CHEMISTRY

CLASS – XII

1-SOLUTION

Multiple Choice Questions

1. Colligative properties depends upon

   Ans: Number of particles of solute in solution
2. Unit of cryoscopic constant is

   Ans: Kg K mol^{-1}
3. Low concentration of oxygen in tissues (anoxia) of people living at high altitude is due to Ans: Low atmospheric pressure (oxygen partial pressure)
4. Which of NaOH and glucoce equimolar aqueous solutions should have highest boiling point (see association or dissociation) Ans: NaOH
5. Characteristics of an ideal solution is

   Ans: Obeys Raoult's law, $\Delta H_{mix} = 0$, $\Delta V_{mix} = 0$
6. The values of van't Hoff factors for KCl, NaCl and K_2SO_4, respectively, are Ans: 2, 2 and 3
7. Isotonic solutions must have the same Ans: osmotic pressure
8. Suggest a binary mixture which will have same composition in liquid and vapour phase?

   (Azeotropic mixture)

   Ans: Water and alcohol **OR** water and nitric acid.
9. With increase of temperature, which will be affected molarity or molality? Ans: Molarity
10. Amount of NaOH required to prepare 0.1M solution in 250 ml. Ans: 1g
11. Molarity of pure water is Ans: 55.6
12. Solubility of gas in liquid increases with

    Ans: Decreasing temperature or increasing pressure
13. Write a mixture which shows positive deviation Ans: Methanol and acetone
14. Which unit is useful in relating concentration of solution with its vapour pressure? Ans: mole fraction
15. Which mixture will form maximum boiling azeotrope ? Ans: Conc. HNO_3 and water
16. The factors $\Delta T_b/K_b$ represents Ans: Molality
17. When NaCl is added to water a its freezing point is Ans: decreased.

18. **Assertion:** Molarity of a solution in liquid state changes with temperature.

Reason: The volume of a solution changes with change in temperature

Ans: Both Assertion and Reason are correct and Reason is the correct explanation of Assertion.

19. **Assertion:** The sum of mole fractions of all components of a solution is unity.

Reason: Mole fraction is independent of temperature.

Ans: Both Assertion and Reason are correct and Reason is not the correct explanation of Assertion.

20. **Assertion:** An ideal solution obeys Henry's law

Reason: Raoult's law is special case of Henry law.

Ans: Both Assertion and Reason are correct and Reason is not the correct explanation of Assertion.

<u>Descriptive Answer Questions:</u>

1. Why osmotic pressure is a colligative property?

Ans: Osmotic pressure is a colligative property because it depends on the number of the particles.

2. Carbon tetra chloride and water are immiscible whereas ethanol and water are missible in all proportions. Why?

Ans: Carbon tetra chloride and water are immiscible because O-H bonds in water are polar whereas (C –Cl) carbon tetra chloride bonds have low polarity, hence do not interact with each other. Water and alcohol are miscible in all proportions because water molecules can form Hydrogen bonds with alcohol molecules.

3. Why molality is preferred over molarity?

Ans: Molality is unaffected by temperature as it does not involve volume. 4.
Why some time we get abnormal molar mass using colligative properties?

Ans: Due to the association or dissociation of the solute in the solution.

5. Define Raoults law.

Ans: It states that partial vapour pressure of a volatile component in solution is proportional to its mole fraction.

6. Define the term mole fraction?

Ans: Mole fraction is defined as the ratio of no. of moles of a component to the total no. of moles of all the components of the solution.

7. What is the effect of temperature on the solubility of solids in liquids?

Ans: It increases with increase in temperature.

8. What is depression constant or cryoscopy constant?

Ans: It is defined as the depression in freezing point when 1 mole of a solute is dissolved in 1 kg of the solvent.

9. Equimolar solutions of NaCl and glucose are not isotonic. Why?

Ans: because NaCl gets dissociated in two ions but glucose does not. Hence osmotic pressure of former is double.

10. Why glycol is used to clear snow on roads ?

Ans. glycol clears snow by decreasing the freezing point of water.

11. Define Colligative Properties and give one example.

Ans: The properties which depends on number of solute particles but independent of its nature. e.g. Elevation in boiling point.

12. Define Azeotropes? What are maximum and minimum boiling azeotropes? Explain with example.

Ans: Azeotropes are constant boiling mixture which has same composition in liquid phase as well as in vapour phase.

The non-ideal solutions which exhibit negative deviation from ideal solution at a particular composition are called as maximum boiling azeotropes. e.g 68% aqueous solution of HNO_3 or any other suitable example.

The non-ideal solutions which exhibit positive deviation from ideal solution at a particular composition are called as minimum boiling azeotropes. e.g 95% aqueous ethanol by volume or any other suitable example

13. Why do we observe abnormal colligative properties?

Ans: Because of –

(i) Association of particles of solute after dissolution. It decreases number of particles of solute so as the value of colligative property.

(ii) Dissociation of particles of solute after dissolution. It increases number of particles of solute so as the value of colligative property.

14. Why is benzene insoluble in water but soluble in toluene?

Ans: Benzene is non polar, therefore insoluble in water (polar solvent) where as it is soluble in touene which is non-polar solvent i.e. non polar compounds are soluble in nonpolar solvents and polar compounds are soluble in polar solvents.

15. State Henry's Law and mention its two important applications?

Ans: Henry's Law states that the solubility of a gas in liquid is directly proportional to the partial pressure of the gas.

Applications: - 1) In
deep sea diving.

2) In aerated water e.g. soft drinks.

16. What happens when a plant cell is placed in (a). Hypertonic solution (b). Hypotonic solution Ans: (a)its protoplasm shrink but its shape remain same due to rigid cell wall.this is called plasmolysis.

(b) its protoplasm swell and apply pressure on the cell wall.but do not burst due to rigid wall.

17. Determine the osmotic pressure of a solution prepared by dissolving 2.5mg of K_2SO_4 in 2L of water at 25°C, assuming that it is completely dissociated.

Ans: $\Pi = \frac{i\,w\,R\,T}{MV}$

i of K_2SO_4 = 3

w= 0.0025g

R =0.0821L atm/K/mole

T=298K

M of K_2SO_4 =174

V=2L

$$\Pi = \Pi = \frac{3 \times 0.0025 \times 0.0821 \times 298}{174 \times 2}$$

= 0.000527 atm.

18. 0.1 mole of CH_3COOH, dissolved in 1 Kg of a solvent, shows depression in freezing point equal to 0.09 K. What is the value of Van't Hoff factor.

Ans: $i = \frac{\Delta T_f}{K_f . m}$

= 0.09 / (1.86 × 0.1)

= 0.484

19. A solution of urea in water has boiling point of 373.328 K. calculate the freezing point of same solution.

Ans: $\frac{\Delta T_f}{\Delta T_b} = \frac{K_b}{K_f}$

$\Delta T_f = K_f \times \Delta T_b$
$/ K_b$ $K_f = 1.86$

$K_b = 0.52$

$\Delta T_b = 373.328 – 373.15 = 0.178$ K

$\Delta T_f = (0.178 \times 1.86) / 0.52 = 0.6367$ K

$T_f = 373.15 – 0.6367 = 372.513$ K

20. A solution containing 18 g of non-volatile solute in 200 g of water, freezes at 272.07 K. calculate molar mass of the solute.

Ans: $\Delta T_f = i \frac{K_f \times w_2 \times 1000}{M_2 \times w_1}$

$M_2 = i \frac{K_f \times w_2 \times 1000}{\Delta T_f \times w_1}$

$i = 1$ $w_2 =$
18 g $w_1 =$
200 g

$K_f = 1.86$

$\square T_f = 273.15 – 272.07 = 1.08$ K

$M_2 = (1 \times 1.86 \times 18 \times 1000) / (1.08 \times 200)$

= 155 g/mol

2-ELECTROCHEMISTRY

Multiple Choice Questions

1. In a lead storage battery, the concentration of electrolyte H_2SO_4 solution is Ans: 38%
2. The relationship between standard reduction potential of cell and equilibrium constant is given by

   Ans: $E^o_{cell} = \frac{0.059}{n} \log K_c$

3. $\Lambda^o_{m(NH_4Cl)} + \Lambda^o_{m(NaOH)} - \Lambda^o_{m(NaCl)}$ is the $\Lambda^o{}_m$ of

   Ans: NH_4OH

4. What are the products of electrolysis of aqueous solution of NaCl? Ans: H_2 at cathode and Cl_2 at anode
5. The number of moles of MnO_4^- reduced to Mn^{2+} by the addition of 1 mole electrons (1 F) in MnO_4^- Ans: 1/5
6. When the concentration of all species is unity, the electrode potential is known as Ans: Standard electrode potential
7. The products of electrolysis of an aqueous solution of $AgNO_3$ with Pt electrode are Ans: H_2 gas at anode and Ag and cathode.
8. An electrochemical cell can behave like an electrolytic cell when Ans: $E_{ext} > E_{cell}$
9. The quantity of charge required to obtain one mole of aluminium from Al_2O_3 is Ans: 3F
10. Molar conductivity of ionic solution depends on Ans: concentration of electrolytes in solution
11. For the given cell, Mg | Mg^{2+} || Ag^+ | Cu, cell reaction is

    Ans: $Mg + Ag^+ \rightarrow Mg^{2+} + Ag$

12. Under what condition is $E_{cell} = 0$ or $\Delta_rG = 0$

    Ans: When the cell reaction reaches equilibrium

13. In a galvanic cell, the salt bridge

    Ans: Stops diffusion of ions from one electrode to another

14. The reaction in a galvanic cell is spontaneous or non- spontaneous Ans: Spontaneous
15. Nernst equation for the cell, $Mg|Mg^{2+}||Ag^+|Cu$

    Ans: $E_{cell} = E^o_{cell} - \frac{0.059}{n} \log \frac{[Mg^{2+}]}{[Ag^+]^2}$

16. $ZnCl_2$ application in Leclanche cell

    Ans: to increase conductivity of electrolyte and to capture NH_3 gas

17. The electrolyte used in a mercury cell is a paste of KOH and Ans: ZnO
18. Assertion: Molar conductivity is increased on increasing dilution.

    Reason: No. of ions increased on dilution.

    Ans: Assertion is correct but reason is not correct.

19. Assertion: Anode is always is a positive electrode of cell Reason: Oxidation always occurs on anode.

    Ans: Assertion is incorrect but reason is correct

20. Assertion: Halogens are strong oxidizing agents

    Reason: standard electrode potential of halogens are much greater.

    Ans: Both Assertion and reason are correct and reason is the correct explanation of assertion.

Descriptive Answer Questions:

1. What is unit of molar conductivity?

   Ans: $ohm^{-1}cm^{-1}mol^{-1}$

2. What is meant by limiting molar conductivity?

   Ans: The molar conductivity of a solution at infinity dilution is called limiting molar conductivity.

3. Give the relationship between molar conductivity and specific conductivity?

4. What is cell constant? What are its units?

   Ans: Cell constant = l/A, where l is the distance of separation of two electrodes (in cm) of the area of cross section 'a' cm^2. Its units are cm^{-1} or m^{-1}.

5. What is the effect of temperature on molar conductivity? Ans: molar conductivity increased.

6. Give the relationship between free energy change and EMF of a cell. Ans: $\Delta_rG = -nFE^o_{cell}$

7. State Kohlrausch law.

   Ans: limiting molar conductivity of an electrolyte can be represented as the sum of the individual contributions of the anion and cation of the electrolyte.

   In general, if an electrolyte on dissociation gives n+ cations and n–anions then its limiting molar conductivity is given by: $\Lambda^o{}_m = \nu_+ \Lambda_+ + \nu_- \Lambda_-$

8. How corrosion and rusting are different? Suggest on method of preventing rusting.

   Ans: Corrosion is the arial oxidation of any metal while arial oxidation of iron is called rusting. Methods of preventing rusting: alloying, electroplating and painting

9. Write reactions occurring in lead storage battery

   Ans: Anode: $Pb(s) + SO_4^{2-}(aq) \rightarrow PbSO_4(s) + 2e^-$

   Cathode: $PbO_2(s) + SO_4^{2-}(aq) + 4H^+(aq) + 2e^- \rightarrow PbSO_4(s) + 2H_2O(l)$ overall cell reaction consisting of cathode and anode reactions is:

   $Pb(s) + PbO_2(s) + 2H_2SO_4(aq) \rightarrow 2PbSO_4(s) + 2H_2O(l)$

   On charging the battery the reaction is reversed

10. What is a fuel cell. Write reactions occurring in fuel cell.

    Ans: Galvanic cells that are designed to convert the energy of combustion of fuels like hydrogen, methane, methanol, etc. directly into electrical energy are called fuel cells.

    Cathode: $O_2(g) + 2H_2O(l) + 4e^- \rightarrow 4OH^-(aq)$

    Anode: $2H_2(g) + 4OH^-(aq) \rightarrow 4H_2O(l) + 4e^-$

11. Calculate the free energy for a cell in which following reaction occurs:

    $Cu(s) + 2Ag^+(aq) \rightarrow Cu^{2+}(aq) + 2Ag(s)$, $E^o_{cell} = 0.46$ V

    Ans. $\Delta_rG^o = -nFE^o_{cell}$

    $\Delta_rG^o = -2 \times 96487 \times 0.46 =$

    – 88768 J

12. The molar conductivity of $\frac{M}{10}$ solution of acetic acid at 25^oC is $14.3\ ohm^{-1}cm^2eq^{-1}$. Calculate the degree of dissociation of CH_3COOH if $\Lambda_\infty CH_3COOH$ is 390.71 $ohm^{-1}cm^2eq^{-1}$.

    Ans: $\Lambda_\infty CH_3COOH = 390.71\ ohm^{-1}cm^2eq^{-1}$

    $\Lambda_{CH_3COOH} = 14.3\ ohm^{-1}cm^2eq^{-1}$

    Degree of dissociation, $\alpha = \frac{\Lambda}{\Lambda_\infty} = \frac{14.3}{390.71}$

    $= 0.0366$ i.e. 3.66% dissociation

13. Represent the cell in which the following reaction takes place

$Mg(s) + 2Ag^{+}(0.0001M) \rightarrow Mg^{2+}(0.130M) + 2Ag(s)$

Calculate its E_{cell}, if $E^{o}_{cell} = 3.17$ V.

Ans: The cell can be written as $Mg \square Mg^{2+}(0.130M) \square\square Ag^{+}(0.0001M) \square Ag$

$$E_{(cell)} = E^{\ominus}_{(cell)} - \frac{RT}{2F} \ln \frac{[Mg^{2+}]}{[Ag^{+}]^{2}}$$

$$= 3.17\ V - \frac{0.059V}{2} \log \frac{0.130}{(0.0001)^{2}}$$

$$= 3.17\ V - 0.21V = 2.96\ V.$$

14. Calculate the equilibrium constant of the reaction:

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

$E^{o}_{cell} = 0.59$ V Ans:

$$E^{\ominus}_{(cell)} = \frac{0.059\ V}{2} \log K_{C}$$

Log Kc = 0.59 × 2 / 0.059 = 20

Kc = antilog 20 = 1.0×10^{20}

15. Define Faraday's laws of electrolysis.

Ans: (i) First Law: The amount of chemical reaction which occurs at any electrode during electrolysis by a current is proportional to the quantity of electricity passed through the electrolyte.

(ii) Second Law: The amounts of different substances liberated by the same quantity of electricity passing through the electrolytic solution are proportional to their chemical equivalent weights.

16. If a current of 0.5 ampere flows through a metallic wire for 2 hours, then how many electrons would flow through the wire? Ans: q = i.t

i = 0.5 A

t = 2 × 60 × 60 s = 7200 s

q = 0.5 × 7200 C

= 3600 C

17. The resistance of a conductivity cell containing 0.001M KCl solution at 298K is 1500 Ω. What is the cell constant if conductivity of 0.001M KCl solution at 298 K is 0.146×10^{-3} S cm^{-1}.

Ans: Conductivity, □ = 0.146×10^{-3} S cm−1

Resistance, R = 1500 Ω

Cell constant G* = k × R

= $0.146 \times 10^{-3} \times 1500$

= 0.219 cm^{-1}

18. Conductivity of 0.00241 M acetic acid is 7.896×10^{-5} S cm^{-1}. Calculate its molar conductivity. If $\square^{o}_{m}$ for acetic acid is 390.5 S cm^{2} mol^{-1}, what is its dissociation constant? Ans: κ = 7.896×10^{-5} S m^{-1} c = 0.00241 mol L^{-1}

molar conductivity, $\square_{m}$ = κ × 1000 / c

= $7.896 \times 10^{-5} \times 1000 / 0.00241$

= 32.76 S cm^{2} mol^{-1}

$\square^{o}_{m}$ = 390.5 S cm^{2} mol^{-1}

□ = $\square_{m} / \square^{o}_{m}$

= 32.76 / 390.5

= 0.084

Dissociation constant, $K_a = c.\alpha^2 / (1-\alpha)$

$= 0.0024 \times (0.084)^2 / (1–0.084)$

$= 1.85 \times 10^{-5}$ mol L^{-1}

19. Write the redox reactions for rusting of iron.

Ans: Anode: $2\ Fe(s) \rightarrow 2\ Fe^{2+} + 4\ e^-$ Cathode:

$O_2(g) + 4\ H^+(aq) + 4\ e^- \rightarrow 2H_2O$

The overall reaction

$2Fe(s) + O_2(g) + 4H^+(aq) \rightarrow 2Fe^{2+}(aq) + 2H_2O$

20. $\square^{o}_{m}$ for NaCl, HCl and NaAc are 126.4, 425.9 and 91.0 S cm^2 mol^{-1} respectively. Calculate Λ^{o}_{m} for HAc.

Ans: $\Lambda^{o}_{m(HAc)} = \lambda^{o}_{H^+} + \lambda^{o}_{Ac^-} = \lambda^{o}_{H^+} + \lambda^{o}_{Cl^-} + \lambda^{o}_{Ac^-} + \lambda^{o}_{Na^+} - \lambda^{o}_{Cl^-} - \lambda^{o}_{Na^+}$

$= \Lambda^{o}_{m(HCl)} + \Lambda^{o}_{m(NaAc)} - \Lambda^{o}_{m(NaCl)}$

$= (425.9 + 91.0 – 126.4)$ S cm^2 mol^{-1}

$= 390.5$ S cm^2 mol^{-1}

3-CHEMICAL KINETICS

Multiple Choice Questions

1. In the reaction A + B □ product, if B is taken in excess, then it is an example of Ans: Pseudo first order reaction
2. The first order rate constant for the decomposition of N_2O_5 is 6.2×10^{-3} sec^{-1}. The $t_{1/2}$ of the decomposition Ans: 111.7 sec
3. The ratio $t_{1/8}$: $t_{1/2}$ for the first order reaction is Ans: 3
4. Order of reaction $CHCl_3 + Cl_2$ □ $CCl_4 + HCl$, if Rate = k $[CHCl_3]$ $[Cl_2]^{1/2}$ Ans: 1½
5. Unit of rate constant is expressed by

   Ans: $(mol\ L^{-1})^{1-n}\ s^{-1}$
6. Rate determining step is the ___________ step which decides the order of reaction. Ans: Slowest step
7. Write integrated rate equation which resembles with linear equation, y=mx+c

   Ans: $log \frac{[R]_o}{[R]} = \left(\frac{k}{2.303}\right) t + 0$
8. Radioactive disintegration is an example of Ans: First order reaction
9. Half life of which reaction does not depend on concentration Ans: First order reaction ($t_{1/2}$ = 0.6932/k)
10. For the reaction, $CH_3COOC_2H_5 + H_2O \xrightarrow{H} CH_3COOH + C_2H_5OH$, rate is given by

    Rate = k $[CH_3COOC_2H_5]^x$ $[H_2O]^y$, What are the values of x and y Ans:

    1 and 0
11. Catalyst affects the

    Ans: Activation energy (E_a)
12. Integrated Arrhenius equation can be written as

    Ans: $\ln K = -\frac{E_a}{RT} + \ln A$
13. For the reaction, $NO_2(g) + CO(g)$ □ $NO(g) + CO_2(g)$, the correct expression for the rate of the reaction is

    Ans: rate = $-\frac{d[NO_2]}{dt}$ or rate = $-\frac{d[CO]}{dt}$
14. When initial concentration of reactant is double in a reaction, the half-life period is not affected. The order of reaction is

    Ans: First order reaction
15. Higher order (>3) reactions are rare due to

    Ans: Low probability of simultaneous collision of all reacting species.
16. How catalyst affects the equilibrium constant?

