केन्द्रीय विद्यालय संगठन

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CLASS XII
CHEMISTRY
QUESTION BANK

KENDRIYA VIDYALAYA SANGATHAN
ZONAL INSTITUTE OF EDUCATION AND TRAINING
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SUPPORT MATERIAL
CLASS -XII

SUBJECT- CHEMISTRY (043)
SESSION- 2024-25

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Time : 3 Hours

CLASS XII (2024-25) (THEORY)

70 Marks

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

CLASS XII

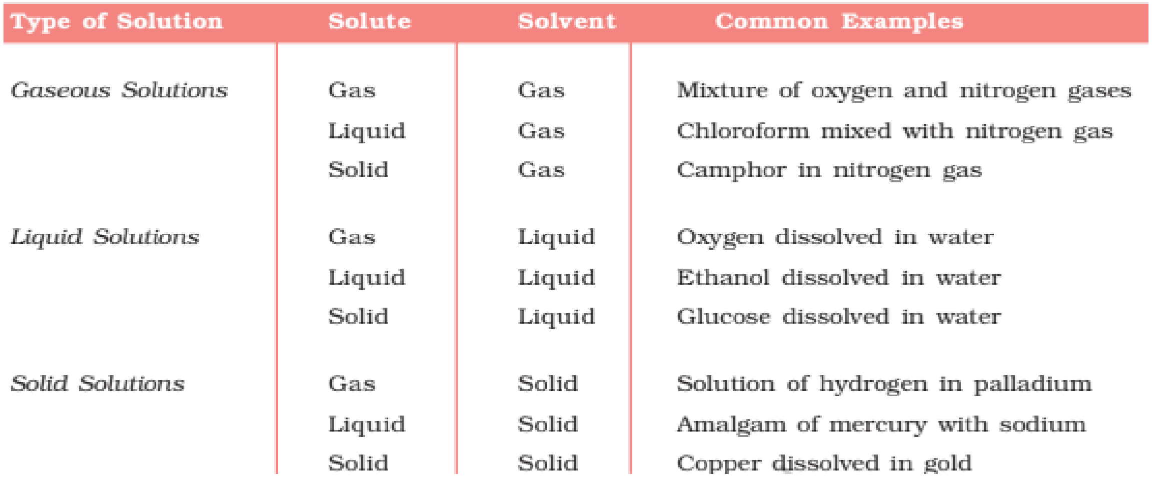
CHAPTER 1: SOLUTIONS

Solution: A homogeneous mixture of two or more chemically non- reacting substances whose composition can be varied within certain limit.

Solution → Solute (component present in lesser amount)

Solution → Solvent (component present in larger amount)

Types of Solution (depending upon physical state of solute & solvent)



Type of Solution	Solute	Solvent	Common Examples
Gaseous Solutions	Gas	Gas	Mixture of oxygen and nitrogen gases
	Liquid	Gas	Chloroform mixed with nitrogen gas
	Solid	Gas	Camphor in nitrogen gas
Liquid Solutions	Gas	Liquid	Oxygen dissolved in water
	Liquid	Liquid	Ethanol dissolved in water
	Solid	Liquid	Glucose dissolved in water
Solid Solutions	Gas	Solid	Solution of hydrogen in palladium
	Liquid	Solid	Amalgam of mercury with sodium
	Solid	Solid	Copper dissolved in gold

Expressing Concentration of Solutions

Concentration: Amount of solute present in a specified amount of solvent or solution.

i. $$\text{Mass percentage (w/w)} = \frac{\text{Mass of the component in the solution}}{\text{Total mass of the solution}} \text{ X } 100$$

ii. $$\text{Volume percentage (V/V)} = \frac{\text{Volume of the component}}{\text{Total volume of the solution}} \text{ X } 100$$

iii. $$\text{Mass by volume percentage (w/V)} = \frac{\text{Mass of the component in the solution}}{\text{Volume of solution}} \text{ X } 100$$

iv. $$\text{Parts per million (ppm)} = \frac{\text{no. of parts of the component}}{\text{Total no. of parts of all the components}} \text{ X } 10^6$$

v. $$\text{Mole fraction } (\times) = \frac{\text{no. of moles of the component}}{\text{Total no. of moles of all the components}}$$

vi. $$\text{Molarity (M)} = \frac{\text{Moles of solute}}{\text{Volume of solution in litre}}$$

vii. $$\text{Molality (m)} = \frac{\text{Moles of solute}}{\text{Mass of solvent in kg}}$$

Solubility

The solubility of a substance depends upon

i. Nature of solute and solvent
ii. Temperature
iii. Pressure (for solution of gas dissolved in liquid)

Nature of solvent:

A polar solute will be soluble in polar solvent and a non-polar solute will be soluble in non-polar solvent

Temperature:
If dissolution is exothermic, solubility decreases with increase in temperature

If dissolution is endothermic, solubility increases with increase in temperature.

Pressure:
Pressure has no effect on solubility of a solid or liquid in liquid.

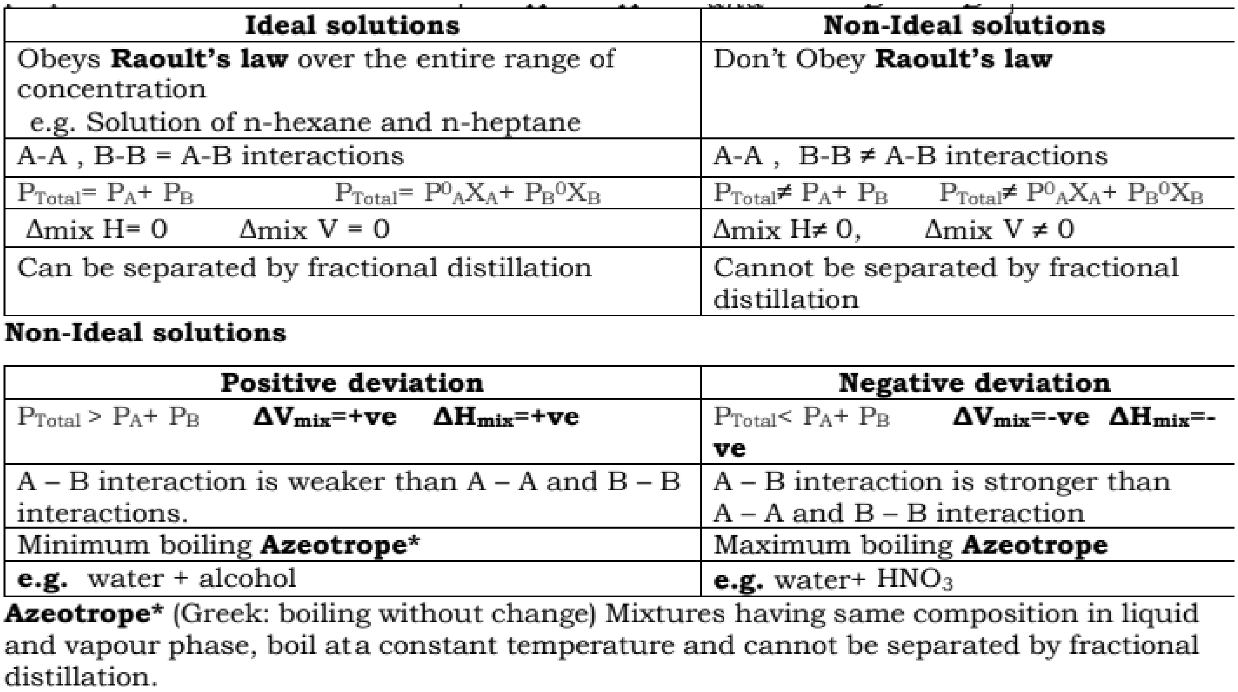
Henry's law
The amount of gas that is dissolved in a liquid is directly proportional to the partial pressure of that gas above the liquid when the temperature is kept constant. [**Henry's law**]

APPLICATIONS: Soft drinks are sealed under high pressure to increase solubility of CO_2.

To avoid BENDS, the tanks used by scuba divers are filled with air diluted with helium (less soluble than N_2)

Anoxia problem at higher altitudes due to low pressure low concentration of O_2 in Blood cells.

Raoult's Law
The vapour pressure of any volatile component in the solution is directly proportional to its mole fraction.
$P_{solution} = X_{solvent} P^0_{solvent}$

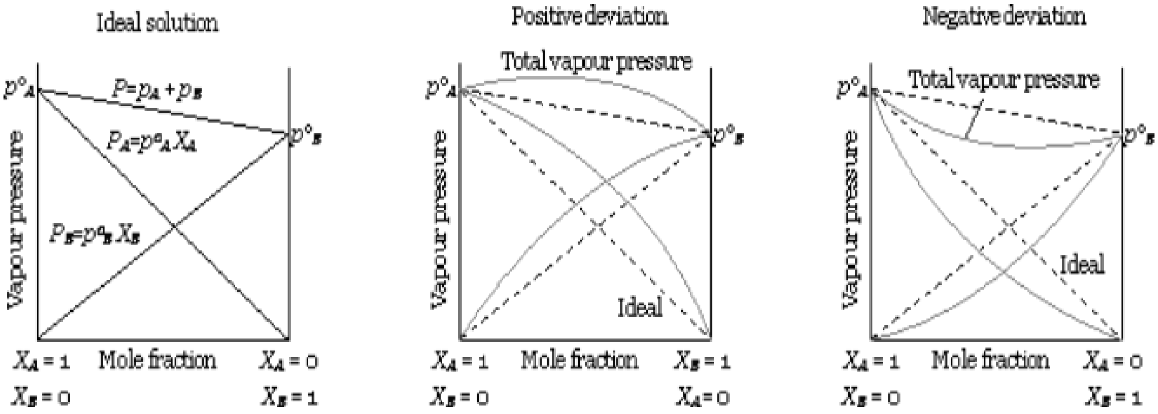


Ideal solutions	Non-Ideal solutions
Obeys **Raoult's law** over the entire range of concentration e.g. Solution of n-hexane and n-heptane	Don't Obey **Raoult's law**
A-A , B-B = A-B interactions	A-A , B-B ≠ A-B interactions
$P_{Total} = P_A + P_B$ $P_{Total} = P^0_A X_A + P_B^0 X_B$	$P_{Total} \neq P_A + P_B$ $P_{Total} \neq P^0_A X_A + P_B^0 X_B$
$\Delta mix\ H = 0$ $\Delta mix\ V = 0$	$\Delta mix\ H \neq 0$, $\Delta mix\ V \neq 0$
Can be separated by fractional distillation	Cannot be separated by fractional distillation

Non-Ideal solutions

Positive deviation	Negative deviation
$P_{Total} > P_A + P_B$ $\mathbf{\Delta V_{mix} = +ve}$ $\mathbf{\Delta H_{mix} = +ve}$	$P_{Total} < P_A + P_B$ $\mathbf{\Delta V_{mix} = -ve}$ $\mathbf{\Delta H_{mix} = -ve}$
A – B interaction is weaker than A – A and B – B interactions.	A – B interaction is stronger than A – A and B – B interaction
Minimum boiling **Azeotrope***	Maximum boiling **Azeotrope**
e.g. water + alcohol	**e.g.** water+ HNO_3

Azeotrope* (Greek: boiling without change) Mixtures having same composition in liquid and vapour phase, boil at a constant temperature and cannot be separated by fractional distillation.



QUESTIONS

1. K_H value for Ar(g), CO2(g), HCHO (g) and CH4(g) are 40.39, 1.67, 1.83 × 10-5 and 0.413 respectively. Arrange these gases in the order of their increasing solubility.

a) HCHO < CH4 < CO2 < Ar b) HCHO < CO2 < CH4 < Ar

c) Ar < CO2 < CH4 < HCHO d) Ar < CH4 < CO2 < HCHO

2. When a non-volatile solid is added to pure water it will:

a) boil above 100^{o}C and freeze above 0^{o}C

b) boil below 100^{o}C and freeze above 0^{o}C

c) boil above 100^{o}C and freeze below 0^{o}C

d) boil below 100^{o}C and freeze below 0^{o}C

3. Molarity of a solution at 60^{o}C is-------- than molarity at 30^{o}C

a) More b) less c) same d) no effect of temperature

ANSWERS

1 (a), 2 (a), 3 (b),

4. Aquatic species are more comfortable in cold waters rather than in warm waters. Give reason.

Answer

Solubility of gases increases with decrease in temperature as it is an exothermic process.

5. Aarav Sharma is very fond of a special drink made by his grandmother using different fruits available in their hometown. It has an outstanding taste and also provides great health benefits of natural fruits. He thought of utilizing his grandmother recipe to create a new product in the beverage market that provide health benefits and also contain fizziness of various soft drinks available in the market. Based on your understanding of solutions chapter, help Aarav Sharma to accomplish his idea by answering following:

(a) How he can add fizz to the special drink made by his grandmother? 1

(b) What is the law stated in the chapter that can help Aarav to make his drink fizzy? 1

(c) What precautions he should take while bottling so that his product does not lose fizz during storage and handling across long distances? 2

Answer

a) Carbon dioxide is a gas which provides fizz and tangy flavour. He can dissolve Carbon dioxide gas in the drink.

b) Henry's law which states that solubility of a gas in liquid is directly proportional to partial pressure of the gas.

(c) Bottles should be sealed under high pressure of CO and capping should be done perfectly to avoid leakage of CO2 as any loss of partial pressure will result into decrease in solubility.

CHAPTER 2: ELECTROCHEMISTRY

PART-A: MULTIPLE CHOICE QUESTIONS

Q1. Galvanised iron sheets are coated with

(a) Carbon

(b) Copper

(c) Zinc

(d) Nickel

Q2. How many coulombs are required for the oxidation of 1 mole of H_2O to O_2?

(a) 1.93×10^5 C

(b) 9.65×10^4 C

(c) 3.86×10^5 C

(d) 4.825×10^5 C

Q3. Rust is a mixture of

(a) FeO and $Fe(OH)_3$

(b) FeO and $Fe(OH)_2$

(c) Fe_2O_3 and $Fe(OH)_3$

(d) Fe_3O_4 and $Fe(OH)_3$

Q4. The Standard electrode potentials for the half cell reactions are as follows

Zn ? $Zn^{2+} + 2e^-$ [E° = 0.41 V]

Fe ? $Fe^{2+} + 2e^-$ [E° = 0.76 V]

(a) -0.35 V

(b) 0.35 V

(c) + 1.17 V

(d) -1.17 V

Q5. The standard reduction potentials of Cu^{2+}/Cu and Cu^{2+}/Cu^+ are 0.337 and 0.153 respectively. The standard electrode potential of Cu^+/Cu half cell is

(a) 0.184 V

(b) 0.827 V

(c) 0.521V

(d) 0.490 V

Q6. The standard reduction potentials of X, Y, Z metals are 0.52, -3.03, -1.18 respectively. The order of reducing power of the corresponding metals is:

(a) Y > Z > X

(b) X > Y > Z

(c) Z > Y > X

(d) Z > X > Y

Q7. Which of the following is not a good conductor?

