it boils at 100°C if the mol are levation constant for water is 0.52 K kg mol^{-1} and the boiling point of water at 750 mm Hg is 99.63°C?

Answer:ΔT_b=100 – 99.63=0.37^0, w_B =121.67 g,

The amount of sucrose that is to be added is 121.67 g

Assertion and Reason Type Questions

In the following questions two statements are given- one labeled Assertion (A) and the other labeled Reason (R). Select the correct answer from the codes (a), (b), (c) and (d) as given below:

(a) Both Assertion (A) and Reason (R) are correct statements and Reason (R) is the correct explanation of Assertion (A).

(b) Both Assertion (A) and Reason (R) are correct statements but Reason (R) is not the correct explanation of Assertion (A).

(c) Assertion (A) is correct but Reason (R) is incorrect statement.

(d) Assertion (A) is incorrect but Reason (R) is correct statement.

1. Assertion (A) : A mixture of chloroform and acetone forms a non-ideal solution with positive deviation.
Reason (R) : Acetone is more volatile than chloroform.

2. Assertion (A) : In reverse osmosis, pressure higher than osmotic pressure has to be applied.
Reason (R) : Higher pressure pushes the solution from one side of the semipermeable membrane to the other side

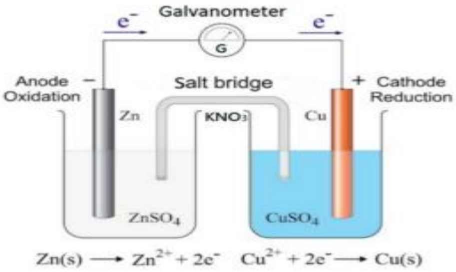
3. Assertion (A) : Out of various colligative properties, osmotic pressure is used for determination of molecular masses of polymers.
Reason (R) : polymer solutions do not possess constant boiling point or freezing point.

4. Assertion (A) : Molarity of a solution in liquid state changes with temperature.
Reason (R) :The volume of a solution changes with change in temperature.

5. Assertion (A) : When methyl alcohol is added to water, boiling point of water increases.
Reason (R) : When a volatile solute is added to a volatile solvent, elevation in boiling point is observe**d.**

1. (d) 2. (c) 3. (b) 4. (a) 5. (d)

UNIT II ELECTROCHEMISTRY



Electrochemical cell: A device in which chemical energy of the redox reaction is converted into electrical energy. e.g., Daniel cell or Galvanic cell The overall cell reaction is:

$Zn(s) + Cu2+ (aq) \rightarrow Zn2+ (aq) + Cu(s)$

The Daniel cell is represented as :

$Zn(s)| Zn2+(aq)(C1) || Cu2+(aq) (C2)| Cu(s)$

Oxidation half Reduction half

Salt Bridge and Its Functions: It consists KCl, KNO3 or NH4Cl .It helps in flow of ions by completing the circuit and maintains electrical neutrality.

Measurement of electrode potential: Potential of individual half-cell cannot be measured but we can measure the difference between the two half-cell potentials that gives the emf of the cell by using SHE (Standard Hydrogen electrode).

$E^0_{cell} = E^0_{cathode} - E^0_{anode} = E^0_{Riglit} - E^0_{Left}$

Nernst equation: It is an equation which gives the relationship between electrode potential and the concentration of ions. For an electrode reaction (reduction reaction), Mn+ (aq) + ne– → M(s),

Nernst equation can be written as:

$$E_{M^{n+}/M} = E^o_{M^{n+}/M} - \frac{RT}{nF}\ln\frac{[M]}{[M^{n+}]}$$

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

Where, $E_{Mn+/M}$ = Electrode potential,

$E^o_{Mn+/M}$ = Standard electrode potential

R = 8.314JK /mol,

T = Temperature in kelvin,

n = No. of electrons gained, F = Faraday constant (96500 C /mol)

Substituting the value of R and F we get

$$E_{M^{n+}/M} = E^o_{M^{n+}/M} - \frac{0.0591}{n}\log\frac{1}{[M^{n+}]} \quad \text{at 298 K}$$

Thus, the reduction potential increases with the increase in the concentration of ions.

Nernst equation can be written as for a general reaction

aA+ bB → cC + dD

$$E_{cell} = E^o_{cell} - \frac{2.303RT}{nF}\log\frac{[C]^c[D]^d}{[A]^a[B]^b}$$

Electrochemical cell and Gibbs Free Energy:

The work done by a reversible galvanic cell is equal to decrease in its free energy.

Mathematically, $\Delta rG = -nFE$cell

If concentration of all the reacting species is unity, then Ecell = $E°$cell

and we get, $\Delta rG = -nFE°$cell

$\Delta rG = -RT\ln Kc$ or $\Delta rG = -2.303RT\log Kc$

Measurement of Conductance: The resistance of electrolytic solution is determined by Wheatstone bridge method having variable resistance (R1), fix resistance (R3 andR4) and unknown resistance (R2 = R) of electrolyte solution. A null point detected by P detector such that, $R1/R2 = R3/R4$ or $R2 = R1R4/R3$ The reciprocal of $R2$ gives the conductance (G)of the solution as,

$\kappa = \frac{1 \times l}{R \times A} = G \times G^*$ l/A = G* (called as cell constant).

Conductance of Electrolytic solutions:

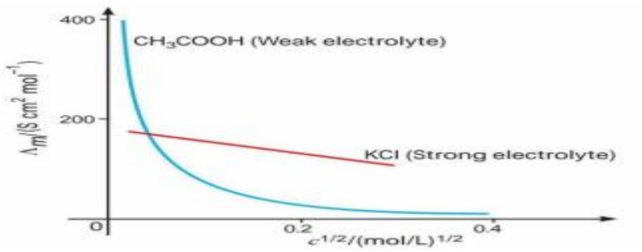
Resistance (R) - Obstruction to the flow of current, $R = \rho\ l/A$, Its SI unit is ohm.

Resistivity(ρ) - Electrical resistance of a conductor of unit cross-sectional area and unit length.

$\rho = R\ A\ /l$, Its SI unit is ohm metre

Limiting molar conductivity: When concentration approaches zero i.e., at infinite dilution, the molar conductivity is known as limiting molar conductivity (Λ° m).

Variation of Conductivity and Molar Conductivity with Concentration:



For strong and weak electrolytes:. Λn increases as concentration decreases but does not reach a constant value even at infinite dilution. Hence, their Λ°m cannot be determined experimentally.

Kohlrausch's Law: It states that the limiting molar conductivity of an electrolyte can be represented as the sum of the individual contributions of the anion and cation of the electrolyte. $\Lambda^{o} = v{+}\lambda_{+}{}^{\circ} + v{-}\lambda$

Applications of Kohlrausch's law:

(a) Calculation of molar conductivities of weak electrolyte at infinite dilution i.e.,

Λ°(CH3COOH) = Λ°m(CH3COONa) + Λ°m(HCl) − Λ°m(NaCl)

(b) Determination of degree of dissociation of weak electrolytes: Degree of dissociation $(\alpha) = \Lambda m\ /\ \Lambda^{\circ}m$

(c) Determination of dissociation constant (K) of weak electrolytes: Ka = Cœ^{2}/ 1-œ.

Faraday's first law of electrolysis: The amount of chemical reaction which occurs at any electrode during electrolysis is proportional to the quantity of electricity passed through the electrolyte.

$m = Z \times I \times t$ where Z = Electrochemical equivalent

Faraday's second law of electrolysis: amount of various substances liberated by the same quantity of electricity passed through the electrolytic solution is proportional to their chemical equivalent weights.

W1/E1 = W2/E2

Battery: Combination of galvanic cells in series and used as a source of electrical energy.

(i) Primary batteries are non-chargeable batteries such as Leclanche cell and Dry cell.

(ii) Secondary batteries are chargeable cells involving reversible reaction.

Example, Lead storage battery and Nickel-cadmium cells.

Dry cell (Leclanche cell): The anode consists of a zinc container and the cathode is a graphite electrode surrounded by powdered MnO2 and C. The space is filled with paste of NH4Cl and ZnCl2.

At anode: Zn(s) → Zn2+(aq) + 2e– At cathode: MnO2 (s) + NH4 +(aq)+ 2e– → MnO(OH) + NH3

The net reaction: Zn + NH4^{+}(aq) + MnO2 → Zn^{2+} + MnO(OH) + NH$_3$

Mercury cell: consists of zinc–mercury amalgam as anode and a paste of HgO and carbon as the cathode. The electrolyte is a paste of KOH and ZnO. The electrode reactions are:

Anode: Zn(Hg) + 2OH-⟶ ZnO(s) + H2O + 2e –

Cathode: HgO(s) + H2O + 2e- ⟶ Hg (l) + 2OH–

Lead storage battery: Anode – lead . cathode – lead oxide

At anode : Pb(s) +SO4 2–(aq) → PbSO4 (s) +2e–

At cathode: PbO2 (s) + 4H+(aq) + SO4 2–(aq) + 2e– → PbSO4 (s) + 2H2O(l)

Complete cell reaction: Pb(s) + PbO2 (s) + 2H2 SO4 (aq) → 2PbSO4 (s) + 2H$_2$O(l)

Recharge reaction of cell: PbSO4 (s) + 2H2O(l) → Pb(s) + PbO2 (s) + 2H2SO4 (aq)

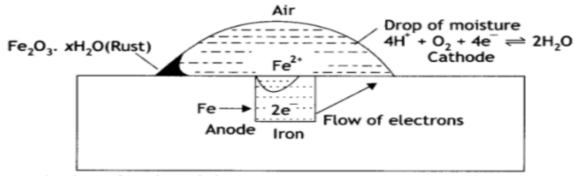
Nickel–cadmium cell which has longer life than the lead storage cell but is costly.

overall reaction $Cd(s) + 2Ni(OH)3\ (s) \rightarrow CdO(s) + 2Ni(OH)2\ (s) + H2O(l)$

Fuel cells: Electrical cells that are designated to convert the energy from the combustion of fuelssuch as hydrogen, carbon monoxide or methane directly into electrical energy are called fuel cells. the cell reactions are: Anode: $2H2\ (g) + 4OH–\ (aq) \rightarrow 4H2\ O\ (l) + 4e-$,

Cathode: $O2\ (g) + 2H2\ O(l) + 4e– \rightarrow 4OH–\ (aq)$ Net reaction: $2H2\ (g) + O2\ (g) \rightarrow 2H2O\ (l)$

Corrosion: The process of slow conversion of metals into their undesirable compounds by reaction with moisture and other gases present in the atmosphere. Rusting of iron:



Mechanism of rusting of air.

Oxidation: $Fe(s) \rightarrow Fe+2\ (aq) + 2e-$

Reduction: $O2(g) + 4H+(aq) + 4e- \rightarrow 2H2O(l)$

Atmospheric oxidation $2Fe+2(s) + ½\ O2\ (g) + 2H2O(l) \rightarrow Fe2O3 + 4H+(aq)$, $Fe2O3 + xH2O \rightarrow Fe2O3.xH2O$

Prevention of Corrosion: (i) Barrier protection: By covering the surface with paint or a thin film of grease or by electroplating. (ii) Sacrificial protection: By galvanization. (iii) Alloying

Name of cell/ battery	Anode	Cathode	Electrolyte
Dry cell	Zinc	Graphite; MnO2 + C (touching cathode)	NH4Cl + ZnCl2 (touching anode)
Mercury cell (used in watches,hearing aids)	Zinc-mercury amalgam	Paste of HgO & carbon	Paste of KOH & ZnO
Lead storage battery	Lead	Lead dioxide PbO2	H2SO4 (38%)
Ni-Cd cell	Cadmium	[Ni(OH)3]	KOH solution
H2O2 Fuel cell	Porous carbon containing catalysts (H2 passed)	Porous carbon containing catalysts (O2 passed)	Conc. Aq. NaOH solution

MULTIPLE CHOICE QUESTIONS (1 MARKS)

Q1. Which metal is used as electrode which do not participate in the reaction but provides surface for conduction of electrons? (a) Cu (b) Pt (c) Zn (d) Fe

Q2. An electrochemical cell can behave like an electrolytic cell when

(a) Ecell = 0 (b) Ecell > Eext (c) Eext > Ecell (d) Ecell = Eext

Q3. Fused NaCl on electrolysis gives ………….. on cathode.

(a) Chlorine (b) Sodium (c) Sodium amalgam (d) Hydrogen

Q4. The charge required for reducing 1 mole of MnO4 - to Mn 2+ is

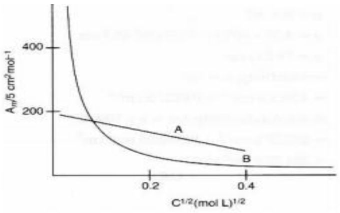
(a) 1.93×10^5 C (b) 2.895×10^5 C (c) $4.28 \times {}^5$C (d) 4.825×10^5 C

Q5. Which of the following is supplied to the cathode of a fuel cell?

(a) Hydrogen (b) Nitrogen (c) Oxygen (d) Chlorine

Q6. The electrolyte used in the mercury cell is
(a) paste of NH4Cl and ZnCl2 (b) paste of HgO and carbon
(c) paste of KOH and ZnO (d) paste of PbO and H2SO4
Q7. A device that converts energy of combustion of fuels like hydrogen and methane directly into electrical energy is known as: (a) dynamo (b) Ni-Cd cell (c) fuel cell (d) electrolytic cell
Q8. If limiting molar conductivity of Ca2+ and Cl– are 119.0 and 76.3 S cm2 mol-1, then the value of limiting molar conductivity of CaCl2 will be
(a) 195.3 S cm2 mol-1 (b) 271.6 S cm2 mol-1 (c) 43.3 S cm2 mol-1 (d) 314.3 S cm2 mol-1
Q9. Charge carried by 1 mole of electrons is
(a) 6.023 × 1023 coulomb (b) 9.65 × 104 coulomb (c) 1.6 × 10–19 coulomb (d) 6.28 × 1019 coulomb
Q10. The potential of a hydrogen electrode at pH 10 is
(a) 0.51 volt (B) 0 volt (C) -0.591 volt (D) 0.059 volt
Answers : 1(b), 2(c), 3(b), 4(d), 5(c), 6(c), 7(c), 8(b), 9(b), 10(c)

VERY SHORT ANSWER TYPE QUESTIONS (2 MARKS)



Q11. In the plot of molar conductivity (Λm) vs square root of concentration (C1/2), following curves are obtained for two electrolytes A and B.
Answer the following:
(i) Predict the nature of electrolytes A and B.
(ii) What happens on extrapolation of Λm to concentration approaching zero for electrolytes A and B?
Ans. (i) A is a strong electrolyte while B is a weak electrolyte. (ii) Λm increases steeply on dilution and extrapolation to zero concentration is not possible.Hence, molar conductivity at infinite dilution cannot be determined.
Q12. Calculate $\Delta rG\circ$ and logKc for the following reaction at 298 K :
2Cr(s) + 3Fe2+(aq) ⟶ 2Cr3+(aq) + 3Fe(s) Given: E°cell = 0.30 V
Ans. Here n=6, ΔG° = -nFE°cell = 6x96500x.3 = -1737.7KJ/mol,
E°cell = 0.059 log Kc/n or logKc = n x E°cell$/0.059 =$ 30.5084
Q13. Three iron sheets have been coated separately with three metals A, and C whose standard electrode potentials are given below. Identify in which rusting will takes place faster when coating is damaged.

Metal	A	B	C	Iron
$E°$	−0.46 V	−0.66 V	−0.20 V	−0.44 V

Ans. As iron (−0.44 V) has lower standard reduction potential than C(−0.20 V) only and therefore when coating is broken, rusting will take place faster.
Q14. Can you store copper sulphate solutions in a zinc pot?
Ans. For this we have to check whether the following reaction will take place or not.
Zn(s) + CuSO4 (aq) ⟶ ZnSO4 (aq) + Cu(s) E°cell = E°Cu2+/Cu − E°Zn2+/Zn = 0.34 − (−0.76) = 1.10 V
As E°cell is positive, the reaction will take place so No.
Q15. Write the cell reaction of a lead storage battery when it is discharge electrolyte change when the battery is discharged?
Ans. Pb+ PbSO4 + 2H:SO4⟶ 2PbSO4 + 2H0
Density of electrolyte decreases because water is formed and sulphuric during discharge of the battery.
Q16. Why on dilution the Λm of CH3COOH increases drastically while that of CH3COONa increases gradually?
Ans. CH3COOH is a weak electrolyte, the number of ions increase on dilution due to an increase in degree of dissociation.

Q17. (a) Which type of a metal can be used in cathodic protection of iron against rusting?

(b) Write the name of the electrolyte used in fuel cell

Ans. (a) More electropositive than iron such as Al, Zn, Mg etc.

(b) Conc. Aq. KOH solution

Q18. A solution of CuSO4 is electrolysed for 10 minutes with a current of 1 copper deposited at the cathode?

Ans. t= 10 x 60 = 600 s Q =IXt=1.5 A x 600 s=900 C According to the reaction: Cu' (aq) + 2e = Cu(s)

We require 2F or 2x 96500 C to deposit 1 mol or 63 g of Cu. For 900 C, the mass of Cu deposited

= (63 g mol x 900 C)/ (2 x 96500 C mol) =567/ 1930 g =0.2938 g.

Q19. The standard electrode potential for Daniell cell is 1.1V. Calculate reaction: Zn(s) + Cu^2 (aq) Zn (aq) + Cu(s) Ans. ΛG°=-nFE'cell The value of n in the above equation is 2, F = 96500 C moll and Ecell Therefore, ΛG° =-2x 1.1V x 96500C mol-! ΛG° =212300 J mol-! ΛG° =212.3 kJ mol

Q20. (a) What is the role of ZnCl2 in a dry cell (b) Unlike dry cell, the mercury cell has a constant cell potential throughout its useful life. why?

Ans (a) ZnCl2 combines with the NH3 produced to form the complex salt [Zn(NH3)2 Cl2] Other wise the pressure developed due to NH3 would crack the seal of the cell (b) Ions are not involved in the overall cell reaction of mercury cells

SHORT ANSWER TYPE QUESTIONS (3 MARKS)

Q21. (i) State Kohlrausch law.

(ii) Why on dilution the Λ_m of CH3COOH increases drastically while that of CH3COONa increases gradually?

Ans: (i) limiting molar conductivity of an electrolyte can be determined by sum of individual contributions of the anion and cation of the electrolyte

(ii) In the case of CH3COOH, it is a weak electrolyte, the number of ions increases on dilution due to an increase in degree of dissociation but in CH3COONa dissociates completely.

Q22. The molar conductivity of sodium acetate, sodium chloride and hydrochloric acid are 83,127 and 426 mho cm2mol−1 at 250∘C respectively. Calculate the molar conductivity of acetic acid solution.

Ans. Λ°m(CH3COOH) = Λ°m (CH3COONa) + Λ°m (HCl) − Λ°m(NaCl)

Or Λ°m(CH3COOH) = 83 + 426 − 127 = 382 mho cm2mol−1

Q23. The electrical resistance of a column of 0.05 mol L^{-1} NaOH solutions of diameter 1 cm and length 50 cm is 5.55×10^3 ohm. Calculate its resistivity, conductivity and molar conductivity.

Solution: $A = \pi r2 = 3.14 \times 0.52\ cm^2 = 0.785\ cm^2 = 0.785 \times 10^{-4}\ m^2$

l = 50 cm = 0.5 m

R = ρ l/ A

ρ (resistivity) = RA/l = $[5.55 \times 10^3$ ohm x $0.785\ cm^2]$ / 50 cm = 87.135 ohm cm

Conductivity (κ) = 1/ ρ = [1 / 87.135] S cm^{-1} = 0.01148 S cm^{-1}

Molar conductivity, Λ_m = [κ (S cm^{-1}) x 1000 (cm^3/L)] / Molarity (mol/L)

= [0.01148 ×1000]/ 0.05

= 229.6 S $cm^2\ mol^{-1}$

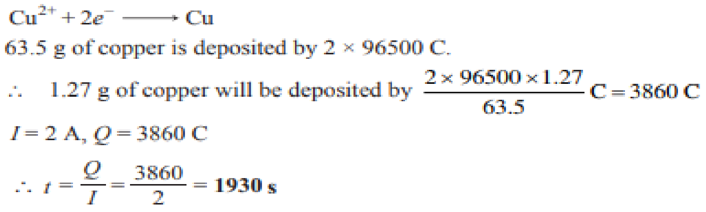
Q24. What will be the sign of ΔG for an electrochemical cell and an electrolytic cell?

Ans. ΔG for an electrochemical cell is -ve and ΔG for an electrolytic cell is +ve.

Q25. Using the E° values of A and B, predict which one is better for coating the surface of iron [E°(Fe2+/Fe) = – 0.44V] to prevent corrosion and why? Given: E°(A2+|A) = -2.37 V and E°(B2+|B) = – 0.14 V

Answer: 'A' will prevent iron from rusting. So, we can coat the iron surface with metal A because it has more negative value

Q26. For the given cells: Lead storage cell, Mercury cell, Fuel cell and Dry cell
Answer the following: (i) Which cell is used in hearing aids? (ii) Which cell was used in Apollo space programme? (iii) Which cell is used in automobiles and inverters? (iv) Which cell does not have long life?
Ans. (i) Mercury cell (ii) Fuel cell (iii) Lead storage cell (iv) Dry cell
Q27.Calculate the time to deposit 1.27 g of copper at cathode when a current of 2 A was passed through the solution of CuSO4. (Molar mass of Cu = 63.5 g mol–1, 1 F = 96500 C mol–1)
Ans.



$Cu^{2+} + 2e^- \longrightarrow Cu$

63.5 g of copper is deposited by 2 × 96500 C.

$\therefore$ 1.27 g of copper will be deposited by $\frac{2 \times 96500 \times 1.27}{63.5}$ C = 3860 C

$I = 2$ A, $Q = 3860$ C

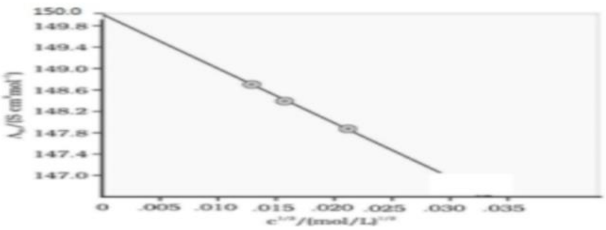
$\therefore t = \frac{Q}{I} = \frac{3860}{2} = \mathbf{1930\ s}$

Q28. The resistance of a conductivity cell containing 0.001 M KCl solution at 298 K is 1500 W. What is the cell constant if conductivity of 0.001 M KCl solution at 298 K is 0.146 × 10–3 S cm–1?
Ans. Conductivity (k) = 1/ Resistance × Cell constant k = 0.146 × 10–3 S cm–1, R = 1500 **Ω**
0.146 × 10–3 S cm–1 = 1/1500 X × Cell constant Cell constant = 0.146 × 10–3 S cm–1 × 1500 **Ω**
= 219 × 10^{-3} cm–1 **= 0.219 cm–1**
Q29. The chemistry of corrosion of iron is essentially an electrochemical phenomenon. Explain the reactions occurring during the corrosion of iron in the atmosphere.
Ans. The redox reaction involves At anode : Fe(S) → Fe2+ (aq) + 2e–
Then net resultant Redox reaction is 2Fe(s) + O2 (g) + 4H+ → 2Fe2+ + 2H2O
Q30. Write the name of the cell which is generally used in transistors. Write the reactions taking place at the anode and the cathode of this cell.
Ans. Leclanche cell is used in transistors. Reaction at Anode: Zn(s) → Zn2+ + 2e–
At Cathode: MnO2 + NH4 + + e– → MnO(OH) + NH3

LONG ANSWER TYPE QUESTIONS (5 MARKS)

Q31. (i) Define limiting molar conductivity and fuel cell.
(ii) Resistance of a conductivity cell filled with 0.1 mol L–1 KCl solution is 100 ohm. If the resistance of the same cell when filled with 0.02 mol L–1 KCl solution is 520 ohm, calculate the conductivity and molar conductivity of 0.02 mol L–1 KCl solution. The conductivity of 0.1 molL–1 KCl solution is 1.29 × 10–2 ohm–1 cm–1.
Ans (i) Limiting Molar conductivity -limiting value of molar conductivity when concentration approaches to zero. Fuel cell - device which converts energy produced during the combustion of fuels directly into electrical energy.
(ii) cell constant = conductivity x resistance = 1.29 cm–1, Conductivity, k = Cell constant/Resistance = 0.00248 ohm–1 cm–1, Λm = k X 1000/M = 124 ohm–1 cm2 mol–1
Q32. (i) State two advantages of H2—O2 fuel cell over ordinary cell.
(ii) Silver is electrodeposited on a metallic vessel of total surface area 500 cm2 by passing a current of 0.5 amp for two hours. Calculate the thickness of silver deposited [Given: Density of silver = 10.5 g cm–3, Atomic mass of silver = 108 amu, F = 96,500 C mol–1]
Ans. (i) pollution free, 75% efficiency, continuous source of energy. (ii) m=ZIt = 4.029g, V=m/d = 0.3837 cm3, thickness of Ag deposited is x, V= A . x = 7.67x10-4cm

Q33. (i) The following figure, represents variation of (Am) vs vc for an electrolyte. Here Am is the molar conductivity and c is the concentration of the electrolyte.



a) Define molar conductivity

b) ldentify the nature of electrolyte on the basis of the above plot. Justify your answer.

c) Determine the value of Am° for the electrolyte.

d) Show how to calculate the value of A for the electrolyte using the above graph.

Ans: (i) (a) Molar conductivity ofa solution at a given concentration is the conductance of the volume V of solution containing one mole of electrolyte kept between two electrodes with area cross section A and distance of unit length (b) Strong electrolyte, For strong electrolytes, Am increases slowly with dilution

(c) Λ m = Λ° m – Ac2 Therefore Λ m = 150 Scm^{2}mol-1 (d) A =-slope = - (149 – 147.8/ 0.010-0.022) = 100 Scm'mol-1

Q34. The conductivity of 0.001028 M of acetic acid is 4.95×10-5 S cm-1. Calculate its dissociation constant if molar conductance for acetic acid is 390.5 S cm2 mol

Ans.

$$\Lambda = \frac{4.95\times10^{-5}\times1000}{1.028\times10^{-3}} = 48.15\,Scm^{2}mol^{-1}$$

$$\alpha = \frac{48.15}{390.5} = 0.1233$$

$$K_a = \frac{C\alpha^2}{1-\alpha} = \frac{1.028\times10^{-3}\times(0.1233)^2}{1-0.1233} = 1.78\times10^{-5}$$

Q35. Q Conductivity of 2.5 × 10 – 4 M methanoic acid is 5.25 × 10 – 5 S cm–1. Calculate its molar conductivity and degree of dissociation.Given: lo (H+) = 349.5 S cm2 mol –1 and lo (HCOO–) = 50.5 S cm2 mol –1.

Ans.

$$\Lambda_m^c = \frac{\kappa\times1000}{M}$$

$$\Lambda_m^c = \frac{5.25\times10^{-5}\ \text{S cm}^{-1}\times1000\ \text{cm}^3\ \text{L}^{-1}}{2.5\times10^{-4}\ \text{mol L}^{-1}}$$

$$\Lambda_m^c = \mathbf{210\ S\ cm^2\ mol^{-1}}$$

$$\begin{aligned}\Lambda_m^o(\text{HCOOH}) &= \Lambda_{\text{HCOO}^-}^o + \Lambda_{\text{H}^+}^o\\ &= 50.5\ \text{S cm}^2\ \text{mol}^{-1} + 349.5\ \text{S cm}^2\ \text{mol}^{-1}\\ &= 400\ \text{S cm}^2\ \text{mol}^{-1}\end{aligned}$$

$$\text{Degree of dissociation, } \alpha = \frac{\Lambda_m^c}{\Lambda_m^o} = \frac{210\ \text{S cm}^2\ \text{mol}^{-1}}{400\ \text{S cm}^2\ \text{mol}^{-1}} = 0.525$$

$$\text{or} \qquad \alpha = \mathbf{52.5\%}$$

<u>Assertion and Reason Type Questions</u>

1. Assertion (A) : The daniell cell becomes dead after some time.
   Reason (R) : Oxidation potential of zinc anode decrease and that of copper cathode increases.
2. Assertion (A) : Copper liberates hydrogen from a dilute solution of hydrochloric acid.
   Reason (R) : Copper is below hydrogen in the electrochemical series.
3. Assertion (A) : F_2 is stronger oxidising agent than Cl_2.
   Reason (R) : Oxidation potential of F_2 is greater than that of Cl_2.
4. Assertion (A) : $H_2 – O_2$ fuel cell gives a constant voltage throughout its life.
   Reason (R) : In this cell, H_2 reacts with OH^- ions, yet the overall concentration of OH^- ions does not change
5. Assertion (A) : Molar conductivity of a weak electrolyte at infinite dilution cannot be determined experimentally.
   Reason (R) : Kohlrausch law helps to find molar conductivity of a weak electrolyte at infinite dilution.

Ans:- 1. (a) 2. (d) 3. (c) 4. (a) 5. (b)

UNIT III CHEMICAL KINETICS

Chemical Kinetics the branch of chemistry, which deals with the study of reaction rates and their mechanisms.

Rate of a Chemical Reaction: the rate of a reaction can be defined as the change in concentration of a reactant or product in unit time. It can be expressed in terms of:

(i) The rate of decrease in concentration of any one of the reactants.

(ii) The rate of increase in concentration of any one of the products.

Consider a hypothetical reaction, R ---> P

Rate of disappearance of R = Decrease in concentration of R / Time taken = - R/t

Rate of appearance of P = Increase in concentration of P /Time taken = P/t

Units of rate of a reaction: The units will be **mol $L^{-1}s^{-1}$**.

In gaseous reactions, the units of the rate equation will be **atm s^{-1}**.

Factors affecting rate of reaction: The important factors are:

1. Concentration of the reacting species.
2. Temperature of the system.
3. Nature of reactant and products.
4. Presence of a catalyst.
5. Surface area.
6. Exposure to radiation.

Rate Law and Rate Constant:

Consider a general reaction: aA + bB ----------------- > cC + dD

Where a, b, c and d are the stoichiometric coefficients of reactants and products. The rate expression for this reaction is Rate $\propto [A]^x [B]^y$

Where exponents x and y may or may not be equal to the stoichiometric coefficients (a & b) of the reactants. Above equation can also be written as

Rate = $k [A]^x [B]^y$ Where exponents x and y may or may not be equal to the stoichiometric coefficients a & b

$-d[R]/dt = k[A]^x [B]^y$ This form of equation is known as differential rate equation,

where k is a proportionality constant called rate constant**.**

Order of reaction: Rate = $k [A]^x [B]^y$

x + y in above equation gives the overall order of a reaction. Whereas x and y represent the order with respect to the reactants A and B respectively.

Order of reaction is defined as the sum of powers of the concentration of the reactants in the rate law expression is called the order of that chemical reaction.

Order of a reaction can be 0, 1, 2, 3 and even a fraction.

A zero-order reaction means that the rate of reaction is independent of the concentration of reactants.

Units of rate constant:

Zero order rate of reaction: mol L^{-1} s^{-1}

First order rate of reaction: s^{-1}

Second order rate of reaction: L mol^{-1} s^{-1}

Important points of distinction between order and molecularity

S.No.	**Order**	**Molecularity**
1	**Order** is the sum of powers of the concentration terms in the rate law expression.	**Molecularity** is the number of reacting species undergoing simultaneous collision in the elementary or simple reaction.
2	Order of a reaction is determined experimentally.	Molecularity is a theoretical concept.
3	Order of a reaction can be negative, zero or fractions.	Molecularity of a reaction cannot be negative, zero or fractions..

Integrated rate equations:

Zero order reaction: Zero order reaction means that the rate of the reaction is proportional to zero power of the concentration of reactants.

Consider the reaction, R---------> P

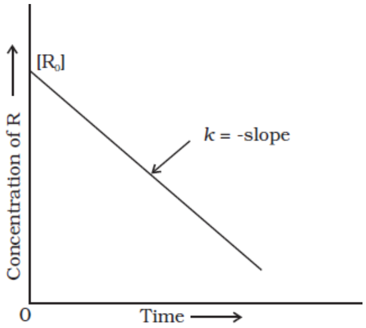
$$\text{Rate} = -d[R]/dt = k[R]^0$$

$$\mathbf{k = \{[R]_0 - [R]\}/t}$$

Variation in the concentration Vs time plot for a zero-order reaction

Example of Zero order reaction is the decomposition of gaseous ammonia.

$2NH_3\,(g)$ ------------------- > $N_2\,(g) + 3\,H_2\,(g)$ Rate = $k\,[NH_3]^0 = k$



First Order Reactions: The rate of the reaction is proportional to the first power of the concentration of the reactant R. For example:

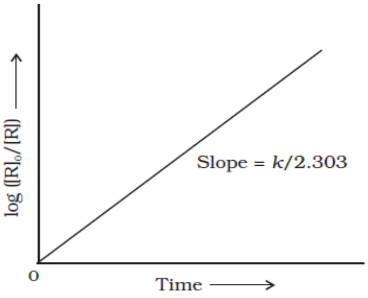
R---------> P

$$\text{Rate} = -d[R]/dt = k[R]$$

$$\mathbf{k = (1/t)\ \ln \{[R]_0/[R]\}}$$

We know that, ln a = 2.303 log a

$$\mathbf{k = (2.303/t)\ \log \{[R]_0/[R]\}}$$



If we plot a graph between log $[R]_0/[R]$ Vs t, the slope is k/2.303 for first order reaction

Half-life of a reaction: The half-life of a reaction is the time in which the concentration of a reactant is reduced to one half of its initial concentration. It is represented as $t_{1/2}$.

For a zero-order reaction,	For a first order reaction
$t_{1/2} = [R]_0/2k$	$t_{1/2} = 0.693/k$

For zero order reaction $t_{1/2} \propto [R]_0$.

For first order reaction $t_{1/2}$ is independent of $[R]_0$.

Temperature Dependence of the Rate of a Reaction:

The rate of a reaction becomes almost doubled for every 10° rise in temperature due to the increase in number of effective collisions.

The temperature dependence of the rate of a chemical reaction can be accurately explained by Arrhenius equation.

$$k = A\,e^{-Ea/RT}$$

Where A is the Arrhenius factor, R is gas constant and Ea is activation energy measured in joules/mole (J mol $^{-1}$).

Taking logarithm both side

$$\ln k = -\frac{E_a}{RT} + \ln A$$

$\log k = \log A – E_a/2.303\ RT$

Let k1 and k2 are the rate constants for the reaction at two different temperatures T1 and T2 respectively.

$$\log\frac{k_2}{k_1} = \frac{E_a}{2.303R}\left[\frac{T_2 - T_1}{T_1 T_2}\right]$$

Collision Theory of Chemical Reactions:

Collision frequency: It is defined as the number of collisions per second per unit volume of the reaction mixture is known as collision frequency (Z).

Effective collision: The collisions in which molecules collide with proper orientation, breaking of bonds between reacting species and formation of new bonds to form products are called as **effective collisions.**

Ineffective collision: The collisions in which molecules collide with improper orientation no products are formed are called as ineffective collisions.

Rate of reaction is proportional to

(i) the number of collisions per unit volume per second (collision frequency,Z) between the reacting species.

(ii) the fraction of effective collisions or probability factor (P)

$K = P\ Z\ e^{-Ea/RT}$

MULTIPLE CHOICE QUESTIONS (1 MARKS)

1. Rate law for a reaction A+2B-C is found to be Rate = k[A][B] Concentration of B is doubled keeping the concentration of A is constant. The rate of the reaction will get

A. Doubled B. Halved C. Quadruples D. remains same

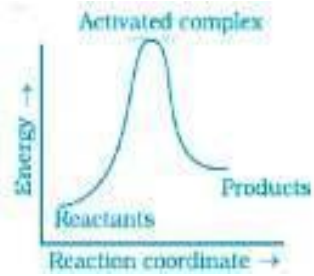
2. A reaction 2A-B, has been found to have rate constant 3.5molL -1 s -1 What is the order of the reaction

A. 1 B. 2 C. 3 D. 0

3. Half life period of a first order reaction is 4 hours. How many hours will it take for 20g of the reactant to reduce to 5g

A. 4 hours B. 16 hours C. 8 hours D. 1 hour

4. This graph represents



A. Exothermic Reaction B. Endothermic Reaction C. insufficient information D. None of these

5. For the reaction A+B → C+D, the rate of reaction quadruples when the concentration of A doubles, whereas on making the concentration of B two times.the rate doubles up. What is overall order of the reaction?

A. 2 B. 3 C. 4 D. 1

6. For a reaction X + 2Y → Z The Rate law expression is Rate = $k[X][Y]^{1/2}$ What is the order of the reaction

A. 1 B. 2 C. 1.5 D. 3

7. A first order reaction is 50% complete in 10s.How much time will it take for 100% completion?

A. 20s B. 10s C. 100s D. Infinite

8. A substance ‘A’ decomposes by a first-order reaction starting initially with [A] = 2.00M and after 200min, [A] becomes 0.15M. For this reaction $t_{1/2}$ is

(a) 53.72 min (b) 50.49 min (c)48.45 min (d)46.45 min

9. Which of the following is altered by a catalyst in a chemical reaction?

(a) Entropy (b) Enthalpy (c) Internal energy (d) Activation energy

10. During different experiments conducted for a reaction it is observed that it takes the same time to reduce the concentration

i) from 100g to 50g ii) 10g to 5 g iii) 500g to 250g We can infer from the observations that

(a) It is a slow reaction (b) it is a zero order reaction

(c) it is a first order reaction (d) it is a second order reaction

Ans. 1-A 2-D 3-C 4-B 5-B

6-C 7-d 8-a 9-d 10-c

11. For a reaction, A + B → Product, the rate law is given by $r = k[A]^{1/2}[B]^2$ .What is the order ofthe reaction?

Ans. Order of reaction (n) = ½ + 2 = 3/2 = 1.5

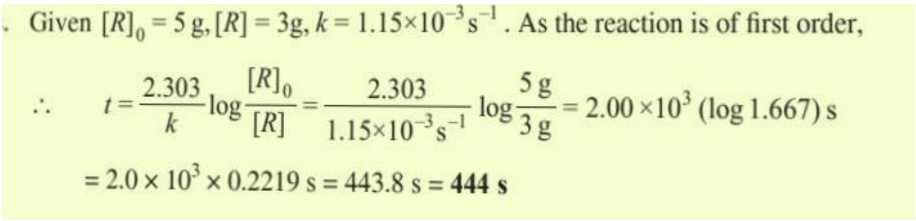
12. The conversion of molecule X to Y follows second order kinetics. If concentration of X is increasedto three times, how will it affect the rate of formation of Y?

Ans rate = $k[X]^2$ rate = $k[3X]^2$ rate = 9k

Rate of formation of Y will increase by 9 times.

13. A first order reaction has a rate constant 1.15 × 10–3 s–1. How long will 5 g of this reactant take to reduce to 3 g?

Ans.



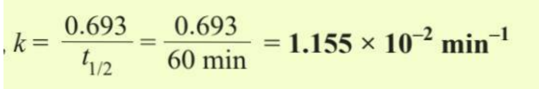
. Given $[R]_0 = 5\text{ g}, [R] = 3\text{g}, k = 1.15\times10^{-3}\text{ s}^{-1}$. As the reaction is of first order,

$$\therefore \quad t = \frac{2.303}{k}\log\frac{[R]_0}{[R]} = \frac{2.303}{1.15\times10^{-3}\text{ s}^{-1}}\log\frac{5\text{ g}}{3\text{ g}} = 2.00\times10^3 (\log 1.667)\text{ s}$$

$$= 2.0\times10^3\times0.2219\text{ s} = 443.8\text{ s} = \mathbf{444\ s}$$

14. Time required to decompose SO2Cl2 to half of its initial amount is 60 minutes. If the decomposition is a first order reaction, calculate the rate constant of the reaction.

Ans.



$$k = \frac{0.693}{t_{1/2}} = \frac{0.693}{60\text{ min}} = \mathbf{1.155\times10^{-2}\ min^{-1}}$$

15. What is the effect of temperature on the rate constant of a reaction? How can this effect of temperature on rate constant be represented quantitatively?

Ans. The rate constant of a reaction increases with increase in temperature and becomes nearly double for every 10°C rise of temperature. The effect can be represented quantitatively by

Arrhenius equation K = Ae- Ea/RT

where Ea is the activation energy of the reaction and A is the frequency factor.

16. What is the effect of adding a catalyst on

(i) Activation energy (Ea), and (ii) Gibbs energy of a reaction?

Ans. i) Decreases (ii) No effect

17. What do you understand by the rate law and rate constant of a reaction? Identify the order of a reaction if the units of its rate constant are: (i) L–1 mol s–1 (ii) L mol–1 s–1.

Ans. An experimentally determined expression which relates the rate of reaction with the concentration of reactants is called rate law while the rate of reaction when concentration of each reactant is unity in a rate law expression is called rate constant.

(i) zero order reaction (ii) second order reaction

18. Define the following terms:

(i) Pseudo first order reaction   (ii) Half life period of reaction ($t_{1/2}$)

Ans. (i) A reaction which is not truely of first order but under certain conditions becomes a reaction of first order is called pseudo first order reaction, e.g., acid hydrolysis of ethyl acetate.

CH3COOC2H5 + H2O ---------> CH3COOH + C2H5OH

Rate ∝ [CH3COOC2H5]   as H2O is in excess.

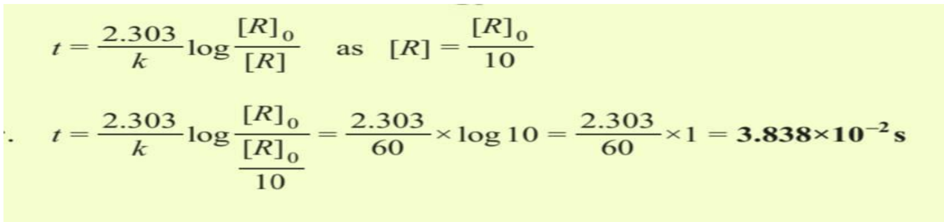
ii) The half life (t1/2) of a reaction is the time in which the concentration of reactant is reduced to one half of its initial concentration $[R]_0$.

For a first order reaction, t1/2 = k/0.693 , i.e., independent of [R]0.

For a zero order reaction, t1/2 = [R]0/2k   i.e., t1/2 ∝ [R]0

19. The rate constant for a first order reaction is 60 s–1. How much time will it take to reduce the initial concentration of the reactant to 1/10 th of its initial value?

Ans.



$$t = \frac{2.303}{k}\log\frac{[R]_0}{[R]} \quad \text{as} \quad [R] = \frac{[R]_0}{10}$$

$$\therefore \quad t = \frac{2.303}{k}\log\frac{[R]_0}{\frac{[R]_0}{10}} = \frac{2.303}{60}\times\log 10 = \frac{2.303}{60}\times 1 = \mathbf{3.838\times10^{-2}\,s}$$

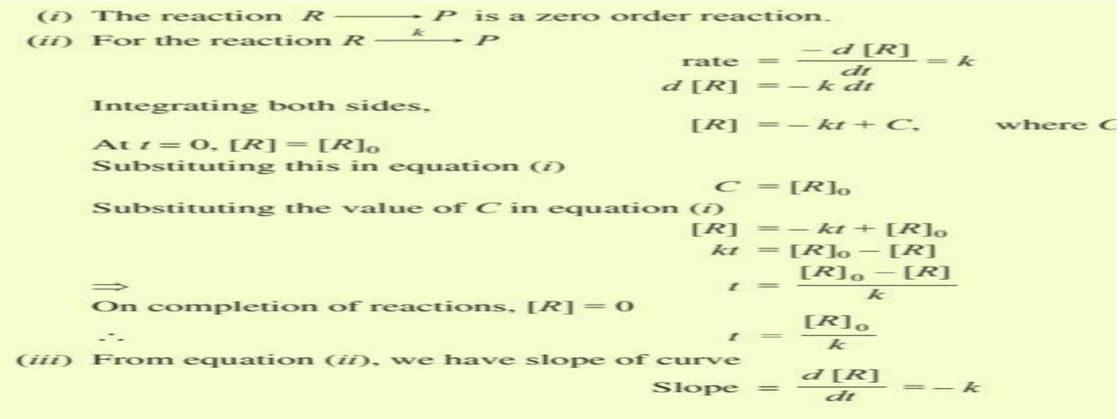
20. Consider the reaction R --------P.The change in concentration of R with time is shown in the following plot:

(i) Predict the order of the reaction.