    Ans: does not affect.
17. The rate of reaction increase with increase in temperature because Ans: No. of molecules possessing activation energy are more.
18. Temperature coefficient of a reaction at T and T+10K is

    Ans: $\frac{T_{k+10}}{T}$
19. Assertion: Molecularity is given only for elementary reactions.

    Reason: Complex reactions have more than one steps.

    Ans: Both Assertion and Reason are correct but Reason is not correct explanation of Assertion.

20. Assertion: Concentration of reactants is changed in zero order reaction.

Reason: Concentration of reactants does not change in first order reaction.

Descriptive Answer Questions:

1. Why rate of the reaction does not remain constant throughout?

Ans: Rate of reaction depends upon concentration of reactants which keep on decreasing with time. Hence, rate of reaction does not remain constant throughout

2. Define rate constant or specific reaction rate.

Ans: When the molar concentration of each reactant is unity, the rate of reaction is called specific reaction rate.

3. What will be the effect of temperature on rate constant?

Ans: The rate constant of a reaction is nearly doubled with a 10^o rise in temperature. However, the exact dependence of the rate of a chemical reaction on temperature is given by Arrhenius equation,

$$K=Ae_{-Ea/RT}$$

Where, A is the Arrhenius factor or the frequency factor, T is the temperature, R is the gas constant, E_a is the activation energy.

4. Mention the factors that affect the rate of a chemical reaction.

Ans: The factors that affect the rate of a reaction are as follows.

(i) Concentration of reactants (pressure in case of gases)

(ii) Temperature

(iii) Presence of a catalyst

5. Differentiate between the activation energy and threshold energy?

Ans. The energy requied by the reacting species to form the activated complex is called Activation energy.

Minimum energy associated with reacting species to cross over the potential barrier is called threshold energy.

$$E_{th} = \text{Average K.E} + E_a$$

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

Ans. The reaction follows second order kinetics.

Therefore, the rate equation for this reaction will be: Rate = k $[X]^2$

If the concentration of X is increased to three times, then the rate of formation will increase by 9 times.

7. Time required to decompose SO_2Cl_2 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.** We know that for a 1st order reaction,

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

It is given that

$$t_{1/2} = 60 \text{ min}$$

$$k = \frac{0.693}{t_{1/2}} = \frac{0.693}{60}$$

$= 1.11 \times 10^{-2}$ min^{-1}

8. A first order reaction has a rate constant 1.15×10^{-3} **sec**$^{-1}$. How long will 5 g of this reactant take to reduce to 3 g?

Ans. From the question, we can write down the following information:

Initial amount $[R]_o$= 5 g

Final concentration [R] = 3 g

Rate constant = 1.15×10^{-3} **sec^{-1}**

We know that for a 1st order reaction,

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

$$=\frac{2.303}{1.15\times10^{-3}}\log\frac{5}{3}$$

$$=\frac{2.303}{1.15\times10^{-3}}\times0.2219$$

= 444.38 s = 444 s (approx.)

9. The rate constant for first order reaction is 60/s. How much time will it take to reduce the concentration of the reaction to 1/10 of its initial value. Ans:

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

t= 2.303/60 log $[R]_o/[R]_o$ × (1/10) t

= 2.303/60 × log10

t = 2.303 / 60 = 3.38×10^{-2} s^{-1}

10. Following reaction takes place in one step

$2NO + O_2 \rightarrow 2NO_2$

How will the rate of the reaction of the above reaction change if the volume of reaction vessel is diminished to 1/3 of its original volume? Will there be any change in the order of reaction with reduced volume?

Ans. $2NO+ O_2 \rightarrow 2NO_2$

$dx/dt = k[NO]^2[O_2]$

If the volume of reaction vessel is diminished to 1/3, concentration of both NO and O_2 will become 3 time, the rate of reaction increased 27 times.

There will be no any change in the order of reaction.

11. Write two points of difference between order and molecularity of a reaction. Ans:

S. No.	Order of a reaction	Molecularity of a reaction
1	It is the sum of the powers of concentration terms of reactants in the rate law expression.	It is the total no. of reacting species which actually bring about the reaction.
2	It may be fractional number or zero.	It is always a whole number.it is never zero.

12. What will be the time of completion of 90% of a first order reaction in terms of half life (approximately).

Ans: For first order reaction

$$K=\frac{2.303}{t}\log\frac{a}{(a-x)}$$

$$t=\frac{2.303}{k}\log\frac{100}{(100-90)}=\frac{2.303\times t_{1/2}}{0.593}\times\log\frac{100}{10}$$

$$=3.3\times t_{1/2}\times\log 10=3.3\ t_{1/2}$$

13. The half-life for radioactive decay of ^{14}C is 5730 years. An archaeological artifact containing wood had only 80% of the ^{14}C found in a living tree. Estimate the age of the sample.

Ans:

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

$$= \frac{0.693}{5730} \text{ years}^{-1}$$

It is known that,

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

$$= \frac{2.303}{\frac{0.693}{5730}} \log \frac{100}{80}$$

= 1845 years (approximately)

Hence, the age of the sample is 1845 years.

14. During nuclear explosion, one of the products is ^{90}Sr with half-life of 28.1 years. If 1µg of ^{90}Sr was absorbed in the bones of a newly born baby instead of calcium, how much of it will remain after 10 years and 60 years if it is not lost metabolically.

Ans:

$$k = \frac{0.693}{t_{1/2}} = \frac{0.693}{28.1} \text{ y}^{-1}$$

It is known that,

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

$$\Rightarrow 10 = \frac{2.303}{\frac{0.693}{28.1}} \log \frac{1}{[R]}$$

$$\Rightarrow 10 = \frac{2.303}{\frac{0.693}{28.1}} \left(-\log[R]\right)$$

$$\Rightarrow \log[R] = -\frac{10 \times 0.693}{2.303 \times 28.1}$$

$$\Rightarrow [R] = \text{antilog } (-0.1071)$$

$$= \text{antilog}\left(\bar{1}.8929\right)$$

$$= 0.7814 \mu\text{g}$$

Therefore, 0.7814 µg of ^{90}Sr will remain after 10 years.

Again,

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

$$\Rightarrow 60 = \frac{2.303}{\frac{0.693}{28.1}} \log \frac{1}{[R]}$$

$$\Rightarrow \log[R] = -\frac{60 \times 0.693}{2.303 \times 28.1}$$

$$\Rightarrow [R] = \text{antilog}\ (-0.6425)$$

$$= \text{antilog}(\bar{1}.3575)$$

$$= 0.2278 \mu g$$

Therefore, 0.2278 μg of ^{90}Sr will remain after 60 years.

15. Sucrose decomposes in acid solution into glucose and fructose according to the first order rate law, with $t_{1/2}$ = 3.00 hours. What fraction of sample of sucrose remains after 8 hours?

Ans:- For a first order reaction,

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

It is given that, $t_{1/2}$ = 3.00 hours

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

$$= \frac{0.693}{3}\ h^{-1}$$

= 0.231 h^{-1}

Then, 0.231 h^{-1} $= \frac{2.303}{8\ h} \log \frac{[R]_0}{[R]}$

$$\log \frac{[R]_0}{[R]} = \frac{0.231\ h^{-1} \times 8\ h}{2.303}$$

$$\frac{[R]_0}{[R]} = \text{antilog}(0.8024)$$

$$\frac{[R]_0}{[R]} = 6.3445$$

$$\frac{[R]}{[R]_0} = 0.1576\ \text{(approx)}$$

$$= 0.158$$

Hence, the fraction of sample of sucrose that remains after 8 hours is 0.158.

16. A first order reaction takes 40 min for 30% decomposition. Calculate $t_{1/2}$.

Ans: For a first order reaction,

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

$$k = \frac{2.303}{40\ \text{min}} \log \frac{100}{100-30}$$
$$= \frac{2.303}{40\ \text{min}} \log \frac{10}{7}$$
$$= 8.918 \times 10^{-3}\ \text{min}^{-1}$$

Therefore, $t_{1/2}$ of the decomposition reaction is

$$t_{1/2} = \frac{0.693}{k}$$
$$= \frac{0.693}{8.918 \times 10^{-3}}\ \text{min}$$

= 77.7 min (approximately)

17. 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, the time required for 99% completion is

$$t_1 = \frac{2.303}{k} \log \frac{100}{100-99}$$
$$= \frac{2.303}{k} \log 100$$
$$= 2 \times \frac{2.303}{k}$$

$$t_2 = \frac{2.303}{k} \log \frac{100}{100-90}$$
$$= \frac{2.303}{k} \log 10$$
$$= \frac{2.303}{k}$$

Therefore, $t_1 = 2t_2$ For a first order reaction, the time required for 90% completion is

18. The decomposition of NH_3 on platinum surface is a zero-order reaction. What are the rate of productions of N_2 and H_2. If k= 2.5 x 10^{-4}

Ans. $2NH_3 \rightarrow N_2 + 3H_2$

$$-\frac{1d[NH3]}{2\ \ dt} = \frac{d[N2]}{dt} = \frac{1d[H2]}{3\ \ dt}$$

rate = k × $[NH_3]^0$ = 2.5 × 10^{-4} mol $L^{-1}sec^{-1}$

$$\frac{d[N2]}{dt} = \frac{1d[H2]}{3\ \ dt}$$

$= \frac{1}{2} \times 2.5 \times 10^{-4}$ mol $L^{-1}sec^{-1}$

$d[H_2]/dt = -3/2(d[NH_3]/dt) = 3/2 \times 2.5 \times 10^{-4}$

$= 3.75 \times 10^{-4}$ mol L^{-1} sec^{-1}

Rate = $-d[NH_3]/dt = k \times [NH_3]^0$

$= 2.5 \times 10^{-4}$ mol$L^{-1}sec^{-1}$

Rate of production of $N_2 = 2.5 \times 10^{-4}$ mol $L^{-1}sec^{-1}$

19. The rate law for the reaction, $2Cl_2O \rightarrow 2Cl_2 + O_2$ at 200 °C is found to be rate = $k[Cl_2O]^2$ (a) How would the rate change if $[Cl_2O]$ is reduced to one-third of its original value?

(b) How should the [Cl_2O] be changed in order to double the rate?

(c) How would the rate change if [Cl_2O] is raised to threefold of its original value? Ans:

(a) Rate equation for the reaction,

$r = k[Cl_2O]^2$

Let the new rate be r'; so

$r' = k[(Cl_2O)⅓]^2 = \frac{1}{9}$ times

(b) In order to have the rate = 2r, let the concentration of Cl_2O be x. So

$2r = kx^2$

We know that $r = k[Cl_2O]^2$

$\frac{2r}{r} = \frac{kx2}{k|Cl2O|2}$

or $2 = \frac{x2}{|Cl2O|2}$ or $x^2 =$

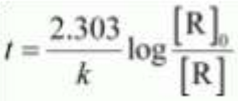
$2[Cl_2O]^2$ or $x = [Cl_2$

$O] \times \sqrt{2}$

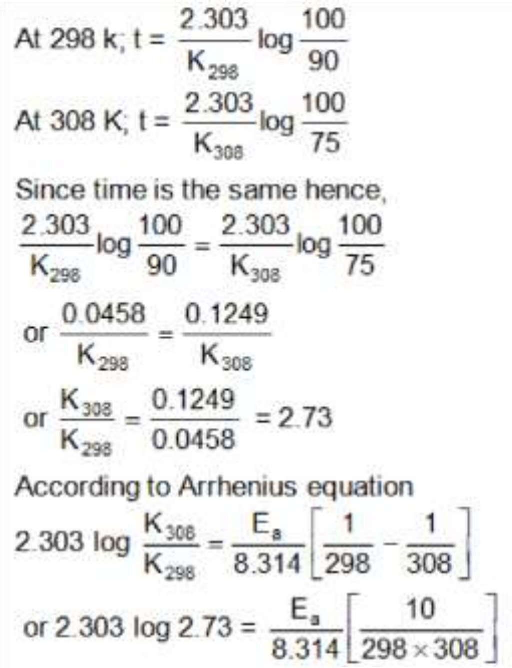
(c) New rate = $k[3Cl_2O]^2 = 9k[Cl_2O]^2 = 9r$

20. The time required for 10% completion of first order reaction at 298 K is equal to that required for its 25% completion at 308K. Calculate the energy of activation.

Ans: For first order reaction



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



At 298 k; $t = \frac{2.303}{K_{298}} \log \frac{100}{90}$

At 308 K; $t = \frac{2.303}{K_{308}} \log \frac{100}{75}$

Since time is the same hence,

$$\frac{2.303}{K_{298}} \log \frac{100}{90} = \frac{2.303}{K_{308}} \log \frac{100}{75}$$

or $\frac{0.0458}{K_{298}} = \frac{0.1249}{K_{308}}$

or $\frac{K_{308}}{K_{298}} = \frac{0.1249}{0.0458} = 2.73$

According to Arrhenius equation

$$2.303 \log \frac{K_{308}}{K_{298}} = \frac{E_a}{8.314}\left[\frac{1}{298} - \frac{1}{308}\right]$$

or $2.303 \log 2.73 = \frac{E_a}{8.314}\left[\frac{10}{298 \times 308}\right]$

$Ea = 2.303 \times 0.4361 \times 8.314 \times 9178.4$

$Ea = 76.64$ kJ/mol

4- d- & f-BLOCK ELEMENTS

Multiple Choice Questions

1. Which metal of 3d series is not considered as transition metal?
   Ans: Zn

2. Which configuration of d^{1-10} configurations does not find in ground state in 3d series? Ans: d^4 and d^9
3. What factor is responsible for interatomic interaction in transition metals?

   Ans: Presence of unpaired electrons in d sub-shell.
4. Which metal atom has smallest radii in 3d series? Ans: Ni
5. Transition elements exhibit higher enthalpies of atomisation due to Ans: presence of unpaired electrons and greater interatomic interaction.
6. Zn has the lowest enthalpy of atomization due to Ans: presence of all paired electrons
7. Which element of 3d series shows the highest oxidation state+7, lowest oxidation state +1, only +2 and only +3 oxidation states respectively Ans: Mn, Cu, Zn and Sc.
8. Higher oxidation states of transition metals are found with Ans: Fluorine and oxygen
9. In MnO_4^-, Mn is present as

   Ans: Tetrahedral, and d^3s hybridized
10. Which oxidation state is most common among the lanthanoid is Ans: +3
11. The magnetic moment of $[NiCl_4]^{2-}$ is Ans: 2.82
12. Colour of d-Block element ion is due to Ans: presence of unpaired electrons
13. $VH_{0.56}$ and $TiH_{1.7}$ are the examples of Ans: interstitial compounds
14. Chromite ore and pyrolusite ore are respectively Ans: $FeCr_2O_4$ and MnO_2
15. $K_2Cr_2O_7$ is converted to K_2CrO_4 by Ans: KOH
16. Lanthanoid contraction is due to

    Ans: imperfect shielding of d- and f-subshell electrons.
17. Which lanthanoid element gives IV oxidation state? Ans: Ce.
18. What is the main composition of mischmetal Ans: ~95% Lanthanoids and ~5% iron.
19. Assertion: Actinoid contraction is greater than lanthanoid contraction.

    Reason: In Actinoids 5f subshell is present with very poor shielding of electrons.

    Ans: Both assertion and reason are correct and reason is the correct explanation of assertion.
20. Assertion: Transition metal Fe is used as catalyst in ammonia production.

    Reason: Fe is consumed in the reaction to produce good yield of products. Ans: Assertion is correct but reason is not correct.

Descriptive Answer Questions:

1. Why do transition elements show variable oxidation states?

   Ans: Small energy gap between ns and (n-1) d sub shells, both ns and (n-1) d electrons take part in bond formation.

2. Write electronic configuration of following species.

(i) Cr (ii) Mn^{2+} (iii) Cu^{+}

Ans: (i) Ar[18], $3d^5$, 4s1 (ii) Ar[18] $3d^5$ (iii) Ar[18] $3d^{10}$

3. Describe the method of preparation of KMnO4 from MnO2.

Ans: $KMnO_4$ is prepared by fusion of pyrolusite ore (MnO_2) with KOH (alkali) and an oxidising agent like KNO_3. This produces the dark green K_2MnO_4 which disproportionates in acidic solution to give $KMnO_4$.

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

$3K_2MnO_4 + 2H_2SO_4$ $2KMnO_4 + MnO_2 + 2H_2O + 2K_2SO_4$

4. Write the steps involved in the preparation of $K_2Cr_2O_7$ from chromite ore.

Ans: (i) Conversion of chromite ore into sodium chromate

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

(ii) Conversion of sodium chromate into sodium dichromate

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

(iii) Conversion of sodium dichromate into potassium dichromate $Na_2Cr_2O_7 + 2KCl \rightarrow K_2Cr_2O_7 + 2NaCl$

5. Explain why Cu^+ is not stable in aqueous medium?

Ans: Cu^+ disproportionates into Cu^{2+} ion and Cu atom. This happens due to the higher hydration enthalpy of Cu^{2+}.

6. Transition metals and their many compounds act as good catalyst.

Ans: Transition metals and their many compounds act as good catalyst It is due to (a) partially filled(n-1) d orbital (b) Variable oxidation state (c) Ability to change oxidation state frequently

7. Transition metals have a strong tendency to form complexes.

Ans: Transition metals have a strong tendency to form complexes. Most of transition elements form complex compounds due to (a) small size (b) high charge (c) presence of vacant d-orbital of suitable energy.

8. Assign giving suitable reason which of the following pairs exhibits the property indicated against each.

(i) Sc^{3+} or Cr^{3+} exhibits Para magnetism

(ii) V or Mn exhibits a greater number of oxidation states exhibits

(iii) V^{4+}or V^{5+}exhibits colour

Ans: (i) Cr^{3+}has three unpaired electron in 3d – sub shell hence it is paramagnetic.

(ii) Mn exhibits more no. of oxidation states as it has five unpaired electrons in (n-1) d and two electrons in ns orbital take part in bonding.

(iii) V^{4+} is coloured as it has $3d^1$ configuration while V^{5+}has $3d^0$ configuration, hence electrons on V^{4+} undergoes d-d transition.

9. $La(OH)_3$ is stronger base than $Lu(OH)_3$Why?