(a) Cu

(b) NaCl (aq)

(c) NaCl (molten)

(d) NaCl(s)

Q8. The e.m.f. of the cell Zn/Zn^{2+} (0.01 M) || Fe^{2+} (0.001 M) Fe at 298 K is 0.2905 volt. Then the value of equilibrium constant for the cell reaction is:

(a) $e^{0.32/0.0295}$
(b) $10^{0.32/0.0295}$
(c) $10^{0.26/0.0295}$
(d) $10^{0.32/0.0591}$
Q9. The volume of H_2 gas at NTP obtained by passing 4 amperes through acidified H_+O for 30 minutes is:
(a) 0.0836 L
(b) 0.0432 L
(c) 0.1672 L
(d) 0.836 L
Q10. 4.5 g of aluminium (at. mass 27 amu) is deposited at cathode from Al^{3+} solution by a certain quantity of electric charge. The volume of hydrogen produced at STP from H+ ions in solution by the same quantity of electric charge will be:
(a) 44.8 L
(b) 11.2 L
(c) 22.4 L
(d) 5.6 L
Q11. The amount of electricity required to deposit 1 mol of aluminium from a solution of $AlCl_3$ will be
(a) 0.33 F
(b) 1 F
(c) 3 F
(d) 1 ampere
Q12. A current of 2.0 A passed for 5 hours through a molten metal salt deposits 22.2 g of metal (at. wt. = 177). The oxidation state of the metal in the metal salt is
(a) +1
(b) +2
(c) +3
(d) +4
Q13. Ionic mobility of Ag^+ ions? [$_{Ag}^{+} = 5 \times 10^{-4}$ ohm^{-1} cm² eq^{-1}] is
(a) 5.2×10^{-9}
(b) 2.4×10^{-9}
(c) 1.52×10^{-9}
(d) 8.25×10^{-9}
Q14. For a cell reaction involving two electron change the standard emf of the cell is found to be 0.295 V at 25°C. The equilibrium constant for the reaction at 25°C will be:
(a) 2.95×10^2
(b) 10
(c) 1×10^{10}
(d) 1×10^{-10}
Q15. If the equivalent conductance of 1 M benzoic acid is 12.8 ohm^{-1} cm² and if the conductance of benzoate ion and H^+ ion are 42 and 288.42 ohm^{-1} cm² respectively, its degree of dissociation is:
(a) 39%
(b) 3.9%
(c) 0.35%
(d) 0.039%

ANSWERS FOR MCQS:

1. ZINC
2. 1.93×10^5 C
3. Fe_2O_3 and Fe $(OH)_3$
4. 0.35 V
5. 0.521V
6. Y > Z > X
7. NaCl(s)
8. $10^{0.32/0.0295}$
9. 0.0836 L
10. 44.8 L
11. 3 F
12. +3
13. 5.2×10^{-9}
14. 1×10^{10}
15. 3.9%

PART-B: 2 MARKS QUESTIONS

Q1. Why should we use mercury cells?

Q2. What do you understand about normal hydrogen electrodes? Why is it important?

Q3. Write the equation that shows the effect of concentration on the electrode potential.

Q4. A cell reaction is considered spontaneous if the overall emf of the cell is positive. Comment.

Q5. What is corrosion?

Q6. Describe the oxidation and reduction potential.

Q7. What is a cell constant? How do you determine it?

Q8. Electrolysis of KBr solution gives Br_2 ions at the anode, but the solution of KF does not produce any F_2 ions. Give a reason.

Q9. Corrosion of motor cars is a common problem in winter when salt is spread on roads to melt the snow. Give a reason.

Q10. What is the reason that in concentrated solutions, strong electrolytes deviate from the Debye-Huckel-Onsager equation?

ANSWER FOR 2 MARKS QUESTIONS:

Ans1. In a mercury cell, the overall cell reaction does not include any ions from the solution. So, the concentration of the solution remains constant. As a result, mercury cells give a constant voltage. Therefore, mercury cells are more advantageous.

Ans2. Standard Hydrogen Electrode or better known as the normal hydrogen electrode is used as a reference for half-cell potential reactions.

By using a hydrogen electrode, it is possible to calculate cell potentials using different electrodes. This is also a standard measurement of electrode potential for the thermodynamic scale of redox potential.

Ans3. The equation that shows the effect of concentration on electrode potential is known as the Nernst Equation. It can be written as follows:
$E_{cell} = E^{o}_{cell} – (RT/nF) \ln Q$
Where,
E_{cell} = the reduction potential at current potential
E_{cell} = the standard reduction potential relative to the reduction potential of hydrogen at 25ºC
R = universal gas constant
T =temperature in K
n = the moles of electrons transferred between the positive and negative terminals of an electrochemical system.
F =Faraday's Constant
Q = reaction quotient

Ans4. When the emf of a cell is positive, then the Gibbs free energy of the overall reaction is less than zero.
$\Delta G = -nFE_{cell}$
Hence, the cell reaction is considered spontaneous.

Ans 5. Corrosion can be defined as the process of deterioration of metals because of their reaction with air and water. In this process, sulphides, oxides, carbonates, hydroxides, etc. are produced that slowly damage the metals. Rusting of iron is an example of corrosion. Rust is nothing but an oxide of iron (Fe_2O_3, x H_2O).

Ans 6. The oxidation potential of a chemical element refers to its propensity to be oxidised by losing one or more electrons at an electrode. Reduction potential, on the other hand, refers to the tendency of a chemical element to be reduced at the electrode by gaining one or more electrons.\

Ans 7. Cell constant can be defined as the ratio of the distance between the electrodes of a conductivity cell to their surface area. It can be determined by calculating the resistance of a cell of known conductivity.

Ans 8. We get the negative ions at the anode because it is the electrode where oxidation takes place. The oxidation process becomes easy if the oxidation potential of the solution is high. Br- has the highest oxidation potential, followed by H_2O, and finally F–.
So, in the aqueous solution of KBr, Br− ions are oxidised to Br_2 in preference to H_2O. On the other hand, in the aqueous solution of KF, H_2O is oxidised in preference to F−. Hence, in this case, oxidation of H_2O at the anode gives O_2 and thus no F_2 is produced at the anode.

Ans 9. When two metals are brought together under the surface of an electrolyte, a short-circuited cell is formed. Motor cars contain metals like lead, chromium and salt (NaCl) sprinkled over ice that acts as an electrolyte. Thus, a short-circuited cell is formed when cars move on the salt spread on the ice. So, corrosion on cars becomes a great problem in winter.

Ans 10. Strong electrolytes in concentrated solutions deviate from the Debye-Huckel-Onsager equation due to the large interionic forces of attraction.

PART-C: 3 MARKS QUESTIONS

Q1. Write three differences between potential difference and emf.

Q2. What is meant by “electrolytic conductance”? Name the factors that determine electrolytic conduction. What is the effect of temperature on it?

Q3. How is electrolytic conductance measured?

Q4. Iron does not rust even if a zinc coating is broken in a galvanised iron pipe, but rusting occurs much faster if the tin coating over iron is broken. Why?

Q5. What do you mean by Kohlrausch’s law: from the following molar conductivities at infinite dilution

λ_m Ba $(OH)_2$ = 457.6 Ω-1cm2mol-1

λ_m $BaCl_2$ = 240.6 Ω-1cm2mol-1

λ_m NH_4Cl = 129.8 Ω-1cm2mol-1

Calculate λ m for NH_4OH.

Q6. State Faraday’s Laws of electrolysis?

Q7. How many g of chlorine can be produced by the electrolysis of molten NaCl with a current of 1 ampere for 15 min?

Q8. What do you mean by primary and secondary battery?

Q9. a) Why does the conductivity of a solution decrease with dilution?

b) Can you store copper sulphate solutions in a zinc pot?

Q10.**At 298 K , the molar conductivities at infinite dilution of NH_4OH, NaOH and NaCl are 129.8 , 217.4 and** $108.9\ s\ cm^2\ mol^{-1}$ **respectively .It molar conductivity of 0.01M NH_4OH solution is** $9.33\ s\ cm^2\ mol^{-1}$ **,calculate the degree of dissociation of at this NH_4OH dilution?**

ANSWER FOR 3 MARKS QUESTIONS

Ans 1. Potential difference is the difference of potential of electrodes when there is a flow of electricity in the circuit; whereas emf refers to the electrode potential of two electrodes when there is no flow of electricity in the circuit.

The value of the potential difference is less than the maximum voltage obtained from the cell. Emf, on the other hand, is the maximum voltage obtained from a cell.

Potential difference is not responsible for a steady flow of current. Emf is responsible for the steady flow of the current in a circuit.

Ans 2. The ability of the electrolytic solutions to let the electric current pass through them is called electrolytic conductance.

The factors on which electrolytic conductance depends are as follows:

1. Temperature
2. The concentration of ions in the solution
3. Nature of the electrolyte

The ability of electrolytes to get dissolved in a solution changes with the change in temperature. When temperature increases, the solubility also increases, and hence, the electrolytic conductance also increases.

Ans 3. The resistance between two nodes helps determine the conductance of electrolytes. When electricity passes through the solution, it produces positive ions and negative ions in the solution. The conductance of electrolytes can be measured by using galvanic cells or the method of electrolysis.
Ans 4. Iron is less electropositive than zinc. So, the coating of zinc on the surface of the iron pipe acts as an anode and the iron pipe itself acts as a cathode. As a result, the iron pipe does not get damaged easily. Thus, rusting on galvanised iron is prevented by the coating of zinc.
On the other hand, zinc is more electropositive than tin. If the coating of tin is broken anywhere, or any pores or breaks are observed on the pipe, the parts where the iron is exposed are rusted easily.
Ans 5. According to Kohlrausch's Law, "An infinite dilution of each ion migrates independently of its co-ion and makes its own contribution to the total molar conductivity of an electrolyte irrespective of nature."
$\lambda_m NH_4OH = \lambda_{m+} + \lambda_{m-}$
$= 2NH_4^+ + 2Cl^- + Ba^{2+} + 2\,OH^- - Ba^{2+} + 2\,Cl^-$
$= 2\,\lambda_m(NH_4Cl) + \lambda_m Ba(OH)_2 - \lambda_m BaCl_2$
$=2\,\lambda_m(NH_4OH)$
$= 238.3\ \Omega^{-1}cm^2mol^{-1}$

Ans 6. Faraday's Laws of electrolysis
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.
Second Law: The amount of different substances liberated by the same quantity of electricity passing through the electrolytic solution is proportional to their chemical equivalent weights.

Ans 7. $Q = It \quad = 1\times 15\times 60 = 900C$
The reaction is $2Cl^- \; Cl_2 + 2e^-$
2mol 1mol 2mol
$\therefore$ 2F . produces 1 mol of Cl_2
1mol of $Cl_2 = 71g$
$\therefore$ 2× 96500 C produces 71g of Cl_2
900 C will produce $\frac{71}{2}\times\frac{900}{96500}$ g $= 0.331\ g\ of\ Cl_2$.

Ans 8. In the primary batteries, the reaction occurs only once and after the use over a period of time battery becomes dead and cannot be reused again. A secondary battery , after used, can be recharged by passing current through it in the opposite direction so that it can be used again.

Ans 9. a) The conductivity of a solution is the conductance of ions present in a unit volume of the solution. The number of ions (responsible for carrying current) decreases when the solution is diluted. As a result, the conductivity of a solution decreases with dilution.

b) Zinc is more reactive than copper. Therefore, zinc can displace copper from its salt solution. If copper sulphate solution is stored in a zinc pot, then zinc will displace copper from the copper sulphate solution.

$Zn + CuSO_4 \rightarrow ZnSO_4 + Cu$

Ans 10.

λ_m^0 $(NH_4OH) = \lambda_m^\circ$ $(Na_4Cl) + \lambda_m^\circ$ $(NaOH) - \lambda_m^\circ$ $(NaCl)$

= 129.8 +217.4 – 108.9 $= 237.35\ cm^2 / mol$

Degree of dissociation, $\alpha = \frac{\lambda m}{\lambda m^0} = \frac{9.33\,5\ cm^2 / mol}{237.3\,5\ cm^2 / mol}$

= 0.039 or 3.9 %.

CASE BASED QUESTIONS

CASE BASED QUESTION 1.

Boiling point or freezing point of liquid solution would be affected by the dissolved solids in the liquid phase. A soluble solid in solution has the effect of raising its boiling point and depressing its freezing point. The addition of non-volatile substances to a solvent decreases the vapor pressure and the added solute particles affect the formation of pure solvent crystals. According to many researches the decrease in freezing point directly correlated to the concentration of solutes dissolved in the solvent. This phenomenon is expressed as freezing point depression and it is useful for several applications such as freeze concentration of liquid food and to find the molar mass of an unknown solute in the solution. Freeze concentration is a high quality liquid food concentration method where water is removed by forming ice crystals. This is done by cooling the liquid food below the freezing point of the solution. The freezing point depression is referred as a colligative property and it is proportional to the molar concentration of the solution (m), along with vapor pressure lowering, boiling point elevation, and osmotic pressure. These are physical characteristics of solutions that depend only on the identity of the solvent and the concentration of the solute. The characters are not depending on the solute's identity. (Jayawardena, J. A. E. C., Vanniarachchi, M. P. G., & Wansapala, M. A. J. (2017). Freezing point depression of different Sucrose solutions and coconut water.)

1. When anon volatile solid is added to pure water it will:

a. boil above 100^oC and freeze above 0^oC

b. boil below 100^oC and freeze above 0^oC

c. boil above 100^oC and freeze below 0^oC

d. boil below 100^oC and freeze below 0^oC

2. Colligative properties are:

a. dependent only on the concentration of the solute and independent of the solvent's and solute's identity.

b. dependent only on the identity of the solute and the concentration of the solute and independent of the solvent's identity.

c. dependent on the identity of the solvent and solute and thus on the concentration of the solute.

d. dependent only on the identity of the solvent and the concentration of the solute and independent of the solute's identity.

3. Assume three samples of juices A, B and C have glucose as the only sugar present in them. The concentration of sample A, B and C are 0.1M, .5M and 0.2 M respectively. Freezing point will be highest for the fruit juice:
a. A
b. B
c. C
d. All have same freezing point
4. Identify which of the following is a colligative property :
a. freezing point b. boiling point
c. osmotic pressure d. all of the above

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

<u>CASE BASED QUESTION 2</u>.

All chemical reactions involve interaction of atoms and molecules. A large number of atoms/molecules are present in a few gram of any chemical compound varying with their atomic/molecular masses. To handle such large number conveniently, the mole concept was introduced. All electrochemical cell reactions are also based on mole concept. For example, a 4.0 molar aqueous solution of NaCl is prepared and 500 mL of this solution is electrolysed. This leads to the evolution of chlorine gas at one of the electrode. The amount of products formed can be calculated by using mole concept.

(i)The total number of moles of chlorine gas evolved is
(a) 0.5
(b) 1.0
(c) 1.5
(d) 1.9
(ii) If cathode is a Hg electrode, then the maximum weight of amalgam formed from this solution is
(a) 300g
(b) 446 g
(c) 396 g
(d) 256 g

or

The total charge (coulomb) required for complete electrolysis is
(a) 186000
(b) 24125
(c) 48296
(d) 193000

(iii) In the electrolytes, the number of moles of electrons involved are

(a) 2

(b) 1

(c) 3

(d) 4

(iv) In electrolysis of aqueous NaCl solution when Pt electrode is taken, then which gas is liberated at cathode?