(ii) Derive the expression for the time required for the completion of the reaction.

(iii) What does the slope of the above line indicate?

Ans.



(*i*) The reaction $R \longrightarrow P$ is a zero order reaction.

(*ii*) For the reaction $R \xrightarrow{k} P$

$$\text{rate} = \frac{-d[R]}{dt} = k$$

$$d[R] = -k\,dt$$

Integrating both sides,

$$[R] = -kt + C, \qquad \text{where } C$$

At $t = 0$, $[R] = [R]_0$

Substituting this in equation (*i*)

$$C = [R]_0$$

Substituting the value of C in equation (*i*)

$$[R] = -kt + [R]_0$$

$$kt = [R]_0 - [R]$$

$$\Rightarrow \qquad t = \frac{[R]_0 - [R]}{k}$$

On completion of reactions, $[R] = 0$

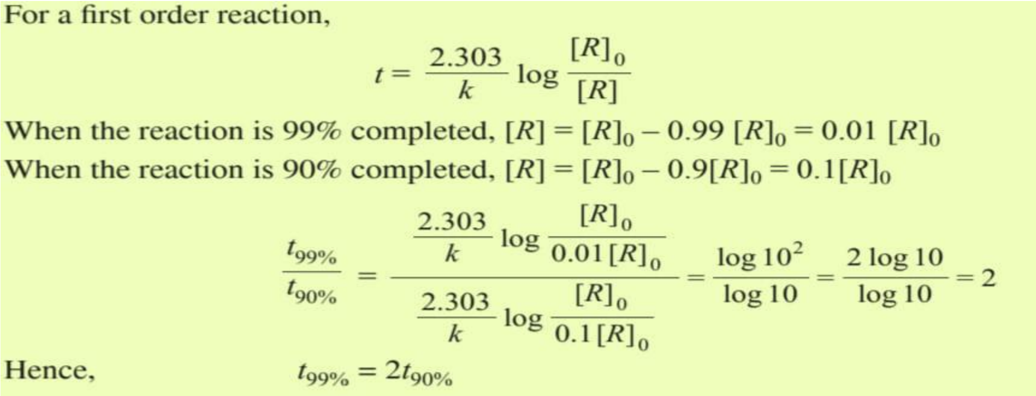
$$\therefore \qquad t = \frac{[R]_0}{k}$$

(*iii*) From equation (*ii*), we have slope of curve

$$\text{Slope} = \frac{d[R]}{dt} = -k$$

21. For a first order reaction, show that time required for 99% completion is twice the time required for the completion of 90% of reaction.

ANS.



For a first order reaction,

$$t = \frac{2.303}{k}\log\frac{[R]_0}{[R]}$$

When the reaction is 99% completed, $[R] = [R]_0 - 0.99\,[R]_0 = 0.01\,[R]_0$

When the reaction is 90% completed, $[R] = [R]_0 - 0.9[R]_0 = 0.1[R]_0$

$$\frac{t_{99\%}}{t_{90\%}} = \frac{\frac{2.303}{k}\log\frac{[R]_0}{0.01[R]_0}}{\frac{2.303}{k}\log\frac{[R]_0}{0.1[R]_0}} = \frac{\log 10^2}{\log 10} = \frac{2\log 10}{\log 10} = 2$$

Hence, $\qquad t_{99\%} = 2t_{90\%}$

22. (a) Identify the reaction order from each of the following rate constants. (i) $k = 2.3 \times 10^{-5}$ L mol^{-1} s^{-1} (ii) $k = 3 \times 10^{-4}$ s^{-1}

(b) The rate of the chemical reaction doubles for an increase of 10K in absolute temperature from 298K. Calculate Ea.

Ans. (a) i) Second order reaction (ii) first order reaction.

(b) $\log k_2 - \log k_1 = Ea/2.303\ R\ [1/T_1 - 1/T_2]$

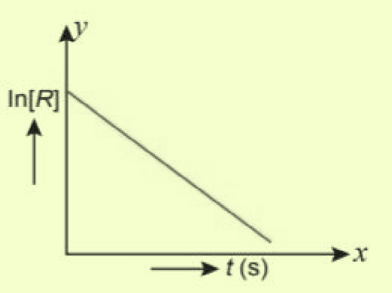
$\log k_2/k_1 = Ea/2.303\ R\ [1/T_1 - 1/T_2]$

$\log 2 = (Ea/2.303 \times 8.314)\ [1/298 - 1/308]$

$$Ea = \frac{\log 2 \times 2.303 \times 8.314 \times 298 \times 308}{308 - 298}$$

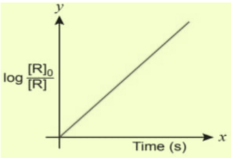
Ea = 52.898 kJ

23. For a certain chemical reaction variation in the concentration ln [R] vs. time plot is given alongside. For this reaction



(i) what is the order of the reaction?
(ii) what are the units of rate constant k?
(iii) give the relationship between k and t1/2 (half-life period).
(iv)what is the slope of the curve?
(v)draw the plot log [R]0 /[R] vs timet(s).

ANS; (i) First order
(ii) time–1 (s–1)
(iii) $t_{1/2} = 0.693/k$
(iv)slope = – k (rate constant)
(v)



Assertion and Reason Type Questions

1. Assertion (A) : Order of reaction is never negative with respect to a reactant or product.
Reason (R) : The rate of reaction is always positive.
2. Assertion (A) : Rate constant of a zero order reaction has the same units as those of the rate of reaction.
Reason (R) : For a zero order reaction, Rate = Rate constant.
3. Assertion (A) : Greater the half-life period, faster is the reaction.
Reason (R) : Half life period depends upon initial concentration as well as order of reaction.
4. Assertion (A) : In the presence of catalyst, enthalpy change of the reaction decreases.
Reason (R) : In the presence of catalyst, activation energy of the reaction decreases.
5. Assertion (A) : According to collision theory, the rate of reaction does not depend on the total number of collision.
Reason (R) : The overall rate of reaction depends upon the number of effective collisions.

Answer 1. (d) 2. (a) 3. (d) 4. (d) 5. (c)

UNIT IV d- AND f- BLOCK ELEMENTS

d-block elements : The elements of periodic table belonging to **group 3 to 12** are known as d-Block elements. Because in these elements last electron enters in d sub shell or d orbital .

Transition Series:There are four series of the transition metals,

***3d* series** (Sc to Zn),

***4d* series** (Y to Cd)

***5d* series** (La to Hg, omitting Ce to Lu).

***6d* series** which begins with Ac is still incomplete

d- Block elements are collectively known as Transition Elements because properties of these elements vary in between s-Block and p-Block elements.

The general electronic configuration of these elements is $(n-1)d^{1-10}$ ns^{1-2}

Transition element: A transition element is defined as the one which has incompletely filled *d* orbitals in its ground state or in any one of its oxidation states.i.e. A transition element should have partially filled (n-1) d orbital.

Zinc, cadmium and mercury of group 12 have full d^{10} configuration in their ground state as well as in their common oxidation states and hence, are not regarded as transition metals

High Melting points& Boiling points of transition elements: due to strong **metallic bonding**

High Enthalpy of atomization: due to strong **metallic bonding**

Variation in Atomic Size of Transition Metals along 3d transition series: The atomic radii decreases from group 3 to 6 (i.e. Sc to Cr) because of increase in effective nuclear charge gradually, The atomic radii of group 7,8 9 &10 elements (i.e. Fe,Co,Ni) is almost same because Screening effect counter balances increased effective nuclear charge, Group 11 &12 elements i.e. Cu & Zn have bigger size due to increaseinter-electronic repulsion as result electron cloud expands and size increases.

Members of second(4d) and the third (5*d*) series in each group of transition elements have similar radii and shows similar properties because **lanthanoid contraction** essentially compensates for the expected increase in atomic size with increasing atomic number.

Zr (160 pm) &Hf (159 pm) and have very similar physical and chemical properties because Zr & Hf belongs to same group of second(4d) and the third (5*d*) series ,as a result they have similar radii due to **lanthanoid contraction.**

Oxidation States: The transition elements show variable oxidation state due to small energy difference between (n-1)d & ns orbital. The highest oxidation state of an element is equal to number of unpaired e^- present in (n-1) d & ns orbital.

Formation of Coloured Ions: due to **d – d transitions** occurring in a transition metal ions by absorption of visible light that they appear coloured.

Magnetic Properties: due to unpaired electron

The magnetic moment is determined by the number of unpaired electrons and is calculated by using the formula $\mu = \sqrt{n(n+2)}$

where n is the number of unpaired electrons and μ is the magnetic moment in units of Bohr magneton (BM)..

Formation of Complex Compounds:. due to **smaller sizes of the metal ions, their high ionic charges and the availability of *d* orbitals for bond formation**.A few examples are: $[Fe(CN)6]^{3-}$, $[Fe(CN)6]^{4-}$,$[Cu(NH3)4]^{2+}$ and $[PtCl4]^{2-}$

Catalytic Properties: due to **Variable oxidation states and Large surface area**

Formation of Interstitial Compounds:. Interstitial compounds are those which are formed when small atoms like H, C or N are trapped inside the crystal lattices of metals. Transition elements form interstitial compounds because size of C, N, O, and B is similar to size of interstitial voids of transition metal

Alloy Formation: Because of **similar radii**

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 effective nuclear charge .e.g. MnO (basic), Mn3O4 (amphoteric), Mn2O7 (acidic).

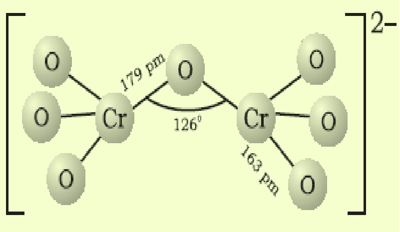
POTASSIUM DICHROMATE $K_2Cr_2O_7$

- **Preparation:** chromite ore ($FeCr_2O_4$ or $FeO.Cr_2O_3$)

$$4\,FeCr_2O_4 + 8\,Na_2CO_3 + 7\,O_2 \rightarrow 8\,Na_2CrO_4 + 2\,Fe_2O_3 + 8\,CO_2$$

$$2Na_2CrO_4 + 2\,H^+ \rightarrow Na_2Cr_2O_7 + 2\,Na^+ + H_2O$$

$$Na_2Cr_2O_7 + 2\,KCl \rightarrow K_2Cr_2O_7 + 2\,NaCl$$



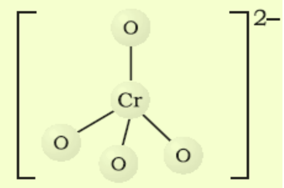
Dichromate ion

- **The chromates and dichromates are interconvertible in aqueous solution depending upon pH of the solution**

$$2\,CrO_4^{2-} + 2H^+ \rightarrow Cr_2O_7^{2-} + H_2O$$

Chromate (yellow) dichromate (orange)

$$Cr_2O_7^{2-} + 2\,OH^- \rightarrow 2\,CrO_4^{2-} + H_2O$$



Chromate ion

Potassium dichromate is used as

i)an oxidising agent ($Cr_2O_7^{2-} + 14H^+ + 6e^- \rightarrow 2Cr^{3+} + 7H_2O$)

It oxidize the following as (a) $2\,I^- \rightarrow I_2 + 2\,e^-$

(b) $H_2S \rightarrow 2H^+ + S + 2e^-$

(c) $Sn^{2+} \rightarrow Sn^{4+} + 2\,e^-$

(d) $Fe^{2+} \rightarrow Fe^{3+} + e^-$

POTASSIUM PERMANGANATE ($KMnO_4$)

- **Preparation:** From Pyrolusite ore(MnO_2)

1.fusion of MnO_2 with an alkali metal hydroxide and an oxidising agent

$$2MnO_2 + 4KOH + O_2 \rightarrow 2K_2MnO_4 + 2H_2O$$

2. dark green K_2MnO_4**disproportionates** in a neutral or acidic solution to give permanganate.

$$3MnO_4^{2-} + 4H^+ \rightarrow 2MnO_4^- + MnO_2 + 2H_2O$$

Tetrahedral permanganate (purple) ion

Properties of $KMnO_4$

- **Thermally unstable** (cannot act as primary standard)

$$2KMnO_4 \rightarrow K_2MnO_4 + MnO_2 + O_2$$

Acts as **oxidizing agent** in acidic as well as basic/neutral medium

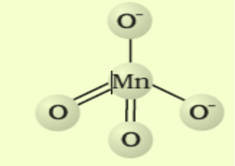
$$MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O$$

Strongly Acidic medium

- ***In*** Acidic medium $10\,I^- + 2MnO_4^- + 16H^+ \longrightarrow 2Mn^{2+} + 8H_2O +$ **$5I_2$**

In Alkaline medium $I^- + 2MnO_4^- + H_2O \longrightarrow 2MnO_2 + 2OH^- +$ **IO_3^-**

- In permanganate titrations, **HCl or HNO_3 cannot** be used to make the medium acidic



Tetrahedral manganate (green) ion

LANTHANOIDS

1. The 14 elements after Lanthanum having atomic number 58 to 71 are collectively known as Lanthanoids.

2. Electronic Configurations: The general electronic configuration of these elements is [Xe] $4f^{1-14}$, $5d^{0-1}$,$6s^2$.

3. Atomic and Ionic Sizes (lanthanoid contraction): The overall decrease in atomic and ionic radii from lanthanum to lutetium is due to poor shielding of 4f electrons is known as **lanthanoid contraction.**

Consequence of the lanthanoid contraction :

(i) Almost identical radii of Zr(160 pm) and Hf (159 pm),

(ii) In separation of lanthanoid elements

(iii) Basic character decreases from $La(OH)_3$ to $Lu(OH)_3$

4. OxidationStates: Most common oxidation state of these elements is +3,However, occasionally +2 and +4 ions in solution or in solidcompounds are also obtained. This irregularity arises mainly from the extra stability of empty, half-filledor filled *f* subshell.

- The formation of Ce(IV) is favoured by its noble gas configuration, but it is a strong oxidant reverting to the common +3 state.

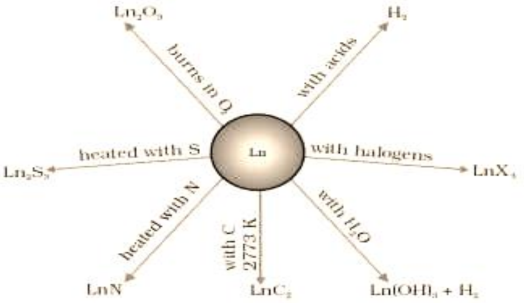
5. Colour Formation :Many trivalent lanthanoid ions are coloured both in the solid state and in aqueous solutions. Colour of these ions may be attributed to the presence of *unpaired* electrons in f subshell. Neither La^{3+}(f^0) nor Lu^{3+}(f^{14})ion shows any colour due to absence of *unpaired* electrons in f subshell.

6. Magnetic Behaviour: The lanthanoid ions other thanthe f^0 type (La^{3+} and Ce^{4+}) and the f^{14} type (Yb^{2+} and Lu^{3+}) are all paramagnetic. The paramagnetism rises to maximum in neodymium.

7. The first **ionisation enthalpies** of the lanthanoids are around600 kJ mol^{-1}, the second about 1200 kJ mol^{-1} comparable with thoseof calcium.

8. In their **Chemical behaviour**, in general, the earlier members of the seriesare quite reactive similar to calcium but, with increasing atomic number,they behave more like aluminium.

9. Chemical reactions of the lanthanoids.



10. Uses of Lanthanoids:

- Production of alloy steels for plates and pipes.
- A well known alloy is *mischmetall* which consists of a lanthanoid metal(~ 95%) and iron (~5%) and traces of S, C, Ca and Al. A good deal of mischmetall is used in Mg-based alloy to produce bullets, shell and lighter flint.
- Mixed oxides of lanthanoids are employed as catalysts inpetroleum cracking. Some individual Ln oxides are used as phosphorsin television screens and similar fluorescing surfaces.

ACTINOIDS

1. The 14 elements after Actinium having atomic number 90 to 113 are collectively known as Actinoids. They are radioactive elements.

2. **Electronic Configurations:** The general electronic configuration of these elements is [Rn] 5^{f1-14}, 6^{d0-1} ,7^{s2}

3. Ionic Sizes(Actinoid contraction): The overall decrease in atomic and ionic radii across the seriesdue to poor shielding of 5f electrons is known as **Actinoid contraction**

4. The actinoidcontraction is, however, greater from element to elementin this series resulting from poor shielding by 5f electrons.

5. **Oxidation States:**The actinoids show in general +3 oxidation state.The actinoids exhibit a larger number of oxidation states, which is in part attributed tothe fact that the 5*f*, 6*d* and 7*s* levels are of comparable energies.

SIMILARITIES between Lanthanoids & Actinoids

1) In both,electrons progressively enter f subshell
2) Both have main O.S +3
3) Both are electropositive & reactive
4) Both show decrease in atomic and ionic size(Lanthanoids / Actinoids contraction)

DIFFERENCES between Lanthanoids & Actinoids

Property	**Lanthanoids**	**Actinoids**
1.Oxidation states	Lanthanoids show mainly +3 Oxidation state except in a few cases where it is +2 and +3	more variety in O.S +4, +5, +6 ,+7
4. Tendency to form complexes	Lesser tendency to form complexes.	Greater tendency to form complexes .
5.Basic character	Lanthanoid compounds are less basic	Actinoid compounds are more basic
6.Tendency to form oxo ions	They do not form oxo ions	They form oxo ions such as UO_2^+ ,NpO_2^+ , PuO_2^+,UO_2^+
7.Radioactivity	non-radioactive(Except promethium)	All the actinoids are radioactive
8.Reactivity	Relatively less reactive	Highly reactive
9.Paramagnetic character	They are paramagnetic and their magnetic properties can be easily explained	They are also paramagnetic but their magnetic properties cannot be easily explained

A. MCQ TYPE:

1. Zinc and mercury do not show variable valency like d-block elements because
A. they are soft B. their d-shells are complete
C. they have only two electrons in the outermost subshell D. their d-shells are incomplete

2. Lanthanoid contraction is due to increase in
(a) Size of 4f orbital (b) shielding effect by 4f electrons (c) effective nuclear charge (d) atomic number

3. The magnetic nature of elements depends on the presence of unpaired electrons. Identify the configuration of transition element, which shows highest magnetic moment.
(i) $3d^7$ (ii) $3d^5$ (iii) $3d^8$ (iv) $3d^2$

4. Which of the following oxidation state is common for all lanthanoids?
(i) +2 (ii) +3 (iii) +4 (iv) +5

5. Although Zirconium belongs to *4d* transition series and Hafnium to *5d* transition series even then they show similar physical and chemical properties because____________.
(i) both belong to *d*-block.
(ii) both have same number of electrons.
(iii) both have similar atomic radius.
(iv) both belong to the same group of the periodic table.

6. Which of the following ions show higher spin only magnetic moment value?
(i) Ti^{3+} (ii) Mn^{2+} (iii) Fe^{2+} (iv) Co^{3+}

7. The pair that has similar atomic radii is
A. Mn and Re B. Ti and Hf C. Sc and Ni D. Zr and Hf

8. Colour of transition metal ions are due to absorption of some wavelength. This results in
A. d-s transition B. s-s transition C. s-s transition D. d-d transition

9. Transition metals form complex compound they have
(A)Small size (B) High nuclear charge
(C) A number of vacant orbitals of equivalent energy (D)All of these

10. The number of unpaired electron in Fe^{2+}(Z=26) are
(a) 4 (b) 5 (c) 6 (d) 3

Ans: **1-B** **2-b** **3-(ii)** **4-(ii)** **5-(iii)**
6-(ii) **7-D** **8-D** **9-D** **10-a**

11.Why Mn has unusually lower melting point though it possess maximum number of unpaired electron?
Ans.Due to half filled $(n-1)d^5$ and full filled ns^2 configuration Mn,is stable which reduce delocalisation of electrons.

12. Why does Cu not replace Hydrogen from Acid.
Ans. Cu shows E^0 positive value.

13. Although +3 oxidation states is the characteristic oxidation state of lanthanoids but cerium shows +4 oxidation state also. Why?
Ans: It is because after losing one more electron Ce acquires stable $4f^0$ electronic configuration.

14. HCl is not used in permanganate titration.Why?
Ans: Permanganate oxidizes HCl into chlorine.

15.Most of the transition metals exhibit paramagnetic behavior .Why?
Ans. In transition metals, d- subshell of (n-1) shell contain unpaired electrons (exception Zn, Cd and Hg) Because of the presence of unpaired electrons transition metals exhibit paramagnetic behavior.

16.Why is $La(OH)_3$ more basic then $Lu(OH)_3$?
Ans: $La(OH)_3$ is more basic then $Lu(OH)_3$ because the latter has greater covalent character as compared to the former on account of lanthanoid contraction. The release of OH^- ion from $Lu(OH)_3$ is more difficult and less basic than $La(OH)_3$

17.Why Cu+ is coloueless where as Cu+2 is coloured
Ans. Cu+ has $3d^{10}$ configuration(no d-d transition of electron) where as Cu+2 ion has $3d^9$ configuration(d-d transition of electron possible)

18.Zn, Cd and Hg are soft and have low melting point .Why?
Ans. It is because the have weak metallic bonds due to absence of unpaired electrons.

19. Chrimium is a typical hard metal whereas mercury is a liquid.Why?
Ans.Due to presence of more no of unpaired electrons from 3d and 4s subshell metal- metal interactions are strong in Chromium while in mercury all the electrons from 5d and 6s are paired thus metal metal interactions are weak.

20. Out of Cu_2Cl_2 and $CuCl_2$, which is more stable and why?
Ans: $CuCl_2$ is more stable than Cu_2Cl_2. The stability of Cu^{2+} (aq.) rather than Cu^+(aq.) is due to the much more negative $\Delta_{hyd}H$ of Cu^{2+} (aq.) than Cu^+(aq.)

21. Scandium is a transition element but Zinc is not. Why

Ans: Scandium is a transition because it has incompletely filled *d* orbitals in its ground state but Zinc have full d^{10} configuration in their ground state as well as in their commonoxidation state**.**

22. Copper atom has completely filled d orbital ($3d^{10}$) in its ground state, yet it is transition element. Why

Ans: Copper (Z = 29) can exhibit +2 oxidation state wherein it will have incompletely filled *d*-orbitals (3*d*), hence a transition element**.**

23. (i) Higher oxidation state of Mn with F is +4 whereas with oxygen is +7.Why? Or

The highest oxidation state of a metal is exhibited in its oxide or fluoride.Why?

Ans: Ability to form multiple bond by oxygen.

24. Complete and balance the following equation:-

(a.) $MnO_4^- + I^- + H^+$ --$\rightarrow$

(b) Na2Cr2O7 + KCl---$\rightarrow$

Ans (a) $2\ MnO_4^- + 10\ I^- + 16\ H^+ \rightarrow 2Mn^{+2} + 5I_2 + 8\ H_2O$

(b) $Na_2Cr_2O_7 + 2\ KCl \rightarrow K_2Cr_2O_7 + 2\ NaCl$

25. Give reasons for the following:

(i) The only oxidation state shown by scandium is +3

(ii) $[Ti(H_20)_6]^{4+}$ is colourless.

(iii) Mn0 is basic while Mn_20_7 is acidic.

Ans. (i) Sc(21) has electronic configuration : [Ar] $3d^1\ 4s^2$. At +3 oxidation state , stable d^0 is obtained.

(ii) $[Ti(H_20)_6]^{4+}$ is colourless it cannot undergo d-d transition as it do not have unpaired electrons

(iii) The oxide in the lower oxidation state of a metal is basic and in the higher oxidation state of the metal , it is acidic . That is why , MnO (oxidation state is +2) is basic whereas Mn_2O_7 (oxidation state +7) is acidic.

26. **A.** The element of 3d transition series are given as:- Sc Ti V Cr Mn Fe Co Ni Cu Zn

Answer the following:-

(a) Which element has highest mp and bp why?

(b) Which element is a strong oxidizing agent in oxidation agent +3 oxidation state and why?

(c) Which element is soft and why?

B.Write the equation involved in the preparation of $K_2Cr_2O_7$ from sodium chromate.

Ans.**A**. (a) Cr, the highest mp of Cr is attributed to the involvement of greater no of electrons from 3d in addition 4s electrons in inter atomic metallic bonding.

(b) Mn, because the change from Mn^{+3} (d^4) to Mn^{+2}(d^5) results in the half filled configuration which has extra stability.

(c) Zn, in Zn ($3d^{10}\ 4s^2$) all the electrons present in d- orbitals are paired and hence metallic bonds present in it are weak.

B. Chromite ore is treated with alkali in presence of air

$$4\ FeCr_2O_4 + 8\ Na_2CO_3 + 7\ O_2 \rightarrow 8\ Na_2CrO_4 + 2\ Fe_2O_3 + 8\ CO_2$$

Sodium chromate is acidified with sulphuric acid to give a solution of sodium dichromate.

$$2Na_2CrO_4 + 2\ H^+ \rightarrow Na_2Cr_2O_7 + 2\ Na^+ + H_2O$$

sodium dichromate is more stable then potassium dichromate hence sodium dichromate is treated with potassium chloride.

$$Na_2Cr_2O_7 + 2\ KCl \rightarrow K_2Cr_2O_7 + 2\ NaCl$$

27. A. In addition of FeSO4 with KMnO4 in the acidic medium, Why is dil. H2SO4 used instead of dil. HCl

B. Give Reason:-

(a) Among the transition metals, the highest oxidation state is exhibited in oxoanions of a metal

(b) Ce^{+4} is used an oxidizing agent in volumetric analysis.

(c) Zn^{+2} salts are white while Cu^{+2} salts are blue.

Ans A. Dil. H2SO4 is an oxidizing agent and oxidize FeSO4 to Fe2(SO4)3. Dil Hcl is reducing agent and liberates chlorine gas on reaction with KMnO4.

B. (a) 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.

(b) Ce^{+4} has the tendency to attain +3 oxidation states which is more stable and so it is used as an oxidizing agent in volumetric analysis.

(c) Zn^{+2} ion has all its orbitals completely filled where as Cu+2 ion there is incompletely filled orbitals. Therefore d-d transition Cu^{+2} has a tendency to form coloures salts

28. **A.** (a) Transition metals form large no of complex compounds.

(b) The lowest oxides of transition metal is basic where the highest oxide is amphoteric or acidic

(c) E^0 value for the Mn+3/ Mn+2 couple is highly positive (+1.57V) as compare to Cr+3/ Cr+2.

B. Write one similarty and one difference between the chemistry of lanthanoids and actinoid elements.

Ans. **A** (a) The tendency to form complex compounds is due to:Small size and high charge on metal ion.

- The avaibility of d- orbitals for accommodating electrons donated by the ligands.

(b) In low oxidation of metals, some of the valence electrons of the metalatom are not involved in bonding. Hence, it can donate electrons and behave as a base. In case of higher oxidation states of the metal, valence electrons are involved in bonding and are not avaible. Hence effective nuclear is high and it can accept electrons and behave an acid.

(c) Large third ionization energy of Mn (3d5) is mainly reason for this.

B . Similarty In both,electrons progressively enter f subshell and Both have main O.S is +3

Difference –Lanthanoids are non-radioactive (Except promethium) while Actinoids are radioactive

29. Assign reason for the following:-

(a) The enthalpies of atomization of tranisition elements are high.

(b) The transition metals and many of their compounds act as good calalyst.

(c) From element to element , the actinoid contraction is greaterthe lanthanoids contraction.

(d)) E^0 value for the Mn+3/ Mn+2 couple is highly positive (+1.57V) as compare to Cr+3/ Cr+2.

(e) Sc (21) doesnot exhibit variable oxidation states and yet it is regarded as a transition elements.

Ans.

(a) Transition metals have strong metallic bonds as they have large no of unpaired electrons.

(b) The catalytic activity of transition metals are due to :-

- Variable oxidation states due to which it form unstable intermediate compounds and provide a newpath with lower activation energy for the reaction. In some cases, the transition metals provide large surface area with free valancieson which reactants are adsorbed.

(c) This is due to poorer shielding by 5f- electrons in actinoidsthan 4f- electrons in the lanthanoids.

(d) Large third ionization energy of Mn (3d5) is mainly reason for this.

(e)This is because Sc has partially filled d- orbitals in the ground states ($3d^1 4s^2$)

30. Explain giving reasons:

(i) Transition metals and many of their compounds show paramagnetic behaviour.

(ii) The enthalpies of atomization 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) Scandium ($Z = 21$) is a transition element but zinc ($Z = 30$) is not?

Ans. (i) due to unpaired electrons.

(ii) Because of large number of unpaired electrons in their atoms they have stronger interatomic interaction and hence stronger bonding between atoms resulting in higher enthalpies of atomization.

(iii) d-d transition

(iv) Due to the presence of vacant orbitals or their tendency to form variable oxidation state.

(v) On the basis of incompletely filled 3*d* orbitals in case of scandium atom in its ground state ($3d^1$), it is regarded as a transition element. On the other hand, zinc atom has completely filled *d* orbitals ($3d^{10}$) in its ground state as well as in its oxidised state; hence it is not regarded as a transition element.

Assertion and Reason Type Questions

1. Assertion (A): Zn, Cd and Hg cannot be regarded as transition elements.
   Reason (R) : These elements do not belong to the d- block of the periodic table.
2. Assertion (A): The highest oxidation state of the 3d metals depends only on electronic configuration of the metal.
   Reason (R) : The number of electrons in (n-1) d and ns sub shells determine the oxidation states exhibited by the metal.
3. Assertion (A): Separation of Zr and Hf is very difficult.
   Reason (R) : Zr and Hf lie in the same group of the periodic table.
4. Assertion (A): A solution of ferric chloride on standing gives a brown precipitate.
   Reason (R) : Ferric chloride possesses covalent bonds and chlorine bridge structure.
5. Assertion (A): Actinides form relatively less stable complexes as compared to lanthanides.
   Reason (R) : Actinides can utilize their 5f orbitals along with 6d orbitals in bonding but lanthanides do not use their 4f orbitals for bonding.

[Ans: 1. (c) 2. (d) 3. (a) 4. (b) 5. (d).]

UNIT V COORDINATION COMPOUNDS

Difference between coordination compound and double salt:

Coordination compound	**Double salt**
-contains a central metal atom or ion surrounded by number of oppositely charged ions or neutral molecules. These ions or molecules are known as ligand and are bonded to the metal atom or ion by a coordinate bond.	When two salts in stoichiometric ratio are crystallised together from their saturated solution they are called double salts.
Example: $K_4[Fe(CN)_6]$	Example: $FeSO_4$. $(NH_4)2SO_4$. $6H_2O$ (Mohr's
They do not dissociate into simple ions when dissolved in water.	They dissociate into simple ions when dissolved in water.

Werner's coordination theory: Werner was able to explain the nature of bonding in complexes. The postulates of Werner's theory are:

a. In coordination compounds metals show two types of linkages (valences)-primary and secondary.
b. The primary valences are normally ionisable and are satisfied by negative ions.
c. The secondary valences are non-ionisable. These are satisfied by neutral molecules or negative ions.

The secondary valence is equal to the coordination number and is fixed for a metal.

Definitions of Some Important Terms Pertaining to Coordination Compounds

(a) Coordination entity: A coordination entity constitutes a central metal atom or ion bonded to a fixed number of ions or molecules. For example, $[CoCl_3(NH_3)_3]$ is a coordination entity in which the cobalt ion is surrounded by three ammonia molecules and three chloride ions. Other examples are $[Ni(CO)_4]$, $[PtCl_2(NH_3)_2]$, $[Fe(CN)_6]^{4-}$, $[Co(NH_3)_6]^{3+}$.

b) 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. For example, the central atom/ion in the coordination entities: $[NiCl_2(H_2O)_4]$, $[CoCl(NH_3)_5]^{2+}$ and $[Fe(CN)_6]^{3-}$ are Ni^{2+}, Co^{3+} and Fe^{3+}, respectively. These central atoms/ions are also referred to as **Lewis acids**.

c) Ligands: The ions or molecules bound to the central atom/ion in the coordination entity are called ligands. Example: Cl^-, H_2O, NH_3, $H_2NCH_2CH_2NH_2$, $N(CH_2CH_2NH_2)_3$ etc.

d) Unidentate ligand: When a ligand is bound to a metal ion through a single donor atom, as with Cl^-, H_2O or NH_3, the ligand is said to be **unidentate.**

e) Didenate Ligand: When a ligand can bind through two donor atoms as in $H_2NCH_2CH_2NH_2$ (ethane-1,2-diamine) or $C_2O_4^{2-}$ (oxalate),

f) Polydentate -when several donor atoms are present in a single ligand as in $N(CH_2CH_2NH_2)_3$, the ligand is saidto be **polydentate**.Ethylenediaminetetraacetate ion ($EDTA^{4-)}$ is an important hexadentate ligand. It can bind through two nitrogen and four oxygen atoms to a central metal ion.

When a di- or polydentate ligand uses its two or more donor atoms to bind a single metal ion, it is said to be a c**helate** ligand. The number of such ligating groups is called the **denticity** of the ligand. Ligand which can ligate through two different atoms is called **ambidentate ligand**. Examples: NO_2^- and SCN^- ions. NO_2^- ion can coordinate either through nitrogen or through oxygen to a central metal atom/ion.

Similarly, SCN– ion can coordinate through the sulphur or nitrogen atom.

(f) Coordination number: is defined as the number of ligand donor atoms to which the metal is directly bonded. For example, in the complex ions, $[PtCl_6]^{2-}$ and $[Ni(NH_3)_4]^{2+}$, the coordination number of Pt and Ni are 6 and 4 respectively.

(g) Coordination sphere: The central atom/ion and the ligands attached to it are enclosed in square bracket and is collectively termed as the **coordination sphere**. The ionisable groups are written outside the bracket and are called counter ions. Example: in the complex $K_4[Fe(CN)_6]$, the coordination sphere is $[Fe(CN)_6]^{4-}$ and the counter ion is K^+.

(h) Oxidation number of central atom: in a complex is defined as the charge it would carry if all the ligands are removed along with the electron pairs that are shared with the central atom. The oxidation number is represented by a Roman numeral in parenthesis following the name of the coordination entity. Example: oxidation number of copper in $[Cu(CN)_4]^{3-}$ is +1 and it is written as Cu(I).

i) Homoleptic and heteroleptic complexes: Complexes in which a metal is bound to only one kind of donor groups, e.g., $[Co(NH_3)_6]^{3+}$, are known as homoleptic. Complexes in which a metal is bound to more than one kind of donor groups, e.g., $[Co(NH_3)_4Cl_2]^+$, are known as heteroleptic.

Formulas of Mononuclear Coordination Entities:

(i) The central atom is listed first.

(ii) The ligands are then listed in alphabetical order. The placement of a ligand in the list does not depend on its charge.

(iii) Polydentate ligands are also listed alphabetically. In case of abbreviated ligand, the first letter of the abbreviation is used to determine the position of the ligand in the alphabetical order.

(iv) The formula for the entire coordination entity, whether charged or not, is enclosed in square brackets. When ligands are polyatomic, their formulas are enclosed in parentheses. Ligand abbreviations are also enclosed in parentheses.

(v) No space between the ligands and the metal within a coordination sphere.

(vi) When the formula of a charged coordination entity is to be written without that of the counter ion, the charge is indicated outside the square brackets as a right superscript with the number before the sign. Example: $[Co(CN)_6]^{3-}$, $[Cr(H_2O)_6]^{3+}$, etc.

(vii) The charge of the cation(s) is balanced by the charge of the anion(s).

Naming of Mononuclear Coordination Compounds:

(i) The cation is named first than anion.

(ii) If complex ion is there than ligand named first.

(iii) The ligands are named in an alphabetical order before the name of the central atom/ion. (This procedure is reversed from writing formula).

(iv) Names 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 ( ).

(v) Prefixes mono, di, tri, etc., is used for multiligands 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 parentheses.

Example, $[NiCl_2(PPh_3)_2]$ is named as dichlorobis(triphenylphosphine)nickel(II).

(vi) Oxidation state of the metal in cation, anion or neutral coordination entity is indicated by Roman numeral in parenthesis.

(vii) If the complex ion is a cation, the metal is named same as the element. For example, Co in a complex cation is called cobalt and Pt is called platinum.

(viii) If the complex ion is an anion, the name of the metal ends with the suffix – ate. For example, Co in a complex anion, Co $(SCN)_4^{2-}$ is called cobaltate. For some metals, the Latin names are used in the complex anions, *e*.g., ferrate for Fe.

(ix) The neutral complex molecule is named similar to that of the complex cation.

Examples:

1. $[Cr(NH_3)_3(H_2O)_3]Cl_3$ is named as: triamminetriaquachromium(III) chloride
2. $[Co(H_2NCH_2CH_2NH_2)_3]2(SO_4)_3$ is named as: tris(ethane-1,2–diammine)cobalt(III) sulphate
3. $[Ag(NH_3)_2][Ag(CN)_2]$ is named as: diamminesilver(I) dicyanoargentate(I)

- **Types of isomerism:**

a) **Structural isomerism**

i. Linkage isomerism

ii. Solvate isomerism or hydrate isomerism

iii. Ionisation isomerism

iv. Coordination isomerism—due to

b) **Stereoisomerism**

i. Geometrical isomerism

ii. Optical isomerism

(a) **Structural isomerism:**It arises due to the difference in structures of coordination compounds.

- **Ionisation isomerism:** It 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. Example: $[Co(NH_3)_5Br]\ SO_4$ and $[Co(NH_3)_5\ SO_4]\ Br$
- **Solvate isomerism:** It is isomerism in which solvent is involved as ligand.If solvent is water it is called hydrate isomerism, e.g., $[Cr(H_2O)_6]Cl_3$ and$[CrCl_2(H_2O)_4]\ Cl_2.\ 2H_2O$.
- **Linkage isomerism:**It arises in a coordination compound containing ambidentate ligand.In the isomerism, a ligand can form linkage with metal through different atoms.Example: $[Co(NH_3)_5ONO]Cl_2$ and $[Co(NH_3)_5NO_2]Cl_2$.
- **Coordination isomerism:**This type of isomerism arises from the interchange of ligands between cationic and anionic entities of different metal ions present in a complex.Example: $[Co(NH_3)_6][Cr(C_2O_4)_3]$ and$[Cr(NH_3)_6][Co(C_2O_4)_3]$.

(b) **Stereoisomerism:** This type of isomerism arises because of different spatial arrangement.

- **Geometrical isomerism:**

  It arises in heteroleptic complexes due to different possible geometrical arrangements of ligands.
- **Optical isomerism:** Optical isomers are those isomers which are non-superimposable mirror

Valence Bond Theory : The metal atom or ion under the influence of ligands can use its (n-1)*d*, n*s*, n*p* or n*s*, n*p*, n*d* orbitals for hybridisation to yield a set of equivalent orbitals of definite geometry such as octahedral, tetrahedral, square planar and so on . These hybridised orbitals are allowed to overlap with ligand orbitals that can donate electron pairs for bonding.

Coordination number	Type of hybridization	Distribution of hybrid orbitals in space
4	sp^3	Tetrahedral
4	dsp^2	Square planar
5	sp^3d	Trigonal bipyramidal
6	sp^3d^2	Octahedral
6	d^2sp^3	Octahedral

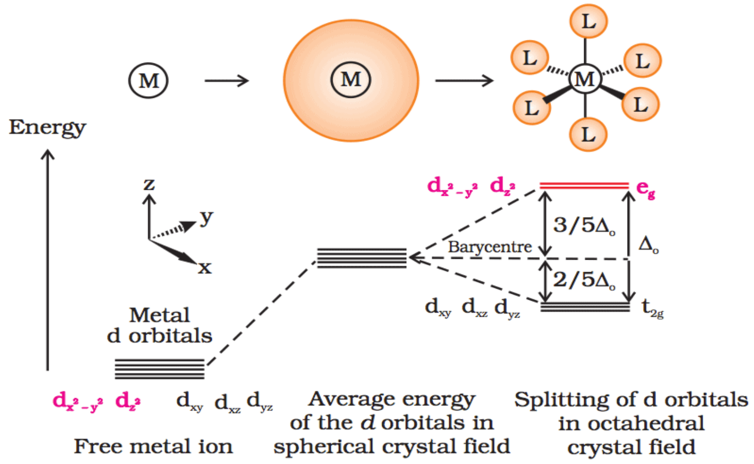
Magnetic properties of coordination compounds: A coordination compound is paramagnetic in nature, if it has unpaired electrons and diamagnetic if all the electrons in the coordination compound are paired. Magnetic moment = $[n (n + 2)]^{1/2}$ where n is number of unpaired electrons.

- **Crystal Field Theory:**

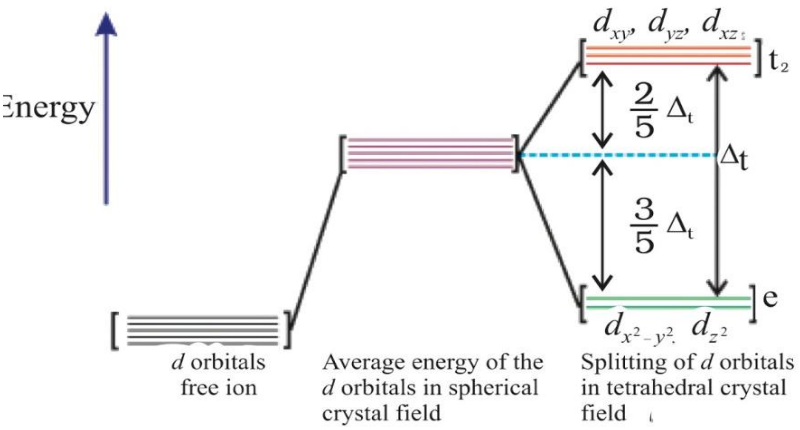
a) It assumes the ligands to be point charges and there is electrostatic force of attraction between ligands and metal atom or ion.

b) It is theoretical assumption.

- **Crystal field splitting in octahedral coordination complexes:**



- **Crystal field splitting in tetrahedral coordination complexes:**



- For the same metal, the same ligands and metal-ligand distances, the difference in energy between eg and t2g level is $\Delta_t = - 4/9\Delta_o$

MULTIPLE CHOICE QUESTIONS

1. Which of the following is a complex of metal other than transition metal?
(a) Haemoglobin (b) Chlorophyll (c) Ferrocene (d) Vitamin B12
2. Which of the following is not a double salt but a coordinate compound?
(a) $KCl.MgCl_2.6H_2O$ (b) $FeSO_4.(NH_4)_2SO_4.6H_2O$
(c) $K_2SO_4.Al_2(SO_4)_3.24H_2O$ (d) $4KCN.Fe(CN)_2$
3. The donor atoms in ethylenediaminetetraacetate ion is
(a) two N and two O (b) two N and four O
(c) four N and two O (d) three N and three O
4. The correct I.U.P.A.C. name of the complex, $Fe(C_5H_5)_2$ is
(a) cyclopentadienyliron(II) (b) bis(cyclopentadienyl)iron(II)
(c) dicyclopentadienyliron(II) (d) ferrocene(0)
5. The geometrical isomerism in coordination compounds is exhibited by
(a) square planar and tetrahedral complexes (b) square planar and octahedral complexes
(c) tetrahedral and octahedral complexes (d) square planar, tetrahedral, octahedral comp.
6. Which of the following is not optically active?
(a) $[Co(en)_3]^{3+}$ (b) $[Cr(ox)_3]^{3-}$
(c) cis-$[CoCl_2(en)_2]$+ (d) trans-$[CoCl_2(en)_2]^+$
7. The complex ion $[Cu(NH_3)_4]^{+2}$ is
(a) tetrahedral and paramagnetic (b) tetrahedral and diamagnetic
(c) square planar and paramagnetic (d) square planar and diamagnetic
8. The hybrid state of Co in high spin complex, $K_3[CoF_6]$ is
(a) sp^3d^2 (b) sp^3 (c) d^2sp^3 (d) sp^3d
9. In an octahedral crystal field, the t2g orbital are
(a) raised in energy by 0.4 Δo (b) lowered in energy by 0.4 Δo
(c) raised in energy by 0.6 Δo (d) lowered in energy by 0.6 Δo
10. If $\Delta o < P$, then the correct electronic configuration for d4 system will be
(a) t^2g^4 eg0 (b) t^2g^3 eg1 (c) t^2g^0 eg^4 (d) $t2g^2$ eg^2
(a) 3 (b) 6 (c) 5 (d) 4

Answer key: 1 b, 2 d , 3 b, 4 b, 5 b, 6 d, 7 c, 8 a, 9 b, 10 b

Q11)The spin only magnetic moment of [MnBr]2– is 5.9 BM. Predict the geometry of the complexion.
Ans. Co-ordination No. of Mn2+ion is 4; it has a tetrahedral geometry.