Ans: Due to larger size of La^{3+} as compared to Lu^{3+}, it has a greater ionic character hence gives more no. of –OH ions.

10. Comment on the following:

(i) Zr and Hf have similar sizes ii) Actinoids show greater no. of oxidation state than Lanthanoids.

Ans: i) As a consequence of Lanthanoid contraction Zr and Hf have similar sizes. ii) As energies of 5f, 6d and 7s are comparable in actinoids, therefore electrons can easily be promoted from lower to higher orbital, hence more no. of oxidation states is shown.

11. Give reasons for the following:

(i) Zn is a soft metal.

(ii) $[Ti(H_2O)_6]^{3+}$ is coloured while $[Sc(H_2O)_6]^{3+}$ is colourless.

Ans: (i) This is because Zn ($3d^{10}4s^2$) has no any unpaired electrons in 3d-subshell. Hence metallic bonding is week in Zn metal.

(ii) The oxidation state of Ti in $[Ti(H_2O)_6]^{3+}$ is +3 and its configuration is [Ar] $3d^1$i.e one unpaired electron and hence it is coloured. Whereas the oxidation state of Sc in $[Sc(H_2O)_6]^{3+}$ is +3 and its configuration is [Ar] $3d^0$ i.e no unpaired electron and hence it is colourless.

12. The enthalpies of atomization of the transition metals are high. Why?

Ans: The enthalpies of atomization of the transition metals are high because of large number of unpaired electrons in their atoms, they have stronger inter atomic interaction and hence strong metallic bonding is present between atoms.

13. The transition metals generally form coloured compounds. Why?

Ans: The transition metals generally form coloured compounds due to presence of unpaired electrons in(n-1) d orbital and thus they can undergo d-d transition.

14. Transition elements form interstitial compounds. Why?

Ans: The transition metals can accommodate the small non-metallic atoms because of spaces between the metal atoms. These spaces are present because of their defects in their structures and existence of variable oxidation states.

15. Cr^{2+} is strongly reducing while Mn3+ is strongly oxidising although these have d4 configuration. Explain.

Ans: Cr^{2+} is strongly reducing because its configuration changes from 3d4 to 3d3 which is stable because of half-filled t2g subshell. On the other hand Mn(III) is strongly oxidising because of halffilled 3d5 configuration.

16. What is the cause and consequences of lanthanoid contraction? Ans: On moving left to right in lanthanoid series i) nuclear charge increases by 1 unit.

ii) one electron is added in 4f.

However, 4f electrons shield each other from nuclear charge poorly due to highly diffused shape of f-orbital therefore nuclear charge becomes more effective and causes very gradual decrease in size.

Consequences: -

(i) Resemblance of 2nd and 3rd transition series.

(ii) Similarity among lanthanoids.

(iii) Bascity difference.

17. Copper I compounds are white and diamagnetic but copper II compounds are coloured and paramagnetic. Why?

Ans: In copper I ion all orbitals are completely filled so its compounds are white and diamagnetic. The electronic configuration of copper II ion is $1s^22s^22p^63s^23p^63d^9$. it has one unpaired electron so it is paramagnetic and forms blue coloured compounds.

18. Calculate the “spin only” magnetic moment of M^{2+}(aq) ion (Z= 27).

Ans: Electronic configuration of M atom is $1s^22s^22p^63s^23p^63d^74s^2$. It has three unpaired electrons in d orbitals.

Magnetic moment = $\sqrt{}$ n(n+2) BM

= $\sqrt{3}$ (3+2)

= $\sqrt{15}$ = 3.87 BM

19. Complete the following chemical equations:

(i) $Cr_2O_7^{2-} + 6Fe^{2+} + 14H^+$ □

(ii) $2CrO_4^{2-} + 2H^+$ □

(iii) $5C_2O_4^{2-} + 2MnO_4^{-} + 16H^{+} \rightarrow$

(iv) $5S^{2-} + 2MnO_4^{-} + 16H^{+} \rightarrow$

Ans: Complete the following chemical equations:

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

(ii) $2CrO_4^{2-} + 2H^{+} \rightarrow Cr_2O_7^{2-} + H_2O$

(iii) $5C_2O_4^{2-} + 2MnO_4^{-} + 16H^{+} \rightarrow 10CO_2 + 2Mn^{+2} + 8H_2O$

(iv) $5S^{2-} + 2MnO_4^{-} + 16H^{+} \rightarrow 2Mn^{2+} + 8H_2O + 5S$

20. Predict which of the following will be coloured in aqueous solution?

Ti^{3+}, V^{3+}, Cu^{+}, Sc^{3+}, Mn^{2+}, Fe^{3+} and Co^{2+}. Give reasons for each.

Ans: Ions with electrons in the d-orbital will be the only ones that will be coloured, and the ions with empty d-orbital will be colourless.

Element	Atomic Number	Ionic State	Elec. Config. of ion
Ti	22	Ti^{3+}	[Ar] $3d^1$
V	23	V_{3+}	[Ar] $3d^2$
Cu	29	Cu^{+}	[Ar] $3d^{10}$
Sc	21	Sc^{3+}	[Ar]
Mn	25	Mn^{2+}	[Ar] $3d^5$
Fe	26	Fe^{3+}	[Ar] $3d^5$
Co	27	Co^{2+}	[Ar] $3d^7$

All other ions, except Sc^{3+}, will be coloured in an aqueous solution because of d–d transitions. Not $Sc^{3+,}$ as it has an empty d-orbital.

5- COORDINATION COMPOUNDS

Multiple Choice Questions

1. The monodentate ligands which can coordinate with the central atom through more than one site are called

   Ans: ambidentate ligand
2. The complexes in which the metal is bound to only one kind of ligands are termed Ans: Homoleptic complexes
3. Which geometrical isomer of $[Co(en)_2Cl_2]^{+}$ shows optical isomerism Ans: Cis isomer
4. IUPAC name of $K_2[HgI_4]$

   Ans: Potassiumtetraiodidomercurate(II)
5. IUPAC name of $[Pt(NH_3)BrCl(ONO)]^{-}$

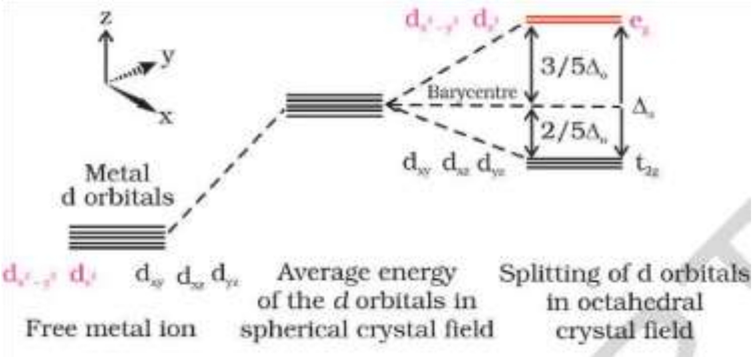
   Ans: Amminebromidochloridonitito-O-platinate(II) ion
6. 1 mole of coordination having formula $NiCl_2.6H_2O$, when treated with $AgNO_3$ solution, 2 moles of AgCl are formed. What is the formula of compound? Ans: $[Ni(H_2O)_6]Cl_2$
7. Which biomolecules are complexes of Mg and Fe respectively? Ans: Chlorophyll and Haemoglobin
8. In which ion d-d transition is not possible?

Ans: Ti^{4+}

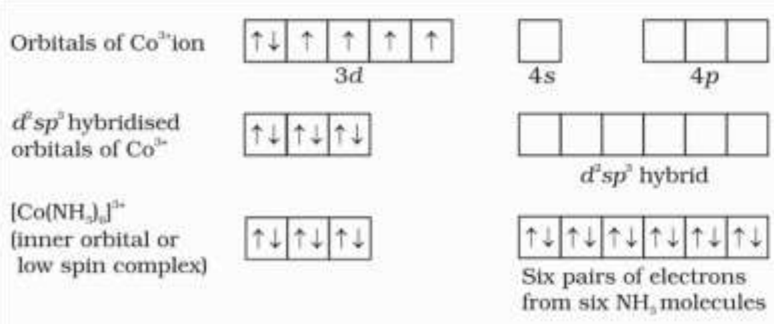
9. The CFSE for octahedral $[CoCl_6]^{4-}$ is 18000 cm^{-1}. The CFSE for tetrahedral $[CoCl_4]^{2-}$ will be Ans: 8000 cm^{-1}
10. Chelate ligands always have Ans: dentacy more than 2
11. If $\Delta_o < P$, the correct electronic configuration for d^4 system will be
    Ans: $t_{2g}^3\ e_g^1$
12. In an octahedral crystal field, the t_{2g} orbitals are
    Ans: lowered in energy by 0.4 Δ_o
13. How many ions are produced from the complex $[CoCl_2(NH_3)_4]Cl$ in solution? Ans: Two
14. Out of $[Fe(CN)_6]^{3-}$, $[Fe(C_2O_4)_3]^{3-}$ and $[Fe(H_2O)_6]^{3+}$ which is the most stable complex species? Ans: $[Fe(C_2O_4)_3]^{3-}$ due to (chelating effect)
15. How many possible isomers are possible with the formula $[Cr(H_2O)_4Cl_2]^+$? Ans: 3 isomers (one pair geometrical and one pair optical)
16. The geometrical isomerism in coordination compounds is exhibited by Ans: square planar and octahedral complexes
17. The tetrahedral complexes are generally high spin. This is because Ans: $\Delta_t < P$
18. Assertion: ($[Fe(CN)_6]^{3-}$ ion shows magnetic moment corresponding to two unpaired electrons.
    Reason: Because it has d^2sp^3 type hybridisation.
    Ans: Assertion is not correct but reason is correct.
19. Assertion: Linkage isomerism arises in coordination compounds containing ambidentate ligand. Reason: Ambidentate ligand has two different donor atoms.
    Ans: (i) Assertion and reason both are true, reason is the correct explanation of assertion.

Descriptive Answer Questions:

1. Arrange the following complexes in the increasing order of conductivity of their solution:
   $[Co(NH_3)_3Cl_3]$, $[Co(NH_3)_4 Cl_2]Cl$, $[Co(NH_3)_6]Cl_3$, $[Cr(NH_3)_5Cl]Cl_2$.
   Ans. Complex which give more ions on dissolution is more conducting.
   $[Co(NH_3)_6]Cl_3 > [Cr(NH_3)_5Cl]Cl_2 > [Co(NH_3)_4Cl_2]Cl > [Co(NH_3)_3Cl_3]$
2. Draw figure to show splitting of d- orbitals in an octahedral crystal field.



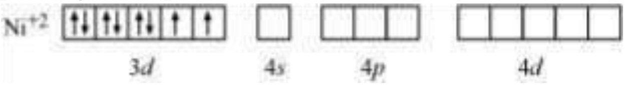
3. Which isomerisms are shown by following
   a) $[CO(NH_3)_5(NO_2)]Cl_2$ and $[CO(NH_3)_5(ONO)]Cl_2$
   b) $[Co(NH_3)_5SO_4]Br$ and $[Co(NH_3)_5Br]SO_4$
   Ans: a) Linkage isomerism b) Ionisation isomerism
4. Explain structure of $[Co(NH_3)_6]^{3+}$ on the basis of valence bond theory.
   Ans: In the diamagnetic octahedral complex, $[Co(NH_3)_6]^{3+}$, the cobalt ion is in +3 oxidation state and has the electronic configuration $3d^6$. The hybridisation scheme is as shown in diagram.



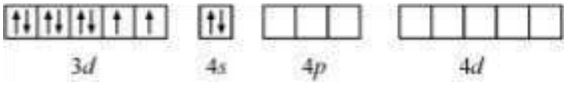
Six pairs of electrons, one from each NH_3 molecule, occupy the six hybrid orbitals. Thus, the complex has octahedral geometry and is diamagnetic because of the absence of unpaired electron. In the formation of this complex, since the inner d orbital (3d) is used in hybridisation, the complex, $[Co(NH_3)_6]^{3+}$ is called an inner orbital or low spin or spin paired complexes.

5. $[NiCl_4]^{2-}$ is paramagnetic while $[Ni(CO)_4]$ is diamagnetic though both are tetrahedral. Why?

Ans: Though both $[NiCl_4]^{2-}$ and $[Ni(CO)_4]$ are tetrahedral, their magnetic characters are different. This is due to a difference in the nature of ligands. Cl^- is a weak field ligand and it does not cause the pairing of unpaired 3*d* electrons. Hence, $[NiCl_4]^{2-}$ is paramagnetic.



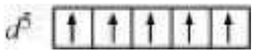
In $Ni(CO)_4$, Ni is in the zero oxidation state i.e., it has a configuration of $3d^8\ 4s^{2.}$



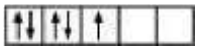
But CO is a strong field ligand. Therefore, it causes the pairing of unpaired 3 *d* electrons. Also, it causes the 4s electrons to shift to the 3d orbital, thereby giving rise to sp^3 hybridization. Since no unpaired electrons are present in this case, $[Ni(CO)_4]$ is diamagnetic.

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

Ans. In both $[Fe(H_2O)_6]^{3+}$and$[Fe(CN)_6]^{3-}$, Fe exists in the +3 oxidation state i.e., in d^5 configuration.



Since CN^- is a strong field ligand, it causes the pairing of unpaired electrons. Therefore, there is only one unpaired electron left in the *d*-orbital.



Therefore,

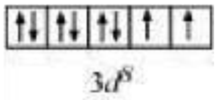
On the other hand, H_2O is a weak field ligand. Therefore, it cannot cause the pairing of electrons.

This means that the number of unpaired electrons is 5.

Therefore, $[Fe(H_2O)_6]^3$ is strongly paramagnetic, while $[Fe(CN)_6]^{3-}$ is weakly paramagnetic.

7. Predict the number of unpaired electrons in the square planar $[Pt(CN)_4]^{2-}$ ion.

Ans: $[Pt(CN)_4]^{2-}$, In this complex, Pt is in the +2 state. It forms a square planar structure. This means that it undergoes dsp^2 hybridization. Now, the electronic configuration of Pd(+2) is $5d^8$.



CN^- being a strong field ligand causes the pairing of unpaired electrons. Hence, there are no unpaired electrons in $[Pt(CN)_4]^{2-}$

8. What is spectrochemical series? Explain the difference between a weak field ligand and a strong field ligand.

Ans: A spectrochemical series is the arrangement of common ligands in the increasing order of their crystal-field splitting energy (CFSE) values. The ligands present on the R.H.S of the series are strong field ligands while that on the L.H.S are weak field ligands. Also, strong field ligands cause higher splitting in the *d* orbitals than weak field ligands.

$I^- < Br^- < S^{2-} < SCN^- < Cl^- < N_3 < F^- < OH^- < C_2O_4^{2-} \sim H_2O < NCS^- \sim H^- < CN^- < NH_3 < en \sim SO_3^{2-}$ $< NO_2^- < phen < CO$

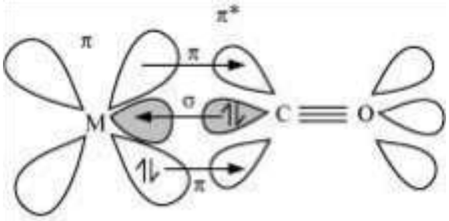
9. A solution of $[Ni(H_2O)_6]^{2+}$ is green but a solution of $[Ni(CN)_4]^{2-}$ is colourless. Explain.

Ans: In $[Ni(H_2O)_6]^{2+}$, H_2O is a weak field ligand. Therefore, there are unpaired electrons in Ni^{2+}. In this complex, the *d* electrons from the lower energy level can be excited to the higher energy level i.e., the possibility of *d−d* transition is present. Hence, $Ni(H_2O)_6]^{2+}$ is coloured.

In $[Ni(CN)_4]^{2-}$, the electrons are all paired as CN^- is a strong field ligand. Therefore, *d-d* transition is not possible in $[Ni(CN)_4]^{2-}$. Hence, it is colourless.

10. Discuss the nature of bonding in metal carbonyls.

Ans: The metal-carbon bonds in metal carbonyls have both σ and π characters. A σ bond is formed when the carbonyl carbon donates a lone pair of electrons to the vacant orbital of the metal. A π bond is formed by the donation of a pair of electrons from the filled metal *d* orbital into the vacant antibonding π* orbital (also known as back bonding of the carbonyl group). The σ bond strengthens the π bond and vice-versa. Thus, a synergic effect is created due to this metal-ligand bonding. This synergic effect strengthens the bond between CO and the metal.



11. What is meant by the *chelate effect*? Give an example.

Ans: When a ligand attaches to the metal ion in a manner that forms a ring, then the metal- ligand association is found to be more stable. In other words, we can say that complexes containing chelate rings are more stable than complexes without rings. This is known as the chelate effect.

For example: $[Ni(en)_3]^{2+}$ is more stable than $[Ni(NH_3)_6]^{2+}$ stable due to chelate effect.

12. Discuss briefly giving an example in each case the role of coordination compounds in: (i) biological system

(ii) medicinal chemistry

(iii) analytical chemistry

Ans: (i) Role of coordination compounds in biological systems:

We know that photosynthesis is made possible by the presence of the chlorophyll pigment. This pigment is a coordination compound of magnesium. In the human biological system, several coordination compounds play important roles. For example, the oxygen-carrier of blood, i.e., haemoglobin, is a coordination compound of iron.

(ii) Role of coordination compounds in medicinal chemistry:

Certain coordination compounds of platinum (for example, *cis*-platin) are used for inhibiting the growth of tumours.

(iii) Role of coordination compounds in analytical chemistry:

During salt analysis, a number of basic radicals are detected with the help of the colour changes they exhibit with different reagents. These colour changes are a result of the coordination compounds or complexes that the basic radicals form with different ligands.

13. Magnetic moment of $[MnCl_4]^{2-}$ is 5.92 BM. Explain giving reason.

Ans: The magnetic moment of 5.92 BM corresponds to the presence of five unpaired electrons in the d-orbitals of Mn2+ ion. As a result, the hybridisation involved is sp^3 rather than dsp^2. Thus, tetrahedral structure of $[MnCl_4]^{2-}$ complex will show 5.92 BM magnetic moment value.

14. Give the electronic configuration of the following complexes on the basis of Crystal Field Splitting theory.

$[CoF_6]^{3-}$, $[Fe(CN)_6]^{4-}$ and $[Cu(NH_3)_6]^{2+}$.

Ans: According to spectrochemical $CN^- > NH_3 > F^-$

Thus CN^- and NH_3 are strong field ligand pair up the t_2g electrons before filling eg set.

$[CoF_6]^{3-}, Co^{3+}(d^6)t_{2g}^4\,e_g^2.$

$[Fe(CN)_6]^{4-}, Fe^{2+}(d^6)t_{2g}^6\,e_g^0.$

$[Cu(NH_3)_6]^{2+}, Cu^{2+}(d^9)t_{2g}^6\,e_g^3.$

15. $CuSO_4.5H_2O$ is blue in colour while $CuSO_4$ is colourless. Why?

Ans. In $CuSO_4.5H_2O$, water acts as ligand as a result it causes crystal field splitting. Hence d-d transition is possible in $CuSO_4.5H_2O$ and shows colour. In the anhydrous $CuSO_4$ due to the absence of water (ligand), crystal field splitting is not possible and hence no colour.