(a) H_2 gas

(b) Cl_2 gas

(c) O_2 gas

(d) None of these

ANSWERS:

(i) b(ii) bord (iii) a(iv) a

CASE BASED QUESTION 3.

The potential of each electrode is known as electrode potential. Standard electrode potential is the potential when concentration of each species taking part in electrode reaction is unity and the reaction is taking place at 298 K. By convention, the standard ectrode potential of hydrogen (SHE) is 0.0 V. The electrode potential value for eacfi electrode process is a measure of relative tendency of the active species in the process to remain in the oxidisedlreduced form. The negative electrode potential means that the redox couple is stronger reducing agent than H+/H2 couple. A positive electrode potential means that the redox couple is a weaker reducing agent than the H+/H2 couple. Metals which have higher positive value of standard reduction potential form the oxides of greater thermal stability.

In these questions (i-iv), a statement of assertion followed by a statement of reason is given. Choose the correct answer out of the following choices.

(i) Assertion : An electrochemical cell can be set-up only if the redox reaction is spontaneous.

Reason : A reaction is spontaneous if the free energy change is negative.

(a) Assertion and reason both are correct statements and reason is correct explanation for assertion.

(b) Assertion and reason both are correct statements but reason is not correct explanation for assertion

(c) Assertion is correct statement but reason is wrong statement.

(d) Assertion is wrong statement but reason is correct statement.

(ii) Assertion : The standard electrode potential of hydrogen is 0.0 V.

Reason : It is by convention.

(a) Assertion and reason both are correct statements and reason is correct explanation for assertion.

(b) Assertion and reason both are correct statements but reason is not correct explanation for assertion

(c) Assertion is correct statement but reason is wrong statement.

(d) Assertion is wrong statement but reason is correct statement.

(iii) Assertion : The negative value of standard reduction potential means that reduction takes place on this electrode with reference to hydrogen electrode.
Reason : The standard electrode potential of a half cell has a fixed value.
(a) Assertion and reason both are correct statements and reason is correct explanation for assertion.
(b) Assertion and reason both are correct statements but reason is not correct explanation for assertion
(c) Assertion is correct statement but reason is wrong statement.
(d) Assertion is wrong statement but reason is correct statement.

(iv) Assertion : The absolute value of electrode potential cannot be determined experimentally.
Reason : The electrode potential values are generally determined with respect to SHE.
(a) Assertion and reason both are correct statements and reason is correct explanation for assertion.
(b) Assertion and reason both are correct statements but reason is not correct explanation for assertion
(c) Assertion is correct statement but reason is wrong statement.
(d) Assertion is wrong statement but reason is correct statement.

ANSWER: (i) (b)
(ii) (a)
(iii) (d) : A negative value of standard reduction potential means that oxidation takes' place on the electrode with reference to SHE.
(iv) (a)

CASE BASED QUESTION 4.

The study of the conductivity of electrolyte solutions is important for the development of electrochemical devices, for the characterization of the dissociation equilibrium of weak electrolytes, and for the fundamental understanding of charge transport by ions. The conductivity of the electrolyte is measured for electrolyte solution with concentrations in the range of 10^{-3} to 10^{-1} mol L^{-1}, as a solution in this range of concentrations can be easily prepared. The molar conductivity (Λm)
of strong electrolyte solutions can be nicely fit by the Kohlrausch equation.

$\Lambda_m = \Lambda^\circ_m - K\sqrt{C}$ …(i)

Where $\Lambda^\circ m$ is the molar conductivity at infinite dilution and C is the concentration of the solution. K is an empirical proportionality constant to be obtained from the experiment. The molar conductivity of weak electrolytes, on the other hand, is dependent on the degree of dissociation of the electrolyte. At the limit of a very dilute solution, the Ostwald dilution law is expected to be followed,

$$\frac{1}{\Lambda_m} = \frac{1}{\Lambda_m^\circ} + \frac{\Lambda_m}{(\Lambda_m^\circ)^2}\frac{C_A}{K_d} \qquad \ldots(ii)$$

where CA is the analytical concentration of the electrolyte and Kd is the dissociation constant. The molar conductivity at infinite dilution can be decomposed into the contributions of each ion.

$$\Lambda_m^\circ = \nu_+\lambda_+^\circ + \nu_-\lambda_-^\circ \qquad \ldots(iii)$$

Where, λ_+ and λ_- are the ionic conductivities of positive and negative ions, respectively and v_+ and v^- are their stoichiometric coefficients in the salt molecular formula.

Which statement about the term infinite dilution is correct?
(a) Infinite dilution refers to a hypothetical situation when the ions are infinitely far apart.
(b) The molar conductivity at infinite dilution of NaCl can be measured directly in solution.
(c) Infinite dilution is applicable only to strong electrolytes.
(d) Infinite dilution refers to a real situation when the ions are infinitely far apart.
Ans: (a) Infinite dilution refers to a hypothetical situation when the ions are infinitely far apart.

Which of the following is a strong electrolyte in aqueous solution?
(a) HNO_2 (b) HCN(c) NH_3 (d) HCl
Answer: (d) HCl
OR

Which of the following is a weak electrolyte in aqueous solution?
(a) K_2SO_4 (b) Na_3PO_4(c) NaOH (d) H_2SO_3
Answer: (d) H_2SO_3
If the molar conductivities at infinite dilution for NaI, CH_3COONa and $(CH_3COO)_2Mg$ are 12.69, 9.10 and 18.78 S cm^2 mol^{-1} respectively at 25°C, then the molar conductivity of MgI_2 at infinite dilution is
(a) 25.96 S cm^2 mol^{-1} (b) 390.5 S cm^2 mol^{-1}
(c) 189.0 S cm^2 mol^{-1}
(d) 3.89 × 10–2 S cm^2 mol^{-1}
Answer: (a) 25.96 S cm^2 mol^{-1}

Which of the following is the correct order of molar ionic conductivities of the following ions in aqueous solutions?

- (a) $Li^+ < Na^+ < K^+ < Rb^+$
- (b) $Li^+ > Na^+ > K^+ > Rb^+$
- (c) $Rb^+ < Na^+ < Li^+ < K^+$
- (d) $Li^+ < Rb^+ < Na^+ < K^+$

Answer: (a) $Li^+ > Na^+ > K^+ > Rb^+$

5 MARLS QUESTIONS

QUS 1. Two half cell reactions of an electrochemical cell are given below :
$MnO^-_4(aq) + 8H^+ (aq) + 5e^- \rightarrow Mn^{2+} (aq) + 4H_2O$ (I), E° = + 1.51 V
$Sn^{2+} (aq) \rightarrow 4\ Sn^{4+} (aq) + 2e^-$, E° = + 0.15 V
Construct the redox equation from the two half cell reactions and predict if this reaction favours formation of reactants or product shown in the equation. (All India 2009)
Answer:
The reactions can be represented at anode and at cathode in the following ways :
At anode (oxidation) :
$Sn^{2+} \rightarrow = Sn^{4+} (aq) + 2e^-\ ] \times 5$ E° = + 0.15 V
At cathode (reduction) :
$MnO^-_4(aq) + 8H^+ (aq) + 5e^- \rightarrow Mn^{2+} (aq) + 4H_2O$ (I)] × 2 E° = + 1.51 V
The Net R × M = $2MnO^-_4(aq) + 16H^+ + 5Sn^{2+} \rightarrow 2Mn^{2+} + 5Sn^{4+} + 8H_2O$

Now $E°_{cell} = E°_{cathode} – E°_{anode}$
= 1.51 – 0.15 = + 1.36 V
∴ Positive value of $E°_{cell}$ favours formation of product.

QUS 2. A zinc rod is dipped in 0.1 M solution of $ZnSO_4$. The salt is 95% dissociated at this dilution at 298 K. Calculate the electrode potential.
[$E°_{Zn}{}^{2+}$ /Zn = – 0.76 V] (Comptt. Delhi 2012)
Answer:
The electode reaction is given as
$Zn^{+2} + 2e \rightarrow Zn$
Using Nernest Equation

$$E_{Zn^{+2}/Zn} = E^{\circ}_{Zn^{2+}/Zn} - \frac{0.0591}{2}\log\frac{1}{[Zn^{+2}]}$$

$$[Zn^{+2}] = \frac{95}{100}\times 0.1 = 0.095$$

$$\begin{aligned} E_{Zn^{+2}/Zn} &= -0.76 - 0.0295 \log \frac{1}{0.095} \\ &= -0.76 - 0.0295\,[\log 1000 - \log 95] \\ &= -0.76 - 0.0295\,[3 - 1.9777] \\ &= -0.76 - 0.03016 = \mathbf{-0.79\ volt} \end{aligned}$$

QUS 3. a) Write the reactions taking place at cathode and anode in lead storage battery when the battery is in use. What happens on charging the battery ?
b) The standard electrode potential (E°) for Daniel cell is +1.1 V. Calculate the ΔG° for the reaction
$Zn(s) + Cu^{2+}(aq) \rightarrow Zn^{2+}(aq) + Cu(s)$
(1 F = 96500 C mol^{-1}).
Answer: a) At Anode: $Pb + SO_4^{-2} \rightarrow PbSO_4 + 2e$
at Cathode : $PbO_2 + SO_4^{-2} + 4H^+ + 2e \rightarrow PbSO_4 + 2H_2O$
On charging the battery, the reaction is reversed and $PbSO_4$ on anode and cathode is converted into Pb and PbO_2 respectively.
b) We know, ΔG° = -nFE°cell
Given :E°cell = 1.1 volt
∴ΔG° = -2 × 96500 C mol^{-1} × 1.1 volt
= -212300 CV mol^{-1}
= -212300 J mol^{-1} = -212.3 KJ mol^{-1}

QUS 4. The conductivity of 0.001 M acetic acid is 4×10^{-5} S/cm. Calculate the dissociation constant of acetic acid, if molar conductivity at infinite dilution for acetic acid is 390 S cm^2/mol.
Answer:
Given : K = 4×10^{-5} S/cm, M = 0.001 M
$\Lambda°m$ = 390 S cm^2/mol, k = ?

Using the formula

$$\Lambda_m^c = \frac{K \times 1000}{\text{Molarity}}$$

$$= \frac{4 \times 10^{-5}\,\text{S cm}^{-1} \times 1000\,\text{cm}^3\text{L}^{-1}}{0.001\,\text{mol L}^{-1}}$$

$$= 40\ \text{S cm}^2\ \text{mol}^{-1}$$

$$\alpha = \frac{\Lambda_m^c}{\Lambda_m^\circ} = \frac{40}{390} = 0.1025$$

$$\begin{array}{ccccc} CH_3-COOH & \rightleftharpoons & CH_3-COO^- & + & H^+ \\ C & & 0 & & 0 \\ C(1-\alpha) & & C\alpha & & C\alpha \end{array}$$

$$k_\alpha = \frac{[CH_3-COO^-][H^+]}{[CH_3-COOH]} = \frac{C\alpha.C\alpha}{C(1-\alpha)} = \frac{C\alpha^2}{1-\alpha}$$

$$k = \frac{10^{-3} \times (1.025 \times 10^{-1})^2}{1-0.1025} = \frac{10^{-5} \times 0.105}{0.8975}$$

$$\therefore \quad k = \mathbf{1.46 \times 10^{-6}}$$

CHAPTER 3: CHEMICAL KINETICS

SECTION A

MULTIPLE CHOICE QUESTIONS

1. What will be the fraction of molecules having energy equal to or greater than activation energy, Ea?
(a) K
(b) A
(c) $Ae^{-Ea/Rt}$
(d) $e^{-Ea/Rt}$

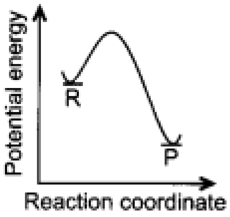
2. $RCOOR' + H_2O \xrightarrow{HCl} RCOOH + R'OH$
What type of reaction is this?
(a) Second order
(b) Unimolecular
(c) Pseudo-unimolecular
(d) Third order

3. Which among the following is a false statement?
(a) Rate of zero order reaction is independent of initial concentration of reactant.
(b) Half life of a third order reaction is inversely proportional to square of initial concentration of the reactant.
(c) Molecularity of a reaction may be zero or fraction.
(d) For a first order reaction, t1/2=0.693K

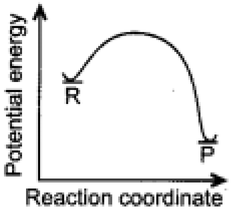
4. Which of the following statements about the catalyst is true?
(a) A catalyst accelerates the rate of reaction by bringing down the activation energy.
(b) A catalyst does not participate in reaction mechanism.
(c) A catalyst makes the reaction feasible by making ΔG more negative.
(d) A catalyst makes equilibrium constant more favourable for forward reaction.

5. An endothermic reaction with high activation energy for the forward reaction is given by the diagram.

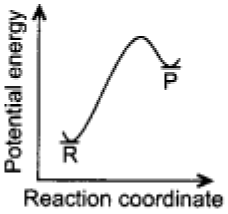
(a)



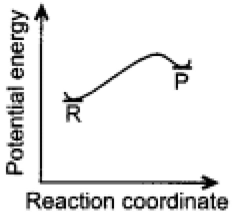
(b)



(c)



(d)



6. For the reaction $N_2 + 3H_2 \rightarrow 2NH_3$ if

Δ[NH3]/Δt = 2 × 10^{-4} mol $L^{-1}s^{-1}$, the value of −Δ[H2]/Δt would be
(a) 1 × 10^{-4} mol $L^{-1}s^{-1}$
(b) 3 × 10^{-4} mol $L^{-1}s^{-1}$
(c) 4 × 10^{-4} mol $L^{-1}s^{-1}$
(d) 6 × 10^{-4} mol $L^{-1}s^{-1}$

7. The rate of a certain hypothetical reaction
A + B + C → products
is given by r = −d[A]/dtK[A]1/2[B]1/3[C]1/4. The order of the reaction is
(a) 13/11
(b) 13/14
(c) 12/13
(d) 13/12

8. In the formation of S02 by contact process;
$2SO_2 + O_2 \rightarrow 2SO_3$, the rate of reaction was measured as −d[O2]/dt=2.5 × 10^{-4} mol $L^{-1}s^{-1}$. at
The rate of formation of of S03 will be
(a) -5.0 × 10^{-4} mol $L^{-1}s^{-1}$
(b) -1.25 × 10^{-4} mol $L^{-1}s^{-1}$
(c) 3.75 × 10^{-4} mol $L^{-1}s^{-1}$
(d) 5.00 × 10^{-4} mol $L^{-1}s^{-1}$

9. For a chemical reaction A→B, it is found that the rate of reaction doubles when the concentration of A is increased four times. The order of reaction is
(a) Two

(b) One
(c) Half
(d) Zero

---

10. The half life of the first order reaction having rate constant K = $1.7 \times 10^{-5}s^{-1}$ is
(a) 12.1 h
(b) 9.7 h
(c) 11.3 h
(d) 1.8 h

SHORT ANSWER QUESTIONS(2M)

11) Define ‘rate of a reaction’

12) Define ‘order of a reaction’

13) Define ‘activation energy’ of a reaction

14) If the rate constant of a reaction is $k = 3 \times 10^{-4}\ s^{-1}$, then identify the order of the reaction.