Q 12) CuSO4.5H2O is blue in colour while CuSO4 is colourless. Why?
Ans. d -d transition is possible in CuSO4.5H2O , so it shows colour. CuSO4 due to the absence of water (ligand) Crystal Field splitting is not possible, so it is not coloured.

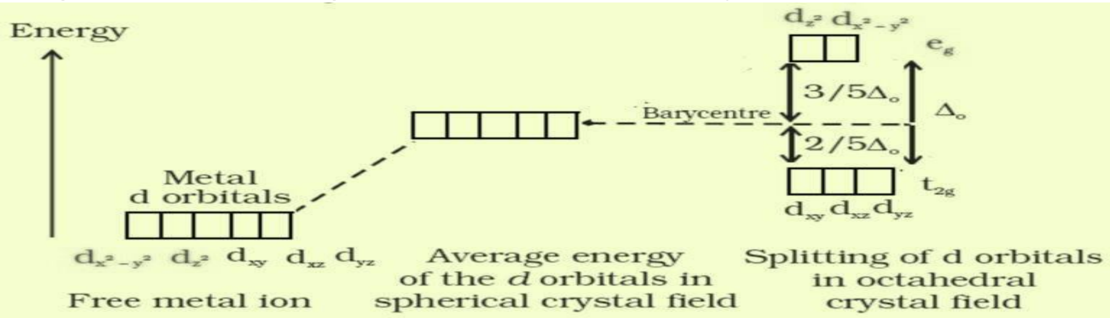
Q13) Write the stateof hybridisation in[Cr(NH3)6]3+ Ans. d2sp3 geometry, octahedral

Q14)Write the formula of the given Coordination compound :–
a) Ni2+ ion is bound to two water molecules and two oxalate ions.
b) Co3+ ion is bound to one chloride ion and one ammonia molecule and two ethylenediamine molecules
Ans. a) [Ni(H2O)2(C2O4)2]2- b) [Co(Cl)(NH3)(en)2]2+

Q15) When 1 mol of CrCl3.6H2O is treated with an excess of AgNO3, 3 mol of AgCl are obtained. Write structural formula & IUPAC name of the compound.
Ans. [Cr(H2O)6]Cl3

Q16.How can you show that [Co(NH3)5Cl]SO4 and [Co(NH3)5SO4]Cl are ionisation isomers?
Ans: the former gives white ppt with BaCl2 solution, latter does not.

Q17) Name (a) the metal ion present in vitamin B12 and (b) the compound used for inhibiting growth of tumours.
Ans:(a) Co3+ (b) cis – platin
Q18) Draw diagram to show splitting of d – orbital in octahedral crystal field.
Ans.



Q19) Explain the two patterns of filling d4 ion in octahedral crystal field.
Ans. b) Electronic configuration for d4 ion if Δo< P the electronic configuration is t 2g4 eg 0 and if Δo> P the electronic configration is t2g 3 eg 1
Q20) Arrange following complex ions in increasing order of crystal field
splitting energy (O) : [Cr(Cl)6]3– , [Cr(CN)6]3–, [Cr(NH3)6]3+
Ans. [Cr(Cl)6]3– , [Cr(NH3)6]3+ [Cr(CN)6]3–
Q21) Discuss the nature of Bonding in metal carbonyls.
[Hint: refer to synergic effect, back bonding and - acid ligand- CO]
Q22) Arrange the following complexes in theorder of increasing electrical conductivity. Give reason.
[Co(NH3)3Cl3], Co(NH3)5Cl]Cl2,[Co(NH3)6]Cl3, [Co(NH3)4Cl2]Cl
Ans. [Hint: refer to no. of ions resulting from dissociation] [Co(NH3)3Cl3]< [Co(NH3)4Cl2]Cl < [Co(NH3)5Cl]Cl2, < [Co(NH3)6]Cl3
Q 23)How many geometrical isomers are possible in the following coordination entities:
(i) $[Cr(C_2O_4)_3]$
(ii) [CoCl3(NH3)3].
Ans. (i) Nil [Hint: oxalate is a symmetrical didentate ligand]
(ii) Two (fac and mer isomer).
Q 24. A solution of [Ni(H2O)6]2+ is green, but a solution of [Ni(CN)4] 2- is colourless. Explain.
Ans.H_2O being weak ligand forms an outer orbital complex with unpaired electros and vacant orbitals. This facilitates d-d transition.
Q 25. Why $[Fe(CN)_6]^{3-}$ is weakly paramagnetic while $[Fe(CN)_6]^{4-}$ is diamagnetic ?
Ans. In [Fe(CN)6]3– Fe is in +3 state having d5 configuration, thus it has one unpaired electron. Therefore it is paramagnetic. While in [Fe(CN)6]4– Fe is in +2 state(d6) and it has no unpaired electrons(inner orbital complex)
Q 26. Why[Ni(CO)4] possesses tetrahedral geometry, while [Pt(NH3)2 Cl2] is a square-planar?
Ans. In [Ni(CO)4] Ni is in) state,CO being strong ligand pushes 4s electrons to 3d and sp3 hybridization takes place. But in Pt2+ even after pairing of 3d electrons one d orbital is available for dsp2 hybridisation.
Q 27.What is the difference between - (a) homoleptic and heteroleptic complexes
(b) didentate and ambidentate ligands
Ans: (a)Homoleptic complexes have only one type of ligand, hetero leptic have more than one type
(c) didentate ligands have two donor sites while ambident ligands donate an electron pair in two different ways.

Q 28) Write the structures and IUPAC names of the -

(a) linkage isomer and the (b) ionisation isomer of [Co(NH3)5(NO2)](NO3)2

Ans: pentaamminenitrito-O-cobalt(III) nitrate

a)$[Co(NH_3)_5ONO](NO_3)_2$ is linkage isomer.

b) $[Co(NH_3)_5(NO_3)]\ NO_2NO_3$ is ionization isomer

Q29) Discuss briefly giving example in each case the role of coordination compounds in:

a.Biological system b.Medicinial chemistry c.Analytical chemistry

d.Extraction/metallurgy of metals e.Phohtography

Ans:a. **Biological system** Chlororophyll a pigment helps in phototo synthesis.It is a coordination compound of magnesium

b.**Medicinial chemistry:** cis platin a coordination compound is used in treatment of cancer.

c.**Analytical chemistry:**during salt analysis a large no, of coordination copmpounds are made/used.e.g. AgCl is a white ppt forms a soluble complex with excess of ammonia.

d**.Extraction/metallurgy of metals:**In extraction of gold and siver the metal is treated with NaCN to form a coordination compound.

e**.Phohtography:** during developing of film in black and white photography AgBr forms a complex when washed with sodium thiosulphte(hypo)solution.

Name the types of isomerism exhibited by [Co(NH3)5(NO2)](NO3)2 .

Ans: linkage isomerism and ionization isomerism

Q30. Write the name & Using VBT Predict the Magnetic behaviour, hybridization, shape of following. Also predict whether it is inner or outer orbital complex in case of octahedral complexes. (1x5)

a) [CoF6]3- b) [Co(NH3)6]3+

c) [Ni(CN)4]2- d) [NiCl4]2- e) [Ni(CO)4]

Ans: a) hexafluoridocobaltate(III) ion,paramagnetic,sp3d2,octahedral

b)hexaamminecobalt(III) ion,diamagnetic,d2sp3,octahedral

c)tetracyanidonickelate(II) ion,diamagnetic,dsp2,square planar

d)tetrachloridonickelate(II) ion,paramagnetic,sp3,tetrahedral

e)tetracarbonylnickel(0),diamagnetic,spp3,tetrahedral

Q31 . $[Fe\ (H_2O)_6]^{3+}$ is strongly paramagnetic whereas $[Fe\ (CN)_6]^{3-}$ is weakly paramagnetic.Explain.

Ans. In both the complexes, Fe is in +3 oxidation state. CN^- is strong field ligand, inner d-orbitals are involved, d^2sp^3 hybridization, one unpaired electron, weakly paramagnetic. H_2O is weak field ligand, outer d-orbitals are involved, sp^3d^2 hybridization, five unpaired electrons, strongly paramagnetic.

Assertion and Reason Type Questions

1. Assertion (A): Linkage isomerism arises in co-ordination compounds containing ambidentate ligands.
   Reason (R) : Ambidentate ligand like NO_2 has two different donor atoms i.e. N and O.
2. Assertion (A): Complexes of MX_6 and MX_5L type do not show geometrical isomerism.
   Reason (R) : Geometrical isomerism is not shown by the complexes of co-ordination number 6.
3. Assertion (A): Toxic metal ions are removed by the chelating ligands.
   Reason (R) : Chelate complexes tend to be more stable.
4. Assertion (A): Mohr's salt, $FeSO_4.(NH_4)_2SO_4.6H_2O$ is not a co-ordination compound.
   Reason (R) : The aqueous solution of this salt gives the test of Fe^{2+}, NH_4^+ and SO_4^{2-} ions.
5. Assertion (A): The complex $[Fe(H_2O)_6]^{2+}$ is paramagnetic in nature.
   Reason (R) : It consists of two unpaired electrons.

[Ans: 1. (a) 2. (b) 3. (a) 4. (b) 5. (c).]

UNIT VI HALOALKANES AND HALOARENES

Alkyl halides or haloalkanes and **aryl halides** or haloarenes are organic compounds obtained by replacement of one or more H-atoms of **aliphatic** and **aromatic** hydrocarbons respectively by **halogen atom**(s).

Types of haloalkanes and haloarenes:

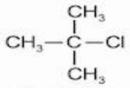
(1) Monohaloalkanes: whether halogen atom is bonded to 1°, 2° or 3° C-atom, e.g.,

$CH_3-CH_2-CH_2-Cl$

1-Chloropropane (1°)

$CH_3-CHCl-CH_3$

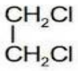
2-Chloropropane (2°)
or Isopropyl chloride



$$CH_3-\overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle CH_3}{|}}{C}}-Cl$$

2-Chloro-2-methylpropane (3°)
or Tert. butyl chloride

(2) Dihaloalkanes and dihaloarenes:

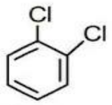


$$\begin{matrix} CH_2Cl \\ | \\ CH_2Cl \end{matrix}$$

1, 2-Dichloroethane
or Ethylene chloride
(vic-dihalide)

CH_3-CHCl_2

1, 1-Dichloroethane
or Ethylidene chloride
(gem-dihalide)



1, 2-Dichlorobenzene
or *o*-Dichlorobenzene

(3) Polyhaloalkanes: $CHCl_3$ (Chloroform), $CHBr_3$ (Bromoform) CHI_3 (Iodoform), CCl_4 (Carbon tetrachloride)

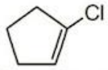
(4) Allylic halides: When halogen atom bonded to sp^3 hybridised C-atom next to carbon, carbon double bond, e.g., $CH_3-CH=CH-CH_2-Cl$, $CH_2=CH-CH_2-Cl$

(5) Benzylic halides: When halogen atom bonded to sp^3 hybridised C-atom next to an aromatic ring. For example $C_6H_5-CH_2-Cl$

(6) Vinylic halides: When halogen atom bonded to sp^2 hybridised C-atom of an aliphatic compound, e.g.,

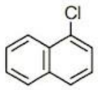
$CH_2=CH-Cl$

Chloroethene

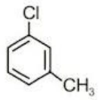


1-Chlorocyclopenten

(7) Aryl halides: When halogen atom bonded to sp^2 hybridised C-atom of an aromatic ring. For example

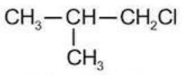


1-Chloronaphthalene



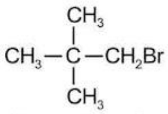
(m-Chlorotoluene)
1-Chloro-3-methylbenzene

IUPAC Nomenclature:



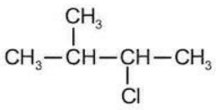
$$CH_3-\underset{\underset{\displaystyle CH_3}{|}}{CH}-CH_2Cl$$

Isobutyl chloride
1-Chloro-2-methylpropane



$$CH_3-\overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle CH_3}{|}}{C}}-CH_2Br$$

Neopentyl bromide
1-Bromo-2-2-dimethylpropane



$$CH_3-\overset{\overset{\displaystyle CH_3}{|}}{CH}-\underset{\underset{\displaystyle Cl}{|}}{CH}-CH_3$$

2-Chloro-3-methylbutane

$CH_3-CF_2-CH_2-CH_3$

2, 2-Difluorobutane (gem)

Preparation of Haloalkanes

1. (1)From Alcohols:

(a) $CH_3CH_2OH + HCl$(in presence of anhydrous $ZnCl_2$) ⟶ $CH_3CH_2Cl + H_2O$

(b) By reaction with phosphorus halides: $CH_3CH_2OH + PCl_5 \longrightarrow CH_3CH_2Cl + POCl_3 + HCl$

(c) By reaction with thionyl chloride: $CH_3CH_2OH + SOCl_2 \longrightarrow CH_3CH_2Cl + SO_2 + HCl$

2. From Hydrocarbons

(i) $CH_3—CH_3 + Cl_2$ (in presence of sunlight) ⟶ $CH_3—CH_2Cl$

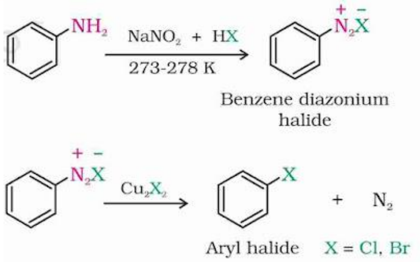
(ii) $CH_3—CH{=}CH_2 + HCl \longrightarrow CH_3—CH(Cl)—CH_3$ (Markovnikov's rule)

3. **Halogen exchange reaction** :-

(i)Finkelstein Reaction): Alkyl chloride or alkyl bromide is treated with NaI in acetone to give alkyl iodide in fairly good yield. $CH_3CH_2Cl + NaI$ (in dry acetone)⟶ $CH_3CH_2I + NaCl$

(ii) **Swarts Reaction** $H_3C – Br + AgF \rightarrow H_3C – F + AgBr$

5. From Diazonium Salt(Sandmeyer reaction)



1. **Physical properties of haloalkanes :**

1. Boiling point orders

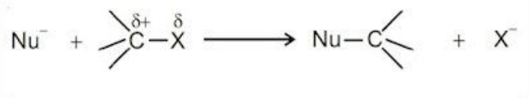
1. R – I > R – Br > R – CI > R – F
2. $CH_3 – (CH_2)_2 – CH_2Br > (CH_3)_2\,CHCH_2Br > (CH_3)_3CBr$
3. $CH_3CH_2CH_2 > CH_3CH_2X > CH_3X$

2. Dipole moment decreases as the **electronegativity of the halogen decreases**.

3. Haloalkanes though polar but are insoluble in water as they **do not form hydrogen bonding with water.**

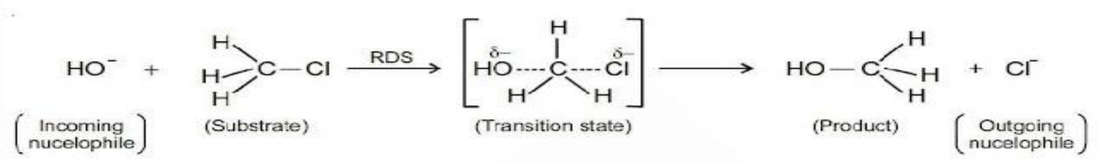
1. Reactions of haloalkanes:

I. Nucleophilic Substitution Reactions



(a) Substitution nucleophilic bimolecular (S_N2)

S_N2 is a **single step bimolecular reaction** in which the incoming nucleophile attacks the C–atom of substrate in a direction opposite to the outgoing nucleophile.



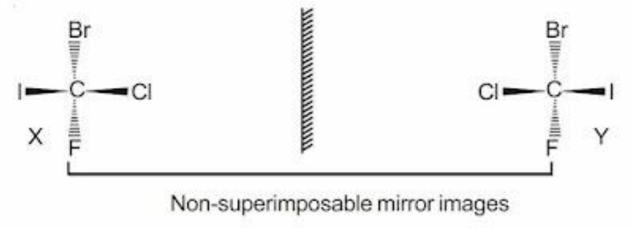
Reactivity of halides towards S_N2 mechanism is 1° > 2° > 3°

Relative reactivity of alkyl halides for same alkyl group is RI > RBr > RCI > RF

(b) <u>Substitution nucleophilic unimolecular (S_N1)</u> S_N1 is a **two step unimolecular** reaction. The first step is the slow ionisation of substrate and is the rate-determining step. The second step is the rapid reaction between the carbocation (formed in the first step) and the nucleophile. SN1 reactions generally proceed in **polar protic solvents** such as H_2O, CH_3OH, CH_3COOH etc. $R—X \longrightarrow R^+ + X^-$ (Step 1)

$R^+ + Nu^- \longrightarrow R—Nu$ (Step 2)

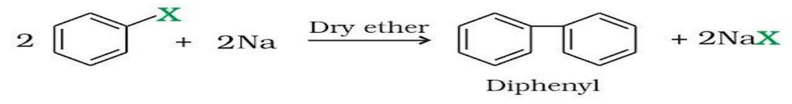
i). Optical Isomerism -When a compound is non super imposable on its mirror image. The compound would be chiral and it will exhibit optical isomerism. All chiral objects rotate plane polarized light.



Chiral and hence X and Y are non-identical. They are enantiomers.
ii). Chiral Carbon If all the four valencies of carbon are satisfied by **4 different group** the carbon is chiral carbon or asymmetric carbon. Presence of chiral carbon never ensure the molecule is optically active.
II. Elimination Reactions Haloalkanes having β-hydrogen atom when heated in presence of alc. KOH undergo dehydrohalogenation forming alkene. $CH_3CH_2(Cl)CH_3$ + alc. KOH $\longrightarrow CH_3CH{=}CH_2 + HCl$
III. Reaction with Metals(Preparation of Grignard reagent)
(a) $CH_3Cl + Mg \longrightarrow CH_3MgCl$ .In this reaction polarity on C is reversed.
(b) **(Wurtz Reaction)** $2CH_3Cl + 2Na$ (in dry ether)$\longrightarrow C_2H_6 + 2NaCl$

2. Reactions of Haloarenes

I. Nucleophilic Substitution Reactions
Haloarenes are very much less reactive than haloalkanes towards nucleophilic substitution reactions.
Reason: (i)The lone pair of electrons on halogen atom is delocalised with the π-electrons of benzene ring. (ii)It acquires **partial double bond character** in carbon halogen bond **due to resonance**. Thus it is more difficult to break carbon-halogen bond in haloarenes.
II. Electrophilic Substitution Reactions
III. Reaction with Metals
Fittig reaction: Haloarenes when treated with sodium in presence of dry ether react in a manner simillar to haloalkanes to give diarenes. This is known as Fittig reaction.



Wurtz-Fittig reaction: When a mixture of haloalkane and haloarene is treated with sodium under identical conditions we get alkyl arene.
e.g.Chlorobenzene to Toluene

Polyhalogen Compound

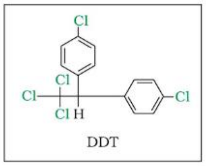
1. Dichloromethane (Methylene chloride)$CH_3Cl + Cl_2 \longrightarrow CH_2Cl_2 + HCl$
2. Trichloromethane (Chloroform) $CCl_4 + H_2 \longrightarrow CHCl_3 + HCl$

Chloroform is slowly oxidised by air in the presence of light to an extremely poisonous gas, carbonyl chloride, also **known as phosgene**. It is therefore stored in closed dark coloured bottles completely filled so that air is kept out.

3. Triiodomethane (Iodoform)It was used earlier as an antiseptic but the antiseptic properties are due to the liberation of free iodine and not due to iodoform itself.

4. Tetrachloromethane (Carbon tetrachloride) $CHCl_3 + Cl_2 \longrightarrow CCl_4 + HCl$

5. p,p'-Dichlorodiphenyltrichloroethane (DDT)



Important questions

1.In Allyl chloride the hybridisation of carbon in C-Cl is

(a) sp (b) sp^2 (c) sp^3 (d) None of the above

2. Which of the following alkyl halides will undergo S_N1 reaction most readily?

(i) $(CH_3)_3C—F$ (ii) $(CH_3)_3C—Cl$ (iii) $(CH_3)_3C—Br$ (iv) $(CH_3)_3C—I$

3. Which of the following is Finkelstein reaction

(a) Halogen (-X) is replaced by iodine (b) Addition of hydrogen halide on alkene

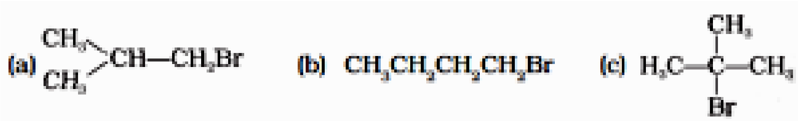
(c) Halogen replaces alcoholic group (d) Halogen replaces the hydrogen of benzoic ring

4. The IUPAC name of the compound $CH_2=C(CH_3)-CH_2Br$ is

(a) 3-bromo-2-methylprop-1-ene (b) 1-bromo-3-methylprop-1-ene

(c) 2-bromo-2-methylprop-1-ene (d) 3-bromo-2-methylprop-2-ene

5. Arrange the following compounds in increasing order of their boiling points.



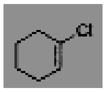
(i) (b) < (a) < (c) (ii) (a) < (b) < (c) (iii) (c) < (a) < (b) (iv) (c) < (b) < (a)

6. Reaction of $C_6H_5CH_2Br$ with aqueous sodium hydroxide follows _______________

(A)S_N1 mechanism (B) S_N2 mechanism

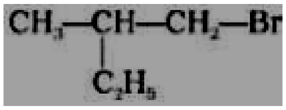
(C) Any of the above two depending upon the temperature of reaction. (D)Saytzeff rule

7. The following compound is



a) Allyl Chloride b) Vinyl Chloride c) Benzyl Chloride d) Aryl Chloride

8.The correct IUPAC name of above compound is



$$CH_3—\underset{\displaystyle C_2H_5}{\underset{|}{CH}}—CH_2—Br$$

(A) 1-Bromo-2-ethyl-2-methylethane (B) 1-Bromo-2-ethylpropane

(C) 1-Bromo-2-methylbutane (D) 2-Methyl-1-bromobutane

9. Molecules whose mirror image is non superimposable over them are known as chiral. Which of the following molecules is chiral in nature?

(i) 2-Bromobutane (ii) 1-Bromobutane (iii) 2-Bromopropane (iv) 2-Bromopropan-2-ol

10. Toluene reacts with a halogen in the presence of iron (III) chloride giving ortho and para halo compounds. The reaction is

(i) Electrophilic elimination reaction (ii) Electrophilic substitution reaction

(iii) Free radical addition reaction (iv) Nucleophilic substitution reaction

Answer: 1(C) , 2(IV), 3(a),4(a),5(iii),6(A),7(b),8(C),9(i),10(ii)

11. Which compound in each of the following pairs will react faster in S_N2 reaction with OH^-?

i. CH_3Br or CH_3I ii. $(CH_3)_3$ CCl or CH_3Cl

Answer: (i) CH_3I as I is better leaving group than Cl

(ii) $(CH_3)_3$ CCl due to formation of stable tertiary carbocation.

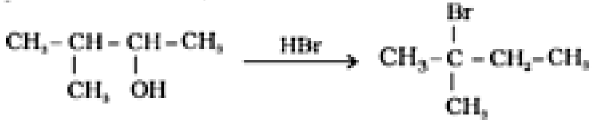
12. Out of o-and p-dibromobenzene which one has higher melting point and why?

Ans. *p*-Dibromobenzene has higher melting point than its *o*-isomer. It is due to symmetry of *p*- isomer which fits in crystal lattice better than the o-isomer.

13 **Why is it necessary to avoid even traces of moisture during the use of a Grignard reagent?**

Ans. Grignard reagents are highly reactive and react with any source of proton to give hydrocarbons.

14. When 3-methylbutan-2-ol is treated with HBr, the following reaction takes place:

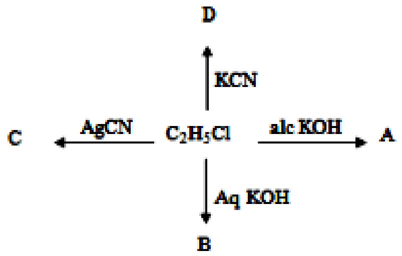


$$CH_3-\underset{\underset{CH_3}{|}}{CH}-\underset{\underset{OH}{|}}{CH}-CH_3 \xrightarrow{HBr} CH_3-\overset{\overset{Br}{|}}{\underset{\underset{CH_3}{|}}{C}}-CH_2-CH_3$$

Give a mechanism for this reaction.

Answer:The secondary carbocation formed in step II rearranges to more stable tertiary carbocation by a hydride ion shift from 3rd carbon atom.

15. Identify A,B,C and D:



Answer: A = Ethene,

B=Ethanol ,

C= C_2H_5NC,

D= C_2H_5CN

16. Why is Sulphuric acid not used during the reaction of alcohols with KI?

Ans. Sulphuric acid is an oxidising agent. It will oxidise HI produced during the reaction to I_2 and therefore, will prevent reaction between an alcohol and HI to form alkyl halide.

17. **Aryl chlorides and bromides can be easily prepared by electrophilic substitution of arenes with chlorine and bromine respectively in the presence of Lewis acid catalysts. But why does preparation of aryl iodides requires presence of an oxidising agent?**

Answer: Iodination reactions are reversible in nature. To carry out the reaction in the forward direction, HI formed during iodination is removed by oxidation. HIO_4 is used as an oxidising agent.

18. Why can aryl halides not be prepared by reaction of phenol with HCl in the presence of $ZnCl_2$?

Answer: C—O bond in phenols is more stable due to resonance effect and it has double bond character, hence breaking of this bond is difficult.

19.Explain the following

(a) Aryl halides have low reactivity.

(b) Organic halogen compounds used as solvents in industry are chlorides rather than bromide and iodide.

(c) Reactivity of HX with alcohols is in the order HI > HBr > HCl.

Ans. (a)In aryl halides, halogen in attached to *sp*^{2} hybridised carbon. So carbon chlorine bond dissociation energy is high due to partial double bond character.

(b)As chlorides are more volatile than bromide and iodide so used as solvents in industry.

(c) Reactivity of halogen acids depends upon bond dissociation energy and the bond energy is in the order HI < HBr < HCl. So HI is more reactive than HBr and HCl.

20. a) What is racemic mixture?

(b)The following haloalkanes are hydrolysed in presence of aq KOH.

(i) 2- Chlorobutane (ii) 2-chloro-2-methylpropane

Which of the above is most likely to give a racemic mixture? Justify your answer.

Answer: (a) Equal proportion of dextro-rotatory and laevorotatory compound.

(b) 2- Chlorobutane. As it is optically active molecule.

20. Allyl chloride is hydrolysed more readily than *n*-propyl chloride. Why?

Answer: Allyl chloride shows high reactivity as the carbocation formed by hydrolysis is stabilised by resonance.

21. (i) Out of $(CH_3)_3C–Br$ and $(CH_3)_3C–I$, which one is more reactive towards SN ^{1}and why?

(ii) Write the product formed when p-nitro Chlorobenzene is heated with aqueous NaOH at 443 K followed by acidification.

(iii) Why dextro and laevo – rotatory isomers of Butan-2-ol are difficult to separate by fractional distillation?

(iv) Some alkylhalides undergo substitution whereas some undergo elimination reaction on treatment with bases. Discuss the structural features of alkyl halides with the help of examples which are responsible for this difference.

Answer : (i) $(CH_3)_3C–I$ is more reactive towards SN ^{1} as I is better leaving group than Cl.

(ii) p-Nitrophenol

(iii) They are enantiomers, they possess identical physical properties like boiling point.

(iv) Primary alkyl halides prefer to undergo substitution reaction by S_N2 mechanism whereas tertiary halides undergo elimination reaction due to the formation of stable carbocation.

22.(a) Identify the chiral molecule in the following pair:

(i) 3-methyl butan-2-ol (ii) 2,4-dimethyl butan-3-ol

(b) Write the structure of the product when Chlorobenzene is treated with methyl chloride in the presence of sodium metal and dry ether.

(c) Write the structure of the alkene formed by dehydrohalogenation of1-bromo-1- methylcyclohexane with alcoholic KOH.

(d) Haloalkanes react with KCN to form alkyl cyanides as main product while AgCN forms isocyanides as the chief product. Explain.

Answer :(a) 3-methyl butan-2-ol

(b) Toluene

(c) 1- methylcyclohexene

(d) KCN is predominantly ionic and provides cyanide ions in solution. The nucleophillic attack takes place mainly through carbon atom and not through nitrogen atom since **C—C bond is more stable than C—N bond**. However, AgCN is mainly covalent in nature and nitrogen is free to donate electron pair forming isocyanide as the main product.

23.(i) Write the structure of major alkene formed by β-elimination when 2-Bromopentane reacts with alcoholic KOH.

(ii) Which one of the compounds in the following pairs is chiral: 2-bromobutane and 3-bromopentane

(iii) Identify A and B in the following:

(iv) Why are aryl halides less reactive towards nucleophilic substitution reactions than alkyl halides? How can we enhance the reactivity of aryl halides?

Answer:(i) Pent-2-ene

(ii) 2-bromobutane

(iii) A is Diphenyl ,B is Phenyl magnesium bromide.

(iv) C-X bond in aryl halide is difficult to break due to partial double bond character. Reactivity can be increased by introduction of electron withdrawing group in ortho and para position.

24. (i) Convert Chloroethane to but-1-yne

(ii)Primary alkyl halide C_4H_9Br (a) reacted with alcoholic KOH to give compound (b).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}which is different from the compound formed when n-butyl bromide is reacted with sodium. Give the structural formula of (a) and write the equations for all the reactions.

Answer : (i) $C_2H_5Cl + HC\equiv CNa \rightarrow C_2H_5\text{-}C\equiv CH$

(ii)There are two primary alkyl halides having the formula, C_4H_9Br. They are *n* - butyl bromide and isobutyl bromide. Therefore, compound (a) is either *n*-butyl bromide or isobutyl bromide.

Now, compound (a) reacts with Na metal to give compound (b) of molecular formula, $C_8H_{18,}$ which is different from the compound formed when *n*-butyl bromide reacts with Na metal. Hence, compound (a) must be isobutyl bromide. Thus, compound (d) is 2, 5-dimethylhexane.It is given that compound (a) reacts with alcoholic KOH to give compound (b). Hence, compound (b) is 2- methylpropene.

Also, compound (b) reacts with HBr to give compound (c) which is an isomer of (a). Hence, compound (c) is 2-bromo 2-methylpropane.

25 .What happens when

(i) methyl chloride is treated with AgCN

(ii) bromobenzene is treated with Mg in the presence of dry ether,

(iii) chlorobenzene is subjected to hydrolysis,

(iv) ethyl chloride is treated with aqueous KOH,

(v) methyl bromide is treated with sodium in the presence of dry ether,

(vi) n-butyl chloride is treated with alcoholic KOH.

Answer :

(i) When methyl chloride is treated with AgCN, it undergoes a substitution reaction to give methyl isocyanide

(ii) When bromobenzene is treated with Mg in the presence of dry ether, phenylmagnesium bromide is formed.

(iii) Chlorobenzene does not undergo hydrolysis under normal conditions. However, it undergoes hydrolysis when heated in an aqueous sodium hydroxide solution at a temperature of 623 K and a pressure of 300 atm to form phenol.

(iv) When ethyl chloride is treated with aqueous KOH, it undergoes hydrolysis to form ethanol.

(v) When methyl bromide is treated with sodium in the presence of dry ether, ethane is formed. This reaction is known as the Wurtz reaction.

(vi). When n - butyl chloride is treated with alcoholic KOH, the formation of but - l - ene takes place. This reaction is a dehydrohalogenation reaction.

Assertion and Reason Type Questions

(A) Both Assertion and reason are true and reason is correct explanation of assertion.

(B) Assertion and reason both are true but reason is not the correct explanation of assertion.

(C) Assertion is true, reason is false.

(D) Assertion is false, reason is true.

1. Assertion: Aryl halides undergo nucleophilic substitution reactions with ease.
Reason: The carbon halogen bond in aryl halides has partial double bonds character.

2 Assertion – Treating alcohols with thionyl chloride is the most preferred method to prepare haloalkanes.
Reason – In this method, the byproducts are escapable gases.

3. Assertion - When Hydrogen Bromide is added to propene, 2-bromopropane is the major product.
Reason –Br- is added to that double bonded carbon, which has more number of hydrogen atoms bonded to it.

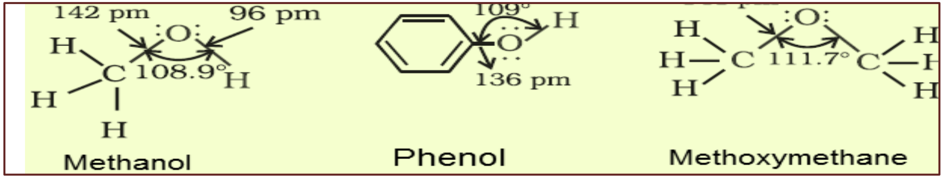
4. Assertion: C – X bond in aryl halides is less polar than the C – X bond in alkyl halides.
Reason**:** In aryl halides, the electron withdrawing inductive effect is opposed by electron releasing resonance effect.

Answer: 1(D) , 2(A), 3(C), 4(A),

UNIT VII ALCOHOLS, PHENOLS AND ETHERS

Compound	Common name	IUPAC name
Alcohol [R-OH]	Alkyl alcohol	Alkanol
Phenol [Ar-OH]	Phenol	Phenol
Ether[R-O-R’]	Alkyl alkyl ether [alphabetical order in alkyl or dialkyl if two same alkyls are present]	Alkoxy alkane

Structures of Functional Group-



1. Primary alcohols can be obtained by
(i) reduction of aldehydes
ii) reaction of Grignard reagents with HCHO
(iii) reduction of carboxylic acids and esters
(iv) hydrolysis of 1" alkyl halides
(v) hydration of alkenes.
2. Secondary Alcohols can be prepared by
(i) reduction of ketones
(ii) reaction of Grignard reagents with aldehydes
(iii) hydration of alkenes
(iv) hydrolysis of alkyl halides.
3. Tertiary Alcohols can be obtained by
(i) reaction of Grignard reagents on ketones
(ii) reaction of excess Grignard reagents with esters
(iii) hydration of alkenes.
4.Alcohols have higher boiling points than corresponding alkyl halides or alkanes due to their ability to form intermolecular hydrogen bonds.
5. Lower alcohols are soluble in water. Solubility in water decreases with increase in size of alkyl group. Among isomeric alcohols straight chain alcohols are less soluble in water than the branched chain alcohols.
6. Order of acidic strength among alcohols is: 1° > 2° >3.
7. Order of reactivity of alcohols in reactions involving cleavage of oxygen-hydrogen bond is: 1° > 2° >3.
8. Order of reactivity of alcohols in reactions involving cleavage of carbon-oxygen bond in: $3^0 > 2^0 > 1^0$
9. Order of acidity: Phenol > H_2O > ROH
10. In phenol electrophilic substitution occurs very easily and mainly at ortho and para positions.
11. In Kolbe reaction, electrophilic species involved in CO_2 and in Reimer Tiemann reaction, electrophilic species involved in CCl_2
12. **3^0 , 2^0 , 1^0** alcohols can be distinguished by Lucas test
13. Phenol can be distinguished from alcohols by reaction with
(i) $FeCl_3$ solution (ii) litmus solution
(iii) NaOH solution (phenol is soluble in NaOH solution) (iv) Bromine water.

ETHERS

16. Ethers are dialkyl derivatives of water or monoalkyl derivatives of alcohols. Ethers can be prepared by Williamson synthesis reaction $R\text{-}X + RONa \rightarrow R\text{ - }O\text{ - }R' + NaX$

The alkyl halide used in this reaction should preferably be primary because tertiary and secondary alkyl halides have greater tendency to undergo elimination in the presence of strong base, sodium alkoxide.

17. Aromatic ethers can be prepared by reaction of sodium phenoxide with alkyl halides and not by reaction of sodium alkoxide with alkyl halide.

18. C-O-C bond in ether is bent and hence polar.

19. Ethers are relatively inert and hence are used as solvents in many reactions.

Ethers can be cleaved by acids. Aromatic ethers on cleavage with halogen acids give phenol and alkyl halide. Alkoxy group activates the benzene ring towards electrophilic substitution and directs the incoming electrophile towards ortho and para positions.

Important questions

1. To get carboxylic acids directly from alcohol, which of the following oxidising agents is used?

a) Alkaline $KMnO_4$ b) Aqueous $KMnO_4$

c) Acidified $KMnO_4$ d) Anhydrous CrO_3

Answer: c

Explanation: Strong oxidizers, such as acidified potassium permanganate or acidified potassium dichromate, convert alcohol to carboxylic acid immediately. Using CrO_3 as the oxidising agent in an anhydrous media, however, only aldehyde can be produced.

2. When phenol reacts with bromine water, what is the result?

a) Brown liquid b) Colourless gas

c) White precipitate d) No reaction

Answer: c

Explanation: When phenol is treated with bromine water, a white precipitate is formed, which is 2,4,6-Tribromophenol.

3. The Lucas test was carried out on three different compounds: A, B, and C. Compounds A and B were turbid at ambient temperature, while compound C did not become turbid until it was heated. Which one of the compounds is tertiary in structure?

a) A b) B c) C d) can not be determined

Answer: d

Explanation: It is stated that A and B exhibit turbidity at room temperature, however, it is not stated whether the turbidity appears immediately or over a period of time. So compounds A and B may be tertiary or secondary depending on whether turbidity appears immediately or after 5 minutes respectively. Compound C may be primary.

4. Which of the following compounds is formed when secondary alcohols are oxidised by nascent oxygen[O]?

a) Ether b) Aldehyde c) Ketone d) Amine

Answer: c

Explanation: The oxidation of secondary alcohols by a nascent oxygen atom [O] yields the ketone molecule.

5. Which of the following processes does not result in the production of alcohol?

a) Acid catalysed hydration of alkenes b) Free radical halogenation of alkanes

c) Reduction of aldehydes d) Hydroboration-oxidation of alkenes

Answer: b

Explanation: When alkanes are halogenated by free radicals, give haloalkane not alcohol.

6. The conversion of trialkyl borane to an alcohol does not require which of the following?

a) Sodium hydroxide b) Water c) Diborane d) Hydrogen peroxide

Answer: c

Explanation: In the presence of aqueous NaOH, trialkyl boranes are oxidised by hydrogen peroxide to produce alcohol. This conversion does not require diborane, although it is required for the creation of trialkyl boranes.

7. Ethers may be used as solvents because they react only with which of the following reactants?

a) Oxidising agent b) Bases c) Acids d) Reducing agents

Answer: c

Explanation: Nucleophiles and bases cannot attack ether. However, because of their capacity to solve cations by giving an electron pair from an oxygen atom, they are excellent solvents in many chemical reactions. Ethers are less reactive than alcohols and react only with acids.

8. An aryl carbon can be found in which of the following compounds?

a) Ethanol b) Phenol c) Vinyl alcohol d) Benzyl alcohol

Answer: b

Explanation: An aryl carbon is the sp^2 hybridised carbon of an aromatic ring to which the hydroxyl group is connected. The OH group is connected to an aryl carbon in phenol.

9. Which type of ether is called when the alkyl groups connected to either side of the oxygen atom in an ether are different.

a) mixed b) symmetrical c) simple d) diethyl

Answer: a

Explanation: A mixed or unsymmetrical ether is one in which the alkyl or aryl groups on either side of the O atom differ.

10. Which of the following alcohols is not polyhydric?

a) Propylene glycol b) Ethylene glycol c) Cyclohexanol d) Benzene-1,2-diol

Answer: c

Explanation: Polyhydric alcohols include two or more hydroxyl groups and are classified as glycols in the common system or diols and triols in the IUPAC system.

Q11. Give reason for the following-

(a) Propanol has higher boiling point than butane.

(b) O-nitrophenol is less soluble in water than p-nitrophenol.

Ans-(a) Since in propanol molecules are associated with strong H-bonds whereas butane has weak dispersion forces.

(b) O-nitrophenol shows intramolecular H- bonding.

Q12. Name the reagents used in the following reactions-

a) Oxidation of a primary alcohol to carboxylic acid.

b) Oxidation of a primary alcohol to aldehyde.

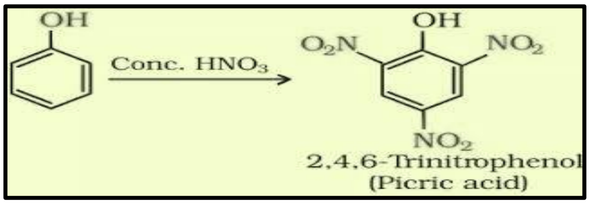
Ans- a) $KMnO_4$ /H + or $K_2Cr_2O_7/H^+$ or Dil HNO_3

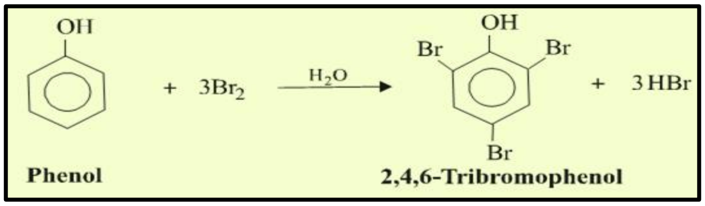
b) CrO_3 in anhydrous medium or Pyridiniumchlorochromate PCC

Q13. Give equations of the following reactions-

a. Dilute HNO_3 with phenol b. Bromine water with phenol.

Ans:





Q14

. Write the suitable test to distinguish the following pair of organic compounds-

(a) Phenol and Benzoic acid (b) n-Butanol and tert butyl alcohol

Ans-

Test	Phenol	Benzoic acid
1. $Na_2CO_3/NaHCO_3$ test	No brisk effervescence of CO_2 is seen.	A brisk effervescence of CO_2 is seen.
2. Neutral $FeCl_3$	A violet coloured complex is seen.	No violet coloured complex is seen.
	n-Butanol	tert butyl alcohol
1. Lucas test [alcohol+ concHCl $+ZnCl_2$]	Turbidity appears only upon heating.	Turbidity appears immediately on adding reagent.

Q15. Arrange the following compounds in increasing order of their strength.

a) Propanol, O-nitrophenol, O-cresol, phenol b) Propanol, propanoic acid, phenol

Ans- a). Propanol, <O-cresol, < phenol < O-nitrophenol. b) Propanol,< phenol <propanoic acid.

Q16 (i) Diethyl ether does not react with sodium.

(ii) Phenols do not undergo substitution of the –OH group like alcohols.