16. How many EDTA ligand are required to make an octahedral coordination compound with Ca^{2+} ion and why?

Ans: One EDTA ligand because it is hexadentate ligand

17. What is synergic effect?

Ans: In metal carbonyl compounds CO ligands donate it's electron pairs in vacant d orbital of metal through sigma bond and metal also donate it's electron in vacant antibonding orbital of CO ligand, this is known as synergic effect.

18. Aqueous copper sulphate solution (blue in colour) gives:

(i) a green precipitate with aqueous potassium fluoride, and

(ii) a bright green solution with aqueous potassium chloride Explain these experimental results.

Ans: Aqueous $CuSO_4$ exists as $[Cu(H_2O)_4]SO_4$. It is blue in colour due to the presence of $[Cu[H_2O)_4]^{2+}$ ions.

(i) When KF is added:

$$\left[Cu(H_2O)_4\right]^{2+} + 4F^- \longrightarrow \underset{(green)}{\left[Cu(F)_4\right]^{2-}} + 4H_2O$$

(ii) When KCl is added:

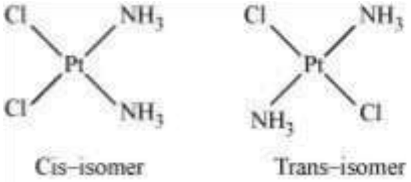
$$\left[Cu(H_2O)_4\right]^{2+} + 4Cl^- \longrightarrow \underset{(bright\ green)}{\left[CuCl_4\right]^{2-}} + 4H_2O$$

In both these cases, the weak field ligand water is replaced by the F^- and Cl^- ions.

19. What is the coordination entity formed when excess of aqueous KCN is added to an aqueous solution of copper sulphate? Why is it that no precipitate of copper sulphide is obtained when $H_2S(g)$ is passed through this solution?

Ans: When excess of KCN is added to copper sulphate solution a complex [Co(CN)6]3– is formed. It does not form precipitate with H2S because copper ions are not free they are present in combined state as a complex.

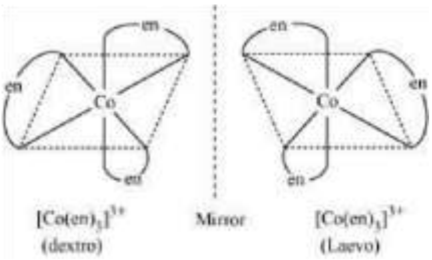
20. List various types of isomerism possible for coordination compounds, giving an example of each. Ans: (a) Geometric isomerism: This type of isomerism is common in heteroleptic complexes. It arises due to the different possible geometric arrangements of the ligands. For example:



Cis–isomer Trans–isomer

(b) Optical isomerism:

This type of isomerism arises in chiral molecules. Isomers are mirror images of each other and are non-superimposable.



$[Co(en)_3]^{3+}$ (dextro) $[Co(en)_3]^{3+}$ (Laevo)

(c) Linkage isomerism: This type of isomerism is found in complexes that contain ambidentate ligands. For example: $[Co(NH_3)_5(NO_2)]Cl_2$ and $[Co(NH_3)_5(ONO)Cl_2$

Yellow form Red form

(d) Coordination isomerism: This type of isomerism arises when the ligands are interchanged between cationic and anionic entities of differnet metal ions present in the complex.

$[Co(NH_3)_6][Cr(CN)_6]$ and $[Cr(NH_3)_6][Co(CN)_6]$

(e) Ionization isomerism: This type of isomerism arises when a counter ion replaces a ligand within the coordination sphere. Thus, complexes that have the same composition, but furnish different ions when dissolved in water are called ionization isomers. For e.g., $Co(NH_3)_5SO_4)Br$ and $Co(NH_3)_5Br]SO_4.$

(f) Solvate isomerism: Solvate isomers differ by whether or not the solvent molecule is directly bonded to the metal ion or merely present as a free solvent molecule in the crystal lattice.

$[Cr[H_2O)_6]Cl_3$	$[Cr(H_2O)_5Cl]Cl_2.H_2O$	$[Cr(H_2O)_5Cl_2]Cl.2H_2O$
Violet	Blue-green	Dark green

6- HALOALKANES & HALOARENES

Multiple Choice Questions

1. Which four carbon alcohol is a chiral molecule? Ans: Butan-2-ol
2. Addition of halogen acid to an alkene to form haloalkane is guided by Ans: Markovnikovs rule
3. Formation of product in dehydrohalogenetion of haloalkanes is guided by Ans: Saytzeffs Rule
4. How many isomers are possible of the monosubstituted haloalkane formula $C_5H_{11}Cl$ Ans: Eight
5. IUPAC name of $ClCH_2C\equiv CCH_2Br$ is Ans: 1-bromo-4-chlorobut-2-yne
6. 1-chlorobutane is treated with KI in dry acetone. Name of the reaction is Ans: Finkelstein reaction
7. Which of the monohalo derivatives of methane will has maximum dipole moment? Ans: CH_3F
8. Products in the following reaction respectively

   $CH_3CH_2I + NaCN \rightarrow$

   $CH_3CH_2I + AgCN \rightarrow$

Ans: CH_3CH_2CN and CH_3CH_2NC

9. The Synthesis of Alkyl Fluoride is best accomplished by Ans: Swarts Reaction
10. The best reagent to convert alcoholic group to halogen group Ans: $SOCl_2$/Pyridine
11. Lucas' reagent is a mixture of

Ans: Anhydrous $ZnCl_2$ in conc. HCl

12. In Dow's process, preparation of Phenol becomes faster on applying which of the group on Benzene? Ans: Electron Withdrawing Group
13. How many monosubstituted product would be obtained on free radical halogenation of neopentane? Ans: One
14. When HCl gas is treated with propene in presence of benzoyl peroxide, it gives Ans: 2-chloropropane (Markovnikov Rule followed)
15. Aryl halides cannot be prepared by the reaction of aryl alcohols with PCl_3, $SOCl_2$ because Ans: carbon-oxygen bond in phenols has a partial double bond character (Resonance effect).
16. The reaction of 2-bromobutane with KOH in presence of ethanol would result in the formation of Ans: but-2-ene
17. A mixture of methyl chloride and ethyl chloride on treatment with sodium and dry ether results in the formation of

Ans: Mixture of ethane, propane and butane

18. Haloarenes are less reactive than haloalkanes towards nucleophilic substitution reactions due to Ans: bond length of C-X is shorter in haloarenes
19. Assertion: Treating alcohols with thionyl chloride is the most preferred method to prepare haloalkanes.

Reason: In this method, the by products are escapable gases.

Ans: Both Assertion and reason are correct and reason is the correct explanation of assertion.

20. Assertion: Toluene produces two different monohaogenated product in presence of light or in absence of light.

Reason: in present of light benzyl chloride is formed by free radical mechanism.

Ans: Both Assertion and reason are correct and reason is the correct explanation of assertion.

Descriptive Answer Questions:

1. The correct order of boiling point of all isomers of formula C_4H_9Cl

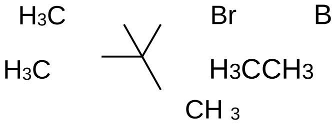
Ans: $CH_3CH_2CH_2CH_2Br > CH_3CH_2CH_2CH(Br)CH_3 > (CH_3)_2CHCH_2Br > (CH_3)_3CBr$

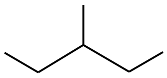
2. Electrophilic reactions are given by haloarenes and nucleophilic substitution reaction can also be given. Justify.

Ans: because the halo-groups are the only ortho - para directing but they are deactivating groups

3. In the following pairs of halogen compounds, which undergo faster S_N1 reaction?

(a)





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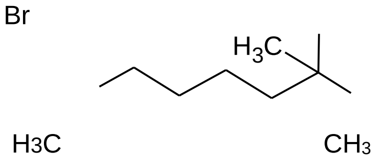
(b)



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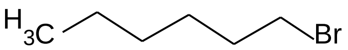
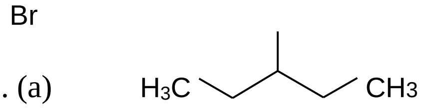
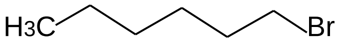


Ans. (a)  (b) 

4. What is racemic mixtures?

   Ans: equimolar mixture of enantiomers of a compound is called racemic mixture.

5. What is Saytzaffrule? Give example

   Ans: During dehydrohalogination of alkyl halide, formation of such alkene is preferred which has a greater number of alkyl group with doubly bonded carbon atom. (More symmetrical alkene)

   $CH_3CH(Br)CH_2CH_3 \xrightarrow{alc.\ KOH} CH_3CH{=}CHCH_3 + CH_3CH_2CH{=}CH_2$

   But-2-ene (major) But-1-ene (minor)

6. Write two differences between S_N1 and S_N2 reaction.

   Ans: (i) Carbocation is formed in S_N1 and given by tertiary alkyl halide while S_N2 is given by primary alkyl halide where carbocation is not formes.

   (ii) 50% inversion and 50% retention takes place in S_N1 while 100% inversion takes place in S_N2 is due to lack of steric hindrance.

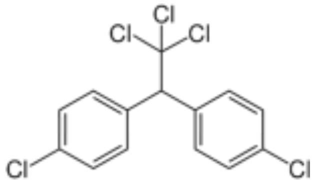
7. Write the name and structures of any three polyhalogen compounds with their uses.

   Ans: Chloroform (Trichloromethane) - $CHCl_3$ Used as anaesthetic

   Iodoform (Triiodomethane) - CHI_3

   Used as antiseptic

   DDT (p,p'-dichlorodiphenyltrichloromethane) Used as insecticide



8. Which is -

   (a) better nucleophile Br^- or I^-

   (b) ambident nucleophile CN^- or Cl^-

   (c) show nucleophilic substitution C_6H_5Cl or CH_3Cl

   Ans: (a) I^-

   (b) CN^-

   (c) CH_3Cl

9. Give reason why-

   (i) Aryl halides are less reactive towards nucleophilic substitution reaction than Alkyl halides (ii) Chloromethane react with KCN to form ethanenitrile as the main product but with AgCN it form methyl carbylamines

   (iii) Alkyl chloride react with aqueous KOH leads to the formation of alcohols but in presence of alcoholic KOH leads to formation of alkenes.

   Ans: (i) Aryl halide are less reactive because its C-X bond has partial double bond character due to resonance.

   (ii) Because KCN is ionic while AgCN is covalent in nature.

   (iii)Because aq. KOH contains OH^- ions which are strong nucleophiles but Alc. KOH contains alkoxide ions which are more stronger base and will remove H^+.

10. How can you convert the following- (a) But-1-ene into 1-Bromobutane

(b) 2- Bromobutane into But-2-ene

(c) Chloromethane into Ethane

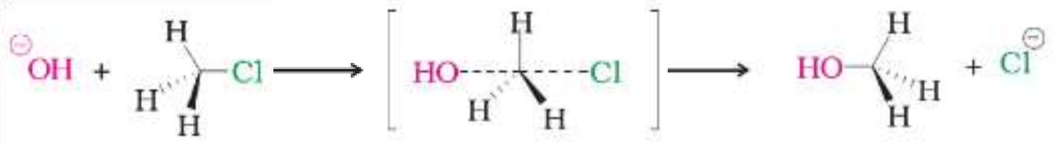
Ans: (a) $CH_3\text{-}CH_2\text{-}CH{=}CH_2 + HBr$ (with peroxide) $\rightarrow CH_3\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}Br$

(b) $CH_3\text{-}CH_2\text{-}CH(Br)\text{-}CH_3$ + alc. $KOH \rightarrow CH_3\text{-}CH{=}CH\text{-}CH_3 + KBr + H_2O$

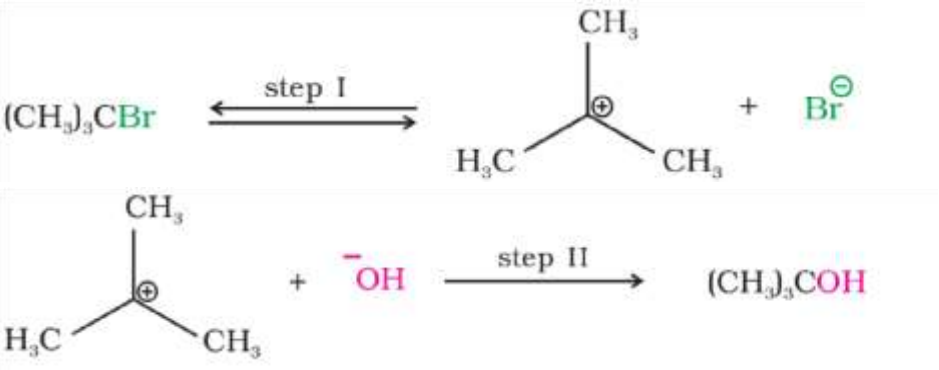
(c) $2CH_3Cl + 2Na$ (with dry ether) $\rightarrow CH_3\text{-}CH_3 + 2NaCl$

11. Explain S_N1 and S_N2 mechanism.

Ans: The reaction between CH_3Cl and hydroxide ion to yield methanol and chloride ion follows a second order kinetics, i.e., the rate depends upon the concentration of both the reactants.



The reaction between tert-butyl bromide and hydroxide ion yields tert-butyl alcohol and follows the first order kinetics. It occurs in two steps. In step I, the polarised C—Br bond undergoes slow cleavage to produce a carbocation and a bromide ion. The carbocation thus formed is then attacked by nucleophile in step II to complete the substitution reaction.



12. Predict the order of reactivity of the following compounds in S_N1 and S_N2 reactions:

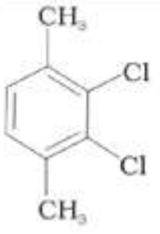
$C_6H_5CH_2Br$, $C_6H_5CH(C_6H_5)Br$, $C_6H_5CH(CH_3)Br$, $C_6H_5C(CH_3)(C_6H_5)Br$

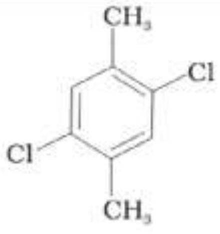
Ans:

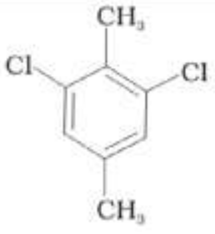
$C_6H_5C(CH_3)(C_6H_5)Br > C_6H_5CH(C_6H_5)Br > C_6H_5CH(CH_3)Br > C_6H_5CH_2Br$ (S_N1)

$C_6H_5C(CH_3)(C_6H_5)Br < C_6H_5CH(C_6H_5)Br < C_6H_5CH(CH_3)Br < C_6H_5CH_2Br$ (S_N2)

13. Which of the following compounds will have the highest melting point and why?


(I)


(II)


(III)

Ans: II, due to symmetry of para-positions; it fits into crystal lattice better than other isomers.

14. Give reasons: (i) C-Cl bond length in chlorobenzene is shorter than C-Cl bond length in CH3-Cl. (ii) The dipole moment of chlorobenzene is lower than that of cyclohexyl chloride

Ans: (i) In chlorobenzene each carbon atom is sp^2 hybridised. Due to resonance, there is a partial double bond character, so bond length is short.

(ii) In chlorobenzene carbon to which chlorine is attached is sp^2 hybridised and and is more electronegative than the corresponding carbon in cyclohexyl chloride which is sp^3 hybridised.

15. Why Grignard reagent should be prepared under anhydrous conditions?

Ans: Grignard reagent react with water to form alkanes, therefore they are prepared under anhydrous conditions.

16. p- dichlorobenzene has highest m.p. than those of ortho and meta –isomers?

Ans: p- Dichlorobenzene is symmetrical, fits into the crystal lattice more readily and has higher melting point.

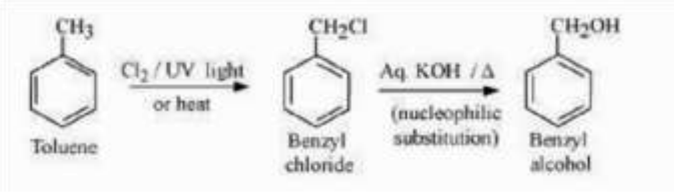
17. How do you convert the following

(i) Toluene to benzylalcohol

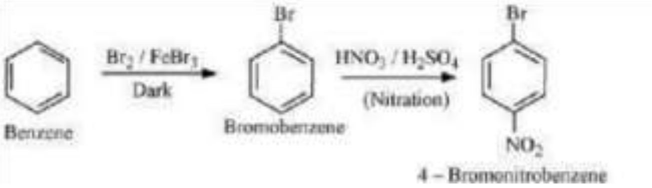
(ii) Benzene to 4-bromonitrobenzene

(iii) Benzylalcohol to 2-phenylethanoicacid

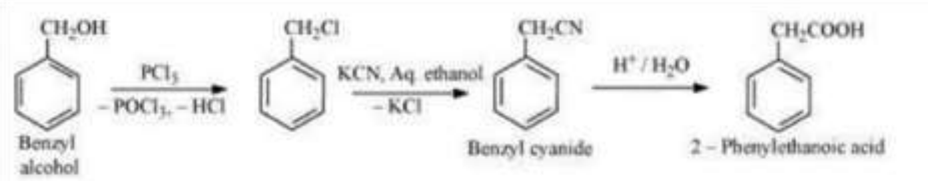
Ans: (i)



(ii)



(iii)



18. How can you distinguish between 1,1-dichloroethane and 1,2-dichloroethane? Give reactions also.

Ans: 1,1-Dichloroethane on reaction with aq. KOH gives ethanal a pungent smelling aldehyde, which gives insoluble yellow 2,4-DNP derivative with 2,4-dinitrophenylhydrazine.

$CH_3–CHCl_2 \xrightarrow{aq.KOH} CH_3–CHO \xrightarrow{2,4-DNP}$ Yellow ppt.

1,1-Dichloroethane Ethanal

1,2-Dichloroethane on reaction with aq. KOH gives ethane-1,2-diol which is odourless and gives no ppt. with 2,4 - DNP reagent.

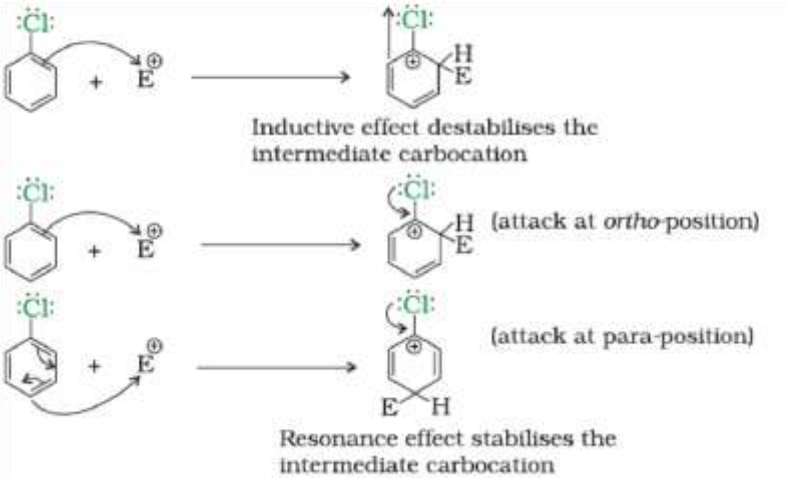
$CH_2Cl–CH_2Cl$ + aq. KOH $HOCH_2–CH_2OH$ Yellow ppt.