15) Write the unit of rate constant for a zero order reaction.

16) Define rate constant (K)

17) For a reaction R → P, half-life ($t_{1/2}$) is observed to be independent of the initial concentration of reactants. What is the order of reaction?

18) Define Elementary step in a reaction

19)Define Activation energy of a reaction

20)What is meant by rate constant

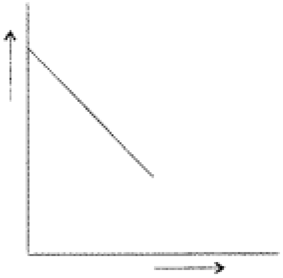
SHORT QUESTIONS(3M)

21) Write two differences between ‘order of reaction’ and ‘molecularity of reaction’.

22)Define the following terms :
(a) Pseudo first order reaction.
(b) Half life period of reaction ($t_{1/2}$).

23) Explain the following terms :
(i) Rate constant (k)
(ii) Half life period of a reaction ($t_{1/2}$)

24) For a chemical reaction R → P, the variation in the f concentration (R) vs. time (f) plot is given as
(i) Predict the order of the reaction.
(ii) What is the slope of the curve? (All India 2014)



25)) For a reaction, A + B → Product, the rate law is given by, Rate = $k[A]^1[B]^2$. What is the order of the reaction?
(b) Write the unit of rate constant 'k' for the first order reaction

26) For a reaction A + B → P, the rate is given by Rate = $k[A]\,[B]^2$
(i) How is the rate of reaction affected if the concentration of B is doubled?
27) What is the physical significance of energy of activation ? Explain with diagram

28) Following data are obtained for the reaction:
$N_2O_5 \rightarrow 2NO_2 + 1/2O_2$

t/s	**0**	**300**	**600**
$[N_20_5]$/mol L^{-1}	1.6×10^{-2}	0.8×10^{-2}	0.4×10^{-2}

(a) Show that it follows first order reaction.
(b) Calculate the half-life.
(Given log 2 = 0.3010 log 4 = 0.6021)

29) The rate constant for a first order reaction is 60 s^{-1}. How much time will it take to reduce the initial concentration of the reactant to its l/10th value?

30) The rate constant for the first order decomposition of H_2O_2 is given by the following equation:
$\log k = 14.2 - 1.0\times10^4 TK$
Calculate E_a for this reaction and rate constant k if its half-life period be 200 minutes.
(Given: R = 8.314 J K^{-1} mol^{-1})

SECTION D(LONG ANSWER QUESTIONS)-5M

31) For the hydrolysis of methyl acetate in aqueous solution, the following results were obtained:

t/s	0	10	20
$[CH_3COOCH_3]$/mol L^{-1}	0.10	0.05	0.025

(i) Show that it follows pseudo first order reaction, as the concentration of water remains constant.
(ii) Calculate the average rate of reaction between the time interval 10 to 20 seconds. (Given : log 2 = 0.3010, log 4 = 0.6021) (All India 2015)

32) a) For a reaction A + B → P, the rate is given by Rate = $k[A][B]^2$
(i) How is the rate of reaction affected if the concentration of B is doubled?
(ii) What is the overall order of reaction if A is present in large excess?
(b) A first order reaction takes 30 minutes for 50% completion. Calculate the time required for 90% completion of this reaction.

33) (a) For a reaction A + B → P, the rate is given by Rate = $k[A][B]^2$
(i) How is the rate of reaction affected if the concentration of B is doubled?
(ii) What is the overall order of reaction if A is present in large excess?
(b) A first order reaction takes 30 minutes for 50% completion. Calculate the time required for 90% completion of this reaction.
(log 2 = 0.3010)

34) The decomposition of A into products has a value of K as 4.5×10^3 s^{-1} at 10°C and energy of activation 60 kj mol-1. At what temperature would K be 1.5×10^4 s^{-1}?
(b) (i) If half life period of a first order reaction is x and 3/4,th life period of the same reaction is y, how are x and y related to each other?
(ii) In some cases it is found that a large number of colliding molecules have energy more than threshold energy, yet the reaction is slow. Why?

35) A first order reaction takes 100 minutes for completion of 60% of the reaction. Find the time when 90% of the reaction will be completed.
(b) With the help of diagram explain the role of activated complex in a reaction

SECTION E (CASE BASED QUESTIONS)-4M

36) The integrated rate law for the second-order reaction A → products is 1/[A]_t = kt + 1/[A]_0. Because this equation has the form y = mx + b, a plot of the inverse of [A] as a function of time yields a straight line. The rate constant for the reaction can be determined from the slope of the line, which is equal to k.

A reaction is second order in A and first order in B.
(36.i) Write the differential rate equation(1m),
(36.ii) How is the rate affected on increasing the concentration of A three times?(1m)
(36.iii) How is the rate affected when the concentrations of both A and B are doubled?(2m)

37) Molecularity is the number of reacting species involved in simultaneous collisions in an elementary or simplest reaction. Order is an experimentally determined quantity. It may be equal to zero, positive, negative, whole number or fractional number. Molecularity is a theoretical concept, it is always in whole numbers.

Explain the following terms :
(37.i) Order of a reaction(1m)
(37.ii) Molecularity of a reaction(1m)
(37.iii) The rate of a reaction increases four times when the temperature changes from 300 K to 320 K. Calculate the energy of activation of the reaction, assuming that it does not change with temperature. (R = 8.314 J K^{-1} mol^{-1})(2m)

38) For the reaction
$2NO(g) + Cl_2(g) \rightarrow 2NOCl(g)$ the following data were collected. All the measurements were taken at 263 K :

Experiment No.	**Initial [NO](M)**	**Initial $[Cl_2]$(M)**	**Initial rate of tlisa/ipcarance of Cl_2 (M/min)**
1	0.15	0.15	0.60
2	0.15	0.30	1.20
3	0.30	0.15	2.40
4	0.25	0.25	?

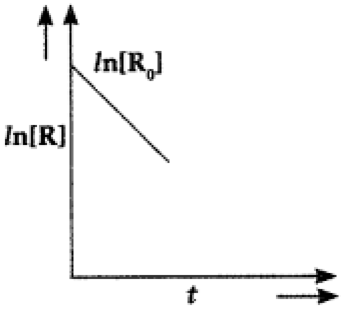
(a) Write the expression for rate law.

(b) Calculate the value of rate constant and specify its units.

(c) What is the initial rate of disappearance of Cl_2 in exp. 4?

39) For a chemical reaction R → P, variation in ln[R] vs time (f) plot is given below:
For this reaction:

(39.i) Predict the order of reaction



(39.ii) What is the unit of rate constant (k)?

Answer:

(39.iii) Write the rate equation for the reaction $A_2 + 3B_2 \rightarrow 2C$, if the overall order of the reaction is zero.

ANSWERS TO CHEMICAL KINETICS PART-1

SECTION A (MCQ)

1.d

2.c

3. c

4.a

5.c

6.b

7.d

8.d

9.c

10.c

Short answers(2m)

11) **Rate of a reaction:** Either, The change in the concentration of any one of the reactants or products per unit time is called rate of a reaction. Or, The rate of a chemical reaction is the change in the molar concentration of the species taking part in a reaction per unit time.

12) The sum of powers of the concentration of the reactants in the rate law expression is called the order of reaction

13) The minimum extra amount of energy absorbed by the reactant molecules to form the activated complex is called activation energy.
The activation energy of the reaction decreases by the use of catalyst.

14) S^{-1} is the unit for rate constant of first order reaction.

15) Mol L^{-1} S^{-1} is unit of rate constant for a zero order reaction

16) Rate constant. It is defined as the rate of reaction when the concentration of reaction is taken as unity.

17) The $t_{1/2}$ of a first order reaction is independent of initial concentration of reactants.

18) Those reactions which take place in one step are called elementary reactions.
Example : Reaction between H_2, and I_2 to form 2HI
$H_2 + I_2 \rightarrow 2HI$
19) The minimum extra amount of energy absorbed by the reactant molecules to form the activated complex is called activation energy.

SECTION B(Short Answer questions (3m))

21)

Order of reaction	**Molecularity of reaction**
(i) It is the sum of tire concentration terms on which die rate of reaction actually depends.	It is the number of atoms, ions or molecules that must collide with one another simultaneously so as to result into a chemical reaction.
(ii) It can be fractional as well as zero.	it is always a whole number.

22) (a) Those reactions which are not truly of the first order but under certain conditions become first order reactions are called pseudo first order reaction.
(b) The time taken for half of the reaction to complete is called half life period.

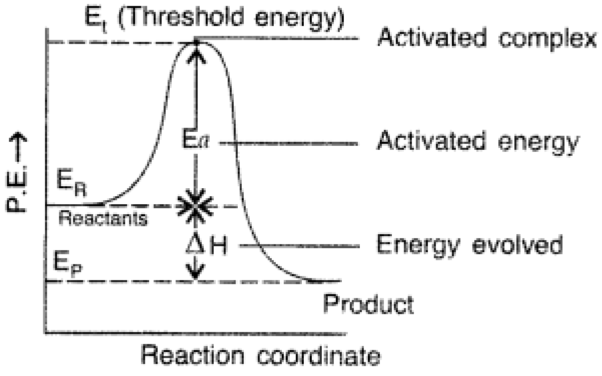
23) **i) Rate constant (k):** It is a proportionality constant and is equal to the rate of reaction when the molar concentration of each of the reactants is unity.
(ii) Half life period of a reaction ($t_{1/2}$): The time taken for half of the reaction to complete is called half life penod.(R)t

24)) It is zero order reaction.
(ii) Slope of the curve = -K

25) a) For a reaction, A + B
Rate = k $[A]^1$ $[B]^2$
This is the third order of reaction.
(b) Unit of rate constant for first order reaction is S^{-1}

26) For the reaction A + B → P rate is given
by Rate = $k[A]^1[B]^2$
(i) r_1 = k[A]1 [B]2
$r_2 = k[\ A]^1[2B]^2 =$
$r_2 = k[A]^1\ [2B]^2 = 4k[A]^1\ [B]^2$
$r_1 = 4r_2$, rate will increase four times of actual rate.

27) The minimum extra amount of energy absorbed by the reactant molecules so that their energy becomes equal to threshold value is called activation energy. Less is the activation energy, faster is the reaction or greater is the activation energy, slower is the reaction



28) (a) Show that it follows first order reaction.
(b) Calculate the half-life.
(Given log 2 = 0.3010 log 4 = 0.6021) (Delhi 2016)
Answer:

(a) For first order reaction:

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

$$k = \frac{2.303}{t}\log\frac{[N_2O_5]_0}{[N_2O_5]_t}$$

At $t = 300$ s

$$k = \frac{2.303}{300}\log\frac{1.6\times10^{-2}}{0.8\times10^{-2}}$$

$$= \frac{2.303}{300}\log 2 = \frac{2.303}{300}\times 0.3010$$

$\therefore \quad k = 0.0023106$

At $t = 600$ s

$$k = \frac{2.303}{600}\log\frac{1.6\times10^{-2}}{0.4\times10^{-2}}$$

$$= \frac{2.303}{600}\log 4 = \frac{2.303}{600}\times 0.6020$$

$\therefore \quad \mathbf{k = 0.0023106}$

Since the value of k comes to nearly constant therefore it follows the first order reaction.

(*b*) $t_{1/2} = \frac{0.693}{k} = \frac{0.693}{0.0023106} = 299.9 = \mathbf{300\ s}$

29) Given : $k = 60\ s^{-1}$, t = ?

If initial concentration is $[A_0]$

Then $\frac{1}{10}$th of initial concentration is $\frac{[A_0]}{10}$

Using expression for first order reaction,

$$k = \frac{2.303}{t}\log\frac{[A_0]}{[A]} \qquad t = \frac{2.303}{k}\log\frac{[A_0]}{[A]}$$

Substituting values,

$$t = \frac{2.303}{60\,s^{-1}}\log\frac{[A_0]}{[A_0]/10} \Rightarrow t = \frac{2.303}{60\,s^{-1}}\log 10$$

$$\Rightarrow t = \frac{2.303}{60\,s^{-1}}\times 1 \qquad \therefore\ t = 0.0383\ s$$

30) Given: $t_{1/2}$ = 200 min E_a = ?, T = ?

Using Arrhenius equation

$$\log k = \log A - \frac{E_a}{2.303\ RT}$$

On comparing above equation with the given equation

$$i.e.\ \log k = 14.2 - \frac{1.0\times 10^4}{T}K$$

$$\therefore \qquad \frac{E_a}{2.303\ RT} = \frac{1.0\times 10^4}{T}K$$

$$E_a = 1.0 \times 10^4 \times 2.303 \times 8.314\ (\text{J mol}^{-1})$$

$$= 191471.42\ \text{J mol}^{-1} = \mathbf{191.471\ K\ J\ mol^{-1}}$$

For first order reaction;

$$k = \frac{0.693}{t_{1/2}} = \frac{0.693}{200\ \text{min}} = \mathbf{0.0034\ min^{-1}}$$

SECTION C (LONG ANSWERS-5M)

(*i*) $[A]_0 = 0.10$ mol/L, $[A] = 0.5$ mol/L, $t = 10$s
$[A]_0 = 0.10$ mol/L, $[A] = 0.25$ mol/L, $t = 20$s

$$k = \frac{2.303}{t}\log\frac{[A_0]}{[A]}$$

$$k_1 = \frac{2.303}{10}\log\frac{0.1}{0.05}$$

$$k_1 = \frac{2.303}{10}\times\log 2$$

$$k_1 = \frac{2.303\times 0.3010}{10}$$

$$k_1 = \frac{0.693}{10} = 0.0693\ \text{sec}^{-1}$$

$$k = \frac{2.303}{t}\log\frac{[A_0]}{[A]}$$

$$k_2 = \frac{2.303}{20}\log\frac{0.1}{0.025}$$

$$k_2 = \frac{2.303}{20}\times\log 4$$

$$k_2 = \frac{2.303\times 2\log 2}{20}$$

$$k_2 = \frac{2.303\times 0.3010\times 2}{20}$$

$$= 0.0693\ \text{sec}^{-1}$$

31)

As k_1 and k_2 are equal, hence pseudo rate constant is same.

It follows the pseudo first order reaction.