Ans: (i). Since diethyl ether does not contain an active hydrogen.

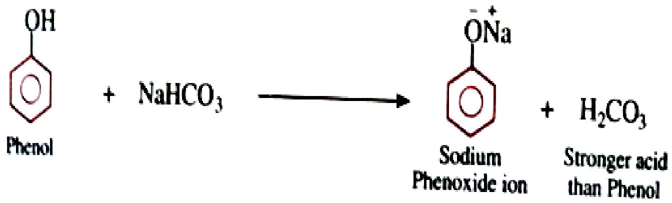
ii) The C-O bond in phenol has some double bond character due to resonance and hence cannot be easily cleaved by nucleophile.

Q17.Account for the following

(i) phenol does not react with $NaHCO_3$ whereas carboxylic acids react

(ii) phenol is more easily nitrated than benzene

Ans. (i) $RCOOH + NaHCO_3 \longrightarrow RCOONa + \underset{\text{than RCOOH}}{\underset{\text{Weaker acid}}{H_2CO_3}}$



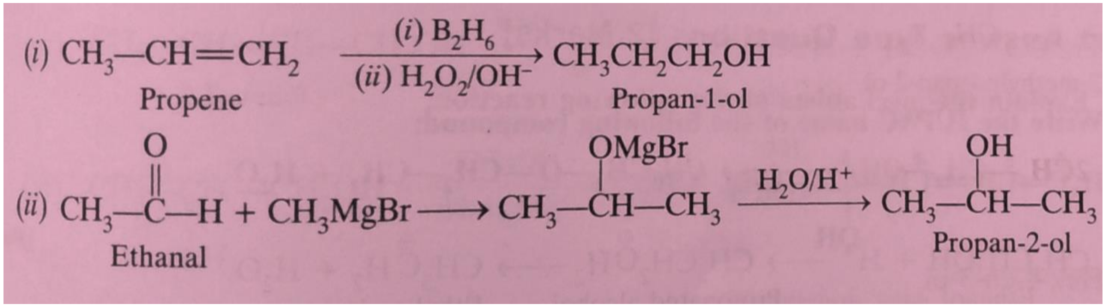
Such acid- base reaction takes place only if the acid formed is weaker than the reacting acid.H_2CO_3 is stronger acid than phenol so it does not react.

(ii) nitration involves attack of electrophile nitronium ion NO_2^+ on benzene ring.Due to +R effect of –OH group electron density on benzene increases. Therefore , phenol is more easily nitrated as compared to benzene.

Q18.How are the following conversions carried out?

(i) Propene to propan-1-ol (ii) Ethanol to propan-2-ol

Ans:

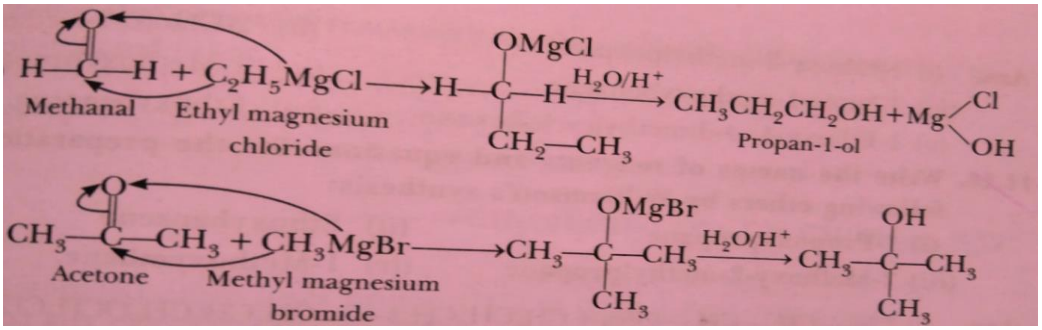


$$(i)\ \underset{\text{Propene}}{CH_3{-}CH{=}CH_2} \xrightarrow[(ii)\ H_2O_2/OH^-]{(i)\ B_2H_6} \underset{\text{Propan-1-ol}}{CH_3CH_2CH_2OH}$$

$$(ii)\ \underset{\text{Ethanal}}{CH_3{-}\overset{\overset{O}{\|}}{C}{-}H} + CH_3MgBr \longrightarrow CH_3{-}\overset{\overset{OMgBr}{|}}{C}H{-}CH_3 \xrightarrow{H_2O/H^+} \underset{\text{Propan-2-ol}}{CH_3{-}\overset{\overset{OH}{|}}{C}H{-}CH_3}$$

Q19. How are

the following conversions carried out?
(i) Ethyl magnesim chloride to propanol
(ii) Methyl magnesim bromide to 2-methylpropan-2-ol
Ans:



Q20.Distinguish between
(i) Ethanol and diethyl ether (ii) Propanol and t-butyl alcohol

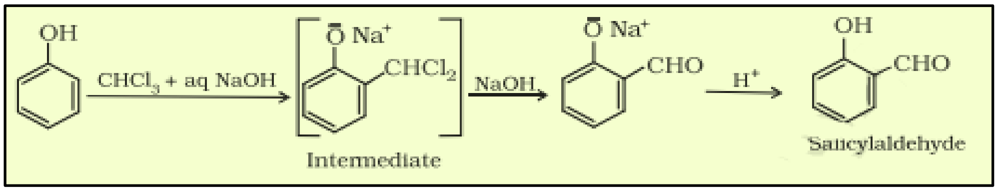
Ans: (i) ethanol on warming with I_2 and NaOH to form yellow precipitate of iodoform .on the other hand diethyl ether does not give iodoform.

$$\text{H-CH(OH)-CH}_3 + 4I_2 + 6NaOH \rightarrow$$
$$HCOONa + CHI_3 + 5\ NaI + 5H_2O$$
(Yellow ppt)

(ii) t-butyl alcohol being a tertiary(3^0) alcohol, it gives turbidity immediately on treatment with Lucas regent(Conc. HCl + anhydrous $ZnCl_2$), but propanol does give turbidity at room temperature because of 1^0-alcohol.

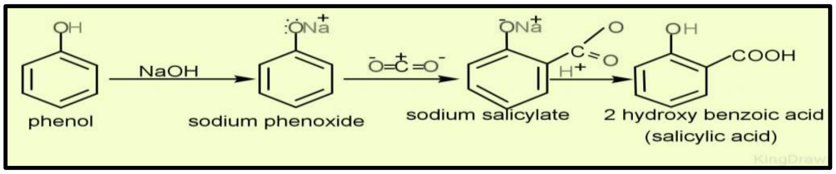
Q21. Write the equations for following name reactions-
a) Reimer-Tiemann reaction b) Williamson synthesis c) Kolbe reaction

Ans: a) Reimer-Tiemann reaction



b) Williamson synthesis
CH_3I + CH_3CH_2ONa $\longrightarrow$ $CH_3\text{-O-}CH_2CH_3 + NaI$
Methyl iodide Sod. Ethoxide Ethyl methyl ether

c) Kolbe reaction:

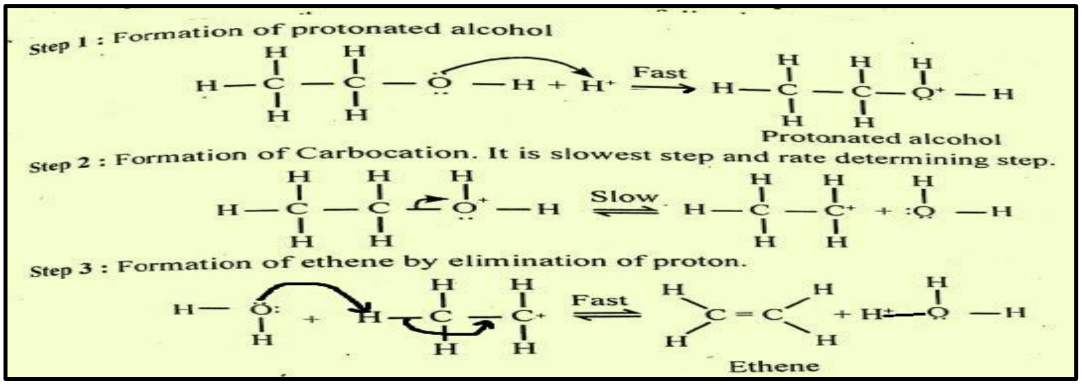


Q22. Write the names of reagents and equations for the preparation of the following ethers by Williamson's synthesis:
(i) 1-Propoxypropane (ii) Ethoxybenzene (iii) 1-Methoxyethane

Ans- (i) $CH_3CH_2CH_2ONa + CH_3CH_2CH_2Br \rightarrow CH_3CH_2CH_2OCH_2CH_2CH_3 + NaBr$
(ii) $C_6H_5\text{-ONa} + CH_3CH_2Br \rightarrow C_6H_5\text{-O-}CH_2CH_3 + NaBr$
(iii) $CH_3CH_2ONa + CH_3Br \rightarrow CH_3CH_2OCH_3 + NaBr$

Q23. Write the mechanism of hydration of ethene to yield ethanol.

Ans:



Q24. Explain the following with suitable reason.

a) Bond angles in ether is slightly more than the tetrahedral angle.

b) orthonitrophenols more acidic than orthomethoxyphenol .

c) The –OH group attached to a carbon of benzene ringactivates it towards electrophilic substitution.

Ans: a) The bond angle in ether is slightly greater than the tetrahedral angle due to the repulsive interaction between the two bulky (–R) groups.

b) The electron withdrawing group nitro group due to the effectivedelocalisation of negative charge present over carbon atom in benzene ring. Whereas methoxy an electron releasing group causes accumulation of charge.

c) Since lone pair of electrons on oxygen is in resonance with benzene ring and increases the electron density on benzene ring.

Q25.(a)What is iodoform test? write the reactions of alcohols giving this test.

b) Name a primary alcohol which gives iodoform test.

c) How can 2-propanol and 1-propanol be distinguished?

Ans:a) An alcohol having formula $R\text{-}CH(OH)\text{-}CH_3$ is reacted with I_2 in presence of NaOH to form yellow ppt. of iodoform is called iodoform test.$R\text{-}CH(OH)\text{-}CH_3 + 4I_2 + 6NaOH \rightarrow RCOONa + CHI_3 + 5 NaI + 5H_2O$

(Yellow ppt)

b) Ethanol is the only primary alcohol which gives iodoform test

c) 2-propanol gives iodoform test but propanol dose not give.

Q26. Give the structures and IUPAC names of the products expected from the following reactions:

(a) Catalytic reduction of butanal.

(b) Hydration of propene in the presence of dilute sulphuric acid.

(c) Reaction of propanone with methyl magnesium bromide followed by hydrolysis.

Ans- (a) $CH_3CH_2CH_2CH_2OH$ [Butan-1-ol]

(b) $CH_3\text{-}CH(OH)\text{-}CH_3$[propan-2-ol]

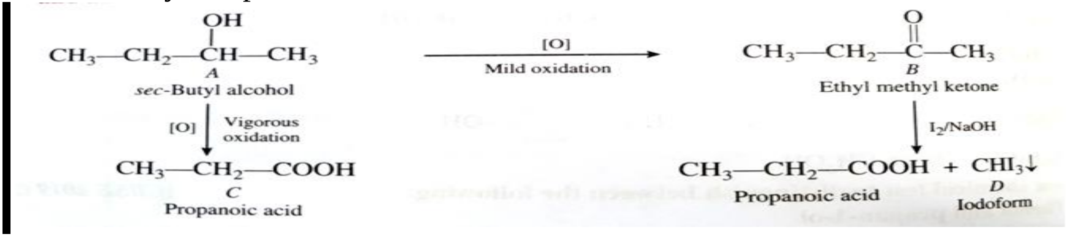
(c) $CH_3\text{-}C\text{-}(CH_3)(OH)\text{-}CH_3$ [2-Methylpropan-2-ol]

Q27. A compound ‘A’ is optically active. On mild oxidation, it gives a compound ‘B’ but on vigorous oxidation gives another compound ‘C’. C along with D is also formed from B by reaction with iodine and alkali. Deduce the structures of A, B, C and D.

Ans: [A = 2-hydroxybutane, B = Butan-2-one, C = Propanoic acid , D = Iodoform]

Q28. An alcohol A ($C_4H_{10}O$) on oxidation with acidified $K_2Cr_2O_7$ gives a carboxylic acid B ($C_4H_8O_2$). Treatment of C with warm aq. H_2SO_4 gives D($C_4H_{10}O$) ,an isomer of A. The compound D is resistant to oxidation. Identify compounds A,B,C and D. Write all the reactions involved.

Ans:



Q29.(a) Why phenol is more acidic than ethanol?

(b) $(CH_3)_3C\text{-}O\text{-}CH_3$ on reaction with HI gives CH_3OH and $(CH_3)_3C\text{-}I$ as the main products and not $(CH_3)_3C\text{-}OH$ and CH_3I

(c) boiling point of ethanol is higher in comparision to methoxymethane.

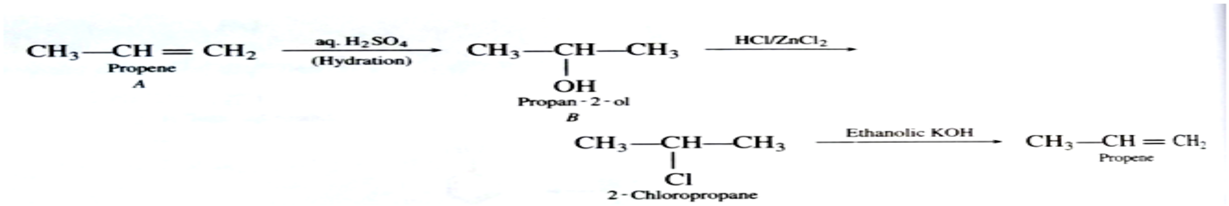
Ans: (a) it is because phenoxide ion is more stable than methoxide ion

(b) It is because $(CH_3)_3C^+$ (tert.carbocation) is more stable, reacts with I^- to form tert.butyl iodide.

(c) Ethanol is associated with intermolecular H- bonding, whereas methoxymethasne is not.

Q30. An organic compound 'A' having molecular formula C_3H_6 on treatment with aqueous H_2SO_4 gives 'B' which on treatment with $HCl/ZnCl_2$ gives 'C'.The compound C on treatment with ethanolic KOH gives back the compound 'A'. Identify the compounds A,B,C.

Ans: Propene, B= 2-Propanol,C= 2-Chloropropane



Q31.(a) How would you convert the following:

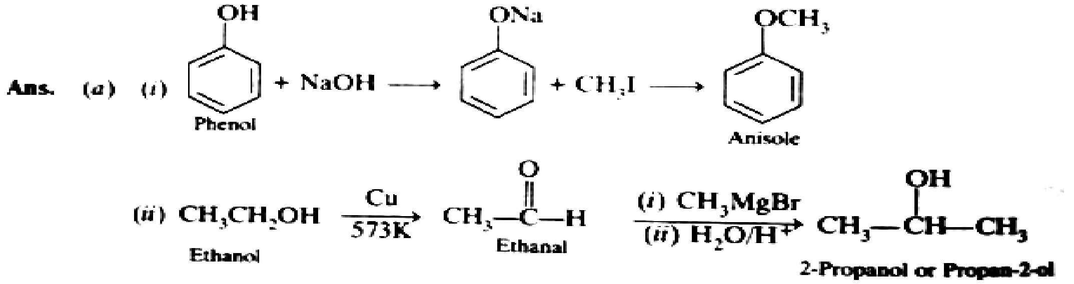
(i) Phenol to anisole (ii) Ethanol to propan-2-ol

(b)Write the mechanism for the following reactions:

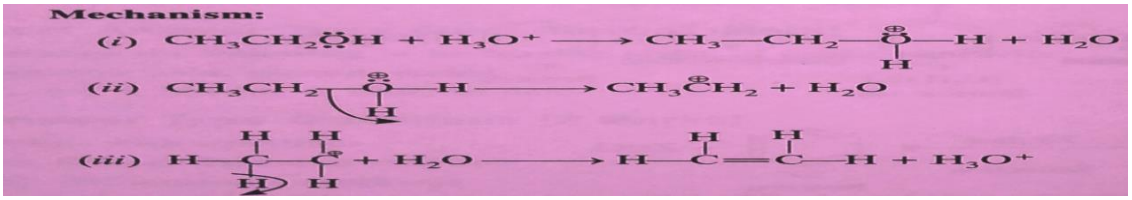
$$CH_2\text{-}CH_2\text{-}OH \xrightarrow{H_2SO_{4/}/443K} CH_2{=}CH_2 + H_2O$$

(c) Why phenol undergoes electrophilic substitution more easily than benzene?

Ans(a)



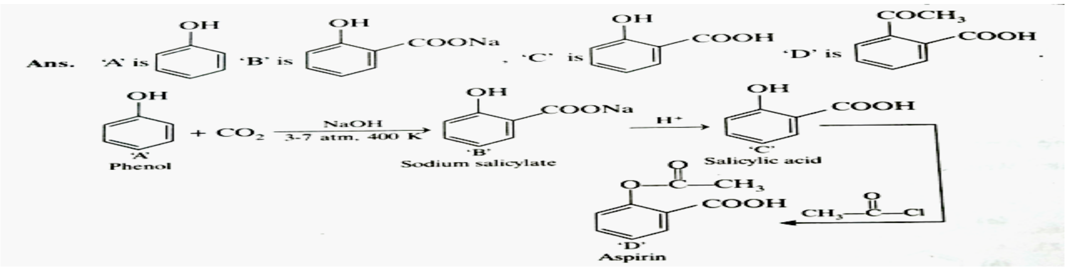
Ans : b)



c) it is because –OH group is electron releasing, activating, therefore, it undergoes electrophilic substitution more readily than benzene due to +R-effect.

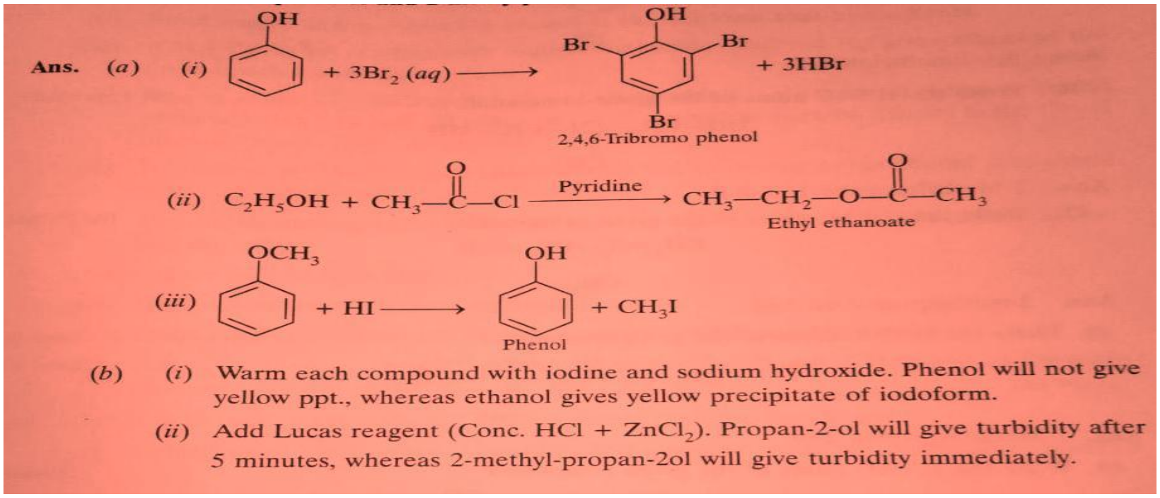
Q32. An organic compound 'A' having molecular formula C_6H_6O gives a characteristic colour with aq. $FeCl_3$ solution. When 'A' is treated with CO_2 and NaOH at 400 K under pressure 'B' is formed. The compound 'B' on acidification gives 'C' which reacts with acetyl chloride to form 'D' which is popular pain killer. Write the structure of 'A', 'B' , 'C' and 'D

Ans: 'A' gives a characteristic colour with aq. $FeCl_3$ solution , indicating the presence of phenolic group C_6H_5-OH
.



Q33 (a) What happens when
(i) Phenol reacts with bromine water?
(ii) Ethanol reacts with CH_3COCl /pyridine?
(iii) Anisole reacts with HI?
Write the chemical equations involved in the above reactions.
(b) distinguish between: (i) ethanol and phenol (ii) propan-2-ol and 2-methylpropan-2-ol

Ans:-



Ans. (*a*) (*i*) OH + $3Br_2\,(aq) \longrightarrow$ OH Br Br Br + 3HBr
2,4,6-Tribromo phenol

(*ii*) $C_2H_5OH + CH_3-\overset{\overset{O}{\|}}{C}-Cl \xrightarrow{\text{Pyridine}} CH_3-CH_2-O-\overset{\overset{O}{\|}}{C}-CH_3$
Ethyl ethanoate

(*iii*) OCH_3 + HI $\longrightarrow$ OH + CH_3I
Phenol

(*b*) (*i*) Warm each compound with iodine and sodium hydroxide. Phenol will not give yellow ppt., whereas ethanol gives yellow precipitate of iodoform.

(*ii*) Add Lucas reagent (Conc. HCl + $ZnCl_2$). Propan-2-ol will give turbidity after 5 minutes, whereas 2-methyl-propan-2ol will give turbidity immediately.

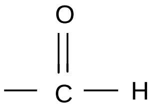
Assertion and Reason Type Questions

1. Assertion- Benzenediazonium chloride on boiling with water gives phenol.
   Reason – C---N bond is polar.
2. Assertion- Neopentyl alcohol on treatment with HCl gives neopentyl chloride.
   Reason – Neopentyl alcohol is a tertiary alcohol.
3. Assertion-Hydroxyl ketones are not directly used in Grignard reagent.
   Reason – Grignard reagents react with hydroxyl group.
4. Assertion- p- Nitrophenol is a stronger acid than o- Nitrophenol.
   Reason – Intramolecular hydrogen bonding makes o- isomers weaker than p-isomer.
5. Assertion- Alcohols nave higher boiling point than ethers of comparable molecular mass.
   Reason – Alcohols and ethers are isomeric in nature.
   Ans. 1-(b) 2-(d) 3-(a) 4-(a) 5-(b)

UNIT VI ALDEHYDES, KETONES AND CARBOXYLIC ACID

FUNCTIONAL GROUP & NOMENCLATURE:

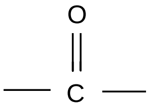
ALDEHYDE-



$$-\overset{\overset{O}{\|}}{C}-H$$

Alkane - e + al ⟶ Alkanal

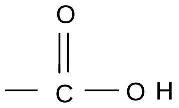
KETONE:-



$$-\overset{\overset{O}{\|}}{C}-$$

Alkane - e + one ⟶ Alkanaone

CARBOXYLIC ACID:-

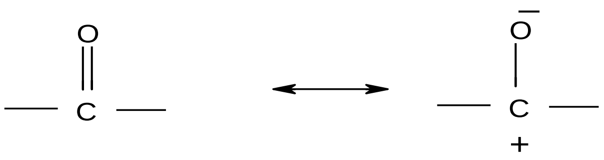


$$-\overset{\overset{O}{\|}}{C}-OH$$

Alkane -e + oic acid ⟶ Alkanoic acid

STRUCTURE OF CARBONYL GROUP:

The carbonyl group has a planar structure with sp^2 hybridized carbon having three sigma bonds and a pi bond. The carbon oxygen double bond is polarized due to higher electronegativity of oxygen atom.



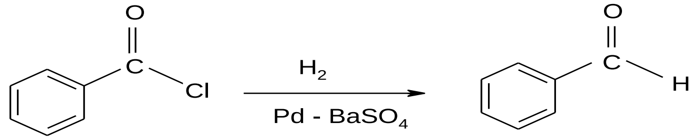
PREPARATION OF ALDEHYDES AND KETONES:

1. Oxidation of alcohol:

$$\begin{tikzcd}
\text{Aldehyde} & \text{Primary alcohol} \arrow[l, "Cu/Ag"'] \arrow[r, "alk\ KMnO_4"] \arrow[d, "PCC/PDC"] & \text{Aldehyde} \arrow[r, "alk\ KMnO_4"] & \text{Carboxylic acid} \\
& \text{Aldehyde} & &
\end{tikzcd}$$

$$\text{Ketone} \xleftarrow{Cu/Ag} \text{Secondary alcohol} \xrightarrow{[O]} \text{Ketone}$$

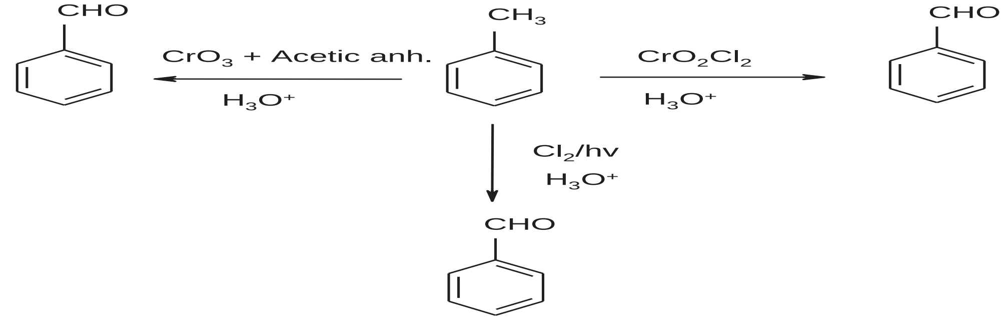
2. Rosenmund's Reduction: Acid chlorides on hydrogenation in presence of palladium on barium sulphate gives an aldehyde.



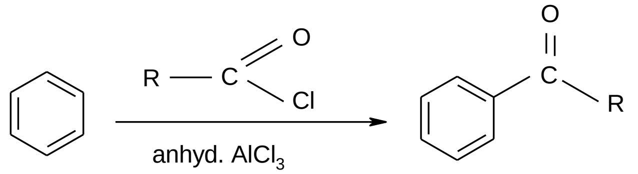
3. Stephen's Reaction:

$$R-CN \xrightarrow{SnCl_2 + HCl} RCH=NH \xrightarrow{H_3O^+} RCHO$$

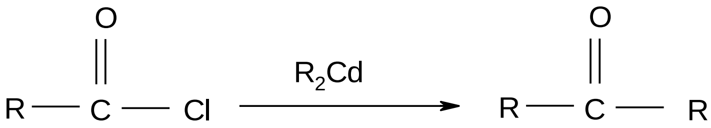
4. From hydrocarbons:



5. Friedel Craft's Acylation:



6. Preparation of ketone from acid chloride:



$$R-\overset{\overset{\displaystyle O}{\|}}{C}-Cl \xrightarrow{R_2Cd} R-\overset{\overset{\displaystyle O}{\|}}{C}-R$$

PROPERTIES:

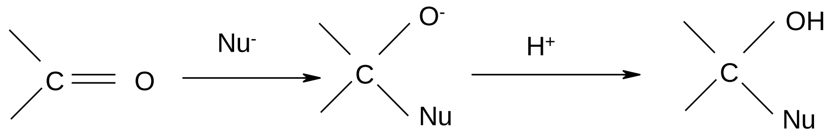
1. Aldehydes and ketones can form H- bond with water and therefore they are soluble in it. Solubility decreases with the increase in the no. of carbon atoms.

2. These molecules are polar in nature and have higher m.p and b.p than the hydrocarbons of comparable molar mass.

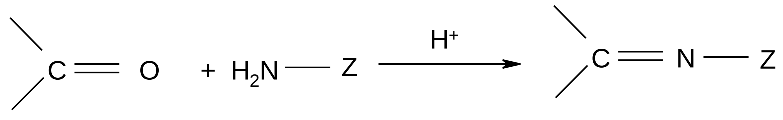
3. Nucleophilic addithion:-

(a) Due to the polar nature of Carbonyl group aldehydes and ketone undergo nucleophilic addition.

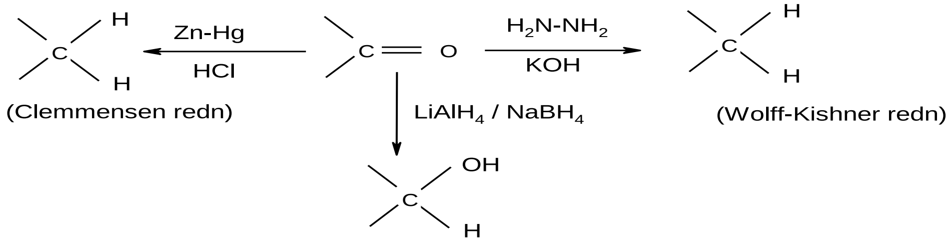
(b) Aldehydes are generally more reactive than ketones towards the nucelophilic addition as ketones have two bulky alkyl groups and its carbonyl carbon is more hindered than that of aldehydes.



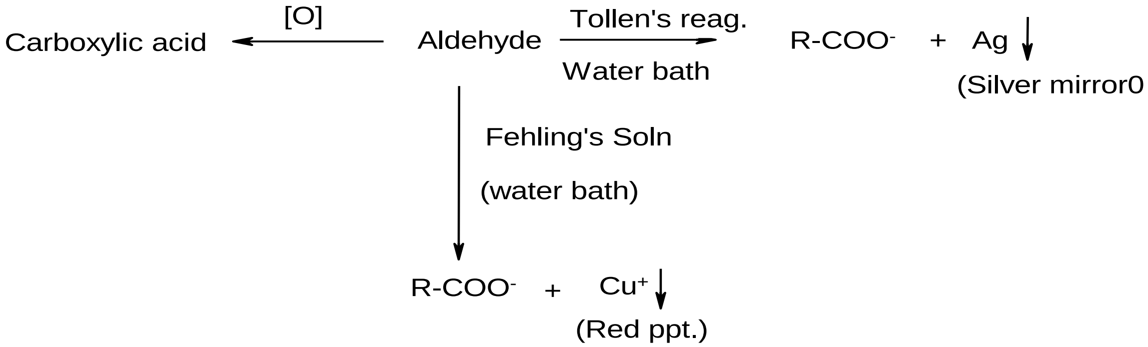
4.Addition of Ammonia and its derivatives:



5. Reduction:

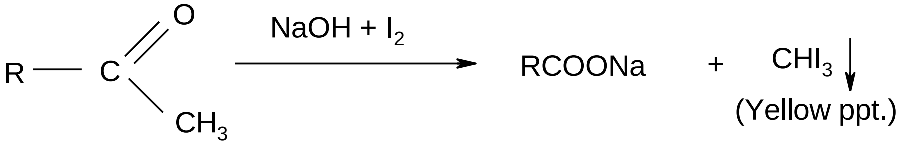


6. Oxidation:



(Ketones do not react with Fehling's solution or Tollen's reagent)

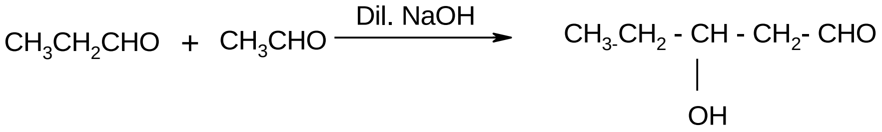
7. Oxidation of methyl ketones:



8. **Aldol Condensation**: Aldehydes or ketones having at least an α- H undergo self condensation in presence of a strong alkali to give a β- hydroxyl aldehyde called aldol and the process is called aldol condensation.

$$2\,HCHO \xrightarrow{\text{Conc. NaOH}} CH_3OH + HCOONa$$

When Aldol condensation is carried out between two different aldehydes or ketones it is called **Cross Aldol Condensation.**



$$CH_3CH_2CHO + CH_3CHO \xrightarrow{\text{Dil. NaOH}} CH_3\text{-}CH_2 - \underset{\displaystyle OH}{\underset{|}{CH}} - CH_2 - CHO$$

9. **Cannizzaro's reaction**: Aldehydes having no α- H undergo self oxidation and reduction in presence of conc. alkali to give an alcohol and a salt of carboxylic acid.

$$2\,HCHO \xrightarrow{\text{Conc. NaOH}} CH_3OH + HCOONa$$

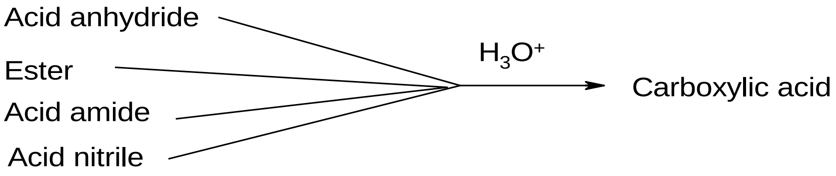
CARBOXYLIC ACID

PREPARATION:

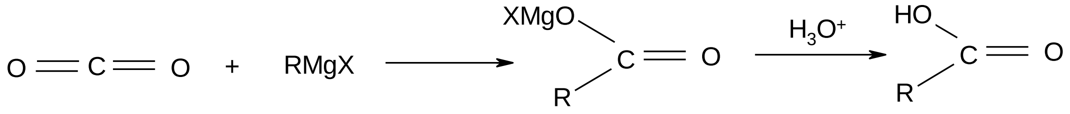
1. Oxidation of alcohols:

$$\text{Primary alcohol} \xrightarrow{\text{alk } KMnO_4} \text{Carboxylic acid}$$

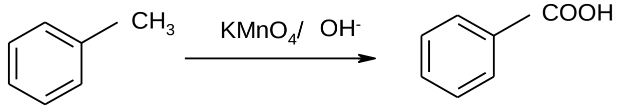
2. Hydrolysis of the acid derivatives



3. By the action of Grignard reagent on carbon dioxide



4. From alkyl benzenes



PROPERTIES:

1. Soluble in water as they can form H- bond with water. Solubility decreases with the increase in the length of the carbon chain.

2. M.P. and B.P of carboxylic acids are higher than those of the corresponding alcohols as they exist in the dimeric form even in their vapour phase.

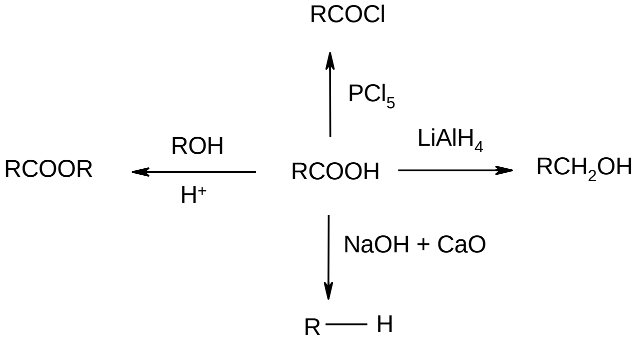
3. Acidic nature:

(a) Carboxylic acids are stronger acids than phenols due to symmetrical resonance.

(b) Presence of electron releasing group (+I effect) causes the acidic strength of carboxylic acids to decrease.

(c) Presence of electron withdrawing group (-I effect) causes the acidic strength of the carboxylic acids to increase.

4. **General reactions:**



5. **<u>Hell Volhard Zelinsky (HVZ) reaction</u>**:-

When Carboxylic acids containing α-H are treated with red phosphorus and X_2 α- halogen substituted carboxylic acids are obtained.

$$CH_3COOH \xrightarrow{\text{Red } P_4 + X_2} CH_2XCOOH$$

Multiple Choice Questions

1. The conversion of a carboxylic acid to α-bromocarboxylic acid using red phosphorus and bromine is-

(a) Cannizzaro's reaction (b) Aldol condensation

(c) Kolbe's reaction (d) Hell-Volhard- Zelinsky reaction

Ans-(d) Hell-Volhard- Zelinsky reaction

2. Decarboxylation of sodium benzoate on heating with soda lime gives

(a) Benzene (b) toluene (c) benzaldehyde (d) benzoic acid

Ans-(a) Benzene

3. The reaction of HCHO + CH_3MgBr followed by hydrolysis gives-

(a) Primary alcohol (b) Secondary alcohol (c) Tertiary alcohol (d) None of these

Ans- (a) Primary alcohol

4. Which of the following is most reactive towards nucleophilic addition reactions?

(a) CH3COCH3 (b) CH3CHO (c) CH3COCH2CH3 (d) HCHO

Ans- (d) HCHO

5. In the carbonyl group, carbon has hybridisation of –

(a) sp (b) sp2 (c) sp3 (d) sp3d

Ans- (b) sp2

6. Which of the following gives iodoform test?

(a) CH3OH (b) CH3COCH2CH3 (c) HCHO (d) CH3COOH

Ans- (b) CH3COCH2CH3

7. Acetaldehyde and acetone can be distinguished by-

(a) NaHSO3 (b) AgNO3 (c) Conc. H2SO4 (d) Fehling solution

Ans- (d) Fehling solution

8. Which of the following will not undergo aldol condensation?

(a) Acetaldehyde (b)Propanaldehyde (c) Benzaldehyde (d) Propanone

Ans- (c) Benzaldehyde

9. The –OH group of an alcohol or –COOH group of a carboxylic acid can be replaced by –Cl by using

(a) Hypochlorous acid (b) chlorine

(c) hydrochloric acid (d) phosphorus pentachloride

Ans- (d) phosphorus pentachloride

10. Clemmensen reduction of a ketone is carried out in the presence of which of the following?

(a) Glycol with KOH (b) Zn-Hg with HCl (c) LiALH4 (d) H2+Pt

Ans- (b) Zn-Hg with HCl

Very Short Answer Questions

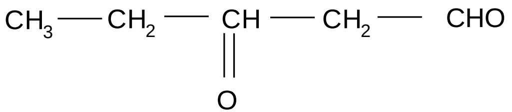
11. Write the IUPAC name –(i) (CH3)2CHCHO (ii)COOH-COOH

Ans- (i) 2-Methyl propanal (ii) Ethane1,2-dioic acid

12. Write the structure of the following compounds- (i)3-oxopentanal (ii) Phthalic acid

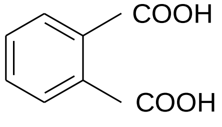
Ans:

(i) 3- oxopentanal



$$CH_3-CH_2-\underset{\displaystyle\|\atop\displaystyle O}{CH}-CH_2-CHO$$

(ii) Phthalic acid



13. Arrange the following as directed-

(i) CH3CHO, CH3CH2OH, CH3OCH3, CH3CH2CH3 [Increasing order of boiling point]

(ii) Ethanal, propanal, propanone, butanone [In increasing order towards nucleophilic addition reaction]

Ans- (i) CH3CH2CH3 < CH3OCH3< CH3CHO< CH3CH2OH

(ii) Butanone < propanone < propanal < ethanol

14. Write chemical reactions to affect the following transformations-

(i) Butanal to Butanoic acid (ii) Butanal to Butane

Ans- (i) CH3CH2CH2CHO------Ammoniacal AgNO3 or Tollen's reagent----CH3CH2CH2COOH

(ii) CH3CH2CH2CHO----Na-Hg+Conc HCl-→ CH3CH2CH2CH3

15. Which acid of each pair shown here would you expect to be stronger and why?

(i) CH3COOH or CH2FCOOH (ii) CH2FCOOH or CH2ClCOOH

Ans- (i) CH2FCOOH due to –I effect of F atom, the release of proton is easier.

(ii) CH2FCOOH due to more stronger –I effect of F atom than Cl atom because of higher electronegativity.

16. Explain the following reactions-

(i) Clemmensen reduction (ii) Rosenmund reduction

Ans- (i) Clemmensen reduction- Reduction of the carbonyl group of aldehydes and ketones to CH2 group on treatment with zinc-amalgam and Conc. HCl. CH3CH2CH2CHO----Na-Hg+Conc HCl-→ CH3CH2CH2CH3

(ii) Rosenmund reduction-Hydrogenation of acid chloride using catalyst Pd on BaSO4.

RCOCl + H2 -------Pd/BaSO4---→ R-CHO

17. Give suitable reasons for the following-

(i) Carboxylic acid does not give the characteristics reactions of a carbonyl group.

(ii) Carboxylic acid s show abnormal molar mass.

Ans- (i) Due to resonance of carbonyl group with hydroxyl group.

(ii) They form dimmers due to hydrogen bonds.

18. Give a suitable chemical test to distinguish between the following pair of compounds.

(i) Propanal and propanone (ii) Phenol and Benzoic acid

Ans- (i)

(i) Test	Propanal	Propanone
Tollen's test	Gives silver mirror on heating with ammoniacal AgNO3.	Does not give silver mirror on heating with ammoniacal AgNO3.
(ii)	Phenol	Benzoic acid
Neutral FeCl3 test	A violet coloured complex is formed.	A violet coloured complex is not formed.

19. Write a suitable reagent to bring about the following conversion?

(i) Butan-1-ol to butanoic acid (ii) Formaldehyde to ethanol

Ans- (i) Oxidation using acidified KMnO4 or K2Cr2O7

(ii) Methyl magnesium bromide followed by hydrolysis.

20. Write the expected product(s) in following cases-

(i) C6H5-CHO + Conc KOH---------→

(ii) CH3CHO + NH2-NH2 ------H+--→

Ans- (i) C_6H_5-OH + C_6H_5COOK

(ii) $CH_3CH=N-NH_2$

21. Give IUPAC name of the following compound-

(i) $(CH_3)_2C=CH-COCH_3$ (ii) $CH_2=CH-CO-CH_3$ (iii) $(CH_3)_3$-C-CH(Cl)CHO

Ans- (i) 4-Methylpent-3-en-2-one

(ii) But-3-en-2-one

(iii) 2-chloro-3,3-dimethylbutanal

22. Give suitable reasons for the following-

(i) Carboxylic acid does not undergo Friedel Craft's reaction.

(ii) Aldehydes undergoes nucleophilic addition reaction with ease than ketone.

(iii) Why catalyst is poisoned in Rosenmund reduction.

Ans- (i) Because carboxylic acid is deactivating and catalyst $AlCl_3$ gets bonded to –COOH group.

(ii) Since in aldehyde, due to hydrogen positive polarity on carbonyl carbon is high and steric hinderence is lesser.

(iii) To prevent the reduction of aldehyde to carboxylic acid.

23. Explain the following reactions-

(i) Wolff-kishner reduction

(ii) Aldol condensation

(iii) Cannizzaro reaction

Ans- (i) Wolff-kishner reduction- Reduction of the carbonyl group of aldehydes and ketones to CH_2 group on treatment with hydrazine followed by heating with sodium or potassium hydroxide in high boiling solvent.

$CH_3CH_2CHO + NH_2\text{-}NH_2 \rightarrow CH_3CH_2CH{=}N\text{-}NH_2 \text{-----KOH/HBS + heat -}\rightarrow CH_3CH_2CH_3$

(ii) Aldol condensation---Aldehydes and ketones having at least one $\alpha -$H atom undergo a reaction in the presence of dilute alkali as catalyst to form β-hydroxy aldehydes (aldol) or β-hydroxy ketones (ketol) respectively. $2\ CH_3\text{-}CHO \text{----dil NaOH} \rightarrow CH_3\text{-}CH(OH)\text{-}CH_2\text{-}CHO \text{---Heat}\rightarrow CH_3\text{-}CH{=}CH\text{-}CHO$

(iii) Cannizzaro reaction—Aldehydes having no α- H atom undergo self oxidation and reduction in presence of conc. alkali. $C_6H_5\text{-}CHO + \text{Conc KOH} \text{---------}\rightarrow C_6H_5\text{-}OH + C_6H_5\text{-}COOK$

24. Give a suitable chemical test to distinguish between the following pair of compounds.

(i) Acetophenone and Benzophenone

(ii) Ethanal and Propanal

(iii) Benzoic acid and Ethyl benzoate

Ans-

Test	Acetophenone	Benzophenone
Iodoform test	Gives yellow precipitate on treatment with I_2 + NaOH	Does not give yellow precipitate on treatment with I_2 + NaOH.

Test	Ethanal	Propanal
Iodoform test	Ethanal gives yellow ppt of CHI_3 when warmed with I_2+NaOH.	Propanal does not give yellow ppt of CHI_3 when warmed with I_2+NaOH.