1,1-Dichloroethane Ethanal

19. Although chlorine is an electron withdrawing group, yet it is *ortho*-, *para*- directing in electrophilic aromatic substitution reactions. Why?

Ans: Chlorine withdraws electrons through inductive effect and releases electrons through resonance. Through inductive effect, chlorine destabilises the intermediate carbocation formed during the electrophilic substitution

Through resonance, halogen tends to stabilise the carbocation and the effect is more pronounced at *ortho*- and *para*- positions. The inductive effect is stronger than resonance and causes net electron withdrawal and thus causes net deactivation. The resonance effect tends to oppose the inductive effect for the attack at *ortho*- and *para* positions and hence makes the deactivation less for *ortho*- and *paraattack*. Reactivity is thus controlled by the stronger inductive effect and orientation is controlled by resonance effect.



20. What happens when

(i) n-butyl chloride is treated with alcoholic KOH,

(ii) ethyl chloride is treated with aqueous KOH,

(iii) methyl bromide is treated with sodium in the presence of dry ether, (iv) methyl chloride is treated with KCN?

(v) methyl chloride is treated with AgCN?

Ans: (i) Dehydrohalogenation occurs and But-1-ene will be formed.

$CH_3CH_2CH_2CH_2Cl + \text{alc. KOH} \rightarrow CH_3CH_2CH{=}CH_2$

(ii) Ethanol is formed by SN2 mechanism.

$CH_3CH_2Cl + \text{aq. KOH} \rightarrow CH_3CH_2OH$

(iii) Its Wurtz reaction. Ethane will be formed.

$2CH_3Cl + 2Na \rightarrow CH_3\text{-}CH_3 + 2NaCl$

(iv) Nucleophilic substitution takes place and methyl cyanide is formed.

$CH_3Cl + KCN \rightarrow CH_3CN$

(v) Methyl isocyanide is formed because AgCN is predominantly covalent in nature and nitrogen is free to donate electron pair forming isocyanide as the main product.

$CH_3Cl + AgCN \rightarrow CH_3NC$

7- ALCOHOLS, PHENOLS AND ETHERS

Multiple Choice Questions

1. Which type of compound gives idoform test. Ans: Compound containing –$COCH_3$
2. Alcohols can be converted to aldehydes by

   Ans: CrO_3 or PCC
3. Ethyl alcohol can be prepared from Grignard reagent by the reaction of Ans: HCHO
4. Phenol is more acidic than alcohol because

   Ans: phenoxide ion is resonance stabilised, alkoxide ion is unstable.
5. Which compound is obtained by dehydrogenation of secondary alcohols? Ans: Ketones
6. The reaction of carboxylic acid with catalysed by conc.H_2SO_4 is called? Ans: Esterification
7. On heating aqueous solution of benzene diazonium chloride, which compound is formed? Ans: Chlorobenzene (Sandmeyer rea
8. When phenol is heated with $CHCl_3$ and alcoholic KOH when salicyladehyde is produced. This reaction is known as

   Ans: Reimer-Tiemann reaction
9. Bond angle is greater in alcohols, phenols or ethers.

   Ans: In ethers, due to two carbons connected to oxygen.
10. Phenol is distinguished by treating with Ans: $FeCl_3$
11. What is the correct order of reactivity of alcohols in the following reaction?

    $R–OH + HCl \xrightarrow{ZnCl_2} R–Cl + H_2O$

    Ans: $3^o > 2^o > 1^o$
12. Phenol is more acidic than Ans: p-cresols
13. Phenol is less acidic than Ans: p-nitrophenol
14. Primary, secondary and tertiary alcohols are differentiated by Ans: Lucas Test
15. Dehydration of alcohol at lower temperature (413K) yields Ans: ether
16. Asprin is prepared by esterification reaction between Ans: Salicylic acid and acetic anhydride
17. Denaturation of ethanol is done by mixing in it Ans: Copper sulphate and pyridine
18. Oxidation of phenol by potassium dichromate gives Ans: Benzoquinone
19. Assertion: In case of phenol, bromination takes place even in absence of Lewis acid whereas bromination of benzene takes place in presence of Lewis acid like FeBr3.

    Reason: –OH group attached to benzene ring is highly activating

    Ans: Both Assertion and reason are correct and reason is the correct explanation of assertion.
20. Assertion: In Lucas test, 3^o alcohols react immediately.

    Reason: An equimolar mixture of anhydrous $ZnCl_2$ and conc. HCl is called Lucas reagent.

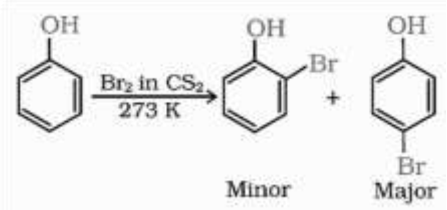
    Ans: Both Assertion and reason are correct and reason is not the correct explanation of assertion.

Descriptive Answer Questions:

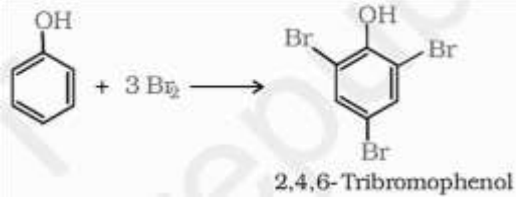
1. Name the chemical test used to distinguish between Phenol and Ethanol?

   Ans: Phenol is distinguished by $FeCl_3$ and ethanol is identified by ceric ammonium nitrate. Phenol gives blue colour with $FeCl_3$ while ethanol gives red colour with ceric ammonium nitrate.

2. Write the reaction of Bromine in CS_2 and bromine water with phenol. Ans: Bromine in CS_2 gives o-bromophenol and p-bromophenol



   Bromine water gives 2,4,6-tribromophenol



3. Name simple alcohol, aldehyde and ketone which give iodoform test. Ans: Ethanol, ethenal and propanon

4. Arrange the following compounds in the decreasing order of acid strength.

   Propan-1-ol, 2, 4, 6-trinitrophenol, 3-nitrophenol, 3,5-dinitrophenol Ans:

   2, 4, 6-trinitrophenol > 3,5-dinitrophenol > 3-nitrophenol > propan-1-ol

5. Alcohols are highly soluble in water. Why?

   Ans: Due to the formation of H-Bonding between alcohols and water.

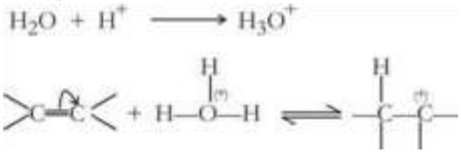
\6. Arrange the following alcohols in the order of increasing reactivity towards Lucas reagent.

   2-butanol, 1-butanol, 2-methyl-2-propanol

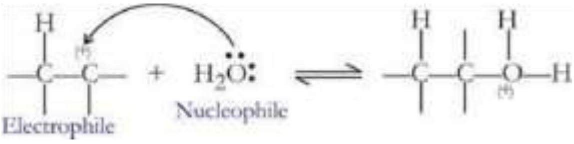
   Ans: 1-butanol < 2-butanol < 2-methyl-2-propanol

7. Write the mechanism of hydration of ethene to form ethanol.

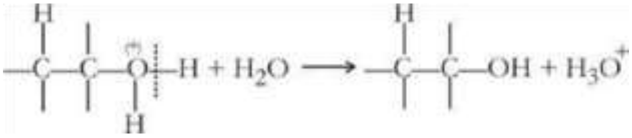
   Ans: Step 1. Protonation



   Step 2. Nucleophilic attack of water on carbocation

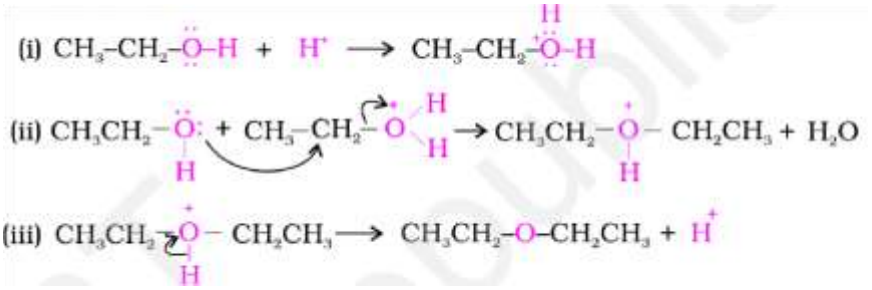


   Step 3. Deprotonation



8. Write the mechanism of dehydration of ethanol using Conc. H_2SO_4 at 413 K.

   Ans:



9. Why is sulphuric acid not used during the reactions of alcohols with KI?

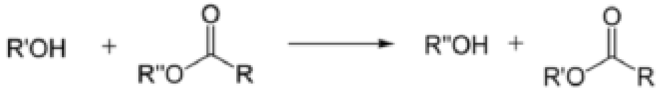
Ans: Sulphuric acid is an oxidizing agent. It oxidizes HI produced during the reaction, to I_2.

$$2KI + H_2SO_4 \longrightarrow 2KHSO_4 + 2HI$$

$$2HI + H_2SO_4 \longrightarrow H_2O + I_2 + SO_2$$

10. Write short notes on transesterification.

Ans. When an ester is treated with excess of another alcohol other than the one from which ester has been derived in presence of corresponding sodium or potassium Alkoxide or an acid H_2SO_4/HCl as catalyst a new ester is formed.



11. Ethers are cleaved by acids not by bases. Why?

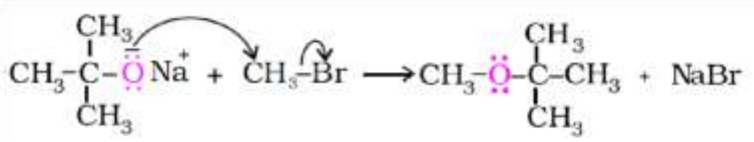
Ans. The C-O-C bond in ethers is very strong. The addition of acid shall protonate the oxygen atom as a result, the attack by nucleophiles as Br^- /I^- on the less hindered alkyl group makes the process facile.

12. Explain following named reactions.

(i) Williamson's synthesis (ii)
Kolbe's reaction

(iii) Reimer-Tiemann reaction

Ans: (i) Williamson's synthesis: In this reaction, an alkyl halide is allowed to react with sodium alkoxide to form an ether. Better results are obtained if the alkyl halide is primary.



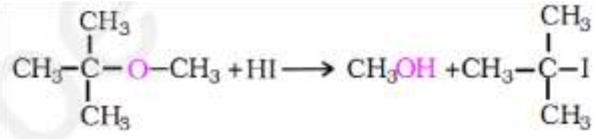
(ii) Kolbe's reaction

Phenoxide ion generated by treating phenol with sodium hydroxide is even more reactive than phenol towards electrophilic aromatic substitution. Hence, it undergoes electrophilic substitution with carbon dioxide, a weak electrophile. Ortho hydroxybenzoic acid is formed as the main reaction product.

(iii) Reimer-Tiemann reaction

On treating phenol with chloroform in the presence of sodium hydroxide, a –CHO group is introduced at ortho position of benzene ring. This reaction is known as Reimer - Tiemann reaction.

13. What will be the products when HI reaction with methyl-tert-butylether. Ans: Tertiary butyl iodide and methanol is formed.



$$CH_3-C(CH_3)_2-O-CH_3 + HI \longrightarrow CH_3OH + CH_3-C(CH_3)_2-I$$

14. Account for the following:

(a) Propanol has higher boiling point than butane

(b) O-nitrophenol is more acidic than o- methoxyphenol

(c) Phenol does not give protonation reaction readily

Ans. (a) both are of comparable masses but because of intermolecular H-bonding in propanol which is not present in butane due to absence of –OH group. There are only weak Van Der Waals forces in butane and hence has lower boiling point.

(b) $-NO_2$ group is an electron withdrawing group and tend to decrease the electron density on –OH thereby increasing its tendency to lose H^+ ions, consequently increasing the acidic nature. but in case of o-methoxyphenol, $-OCH_3$ group has +I effect and hence less acidic.

(c) C-OH in phenol is stabilized due to resonance and electron pair at oxygen atom in phenol is not readily available to proton, thus protonation not occurs readily.

15. Why 1% ethanol should be added to chloroform sample while storing?

Ans: Chloroform forms phosgene gas which is highly poisonous. Ethanol reacts with phosgene to give harmless diethyl carbonate

$COCl_2 + 2C_2H_5OH \rightarrow (C_2H_5)_2CO_3 + 2HCl$

16. Give chemical test to distinguish b/w

(i) Phenol and benzyl alcohol

(ii) Butan-2-ol and 2-methylpropan-2-ol

Ans: (i) phenol decolorizes bromine water giving a white ppt but benzyl alcohol does not. Phenol also gives violet colouration with neutral $FeCl_3$ solution.

(ii) Lucas test: butan-2-ol react with Lucas reagent and turbidity appears within 5 min but second one react with the same to give turbidity immediately.

17. Name the reagents used in the following reactions:

(i) Oxidation of a primary alcohol to carboxylic acid.

(ii) Oxidation of a primary alcohol to aldehyde.

(iii) Bromination of phenol to 2,4,6-tribromophenol.

(iv) Benzyl alcohol to benzoic acid.

(v) Dehydration of propan-2-ol to propene.

(vi) Butan-2-one to butan-2-ol.

Ans: (i) $KMnO_4/H^+$

(ii) PCC or CrO3

(iii) Bromine water

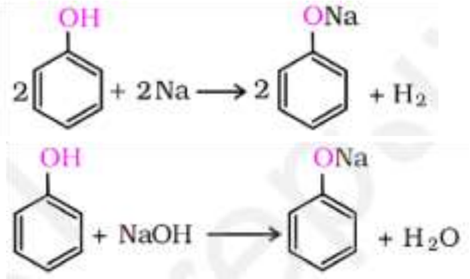
(iv) $KMnO_4/H^+$

(v) Conc. H_2SO_4

(vi) $LiAlH_4$

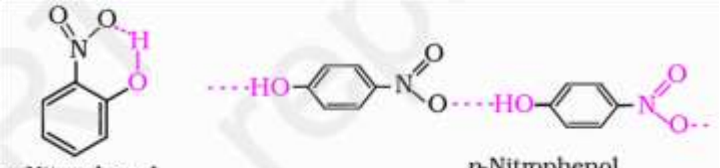
18. Give two reactions that show the acidic nature of phenol. Compare acidity of phenol with that of ethanol.

Ans: When phenol reacts with sodium metal and sodium hydroxide forms sodium phenoxide. These reactions show the acidic nature of phenol.



19. While separating a mixture of ortho and para nitrophenols by steam distillation, name the isomer which will be steam volatile. Give reason.

Ans: Ortho-nitrophenol is steam volatile. The reason is chelation due to intramolecular H-bonding. So, it can be separated by steam distillation from p-nitrophenol. Para-nitrophenol is not steam volatile due to the presence of intermolecular H-bonding.



o-Nitrophenol (Intramolecular H-bonding)

p-Nitrophenol (Intermolecular H-bonding)

20. How are the following conversions carried out? (i) Propene □ Propan-2-ol.

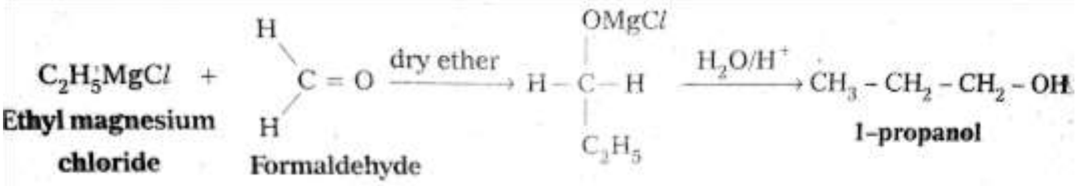
(ii) Benzyl chloride □ Benzyl alcohol.

(iii) Ethyl magnesium chloride □ Propan-1-ol.

Ans: (i) $CH_3CH=CH_2 \xrightarrow{H_2O/H^+} CH_3CH(OH)CH_3$

(ii) $C_6H_5Cl \xrightarrow{NaOH-(623K)} C_6H_5OH$

(iii)



8- ALDEHYDES, KETONES AND CARBOXYLIC ACIDS

Multiple Choice Questions

1. Correct order of chloroderivative of acetic acid.

   Ans: $CH_3COOH < CH_2ClCOOH < CHCl_2COOH < CCl_3COOH$

2. The reagent which does not react with both, acetone and benzaldehyde

   Ans: Fehling’s solution

3. Being an aldehyde benzaldehyde does not give

   Ans: Fehling’s Test

4. Cannizzaro’s reaction is given by

   Ans: HCHO and C_6H_5CHO (Don’t bear □-hydrogen)

5. complete reduction of carbonyl group (>C=O) is done by

   Ans: Clemmensen’s reduction or Wolf-Kishner reduction

6. □-Halo derivative of acid is prepared by Ans: HVZ reaction

7. The reagent(s) which can be used to distinguish acetophenone from benzophenone is (are) Ans: I_2 & KOH (iodoform test)
8. Carboxylic acid group doesn't give the usual addition & elimination reaction of aldehydes & ketones because

   Ans: Carboxylate ion gets stabilized by resonance.
9. Etard reaction, Rosenmund reduction and Gattermann-Koch reaction are common in Ans: Product is benzaldehyde
10. Write characteristic test for formaldehyde and acetaldehyde

    Ans: all aldehyde gives Tollens test, acetaldehyde gives iodoform test

11 formic acid and acetic acid

Ans: All acids give $NaHCO_3$ test, formic acid gives Tollens test.

12. The chemical that undergoes self-oxidation & self-reduction in the same reaction is Ans: formaldehyde (Cannizzaro reaction)
13. The product formed in Aldol condensation is Ans: a beta hydroxyaldehyde or ketone
14. Correct order of alcohol, aldehyde and acid of same no. of carbons (4 carbons)

    Ans: $CH_3CH_2CH_2CHO < CH_3CH_2CH_2CH_2OH < CH_3CH_2CH_2COOH$
15. □-Hydrogen is necessary for

    Ans: Aldol condensation and Hell-Volhard-Zelinsky reaction
16. What happens when acetic acid is dissolved in CCl_4. Ans: It forms dimers
17. Benzoic acid does not give Friedel-Crafts reaction because Ans: $AlCl_3$ gets bonded to the carboxyl group
18. Assertion: Compounds containing —CHO group are easily oxidised to corresponding carboxylic acids.

    Reason: Carboxylic acids can be reduced to alcohols by treatment with $LiAlH_4$.

    Ans: Both Assertion and reason are correct and reason is not the correct explanation of assertion.
19. Assertion: Aromatic aldehydes and formaldehyde undergo Cannizzaro reaction.

    Reason: Aromatic aldehydes are almost as reactive as formaldehyde. Ans:
    Assertion is correct but reason is not correct
20. Assertion: Aldehydes and ketones, both react with Tollen's reagent to form silver mirror.

    Reason: Both, aldehydes and ketones contain a carbonyl group.