(ii) Average rate of reaction between 10 to 20 seconds

= −Δ[R]Δt=−(0.025−0.05)(20−10)=0.02510

= 0.0025 mol lit^{-1} sec^{-1}

32) a) For the reaction A + B → P

rate is given by Rate = $k[A]^1[B]^2$

(i) $r_1 = k[A]^1\ [B]^2$

$r_2 = k[A]^1\ [2B]^2 = 4k[A]^1\ [B]^2$

$r_1 = 4r_2$ (rate of reaction becomes 4 times)

(ii) When A is present in large amounts, order w.r.t. A is zero.
Hence overall order = 0 + 2 = 2

(b) $t_{\frac{1}{2}} = \frac{0.693}{k}$ $t_{\frac{1}{2}} = 30$ minutes $k = \frac{0.693}{30}\ \text{min}^{-1}$

$$k = 0.0231\ \text{min}^{-1}$$

$$k = \frac{2.303}{t}\log\frac{[A_0]}{[A]}$$

$$t = \frac{2.303}{0.0231}\log\frac{100}{10} \quad t = \frac{2.303}{0.0231}\ \text{min}$$

$$\therefore \quad t = \mathbf{99.7\ min}$$

33) a) For the reaction A + B → P rate is given
by Rate = $k[A]^1[B]^2$
(i) r_1 = k[A]1 [B]2
$r_2 = k[\ A]^1[2B]^2 =$
$r_2 = k[A]^1\ [2B]^2 = 4k[A]^1\ [B]^2$
$r_1 = 4r_2$, rate will increase four times of actual rate.

(ii) When A is present in large amount, order w.r.t. A is zero.
Hence overall order = 0 + 2 = 2, second order reaction.

(b) $t_{\frac{1}{2}} = 30$ minutes, $t_{\frac{1}{2}} = \frac{0.693}{k}$

$$\Rightarrow \quad 30\ \text{min} = \frac{0.693}{k}$$

$$\Rightarrow \quad k = \frac{0.693}{30}\ \text{min}^{-1} \quad \Rightarrow k = 0.0231\ \text{min}^{-1}$$

$$k = \frac{2.303}{t}\log\frac{[A_0]}{[A]}$$

$$t = \frac{2.303}{0.0231}\log\frac{100}{10} \quad \Rightarrow t = \frac{2.303}{0.0231}\ \text{min}$$

$$\therefore \quad t = \mathbf{99.7\ minutes}$$

34) (a) Given : $K_1 = 4.5 \times 10^3\ s^{-1}$,
T_1 = 10K + 273K = 283K
$K_2 = 1.5 \times 10^4\ s^{-1}$, T_2 = ?
$E_a = 60$ KJ mol^{-1}
Using formula :

$$\log : \frac{K_2}{K_1} = \frac{E_a}{2.303R}\left(\frac{T_2 - T_1}{T_1 T_2}\right)$$

$$\log \frac{1.5 \times 10^4}{4.5 \times 10^3} = \frac{60000\,\text{J mol}^{-1}}{2.303 \times 8.314\,\text{JK}^{-1}\text{mol}^{-1}}\left(\frac{T_2 - 283}{283T_2}\right)$$

$$\Rightarrow \quad \log 3.333 = 3133.63 \left(\frac{T_2 - 283}{283T_2}\right)$$

$$\Rightarrow \quad \frac{0.5228}{3133.63} = \frac{T_2 - 283}{283T_2}$$

$$\Rightarrow \quad 0.0472\ T_2 = T_2 - 283$$

$$\Rightarrow \quad 0.9528\ T_2 = 283$$

$$\Rightarrow \quad T_2 = \frac{283}{0.9528} = 297\ \text{K}$$

∴ Temperature, T_2 will be = 297° – 273° = 24° C

(b) (i) $t_{1/2} = 0.693K$ (For first order reaction)

$t_{3/4} = K \Rightarrow t_{3/4} = 1.3864K$

According to condition

(The value 1.3864 is double of 0.693)

From the above equation it is clear that

$t_{3/4} = 2t_{1/2}$ ∴ $y = 2X$

(ii) It is due to improper orientation of the colliding molecules at the time of collision.

35)) For the first order reaction,

$$k = \frac{2.303}{t}\log\frac{a}{a-x}$$

When reaction is 60% complete

$$x = \frac{60}{100}a = 0.6a,$$

$t = 100\ \text{min}^{-1}$ (Given)

$$\text{then } k = \frac{2.303}{100}\log\frac{a}{a-0.6a}$$

$$\Rightarrow \quad k = \frac{2.303}{100}\log\frac{a}{0.4a}$$

$$\Rightarrow \quad k = \frac{2.303}{100}\log 2.5 \qquad \ldots(i)$$

t = ?, ***when reaction is 90% complete***

$x = 0.9a$

$$\text{then } k = \frac{2.303}{t}\log\frac{a}{a-x}$$

$$\Rightarrow \quad k = \frac{2.303}{t}\log\frac{a}{a-0.9a}$$

$$\Rightarrow \quad k = \frac{2.303}{t}\log 10 \qquad \ldots(ii)$$

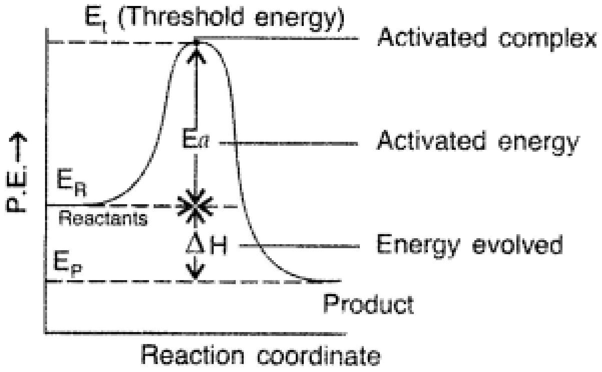
Taking equations (*i*) and (*ii*), we get

$$\frac{2.303}{100}\log 2.5 = \frac{2.303}{t}\log 10$$

$$\Rightarrow \quad \frac{0.3979}{100} = \frac{1}{t} \qquad \Rightarrow t = \frac{100}{0.3979}$$

$\therefore$ **t = 251.31 minutes**

(b) In order that the reactants may change into products, they have to cross an energy barrier as shown in the diagram



This diagram is obained by plotting potential energy vs. reaction coordinate. It is believed that when the reactant molecules absorb energy, their bonds are loosened and new bonds are formed between them. The intermediate complex thus formed is called activated complex. It is unstable and immediately dissociates to form the stable products.

36.i) Differential rate equation :

dxdt = K $[A]^2[B]$

(36.ii) When concentration of A is increased to three times, the rate of reaction becomes 9 times

$r = K[3A]^2B \therefore r = 9KA^2B$ i.e. = 9 times

(36.iii) $r = K[2A]^2[2B] \therefore r = 8KA^2B$ i.e. = 8 times

37.**i) Order of a reaction:** It is the sum of powers of the molar concentrations of reacting species in the rate equation of the reaction.

(37.ii) Molecularity of a reaction :

- It is the total number of reacting species (molecules, atoms or ions) which bring the chemical change.
- It is always a whole number.
- It is a theoretical concept.
- It is meaningful only for simple reactions or individual steps of a complex reaction. It is meaningless for overall complex reaction.

(37.iii) Given : $T_1 = 300$ K $T_2 = 320$ K

$K_1 = K$ (Consider)

$K_2 = 4$ K $R = 8.314$ $E_a = ?$

Substituting these values in the formulae,

$$\log \frac{K_2}{K_1} = \frac{E_a}{2.303R}\left(\frac{T_2 - T_1}{T_1 T_2}\right)$$

$$\therefore \quad \log \frac{4K}{K} = \frac{E_a}{2.303 \times 8.314}\left(\frac{320 - 300}{320 \times 300}\right)$$

$$\text{or} \quad \log 4 = \frac{E_a}{19.1471} \times \frac{20}{96000}$$

$$\text{or} \quad 0.6020 = \frac{E_a}{19.1471} \times \frac{20}{96000}$$

$$\text{or} \quad E_a = \frac{0.6020 \times 19.1471 \times 96000}{20} = 55327.46$$

$\therefore$ Energy of activation, $E_a = 55327.46 = 55.3$ KJ mol^{-1}

38.i) Rate law = $K[NO]^2\,[Cl_2]$

(38.ii) 0.60 M $min^{-1} = K[0.15]^2\,[0.15]$ M^3

$\therefore K = 177.7$ M^{-2} min^{-1}

(38.iii) Initial rate of disappearance of Cl_2 in exp. 4

Formula : Rate = $K[NO]^2\,[Cl_2]$

$\therefore$ Initial rate = $177.7M^{-2}$ $min^{-1} \times (0.25)^2 \times (0.25)M^3$

= 2.8 M min^{-1}

39.i) It is zero order reaction.

(39.ii) The unit of rate constant (k) is mol L^{-1} S^{-1}.

39.iii) (ii) $A_2 + 3B_2 \rightarrow 2C$

Rate = (dxdt) = $K[A]^0\,[B]^0$ = K (rate constant)

S NO.	**CHAPTER 4: THE D & F BLOCK ELEMENTS**	MARKS
Q.1	Which of the following is a strong oxidising agent? (At. No. Mn =25 Zn=30, Cr=24 Sc=21) (a) Mn^{3+} (b) Zn^{2+} (c) Cr^{3+} (d) Sc^{3+}	1
Q.2	In which of the following pairs both the ions are coloured in aqueous solution? (a) Sc^{3+} Ti^{3+} (b) $Sc^{3+}Co^{2+}$ (c) Ni^{2+} Cu^{+} (d) $Ni^{2+}Ti^{3+}$	1
Q.3	Which of the following has the same ionic size? (a)Zr^{4+}, Hf^{4+} (b)Zn^{2+}, Hf^{4+} (c) Fe^{2+}, Ni^{2+} (d)Zr^{4+} , Ti^{4+}	1
Q.4	Magnetic moment of 2.83 B.M. is given by which of the following ion? (a)Ti^{3+} (b) Ni^{2+} (c) Cr^{3+} (d)Mn^{2+}	1
Q.5	The correct order of decreasing second ionising enthalpy of Ti(22) V(23) Cr(24) Mn(25) (a) V > Mn < Cr>Ti (b) Mn <Cr <Ti<V (c) Ti> V> Cr > Mn (d) Cr> Mn > V >Ti	1
Q.6	Which property of transition metals enables them to behave as a catalyst ? (a) high melting point (b) high ionisation energy (c) alloy formation (d) variable oxidation state	1
Q.7	The incorrect statement about interstitial compounds is: (a) they are chemically reactive (b) they are very hard (c) they retain metallic conductivity (d) they have high melting point	1
Q.8	Out of the following transition elements, the maximum number of oxidation states is shown by which element: (a) Sc [Z=21] (b) Mn [Z=25] (c) Cr [Z=24] (d) Fe [Z=26]	1
Q.9	KMnO4 is not acidified by HCl instead of H_2SO_4 because (a) H_2SO4 is stronger acid than HCl (b) HCl is oxidised to Cl_2 by $KMnO_4$ (c) H_2SO_4 is dibasic (d) rate is faster in presence of H_2SO_4	1
Q.10	The oxidation state of Cr in final product formed by reaction of KI and acidified dichromate solution is- (a) +4 (b) +6 (c) +2 (d) +3	1
Q.11	The difference between the oxidation number of Cr in chromate and dichromate ion is (a) 1 (b) 2 (c) 3 (d) 0	1

Q.12	Which of the following are d-block elements but not regarded as transition elements? (a) Cu, Ag, Au (b) Zn, Cd, Hg (c) Fe, Co, Ni (d) Ru, Rh, Pd	1
Q.13	Transition elements form alloys easily because they have (a) Same atomic number (b) Same electronic configuration (c) Nearly same atomic size (d) None of the above	1
Q.14	The properties which is not characteristic of transition elements- (a) Variable oxidation state (b) Tendency to form complexes (c) Formation of colour compounds (d) natural radioactivity.	1
Q.15	Which of the following has magnetic moment value of 5.9? (a) Fe^{2+} (b) Fe^{3+} (c) Ni^{2+} (d) Cu^{2+}	1
Q.16	Why transition elements exhibit variable oxidation states?	2
Q.17	Calculate the spin only moment of Co^{+2} by writing the electronic configuration of Co (Z=27) and Co^{+2}.	2
Q.18	Give reason and select one atom or ion which exhibit asked property (a) Sc^{+3} or Cr^{+3} (diamagnetic behaviour) (b) Cr or Cu (high melting and boiling point)	2
Q.19	Explain the followings: (a) Why transition elements act as a catalyst? (b) Why transition elements form alloys?	2
Q.20	Calculate the magnetic moment of a divalent ion in aqueous solution if its at.no is 25. Zn^{2+} salts are white while Cu^{2+} salts are coloured. Why?	2
Q.21	Which is a stronger reducing agent Cr^{2+}or $Fe^{2+}$and why?	2
Q.22	In the following ions: Mn^{3+}, V^{3+}, Cr^{3+}, Ti^{4+} (Atomic no.: Mn=25, V=23, Cr=24, Ti=22) A. Which ion is most stable in an aqueous solution? B. Which ion is strongest oxidizing agent? C. Which ion is colorless? D. Which ion has the highest number of unpaired electrons?	2
Q.23	The elements of 3d transition series are given as: Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn Answer the following: A. Copper has exceptionally positive Eo M^{+2}/M value. Why? B. Which element is a strong reducing agent in +2 oxidation state and why?	2
Q.24	How would you account for the following:- The oxidising power of the following three oxo ions in the series follows the order $VO_2^+ < Cr_2O_7^{2-} < MnO_4^-$	2

Q.25	When pyrolusite ore MnO_2 is fused of with KOH in presence of air,a green coloured compound (A) is obtained which undergoes disproportionation reaction in acidic medium to give purple coloured compound (B). a) Write the formulae of (A) & (B). b) What happens when compound (B) is heated	2
Q.26	Account for the following: (a) Mn_2O_7 is acidic whereas MnO is basic. (b) Though copper has completely filled d-orbital (d^{10}) yet it is considered as a transition metal. (c) transition elements form coloured complexes.	3
Q.27	Explain giving a suitable reason for each of the following – a. Metallic bonding is more frequent for the 4d & 5d series of transition metals than 3d series. b. Cu+ salts are colourless while Cu^{2+} salts are Coloured. c. Mn^{2+} exhibits maximum paramagnetism.	3
Q.28	Account for the following a. Although Zr belongs to 4d and Hf belongs to 5d transition series but it is quite difficult to separate them. b. There is in general increase in density of element from titanium to copper c. Most of the transition metals and their compounds possess catalytic properties.	3
Q.29	Explain the following observations. (a) Mn Shows the highest oxidation state of +7 among 3d series elements. (b) Mn Shows the highest oxidation state of +7 with oxygen but with fluorine it shows the highest oxidation state of +4. (c) Cu^+ is unstable in aqueous solution.	3
Q.30	Account for the following (a) Transition metals are much harder than alkali metals. (b) d^1 configuration is very unstable in ions. (c) E^0 value for the Mn^{2+}/Mn much more than expected.	3
Q.31	Assign reasons for the following: (a) Scandium is a transition element but Zinc is not. (b) Silver atom has completely filled d orbital ($4d^{10}$) in its ground state, yet it is transition element. (c) In the series Sc(Z = 21) to Zn (Z = 30), the enthalpy of atomisation of zinc is the lowest	3