Test	Benzoic acid	Ethyl benzoate
Carbonate/hydrogen carbonate test	Gives a brisk effervescence of CO_2	Does not give a brisk effervescence of CO_2

25. Arrange the following compounds in increasing order of their property as indicated.

(i) Acetaldehyde, Acetone, Di-tert-butyl ketone, Methyl tert-butyl ketone (reactivity towards HCN)

(ii) $CH_3CH_2CH(Br)COOH$, $CH_3CH(Br)CH_2COOH$, $(CH_3)_2CHCOOH$, $CH_3CH_2CH_2COOH$ (acid strength)

(iii) Benzoic acid, 4-nitrobenzoic acid, 3,4-dinitrobenzoic acid, 4-methoxy benzoic acid (Acid strength)

Ans- (i) Di-tert-butyl ketone < Methyl tert-butyl ketone < Acetone< Acetaldehyde

(ii) $(CH_3)_2CHCOOH < CH_3CH_2CH_2COOH < CH_3CH(Br)CH_2COOH < CH_3CH_2CH(Br)COOH$

(iii) 4-methoxy benzoic acid< Benzoic acid <4-nitrobenzoic acid<3,4-dinitrobenzoic acid

26. An organic compound (A) (molecular formula $C_8H_{16}O_2$) was hydrolyzed with dilute sulphuric acid to a carboxylic acid (B) and an alcohol (C). Oxidation of (C) with chromic acid produces (B). (C) on dehydration gives but-1-ene. Identify A, B & C and write equations for the reactions involved.

Ans- A-Butyl butanoate B- Butanoic acid C- Butanol

$CH_3CH_2CH_2\text{-}COOCH_2CH_2CH_2CH_3$ (A) ---dil H_2SO_4→ $CH_3CH_2CH_2\text{-}COOH$(B) + $CH_3CH_2CH_2\text{-}CH_2OH$(C)

$CH_3CH_2CH_2\text{-}COOH$ (B) ---Oxidation using chromic acid --→ $CH_3CH_2CH_2\text{-}CH_2OH$ (C) ---dehydration--→ $CH_3CH_2CH{=}CH_2$

27. Write the products- (i) $C_6H_5\text{-}CH_2CH_3$--------$KMnO_4$+KOH, Heat---→

(ii) $C_6H_5\text{-}CHO$ -----$H_2NCONHNH_2$----→

(iii) $CH_3COCH_2COOC_2H_5$ ----------(i)$NaBH_4$ followed by (ii) H^+--→

Ans- (i) $C_6H_5\text{-}COOK$ potassium benzoate

(ii) $C_6H_5\text{-}CH{=}N\text{-}NHCO\text{-}NH_2$ semicarbazone

(iii) $CH_3CH(OH)CH_2COOC_2H_5$

28. How will you bring about the following conversations in not more than two steps?

(i) Propanone to propene

(ii) Benzoic acid to benzaldehyde

(iii) Ethanol to 3-hydroxybutanal

Ans- (i) CH_3COCH_3---[H]—$CH_3\text{-}CH(OH)\text{-}CH_3$---$Al_2O_3/H^+$ and Heat--→$CH_3\text{-}CH{=}CH_2$

(ii) $C_6H_5\text{-}COOH$----$SOCl_2$-→$C_6H_5\text{-}COCl$----- H_2+Pd/$BaSO_4$---→$C_6H_5\text{-}CHO$

(iii) CH_3CH_2OH----[O]---CH_3CHO---dil NaOH--→ $CH_3\text{-}CH(OH)\text{-}CH_2\text{-}CHO$

29. A carbonyl compound having molecular formula $C_5H_{10}O$ does not reduce Tollen's reagent but forms an addition product with sodium hydrogensulphite and give positive iodoform test. On vigorous oxidation, it gives ethanoic and propanoic acid. Write the possible structure of the compound.

Ans- $CH_3\text{-}CO\text{-}CH_2\text{-}CH_2\text{-}CH_3$ + $NaHSO_3$---→ $CH_3\text{-}C(OH)\ OSO_2Na\text{-}CH_2\text{-}CH_2\text{-}CH_3$

$CH_3\text{-}CO\text{-}CH_2\text{-}CH_2\text{-}CH_3$ + I_2 +NaOH---→CHI_3 + $CH_3\text{-}CH_2\text{-}CH_2\text{-}COONa$

$CH_3\text{-}CO\text{-}CH_2\text{-}CH_2\text{-}CH_3$ ---[O]--→ $CH_3\text{-}COOH$ + $CH_3\text{-}CH_2\text{-}COOH$

30. Give names of the reagents to bring about the following transformations.

(i) Hexan-1-ol to hexanal (ii) Cyclohexanol to cyclohexanone (iii) But-2-ene to ethanol

Ans- (i) Oxidation using PCC (pyridinium chlorochromate)

(ii) $K_2Cr_2O_7$ in acidic medium

(iii) O_3/H_2O-Zn dust

LONG ANSWER QUESTIONS [5 MARKS]

31. Identify A to E in the following sequence:

$$CH_3CH_2COOH \xrightarrow{NH_3} A \xrightarrow{Br_2/KOH} B \xrightarrow{HNO_2} C \xrightarrow{[O]} CH_3COOH$$

$$CH_3COOH \xrightarrow[\text{Dil HCl}]{Ca(OH)_2} D \xrightarrow{LiAlH_4} E$$

[Ans: A = $CH_3CH_2CONH_2$, B = $CH_3CH_2NH_2$ C = CH_3CH_2OH D = CH_3COCH_3 E = $CH_3CH(OH)CH_3$]

32. An organic compound A on treatment with acetic acid in the presence of sulphuric acid produces an ester B. Compound A on mild oxidation gives C. Compound C with 50% KOH followed by acidification of dilute HCl generates A and D. Compound D on reaction with PCl_5 followed by reaction with ammonia gives E. Compound E on dehydration produces hydrocyanic acid. Identify the compounds A, B, C, D and E.

[Ans: Compound A gives an ester with acetic acid so it must be an Alcohol.

Compound C reacts with 50% KOH followed by acidification with HCl to give A and D i.e. it undergoes Cannizzaro's reaction so it must be an aldehyde with no α-H.

Compound E on dehydration give HCN so it must be $HCONH_2$.

D on reacting with PCl_5 followed by NH_3 give E so D must be HCOOH.

$$\underset{D}{HCOOH} \xrightarrow[NH_3]{PCl_5} \underset{E}{HCONH_2} \xrightarrow{-H_2O} HCN$$

As D is formed by the Cannizzaro's reaction of compound C so C must be HCHO and A gives C on oxidation so A must be CH_3OH.

$$\underset{C}{2HCHO} \xrightarrow[\text{Dil. HCl}]{\text{50\% KOH}} \underset{A}{CH_3OH} + \underset{D}{HCOOH}$$

$$\underset{A}{CH_3OH} \xrightarrow{[O]} \underset{C}{HCHO}$$

$$\underset{A}{CH_3OH} + CH_3COO \longrightarrow \underset{E}{CH_3COOCH_3}$$

33. (i) How will you bring about the following conversions

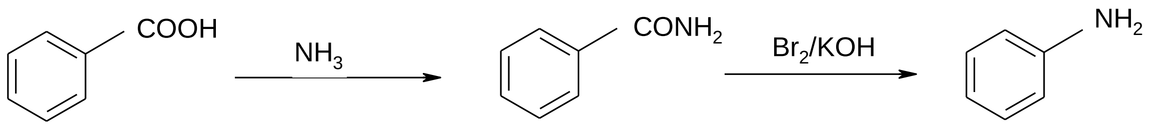
(a) Benzoic acid to aniline

(b) Bromomethane to ethanol

(ii) An alkene with molecular formula C_5H_{10} on ozonolysis gives a mixture of two compounds B and C. Compound B gives positive Fehling's test and also reacts with iodine and NaOH solution. Compound C does not give Fehling's solution test but forms iodoform. Identify the compounds A, B and C.

[Ans:

(i) (a) Benzoic acid to aniline:



(b) Bromomethane to ethanol:

$$CH_3Br \xrightarrow{KCN} CH_3CN \xrightarrow{H_3O^+} CH_3COOH \xrightarrow{LiAlH_4} CH_3CH_2OH$$

(ii) As B give positive Fehiling's solution test and also positive iodoform test so it must be an aldehyde with an acyl group. C does not give positive Fehling's solution test but gives positive iodoform test so it must be a ketone with an acyl group.

So B must be CH_3CHO and C must be CH_3COCH_3 and A will be $CH_3CHC(CH_3)_2$.

$$\underset{A}{CH_3CH = C(CH_3)_2} \xrightarrow[Zn/H_3O^+]{O_3} \underset{B}{CH_3CHO} + \underset{C}{CH_3COCH_3}$$

34. (i) Give simple chemical tests to distinguish between the following pairs of compounds:

(a) Butanal and butan-2-one

(b) Benzoic acid and phenol

(ii)Identify A, B and C in the following reaction

$$CH_3CN \xrightarrow[H_3O^+]{SnCl_2/HCl} A \xrightarrow{\text{Dil. NaOH}} B \xrightarrow{\triangle} C$$

[Ans: (i) (a) Butatnal being an aldehyde gives positive Tollen's reagent test bu Butan-2-one being a ketone does not.

(b) Benzoic acid reacts with $NaHCO_3$ to give CO_2 with brisk effervescence but phenol does not.

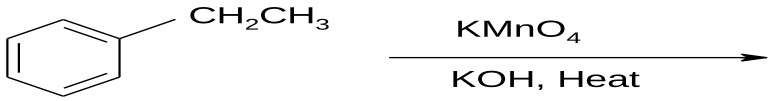
(ii) A = CH_3CHO B = $CH_3CH(OH)CH_2CHO$ C = $CH_3CH = CHCHO$]

35. (i) Write the reactions involved in the following reactions:

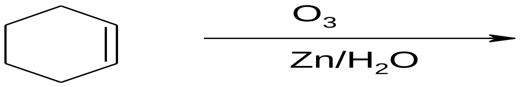
(a) Aldol condensation

(b) Hell- Volhard- Zelinsky reaction.

(ii) Complete the following reactions:

(a) 

(b) $$C_6H_5CHO \xrightarrow{H_2NCONHNH_2}$$

(c) 

[***Ans:***

(i) (a) Aldol Condensation:

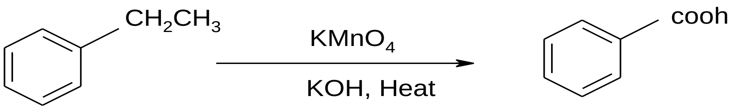
$$2CH_3CHO \xrightarrow{\text{Dil NaOH}} CH_3CH(OH)CH_2CHO$$

(b) Hell- Vilhard- Zelinsky reaction:

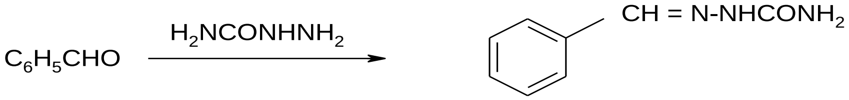
$$R\text{-}CH_2COOH \xrightarrow[H_2O]{X_2 \text{ / Red } P_4} RCH(X)COOH$$

(ii)

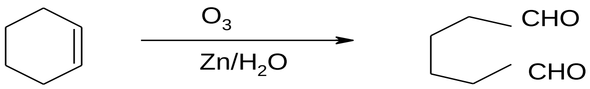
(a)



(b)



(c)



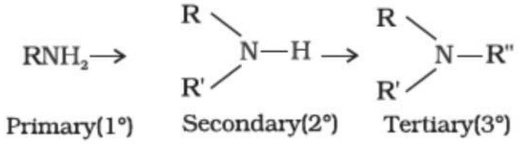
<u>Assertion and Reason Type Questions</u>

1. Assertion- Formaldehyde is a planar molecule.
   Reason – It contains sp^2 hybridised carbon atom.
2. Assertion- Compounds containing –CHO group are easily oxidised to corresponding carboxylic acids.
   Reason – Carboxylic acids can be reduced to alcohols by treatment with LiAlH4
3. Assertion- The α- hydrogen atom in carbonyl compounds is less acidic.
   Reason – The anion formed after the loss of α- hydrogen atom is resonance stabilised.
4. Assertion- Aromatic aldehydes and formaldehydes undergo Cannizaro’s reaction.
   Reason – Aromatic aldehydes are almost as reactive as formaldehydes.
5. Assertion- Aldehydes and ketones both react with Tollen’s reagent to form silver mirror.
   Reason – Both aldehydes and ketones contain carbonyl group.

Ans. 1- (a) 2- (b) 3- (d) 4- (c) 5- (d)

UNIT VI AMINES

- Amines are alkyl or aryl derivatives of ammonia. It is obtained by replacement of one, two or all the three hydrogen atoms by alkyl or aryl groups.
- When one hydrogen atom of ammonia is replaced by alkyl or aryl group then we get Primary amine. If two hydrogen atoms of ammonia are replaced by alkyl or aryl group then we get Secondary amine. Similarly if three hydrogen atoms of ammonia are replaced by alkyl or aryl group then we get tertiary amine.



- Amines can be prepared by

(i) Ammonolysis of alkyl halides,

$$\underset{(1^\circ)}{RNH_2} \xrightarrow{RX} \underset{(2^\circ)}{R_2NH} \xrightarrow{RX} \underset{(3^\circ)}{R_3N} \xrightarrow{RX} \underset{\text{Quaternary ammonium salt}}{R_4\overset{+}{N}\overset{-}{X}}$$

$$R\text{–}\overset{+}{N}H_3\overset{-}{X} + NaOH \longrightarrow R\text{–}NH_2 + H_2O + \overset{+}{Na}\overset{-}{X}$$

(ii) Reduction of nitro compounds

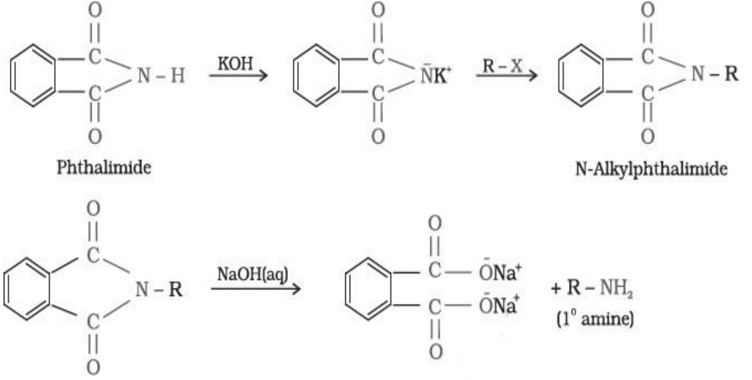
(a) $C_6H_5\ NO_2 \xrightarrow{H2/Pd,\ ethanol} C_6H_5\ NH_2$

(b) $C_6H_5\ NO_2 \xrightarrow{Sn\ +\ HCl\ or\ Fe\ +\ HCl} C_6H_5\ NH_2$

(iii) Reduction of cyanides, amides and oximes,

$$R\text{–}C\equiv N \xrightarrow[Na(Hg)/C_2H_5OH]{H_2/Ni} R\text{–}CH_2\text{–}NH_2$$

(iv) Gabreil Phthalimide synthesis.(phthalimide synthesis cannot be used for preparing 2^0 as well as 3^0 amines and aryl amines.)



(v) Hoffmann's bromamide reaction

$RCONH_2 + Br_2 + 4NaOH \text{ ---> } R\text{-}NH_2 + Na_2CO_3 + 2NaBr + 2H_2O$

- Pure amines are almost colour less but develop colour in air due to oxidation.
- Boiling point of amines increases with increase in molecular weight. The boiling point of Primary and secondary amines are higher than tertiary amines due to formation of H-bond.

- Lower members of amines are soluble in water due to formation of H-bond with water but aromatic amines and higher aliphatic amines are insoluble due to presence of hydrophobic aryl or alkyl group.
- Primary and secondary amines gives Hinsberg's test but tertiary amines do not give Hinsberg's test. Similarly Primary amines gives carbylamines test while Secondary amines do not give Carbylamine test.
- Aniline is O, P-directing but during nitration it form m-nitro aniline also because in strong acidic medium, aniline is protonated to form anilinium ion, which is meta-directing.
- Aniline does not undergo Friedel craft reaction because it form salt with Lewis-acid anhydrous $Alcl_3$.
- Basic strength of amines are in following order-
  - (i) For methyl amines- 2^0 amine > 1^0 amine > 3^0 amine.
  - (ii) For ethyl and other aliphatic amines- 2^0 amine > 3^0 amine > 1^0 amine.
  - (iii) For gaseous amines - 3^0 amine > 2^0 amine > 1^0 amine.
  - (iv) For aromatic amine - 1^0 amine > 2^0 amine > 3^0 amine.
  - (v) Aliphatic amine > NH_3 > aromatic amine.
  - (vi) O, P – directing group in aniline increase its basic strength while m – directing group in aniline decrease its basic strength.

Chemical Reactions:

1. **Basic character of amines:** Amines, being basic in nature, react with acids to form salts.

2. **Alkylation:** Amines undergo alkylation on reaction with alkyl halides.

$$C_2H_5Br \xrightarrow{NH3} C_2H_5NH_2\ (1^0) \longrightarrow (C_2H_5)_2NH\ (2^0) \longrightarrow (C_2H_5)_3N\ (3^0) \longrightarrow (C_2H_5)\ N^+\ Br^-$$

3. **Acylation:** Ethanamine to N-ethyl ethanamide

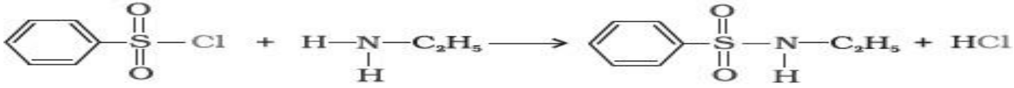
$$C_2H_5NH_2 + CH_3COCl \longrightarrow C_2H_5\ NH - CO - CH_3$$

4. **Carbylamine reaction:** Test for primary amines (Aliphatic and aromatic)

$$R{-}NH_2 + CHCl_3 + 3KOH \xrightarrow{Heat} R{-}NC + 3KCl + 3H_2O$$

5. **Reaction with nitrous acid:** $R{-}NH_2 + HNO_2 \xrightarrow{NaNO_2 + HCl} [R{-}\overset{+}{N_2}\overset{-}{Cl}] \xrightarrow{H_2O} ROH + N_2 + HCl$

6. **Reaction with arylsulphonyl chloride:** Benzenesulphonyl chloride ($C_6H_5SO_2Cl$), which is also known as Hinsberg's reagent, reacts with Ethyl amine to form N-Ethylbenzenesulphonamide.

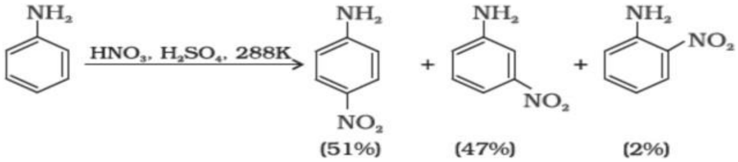


N-Ethylbenzenesulphonamide
(soluble in alkali)

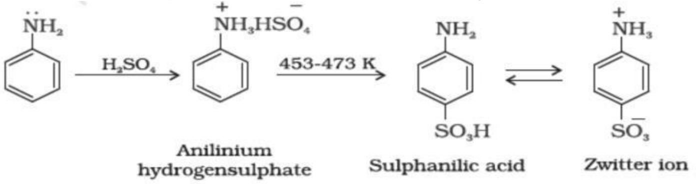
7. Electrophilic substitution:

(a) Bromination: Aniline reacts with bromine water at room temperature to give a white precipitate of 2, 4, 6-tribromoaniline.

(b) Nitration: Aniline reacts with nitric acid to give o-, m- & p-nitro aniline.



(c) Sulphonation: Aniline reacts with conc Sulphuric acid to form anilinium hydrogensulphate which on heating with Sulphuric acid at 453-473K produces p-amino benzene sulphonic acid, known as sulphanilic acid followed by Zwitter ion structure.



- Arenediazonium salts are prepared from Aniline by diazotisation reaction.

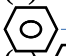
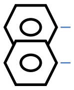
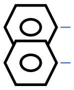
$C_6H_5NH_2 + NaNO_2 + 2HCl \xrightarrow{273\text{-}278} C_6H_5N_2^+Cl^- + NaCl + 2H_2O$

- Benzene diazonium chloride can be converted into benzene, phenol, benzonitrile, benzoic acid, benzyl amine, nitrobenzene, halobenzene, azodyes, etc., by suitable reagents.

Multiple choice question

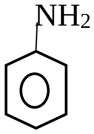
1. The correct IUPAC name for $CH_2 = CH\ CH_2\ NH\ CH_3$ is-
   (a) Allylmethylamine (b) 2 - amino – 4 - Pentene
   (c) 4 – amino Pent – 1 – ene (d) N – methyl Prop – 2en – 1 – amine

2. Methylamine reacts with HNO_2 to form ……………..
   (a) $CH_3\ ONO$ (b) $CH_3\ OCH_3$
   (c) $CH_3\ OH$ (d) $CH_3\ CHO$

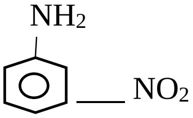
3.  – $CH_2 – NH_2$ on heating with $CHCl_3$ and alcoholic KOH gives foul smell of-
   (a)  – $CH_2\ OH$ (b)  – $CH_2\ NC$
   (c)  – $CH_2\ CN$ (d)  – $CH_2\ Cl$

4. Which of the following has highest PK_b value?
   (a) $CH_3\ CH_2\ NH_2$ (b) NH_3
   (c) $CH_3\ NH_2$ (d) $C_6\ H_5\ NH_2$

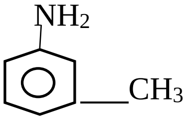
5. The correct increasing order of basic strength for the following compound is ……………….;



(I)



(II)



(III)

   (a) II < III < I (b) III < I < II
   (c) III < II < I (d) II < I < III

6. Among the following, the strongest base in aqueous medium is ………………

(a) $CH_3\ NH_2$ (b) $NC\ CH_2\ NH_2$

(c) $(CH_3)_2\ NH$ (d) $C_6\ H_5\ NH\ CH_3$

7. The source of Nitrogen in Gabriel Synthesis of amines is ……………..

(a) Sodium azide (b) Sodium nitrite

(c) Potassium Cyanide (d) Potassium Phthalimide

8. Which of the following reagents would not be a good choice for reducing an aryl nitro compound to an amine?

(a) H_2 (excess) / Pt (b) Li Al H_4 in ether

(c) Fe and Hel (d) Sn and HCl

9. An organic compound 'A' on treatment with NH_3 gives 'B' which on heating gives 'C'. When C is treated with Br_2 in presence of KOH produces ethylamine. Compound A is-

(a) $CH_3\ CH_2\ CH_2\ COOH$ (b) $CH_3\ COOH$

(c) $CH_3\ CH\ (CH_3)\ COOH$ (d) $CH_3\ CH_2\ COOH$

10. Which of the following will be most stable diazonium salt?

(a) $CH_3\ CH_2\ N_2^+\ X^-$ (b) $C_6\ H_5\ N_2\ {}^+X^-$

(b) $CH_3\ N_2^+X^-$ (d) $C_6\ H_5\ CH_2\ N_2^+X^-$

Answers:- 1 – d; 2 – c; 3 – b; 4 – d; 5 – d;
6 – c; 7 – d; 8 – b 9 – d; 10 – b.

11. Write the IUPAC name of following compounds-

(i) $CH_3 - CH_2 - CH_2 - CO - N(CH_3)_2$ (ii) $C_6\ H_5 - NH - COCH_3$

Ans.- (i) N, N – dimethyl butanamide.

(ii) N – Phenyl ethanamide.

12. Arrange the following as properties indicated-

(i) $C_2\ H_5\ NH_2$, $(C_2\ H_5)_2\ NH$ and $C_6\ H_5\ NH_2$ (Increasing order of solubility in water)

(ii) $C_2\ H_5\ OH$, $(CH_3)_2\ NH$, $C_2\ H_5\ NH_2$ (Increasing Boiling Point)

Ans.- (i) $C_6\ H_5\ NH_2 < (C_2\ H_5)_2\ NH < C_2\ H_5\ NH_2$

(ii) $(CH_3)_2\ NH < C_2\ H_5\ NH_2 < C_2\ H_5\ OH$.

13. How will you distinguish the following pair of compounds-

(i) Methyl amine and dimethyl amine.

(ii) Secondary amine and Tertiary amine.

Ans.- (i) Methyl amine gives carbylamine test while dimethyl amine do not give carbylamine test.

(ii) Secondary amine gives Hinsberg's test while tertiary amine do not give Hinsberg's test.

14. Account for the following-

(i) Aniline does not undergo Friedel crafts reaction.

(ii) Aromatic Primary amine can not be prepared by Gabriel Phthalimide synthesis?

Ans.- (i) Because aniline is basic, which form salt with Lewis acid Al Cl_3.

(ii) Because aryl halide do not undergo nucleophilic substitution with the anion formed by Phthalimide.

15. Give the suitable reagent to convert-

(i) Nitrobenzene to Aniline.

(ii) Methanamine to Methanol

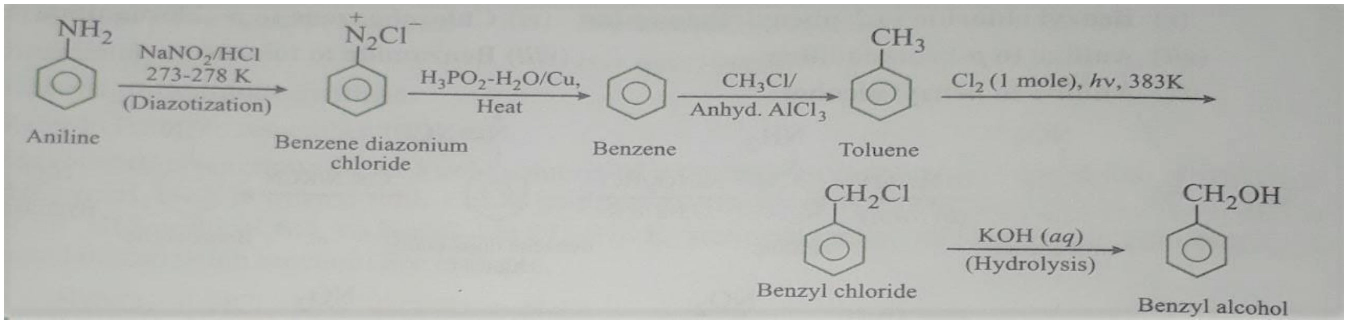
Ans.- (i) Sn | HCl Or Fe | HCl

(ii) $NaNO_2$ | HCl Or HNO_2.

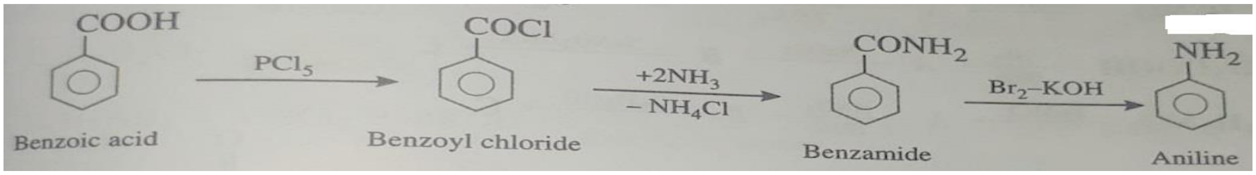
16. How will you convert-

(i) Aniline to benzyl alcohol (ii) Benzoic acid to aniline

Ans.- (i)



(ii)



17. Account for the following-

(i) PKb value of aniline is more than that of methylamine.

(ii) Although amino group is O – and P – directing in aromatic electrophilic substitution reactions but aniline on nitration gives m – nitro aniline also.

Ans.- (i) In aniline Phenyl group is electron withdrawing group while in methylamine, methyl group is electron pushing group.

(ii) Because in strong acidic medium aniline is protonated to form anilinium ion which is meta directing.

18. Arrange the following in order of increasing basic strength-

(i) $C_6H_5NH_2$, $C_6H_5N(CH_3)_2$, $(C_2H_5)_2NH$ and CH_3NH_2

(ii) $C_2H_5NH_2$, $(C_2H_5)_2NH$, $(C_2H_5)_3N$ and NH_3 (In gas Phase)

Ans.- (i) $C_6H_5NH_2 < C_6H_5N(CH_3)_2 < CH_3NH_2 < (C_2H_5)_2NH$

(ii) $NH_3 < C_2H_5NH_2 < (C_2H_5)_2NH < (C_2H_5)_3N$.

19. (i) Draw the zwitter ion structure of sulphanilic acid.

(ii) How can the activation effect of $-NH_2$ group in aniline be controlled?

Ans.- (i)

Sulphanilic acid
(Zwitter ion)

(ii) The activating effect of $-NH_2$ group in aniline be controlled by acylation.

10. (i) What is Hinsberg reagents?

(ii) Why do amines behave as nucleophiles?

Ans.- (i) Hinsberg reagents is Benzene sulphonyl chloride.

(ii) Due to presence of lone pair electrons on nitrogen atoms amines behave as nucleophiles.

***

Short Answer questions (3 marks)

1. Give the reason of following-

   (i) Primary and Secondary amines have higher boiling point than tertiary amines.

   (ii) Aliphatic amines are stronger base than aromatic amines.

   (iii) Amines are less acidic than alcohol of comparable molecular masses.

Ans.- (i) Primary and Secondary amines form intermolecular hydrogen bond but tertiary amine do not form hydrogen bond.

(ii) In aliphatic amine alkyl group is electron pushing group while in aromatic amine aryl group is electron withdrawing group.

(iii) Loss of a proton from an amine gives amide ion while loss of a proton from alcohol gives alkoxide ion. Since ‘O’ is more electronegative than ‘N’. So alkoxide ion RO^- can accommodate the negative charge more easily than amide ion RNH^-.

2. Arrange the following in order of their increasing basic strength-

   (i) $C_2H_5NH_2$, $C_6H_5NHCH_3$, $(C_2H_5)_2NH$ and $C_6H_5NH_2$.

   (ii) CH_3NH_2, $(CH_3)_2NH$, $(CH_3)_3N$, $C_6H_5NH_2$ and $C_6H_5CH_2NH_2$.

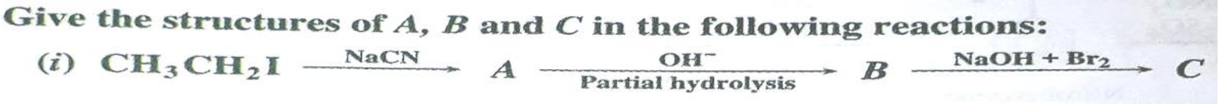
   (iii) aniline, P – nitroaniline and P – toluidine.

Ans.- (i) $C_6H_5NH_2 < C_6H_5NHCH_3 < C_2H_5NH_2 < (C_2H_5)_2NH$

(ii) $C_6H_5NH_2 < C_6H_5CH_2NH_2 < (CH_3)_3N < CH_3NH_2 < (CH_3)_2NH$

(iii) P – nitro aniline < aniline < P – toluidine.

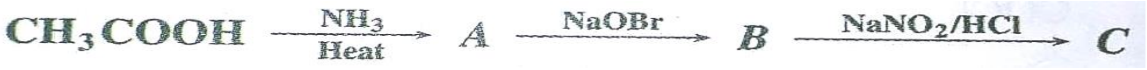
3.



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)



$CH_3COOH \xrightarrow[\text{Heat}]{NH_3} A \xrightarrow{NaOBr} B \xrightarrow{NaNO_2/HCl} C$

Ans.- (i) $A = CH_3CH_2CN$, $B = CH_3CH_2CONH_2$, $C = CH_3CH_2NH_2$

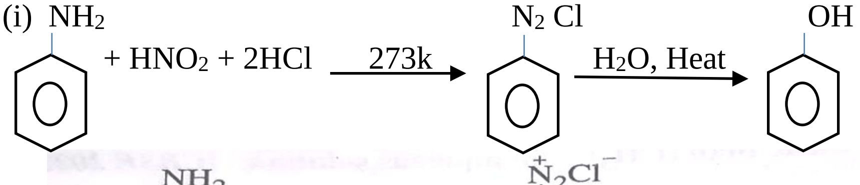
(ii) $A = CH_3CONH_2$, $B = CH_3NH_2$, $C = CH_3OH$.

4. How will you convert-

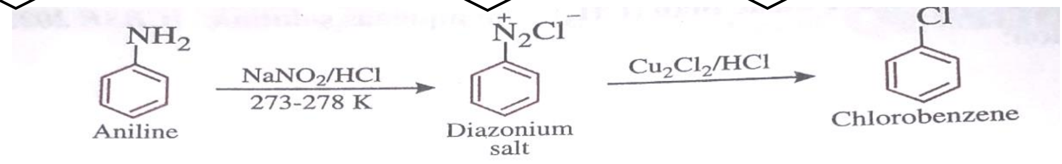
   (i) Aniline to Phenol (ii) Aniline to Chlorobenzene.

   (iii) Nitrobenzene to Aniline.

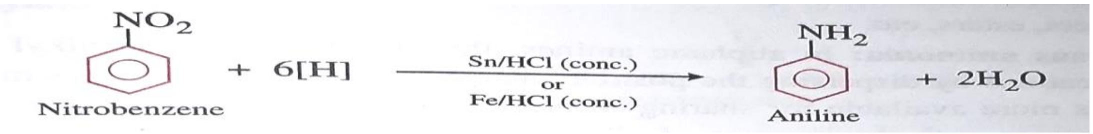
Ans.- (i)



(ii)



(iii)



5. Write short notes on the following-

(i) Carbylamine Reaction.

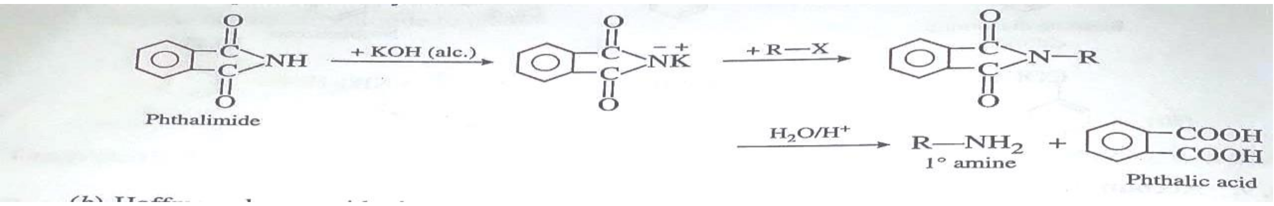
(ii) Hofmann's bromamide reaction

(iii) Gabriel Phthalimide Synthesis.

Ans.- (i) Carbylamine Reaction- When Primary amine is heated with chloform and KOH then Isocyanide is formed. $R\text{-}NH_2 + CHCl_3 + KOH \xrightarrow{\Delta} R\text{-}NC + KCl + H_2O$.

(ii) Hofmann's Bromamide Reaction- When acid amide is treated with Br_2 and NaOH then Primary amine is formed $R\text{-}CO\text{-}NH_2 \xrightarrow{Br_2 + NaOH} R\text{-}NH_2 + Na_2CO_3 + NaBr + H_2O$

(iii) Gabriel phthalimide synthesis- Phthalimide on tractement with KOH gives potassium phthalimide, which on treating with alkyl halide followed by hydrolysis gives Primary amine.



6. Write the product of following reactions-

(i) $C_6H_5NH_2 + CHCl_3 + \text{alc } KOH \longrightarrow$ ……………

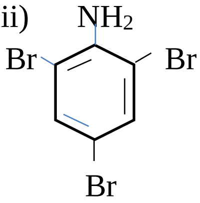
(ii) $C_6H_5N_2Cl + C_2H_5OH \longrightarrow$ …………….

(iii) $C_6H_5NH_2 + Br_2\ (aq) \longrightarrow$ …………….

Ans.- (i) $C_6H_5NC + KCl + H_2O$.

(ii) $C_6H_6 + CH_3CHO + N_2 + HCl$

(iii)



+ HBr

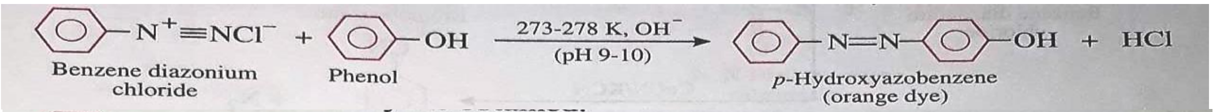
7. Write the following reaction-

(i) Coupling Reaction.

(ii) Diazotisation Reaction.

(iii) Sand Meyer's Reaction.

Ans.- (i)



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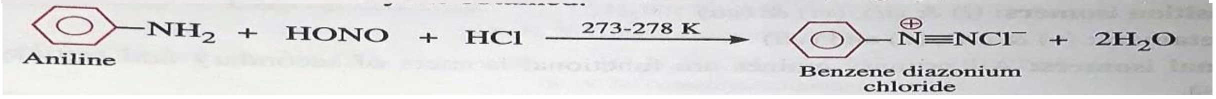

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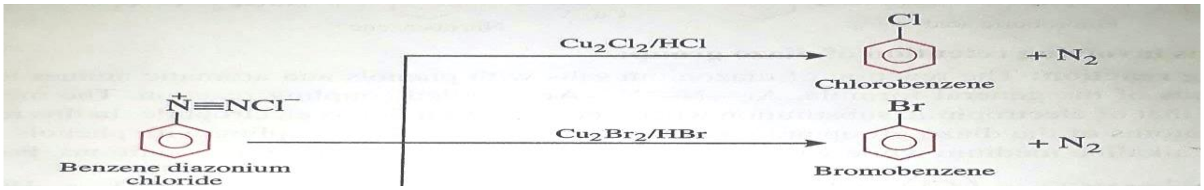
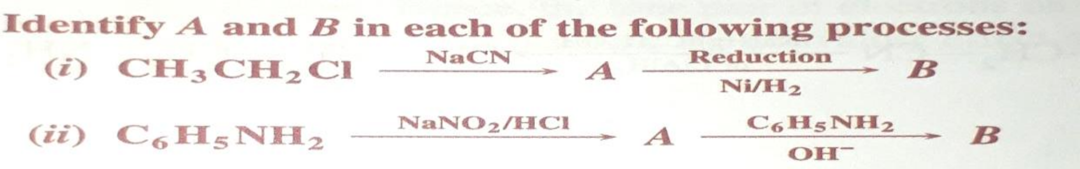
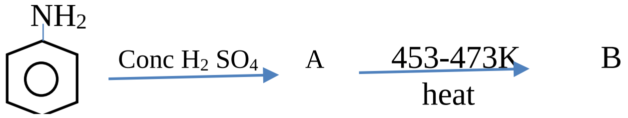


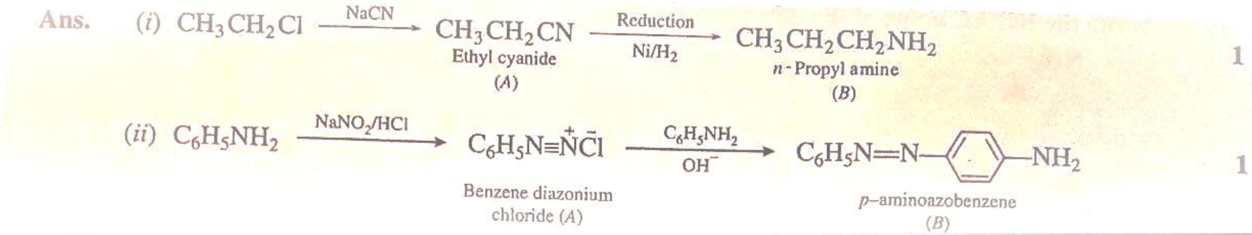
8. 

Identify A and B in each of the following processes:

(i) $CH_3CH_2Cl \xrightarrow{NaCN} A \xrightarrow[Ni/H_2]{Reduction} B$

(ii) $C_6H_5NH_2 \xrightarrow{NaNO_2/HCl} A \xrightarrow[OH^-]{C_6H_5NH_2} B$

(iii) 

Ans. 

Ans. (i) $CH_3CH_2Cl \xrightarrow{NaCN} CH_3CH_2CN \xrightarrow[Ni/H_2]{Reduction} CH_3CH_2CH_2NH_2$ 1

Ethyl cyanide (A) n-Propyl amine (B)

(ii) $C_6H_5NH_2 \xrightarrow{NaNO_2/HCl} C_6H_5\overset{+}{N}\equiv N\overset{-}{Cl} \xrightarrow[OH^-]{C_6H_5NH_2} C_6H_5N{=}N{-}C_6H_4{-}NH_2$ 1

Benzene diazonium chloride (A) p–aminoazobenzene (B)

(iii) 

Anilinium hydrogensulphate (A) Sulphanilic acid (B)

9. Write the reagent to convert-
   - (i) Aniline to chlorobenzene.
   - (ii) Ethanoic acid to methanamine.
   - (iii) Aniline to Phenol

Ans.- (i) $NaNO_2$ | HCl and Cu_2Cl_2| HCl
(ii) NH_3 and Br_2 | KOH
(iii) $NaNO_2$ | HCl and H_2O (Heat)

10. Give a chemical test to distinguish between the following pairs of compounds-
   - (i) Aniline and N-methyl aniline (ii) Aniline and Benzyl amine.
   - (iii) $(CH_3)_2$ NH and $(CH_3)_3$ N,

Ans.- (i) Aniline gives carbylamines(1^0) test but N-methyl aniline (2^0) do not give carbylamines test.
(ii) Aniline give azo dye test ie. Aniline form red-dye with $NaNO_2$ / HCl and 2 naphthol.
Benzyl amine do not give azo dye test.
(iii) $(CH_3)_2$ NH gives Hinsberg's test but $(CH_3)_3$ N do not give Hinsberg's test.

Long answer question (5 marks)

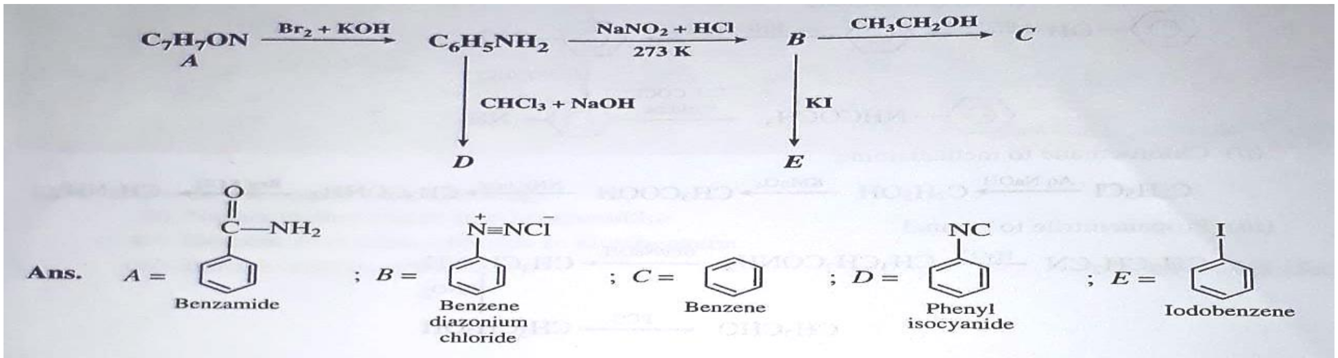
1. An aromatic compound A on treatment with aqueous ammonia and heating forms compound 'B' which on heating with Br_2 and KOH forms compound 'C' of molecular formula $C_6 H_7 N$. Write the structure and IUPAC name of A, B and C. Write the reaction involved.

Ans.- A = $C_6 H_5$ COOH Benzoic acid.
B = $C_6 H_5$ CO NH_2 Benzamide.
C = $C_6 H_5$ NH_2 Aniline.