    Ans: Assertion is not correct but reason is correct

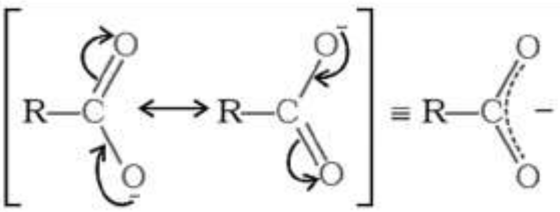
Descriptive Answer Questions:

1. Why Carboxylic acid have higher boiling point than alcohols as both have intermolecular hydrogen bonding?

   Ans: Carboxylic acid forms a dimer due to double H-bonding. Therefore it has higher boiling point than alcohols.
2. Why do Carboxylic acids not give the characteristic reactions of a carbonyl group?

   Ans: Due to resonance, It does not have free carbonyl group.
3. Although phenoxide ion has more no. of resonating structures than carboxylate ion, even though carboxylic acid is a stronger acid why?

   Ans. The phenoxide ion has non-equivalent resonance structures in which negative charge is on less electronegative C atom and positive charge is on more electronegative O-atom. Carboxylate ion has equivalent resonance structure in which negative charge is delocalized on two electronegative Oatoms hence resonance is more effective.



So Carboxylic acid is stronger acid.

4. a) What type of aldehydes undergo Cannizzaro reaction?

   b) Out of acetophenone and benzophenone, which gives iodoform test?

   Ans: a) Aromatic and aliphatic aldehydes which do not contain α hydrogens undergoes Cannizzaro reaction.

   b) The compound should have $CH_3CO–$ group to show the iodoform test. Acetophenone ($C_6H_5COCH_3$) contains the group $CH_3CO–$ attached to carbon and hence given iodoform test while benzophenone does not contain this group and hence does not give iodoform test.

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

   CH_3CHO, CH_3CH_2OH, CH_3OCH_3, $CH_3CH_2CH_3$

   Ans: $CH_3CH_2CH_3 < CH_3OCH_3 < CH_3CHO < CH_3CH_2OH$

6. Why does solubility decreases with increasing molecular mass in carboxylic acid?

   Ans: Because with increase of molecular mass size of hydrophobic carbon chain length increases.

7. Why PCC cannot oxidise methanol to methanoic acid while $KMnO_4$ can oxidise?

   Ans: This is because PCC is a mild oxidizing agent and can oxidize methanol to methanal only. While $KMnO_4$ is strong oxidizing agent which oxidizes it to methanoic acid.

8. Would you expect benzaldehyde to be more reactive or less reactive in nucleophilic addition reactions than propanal? Explain your answer.

   Ans: C-atom of carbonyl group of benzaldehyde is less electrophilic than C-atom of carbonyl group in propanal. Polarity of carbonyl group is in benzaldehyde reduced due to resonance making it less reactive in nucleophilic addition reactions.

   There is no such resonance effect in propanal and so the polarity of carboxyl group in it is more than in benzaldehyde. This makes propanal more reactive than benzaldehyde.

9. Distinguish the following pair of compounds

   (a) Propanal and Propanone

   (b) Acetophenone and benzophenone (c)
   Phenol and benzoic acid

   Ans. (a) Propanal gives a silver mirror on oxidation by Tollen's reagent but propanone does not.

   CH_3CH_2CHO □ $2[Ag□NH_3□_2]^+$ □ $3OH^–$ □ $CH_3CH_2COO^-$ □ $2Ag\downarrow$ □ $2H_2O$ □ $4NH_3$

   Propanal Tollen's reagent silver mirror

   b) Acetophenone gives a positive iodoform test with sodium and NaOH as it has a terminal $-COCH_3$ group unlike benzophenone

   $C_6H_5COCH_3 + 3I_2 + 4NaOH$ □ $CHI_3 + C_6H_5COONa + 3NaI + 3H_2O$

   Acetophenone Iodoform

   c) Benzoic acid on treatment with sodium hydrogen carbonate produces efferversense due to evolution of CO_2, as it is more acidic than phenol.

C_6H_5COOH □ $NaHCO_3$ □ C_6H_5COONa □ $CO_2 \uparrow$ □ H_2O

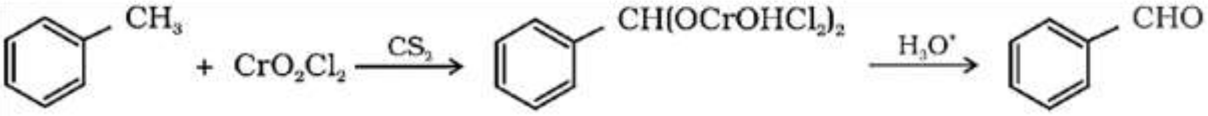
Benzoic acid (effervescence)

10. How will you carry out the following conversions (Write chemical equations):

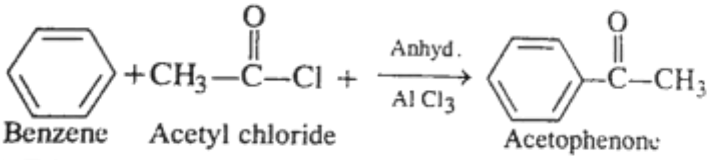
(a) Toluene to Benzaldehyde

(b) Benzene to acetophenone (c) Benzoyl chloride to benzaldehyde

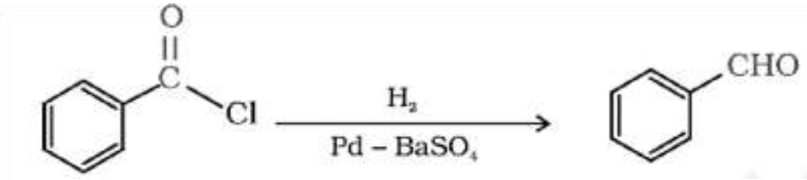
Ans. (a)



(b)



(c)



11. Distinguish the following pair of compounds

a) Benzaldehyde and acetaldehyde

b) Pentan-2-one and Pentan-3-one

c) Formic acid and acetic acid

Ans: a) Acetaldehyde give Fehling's Test but benzaldehyde does not.

b) Pentan-2-one gives a yellow ppt. of iodoform on treatment with a mixture of NaOH and I_2 but not Pentan-3-one.

c) Formic acid gives Tollens Test while acetic acid not.

12. Can Gattermann-Koch reaction be considered similar to Friedel Craft's acylation?

Ans: Yes, the reason being that in Friedel Craft's acylation reactions, benzene is treated with an acid chloride (CH_3COCl) in presence of anyhd. $AlCl_3$. Since HCOCl (Formyl Chloride) is not stable. Therefore, in Gattermann-Koch reaction, it is prepared in situ by reacting CO with HCl gas in presence of anhydrous $AlCl_3$. Thus, Gattermann-Koch "action is similar to F.C. acylation reaction".

13. Why does methanal not give aldol condensation while ethanal gives?

Ans: This is because only those compounds which have α-hydrogen atoms can undergo aldol reaction. Ethanal possesses α-hydrogen and undergoes aldol condensation. Methanal has no alpha hydrogen atoms hence does not undergo aldol condensation.

14. Give the reasons for the following:

(a)Why is the oxidation of toluene to benzaldehyde with CrO_3 carried out in the presence of acetic anhydride?

(b) Why pH of reaction should be carefully controlled while preparing ammonia derivatives of carbonyl compound?

Ans. (a) If acetic anhydride is not used we will get benzoic acid. Acetic anhydride used to prevent oxidation of benzaldehyde to benzoic acid.

(b) In strongly acidic medium ammonia derivatives being basic will react with acids and will not react with carbonyl compound. In basic medium, OH- will attack carbonyl group. So, the pH of a reaction should be carefully controlled.

15. How can you convert the following- (i) ethanal into ethanoic acid

(ii) ethanal into ethanol

(iii) ethanoic acid into ethanol

Ans.(i) $CH_3CHO \xrightarrow{KMnO_4 / H^+} CH_3COOH$

(ii) $CH_3CHO + LiAlH_4 \rightarrow CH_3CH_2OH$

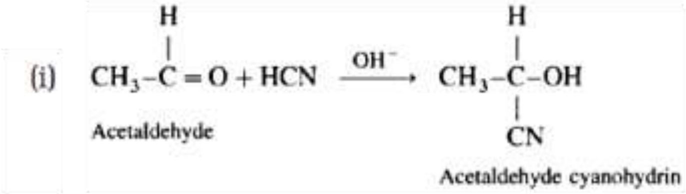
(iii) $CH_3COOH + LiAlH_4 \rightarrow CH_3CH_2OH$

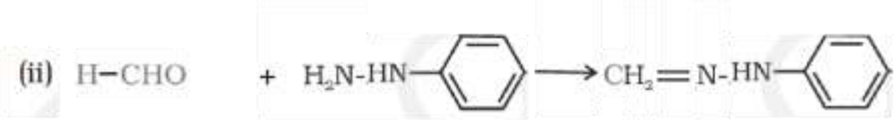
16. What happens when (write equation)

(i) Ethanal react with HCN

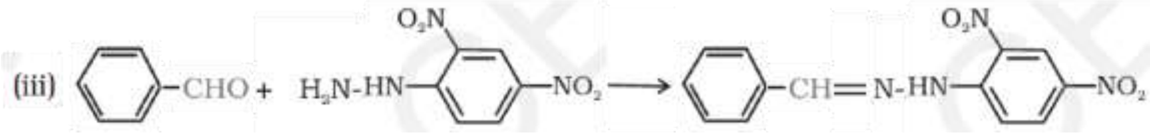
(ii) Formaldehyde reacts with phenyl hydrazine (iii) Benzaldehyde reacts with 2,4-DNP.

Ans:





Formaldehyde Phenylhydrazine Phenylhydrazone



Benzaldehyde 2,4-DNP 2,4 Dinitrophenylhydrazone

17. Arrange the following in increasing order of-

(i) Ethanal, Propanal, Butanal, Butanone (reactivity toward nucleophilic addition)

(ii) Propanal, Propanone, Propanol (boiling point)

(iii) p–tolualdehyde, Benzaldehyde, p-nitrobenzaldehyde, Acetophenone, (reactivity)

Ans. (i) Butanone < Butanal < Propanal < Ethanal

(ii) Propanal < Propanone < Propanol

(iii) Acetophenone < p–tolualdehyde < Benzaldehyde < p-nitrobenzaldehyde

18. (i) Give one use of formalin.

(ii) What is the function of $BaSO_4$ in Rosenmund Reaction?

(iii) What is Rochelle Salt?

Ans. (i) Formalin is used as a disinfectant, preservative for biological specimen and in leather industry.

(ii) $BaSO_4$ act as catalyst poison which prevent the reduction of aldehyde into alcohol. (iii) Sodium potassium tartarate.

19. What is meant by the following terms? Give an example of the reaction in each case.

(i) Cyanohydrin (ii) Hemiacetal

(iii) Acetal (iv) Ketal

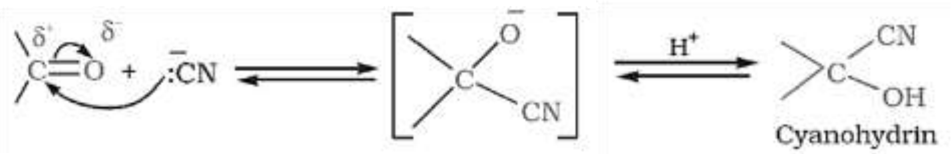
(v) Hydrazone (vi) oxime

(vii) Semicarbazone (viii) 2,4-DNP-derivative

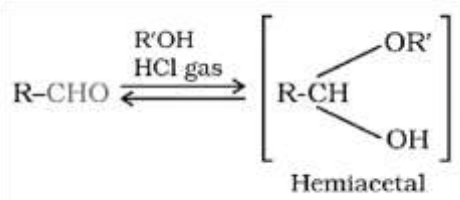
(ix) Aldol (x) Imine

(xi) Schiff's base

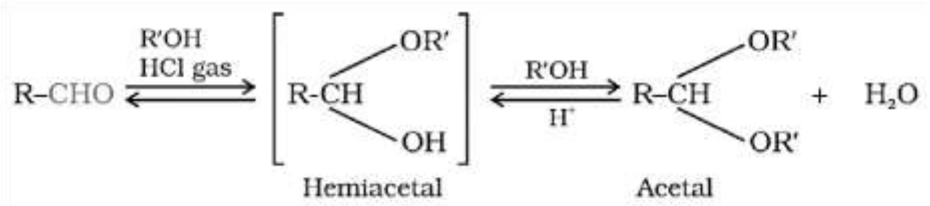
Ans: (i) Cyanohydrin: In the presence of excess sodium cyanide (NaCN) as a precursor to using cyanohydrin, aldehydes and ketones react with hydrogen cyanide (HCN). Such reactions are classified as reactions to cyanohydrins.



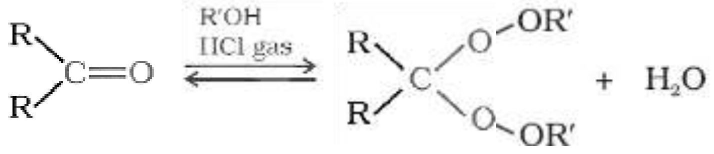
(ii) Hemiacetal: Aldehydes react with one equivalent of monohydric alcohol in the presence of dry hydrogen chloride to yield alkoxyalcohol intermediate, known as hemiacetals.



(iii) Acetal: Aldehydes react with one equivalent of monohydric alcohol in the presence of dry hydrogen chloride to yield alkoxyalcohol intermediate, known as hemiacetals, which further react with one more molecule of alcohol to give a gem-dialkoxy compound known as acetal as shown in the reaction.

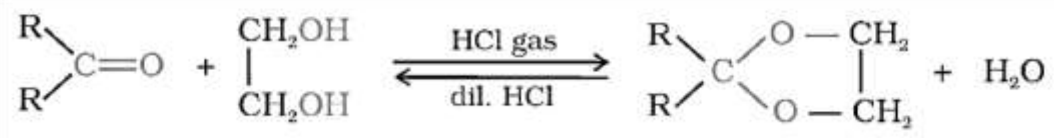


(iv) Ketal: Ketones react with two monohydric alcohols in the presence of dry hydrogen chloride to yield a gem-dialkoxy compound known as ketal.

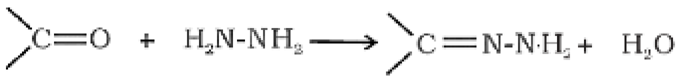


Ketal

Ketones react with ethylene glycol under similar conditions to form cyclic products known as ethylene glycol ketals.

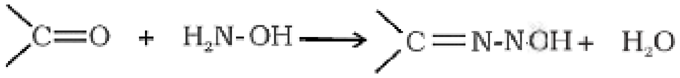


(v) Hydrazone: Nucleophile, such as Hydrazine ($H_2N–NH_2$) adds to the carbonyl group of aldehydes and ketones. The reaction is catalysed by acid and the product formed is called hydrazone.



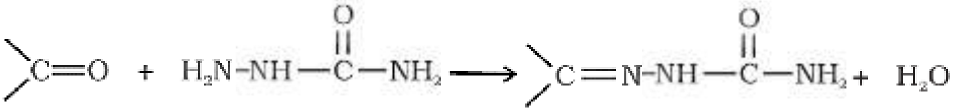
Hydrazine Hydrazone

(vi) Oxime: When hydroxylamine (H_2N-OH) adds to the carbonyl group of aldehydes and ketones, oxime is formed.



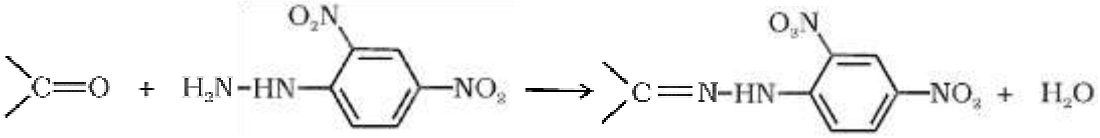
hydroxylamine Oxime

(vii)Semicarbazone: Semicarbazone comes from aldehydes and ketones and is formed by the condensation reaction between a ketone or aldehyde and semicarbazide.



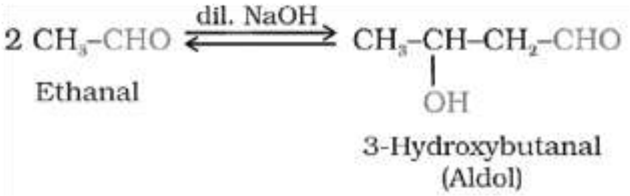
semicarbazide Semicarbazide

(viii) 2,4-DNP derivative: 2, 4-dinitrophenylhydrazone are 2,4−DNP−derivatives which are produced in a weakly acidic medium when aldehydes or ketones react with 2,4−dinitrophenylhydrazine.



2,4−dinitrophenylhydrazine 2, 4-dinitrophenylhydrazone

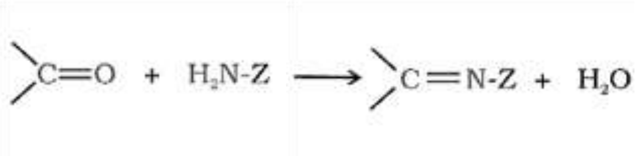
(ix) Aldol: Aldehydes having at least one α-hydrogen undergo a reaction in the presence of an alkali form β-hydroxy aldehydes. This β-hydroxy aldehydes are called aldol.



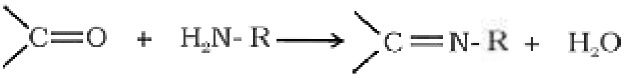
(x) Imine: Imines are chemical compounds which have a double bond between carbon-nitrogen. Imines are formed during Stephen reaction and also in the reactions of aldehydes and ketones with

primary amines.

$$RCN + SnCl_2 + HCl \longrightarrow RCH = NH$$



(x) Schiff's base: Schiff's base is a chemical compound that contains a double bond between carbonnitrogen and the nitrogen atom connected to an aryl or alkyl group.



20. Write a note about the following named reaction.

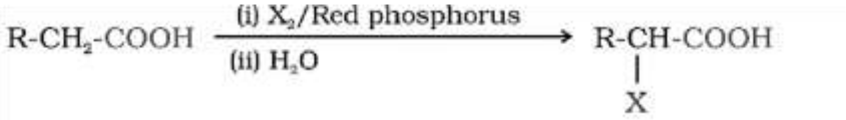
(i) Hell-Volhard-Zelinsky reaction (ii) Cannizzaro reaction

(iii) Clemmensen reduction (iv) Wolff-Kishner reduction

(v) Rosenmund reduction (vi) Etard Reaction

(v) Gattermann Koch reaction

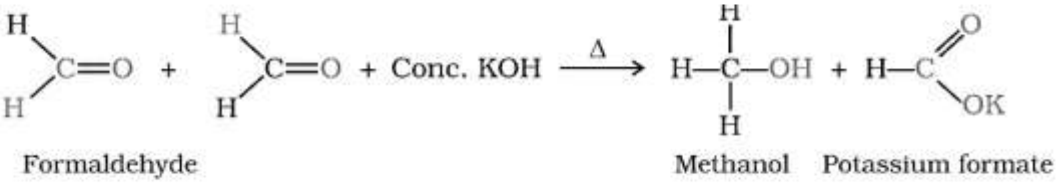
Ans: (i) Hell-Volhard-Zelinsky reaction: Carboxylic acids having an α-hydrogen are halogenated at the α-position on treatment with chlorine or bromine in the presence of small amount of red phosphorus to give α-halocarboxylic acids.