Q.32	Account for the following: (a) Transition elements and their compounds are good catalysts. (b) Cr^{+2} is a good reducing agent. (c) Why are enthalpies of atomisation of transition metals are quite high?	3
Q.33	Give reasons: (a) Transition metals form large variety of complex compounds. (b) Iron has high enthalpy of atomisation than copper (c) Cu^{+2} salts are coloured while Zn^{+2} salts are white.	3
Q.34	Following ions are given: Cr^{+2}, Cu^{+2}, Cu^{+}, Fe^{+2}, Fe^{+3}, Mn^{+3} Identify the ion which is (a) A strong reducing agent (b) Unstable in aqueous solution (c) A strong oxidizing agent	3
Q.35	Give reason for the following: (a) Transition metals form alloys. (b) Zinc is typically soft metal whereas iron and copper are hard. (c) Manganese shows higher oxidation state of +4 with fluorine but shows +7 with oxygen.	3
Q.36	Complete the following chemical equations: (i) 8 MnO_4^{-} + $3S_2O_3^{2-}$ + H_2O → (ii) $Cr_2 O_7^{2-}$ + 3 Sn^{2+} + 14H^{+} →	4
Q.37	How do you prepare? (a) K_2MnO_4 from MnO_2 (b) $Na_2Cr_2O_7$ from Na_2CrO_4	4
Q.38	Explain the following observations : (i) Generally there is an increase in density of elements from titanium (Z = 22) to copper (Z = 29) in the first series of transition elements. (ii) Transition elements and their compounds are generally found to be good catalysts in chemical reactions.	4
Q.39	State reasons for the following: (i) Cu (I) ion is not stable in an aqueous solution. (ii) Unlike Cr^{3+}, Mn^{2+}, Fe^{3+} and the subsequent other M^{2+} ions of the 3d series of elements, the 4d and the 5d series metals generally do not form stable cationic species.	4

Q.40	Account for the following: (i) Transition metals form large number of complex compounds. (ii) The lowest oxide of transition metal is basic whereas the highest oxide is amphoteric or acidic. (iii) Transition metals show variable oxidation states. (iv) Zn, Cd and Hg are soft metals. (v) E° value for the Mn3+/Mn2+ couple is highly positive (+1.57 V) as compared to Cr3+/Cr2+.	5
Q.41	A. Complete and balance the following reactions a) $Cr_2O_7^{2-} + Fe^{2+} + H^+ \rightarrow$ b) $MnO_4^- + H^+ + C_2O_4^{2-} \rightarrow$ c) $Cr_2O_7^{2-} + OH^- \rightarrow$ d) $MnO_4^- + H_2O + I^- \rightarrow$ B. Name the oxo metal anion of one of the transition metals in which the metal exhibits the oxidation state equal to the group number.	5
Q.42	Assign reason for each of the following: Among the elements of 3d series: (a) Write the element which shows maximum number of oxidation states and why? (b) Which element has highest melting point? (c) Which element shows +3 oxidation state only? (d) Sc+3 is colourless in aqueous solution whereas Ti+3 is coloured. (e) It is difficult to obtain oxidation state greater than 2 for copper.	5
Q.43	Assign a reason for each of the following observations: (a) The transition metals (with the exception of Zn, Cd and Hg) are hard and have high melting and boiling points. (b) The ionization enthalpies (first and second) in the first series of the transition elements are found to vary irregularly. (c) Transition elements exhibit paramagnetic behaviour. (d) Co^{2+}. is easily oxidised in the presence of a strong ligand. (e) Many of the transition elements are known to form interstitial compounds.	5

Answer Key

1. (a)
2. (d)
3. (a)
4. (b)
5. (d)
6. (d)
7. (a)
8. (b)

9. (b)
10. (d)
11. (d)
12. (b)
13. (c)
14. (d)
15. (b)
16. Transition elements exhibit variable oxidation state due to less energy gap between ns and (n-1) d orbitals. With same energy (n-1) d electrons also get ejected with ns electrons.
17. Electronic configuration of Co= $3d^7 4s^2$

    $Co^{+2} = 3d^7 4s^0$

    Magnetic moment= 4.9 BM
18. (a) Sc^{+3} is diamagnetic in nature

    (b) Chromium has higher melting and boiling point than copper due to greater number of unpaired electrons.

19. (a) Transition elements act as catalyst due to their high surface area and tendency to show variable oxidation state.

    (b) Transition metals form alloys due to their almost similar sizes.

20. $\mu = 5.92BM$] Cu^{2+} ($3d^9 4s^0$) has one unpaired electron in d-subshell absorbs radiation in visible region resulting in d-d transition and hence Cu^{2+} salts are coloured. Zn^{2+} ($3d^{10} 4s^0$) has completely filled d-orbitals. No radiation is absorbed for d-d transition and hence Zn^{2+} salts are colourless.
21. because change in $3d^4 \rightarrow 3d^3$ occurs in case of Cr^{2+} to Cr^{3+} But $3d^6 \rightarrow 3d^5$ occurs in case of Fe^{2+} to $Fe^{3+.}$ In a medium (like water) d3is more stable as compared to d^5]
22. A. Cr^{3+} because of half filled t_2g level.

    B. Mn^{3+}, as the change from Mn^{3+} to Mn^{2+} results in stable half filled (d^5) configuration.

    C. Ti^{4+}, as Ti^{4+} has empty d-orbitals therefore d-d transition cannot occur in Ti^{4+}.

    D. Mn^{3+} ($3d^4 4s^0$). It has 4 unpaired electrons.

23. A. Because the sum of sublimation enthalpy and hydration enthalpy to convert Cu(s) to $Cu^{2+}(aq)$ is so high that it is not balanced by its hydration enthalpy.

    B. Cr is strongest reducing agent in +2 oxidation state. Cr^{2+} has configuration $3d^4$. After losing one electron it forms Cr3+ which has stable half filled t_2g, level.

24. The oxidizing power of these ions is due to their ability to accept electrons and undergo a change in oxidation state.

25. **(**a) A= K_2MnO_4 B=$KMnO_4$

    (b) $2KMnO_4 \longrightarrow K_2MnO_4 + MnO_2 + O_2$]

26. A. As the oxidation state of the central ion increases, acidity of oxide increases. In Mn_2O_7, Mn has +7 oxidation state, whereas in MnO, Mn has +2 oxidation state.

B. In aqueous solution, Cu exists in +2 oxidation state in which the ion has partially filled d orbitals. That's why copper is considered as a transition element.

C. Due to presence of vacant d orbitals, there are d-d transitions in compounds of transition elements. Therefore, the compounds are coloured.

27. A. Metallic bonding is more frequent for the 4d & 5d series of transition metals than 3d series because of higher enthalpies of atomisation of 4d and 5d as compared to 3d elements.

B. Cu^+ salts are colourless due to absence of unpaired electrons whereas Cu^{+2} salts are coloured due to presence of unpaired electrons.

C. Mn^{+2} has d^5 electronic configuration, therefore it can show maximum paramagnetism.

28. A. Due to lanthanoid contraction, atomic sizes of elements of 4d and 5d series are comparable.

B. There is in general increase in density of element from titanium to copper due to decrease in metallic radius from Ti to Cu coupled with increase in atomic mass.

C. Most of the transition elements have catalytic properties due to their tendency to form variable oxidation states.

29. A. Mn shows highest oxidation state because it can form Mn^{+2} ion by losing all valence electrons ($3d^5$ $4s^2$).

B. Mn can get extra stability by forming d pi- p pi bond with p orbital of oxygen which is not possible in case of fluorine.

C. Due to disproportionation, Cu^+ is unstable in aqueous solution.

30. A. In transition metals, there is extra covalent bonding due to presence of unpaired electrons in d orbitals which causes hardness of transition elements.

B. d^1 configuration is unstable because ions having d^1 electronic configuration tend to undergo either disproportionation or oxidation reactions.

C. Due to extra stability of Mn^{+2} ion, E^0 value for the Mn^{2+}/Mn much more than expected.

31. A. Zinc is not considered as a transition element due to absence of partially filled d orbitals in its elemental or ionic form.

B. Silver in +2 oxidation state has partially filled d orbitals, hence are considered as transition element.

C. Due to absence of unpaired d electrons, zinc has lower value of atomization.

32. A. Transition elements are good catalysts due to their tendency to form variable oxidation state.

B. Cr^{+2} is a good reducing agent, since its configuration is converted to d^3 from d^4, which has higher stability due to half filled t_2g configuration.

C. Enthalpies of atomization depends on number of unpaired electrons present in the element. Therefore, transition elements have greater value of enthalpies of atomization.

33. A. Transition metals form large variety of complex compounds due to their small size and tendency to form variable oxidation states.
    B. Fe has higher enthalpy of atomization than that of Cu due to greater number of unpaired electrons in Fe.
    C. Cu $^{+2}$ compounds are coloured due to presence of unpaired electrons.

34. A. **Cr^{+2}** **B. Cu^+** **C. Mn^{+3}**
35. A. Transition metals form alloys due to their almost similar sizes.
    B. Zinc is typically soft metal due to lack of unpaired electrons which are required for metallic bonding.
    C. Mn can form d pi- p pi bonding with oxygen by using its 2p orbitals which is not possible in case of fluorine.
36. A. $8\ MnO_4^- + 3\ S_2O_3^{2-} + H_2O \rightarrow 8MnO_2 + 2OH^- + 6\ SO_4^{2-}$
    B. $Cr_2O_7^{2-} + 3Sn^{2+} + 14H^+ \rightarrow 2Cr3^+ + 3Sn^{4+} + 7H_2O$

37. A. $MnO_2 + 2KOH + KNO_3 \rightarrow K_2MnO_4 + KNO_2 + H_2O$
    B. $Na_2CrO_4 + H_2SO_4 \rightarrow Na_2Cr_2O_7 + Na_2SO_4 + H_2O$

38. (i) From titanium to copper the atomic size of elements decreases and mass increases as a result of which density increases.
    (ii) The catalytic properties of the transition elements are due to the presence of unpaired electrons in their incomplete d- orbitals and variable oxidation states.
39. (i) Cu^{2+}(aq) is much more stable than Cu^+(aq). This is because although second ionization enthalpy of copper is large but Δ_{hyd} (hydration enthalpy) for Cu^{2+}(aq) is much more negative than that for Cu^+(aq) and hence it more than compensates for the second ionization enthalpy of copper. Therefore, many copper (I) compounds are unstable in aqueous solution and undergo disproportionation as follows : $2Cu^+ \rightarrow Cu^{2+} + Cu$
    (ii) Because high enthalpies of atomisation of 4d and 5d series and high ionization enthalpies, the M.P. and B.P. of heavier transition elements are greater than those of first transition series which is due to stronger intermetallic bonding. Hence 4d and 5d series metals generally do not form stable cationic species.
40. A. Transition metals form large variety of complex compounds due to their small atomic radii and variable oxidation state.

    B. Lower oxides are basic due to lower oxidation state of metal or availability of electrons while higher oxides are acidic due to electron deficiency at transition metal.

    C. Transition metals show variable oxidation states due to less energy difference between (n-1)d and ns orbitals.

    D. Zn, Cd and Hg are soft metals due to unavailability of unpaired d electrons in their ground states.

E. Mn^{+3} is a good oxidizing agent whereas Cr^{+2} is a good reducing agent.

41. (a) $Cr_2O_7^{2-} + 6Fe^{2+} + 14\,H^+ \rightarrow 2Cr^{+3} + 6Fe^{3+} + 7H_2O$
    (b) $2MnO_4^- + 16\,H^+ + 5C_2O_4^{2-} \rightarrow 2Mn^{2+} + 8H_2O + 10CO_2$
    (c) $Cr_2O_7^{2-} + 2\,OH^- \rightarrow 2CrO_4^{2-} + H_2O$
    (d) $2\,MnO_4^- + H_2O + I^- \rightarrow 2MnO_2 + 2OH^- + IO_3^-$

    B. In MnO_4^- ion, the oxidation state of Mn is + 7. It is equal to its group number 7. In CrO_4^{2-}ion, the oxidation state of Cr is + 6. It is equal to its group number 6.

42. (a) Mn shows maximum number of oxidation states.
    (b) Cr has maximum melting point because it has 6 electrons in the valence shell and has strongest interatomic attraction.
    (c) Sc shows +3 oxidation state only because after losing 3 electrons, it attains noble gas configuration.
    (d) Sc^{+3} does not have any unpaired electron, hence it is colourless.
    (e) Due to high value of third ionisation enthalpy.

43. (a) Because of stronger metallic bonding and high enthalpies of atomization.
    (b) Due to irregulaties in the electronic configuration there is irregularities in the enthalpies of atomisation. Hence there is irregular variation in I.E.
    (c) Because of presence of unpaired electrons in their d-subshell in atomic and ionic state.
    (d) Co^{2+} ion is easily oxidised to Co^{3+} ion in presence of a strong ligand because of its higher crystal field energy which causes pairing of electrons to give inner orbital complexes (d^2sp^3).
    (e) The transition metals form a large number of interstitial compounds in which small atoms such as hydrogen, carbon, boron and nitrogen occupy the empty spaces in the crystal lattices of transition metals.

	MULTIPLE CHOICE QUESTIONS:	
1.	Which trivalent lanthanoid ions does not show any colour? (a) Ln $^{3+}$ (b) La $^{3+}$ (c) Ce^{3+} (d) all of these	
2.	Which is the most stable oxidation state of all the lanthanoids? (a) +4 (b) +2 (c) +3 (d) +1	
3.	What do you call the decrease in atomic and ionic radii from lanthanum to lutetium? (a) Lanthanoid repulsion (b) lanthanoid contraction (c) lanthanoid transition (d) lanthanoid shielding	
4.	Which lanthanoid ions are paramangnetic in nature? (a) La 3+ (b) Lu 3+ (c) Ce4+ (d) all of these	
5.	Name the well known alloy having lanthanoid metal. (a) Mischmetall (b) gunmetal (c) german silver (d) all of these	
6.	Actinoid contraction is caused due to : (a) Poor shielding effect of 5f electrons (b) Poor shielding effect of 4f electrons (c) Electronic repulsion of 5f electrons (d) Electronic repulsion of 4f electrons	
7.	Name a member of the lanthanoid series which is well known to exhibit +4 oxidation state. (a) La (b) Ce (c) Pm (d) Lu	
8.	The lanthanides are d-block elements. (a) True (b) False	
9.	What is the general electronic configuration of the lanthanides? (a) (n-2)f 1-14 (n-1)d 1-10 ns2 (b) (n-2)f 1-14 (n-1)d 1-2 ns2 (c) (n-2)f 1-14 (n-1)d 0-1 ns2 (d) (n-2)f 1-14 (n-1)d 0 ns2	
10.	Which property of actinoids cannot be explained? (a) Radioactive (b) Oxidation (c) Magnetic (d) Acidic	
11.	Which of the following is not a consequence of lanthanide contraction? (a) From La^{+3} to Lu^{+3}, the ionic radii changes from 106 pm to 85 pm (b) As the size of the lanthanide ions decreases the basic strength increases (c) The basic character of oxides and hydroxides decreases with increase in atomic number (d) The atomic radii of 4d and 5d series is similar	

12.	What is the most common oxidation state of lanthanides? (a) +2 (b) +4 (c) +6 (d) +3	
13.	Actinoids are mostly attacked by which acid? (a) Hydrochloric acid (b) Nitric acid (c) Sulphuric acid (d) Boric acid	
14.	Which of the following lanthanide ions do not exhibit colour? (a) Lu^{+3} and Ln^{+3} (b) Lu^{+2} and Ln^{+2} (c) Ce^{+3} and Ce^{+3} (d) Pr^{+4} and Ce^{+4}	
15.	Which of the following is the correct order of arrangement of the first five lanthanides according to atomic number? (a) La, Ce, Pr, Nd, Pm (b) La, Pr, Ce, Pm, Nd (c) La, Pr, Ce, Nd, Pm (d) La, Ce, Pr, Pm, Nd	
	ANSWERS	
1.	B	
2.	C	
3.	B	
4.	D	
5.	A	
6.	A	
7.	B	
8.	B	
9.	C	
10.	C	
11.	B	
12.	D	
13.	A	
14.	A	
15.	A	
	Short Answer Question	
1.	Lonisation enthalpies of Ce, Pr and Nd are higher than Th, Pa and U. Why?	