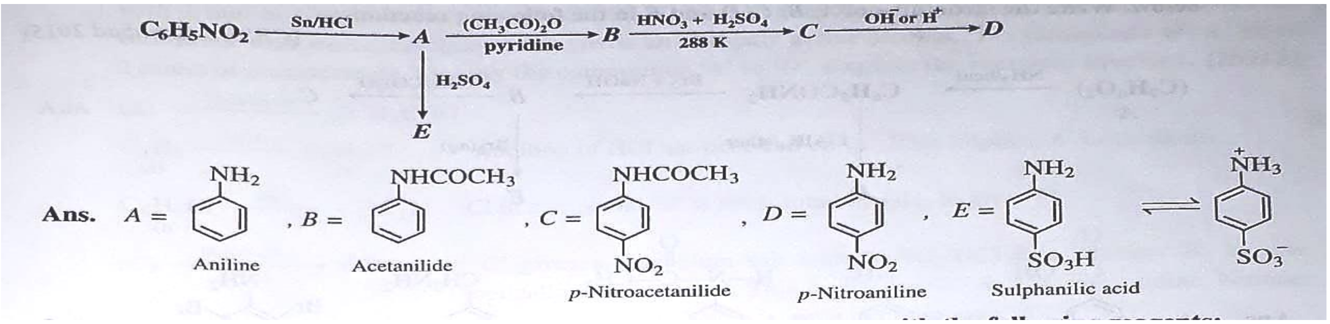
Reaction - $\underset{(A)}{C_6H_5COOH} \xrightarrow{\text{(i) aq } NH_3 \text{ (ii) Heat}} \underset{(B)}{C_6H_5CONH_2}$

$$\underset{(B)}{C_6H_5CONH_2} \xrightarrow{Br_2 \mid KOH} \underset{(C)}{C_6H_5NH_2}$$

2. An aromatic Compound 'A' of molecular formula C_7H_7ON undergoes a series of reactions as shown below. Write the structure of A, B, C, D and E in the following reactions.



3. Write the structure of A, B, C, D and E in the following reactions-



4. (i) Write the structure of main product when aniline reacts with the following reagents-

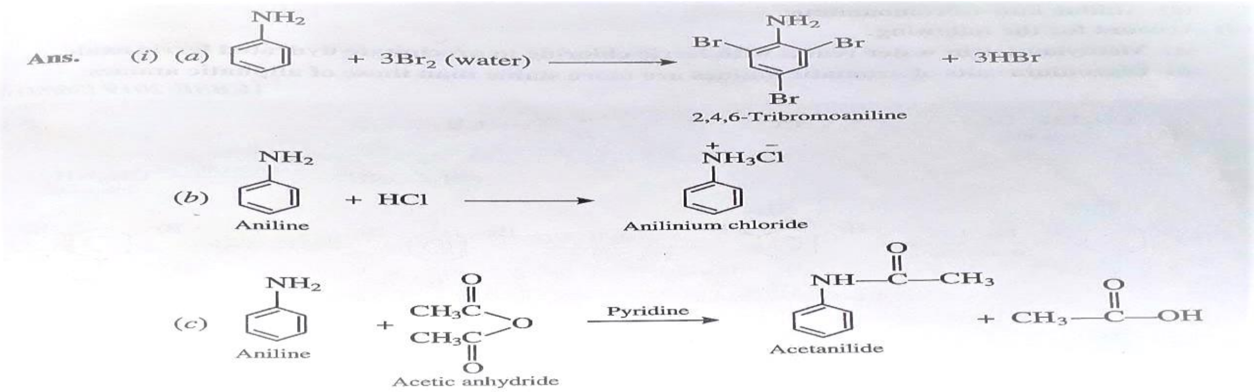
(a) Br_2 – water (b) HCl (C) $(CH_3CO)_2O$ | Pyridine

(ii) Account for the following-

(a) Methyl amine in water reacts with ferric chloride to precipitate hydrated ferric oxide.

(b) Diazonium salts of aromatic amines are more stable than those of aliphatic amines.

Ans.-



(ii)

(a) Methyl amine being more basic than water, accepts a proton from water and liberate OH^- ion. Which combine with Fe^{3+} to form brown precipitate of hydrated ferric oxide.

$$CH_3NH_2 + H_2O \longrightarrow CH_3NH_3^+ + OH^-$$

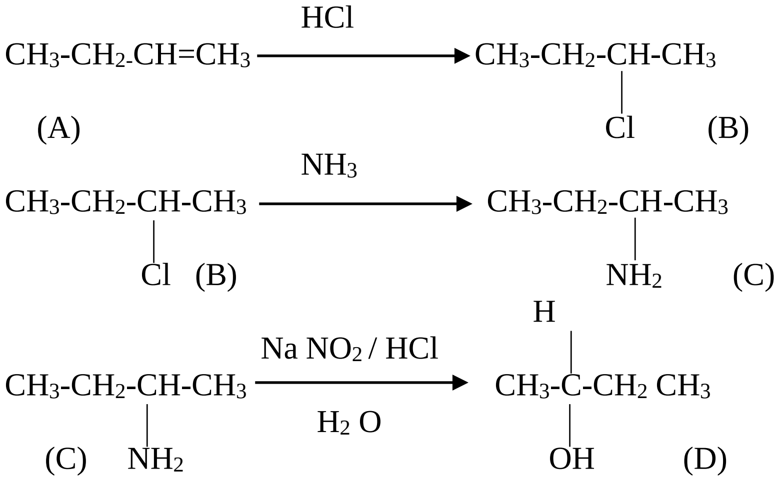
$$FeCl_3 \longrightarrow Fe^{3+} + 3Cl^-$$

$$2Fe^{3+} + 6OH^- \longrightarrow \underline{Fe_2O_3 . 3H_2O}$$

(b) The diazonium salt of aromatic amines are more stable than those of aliphatic amines due to dispersal of the positive charge on the benzene ring.

5. A hydrocarbon ‘A’ ($C_4 H_6$) on reaction with HCl gives a compound ‘B’ ($C_4 H_9 Cl$), which on reaction with 1 mole of NH_3 gives compound ‘C’ ($C_4 H_{11} N$). On reacting with Na NO_2 and HCl following by treatment with water compound ‘C’ yield an optically active alcohol ‘D’. Ozonolysis of ‘A’ gives 2 mole of Acetaldehyde. Identify the compound A to D. Explain the reaction involved.

Ans.-



$$\underset{(A)}{CH_3\text{-}CH_2\text{-}CH{=}CH_3} \xrightarrow{HCl} CH_3\text{-}CH_2\text{-}\underset{\underset{Cl}{|}}{CH}\text{-}CH_3 \quad (B)$$

$$CH_3\text{-}CH_2\text{-}\underset{\underset{Cl}{|}}{CH}\text{-}CH_3 \;(B) \xrightarrow{NH_3} CH_3\text{-}CH_2\text{-}\underset{\underset{NH_2}{|}}{CH}\text{-}CH_3 \quad (C)$$

$$(C)\; CH_3\text{-}CH_2\text{-}\underset{\underset{NH_2}{|}}{CH}\text{-}CH_3 \xrightarrow[H_2O]{Na\,NO_2 / HCl} CH_3\text{-}\overset{\overset{H}{|}}{\underset{\underset{OH}{|}}{C}}\text{-}CH_2\,CH_3 \quad (D)$$

Assertion and Reason Type Questions

1. Assertion-Aniline does not undergo Friedel Crafts reaction .
   Reason – Friedel Crafts is an electrophilic substitution reaction.
2. Assertion- Gabriel phthalimide reaction can be used to prepare aryl and alkyl amines.
   Reason – Aryl halides have reactivity as alkyl halides towards nucleophilic substitution reactions.
3. Assertion- Aniline is weak basic than ammonia .
   Reason – In aniline lone pair is shared by benzene nucleus.
4. Assertion- p- toluidine is a stronger base than m- toluidine.
   Reason – Methyl group from m- position exerts smaller electron donating inductive effect than from p- position.
5. Assertion- Methyl cyanide has higher boiling point than methyl cyanide.
   Reason – Dipole moment of methyl cyanide is higher than that of methyl isocyanide.

Ans. 1 (b) 2 (d) 3-(a) 4-(b) 5-(a)

UNIT X BIOMOLECULES

- **Carbohydrates:** Polyhydroxy aldehydes or polyhydroxy ketones or compounds on hydrolysis give carbohydrates.
- **Classification of carbohydrates:**

Monosaccharides-- Simplest carbohydrates, It cannot be hydrolysed into simpler compounds

Examples – Glucose, mannose

Oligosaccharides Carbohydrates which gives 2 to 10 monosaccharide units on hydrolysis

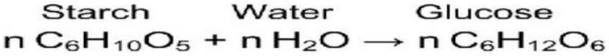
Examples – Sucrose, Lactose, Maltose

Polysaccharides- carbohydrates which on hydrolysis give large number of monosaccharide units.

Examples – Cellulose, starch

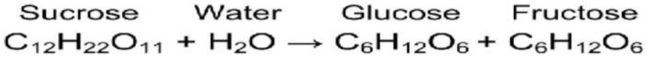
Preparation of Glucose –

From starch-



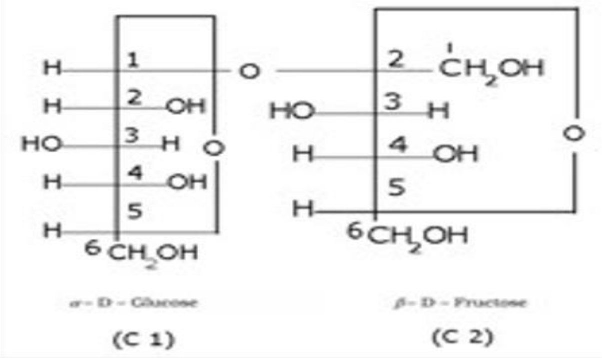
$$\underset{\text{Starch}}{n\,C_6H_{10}O_5} + \underset{\text{Water}}{n\,H_2O} \longrightarrow \underset{\text{Glucose}}{n\,C_6H_{12}O_6}$$

From sucrose -

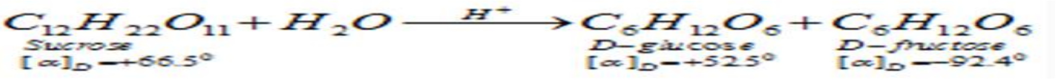


$$\underset{\text{Sucrose}}{C_{12}H_{22}O_{11}} + \underset{\text{Water}}{H_2O} \longrightarrow \underset{\text{Glucose}}{C_6H_{12}O_6} + \underset{\text{Fructose}}{C_6H_{12}O_6}$$

- ❖ Glycosidic linkage: The oxide linkage formed by the loss of a water molecule when two monosaccrides are joined together through oxygen atom is called glycosidic linkage.
- ❖ Sucrose (invert sugar): a) Sucrose is non-reducing sugar because the two monosccharide units are held together by a glycosidic linkage between C1 of α glucose and C2 of β fructose. Since the reducing groups of glucose and fructose are involved in glycosidic bond formation, sucrose is a non – reducing sugar

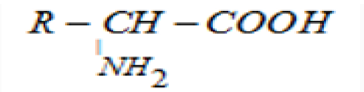


b) Sucrose is dextrorotatory but on hydrolysis it gives dextrorotatory & laevorotatory and the mixture is laevorotatory-



$$\underset{\substack{\text{Sucrose} \\ [\alpha]_D = +66.5^\circ}}{C_{12}H_{22}O_{11}} + H_2O \xrightarrow{H^+} \underset{\substack{D-\text{glucose} \\ [\alpha]_D = +52.5^\circ}}{C_6H_{12}O_6} + \underset{\substack{D-\text{fructose} \\ [\alpha]_D = -92.4^\circ}}{C_6H_{12}O_6}$$

Amino acids:



$$R - \underset{\substack{| \\ NH_2}}{CH} - COOH$$

Amino acids contains amino (-NH_2) and carboxyl (-COOH) functional groups.

Where R – any side chain

Most naturally occuring amino acids have L- Config

Types of amino acid:-

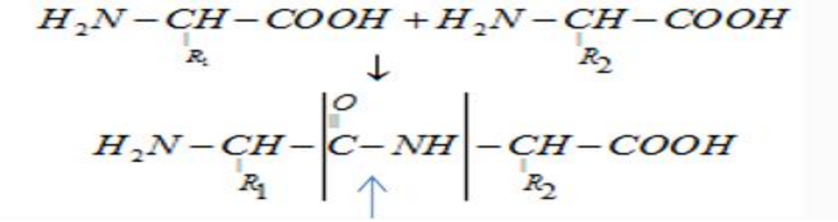
a). **Essential amino acids:** The amino acids which cannot be synthesised in the body and must be obtained through diet, are known as essential amino acids. Examples: Valine, Leucine

b). **Non-essential amino acids:** The amino acids, which can be synthesised in the body, are known as non-essential amino acids. Examples: Glycine, Alanine

- **Zwitterion form of amino acids:**

1. Amino acids behave like salts rather than simple amines or carboxylic acids. This behaviour is due to the presence of both acidic (carboxyl group) and basic (amino group) groups in the same molecule. In aqueous solution, the carboxyl group can lose a proton and amino group canaccept a proton, giving rise to a dipolar ion known as zwitter ion. This is neutral but contains both positive and negative charges.
2. In zwitterionic form, amino acids show amphoteric behaviour as they react both with acids and bases.

- **Isoelectronic point:** The pH at which the dipolar ion exists as neutral ion and does not migrate to either electrode cathode or anode is called isoelectronic point.
- **Proteins:** Proteins are the polymers of α-amino acids and they are connected to each other by peptide bond or peptide linkage. A polypeptide with more than hundred amino acid residues, having molecular mass higher than 10,000u is called a protein.
- **Peptide linkage:** Peptide linkage is an amide linkage formed by condensation reaction between –COOH group of one amino acid and –NH2 group of another amino acid.



$$H_2N-\underset{R_1}{CH}-COOH + H_2N-\underset{R_2}{CH}-COOH \downarrow H_2N-\underset{R_1}{CH}-\left|\overset{O}{C}-NH\right|-\underset{R_2}{CH}-COOH$$

Peptide Linkage :-

- **Primary structure of proteins:** The sequence of amino acids is said to be the primary structure of a protein.
- **Secondary structure of proteins:** It refers to the shape in which long polypeptide chain can exist. Two different types of structures:

α– Helix:

Right handed screw with the NH group of each amino acid residue H – bonded to – C = O of adjacent turn of the helix.

B- Pleated sheet

In this conformation, all peptide chains are stretched out to nearly maximum extension and then laid side by side which are held together by hydrogen bonds.

- **Tertiary structure of proteins:** It represents the overall folding of the polypeptide chain i.e., further folding of the 2° structure.

Two Shapes of Protein :-

Fibrous proteins

a) When the polypeptide chains run parallel and are held together by hydrogen and disulphide bonds, then fibre– like structure is formed.

b) These proteins are generally insoluble in water

c) Examples: keratin (present in hair, wool, silk) and myosin (present in muscles),

Globular proteins

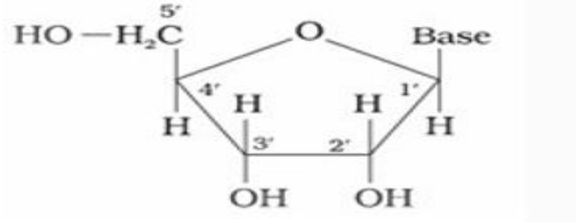
a) This structure results when the chains of polypeptides coil around to give a spherical shape.
b) These are usually soluble in water.
c) Examples: Insulin and albumins

- **Denaturation of proteins:**

1. The loss of biological activity of proteins when a protein in its native form, is subjected to physical change like change in temperature or chemical change like change in pH. This is called denaturation of protein.
2. Example: coagulation of egg white on boiling, curdling of milk.

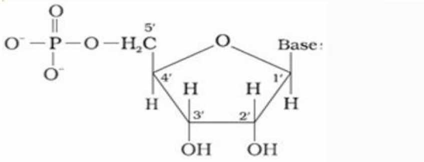
- **Nucleoside:**

1. Base + sugar



- **Nucleotide:**

1. Base + sugar + phosphate group



- **Nucleic acids (or polynucletides):**

1. Long chain polymers ofnucleotides.
2. Nucleotides are joined by phosphodiester linkage between 5' and 3' C atoms of a pentose sugar.

Double helix structure of DNA:

1. It is composed of two right handed helical polynucleotide chains coiled spirally in opposite directions around the same central axis.
2. Two strands are anti-parallel i.e., their phosphodiester linkage runs in opposite directions.
3. Bases are stacked inside the helix in planes ⊥to the helical axis.
4. Two strands are held together by H – bonds ($A = T$, $G \equiv C$).
5. The two strands are complementary to each other because the hydrogen bonds are formed between specific pairs of bases.
6. Adenine forms hydrogen bonds with thymine whereas cytosine forms hydrogen bonds with guanine.

Vitamins: Vitamins are organic compounds required in the diet in small amounts to perform specific biological functions for normal maintenance of optimum growth and health of the organism.

1. Water soluble vitamins **i)** These vitamins are soluble in water.
   ii) Water soluble vitamins must be supplied regularly in diet because they are readily excreted in urine and cannot be stored (except vitamin B12) in our body.
   iii) Example: Vitamin C, B group vitamins.
2. Fat soluble vitamins
   i) These vitamins are soluble in fat and oils but insoluble in water.
   ii) They are stored in liver and adipose (fat storing) tissues.
   iii) Example: Vitamin A, D, E and K

SECTION -A (MCQ)

1. A disaccharide is formed when two monosaccharides are bonded together by a bond.
a) glycosidic
b) peptide
c) ionic
d) phosphodiester
2. Which of the following statements about starch is incorrect?
a) It gives blue colour with iodine
b) It is a polymer of α-D-glucose
c) It is a reducing carbohydrate
d) It consists of branched chains
3. On oxidation with a mild oxidising agent like Br2/H20, the glucose is oxidized to
(a) saccharic acid
(b) glucaric acid
(c) gluconic acid
(d) valeric acid
4. Glycosidic linkage is an
(a) amide linkage
(b) ester linkage
(c) ether linkage
(d) acetyl linkage
5. What are the hydrolysis products of sucrose?
(a) Fructose + Fructose
(b) Glucose + Glucose
(c) Glucose + Galactose
(d) D-Glucose + D-Fructose
6. Which of the following is a non-reducing sugar?
(a) Glucose
(b) Sucrose
(c) Maltose
(d) Lactose
7. Which type of interactions are responsible for making the a-helix structure stable?
(a) Peptide bonds between -NH2 and -CO groups of adjacent carbon chain
(b) Hydrogen bonds between -NH of amino acid in the one turn with -CO of amino acid to adjacent turn
(c) -OH group of one amino acid with -CO group of other amino acid on the turn
(d) Hydrogen bonds between adjacent amino acids
8. Invert sugar is –
(a) a type of cane sugar
(b) optically inactive form of sugar
(c) mixture of glucose and galactose
(d) mixture of glucose and fructose in equimolar quantities.
9. Which of the following treatment will convert starch directly into glucose ?
(a) Heating with dilute H_2SO_4 (b) Fermentation by diastase.
(c) Fermentation by zymase (d) Heating with dilute NaOH
10. Denaturation of protein leads to loss of its biological activity by
(a) formation of amino acids
(b) loss of primary structure
(c) loss of both primary and secondary structure
(d) loss of both secondary and tertiary structures

SECTION -B

11. Write the reaction involved when D- glucose is treated with following reason –

(a) HCN (b) Br_2

12. (i) What type of linkage is present in nucleic acid?

(ii) Give one example each for fibrous protein and globular protein.

13. (i) Write chemical reaction to show that open structure of D-glucose contains the straight chain.

(ii) What type of linkage is responsible for the formation of protein?

14. Write differences between essential amino acid and non- essential amino acid with suitable examples.

15. Name the bases present in RNA. Which one of these is not present in DNA?

16. Explain denaturation with suitable example.

17. Account for the following –

(i) vitamin -c cannot be storage in our body.

(ii) Glucose is a reducing sugar.

18. Answer the following-

(i) What type of linkage is responsible for the primary structure of protein?

(ii) Name the location where protein synthesis occurs in body.

19. (i)What is the water soluble part of the starch called?

(ii)What is the name of the monomers?

20. (i) Name the vitamin responsible for the coagulation.

(ii) Give one example of fat soluble vitamin.

SECTION -C (SHORT ANSWER)

21.Define following terms-

(a) Invert sugar (b) Glycosidic linkage (c) oligosaccharides

22. (a) Give one structural difference between amylose and amylopectin.

(b) Name protein and its shapes present in oxygen carrier in human body.

(c) Name two fat storing tissues in human body.

23. Give reasons for any 3 of the following observation –

(a) Penta-acetate of glucose does not react with hydroxylamine.

(b) Amino acid behaves like salts.

(c) The two strands in DNA are complimentary to each other.

(d) Water soluble vitamins must be taken regularly in diet.

24. Write three differences between fibrous protein and Globular protein.

25. Write three structural differences between RNA & DNA.

26. (a) Which of the following biomolecules is insoluble in water? Justify Insuline, keratin, haemoglobin.

(b) Write one functional difference between DNA & RNA.

(c) α– amino acids have relatively high a melting point then the corresponding halo acids.

27. (a) How do you explain the presence of an aldehydic group in a glucose molecule?

(b) Why are carbohydrates generally optically active?

(c) Name two α-amino acid which form a dipeptide which is 100 times more sweet than can sugar.

28. Write the products

(a) Glucose reaction with Nitric Acid

(b) Glucose reacting with Bromine water.

(c) Glucose reacting with HI

29.(a) Define a 'Peptide linkage'.

(b) Name the four bases present in DNA.

(c)Which one of these is not present in RNA?

30. (a) Which one of the following is a disaccharide: Starch, Maltose, Fructose, Glucose?
(b)What is the difference between fibrous protein and globular protein?
(c) Write the name of vitamin whose deficiency causes bone deformities in children.

SECTION D- LONG ANSWER

31. (a) What does the water present in the egg go after boiling the egg?
(b) What type of linkage are responsible for the formation of –
(i) α-Helix formation (ii) β– sheet structure
(c) Name the following-
(i) A reducing sugar (ii) A vitamin which is neither soluble in water nor in fat.
(iii) A oil soluble vitamins (iv) An α – amino acid which is not optically active

32. (a) What happens when oxidation of following carbohydrate take place?
(i) Gluconic acid (ii) Glucose
(b) Account for the following-
(i) Penta acetate of glucose does not react with hydroxyl amine.
(ii) Vitamin B & C are essential for us.
(iii) Amino acid shows amphoteric nature.

33. (a) Name the deficiency diseases resulting from lack of vitamin A and E in the diet.
(b) Out of four bases name those which are common to both DNA and RNA and why DNA and RNA called acids?
(c) Glucose and fructose are reducing sugar. Why?

34. (a) In which form do amino acid exist? How is the charge distributed in amino acids?
(b) What information is furnished by secondary structure of protein?
(c) How is quaternary structure of proteins formed?
(d) Cellulose is a polysaccharide of β – glucose. What units are given on hydrolysis by cellulose.

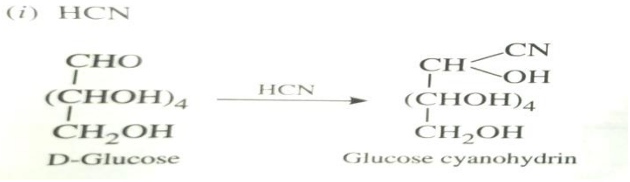
35. (a) Write one important structural and functional difference between DNA and RNA.
(b) What is meant by the inversion of sugar?
(c) Glucose does not give 2,4-DNP test and Schiff's test. Why?
(d) Name the unit formed by the attachment of a base to the 1' position of sugar in a nucleoside.

ANSWERS-

SECTION- A(MCQ)

1-a, 2-c , 3-c , 4-c, 5-d, 6-b, 7-b, 8- d, 9-a, 10- a

SECTION- B 11 (i)



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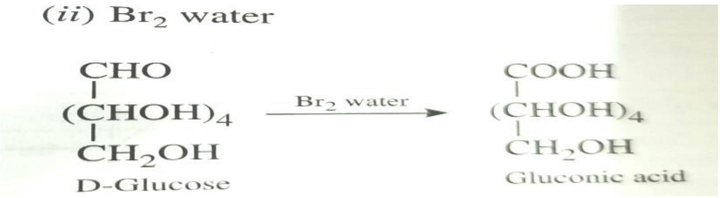
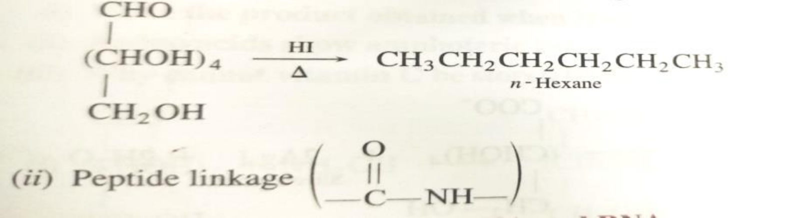


12 (i) Phosphodiester linkage
(ii) fibrous protein :- myosin, keratin, collegen etc
Globular protein :- Insulin, Haemoglobin

13

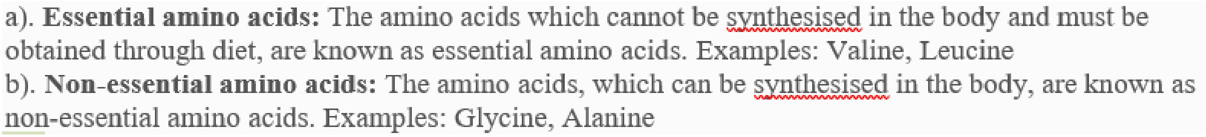


(i) On prolonged heating with HI, glucose gives *n*-hexane.

$$\begin{matrix} CHO \\ | \\ (CHOH)_4 \\ | \\ CH_2OH \end{matrix} \xrightarrow[\Delta]{HI} \underset{n\text{-Hexane}}{CH_3CH_2CH_2CH_2CH_2CH_3}$$

(ii) Peptide linkage $\left(\begin{matrix} O \\ \| \\ -C-NH- \end{matrix} \right)$

14.

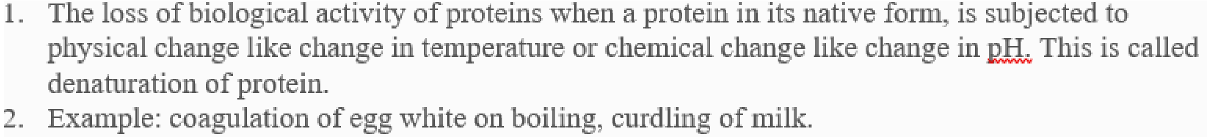


a). **Essential amino acids:** The amino acids which cannot be synthesised in the body and must be obtained through diet, are known as essential amino acids. Examples: Valine, Leucine

b). **Non-essential amino acids:** The amino acids, which can be synthesised in the body, are known as non-essential amino acids. Examples: Glycine, Alanine

15.The bases present in RNA are adenine (a) , guanine (b) , cytosine (c) and uracil (U). Uracil is not present in DNA.

16.



1. The loss of biological activity of proteins when a protein in its native form, is subjected to physical change like change in temperature or chemical change like change in pH. This is called denaturation of protein.
2. Example: coagulation of egg white on boiling, curdling of milk.

17. (i) As vitamin C is water soluble, therefore, it is readily excreted in urine and hence cannot be stored in the body.

(ii)contain free aldehyde group.

18. (i).peptide bonds (ii).ribosomes

19. (i) amylose (ii) glucose

20. (i) vitamin K (ii) vitamin A, D, E and K

SECTION -C (SA)

21. (a) Invert sugar:

Sucrose is dexorotatory which on hydrolysis gives glucose and fructose. This mixture is laevorotatary so it is called invert sugar.

(b)□**Glycosidic linkage:** The oxide linkage formed by the loss of a water molecule when twomonosaccharides are joined together through oxygen atom is called glycosidic linkage.

(c) Oligosaccharides

Carbohydrates which gives 2 to 10 monosaccharide units on hydrolysis

Examples – Sucrose, Lactose, Maltose

22. (a) Amylose is a long unbranched chain polymer of α-D (+) glucose.

Amylopectin is a branched chain polymer of α-D glucose.

(b) Globular protein and its shape is spherical.

(c) Liver and adipose tissue.

23.(a) absence of free-CHO group.

(b) Due to the presence of both acidic (-COOH) and basic ($-NH_2$) group in the same molecule/ formula of zwitter ion.

(c) Because the H-Bonds and formed between specific pairs of bases/ pairing between A & T and Between C & G

(d) They are excreted in urine/ can not be stored in body.

24. **Fibrous proteins**

a) When the polypeptide chains run parallel and are held together by hydrogen and disulphide bonds,then fibre– like structure is formed.

b) These proteins are generally insoluble in water

(c) Examples: keratin (present in hair, wool, silk) and myosin (present in muscles)

Globular proteins

(a) This structure results when the chains of polypeptides coil around to give a sphericalshape.

(b)These are usually soluble in water.

(c)Examples: Insulin and albumins

25.

DNA	RNA
(i) It has double stranded α– helix structure.	(i) It has single stranded α– helix structure.
(ii) The sugar present in DNA is 2- deoxy-D-(-) ribose.	(ii) The sugar present in RNA is D-(-)-ribose.
(iii) It contains cytocine & thymine as pyrimidine.	(iii) It contains cytocine & uracil as pyrimidine.

26. (a) Keratin being a fibrous protein insoluble in water.
    (b) DNA has unique properties of replication but RNA usually does not replicate.
  (b) α-amino acids act as zwitter ions (H_3N-CHR-COO) or dipolar ions.

27. (a) Glucose gives silver mirror with Tollen’s reagent and brick-red ppt with Fehling’s solution.
   (b) All sugar contain at least one asymmetric carbon atom and therefore, are optically active.
   (c) Aspartic acid and phenylalanine

28. (a).Saccharic Acid
   (b).gluconic acid
   (c). n hexane

29. (a) Peptide linkage is an amide linkage form between -COOH group of one α-amino acid and -NH_2 group of otherα- amino acid by loss of water molecule .
    (b).The four bases present in DNA are :A ,T ,G AND C
    (c).In RNA, Thymine (T) is absent. It has Uracil (U) in place of Thymine.

30. (a) Maltose is disaccharide.
    (b) Fibrous proteins have thread like structure and are insoluble in water. Globular proteins form a-helix and are soluble in water.
    (c) Vitamin D

SECTION -D (LONG ANSWER)

31. (a) on boiling point the water soluble globule proteins unfold and helix get uncoiled. During this change intra molecular H-B get disturbed. The water molecule get attached to the uncoiled protein molecules through H-B.

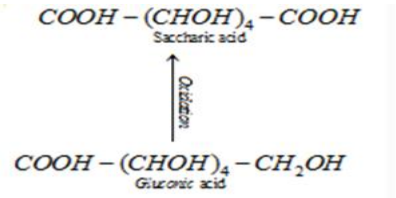
(b) (i) Hydrogen bonds between $\underset{\underset{O}{||}}{-C-}$ and $\underset{\underset{H}{|}}{-N-}$

Groups of the same polypeptide chains.

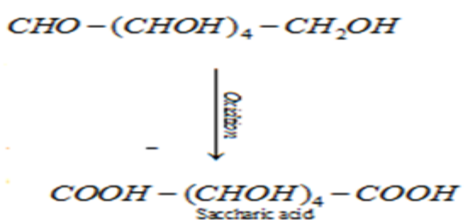
(ii) group belonging to different polypeptide chains.

(c) (i) Glucose (ii) vitamin H (iii) vitamin-D (iv)Glycine

32.(a) (i)



(ii)



(b) (i)Due to absence of free -CHO group.
  (ii) These are soluble in water hence readily excreted in urine and cannot be store in body so must be supplied daily in diet.
  (iii)It contains both amino(-NH_2) and carboxyl (-COOH) group thus react with acids and bases.

33.(a) Due to lack of Vitamin A is Xerophthalmia and vitamin E fragility of RBC and mascular weakness.

(b) Adenine , guanine and cytosine are present in both DNA and RNA.

DNA and RNA are considering as acid because they are from phosphate group which readity remove proton so both are highly acidic.

(c) Both are reducing sugar because both contains free aldehydic & ketonic group which undergo oxidation forming easily carboxylic acid and in the process reactive reagents are reduce easily.

34. (a) The amino acid exist as dipolar ion called zwitter ion, in which proton goes from carboxyl group to the amino group.

(b) Secondary structure of protein tells us about the manner in which the polypeptide chains are arranged and folded i.e. it is helical or pleated structure.

(c) When tertiary structure of proteins undergoes folding, coiling or bonding giving three.

(d) Cellulose on complete hydrolysis give β- glucose.

35. (a) DNA has double stranded α-helix structure while RNA has single α-stranded helix.

(b) Sucrose is dextroratotory on hydrolysis gives glucose & fructose. This mixture is leavo rotatory is called inverse sugar.

(C) Glucose contains an aldehyde group in its open structure but form a cyclic acetalstructure(also called pyranose).

(d) Nucleotides

Assertion and Reason Type Questions

1. Assertion- Fructose does not contain an aldehyde group but still reduces Tollen's reagent.

   Reason – In the presence of base, fructose undergoes rearrangement to form glucose and mannose.
2. Assertion- Glycosides are hydrolysed in acidic medium.

   Reason – Glycosides are acetals.
3. Assertion- Sucrose is non – reducing sugar.

   Reason – It has a Glycosides linkage.
4. Assertion- Insulin is a globular protein.

   Reason – Globular proteins are water soluble.
5. Assertion- All enzymes are proteins but all proteins are not enzymes.

   Reason – Enzymes are biocatalysts and possess a stable configuration having an active site pocket.

Ans. 1- (a) 2-(a) 3-(b) 4-(a) 5-(a)

Kendriya Vidyalaya Sangathan, Ranchi Region

Sample paper 1, 2023-24 (Solved)

TIME: 3 HOURS Max. Marks 70

General Instructions:

Read the following instructions carefully:

- ***(i) All questions are compulsory.***
- ***(i) There are 33 questions in this paper with internal choice.***
- *(ii) **SECTION A** Consists of **16** multiple-choice questions carrying **1 mark** each.*
- *(iii) **SECTION B** Consists of **5** veryshort answer questions carrying**2 marks** each.*
- *(iv) **SECTION C** Consists of **7** short answer questions carrying**3 marks** each.*
- *(v) **SECTION D** Consists of **2 case- based** questions carrying**4 marks** each.*
- (vi) ***SECTION E** Consists of **3 long answer** questions carrying**5 marks** each.*

SECTION A

The following questions are ***multiple-choice questions*** with one correct answer. Each question carries 1 mark

1. An electrochemical cell can behave like an electrochemical cell when---------

(a) E cell =0 (b) E cell > E ext (c) E ext> E cell (d) E cell = E ext

2. Which of the following statement is ***not*** correct for catalyst?

(a) It catalyses the forward and backward reaction to the same extent

(b) It alters Δ G of the reaction.

(c) It is a substance that does not change equilibrium constant of a reaction.

(d) It provides an alternate mechanism by reducing activation energy between reactants and products.

3. When ***initial concentration*** of a reactant is doubled in a reaction, its half life period is not affected. The order of the reaction is: (a) zero (b) first

(c) second (d) more than zero but less than first

4. The half life period of a first order chemical reaction is 6.93 minutes. The time required for ***99% completion*** of the reaction will be : (log 2 = 0.3010)

(a) 230.3 minute (b) 23.03 minute (c) 46.06 minute (d) 460.6 minute

5. Which one of the following shows ***highest*** magnetic moment?

(a) Fe^{2+} (b) Co^{2+} (c) Cr^{3+} (c) Ni^{2+}

6. ***The structure*** of diamagnetic nickel complex,$[Ni(CN)_4]^{2-}$ is

(a) trigonal bipyramidal (b) tetrahedral (c) square planar (d) distorted octahedral

7. The complex having ***minimum*** Δ_0 value

(a) $[Co(NH_3)_6]^{3+}$ (b) $[Cr(H_2O)_6]^{3+}$(c) $[Cr(CN)_6]^{3-}$(d) $[CoCl_6]^{3-}$

8. A primary alkyl halide would ***prefer*** to undergo:

(a) S_N^1 reaction (b) S_N^2 reaction (c) α-elimination (d) racemization

9. Consider the following compounds:

$C_6H_5NH_2$	$C_6H_5CH_2NH_2$	$C_6H_5CH_2CH_2NH_2$
I	II	III

What is the correct order of ***basicity*** of the above compounds

(a) I > II > III (b) III> I >II (c) III > II >I (d) I > III > II

10. Amines that ***can not*** be prepared by Gabriel phthalimide synthesis is

(a) benzylamine (b) aniline (c) methylamine (d) iso-butylamine

11. HCHO was treated with a ***reagent X***. The product formed upon hydrolysis in the presence of an acid gave C_2H_5OH. The reagent X is :

(a) Aqueous KOH (b) alcoholic KOH (c) CH_3MgI (d) alcoholic KCN

12. When phenol is heated with excess of ***bromine water***, it gives :

(a) m-bromophenol (b) o- and p-bromophenol

(c) 2,4-dibromophenol (d) 2,4,6-Tribromophenol

Assertion- Reason Type Questions:

For question No. 13 to 16, select the most appropriate answer from the options given below:

(a) Both A and R are true and R is the correct explanation of A

(b) Both A and R are true but R is not the correct explanation of A.

(c) A is true but R is false.

(d) A is false but R is true.

13. **Assertion :** Amines are more basicthan esters and ethers.

Reason: Nitrogen is less electronegative than oxygen. It is in better position to accommodate the positive charge on the proton.

14. **Assertion :**The boiling point of alcohols is higher than hydrocarbons of comparable molecular mass

Reason: Alcohols show intramolecular hydrogen bonding.

15. **Assertion :**All naturally occurring α-aminoacids except glycine are optically active.

Reason: Most naturally occurring amino acids have L- configuration.

16.**Assertion :**Transition metals have high melting points.

Reason: Transition metals have completely filled d-orbitals.

SECTION- B (2 Marks)

17.(i) Write down the ***IUPAC*** name of the complex : $[Co(NH_3)_5(NO_2)](NO_3)_2$

(ii) Write the ***formula*** of the complex Potassium tetracyanidonickelate(II)

18. The rate of a reaction quadruples when the temperature changes from 293 K to 313 K. Calculate the ***energy of activation*** of the reaction assuming that it does not change with temperature. [log 4=6021]

19. Define the terms: **(a)** Anomers **(b)** Invert sugar

OR

What happens when **D-glucose** is treated with : (i) HI (ii) HNO_3

20. Give ***reasons*** for the following:

(i) Grignard reagent should be prepared under ***anhydrous*** conditions.

(ii) Ethyl iodide undergoes S_N2 reaction ***faster*** than ethyl bromide.

OR

(a) Arrange the given set of compounds in the ***increasing order*** of the boiling points

Bromomethane, Bromoform, Chloromethane, Dibromomethane.

(b) Chloroform is ***stored*** in closed dark coloured completely filled bottles. why?

21. Calculate the ***time*** to deposit 1.5 g of silver at cathode when a current of 1.5 A is passed through the solution of $AgNO_3$

SECTION C(3 Marks)

22. (A),(B) and (C) are three non cyclic functional isomers of a carbonyl compound with molecular formula C_4H_8O. Isomers (A) and (C) give positive Tollen's test whereas isomer (B) does not give Tollen's test but gives positive iodoform test, Isomers (A) and (B) on reduction with Zn(Hg)/conc.HCl give the same product (D). ***Identify*** (A),(B),(C) and (D)

23. A reaction is ***second order*** with respect to a reactant. How is the rate of reaction affected if the concentration of the reactant is (i) doubled (ii) reduced to half?

24. Account for ***any 3*** of the following observations **:**

(a) Ethylamine is ***soluble*** in water whereas aniline is not.
(b) Aniline does ***not*** undergo Friedel-Crafts reaction.
(c) Gabriel phthalimide synthesis is preferred for synthesizing ***primary*** amines.
(d) Primary amines have ***higher*** boiling point than tertiary amines.

25. (i) what type of ***isomerism*** is shown by the complex $[Cr(H_2O)_6]Cl_3$?
(ii) On the basis of Crystal Field Theory write the electronic configuration for d^4 ion if $\Delta_o > P$.
(iii) Write hybridization and shape of $[CoF_6]^{3-}$ (Atomic number of Co=27)

26. Give reasons
(a) ***An increase*** in temperature is observed on mixing chloroform and acetone.
(b) Aquatic animals are more comfortable in ***cold water*** than in warm water.
(c) The preservation of fruits by adding concentrated sugar solution protects against bacterial action.

OR

A 4% solution (w/w) of sucrose ($M=342 gmol^{-1}$) in water has a freezing point of 271.15 K. Calculate the ***freezing point*** of 5% glucose ($M=180 gmol^{-1}$) in water.

27 . (i) Give reason for the following: 1x3=3
(a) o-nitrophenol is ***more*** steam volatile than p-nitrophenol.
(b) Phenol undergoes electrophilic substitution more ***easily*** than benzene.
(ii) Give equation for the reaction when phenol is treated with ***conc.*** HNO_3.

28. (i) Write the ***equations*** involved in the following reactions: 1x2=2
(a) Reimer-Tiemann reaction (b) Kolbe's reaction
(ii) Dipole moment of phenol is ***smaller*** than that of methanol. Why? 1

SECTION D

29.Biomolecules are the organic compounds present as essential constituents of living organisms in different cells, they include carbohydrate, proteins ,enzymes, nucleic acids, vitamins, hormones etc. Glycosidic linkage and peptide bonds are two types of covalent bonds which can be found in living systems. The formation of both these bonds involve removal of water molecules. But the two bonds are different from each other and play a very important role in the existence of living organisms on the earth. There are 13 vitamins known till today four of which are fat soluble (A,D,E,K) and rest of which are water soluble.

Answer the following questions

(a) Name the linkage ***connecting*** monosaccharide units in polysaccharides. **1**
(b) Name the vitamins that are ***stored*** in liver and adipose tissues. (any two) **1**
(c) ***Differentiate*** between peptide linkage and glycosidic linkage. Give two points. **2**

OR

What happens when ***glucose*** reacts with acetic anhydride? What does it suggest about the structure of glucose?

30. SCUBA diving is very fascinating but it is very important to be aware of 'The Bends' a condition in which nitrogen gas bubbles are formed in the body tissues, the nitrogen is soluble in blood and can cause intoxication at sufficient concentration. For this reason the Indian Navy advises divers using compressed air not to go below 130 feet. The total pressure at that depth is 4.8 atm. Solubility of nitrogen in water at 1 atm is 1.8×10^{-3} g/mL and mole percent of nitrogen in air is 78. The condition of 'The Bends' is related to Henry's Law.

(a) ***State*** Henry's Law. 1

(b) Which ***gas*** can be taken or filled in the gas cylinders along with $N_2$to avoid intoxication in the body of deep-sea divers

(c) What will be the ***solubility*** of nitrogen at a depth of 130 feet as per the above informations.

OR

Write ***limitations*** of Henry's law

31. Answer the following:

(i) (a) Why is Cr^{3+} reducing and Mn^{3+} oxidizing when both have d^4 configuration?

(b) Sc^{3+} is ***colorless*** in aqueous solution whereas Ti^{3+} is coloured .why?

(c) Out of Cu_2Cl_2 and $CuCl_2$, which is more ***stable*** and why?

(ii) Complete and balance the following chemical equations:

(a) $Fe^{2+} + MnO_4^- + H^+ \rightarrow$? (b) $Cr_2O_7^{2-} + 3Sn^{2+} + 14H^+ \rightarrow$?

32. (i) Calculate the ***potential*** of hydrogen electrode in contact with a solution whose pH is 10.

(ii) Predict the ***products of electrolysis*** when:

(a) an aqueous solution of $AgNO_3$ is electrolysed using ***silver electrodes***.

(b) a dilute solution of H_2SO_4 using ***platinum*** electrodes.

(iii) Alkaline medium ***inhibits*** rusting of iron .why?