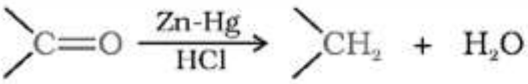
$$R\text{-}CH_2\text{-}COOH \xrightarrow[\text{(ii) } H_2O]{\text{(i) } X_2\text{/Red phosphorus}} R\text{-}\underset{\displaystyle X}{\underset{|}{CH}}\text{-}COOH$$

`

(ii) Cannizzaro reaction: Aldehydes which do not have an α-hydrogen atom, undergo self-oxidation and reduction (disproportionation) reaction on heating with concentrated alkali.

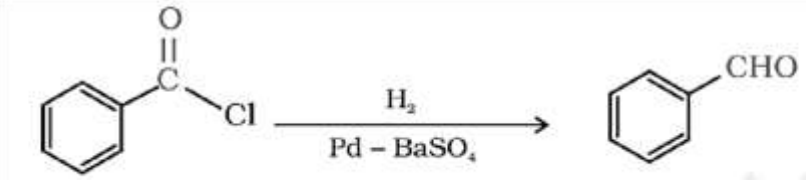


(iii) Clemmensen reduction: The carbonyl group of aldehydes and ketones is reduced to CH2 group on treatment with zinc-amalgam and concentrated hydrochloric acid.

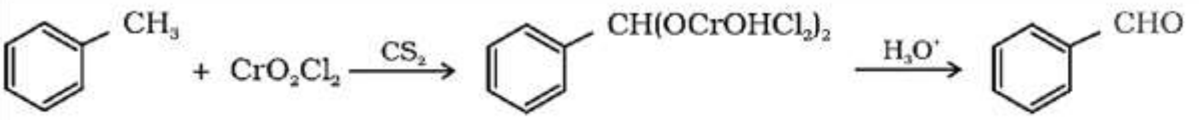


(iv) Wolff-Kishner reduction: The carbonyl group of aldehydes and ketones is reduced to CH2 group on treatment with hydrazine followed by heating with sodium or potassium hydroxide in high boiling solvent such as ethylene glycol.

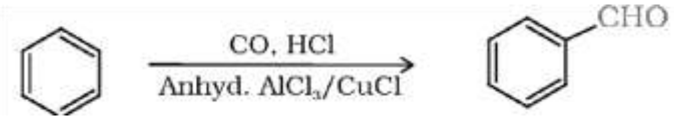
(v) Rosenmund reduction: Benzoil chloride is hydrogenated to benzaldehyde over catalyst, palladium on barium sulphate.



(vi) Etard Reaction: Toluene is oxidised by chromyl chloride followed by hydrolysis to benzaldehyde.



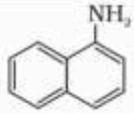
(v) Gattermann Koch reaction: When benzene is treated with carbon monoxide and hydrogen chloride in the presence of anhydrous aluminium chloride, it gives benzaldehyde.



9- AMINES AND DIAZONIUM SALT

Multiple Choice Questions

1. Which of the following is a tertiary amine (3^o)?

(i) 

(ii) 

(iii) $(C_2H_5)_2CHNH_2$ (iv) $(C_2H_5)_2NH$

Ans:

(ii) 

2. Order of basic strength

CH_3NH_2, NH_3, $(CH_3)_2NH$, $(CH_3)_3N$

Ans: $NH_3 < (CH_3)_3N < CH_3NH_2 < (CH_3)_2NH$

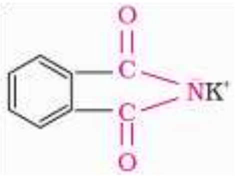
3. Order of basic strength

$C_2H_5NH_2$, NH_3, $(C_2H_5)_2NH$, $(C_2H_5)_3N$

Ans: $NH_3 < C_2H_5NH_2 < (C_2H_5)_3N < (CH_3)_2NH$

4. The source of nitrogen in Gabriel synthesis of amines is

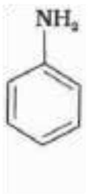
Ans: Potassium phthalimide



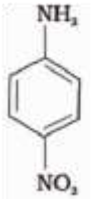
5. Hoffmann Bromamide Degradation reaction is shown by

Ans: an amide ($RCONH_2$)

6. Out of the following compound, which is least basic and which is the most basic?



(i)



(ii)

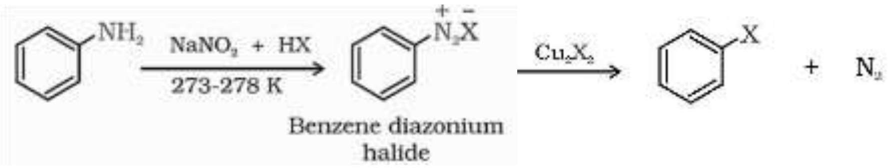
(iii)

Ans: (ii) is least basic and (iii) is the most basic

7. Methylamine reacts with HNO_2. What compound will be formed and which gas will be evolved? Ans: Methanol, N_2 gas

8. Reduction of aromatic nitro compounds by Fe and HCl gives Ans: Aromatic primary amine (Aniline)

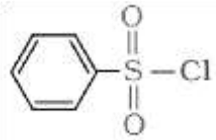
9. Following reaction is called



Ans: Sandmeyer's reaction 10.

What is Hinsberg's Reagent

Ans: Benzenesulphonyl chloride



11. Out of the following amine which will be more volatile?

$CH_3CH_2CH_2NH_2$, $(CH_3)_2CHNH_2$, $(CH_3)_3N$

Ans: $(CH_3)_3N$

12. Which species are involved in the carbylamine test? Ans: Primary amine, chloroform and KOH
13. The reagents that can be used to convert benzenediazonium chloride to benzene are Ans: H_3PO_2 or CH_3CH_2OH
14. Protection of $–NH_2$ group in aniline is done by Ans: Acetylation [Reaction with $(CH_3CO)_2O$]
15. Which type of amines can be prepared by Gabriel synthesis Ans: Aliphatic primary amines
16. Major compounds in the nitration of aniline Ans: p-Nitroaniline and m-Nitroaniline
17. What are the products when $C_6H_5CH_2NH_2$ and $C_6H_5NH_2$ react with HNO_2? Ans. $C_6H_5CH_2OH$ and $C_6H_5N_2Cl$
18. Assertion: Acetanilide is less basic than aniline.

    Reason: Acetylation of aniline results in decrease of electron density on nitrogen. Ans: Assertion is not correct but reason is correct.
19. Assertion: Aromatic 1° amines can be prepared by Gabriel Phthalimide Synthesis.

    Reason: Aryl halides undergo nucleophilic substitution with anion formed by phthalimide. Ans: Both Assertion and reason are correct and reason is correct explanation of assertion.
20. Assertion: Hoffmann’s bromamide reaction produces primary amines.

    Reason: Primary amines are more basic than secondary amines. Ans: Assertion is correct but reason is not correct.

Descriptive Answer Questions:

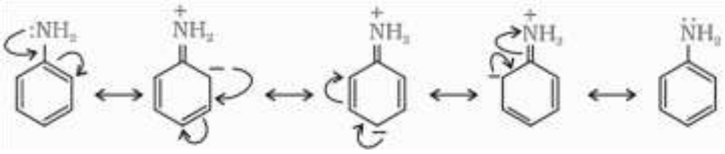
1. Why is $–NH_2$ group of aniline acetylated before carrying out nitration?

   Ans: In the strongly acidic medium, aniline is protonated to form the anilinium ion which is meta directing. That is why besides the ortho and para derivatives, significant amount of meta derivative is also formed.
2. What is the best reagent to convert nitrile to primary amine?

   Ans. Reduction of nitriles with sodium/alcohol or $LiAlH_4$ gives primary amine.
3. Why is benzene diazonium chloride not stored and is used immediately after its preparation? Ans: Benzene diazonium chloride is a colourless crystalline solid. It is readily soluble in water and is stable in cold but reacts with water when warmed. It decomposes easily in the dry state. Due to its instability, the diazonium salt is not generally stored and used immediately after its preparation.
4. Predict the product of reaction of aniline with bromine in non-polar solvent such as CS_2.

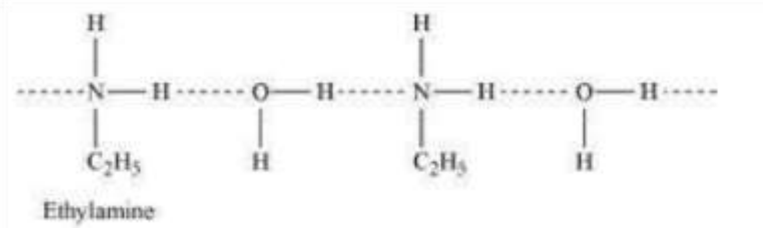
   Ans. A mixture of 2-bromoaniline and 4-bromoaniline is formed.
5. pK_b of aniline is more than that of methylamine. Why?

   Ans: In aniline, lone pair of electrons on N atom is delocalised over the benzene due to which electron density on the nitrogen decreases. On the other hand, electron density on N atom increases in case of methylamine due to +I effect of methy group. So, aniline is less basic than methylamine.and hence pKb value of aniline is more than that of methylamine.



6. Ethylamine is soluble in water whereas aniline is not.

Ans: Ethylamine is soluble in water due to intermolecular hydrogen bonding which is very very less in case of aniline due to large hydrocarbon part in aniline.

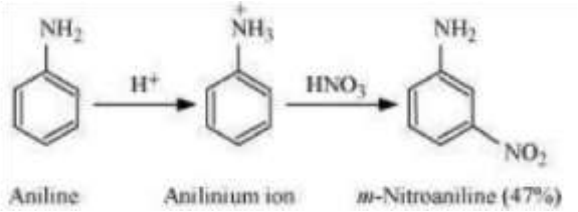


7. State reason that primary amines have higher boiling points than tertiary amines.

Ans: i)Due to extensive intermolecular H-bonding in case of primary amines which is absent in tertiary amines

8. Although –NH_2 group is an ortho and para directing group, nitration of aniline gives along with ortho and para derivatives meta-derivative also.

Ans: Because nitration is carried in acidic conditions and in acidic conditions aniline gets protonated and is converted to anilinium ion which is meta directing group.



9. Aromatic primary amines cannot be prepared by Gabriel phthalimide synthesis. State reason. Ans: Gabriel phthalimide synthesis is used for the preparation of aliphatic primary amines. It involves nucleophilic substitution (S_N2) of alkyl halides by the anion formed by the phthalimide. But aryl halides do not undergo nucleophilic substitution with the anion formed by the phthalimide. Hence, aromatic primary amines cannot be prepared by this process.

10. Give the chemical tests to distinguish between the following pairs of compounds:

(i) Ethylamine and Aniline

(ii) Aniline and N-Methyaniline

Ans: i) These can be distinguished by azodye test.

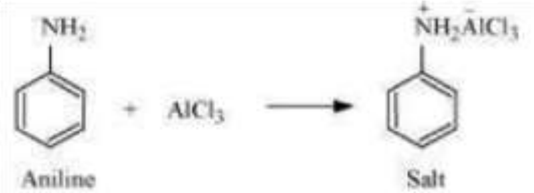
Aniline forms azo dye while ethylamine does not form dye.

ii)These can be distinguished by carbylamine test.

Aniline gives carbylamine test while N-Methylamine does not.

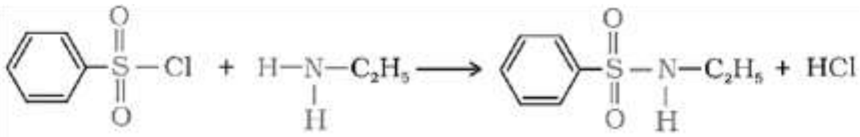
11. Why does aniline not undergo Friedel–Craft's reaction?

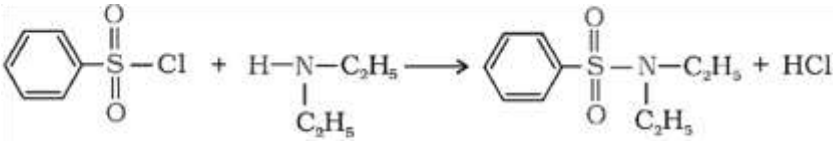
Ans: Because aniline being lewis base reacts with $AlCl_3$, Lewis acid to form salt. Due to this N of aniline acquires + charge and hence acts as strong deactivating group for further reaction.



12. How primary, secondary and tertiary amines are differentiated?

Ans: Out of the three types of amine only 3^o amines don not give reaction with Hinsberg's reagent. Therefore tertiary amine is differentiated.





Out of 1° and 2° amine only 1° amines give carbylamine test.

13. Methylamine in water reacts with ferric chloride to precipitate hydrated ferric oxide. Why?

Ans: With the +I effect of the methyl group it makes methyl amine more basic in nature than water. Thus, methyl amine reacts with water to produce hydroxide ions. The hydroxide ions produced in the reaction further react with ferric chloride to precipitate hydrated ferric oxide ($Fe_2O_3.3H_2O$).

14. Diazonium salts of aromatic amines are more stable than those of aliphatic amines. Give reason.

Ans: Due to resonance-induced positive charge dispersion over the benzene ring, aromatic diazonium salts are more stable than aliphatic diazonium salts.

15. How are the following conversions carried out?

(a) Aniline to nitrobenzene

(b) Nitrobenzene to benzoic acid

(c) Benzene to m-bromophenol

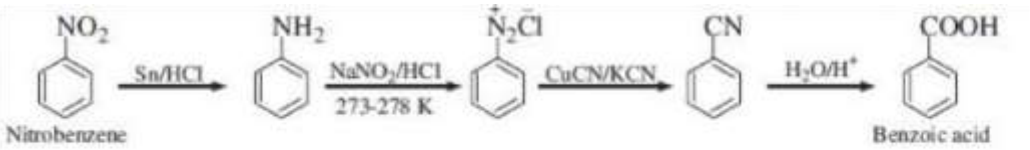
(d) Benzoic acid to aniline

(e) Aniline to 2,4,6-tribromofluorobenzene

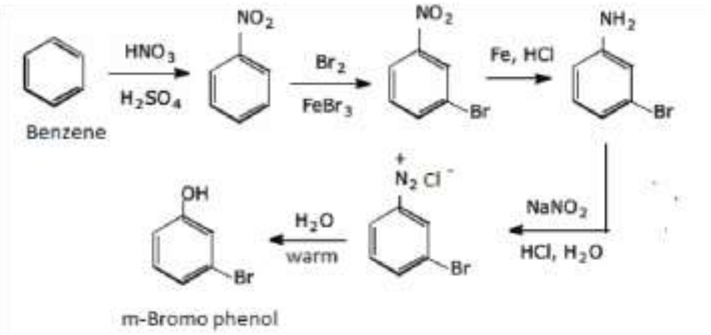
(f) Chlorobenzene to p-chloroaniline

Ans: (a) Aniline to nitrobenzene

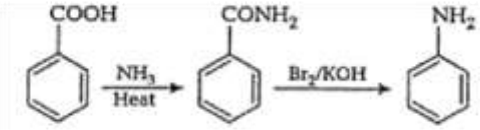
(b) Nitrobenzene to benzoic acid



(c) Benzene to m-bromophenol

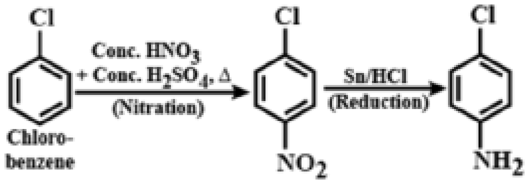


(d) Benzoic acid to aniline



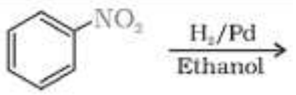
(e) Aniline to 2,4,6-tribromofluorobenzene

(f) Chlorobenzene to p-chloroaniline

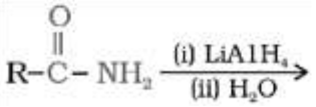


16. Complete the following reactions:

(i)

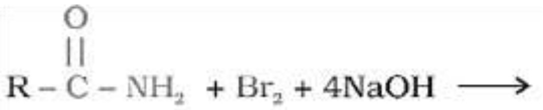


(ii)



$R-\overset{O}{\overset{\|}{C}}-NH_2 \xrightarrow[\text{(ii) } H_2O]{\text{(i) } LiAlH_4}$

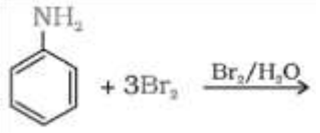
(iii)



$R-\overset{O}{\overset{\|}{C}}-NH_2 + Br_2 + 4NaOH \longrightarrow$

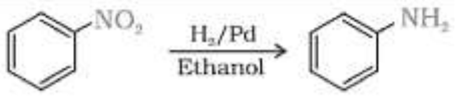
(iv) $R-NH_2 + CHCl_3 + 3KOH \xrightarrow{\text{Heat}}$

(v)

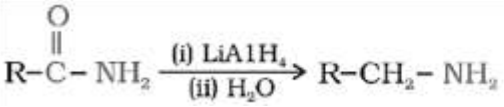


Ans:

(i)

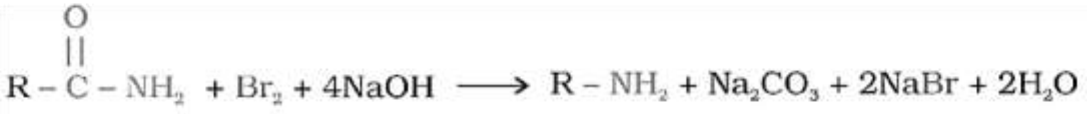


(ii)



$R-\overset{O}{\overset{\|}{C}}-NH_2 \xrightarrow[\text{(ii) } H_2O]{\text{(i) } LiAlH_4} R-CH_2-NH_2$

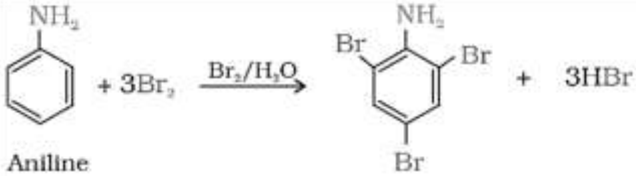
(iii)



$R-\overset{O}{\overset{\|}{C}}-NH_2 + Br_2 + 4NaOH \longrightarrow R-NH_2 + Na_2CO_3 + 2NaBr + 2H_2O$

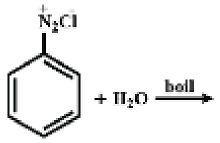
(iv) $R-NH_2 + CHCl_3 + 3KOH \xrightarrow{\text{Heat}} R-NC + 3KCl + 3H_2O$

(v)

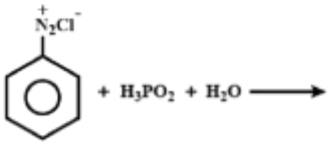


17. Complete the following reactions of diazonium salt

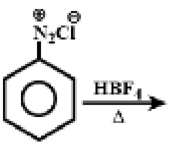
(i)

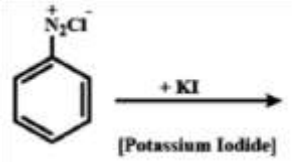


(ii)



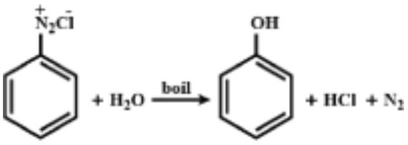
(iii)

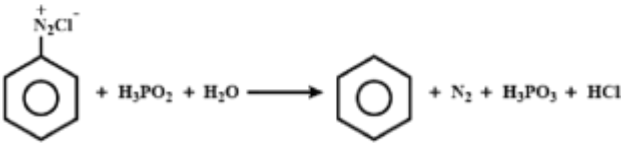




(iv)

Ans: Complete the following reactions of diazonium salt

(i)


(ii)


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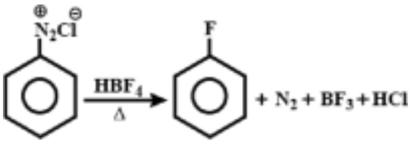
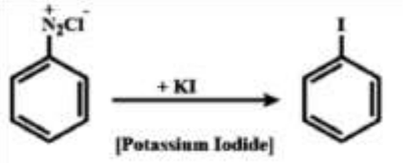
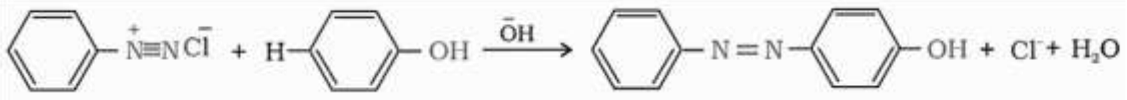


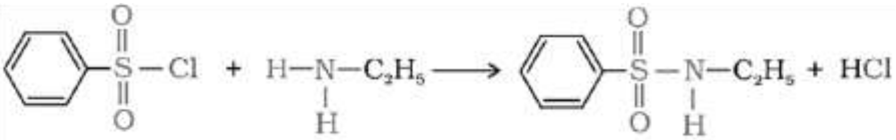
(iv)


18. Comment upon the following
    - (i) coupling reaction
    - (ii) Hinsberg's reaction
    - (iii) Protection of $-NH_2$ group.