2.	Although Zr belongs to 4d and Hf belongs to 5d transition series but it is quite difficult to separate them. Why?	
3.	Although +3 oxidation states is the characteristic oxidation state of lanthanides but cerium shows +4 oxidation state also. Why?	
4.	The +3 oxidation state of lanthanum (Z=57), gadolinium (Z=64) and lutetium (Z=71) are especially stable. Why ?	
5.	Actinoid contraction is greater from element to element than lanthanoid contraction . why?	
6.	Osmium forms a +8 oxidation state with oxygen compound but no such compound is formed with fluorine. Give reason.	
7.	What will happen if we dissolve $KMnO_4$ with conc. H_2SO_4 instead of dil. H_2SO_4?	
8.	Complete and balance the following reaction: $MnO^{4-} + Fe^{2+} + H^+$ □ $Cr_2O_7^{2-} + Fe^{2+} + H^+$ □	
9.	Explain: (a) Transition elements are metals. (b) Lanthanoids are uniformly trivalent.	
10.	Why d- metals are hard metals but Zn, Cd and Hg are soft.	
	ANSWERS	
1.	Ce, Pr and Nd are lanthanoids and have an incomplete 4f shell, while Th, Pa and U are actinoids and have an incomplete 5f shell. When 5f-orbitals begin to be occupied, they will penetrate less into the inner core of electrons. The 5f-electrons will, therefore, be more effectively shielded from the nuclear charge than the 4f electrons of the corresponding lanthanoids. Therefore, outer electrons are less firmly held and are available for bonding in the actinoids.	
2.	Separation of Zr and Hf is pretty tricky because of lanthanoid contraction. Due to lanthanoid contraction, they have almost identical sizes (Zr = 160 pm and Hf =159 pm) and, thus, similar chemical properties. That's why it is tough to separate them by chemical methods.	
3.	After losing one more electron, Ce^{3+} acquires a stable $4f^0$ electronic configuration. Thus, although the +3 oxidation state is the characteristic oxidation state of lanthanoids, cerium shows a +4 oxidation state.	

4.	Lanthanum (57) $5d^1$,$6s^2$, $4f^0$, Lutetium (71) $4f^{14}$, $5d^1$, $6s^2$ and Gadolinium (64) $4f^2$,$5d^1$ $6s^2$ have the same electrical configuration. As a result, they have an empty, fully-filled and half filled 4f -subshell and their +3 oxidation state is stable.	
5.	Due to poor shielding by 5f electrons in actinoids than that by 4f electrons in lanthanoids.	
6.	Cannot accommodate eight fluorine atoms around it.	
7.	With conc. H_2SO4 , highly explosive substance Mn_2O_7 is formed which is responsible for the accident. $2KMnO_4 + H_2SO_4$ -□ $K_2SO_4 + Mn_2O_7 + H_2O$ $2Mn_2O_7$ □ $4MnO_2 + 3O_2$	
8.	$MnO^{4-} + Fe^{2+} + H^+$ □ $Mn^{2+} + 5Fe^{3+} + 4H_2O$ $Cr_2O_7^{2-} + 6Fe^{2+} + 14H^+$ □ $2Cr^{3+} + 7H_2O + 6Fe^{3+}$	
9.	(A) due to low ionisation potentials and presence of vacant d- orbitals (b) +3 is more stable than +2 and +4 oxidation states.	
10.	Absence of partially filled orbitals in them.	
	SHORT ANSWER QUESTIONS (3 MARKS)	
1.	What is Baeyer's reagent ?What happens when $KMnO_4$ is heated?	
2.	What happens when chromates are kept in acidic solution and dichromates are kept in alkaline solution?	
3.	Describe preparation of potassium permanganate from pyrolusite ore.	
4.	Explain why Cu+ is not stable in aqueous solutions?	
5.	Write electronic configuration of Cr3+, Cu+, Ce4+	
6.	Which is a stronger reducing agent Cr2+ or Fe2+ . Why?	
7.	Give reason for the following : (a) Size of trivalent lanthanoid cations decrease with increase in atomic number. (b) Transition metal fluorides are ionic in nature (c) Chemistry of all lanthanoids is quite similar.	
8.	(a) all scandium salts are white. (b) the first ionisation energies of 5d transition elements are higher than those of 3 d and 4d transition elemnets in respective group © Zn salts are white while Cu+2 salts are coloured?	
9.	Write general characteristics of 3d series wrt to (a) Atomic size (b) Enthalpies of atomisation (c) Tendency for complex formation	
10.	Transition metals form a large number of complex compounds. Give reason	
	ANSWERS	
1.	Alkaline solution of $KMnO_4$. It changes into K_2MnO_4, MnO_2 and O_2.	
2.	chromates form dichromates in acidic solution and dichromates form chromates in alkaline solution.	
3.	Refer to text	

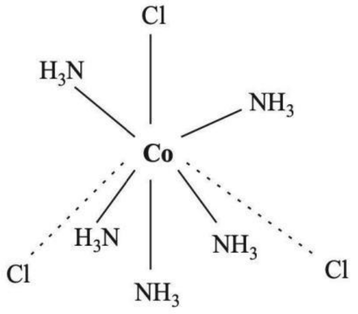
4.	Second ionisation enthalpy of Cu is large and undergo disporpornation reaction. 2Cu + □ Cu2+ + Cu	
5.	Cr3+ = [Ar] 3d3 Cu+ =[Ar] 3d10 Ce 4+ = [Xe]	
6.	Cr2+ . easily oxidised	
7.	(a) because the differentiating electron enter is added in the inner 4f orbital. (B) because the difference in electronegativities of transition metal and fluorine is quite large © their valence shell configuration remains the same because the electrons are added into the inner 4f-subshell	
8.	(a) Sc3+ does not have unpaired electrons, therefore, cannot undergo d-d transition by absorbing light from visible region (b) d elements have much more nuclear charge and the weakest shielding of valence electrons. © Zn2+ ion (3d10) has completely filled d-orbitals and there is ano scope for any electron transition. Therefore, Zn2+ salt are white and not coloured.	
9.	(a) decrease from group 3 to group 6 due to the poor shielding offered by the small number of d-electrons. (b) ansition metals have high **enthalpies of atomisation**. In the **3d series**, from Sc to Zn, only zinc has filled valence shells © they contain vacant d-orbitals ,so that they can accommodate electrons of other elements and form bonds. Transition elements have variable oxidation state like from +2 to +6 which, shows its capacity to form bonds.	
10.	. Transition metals for complex compounds due to, i) small sizes of metal cations ii) their ionic charges and iii) availability of d orbitals for bond formation	
	Long answer questions:	
1	Describe the preparation of potassium permanganate from manganous dioxide How does the acidified permanganate solution react with (a) iron(II) ions (b) oxalic acid and (c) hydrogen sulphide ? Write the ionic equations for the reactions	
Ans	Potassium permanganate is prepared by fusion of MnO2 with an alkali metal hydroxide and an oxidising agent like KNO3. This produces the dark green K2MnO4 which disproportionates in a neutral or acidic solution to give permanganate. 2MnO2 + 4KOH + O2 → 2K2MnO4 + 2H2O +3MnO4 2– + 4H+ → 2MnO4 – + MnO2 + 2H2O (a) Fe2+ ion (green) is converted to Fe3+ (yellow): 5Fe2+ + MnO^{4-} + 8H^{+} ——> Mn2+ + 4H2O + 5Fe3+ (b) Oxalate ion or oxalic acid is oxidised at 333 K: 5C2O4 $^{2-}$ + 2MnO^{4-} + 16H+ ——> 2Mn^{2+} + 8H2O + 10CO2 (c) Hydrogen sulphide is oxidised, sulphur being precipitated: H2S —> 2H+ + S2− 5S2− + 2MnO4 − + 16H+ ——> 2Mn2+ + 8H2O + 5S	

2.	. Name the metal of the 1 st row transition series that i) has highest value for magnetic moment ii) has zero spin only magnetic moment in its +2-oxidation state. iii) exhibit maximum number of oxidation states. Transition metals form a large number of complex compounds. Give reason.	
Ans	i) Chromium ii) Zinc iii) Manganese ii) Transition metals for complex compounds due to, i) small sizes of metal cations ii) their ionic charges and iii) availability of d orbitals for bond formation.	
3.	Write two comparisons of variability in oxidation states of transition metals and non transition elements (p- block elements) ? What happens when (a) A lanthonoid reacts with dilute acids ? (b) A lanthonoid reacts with water?	
Ans	1. In transition elements, variable oxidation state differ from each other by unity, whereas in case of non transition elements, oxidation state differ by units of two.(For example Fe exhibits o.s of +2 and +3 . similarly copper exhibits two o.s of +1 and +2 . on the other hand, Sn, Pb exhibit o.s of +2 and +4.) 2. 2. In transition elements, higher o.s are more favoured in elements of higher atomic mass, whereas in p-block elements lower o.s are favoured by heavier members (due to inert pair effect, For example Mo(VI) and W(VI) are more stable than Cr(VI). On the other hand Pb(II) is more stable than Sn(II)) 3. .(a) When lanthonoid reacts with dilute acids , it liberates hydrogen gas. (b)When lanthonoid reacts with water , it forms lanthanoid hydroxide and liberate hydrogen gas.	
4.	(a). Calculate the 'spin only' magnetic moment of M2+ (aq) ion (Z = 27). (b) The second ionisation enthalpy is high for Cr and Cu , why? © Why first ionisation enthalpy of Cr is lower than that of Zn ? (d) Give two characteristics of transition metal alloys.	
Ans	(a) M (z= 27 , 3d7 4s2) → M+2 (3d7 4s0) hence it has 3 unpaired electrons n= 3 = √3(3+2) = 3.87 BM (b) The second ionisation enthalpy is unusually high values for Cr and Cu because when M+ ion ionize to M+2 ion , the d5 and d10 configurations of the M+ ions (i.e Cr+ or Cu+) are disrupted, with considerable loss of exchange energy . (c) IE1 of Cr is lower, because removal of an electron from Cr does not change the d (3d5 4s1 to 3d5 4s0) configuration . Cr (z= 24 , 3d5 4s1) → Cr+ (3d5 4s0) ------ IE1 IE1 value for Zn is higher, because removal of electron from 4s level needs more energy. Zn (z= 30 , 3d10 4s2) → Zn+ (3d10 4s1) ------ IE1 ∴ IE1 (Zn) > IE1 (Cr) (d) The alloys are hard and have high melting points.	

CHAPTER 5: COORDINATION COMPOUDS

- Coordination compounds have a **central atom (or cation)** that is **coordinated to a number of anions or neutral molecules**, and they usually retain their identity in both solution and solid state.
- These can be **positively, negatively, or neutrally charged** species, such as [Co(NH3)6]3+, [NiCl4]2-, [Ni(CO)4], and so on.
- In 1893, Werner proposed a theory to explain **coordination compound structure and bonding**.
- According to this theory **metals have two types of valencies** in coordination compounds: **primary valency and secondary valency**.
- **Primary valencies are ionisable.**
- **Secondary valencies cannot be ionized**.

On the basis of Werner's theory the structure of [Co(NH3)5Cl]
Cl2 is:



Primary valance (ionizable)(--------)
Secondary valance (non-ionizable) (———)

DIFFERENCE BETWEEN DOUBLE SALTS AND COORDINATION COMPOUNDS.

COORDINATION COMPOUNDS	DOUBLE SALT
A coordination compound contains a central metal atom or ion surrounded by number of oppositely charged ions or neutral molecules. These ions or molecules are bonded to the metal atom or ion by a coordinate bond.	When two salts in stoichiometric ratio are crystallised together from their saturated solution they are called double salts
Example: K4 [Fe(CN)6]	Example: FeSO4 . (NH4)2SO4 .6H2O (Mohr's salt)
They do not dissociate into simple ions when dissolved in water.	They dissociate into simple ions when dissolved in water.

Ligands:

- **Definition:** Ligands are molecules or ions that donate electrons to a metal ion and form coordinate covalent bonds. Ligands can be classified into various types based on their structure and properties.

- **Classification based on denticity:** Ligands can be classified as monodentate, bidentate, tridentate, etc., based on the number of donor atoms they can use to bind to a metal ion.

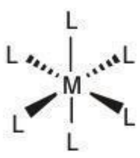
- **Chelating ligands:** Chelating ligands are ligands that can bind to a metal ion through more than one donor atom. Chelating ligands form stable complexes and play an important role in many biological processes.

- **Polydentate ligands:** Polydentate ligands are ligands that have multiple donor atoms and can bind to more than one metal ion. Polydentate ligands play an important role in the formation of coordination polymers and metal complexes with high stability.

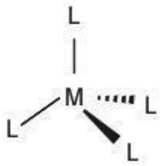
- Coordination sphere & Counter Ions. The central atom/ion and the ligands attached to it are enclosed in square bracket and is collectively termed as coordination sphere and the ionizable groups written outside the coordination sphere is called counter ions etc. In $K_4[Fe(CN_6)]$
  $[Fe(CN)_6]^{4-}$ is coordination sphere
  K^+ is counter ion

  Coordination number: The coordination number in coordination compounds is defined as the number of ligand (donor) atoms/ions surrounding the central metal atom in a complex ion. For example, the coordination number of cobalt in [Co(NH3)6]3+ is six. Similarly the coordination number of Ag+ in [Ag(NH3)2]+ is 2, that of Cu2+ in [Cu(NH3)4]2+ is 4, and that of Fe3+ in [Fe(CN)6]3– is 6.

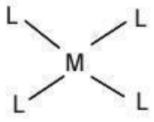
Coordination polyhedra: the spatial arrangement of the ligand atoms which are directly attached to the central atom / ion.



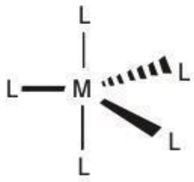
Octahedral



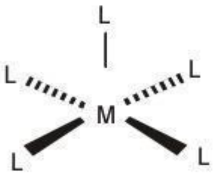
Tetrahedral



Square planar



Trigonal bipyramidal



Square bipyramidal

Oxidation number: Another important property of coordination compound is the oxidation number of the central metal atom. The net charge on a complex ion is the sum of the charges on the central atom and its surrounding ligands. In the [PtCl6]2- ion for example, each chloride ion has an oxidation number of–1, so the oxidation number of Pt must be +4. If the ligands do not bear net charges the oxidation number of the metal is equal to the charge of the complex ion. Thus in [Cu(NH3)4]2+ each NH3 is neutral, so the oxidation number of copper is +2.