OR

(i) In a galvanic cell the following reactions take place

$$2Cr_{(s)} + 3Cd^{2+} \rightarrow 2Cr^{3+} + 3Cd_{(s)}$$

$Cr^{3+}/Cr = -0.74$ V ;E° Cd^{2+}/Cd E° =-0.40 V

Calculate **(a)**the standard cell potentials of **(b)** the standard Gibbs Free Energy change ΔG^0 (**c**) Equilibrium constant (k_c) [Antilog 0.501=3.17]**3**

(ii) Give the reactions taking place while charging and discharging of lead storage battery.**2**

33.(i) Write chemical reactions to bring following conversions; 1x2=2

(a) Benzyl alcohol to phenyl ethanoic acid

(b) Propanone to Propene

(ii)An organic compound with the molecular formula $C_9H_{10}O$ forms 2,4-DNP derivative, reduces Tollen's reagent, and undergoes Cannizzaro reaction. On vigorous oxidation, it gives 1,2-benzenedicarboxylic acid. Identify the compound giving chemical equations . **3**

OR

(i) Give reasons:**1x3=3**

(a) HCHO is more reactive than CH_3CHO towards addition of HCN.

(b) Alpha hydrogen of aldehyde and phenol is acidic in nature.

(c) Carboxylic acid is stronger acid than phenol.

(ii) Give chemical test to ***distinguish*** between ; 1x2=2

(a) Ethanal and Propanal. (b) Phenol and Benzoic acid

CLASS –XII
SUBJECT-CHEMISTRY
SAMPLE PAPER :- 1

Q.No.	ANSWER/SOLUTION	MARKS
1	(c) $E_{ext.} > E_{cell}$	1
2	(b) It alters ΔG of the reaction.	1
3	(b) first	1
4	(c) 46.06 minute $k = \frac{2.303}{t} \log\left(\frac{a}{a-x}\right)$ $\frac{0.693}{t_{1/2}} = \frac{2.303}{t} \log\left(\frac{a}{a-x}\right)$ $\frac{0.693}{6.93} = \frac{2.303}{t} \log\left[\frac{100}{100-99}\right]$ $t = 46.06$ min	1
5	(a) Fe^{2+}	1
6	(c) square planar	1
7	(d) $[CoCl_6]^{3-}$	1
8	(b) S_N2 reaction	1
9	(c) III > II >I	1
10	(b) aniline (As aryl halides do not undergo SN reactions)	1
11	(c) CH_3MgI	1
12	(d) 2,4,6-Tribromophenol	1
13	**(a)** Both A and R are true and R is the correct explanation of A.	1
14	**(c)** A is true but R is false.	1
15	**(b)** Both A and R are true and R is ***not*** the correct explanation of A.	1
16	**(c)** A is true but R is false.	1
17	(i) Pentaamminenitrito-N-cobalt(III) nitrate (ii) $K_2[Ni(CN)_4]$	1
18	$k_2 = 4k_1 \Rightarrow \frac{k_2}{k_1} = 4$ $\log\frac{k_2}{k_1} = \frac{E_a}{2.303\,R}\left[\frac{T_2 - T_1}{T_2 T_1}\right]$ $\log 4 = \frac{E_a}{2.303 \times 8.314}\left(\frac{313 - 293}{293 \times 313}\right)$ $2 \times \log 2 = \frac{E_a}{19.147}\left(\frac{20}{91709}\right)$ $E_a = \frac{2 \times 0.3010 \times 19.147 \times 91709}{20} = 52.85$ kJ/mol	1
19	(a)**Anomers-**Glucose exist in two stereoisomeric forms. In the aqueous solution ,these two forms are in equilibrium through the intermediate open chain form.In the α-D-glucose the -OH group at C_1 is towards right while in β-D-glucose the -OH group at C_1 is towards left. Such pair of stereoisomers which differ in configuration only around C_1 are called anomers. (b) **Invert sugar**- Hydrolysis of sugar brings about a change in sign of rotation from dextro (+) to laevo (-) and the product formed is called invert sugar. **OR** **(i)** D-Glucose with HI gives n-Hexane (correct chemical equation) (ii) D-Glucose with HNO_3 gives Saccharic acid (correct chemical equation)	1x2=2
20.	(i) Grignard reagent reacts with moisture present in apparatus or the starting material to give alkane(hydrocarbon) $RMgX + HOH \rightarrow R\text{-}H + Mg(OH)X$ (ii) I^- ion because of its bigger size and lower electronegativity is a better leaving group than Br^- ion. OR	1 1

(i)Chloromethane<Bromomethane<Dibromomethane< Bromoform, 1

(ii) Chloroform is slowly oxidized by air in the presence of light to an extremely poisonous gas carbonyl chloride(phosgene) $2CHCL3+O2 \xrightarrow{light} 2COCl_2 + 2HCl$ 1

21 At Cathode $Ag^+(aq) \rightarrow Ag(s)$ 1

108g 96500 C 1

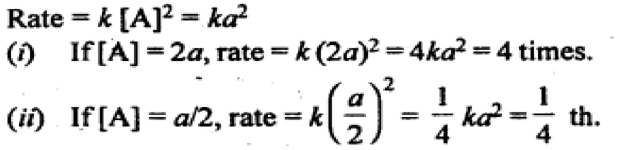
Therefore 1.05 g of silver is deposited by passing charge=96500x1.5/108=1340.27C

Time to deposit 1.5 g of Ag=Q/I=1340.27/1.5 =893.51s or 14.85min

22 **A**=$CH_3CH_2CH_2CHO$, **B**= $CH_3COCH_2\ CH_3$ 1/2x4=2

C= $(CH_3)_2CHCHO$**D**= $CH_3CH_2CH_2\ CH_3$

23



$$\text{Rate} = k\,[A]^2 = ka^2$$

(i) If $[A] = 2a$, rate $= k\,(2a)^2 = 4ka^2 = 4$ times. 1

(ii) If $[A] = a/2$, rate $= k\left(\frac{a}{2}\right)^2 = \frac{1}{4}\,ka^2 = \frac{1}{4}$ th. 1

24 **(a)** Ethylamine when added to water forms intermolecular H-bonds with water but aniline does not undergo H-bonding with water to a very large extent due to the presence of large hydrophobic $-C_6H_5$ 1x3=3

(b) Friedel craft reaction is carried out in presence of $AlCl_3$which is Lewis acid while aniline is Lewis base both form salt.

(c) Gabriel phthalimide synthesis results in the formation of primary amines only.Sec. &tert. amines are not formed in this synthesis.

(d) Due to the presence of H-atoms primary amines undergo extensive intermolecular H-bonding.

25 (i) Solvate isomerism 1x3=3

(ii) Electronic configuration is $t_2g^4\ e_g^0$ or by diagram.

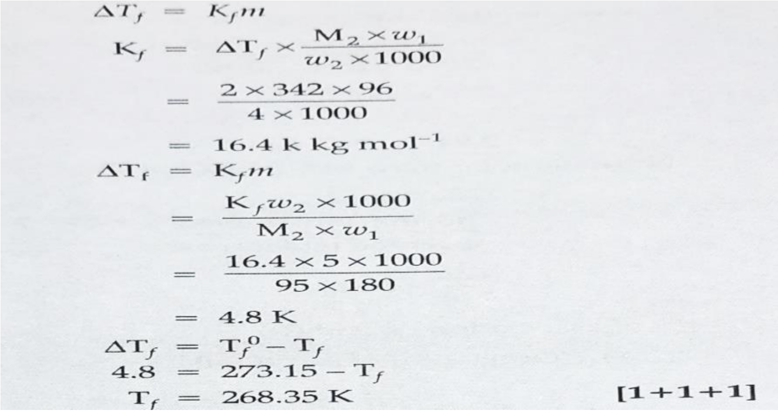
(iii) Hybridization is sp^3d^2 and shape is octahedral.

26 (a) Due to strongerinteraction between chloroform and acetone than pure chloroform or acetone interaction. 1x3=3

(b) K_H value forboth N2 & O2 increases with increase of temperature indicating that solubility of gases increases with decrease of temperature.

(c) Due to osmosis,a bacterium on fruit loses water ,shrivels and dies.

OR



$$\Delta T_f = K_f m$$

$$K_f = \Delta T_f \times \frac{M_2 \times w_1}{w_2 \times 1000}$$

$$= \frac{2 \times 342 \times 96}{4 \times 1000}$$

$$= 16.4 \text{ k kg mol}^{-1}$$

$$\Delta T_f = K_f m$$

$$= \frac{K_f w_2 \times 1000}{M_2 \times w_1}$$

$$= \frac{16.4 \times 5 \times 1000}{95 \times 180}$$

$$= 4.8 \text{ K}$$

$$\Delta T_f = T_f^0 - T_f$$

$$4.8 = 273.15 - T_f$$

$$T_f = 268.35 \text{ K}$$

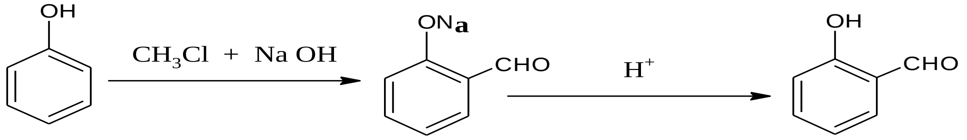
[1+1+1]

27 (i) (a) o-Nitrophenol is steam volatile due to intramolecular hydrogen bonding while p-nitrophenol is less volatile due to intermolecular hydrogen bonding. 1x3=3

(b) The -OH group attached to benzene ring is highly activating group.The lone pair on oxygen is delocalized into benzene ring and makes the phenol more electron rich than benzene.

(ii) 2,4,6-trinitrophenol is formed.

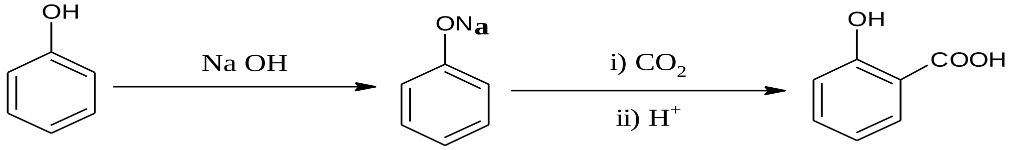
28 (i) (a) Reimer Tiemann Reaction 1



1

1

(b) Kolbe's Reaction



(ii) In phenol (1.54 D),C-O bond is less polar due to electron withdrawing effect of benzene ring, whereas in methanol (1.71D)C-O bond is more polar due to electron releasing effect of $-CH_3$ group.

29 (a) Glycosidic linkage. 1

(b) Vitamin A,D,E,K 1

(c) Peptide linkage is found between amino acids for their linkage, it is between -COOH & $--NH_2$ functional group forming –CONH- linkage

Glycosidic Linkage-It links monosaccharide units and there is –O—linkage. 2

OR

It gives glucose pentaacetate which has five acetyl group in structure it suggests presence of five -OH groups at different carbon atoms

30 (a) Henry's Law states that the partial pressure of the gas in vapour phase is directly proportional to the mole fraction of the gas in solution. 1

(b) Helium 1

(c) Pressure of nitrogen in air=78/100x1=0.78 atm

Acc. to Henry's law S1/S2 =P1/P2 2

$1.8X10^{-3}/S2 = 0.78/4.8 = 0.011 g/100mL$

OR

Henry's law holds good if following conditions are fulfilled

(i) The pressure is not too high.

(ii) The temperature is not very low.

(iii) The gas does not chemically combine with solvent

31 (i) Cr^{3+} has extra stability due to presence of half-filled t_2g^3. Thus Cr^{2+} undergoes oxidation and it acts as reducing agent. 1x5=5

Mn^{2+} has half filled d-subshell with extra stability hence Mn^{3+}undergoes reduction and it acts as an oxidizing agent.

(ii) Absence of unpaired d-electron in Sc^{3+} whereas in Ti3+ there is one unpaired electron or Ti^{3+} shows d-d transition.

(iii) $CuCl_2$ is more stable. As the size of Cu^{2+} is smaller than Cu^+ due to which more is the hydration enthalpy. Hence more will be stability.

(ii) (a) $5Fe^{2+} + MnO_4^- + 8H^+ \rightarrow Fe^{2+} + 4H_2O + 5Fe^{3+}$

(b) $Cr_2O_7 + 3Sn^{2+} + 14H^+ \rightarrow 2Cr^{3+} + 7H_2O + 3Sn^{4+}$

32 For hydrogen electrode,$H^+ + e^- \longrightarrow 1/2\ H_2$, 2 +2+1

Applying Nernst equation,

$$E_{H^+,\frac{1}{2}H_2} = E^\circ_{H^+,\frac{1}{2}H_2} - \frac{0.0591}{n}\log\frac{1}{[H^+]}$$

$$= 0 - \frac{0.0591}{1}\log\frac{1}{10^{-10}} \qquad \left\{\begin{array}{l} pH = 10 \\ \Rightarrow [H^+] = 10^{-10} M \end{array}\right\}$$

$$= -0.0591 \times 10$$

$$= -0.591\ V$$

(*i*) $AgNO_3(s) + aq \longrightarrow Ag^+(aq) + NO_3^-(aq)$

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

At cathode: Ag^+ ions have lower discharge potential than H^+ ions. Hence, Ag^+ ions will be deposited as Ag in preference to H^+ ions.

$$Ag^+(aq) + e^- \longrightarrow Ag(s)$$

At anode: As Ag anode is attacked by NO_3^- ions, Ag of the anode will dissolve to form Ag^+ ions in the solution.

$$Ag(s) \longrightarrow Ag^+(aq) + e^-$$

(b)

$$H_2SO_4(aq) \longrightarrow 2H^+(aq) + SO_4^{2-}(aq)$$

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

At cathode: $H^+ + e^- \longrightarrow H,$

$H + H \longrightarrow H_2(g)$

At Anode: $OH^- \longrightarrow OH + e^-$

$4OH \longrightarrow 2H_2O + O_2(g)$

Thus, H_2 gas is liberated at the cathode and O_2 gas at the anode.

(c) The hydroxyl ions consumes the protons or H+ to form water. Thus, the reaction medium doesn't have any hydronium ion left and the oxidation reaction of iron cannot proceed. Hence, we can say that an alkaline medium inhibits the rusting of iron.

OR

(a) Calculation of E°cell,

$$E^\circ_{cell} = E^\circ_{cathode} - E^\circ_{anode} = -0{\cdot}40 - (-0{\cdot}74) = \mathbf{+\ 0{\cdot}34\ V}$$

Calculation of ΔG°,

$$\Delta G^\circ = -nF\,E^\circ_{cell} = -(6\ mol) \times (96500\ C\ mol^{-1}) \times (0{\cdot}34\ V)$$

$$= -196860\ CV = -196860\ J = \mathbf{-196{\cdot}86\ kJ}$$

Calculation of Equilibrium Constant (K_c)

$$\Delta G^\circ = -2{\cdot}303\ RT\log K_c$$

$$\log K_c = \frac{(-)\,\Delta G^\circ}{2{\cdot}303\ RT} = (-)\frac{(-)\,196860}{2{\cdot}303 \times 8{\cdot}314 \times 298} = 34{\cdot}501$$

$$K_c = \text{Antilog}\ (34{\cdot}501) = \mathbf{3{\cdot}17 \times 10^{34}}$$

(ii)

Pb(s)→Pb(aq)2++2e– (oxidation)

Pb(aq)2++SO4(aq)2–→PbSO4(s) (precipitation)

Pb(s)+SO4(aq)2–→PbSO4(s)+2e– (Overall reaction at anode during discharge)

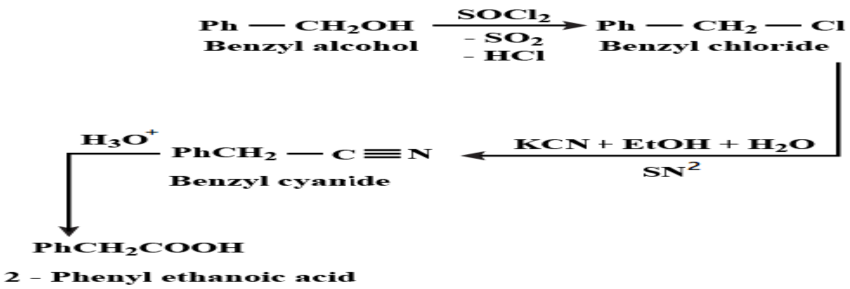
Reduction reaction at cathode:

PbO2(s)+4H(aq)++2e–→Pb(aq)2++2H2O (reduction)

Pb(aq)2++SO4(aq)2–→PbSO4(s) (precipitation)

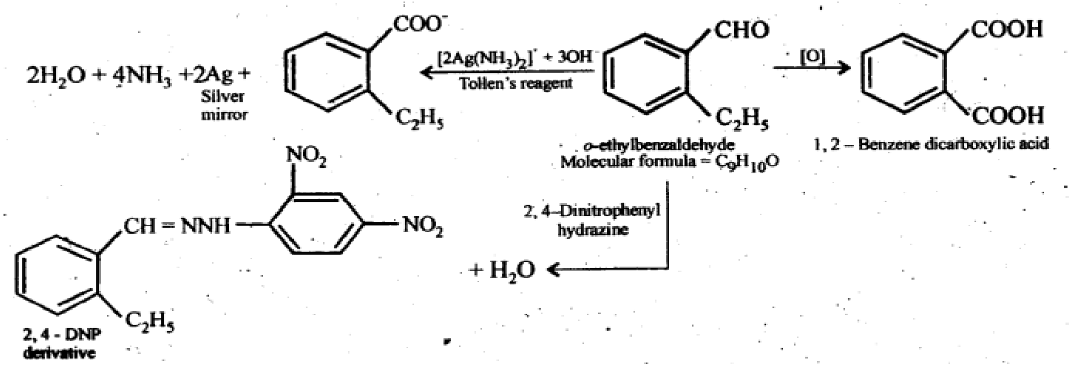
PbO2(s)+4H(aq)++SO4(aq)2–+2e–→PbSO4(s)+2H2O(l) (Overall reaction at cathode during discharge)

33 (i) (a)



(b) $CH_3COCH_3 \xrightarrow{NaBH4} CH_3CH(OH)CH_3 \xrightarrow{Conc.H2SO4} CH_3CH=CH_2$

(ii)**o-ethylbenzaldehyde**

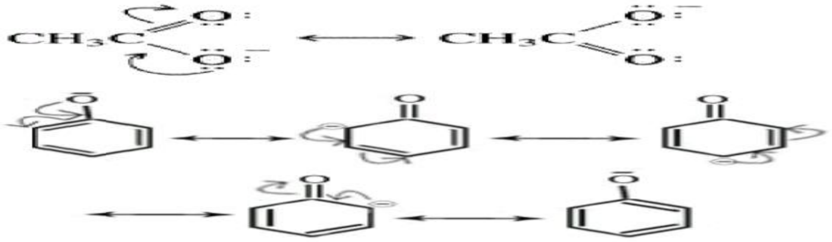


OR

(i) (a) Due to +I effect of methyl group in CH_3CHO 1

(b) Due to the strong electron withdrawing effect of the carbonyl group and resonance stabilization of conjugate base.

(c) The carboxylate ion is more stabilised than phenoxide ion, so carboxylic acids are more acidic than phenols. The conjugate base of carboxylic acid, a carboxylate ion, is stabilised by two equivalent resonance structures in which the negative charge is at the more electronegative oxygen atom. The conjugate base of phenol, a phenoxide ion, has non-equivalent resonance structures in which the negative charge is at the less electronegative carbon atom.



(ii) (a) By Iododform test ethanal gives yellow ppt of iodoform.

(b) Phenol gives violet colour with $FeCl_3$ while benzoic acid does not. Or Benzoic acid gives effervescence with aqueous $NAHCO_3$ while phenol does not.

KENDRIYA VIDYALAYA SANGATHAN RANCHI REGION

SAMPLE PAPER 2[2023-24] (Solved)

CHEMISTRY THEORY (043)

MM:70 Time: 3 hours

General Instructions: Read the following instructions carefully.

a) There are 35 questions in this question paper with internal choice.
b) SECTION A consists of 16 multiple-choice questions carrying 1 mark each.
c) SECTION B consists of 5 very short answer questions carrying 2 marks each.
d) SECTION C consists of 7 short answer questions carrying 3 marks each.
e) SECTION D consists of 2 case- based questions carrying 4 marks each.
f) SECTION E consists of 3 long answer questions carrying 5 marks each.
g) All questions are compulsory.
h) Use of log tables and calculators is not allowed

SECTION A

The following questions are multiple-choice questions with one correct answer. Each question carries 1 mark.

1. Which of the following undergoes nucleophilic substitution exclusively by SN^1 mechanism? 1

(a) Benzyl chloride (b) Ethyl chloride
(c) Chlorobenzene (d) Isopropyl chloride

2. Which of the following organ halogen compound when heated with alcoholic KOH does not undergo dehydrohalogenation reaction? 1

(a) Secondary butyl chloride (b) Tertiary butyl chloride
(c) Isopropyl chloride (d) Neopentyl chloride

3. The number of moles of $KMnO_4$ that are needed to react completely with one mole of ferrous oxalate in acidic solution is 1

(a) 3/5 (b) 2/5 (c) 4/5 (d) 1

4. For a reaction A +B → C, the experimental rate law is found to be $R=k\,[A]^1[B]^{1/2}$. Find the rate of the reaction when [A] = 0.5 M, [B] = 0.1 M and k=0.03. 1

a) $4.74 \times 10^{-2}\ (L/mol)^{1/2}\ s^{-1}$ b) $5.38 \times 10^{-2}\ (L/mol)^{1/2}\ s^{-1}$
c) $5.748 \times 10^{-2}\ (L/mol)^{1/2}\ s^{-1}$ d) $4.86 \times 10^{-2}\ (L/mol)^{1/2}\ s^{-1}$

5. For a certain redox reaction, E° is positive. This means that 1

(a) ΔG° is positive, K is greater than 1 (b) ΔG° is positive, K is less than 1
(c) ΔG° is negative, K is greater than 1 (d) ΔG° is negative, K is less than 1

6. In the reaction $2A + B \rightarrow A_2B$,order of reaction w.r.t.A is 2 and w.r.t B is 1, if the concentration of A is doubled and that of B is halved, then the rate of the reaction will 1

a) increase 2 times b) increase 4 times c) decrease 2 times d) remain the same

7. Which of the following is true for the basicity of amines? 1

(a) Alkyl amines are generally less basic than aryl amines because N is sp hybridised
(b) Aryl amines are generally more basic than alkyl amines due to aryl group
(c) Aryl amines are generally less basic than alkyl amines due to delocalisation of lone pair of electrons in the benzene ring
(d) Alkyl amines are generally less basic than aryl amines because lone pair of electrons on N in the aryl amines are not delocalised in the benzene ring

8. The correct IUPAC name of the following compound is $[Cr(NH_3)_5(NCS)][ZnCl_4]$ 1

(a) Penta amine isothicoyanato chromium (III) tetrachlorozincate (II)
(b) Penta amine isothicocyanatezinc chloridechromate (III)
(c) Penta amine isothicoyanato chromate (II)
(d) isothiocyanatopenta amine chromium (II) zinc chloride (IV)

9. Which of the following alcohols will give the most stable carbocation during dehydration? 1

(a) 2-methyl-1-propanol (b) 2-methyl-2-propanol
(c) 1-Butanol (d) 2-Butanol

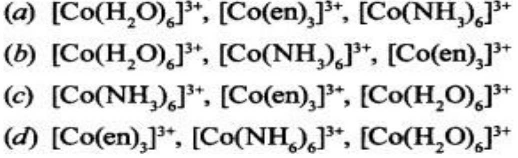
10. The compound that does not liberate CO2, on treatment with aqueous sodium bicarbonate solutionis: 1

a) Benzoic acid b) Salicylic acid
c) Carbolic acid d) Benzenesulphonic acid

11 The decomposition of dimethyl ether is a fractional order reaction. The rate is given by rate =k (PCH3OCH3)$^{3/2}$. If the pressure is measured in bar and time in minutes, then what are the units of rate and rate constant? 1

(a) bar min^{-1}, bar^{2} min^{-1} (b) bar min^{-1}, bar$^{1/2}$ min^{-1}
(c) bar$^{1/2}$ min^{-1}, bar^{2} min^{-1} (d) bar min^{-1}, bar$^{-1/2}$ min^{-1}

12 Correct increasing order of wavelength of absorption in visible region for complex of Co^{3+} is 1



(*a*) $[Co(H_2O)_6]^{3+}$, $[Co(en)_3]^{3+}$, $[Co(NH_3)_6]^{3+}$
(*b*) $[Co(H_2O)_6]^{3+}$, $[Co(NH_3)_6]^{3+}$, $[Co(en)_3]^{3+}$
(*c*) $[Co(NH_3)_6]^{3+}$, $[Co(en)_3]^{3+}$, $[Co(H_2O)_6]^{3+}$
(*d*) $[Co(en)_3]^{3+}$, $[Co(NH_6)_6]^{3+}$, $[Co(H_2O)_6]^{3+}$

Assertion- Reason Type Questions: 1

For question No. 13 to 16, select the most appropriate answer from the options given below:

(a) Both A and R are true and R is the correct explanation of A
(b) Both A and R are true but R is not the correct explanation of A.
(c) A is true but R is false.
(d) A is false but R is true.

13 **Assertion (A)**: Like bromination of benzene, bromination of phenol is also carried out in presence of Lewis acid. 1

Reason (R): Lewis acid polarises the bromine molecule.

14 **Assertion (A)**: Fructose does not contain an aldehyde group but still reduces Tollen's reagent. 1

Reason (R): In the presence of a base, fructose undergoes rearrangement to form glucose and mannose.

15 **Assertion (A)**: N,N-Diethyl benzene sulphonamide is insoluble in alkali 1

Reason (R): Sulphonyl group attached to nitrogen atom is strong electron withdrawing group

16 **Assertion (A)**: Lanthanoids show a limited number of oxidation states whereas actinoids show alarge number of oxidation states. 1

Reason (R): Energy gap between 4f, 5d, and 6s orbitals is small whereas that between 5f, 6d and 7s orbitals is large

SECTION B(2 Marks)

17 Show that in case of a first order reaction, the time taken for completion of 99.9% reaction is tentimes the time required for the half change of the reaction? 2

18. Three amino acids are given below: 2

Alanine $CH_3CH(COOH)(NH_2)$ Aspartic acid $HOOC\text{-}CH_2CH(COOH)(NH_2)$ and Lysine $H_2N\text{-}(CH_2)_4\text{-}CH(COOH)(NH_2)$

a) Make two tripeptides using these amino acids and mark the peptide linkage in both cases.

b) Represent Alanine in the zwitter ion form.

OR

Write the main structural difference between DNA and RNA. Of the four bases, name those which are common to both DNA and RNA.

19. Give Suitable reason: 2

a) Sulphuric acid is not used during the reaction of alcohols with KI.

b) The dipole moment of chlorobenzene is lower than that of cyclohexyl chloride.

20. Write the formula for the complex dichloridobis (ethane-1, 2-diamine) cobalt (III) ion. Draw its geometrical and optical isomers. 2

OR

The spin only magnetic moment of $[MnBr_4]^{-2}$ is 5.9 BM. Predict the geometry of the complex.

21. An aqueous solution of an unknown salt of palladium is electrolysed by a current of 3.0A passing for 1 hour. During electrolysis, 2.997 g of palladium ions are reduced at the cathode. What is the charge on the palladium ions in solution? (Molar mass of Pd=106.4gm/mol) 2

SECTION C(3 Marks)

22. The thermal decomposition of HCOOH is a first order reaction with a rate constant of 2.4×10^{-3} sec^{-1} at a certain temperature. Calculate how long will it take for 3/4th of HCOOH to decompose? 2

(log 4=0.6021, log 3=0.4771, log 0.25= -0.6021)

23. a) Predict the product when Hex-4-en-1-nitrile is treated with DIBALH at -78^0C with water. 2

b) Which is more basic aniline or methyl amine? Why?

c) Arrange the following acids in the increasing order of acidity :

CCl_3COOH, CH_3COOH, $CHCl_2COOH$, CH_2Cl,COOH

24. What happens when: 3

a) 2-Methylbut-1-ol is dehydrated with ConcH_2SO_4.

b) Phenol is oxidized with sodium dichromate/H^+.

c) Benzyl ethyl ether reacts with HI at 373 K.

25. a) A coordination compound with molecular formula $CrCl_3 .4H_2O$ precipitates one mole of AgCl with $AgNO_3$ solution. Its molar conductivity is found to be equivalent to two ions. What is the structural formula? 3

b) Using valence bond theory explain the geometry of $[Co(NH_3)_6\ ]^{+3}$ ion.

26. a) Out of 0.1 molal aqueous solution of glucose and 0.1 molal solution of KCl, which one will have higher boiling point and why? 3

b) A 5% solution (by mass) of cane sugar in water has freezing point of 271K.Calculate the freezing point of 5% glucose in water if freezing point of pure water is 273.15 K.

OR

Give suitable reason to justify your answer:

a) Gases always tend to be less soluble in liquids as temperature is raised.

b) People at higher altitudes suffer from a disease called anoxia.

c) Pure ethyl alcohol cannot be obtained from rectified spirit (95.6% of alcohol) even by fractionaldistillation.

27. Give suitable reason any three to justify your answer: 3

a) Amines are less acidic than alcohols of comparable molecular mass.
b) Methylamine in water reacts with ferric chloride to precipitate hydrated ferric oxide.
c) Diazonium salts of aromatic amines are more stable than those of aliphatic amines.
d) Tertiary amines do not undergo acylation reaction.

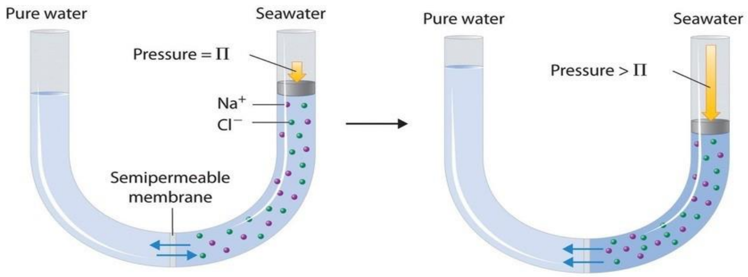
28. Give the IUPAC name of the product formed when: 3

a) 2-Methyl-1-bromopropane is treated with sodium in the presence of dry ether.
b) 1- Methyl cyclohexene is treated with HBr.
c) tert-Butyl bromide is treated with Ethanolic KOH followed with reaction with HBr in presenceof peroxide.

SECTION D (1+1+2=4 Marks)

29 Read the passage given below and answer the following questions:

Trees use osmotic pressure to transport water and other nutrients from the roots to the upper branches. Evaporation of water from the leaves results in a local increase in the salt concentration which generates an osmotic pressure that pulls water up the trunk of the tree to the leaves. Finally, a processcalled reverse osmosis can be used to produce pure water from seawater. As shown in givenFigure applying high pressure to seawater forces water molecules to flow through a semipermeable membrane that separates pure water from the solution, leaving the dissolved salt behind. Large-scale desalinization plants that can produce hundreds of thousands of gallons of freshwater per day are common in the desert lands of the Middle East, where they supply a large proportion of the freshwaterneeded by the population. Similar facilities are now being used to supply freshwater in southern California. Small, hand-operated reverse osmosis units can produce approximately 5 L of freshwater per hour, enough to keep 25 people alive, and are now standard equipment on US Navy lifeboats.



a) What happens when the external pressure applied becomes more than the osmotic pressure ofsolution?

b) Are equimolar solutions of sodium chloride and urea isotonic? Why?

c) A solution prepared by dissolving 8.95 mg of a gene fragment in 35ml of water has an osmotic pressure of 0.335 torr at 25^0C.Assuming the gene fragment is a non-electrolyte, determine its molar mass?(Given R= 0.0821atm.L/mol/K)

OR

c) The osmotic pressure of blood is 8.21 atm at 37^0C.How much glucose should be used per litre for an intravenous injection that is isotonic with blood? (Given R= 0.0821atm.L/mol/K)

30 Read the passage given below and answer the following questions:

Glucose is a simple sugar with the molecular formula $C_6H_{12}O_6$. Glucose is the most abundant monosaccharide, a subcategory of carbohydrates. Glucose is mainly made by plants and most algae during photosynthesis from water and carbon dioxide, using energy from sunlight, whereit is used to make cellulose in cell walls, the most abundant carbohydrate in the world.

In energy metabolism, glucose is the most important source of energy in all organisms. Glucose for metabolism is stored as a polymer, in plants mainly as starch and amylopectin, and in animals. as glycogen. Glucose circulates in the blood of animals as blood sugar. The naturally occurring formof glucose is D-glucose, while L-glucose is produced synthetically in comparatively small amounts and is less biologically active. Glucose is a monosaccharide containing six carbon atoms and an aldehyde group, and is therefore an aldohexose. The glucose molecule can exist in an open-chain (acyclic) as well as ring (cyclic) form. Glucose is naturally occurring and is found in its free state in fruits and other parts of plants. In animals, glucose is released from the breakdown of glycogen in a process known as glycogenolysis.

a) Glucose does not give 2, 4-DNP test and Schiff's test. Why?
b) What type of linkage is there is in amylopectin?
c) How do anomers differ from epimers?

OR

c) Write two function of carbohydrates in plants.

SECTION E (5 Marks each)

31 Give reasons for the following: 5
a) Transition elements act as catalysts
b) Cu^+ ion is not stable in aqueous solution.
c) Of the d^4 species, Cr^{+2} is strongly reducing while Mn^{+3} is strongly oxidising
d) $Cr_2O_7^{-2}$ ion is orange coloured.
e) Among the Lanthanoids, Ce (III) can easily be oxidised to Ce (IV).

32 a) Can Fe^{+3} oxidise Br^- to Br_2 under standard conditions? 5
$Fe^{+3}/Fe^{+2} = 0.77$ V , E^0 Br_2/Br^- $E^0 = 1.08$ V
b) Write Nernst equation and calculate emf of the cell at 298 K:
$Pt(s)/Br_2(1)/Br^-(0.010M)//H^+(0.030M)/H_2(g)$ (1bar)
,Pt(s)Given E^0 : $Br_2/Br^- = 1.08$V , log 1.11=0.0457

OR

i) On the basis of E^o values identify which amongst the following is the strongest oxidizing agent
$Cl_2(g) + 2e^- \rightarrow 2Cl^-$ $E^o = +1.36$ V,
$MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O$ $E^o = +1.51$ V
$Cr_2O_7^{2-} + 14H^+ + 6e^- \rightarrow 2Cr^{3+} + 7H_2O$ $E^o = +1.33$ V

ii) The following figure 2, represents variation of (Λm) vs $\sqrt{c}$ for an electrolyte.

Here Λm is the molar conductivity and c is the concentration of the electrolyte.

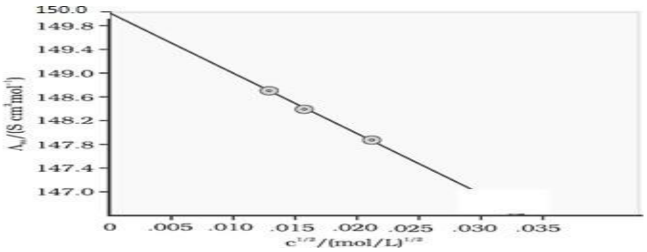


Figure 2

a) Define equivalent conductivity
b) Identify the nature of electrolyte on the basis of the above plot. Justify your answer.
c) The molar conductivity of 0.025 mol L^{-1} methanoic acid is 46.1 S cm^2 mol^{-1}. Calculate its degreeof dissociation and dissociation constant Given $\lambda^\circ(H^+) = 349.6$ S cm^2 mol^{-1} and λ°(HCOO-) = 54.6 S cm^2 mol^{-1}

33 An organic compound with molecular formula C_8H_8O forms an orange red precipitate 2, 4-DNP derivative, and gives yellow precipitate on heating with iodine in presence of NaOH. It neither reduces Tollen's reagents or Fehling's solution, nor does it decolourise bromine water or Baeyer' reagent. It undergoes Aldol condensation. On drastic oxidation with chromic acid, it gives an acid (B) having formula $C_7H_6O_2$. Identify the compounds (A) and (B) and write the reaction involved. 5

OR

i) Write the reaction of cyclohexanecarbaldehyde with the following reagents:
a) PhMgBr and then H_3O^+ (b)Semi carbazide with weak acid.
ii) How will you carry out the following conversions:
a) Ethanal to But-2-enal (b)Benzaldehyde to α-Hydroxyphenyl acetic acid
b) Benzene to *m*-Nitroacetophenone

MARKING SCHEME
SAMPLE PAPER -2

1. (a) Benzyl chloride 1
2. d) Neopentyl chloride 1
3. a) 3/5 1
4. a) 4.74×10^{-2} $(L/mol)^{1/2}$ s^{-1} 1
5. c) ΔG° is negative, K is greater than 1 1
6. a) increase 2 times 1
7. (c) Aryl amines are generally less basic than alkyl amines due to delocalisation of lone pair of electrons in the benzene ring 1
8. (a) Penta amine isothicoyanato chromium (III) tetrachlorozincate (II) 1
9. (b) 2-methyl-2-propanol 1
10. c) Carbolic acid 1
11. (d) bar min^{-1}, $bar^{-1/2}$ min^{-1} 1
12. (d) $[Co(en)_3]^{+3}$, $[Co(NH_3)_6]^{+3}$, $[Co(H_2O)_6]^{+3}$ 1
13. d) Assertion is incorrect statement, but Reason is correct statement 1
14. a) Assertion and reason both are correct statements, and reason is the correct explanation of the Assertion 1
15. b) Assertion and reason both are correct statements, but reason is not the correct explanation of the Assertion 1
16. c) Assertion is correct statement, but Reason is incorrect statement. 1
17. When 99.9% reaction is completed:

$$[R]=[R_0]- \frac{99.9}{100}[R_0] = 0.001[R_0]$$

$$t(99.9\%) = \frac{2.303}{k}\log\frac{[R_0]}{[R]}$$

$$= \frac{2.303}{k}\log\frac{[R_0]}{0.001[R_0]} = \frac{2.303}{k}\log 1000 = \frac{2.303 \times 3}{k} \quad \ldots\ldots\ldots 1$$ 1

When half of reaction is completed

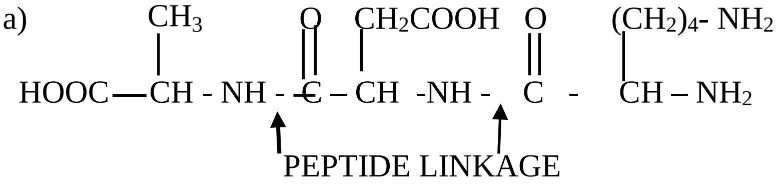
$$[R] = [R_0] - 0.5\,[R] = 0.5\,[R_0]$$

$$t_{(1/2)} = \frac{2.303}{k}\log\frac{[R_0]}{0.5[R_0]} = \frac{2.303}{k}\log 2 = \frac{2.303 \times 0.3010}{k} \quad \ldots\ldots\ldots 2$$

Dividing eq (1) by (2)

$$\frac{t(99.9\%)}{t_{(1/2)}} = \frac{3}{0.3010} = 10 \text{ times}$$ 1

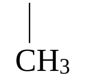
18. a) 1



$HOOC—CH(CH_3)-NH-C(=O)-CH(CH_2COOH)-NH-C(=O)-CH((CH_2)_4-NH_2)-NH_2$

Similarly another tripeptide can be formed.

b) Zwitter ion form of Alanine is: 1



$^{-}OOC—CH(CH_3)–NH_3^{+}$

OR

DNA	RNA	
1. The sugar present in DNA is 2-deoxy-(-) ribose.	1. The sugar present in RNA is D-(-) ribose.	1
2. DNA contains cytosine and thymine as pyrimidine bases.	2. RNA contains cytosine and uracil as pyrimi bases.	
3. DNA has double standard α-helix structure.	3. RNA has single stranded α-helix structure.	1

The base which are common to both DNA and RNA are :

1. Adenine (A)
2. Guanine (G)
3. Cytosine (C)

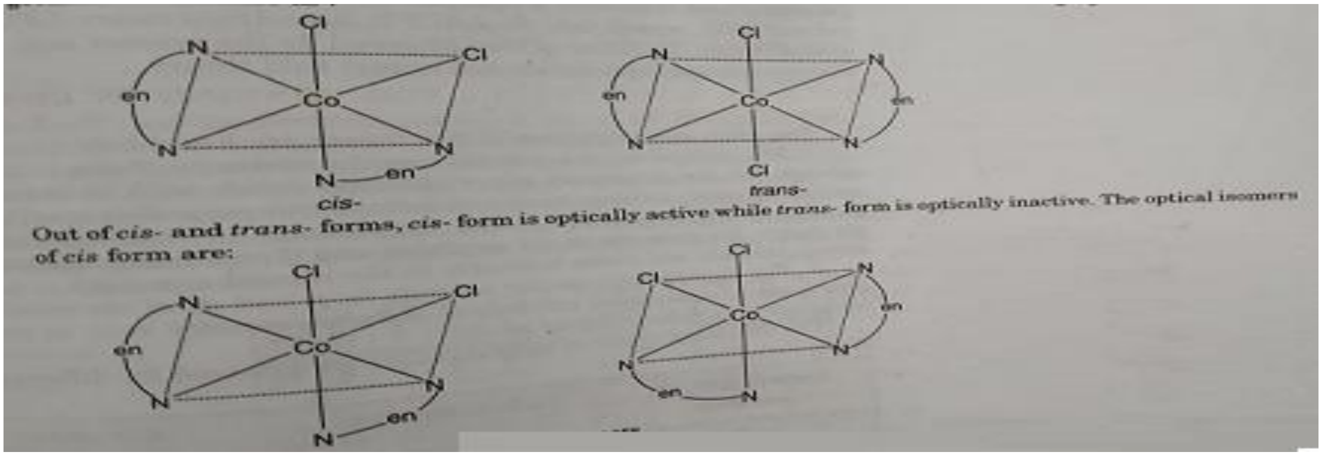
19 a) Sulphuric acid is an oxidising agent. It will oxidise HI produced during the reaction to I_2 and therefore, will prevent the reaction between an alcohol and HI to form alkyl halide. 1

$$2KI + H_2SO_4 \longrightarrow 2KHSO_4 + 2HI$$

$$2HI + H_2SO_4 \longrightarrow H_2 + I_2 + SO_2$$

b) In chlorobenzene the C of C-Cl bond is sp^2 hybridised while the C of C-Cl bond in cyclohexyl chloride is sp^3 hybridised. The magnitude of negative charge is less on Cl atom of chlorobenzene than in cyclohexyl chloride. Due to resonance, C-Cl bond in chlorobenzene acquires some double bond character. Therefore chlorobenzene has lower dipole moment due to lower magnitude of charge on Cl atom and small C-Cl distance. 1

20. The formula for the complex dichloridobis (ethane-1, 2-diamine) cobalt (III) ion is $[Co(en)_2Cl_2]^+$. It exist in two geometrical isomers ½



Out of *cis*- and *trans*- forms, *cis*- form is optically active while *trans*- form is optically inactive. The optical isomers of *cis* form are:

1

½

Cis- form is optically active .The optical isomers are:

OR

The coordination number of Mn+2 ion is 4.The complex has magnetic moment 5.9BM which indicates that it has 5 unpaired electrons.