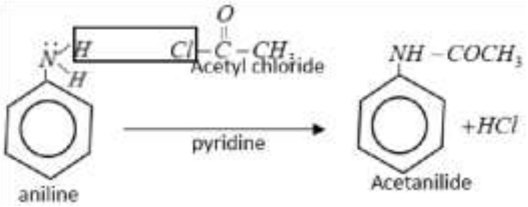
Ans: (i) **coupling reaction:** Benzene diazonium chloride reacts with phenol in which the phenol molecule at its para position is coupled with the diazonium salt to form p-hydroxyazobenzene. This type of reaction is known as coupling reaction.



(ii) **Hinsberg's reaction:** Benzenesulphonyl chloride ($C_6H_5SO_2Cl$), which is also known as Hinsberg's reagent, reacts with primary and secondary amines to form sulphonamides.

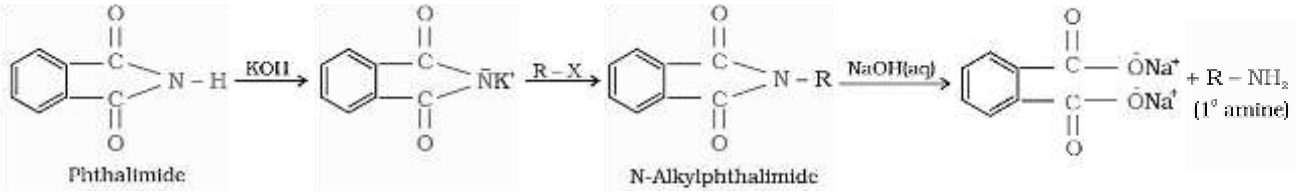


(iii) **Protection of $-NH_2$ group:** Protection of the $-NH_2$ group is the acetylation of $-NH_2$ group with acetic Anhydride. Protection of the $-NH_2$ group controlls the highe reactivity of $-NH_2$ group.



19. Explain Gabriel phthalimide synthesis. What is its limitation

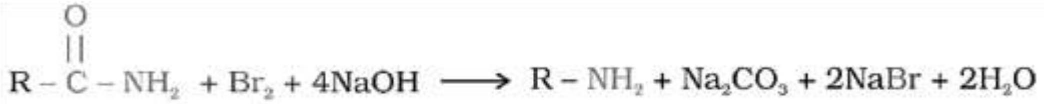
Ans: Phthalimide on treatment with ethanolic potassium hydroxide forms potassium salt of phthalimide which on heating with alkyl halide followed by alkaline hydrolysis produces the corresponding primary amine. Aromatic primary amines cannot be prepared by this method.



20. Explain the following named reactions:

(i) Hoffmann bromamide reaction (ii) Carbylamine reaction (iii) Gatterman reaction:

Ans: (i) **Hoffmann bromamide reaction:** In this degradation reaction, primary amines are prepared by treating an amide with bromine in an aqueous or ethanolic solution of sodium hydroxide.

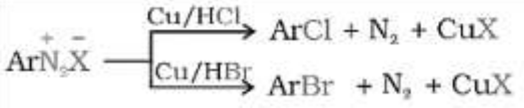


$$R-\overset{\overset{O}{||}}{C}-NH_2 + Br_2 + 4NaOH \longrightarrow R-NH_2 + Na_2CO_3 + 2NaBr + 2H_2O$$

(ii) **Carbylamine reaction:** Aliphatic and aromatic primary amines on heating with chloroform and ethanolic potassium hydroxide form isocyanides or carbylamines which are foul smelling substances.

$$R{-}NH_2 + CHCl_3 + 3KOH \xrightarrow{Heat} R{-}NC + 3KCl + 3H_2O$$

(iii) **Gatterman reaction:** Whene benzene diazonium salt solution is treated with corresponding HCl or HBr presence of copper powder, corresponding halobenzene is formed.



10- BIOMOLECULES

Multiple Choice Questions

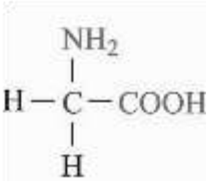
1. α-D-Glucose and β-D-Glucose are Ans: Anomers
2. Which monosaccharide is a non-reducing sugar? Ans: Fructose
3. One mole of sucrose, on hydrolysis gives Ans: 2 moles of glucose
4. The letter ‘D’ in D-glucose signifies

   Ans: configuration at the penultimate chiral carbon
5. Glucose and fructose are: Ans: Functional isomers
6. Which of the following reactions of glucose can be explained only by its cyclic structure?

   Ans: Pentaacetate of glucose does not react with hydroxyl amine.
7. Which of the monosaccharides are isomeric aldohexose? Ans: D-glucose and D-Galactose 8. Which is example of an aldopentose? Ans: Ribose or Deoxyribose
9. Which are the complimentary bases of Cytosine and adenine in DNA strands? Ans: Thymine and guanine
10. The amino acids are brought to the ribosome by: Ans: rRNA
11. The linkage between the nucleotides in nucleic acid molecule is: Ans: Posphodiester linkage

12. Which of the amino acids is optically inactive?

Ans: Glycine



$$H-\overset{\displaystyle NH_2}{\underset{\displaystyle H}{C}}-COOH$$

13. Which monomer compound can exist in a dipolar (zwitter ion) structure? Ans: Amino acid

14. Nucleic acids are the polymers of

Ans: Nucleotides (pentose sugar + nitrogenous base + phospate group)

15. Beri-beri is caused due to deficiency of

Ans: Vitamin B_1

16. Water soluble vitamins are

Ans: Vitamin B complex and vitamin C

17. Maltase and zymase are Ans: Enzymes

18. Assertion- The two strands of DNA are complimentary to each other.

Reason- The hydrogen bonds are formed between specific pairs of bases.

Ans: Both Assertion and reason are correct and reason is correct explanation of assertion.

19. Assertion: α-Helix and β-sheets are the secondary structures of portein.

Reason: Secondary structure is formed by hydrogen bond in a segment of primary structure.

Ans: Both Assertion and reason are correct and reason is correct explanation of assertion.

20. Assertion: Amylose is water soluble component of starch.

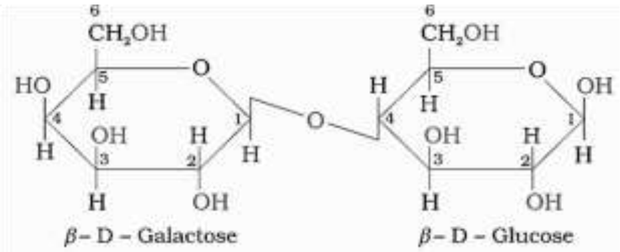
Reason: in amylopectin α-1-4 and α-1-6 glycosidic linkages are present.

Ans: Both Assertion and reason are correct and reason is not correct explanation of assertion.

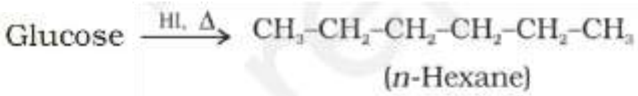
Descriptive Answer Questions:

1. Name the sugar present in milk. How many monosaccharide units are present in it? What are such oligosaccharides called?

Ans. Lactose is 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.

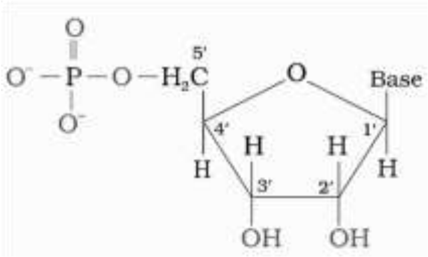


2. How do you explain the presence of all the six carbon atoms in glucose in a straight chain? Ans. On prolonged heating with HI, glucose gives n-hexane.



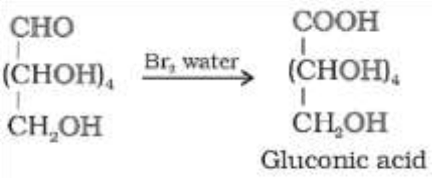
$$\text{Glucose} \xrightarrow{HI,\ \Delta} \underset{(n\text{-Hexane})}{CH_3-CH_2-CH_2-CH_2-CH_2-CH_3}$$

3. At which position of sugar unit is the phosphoric acid linked in a nucleoside to give a nucleotide? Ans. Phosphoric acid is linked at 5′-position of sugar moiety of nucleoside to give a nucleotide



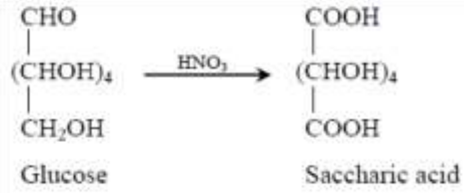
4. Under what conditions glucose is converted to gluconic and saccharic acid?

Ans. Glucose is converted to gluconic acid by bromine water and to saccharic acid by conc. HNO_3.



$$\begin{matrix} CHO \\ | \\ (CHOH)_4 \\ | \\ CH_2OH \end{matrix} \xrightarrow{Br_2\ water} \begin{matrix} COOH \\ | \\ (CHOH)_4 \\ | \\ CH_2OH \end{matrix}$$

Gluconic acid

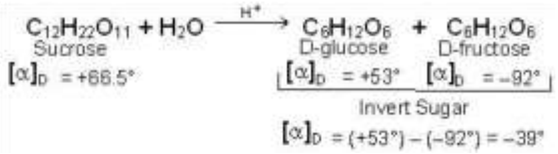


$$\begin{matrix} CHO \\ | \\ (CHOH)_4 \\ | \\ CH_2OH \end{matrix} \xrightarrow{HNO_3} \begin{matrix} COOH \\ | \\ (CHOH)_4 \\ | \\ COOH \end{matrix}$$

Glucose Saccharic acid

5. Which sugar is called invert sugar? Why is it called so?

Ans. Sucrose is dextrorotatory but after hydrolysis gives dextrorotatory glucose and laevorotatory fructose. Since the laevorotation of fructose (-92°) is more than dextrorotation of glucose (+53°), the mixture is laevorotatory. Thus, hydrolysis of sucrose brings about a change in the sign of rotation, from dextro (+) (+66.5°) to laevo (-) (-39°) and the product is named as invert sugar.



$$\underset{\substack{Sucrose \\ [\alpha]_D = +66.5^\circ}}{C_{12}H_{22}O_{11}} + H_2O \xrightarrow{H^+} \underset{\substack{D\text{-glucose} \\ [\alpha]_D = +53^\circ}}{C_6H_{12}O_6} + \underset{\substack{D\text{-fructose} \\ [\alpha]_D = -92^\circ}}{C_6H_{12}O_6}$$

Invert Sugar

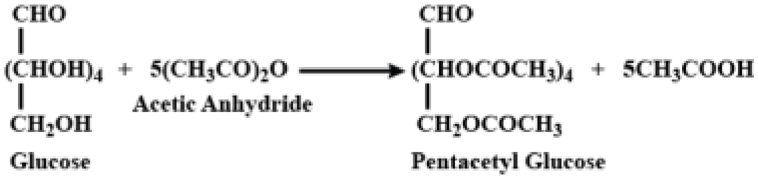
$[\alpha]_D = (+53^\circ) - (-92^\circ) = -39^\circ$

6. During curdling of milk, what happens to sugar present in it?

Ans. When milk is curdeled, its sugar get oxidize to form lactic acid.

7. How do you explain the presence of five —OH groups in glucose molecule?

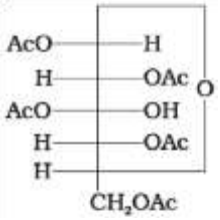
Ans. Acetylation of glucose with acetic anhydride gives glucose pentaacetate which confirms the presence of five —OH groups. Since it exists as a stable compound, five —OH groups should be attached to different carbon atoms.



$$\begin{matrix} CHO \\ | \\ (CHOH)_4 \\ | \\ CH_2OH \end{matrix} + \underset{Acetic\ Anhydride}{5(CH_3CO)_2O} \longrightarrow \begin{matrix} CHO \\ | \\ (CHOCOCH_3)_4 \\ | \\ CH_2OCOCH_3 \end{matrix} + 5CH_3COOH$$

Glucose **Pentacetyl Glucose**

8. Why does pentaester of glucose (given below) not form an oxime?



Ans: Glucose pentaacetate (structure A) doesn't have a free —OH group at C1 and so can't be converted to the open chain form to give —CHO group and hence doesn't form the oxime.

9. Why must vitamin C be supplied regularly in diet?

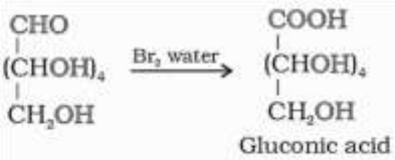
Ans: Vitamin C are soluble in water. Water soluble vitamins must be supplied regularly in diet because they are readily excreted in urine and cannot be stored in our body.

10. Amino acids behave like salts rather than simple amines or carboxylic acids. Explain.

Ans. 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 can accept a proton, giving rise to a dipolar ion known as zwitter ion.

11. How do you explain the presence of an aldehydic group in a glucose molecule?

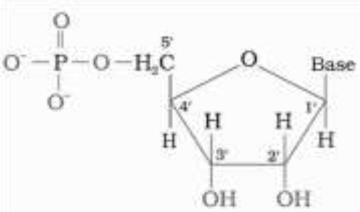
Ans. Glucose gets oxidised to six carbon carboxylic acid (gluconic acid) on reaction with a mild oxidising agent like bromine water. This indicates that the carbonyl group is present as an aldehydic group.



$$\begin{array}{c} CHO \\ | \\ (CHOH)_4 \\ | \\ CH_2OH \end{array} \xrightarrow{Br_2\ water} \begin{array}{c} COOH \\ | \\ (CHOH)_4 \\ | \\ CH_2OH \end{array}$$

12. What is a nucleotide? How many types of nucleotides are present in DNA?

Ans: A unit formed by the attachment of a base to 1′ position of sugar is known as nucleoside. When nucleoside is linked to phosphoric acid at 5′-position of sugar moiety, we get a nucleotide.



13. How do enzymes help a substrate to be attacked by the reagent effectively?

Ans. Enzymes are highly specific. They react with substrate molecule and form intermediate complex. They reduce the magnitude of activation energy and thus increase the rate of biochemical reaction.

14. Coagulation of egg white on boiling is an example of denaturation of protein. Explain it in terms of structural changes.

Ans. During denaturation 2^o and 3^o structures are destroyed but 1^o structure remains intact. The coagulation of egg white on boiling is a common example of denaturation.

15. Write the important structural and functional differences between DNA and RNA.

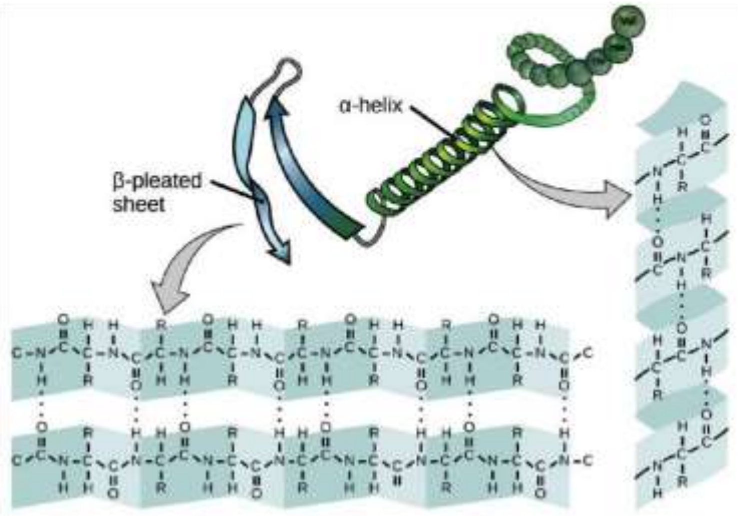
Ans: Strucrural difference: 1. DNA is a double-stranded molecule that has a long chain of nucleotides. RNA is a single-stranded molecule which has a shorter chain of nucleotides.

2. DNA has thymine base while RNA has uracil base.

Difference in function: DNA plays a key role in heredity and to generate RNA strands while RNA plays a key role in protein synthesis.

16. What are the common types of secondary structure of proteins?

Ans: The most common types of secondary structures are the α-helix and the β-sheet. Both structures are held in shape by hydrogen bonds, which form between the carbonyl O of one amino acid and the amino H of another.



17. What are essential and non-essential amino acids? Write any two essential and nonessential amino acids.

    Ans: The amino acids, which can be synthesised in the body, are known as non-essential amino acids. On the other hand, those which cannot be synthesised in the body and must be obtained through diet, are known as essential amino acids.

    Essential amino acids: Valine (Val) and Leucine (Leu) Nonessential amino acids: Glycine (Gly) Alanine (Ala)

18. What is animal starch? Where is it found.

    Ans: Glycogen is known as animal starch. It is the carbohydrates, stored in animal body. its structure is similar to amylopectin and is rather more highly branched. It is present in liver, muscles and brain. When the body needs glucose, enzymes break the glycogen down to glucose.

19. Differentiate between globular and fibrous proteins.

    Ans: Fibrous proteins: When the polypeptide chains run parallel and are held together by hydrogen and disulphide bonds, then fibre– like structure is formed

    Globular proteins: This structure results when the chains of polypeptides coil around to give a spherical shape.

20. What is denaturation of protein and How it affects the structure of proteins?

    Ans: When a protein in its native form, is subjected to physical change like change in temperature or chemical change like change in pH, the hydrogen bonds are disturbed. Due to this, globules unfold and helix get uncoiled and protein loses its biological activity. This is called denaturation of During denaturation 2° and 3° structures are destroyed but 1° structure remains intact.

BEST OF LUCK