$\sqrt{n(n+2)} = 5.9$ so, n= 5 1

Therefore the 3d orbitals are unpaired hence hybridisation is sp3 having tetrahedral geometry. 1

$[MnBr_4]^{-2}$: Mn^{+2}

21. Q=It

Q= 3x 1 x 60 x 60= 10800C

Palladium ions are reduced at cathode as:

$Pd^{+n} + ne^- \longrightarrow Pd$ 1

96500 n coulomb of current reduces palladium ions = 104.4 gm

10800 Coulomb of current reduce palladium ions= $\frac{106.4 \times 10800}{96500\ n}$

Amount of palladium ions reduced = 2.977 gm

$$\frac{106.4 \times 10800}{96500\ n} = 2.977$$

Or n = $\frac{106.4 \times 10800}{96500 \times 2.977}$

n= 4 Therefore charge on Palladium ions is Pd^{+4} 1

22. If initial conc. of A is a then,

$[A] = a - \frac{3}{4}a = \frac{1}{4}a$ 1

$t = \frac{2.303}{2.4 \times 10^{-3}} \log \frac{a}{a/4}$ $t = \frac{2.303 \times \log 4}{2.4 \times 10^{-3}}$ 1

$= \frac{2.303 \times 0.6020}{2.4 \times 10^{-3}}$ 1

= 578 sec

23. 1

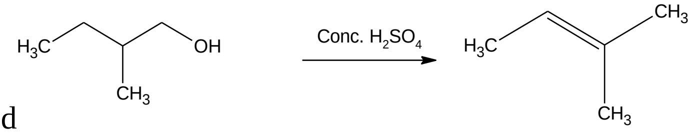
a) $CH_3—CH=CH—CH_2—CH_2—CN \xrightarrow{DIBALH/H_2O,\ -78^0C} CH_3—CH=CH—CH_2—CH_2—CHO$

Hex-4-enal

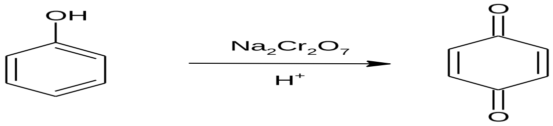
b). Methyl amine, due to +I effect 1

c) $CH_3COOH < ClCH_2COOH < Cl_2CHCOOH < Cl_3CCOOH$ 1

24. 1



a)2-Methylbut-2-ene is formed



1

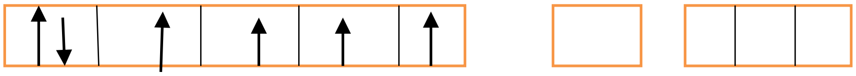
b)Quinone is obtained

c) $C_6H_5CH_2OC_2H_5 \xrightarrow{HI\ /\ 373\ K} C_6H_5CH_2I + C_2H_5OH$ 1

25. a)$[CrCl_2(H_2O)_4]Cl$: Tetraaquadichloridochromium(III)chloride

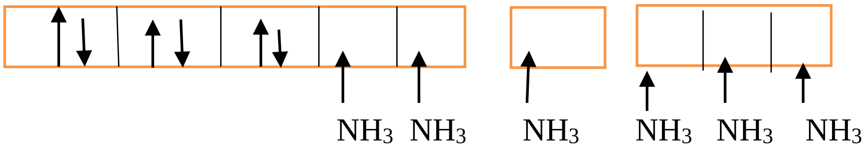
b) Electronic configuration of Co atom in GS= $[Ar]_{18}3d^74s^2$

Electronic configuration of Co(III) ion = $[Ar]_{18}3d^64s^0$



Back pairing of electrons take place as NH_3 is a strong ligand

$[Co(NH_3)_6]^{+3}$



Six pairs of electrons from NH_3 molecules.

Hybridisation: d_2sp^3
Shape: Octahedral
Nature of complex: Inner Orbital
Magnetic nature: Diamagnetic

26. a) 0.1M KCl will have higher boiling point, because it dissociates in water to give two ions whereas glucose does not dissociates. As KCl has greater no of particles so elevation in boiling points will be more. 1

b)For Cane sugar

$\Delta T_f = 273.15 - 271.0 = 2.15$ 1

$$K_f = \frac{2.15 \times 100 \times 342}{5 \times 1000} = 14.706 \text{ K/m}$$

For glucose solution , 1

$$\Delta T_f = \frac{14.706 \times 1000 \times 5}{100 \times 180} = 4.08\text{K}$$

Freezing point = 273.15 – 4.085 = 269.07K

OR

a) The dissolution of a gas in a liquid is exothermic process. Therefore, according to Le-Chatelier's principle with increase in temperature the equilibrium shifts in backward direction. Therefore, the solubility of gas in solution decreases with rise in temperature. 1

Liquid + Gas ⇌ Dissolved Gas ΔH= --ve

b) At higher altitudes, the partial pressure of oxygen is less .This leads to low concentration of oxygen in the blood as well as in tissues. Due to this people become weak and unable to think clearly. 1

c) Because a mixture of 95.6% alcohol and 4.4% water forms an Azeotropic mixture. At this stage liquid and vapour have same composition and therefore, it cannot be further distilled. 1

27. a) Loss of proton from amines give amide ion whereas loss of a proton from alcohol gives an alkoxide ion. 1

$RNH_2 \longrightarrow RNH^- + H^+$

$ROH \longrightarrow RO^- + H^+$

Since O atom is more electronegative than N atom, therefore RO^- can accommodate the –ve charge more easily than RNH^-. Consequently, RO^- is more stable than RNH^-. Thus alcohols are more acidic than amines.

b) Methylamine is more basic than water so it accepts a proton from water forming OH- ions.

$CH_3NH_2 + H{-}OH \longrightarrow CH_3NH_3^+ + OH^-$ 1

These OH^- ions combine with Fe^{+3} ions to form brown ppt. of hydrated ferric oxide.

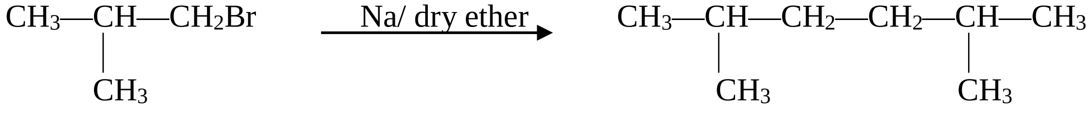
$FeCl_3 \longrightarrow Fe^{+3} + 3Cl^-$

$2Fe^{+3} + 6OH^- \longrightarrow 2Fe(OH)_3$ Brown ppt.

c) The Diazonium salts of aromatic amines are more stable because of dispersal of positive charge on the benzene ring due to resonance. It is not possible in alkyl Diazonium salts. 1

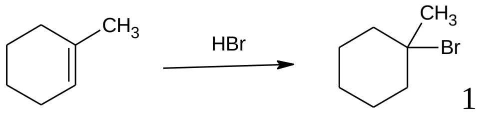
d) Tertiary amines does not have replaceable hydrogen atom which could with acid chloride .So, it does not undergoes acylation reaction.

28. a) 1

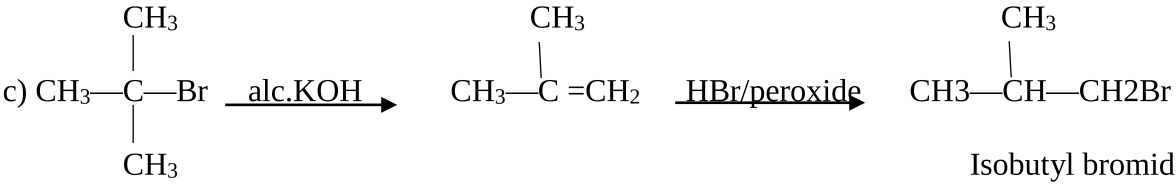


$$CH_3-\underset{\underset{CH_3}{|}}{CH}-CH_2Br \xrightarrow{\text{Na/ dry ether}} CH_3-\underset{\underset{CH_3}{|}}{CH}-CH_2-CH_2-\underset{\underset{CH_3}{|}}{CH}-CH_3$$

2,4-dimethylhexane

b) 

1-Bromo-1-methylcyclohexane 1

c) 

$$CH_3-\underset{CH_3}{\overset{CH_3}{C}}-Br \xrightarrow{alc.KOH} CH_3-\overset{CH_3}{C}=CH_2 \xrightarrow{HBr/peroxide} CH3-\overset{CH_3}{CH}-CH2Br$$

Isobutyl bromide 1

29. a)When external pressure applied becomes more than the osmotic pressure of the solution, then the solvent molecules from the solution pass through the semipermeable membrane to the solvent side. This process is called reverse osmosis.

b)No, as sodium chloride gets dissociated into two ions (Na^+ and Cl^-) so it exerts double osmotic pressure than urea which is non-electrolyte.

c) Mass of gene fragment = 8.95 mg = 8.95×10^{-3} gm

Volume of water = 35ml = 35×10^{-3} L

$\prod$= 0.335 torr = 0.335/760 atm

T = 25^0C + 273 = 298K

$$\prod = \frac{W_A RT}{M_A x\ V}$$

$$\frac{0.335}{760} = \frac{8.95 \times 10^{-3} \times 0.0821 \times 298}{M_A \times 35 \times 10^{-3}}$$

$$M_A = \frac{8.95 \times 10^{-3} \times 0.0821 \times 298 \times 760}{35 \times 10^{-3} \times 0.335}$$ MA = 14193.3 g /mol or 1.42 x 104 g/mol

OR

$\prod$ (blood) = $\prod$ (glucose solution) = 8.21 atm

Now , $\prod V = nRT$

Or n = $\prod$V/RT

n= 8.21 x 1.0 / 0.0821 x 310

n= 10/31

$$\text{Weight of glucose} = \frac{10}{31} \times 180$$

= 58.06 gm.

30. a) Because glucose has a cyclic structure in which –CHO group is not free because it forms a hemiacetal linkage with—OH group at C—5. 1

b) Glycosidic linkage 1

c) Anomers: Carbohydrates which differ in configuration at the glycosidic carbon (i.e.; C_1 in aldoses and C_2 in ketoses) are anomers.

Epimers: Carbohydrates which differ in configuration at nay asymmetric carbon atom other than glycosidic carbon are called epimers. 2

OR

c) 1. They act as main source of energy and is reserve food material in plants
2. Cellulose act as the main material in the cell wall of plants

31. a) Because they have greater surface area moreover, they have tendency to combine with reactant to form intermediate. 1

b) Because of its less enthalpy of hydration than of Cu^{+2} ion. Cu+ ion undergoes disproportionation reaction to form stable Cu^{+2} ion. $2Cu^{+} \longrightarrow 2Cu^{+2} + Cu$ 1

c) Because Cr^{+2} undergoes oxidation to attain stable Cr^{+3} configuration, as t_{2g}^{3} is half filled and more stable. So, it act as reducing agent.

$$\underset{d^4}{Cr^{+2}} \longrightarrow \underset{d^3\ (t_{2g}^{3})}{Cr^{+3}} + e^-$$ 1

Mn^{+3} undergoes reduction to attain stable Mn^{+2} configuration, as d^5 is half filled and more stable. So, it act as oxidising agent.

$$\underset{d^4}{Mn^{+3}} + e^- \longrightarrow \underset{d^5}{Mn^{+2}}$$

d) It is due to charge transfer from O atom to metal atom thereby changing O^{-2} ion to O^- ion and reducing the oxidation state of Cr from +6 to +5. 1

e) Ce (III) has electronic configuration: $4f^15d^06s^0$. It can be easily oxidised because it can readily lose an electron to acquire the stable $4f^0$ configuration and form Ce (IV). 1

32. a) No, because for the reaction, E^0 value is negative so the reaction is not feasible. 1

$$Fe^{+3} + Br^- \longrightarrow Fe^{+2} + \tfrac{1}{2} Br_2$$

$E^0 = 0.771 – 1.09 \quad = --0.319$ V 1

b) Nernst equation for the given cell is:

$$2Br^- + 2H^+ \longrightarrow Br_2 + H_2$$

$E = E^0 – \frac{0.0591}{n} \log \frac{[\text{ anode}]}{[\text{cathode}]}$ $\qquad E^0 = 0- 1.08 = - 1.08V$ 1

$E = -1.08 – \frac{0.0591}{2} \log \frac{[1]}{[Br^-]^2 [H^+]^2}$ 1

$E = -1.08 – \frac{0.0591}{2} \log \frac{[1]}{[0.01]^2 [0.030]^2}$

$E = -1.08 – \frac{0.0591}{2} \log [1.11 \times 10^7]$

$= -1.08 – \frac{0.059}{2} \times 7.0457$

$= -1.08 – 0.208$ 1

$= - 1.288$ V

The given reaction is not feasible. Thus, oxidation will occur at the hydrogen electrode and reduction on the Br_2 electrode to make reaction feasible.

OR

i) MnO_4^- is the strongest oxidizing agent as it has highest value of electrode potential;$E^o= +1.51V$ 1

ii) a)The conducting power of all the ions produced by dissolving one gram equivalent of an electrolyte in solution is called equivalent conductivity. 1

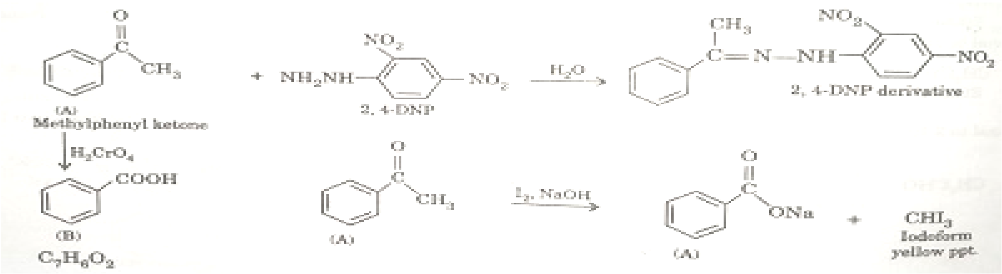
b) The electrolyte is strong. Because it's molar conductivity at infinite dilution can be calculated by extrapolation of the straight line to zero concentration. 1

c) $\wedge^0(HCOOH) = \lambda^0(H^+) + \lambda^0(HCOO^-) \quad = 349.6 + 54.6 \ = 404.2\ Scm^2mol^{-1}$

$\alpha= 46.1/404.2 \ = 0.114$ $\qquad K_c= C\alpha^2 / 1-\alpha$ 1+1

$= \frac{0.025 \times (0.114)^2}{1—0.114} \quad =3.67 \times 10^{-4}$

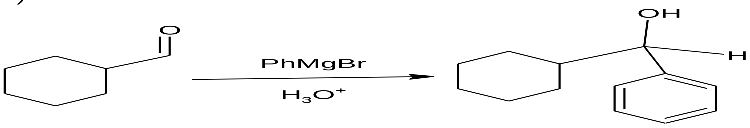
33. Compound **A** is Methyl phenyl ketone & **B** is Benzoic acid 5



OR

Answer of part(i)

a)



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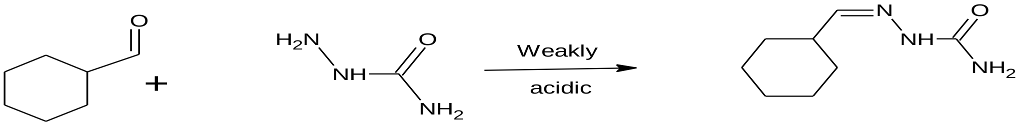
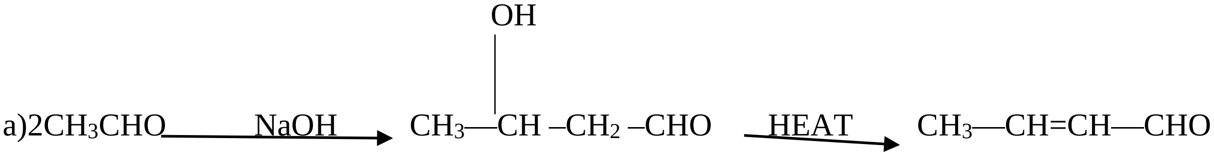
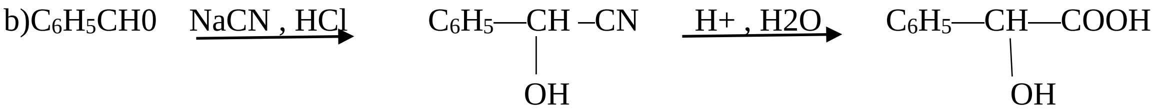


b)

Answer of part (ii) 1

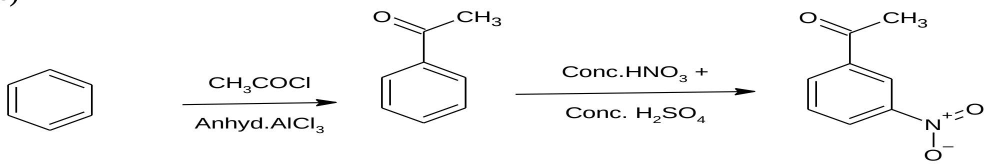


a) $2CH_3CHO \xrightarrow{NaOH} CH_3—\overset{OH}{CH}–CH_2–CHO \xrightarrow{HEAT} CH_3—CH=CH—CHO$



b) $C_6H_5CH0 \xrightarrow{NaCN , HCl} C_6H_5—\underset{OH}{CH}–CN \xrightarrow{H+ , H2O} C_6H_5—\underset{OH}{CH}—COOH$ 1

c)



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KENDRIYA VIDYALAYA SANGATHAN , RANCHI REGION
SESSION 2023-2024 (Unsolved)
SAMPLE QUESTION PAPER – 1 CHEMISTRY (043)

MM: 70 **Time: 3hours**

General Instructions:

Read the following instructions carefully.

There are 33 questions in this question paper with internal choice.

SECTION A consists of 16 multiple-choice questions carrying 1 mark each.
SECTION B consists of 5 very short answer questions carrying 2 marks each.
SECTION C consists of 7 short answer questions carrying 3 marks each.
SECTION D consists of 2 case- based questions carrying 4 marks each.
SECTION E consists of 3 long answer questions carrying 5 marks each.
All questions are compulsory.
Use of log tables and calculators is not allowed

SECTION-A

1 Glucose and fructose are:
a. Structural isomers b. Functional isomers
c. anomers d. geometrical isomers

2 Iodoform test is not given by :
a. Ethanol b. Ethanal c. Pentan-2-one d. Pentan-3-one

Picric acid is:
a. p-Nitrophenol b. 2-Hydroxybenzoic acid
c. 2,4-,6-Tribromophenol d. 2,4-,6-Trinitrophenol

4 Swart reaction is used in the manufacture of from tetrachloromethane:
a. Freon-12 b. DDT c. Phosgene d. Chloroform

5 The most appropriate fact about the diazonium salt is:
a. C6H5CN that can't be obtain by the Nucleophilic substitution of Cl in C6H5Cl but can be easily obtained from diazonium salt
b. Benzene diazonium chloride is a colourless crystalline liquid
c. The alkyldiazonium salts are very much stable
d. Diazotization reaction requires a high temperature to get completed

6 When the temperature rises, what happens to the peak of the curve in the Maxwell-Boltzmann distribution graph?
a) Shifts forward and upward b) Shifts forward and downward
c) Shifts backwards and upward d) Shifts backwards and downward

7 _ _ _ _ _ _ _ _ _ is used in the treatment of lead poisoning
a. AgBr b. EDTA c. [Ni(CO)4] d. Dimethylglyoxime

8 Only the rate of a reaction can be measured easily:
a. Slow b. Fast c. Moderate d. Exceptionally slow

9 The osmotic pressure of a solution increases if:
a. The volume of the solution is increased c. Temperature is decreased
b. The number of solute molecules is increased d. Solution constant (R) is increased

10 Fishes feel comfortable in a lake in Himalayan mountain range than a lake in Udaipur:
a. more b. less c. equally d. extremely less

11 Mischmetalconatains and traces of S, C, Ca and Al.
a. 95% Lanthanoid + 5% Iron c. 5% Lanthanoid + 95% Iron
b. 96% Fe, Ni & Co and 4% Carbond. d. None of these

12 The order of the reaction $HCl_3 + Cl_2$ CCl_4 + HCl is:
a. 1 b. 2 c. 0 d. 3/2

Assertion- Reason Type Questions:

For question No. 13 to 16, select the most appropriate answer from the options given below:

(e) Both A and R are true and R is the correct explanation of A
(f) Both A and R are true but R is not the correct explanation of A.
(g) A is true but R is false.
(h) A is false but R is true.

13 Assertion- Glycosides are hydrolysed in acidic medium.
Reason – Glycosides are acetals.

14 Assertion: Conductivity of an electrolyte increases with decrease in concentration.
Reason: Number of ions per unit volume decreases on dilution.

15 Assertion: Glucose reacts with hydroxylamine to form oxime and also adds a molecule of hydrogencynide to form cynohydrin.
Reason: In open chain structure of glucose, a carbonyl group is present.

16 Assertion: The metal-carbon bond is exceptionally strong in metal carbonyls
Reason: It is due to the synergic effect of ligand to metal bond between the vacant antibonding π-orbital of metal to the filled d-orbital of ligand.

SECTION-B

17 (a) How will you distinguish Propan-1-amine and Propane-2-amine by a chemical test?
(b) Aliphatic amines are stronger bases than ammonia.

18 (a) For non-ideal solutions value of Vont Hoff factor is either greater than 1 or less than 1. What is the value of Vont Hoff's factor if solute molecules are dissociated in solution?
(b) When dehydrated fruits and vegetables are placed in water, they slowly swell and return to original form, why? Also name the type of solutions used also.

19 Account for the following:
(a) Though both Cr^{2+} and Mn^{3+} have d^4 configurations, yet Cr^{2+} is reducing while Mn^{3+} is oxidizing.
(b) Sc^{3+} salts are colourless

OR

A blackish brown solid (A) when fused with alkali metal hydroxide in the presence of air, produces a dark green colored compound (B), which on electrolytic oxidation in alkaline medium gives a dark purple colored compound (C). Identify A, B and C, and write the reactions involved.

20 (a) Illustrate Sandmeyer reaction with suitable example.
(b) Antimarkownikov rule is observed only during the addition of unsymmetrical alkenes to HBr and not with HI. Justify

21 For the reaction:
$2NO(g + Cl_2(g) \longrightarrow 2\,NOCl(g)$

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

Experiment No	Initial Conc. [NO] M	Initial Conc. $[Cl_2]$ 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.

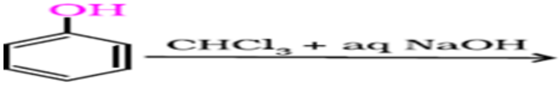
SECTION-C

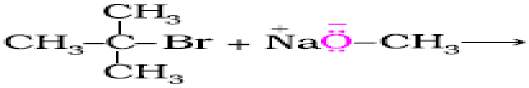
22 (a) Write structures of the compound whose IUPAC name is as follows: 1-Phenylpropan-2-ol
(b) In Phenol, the –OH group activates the benzene ring towards electrophilic substitution and directs the substituent to ortho and para positions in benzene ring. Support your answer with suitable reason.

23 A galvanic cell consists of a metallic zinc plate dipped in 0.01M zinc nitrate solution with a metallic lead plate dipped in 0.002M lead nitrate solution. Write chemical reactions for each electrode and calculate the emf of the cell.
(Given: $E^0\ Zn^{2+} / Zn = -0.76V$;$E^0\ Pb^{2+} / Pb = -0.13V$; log 2=0.3010 ; log 5 =0.6990)

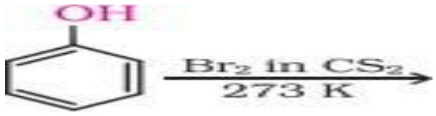
24 (a) Write structures of the compound whose IUPAC name is as follows: 1-Phenylpropan-2-ol
(b) In Phenol, the –OH group activates the benzene ring towards electrophilic substitution and directs the substituent to ortho and para positions in benzene ring. Support your answer with suitable reason.

25 Write the products:

(i)


(ii)


$CH_3-\overset{CH_3}{\underset{CH_3}{C}}-Br + \overset{+}{Na}\overset{-}{\ddot{O}}-CH_3 \longrightarrow$

(iii)


26 a. Rate of a reaction can be experimentally determined for a reaction, but it does not remain constant throughout the reaction process. Why?
b. For a reaction specific rate of reaction is equal to its rate of reaction then find out the order of the reaction and the relation between specific rate of reaction and its half life.

OR

a. If half life for a first order reaction of a reactant is 4 minutes. How long will it take for the initial concentration of reactant to reach its 10%.
b. A first order reaction is 50% completed in 1.26×10^{14} s. How much time would it take for 100%completion

27 Determine the osmotic pressure of a solution prepared by dissolving 25 mg of K_2SO_4 in 2 litre of the solution at 25° C, assuming that K_2SO_4 is completely dissociated.

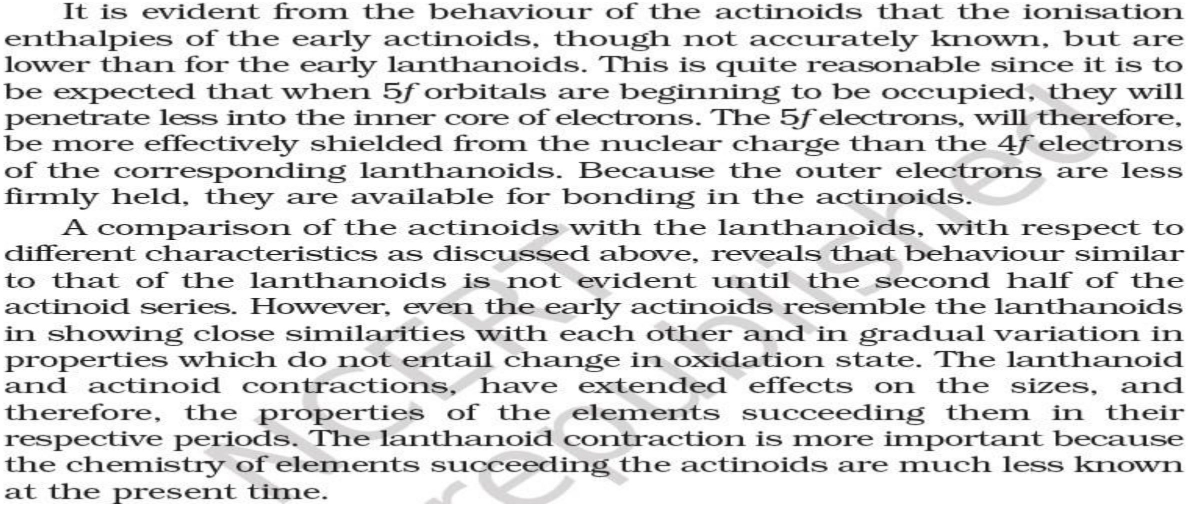
28 Give Reasons for following :-
a. Diazonium salts of aromatic amines are more stable than aliphatic diazonium salts.
b. pK_b of aniline is more than that of methylamine.
c. Ethylamine is soluble in water whereas aniline is not.

OR

a. How will you distinguish Chloroform and dichloromethane by a chemical test
b. Aryl halides do not undergo Nucleophilic Substitution reactions. Why?
c.We cannot prepare Chlorobenzene by reaction of phenol and $SOCl_2$ .Why?

SECTION-D

29 Case-study Based Question-I:



It is evident from the behaviour of the actinoids that the ionisation enthalpies of the early actinoids, though not accurately known, but are lower than for the early lanthanoids. This is quite reasonable since it is to be expected that when 5*f* orbitals are beginning to be occupied, they will penetrate less into the inner core of electrons. The 5*f* electrons, will therefore, be more effectively shielded from the nuclear charge than the 4*f* electrons of the corresponding lanthanoids. Because the outer electrons are less firmly held, they are available for bonding in the actinoids.

A comparison of the actinoids with the lanthanoids, with respect to different characteristics as discussed above, reveals that behaviour similar to that of the lanthanoids is not evident until the second half of the actinoid series. However, even the early actinoids resemble the lanthanoids in showing close similarities with each other and in gradual variation in properties which do not entail change in oxidation state. The lanthanoid and actinoid contractions, have extended effects on the sizes, and therefore, the properties of the elements succeeding them in their respective periods. The lanthanoid contraction is more important because the chemistry of elements succeeding the actinoids are much less known at the present time.

Which is the most common oxidation state of Lanthanoids? 1

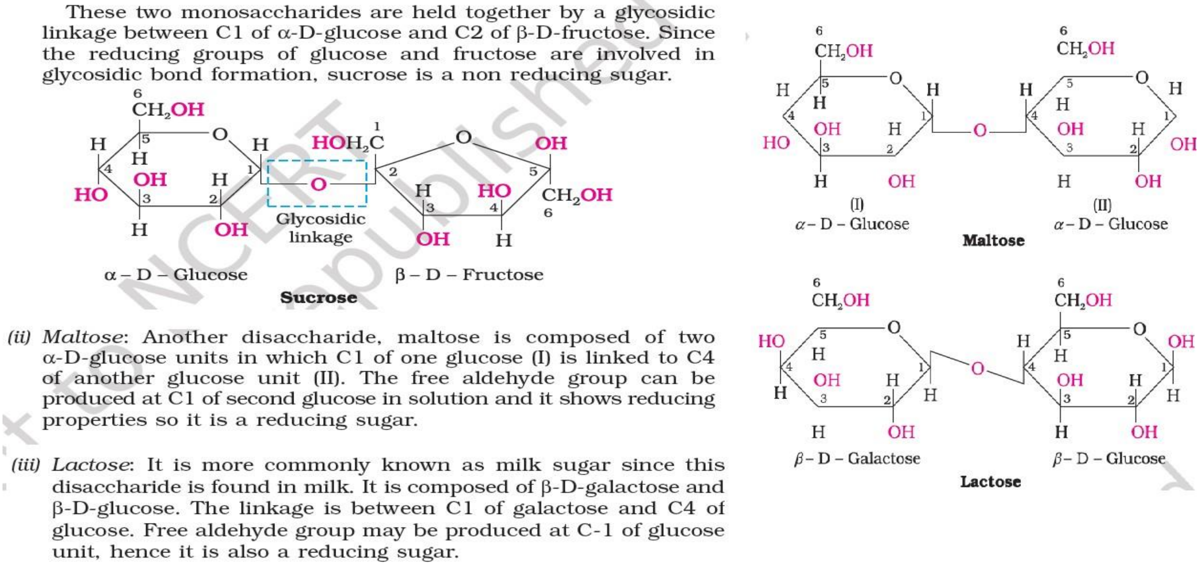
a. What is the main cause for the similarity in atomic size of the elements of second and third transition series? 1

b. Why is the chemistry of the Actinoids much difficult than those of Lanthanoids? Give two reasons at least to support your answer. 2

OR

Use Hund's rule to derive the electronic configuration of Ce^{3+} ion, and calculate its magnetic moment on the basis of 'spin-only' formula.

30 Case-study Based Question-II:



These two monosaccharides are held together by a glycosidic linkage between C1 of α-D-glucose and C2 of β-D-fructose. Since the reducing groups of glucose and fructose are involved in glycosidic bond formation, sucrose is a non reducing sugar.

Sucrose

(ii) Maltose: Another disaccharide, maltose is composed of two α-D-glucose units in which C1 of one glucose (I) is linked to C4 of another glucose unit (II). The free aldehyde group can be produced at C1 of second glucose in solution and it shows reducing properties so it is a reducing sugar.

(iii) Lactose: It is more commonly known as milk sugar since this disaccharide is found in milk. It is composed of β-D-galactose and β-D-glucose. The linkage is between C1 of galactose and C4 of glucose. Free aldehyde group may be produced at C-1 of glucose unit, hence it is also a reducing sugar.

Maltose

Lactose

…a. What is the anomeric carbon? 1

b. What is invert sugar? 1

c. Although both are disaccharides Sucrose is a non-reducing sugar while Maltose is reducing sugar, why? 2 OR

What is the difference between β–D-Glucose and β–D-Galactose? Which linkage is responsible to hold them to make milk sugar?

SECTION-E

31 (a) Write down the chemical formula of *Dibromobis(ethan-1,2diamine)chromate(III) chloride* and write down all the possible isomers of this compound.

(b) Ritika have two test tubes containing aqueous solutions of CuSo4. She added Ammonia solution to test tube A and Aqueous solution to B . Write down the IUPAC names and Formula formed in test tube A and B. (Both of compounds with coordination number 4)

(c) When ammonia solution is mixed in test tube A, the resultant solution does not show Cu $^{+2}$ions. Why?

32 (A) Which of the component of each pair will show higher Conductance and why ? (1×5=5)

(i) 1 M NaOH and 1 M NH_4OH solutions

(ii) Dilute solution of HAc and Concentrated solution of HAc.

(iii) Copper wire and Acetic acid solution at 20^0C

(B) How much electricity is required for the oxidation of-

(i) 1 mol of H_2O to O_2

(ii) 1 mol of FeO to Fe_2O_3

OR

(i) A student prepared 1 molar aqueous solution of silver nitrate solution and stirred the solution with copper spoon. Point out if he has committed any mistake? (E_0Ag^+/Ag =0.80 volt and E^0 Cu^{+2}/Cu=0.34 Volt)

(ii) If aqueous solution of common salt is electrolyzed, Which of the reactions will take place at anode and cathode (mention the reactions)

(iii) Suresh Supplied 2 q charge for the electrolysis of molten NaCl and Mahesh supplied 4 q charge for the same process then Which one will get higher quantity of Na at cathode and Which rule of Faraday is being used to calculate the quantity of Na deposited? Define this rule

33 a. An organic compound A with formula $C_7H_6O_2$ on reacting with ammonia and on subsequent heating gives a compound B which can undergo Hoffmann Bromamide Degradation reaction. A (that may also give baking soda test) can give such a sodium salt which on treating with Soda lime, gives a hydrocarbon C with 6 π e- that fits better in the Huckel's rule (4n +2). Identify A, B & C and write all the reactions involved.

b. Distinguish between Salicylic acid and Salicylaldehyde

c. What is the IUPAC name of β-Hydroxyvalericacid

OR

a. How will you convert: (i) Benzene into Benzaldehyde using Gatterman-Koch reaction

(ii) Toluene into Benzaldehyde using Etard reaction

(iii) β-Phenyl ethyl alcohol into β-Phenyl acetic acid using Jones reagent

b. Give the mechanism of the reaction in which a carboxylic acid is esterified into a sweet fruity smelling organic compound.

KENDRIYA VIDYALAYA SANGATHAN, RANCHI REGION
SESSION 2023-2024 (Unsolved)
SAMPLE QUESTION PAPER -2 CHEMISTRY (043)

MM: 70 **Time: 3hours**

General Instructions:

Read the following instructions carefully.

There are 33 questions in this question paper with internal choice.
SECTION A consists of 16 multiple-choice questions carrying 1 mark each.
SECTION B consists of 5 very short answer questions carrying 2 marks each.
SECTION C consists of 7 short answer questions carrying 3 marks each.
SECTION D consists of 2 case- based questions carrying 4 marks each.
SECTION E consists of 3 long answer questions carrying 5 marks each.
All questions are compulsory.
Use of log tables and calculators is not allowed

Q.1.What is expected value of van't Hoff's factor for K4[Fe(CN)6]?
(a) 2 (b) 4
(c) 10 (d) 5

Q.2. The rate constant for a first order reaction is 60 S^{-1}.How much time will it take to reduce the concentration of the reactant to 1/16 th of its initial value?
(a) 4.62 $x10^{-3}$ s^{-1} (b) 4.62 $x10^{-4}$ s^{-1}
(c) 4.62 $x10^{-2}$ s^{-1} (d) 46.2 $x10^{-2}$ s^{-1}

Q.3. As temperature increases electrolytic conductance
(a) increases (b)decreases
(c) remains unaffected (d)none of the above

Q.4 Pair [Co(NH3)4Cl2]Br2 and [Co(NH3)4Br2]Cl2 will show
(a) Linkage isomerism
(b)Hydrated isomerism
(c) Ionisation isomerism
(d) coordination isomerism

Q.5.The coordination number of Co in the coplex $[Co(en)_{3}]^{+3}$
(a) 3 (b) 6 (c) 4 (d) 5

Q.6.Which one of the following compound is more reactive towards SN1 reaction
(a) CH2=CHCH2Br (b) C6H5CH2Br
(c) C6H5CH(C6H5)Br (d) C6H5CH(CH3)Br

Q.7. The base which is present in DNA and not in RNA is.
(a) cytosine (b)guanine
(c).adenine (d).thymine

Q.8. A primary alkyl halide would prefer to undergo
(a) SN 1 reaction (b) SN 2 reaction
(c) alpha elimination (c) beta elimination

Q.9 Name the linkage that hold the two unit of disaccharide
(a) Nucleoside (b) Glycosidic linkage
(c) Peptide Linkage (d)None of the above

Q.10.p-Nitro phenol is stronger acid than o-Nitro phenol due to
(a) Inter molecular Hydrogen bonding (b) Intramolecular Hydrogen Bonding
(c) Dispersion forces (d) Van der waal forces

Q.11. In clemmensen reduction ,carbonyl compound is treated with----------

(a) zinc amalgam+HCl (b) sodium amalgam+HCl

(c) zinc amalgam + nitric acid (d) Sodium amalgam +HNO3

Q.12.Lanthanoid contraction is due to increase in

(a) Atomic number (b)Effective nuclear charge

(c)Atomic radius (d) Valence electron

For question No. 13 to 16, select the most appropriate answer from the options given below:

(a) Both A and R are true and R is the correct explanation of A

(b) Both A and R are true but R is not the correct explanation of A.

(c) A is true but R is false.

(d) A is false but R is true.

Q.13Given below are two statements labelled as Assertion (A) and Reason (R)

Assertion (A): Amines are basic in nature.

Reason (R): Amines have lone pair of electrons on nitrogen atom.

Q.14. Assertion (A): In Lucas test, 3^0 alcohols react immediately.

Reason (R): An equimolar mixture of anhyd. ZnCl2 and conc. HCl is called Lucas Reagent.

Q.15.Assertion (A): D(+) Glucose is dextrorotatory in nature.

Reason (R): 'D'represents its dextrorotatory in nature.

Q.16.Assertion (A): Transition metals show variable valency.

Reason (R): Transition metals have a large energy difference between the ns^2 and (n – 1)d electrons.

SECTION B

This section contains 5 questions with internal choice in one question and carry 2 marks each.

Q.17.What are the expected products of hydrolysis of lactose and sucrose?

Q.18.Write the equations involved in the following reactions:

(a) Reimer-Tiemann reaction (b) Kolbe's reaction

Q.19.You are given benzene, cone. $H_2S0_4$and NaOH. Write the equations for the preparation of phenol using these reagents.

Q.20. (i) For the reaction R—>P, the concentration of reactant changes from 0.03 M to 0.02 M in 25 minutes. Calculate the average rate of reaction using units of time both in minutes and seconds.

(ii) What is the unit of rate constant for zero order of reaction?

(iii) What are pseudo-first order reactions?

Q.21.(a) Draw figure to show the splitting of d-orbitals in an octahedral crystal field.

(b) How much charge is required for the following reductions:

(i) 1 mol of Al^{3+} to Al? (ii) 1 mol of Cu^{2+} to Cu ?

OR

Write the chemistry of recharging the lead storage battery, highlighting all the materials that are involved during recharging.

SECTION C

This section contains 7 questions with internal choice in one question. The following questions are short answer type and carry 3 marks each.

Q.22.Using valence bond theory, Find the hybridization, the geometry and magnetic behaviour of $[Fe(CN)6]^{4-}$ (At. No. of Fe is 26)

What is lanthanide contraction? What are the consequences of lanthanoid contraction?

OR

(i) Why is the highest oxidation state of a metal exhibited by its fluoride and oxide only?

(ii) Write down the electronic configuration of (a) Cr3+ (b) Pm3+ [At No- Cr(24) & Pm(61)]

Q.23.Explain giving reasons:

(i) Transition metals and many of their compounds show paramagnetic behaviour.

(ii) The transition metals generally form coloured compounds. (iii)Transition metals and their many compounds act **as good catalyst**

Q.24.Write the reactions involved in the following reactions:

Clemmensen reduction
Cannizzaro reaction
Wolff-Kishner reduction

Q.25.Assign reasons for the following:

(a) Pkb value of methyl amine is lower than that of ammonia.

(b) Ethylamine is soluble in water whereas Aniline is not. (c)Distinguish between methyl amine and Dimethyl amine

Q.26. (a) How will you differentiate in between methyl amine and ethyl amines?

(b)Arrange the following in increasing order of basic strength in aq. Solution $(C_2H_5)_3N$, $C_2H_5NH_2$, $(C_2H_5)_2NH$

(c) What is carbyl amine reaction ?

Q.27.(a)State Henry's law. Write two applications of Henry's law.

(b) What is crystal field splitting energy?

(c)Why are low spin tetrahedral complexes not formed?

Q.28Give reasons

(a)Alcohol Alcohols and phenols both are acidic but alcohol does not give positive litmus test whereas phenols do.

(b) Ethanol has higher boiling point than methoxymethane.

(c) Phenols do not give substitution reactions of –OH groups like alcohols.

SECTION D

The following questions are case-based questions. Each question has an internal choice and carries 4 (1+1+2) marks each. Read the passage carefully and answer the questions that follow.

Q.29.Alkyl halides easily undergo Nucleophilic substitution reactions. Nucleophilic substitution reactions are of two types; substitution nucleophilic bimolecular (SN2) and substitution nucleophilic unimolecular (SN1) depending on molecules taking part in determining the rate of reaction. Reactivity of alkyl halide towards SN1 and SN2 reactions depends on various factors such as steric hindrance, stability of intermediate or transition state and polarity of solvent. SN2 reaction mechanism is favoured mostly by primary alkyl halide or transition state and polarity of solvent, SN2 reaction mechanism is favoured mostly by primary alkyl halide then secondary and then tertiary. This order is reversed in case of SN1 reactions.

Answer the following questions:

a) Why do phenyl chloride not undergo nucleophilic substitution reaction easily?
b) Out of Isopropyl chloride and propyl chloride, which undergo SN2 reaction easily.
c) Write two differences between SN1 reaction and SN2 reaction. Or
d) What is walden Inversion?

Q.30.Nucleic acids are giant biomolecules made of monomers called nucleotides. Nucleotides have three components: pentose sugar (5-carbon sugar), phosphate group, and nitrogenous base. The nucleic acids are of two major types: natural and synthetic nucleic acids. The natural nucleic acids are the two known types: ribonucleic acid (RNA) and Deoxyribonucleic acid (DNA). The pentose sugar in RNA is ribose while DNA contains deoxyribose. The other difference is found in the nitrogenous base component. While the nitrogenous bases adenine, guanine, and cytosine are identified in both DNA and RNA, thymine is found only in DNA, and uracil is found only in RNA

Answer the following questions:

What is nucleoside?

Which nitrogenous base only found in DNA but not in RNA?

What are the differences between DNA and RNA? Or

Why DNA is called master molecules?

SECTION E

The following questions are long answer type and carry 5 marks each. All questions have an internal choice

Q.31.(a) Give chemical tests to distinguish between the following pairs of compounds :

(i) Ethanal and Propanal (ii) Phenol and Benzoic acid

How will you bring about the following conversions?

(i)Benzoic acid to benzaldehyde (ii) Ethanal to but-2-enal (iii) Propanone to propene

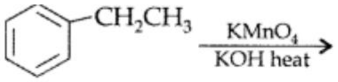
OR

Describe the following giving linked chemical equations :

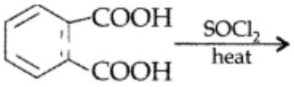
Aldol reaction (ii) Decarboxylation

Complete the following chemical equations

(i)



(ii)



(iii) $C_6H_5CONH_2 \xrightarrow[\text{heat}]{H_3O^+}$

Q.32.(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 acqueous solution containing 10.50 g of $MgBr_2$ in 200 g of water. (Molar mass of $MgBr_2$ = 184 g) (Kf for water = 1.86 K kg mol^{-1})

OR

(a) Explain the following : Raoult'law , positive deviation and negative deviation from ideal behaviour

(b) A solution of glycerol ($C_3H_8O_3$) in water was prepared by dissolving some glycerol in 500 g of water. This solution has a boiling point of 100.42°C. What mass of glycerol was dissolved to make this solution? (Kb for water = 0.512 K kg mol^{-1})

Q.33.(a)Define the following terms :

(i) Limiting molar conductivity (ii) Fuel cell

Resistance of a conductivity cell filled with 0.1 mol L^{-1} KCl solution is 100 **Ω**. If the resistance of the same cell when filled with 0.02 mol L^{-1} KCl solution is 520 **Ω**, calculate the conductivity and molar conductivity of 0.02 mol L^{-1} KCl solution. The conductivity of 0.1 mol L^{-1} KCl solution is 1.29×10^{-2} **Ω**$^{-1}$ cm^{-1}.