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

Rules for naming mononuclear coordination compounds

1. Order of naming ions
   The positive ion (cation) whether simple or complex, is named first followed by the negative ion (anion). The name is started with a small letter and the complex part is written as one word.

2. Naming ligands

3. i) Negative ligands (organic or inorganic) end in −O, eg, CN^- (cyano), Cl^- (chlorido), Br^- (bromido), F- (fluorido), NO_2^- (nitro), OH- (hydroxo), O^{2-} (oxo), H- (hydrido).
   If the name of the anionic ligands ends in −ide, −ite or −ate, the last 'e' is replaced by 'O' giving −ido, −ito and −ato eg, SO_4^{2-} (sulphato), $C_2O_4^{2-}$ (oxalato), NH_2^- (amido), NH^{2-} (imido), ONO^- (nitrito).

   - ii) Neutral ligands have no special ending, NH_3 (ammine), H_2O (aqua), CO (carbonyl)

   - iii) Positive ligands (which are very few) end in -ium, NO^+ (nitrosoium), NO_2^+ (nitronium)

3. Numerical prefixes to indicate number of ligands
   If there are several ligands of the same type, the prefixes like di, tri, tetra, penta and hexa are used to indicate the number of ligands of that type.
   When the name of polydentate ligand includes a number e.g., ethylendediamine, then bis, tris, tetrakis are used as prefixes.

4. Order of naming of ligands
   All ligands whether negative, neutral or positive are named first in the alphabetical order followed by the name of the metal atom/ion.

5. Naming of the complex ion and ending of the central atom
   Ligands are named first followed by the metal atom.

a) If the complex ion is a cation or the coordination compund is non-ionic, the name of the central metal ion is written as such followed by its oxidation state indicated by Roman numeral (such as II, III, IV) in the parentheses at the end of the name of the metal without any space between the two.

b) If the complex ion is anion, the name of the central metal atom is made to end in-ate followed by the oxidation number in brackets without any space between them.

Rules for Writing Formula from the Name of the Mononuclear Complex

Formula of the cation (whether simple or complex) is written first followed by that of the anion.

The formula of the complex ion (coordination entity) (whether charged or not) is written in square brackets called coordination sphere.

Within the coordination sphere, the symbol of the metal atom is written first followed by the symbols/formulas of the ligands arranged alphabetically according to their names irrespective of the charge present on them.
While listing the ligands alphabetically, the following rules should be followed:

i) Polydentate ligands are also listed in the alphabetical order.

ii) The position of abbreviated ligands in the alphabetical order is determined from the first letter of the abbreviation.

iii) The position of ligands with special names (such as aqua for water) in the alphabetical order is determined from the first letter of the special name.

iv) Abbreviations used for the ligands and the formulas of the polyatomic ligands are enclosed in parentheses separately.

v) The metal atom as well as all the ligands are listed without any space between them.

If the formula of the complex ion is to be written without writing the counter ion, the charge on the complex ion is indicated outside the square bracket as a right superscript with the number before the sign. For example, [Fe(CN)6]3-, [Cu(NH3)4]2+, etc.

The number of cations or anions to be written in the formula is calculated on the basis that total positive charge must be equal to the total negative charge, as the complex as a whole is electrically neutral.
Example : Tetraammineaquachloridocobalt(III) chloride has complex ion = [Co(NH3)4(H2O)Cl] and simple ion = Cl-
To balance the charge, the formula will be $[Co(NH_3)_4(H_2O)Cl]Cl_2$

SECTION A:

MCQ (1 MARKS):

1. The correct name of the compound $[Cu(NH_3)_4](NO_3)_2$ according to IUPAC system is

(a) Cuprammonium nitrate

(b)Tetrammonium copper (II) dinitrate

(c) tetraamminecopper (Il) nitrate

(d) tetrammine copper (II) dinitrite

2. Coordination number and oxidation number of Cr in $K_2[Cr(C_2O_4)_3]$ are, respectively?

(a) 4and +2

(b) б aпd +3

©3 aпd +3

(d) 3 aпd 0

3. Which of the following is a negatively charged bidentate ligand?

(a) Dimethylglyximato

(b) Cyano

(c) Ethylenediamine

(d) Acetato

4. The oxidation number of Cobalt in K[Co (CO)4] is

(a) +1

(b) +3

(c) -1

(d) -3

5. Amongst the following ions, which one is highly paramagnetic?

(a) $[Cr(H_2O)_6]^{3+}$

(b) [Fe$(H_2O)_6$**]** $^{2+}$

(c) $[Cu(H_2O)_6]^{2+}$

(d) $[Zn(H_2O)_6]^{2+}$

6. The spin only magnetic moment of $[Ni(Cl_4)]^{2-}$ is

(a) 1.82 BM (b) 5.46 BM **(c) 2.82BM** (d) 1.41 BM

7. The IUPAC name of complex ion ,$[Fe(CN)_6]^{3-}$ is

(a) Hexacyanidoiron(III)ion

(b) Hexacyanatoferrate (III)ion

(c) Hexacyanidoferrate (III)ion

(d) Tricyanoiron(III)ion

8. The geometry and magnetic behaviour of the complex $[Ni(CO)_4]$ are

(a) Square planar and paramagnetic

(b) Tetrahedral and diamagnetic

(c) Square planar and diamagnetic

(d) Tetrahedral and paramagnetic

9. The hybridisation involved in the complex [Ni(CN)4] 2- is

(a) $d^2 sp^2$

(b) $d^2 sp^3$

(c) dsp^2

(d) sp^3

10. The geometry of $[Ni(CN)_4]$ 2- and $[NiCl_4]$ 2- are

(a) Both square planar

(b) Both tetrahedral

(c) Tetrahedral and square planar respectively

(d) Square planar and tetrahedral respectively

11. The diamagnetic species is

(a) $[Ni(CN)_4]^{2-}$

(b) $[NiCl_4]^{2-}$

(c) $[CuCl_4]^{2-}$

(d) $[CoF_6]^{3-}$

12. Correct increasing order for the wavelengths of absorption in the visible region in the complexes of Co3+ is

(a) $[Co(H_2O)6]^{3+}$, $[Co(en)_3]^{3+}$, $[Co(NH_3)_6]^{3+}$

(b) [Co(H2O)6] 3+, [Co(NH3)6] 3+ , [Co (en)3] 3+

(c) [Co(NH3)6] 3+, [Co (en)3] 3+, [Co(H2O)6] 3+

(d) [Co (en)3] 3+,[Co(NH3)6] 3+, [Co(H2O)6] 3+

ASSERTION – REASON TYPE QUESTIONS

In the following questions, a statement of Assertion followed by a statement of Reason is given. Choose the correct option out of the following choices.

(a) Assertion and Reason both are true, Reason is the correct explanation of Assertion .
(b) Assertion and Reason both are true but Reason is not the correct explanation of Assertion
(c) Assertion is true, Reason is false.
(d) Assertion is false, Reason is true.

13. Assertion: The crystal field theory is successful in explaining the formation, structure, colour and magnetic properties of coordination compounds.

Reason: crystal field theory considers the metal-ligand bond to be ionic.

Ans: (b) Assertion and Reason both are true but Reason is not the correct explanation of Assertion

14. Assertion: Linkage isomerism arises in coordination compounds containing ambidentate ligands

Reason: Ambidentate ligand has two different donor atoms

Ans: (a) Assertion and Reason both are true, Reason is the correct explanation of Assertion.

15. Assertion: CO is stronger ligand than NH3 for many metals

Reason: NH3 can form pi bonds by back bonding

Ans: (c) Assertion is true, Reason is false.

SECTION B:

(2MARKS)

16. Give reasons

(i)$CuSO_4$ $5H_2O$ is blue in colour while $CuSO_4$ is colourless.

Ans. In $CuSO_4$ $5H_2O$, water acts as ligand and causes crystal field splitting. Hence d-d transitionis possible and shows colour.

(ii)Low spin tetrahedral complexes not formed

Ans:In a tetrahedral complex, the d-orbital is split too small as compared to octahedral complex. For the same metal and same ligand $\Delta t = 4/9\Delta o$.Hence, the orbital energies are not enough to force pairing. As a result, low spin configurations are rarely observed in tetrahedral complexes.

17. Arrange the following complexes in the increasing order of conductivity of their solution: $[Co(NH_3)3Cl_3]$, $[Co(NH_3)4Cl2]CI$, $[Co(NH_3)6]Cl3$, $[Cr(NH_3)5Cl]Cl_2$

Ans: Co(NH3)3Cl3] < [Co(NH3)4Cl2]Cl < [Cr(NH3)5Cl]Cl2 < [Co(NH3)6]Cl3 Here, the number of ions increases and conductivity increases.

18. A coordination compound CrCl3. 4H2O precipitates silver chloride when treated with silver nitrate. The molar conductance of its solution corresponds to a total of two ions. Write the structural formula of the compound and name it.

Ans: Silver chloride precipitates when treated with silver nitrate because there is chloride ion outside the complex. There is only one chloride ion outside the complex since only two ions are generated. As a result, the compound’s structural formula and nomenclature are: [Co(H2O)4Cl2]Cl – Tetraaquadichloridocobalt(III) chloride

19. Explain why $[Fe(H_2O)_6]^{3+}$ has a magnetic moment value of 5.92 BM whereas $[Fe(CN)_6]$ 3- has a value of only 1.74 BM.

Ans:$[Fe(CN)_6]^{3-}$ involves d2 sp3 hybridisation with one unpaired electron and $[Fe(H_2O)6]$ 3+ involves sp3 d 2 hybridisation with five unpaired electrons. This difference is due to the presence of strong ligand CN– and weak ligand H_2O in these complexes.

20. $[Ni(CN)_4]^{2-}$ is colourless where as $[Ni(H_2O)_6]^{2+}$ is green. Why?

Ans:In $[Ni(CN)_4]$ 2- , Ni is in +2 oxidation state with electronic configuration 3d8 . In the presence of strong CNligand the two unpaired electron in 3d orbital pair up. As there is no unpaired electron, it is colourless. In [Ni(H2O)6] 2+ Ni is +2 oxidation state and electronic configuration 3d8 . The two unpaired electrons do not pair up in the presence of weak ligand H2O. The d-d transition absorbs red lightand complementary green light is emitted.

21.Give the formula of each of the following coordination entities: (i)Co $^{3+}$ ion bound to one Cl^- , one NH3 molecule and two ethylene diamine molecules. (ii)Ni 2+ ion is bound to two water molecules and two oxalate ions.

Ans. (i) $[Co(NH_3)Cl(en)_2]^{2+}$ (ii)$Ni(H_2O)_2(ox)_2]^{2-}$

22. Explain the following terms giving a suitable example in each case : (i) Ambident ligand (ii) Denticity of a ligand

Ans: Denticity : The number of coordinating groups present in a ligand is called the denticity of ligand. For example, bidentate ligand ethane-1, 2-diamine has two donor nitrogen atoms which can link to central metal atom.

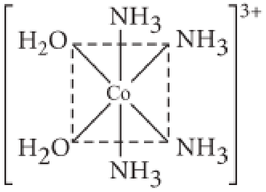
Ambidentate ligand : A unidentate ligand which can coordinate to central metal atom through two different atoms is called ambidentate ligand. For example NO^{2-} ion can coordinate either through nitrogen or through oxygen to the central metal atom/ion.

23. Using IUPAC norms write the formulae for the following coordination compounds : (i) Hexaamminecobalt(III)chloride (ii) Potassiumtetrachloridonickelate(II)

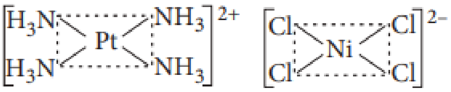
Ans: (i) $[Co(NH_3)_6]Cl_3$ (ii) $K_2[NiCl_4]$

24. Write the name and draw the structures of each of the following complex compounds: (i) $[Co(NH_3)_4(H_2O)_2]Cl_3$ (ii) $[Pt(NH_3)_4][NiCl_4]$

4. (i) Tetraamminediaquacobalt (III) chloride.

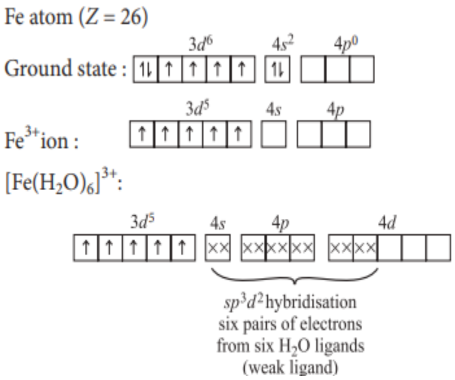


i) Tetraammineplatinum(II)tetrachloridonickelate(II)



25. For the complex $[Fe(H_2O)_6]^{3+,}$ write the hybridization magnetic character and spin of the complex. (At number Fe = 26)

Ans:



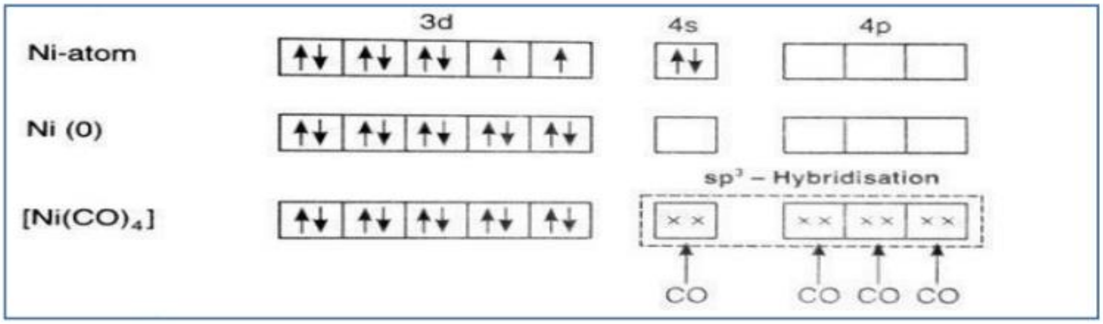
The complex ion has outer orbital octahedral geometry (high spin) and is paramagnetic due to the presence of five unpaired electrons.

SECTION C:

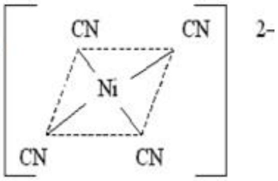
(3MARKS)

26. .[$Ni(CO)_4$] possesses tetrahedral geometry while [$Ni(CN)_4$] $^{2-}$ is square planar. Why?

Ans. In [$Ni(CO)_4$] Ni is in 0 oxidation state and its electronic configuration is $3d^8$ $4s^2$. CO is strong ligand. Hybridization is sp3 and it is tetrahedral.



In $[Ni(CN)_4]^{2-}$] Ni is in +2 oxidation state and its electronic configuration is $3d^8$. CN^- is strongligand. Hybridization is dsp2 and it is square planar.



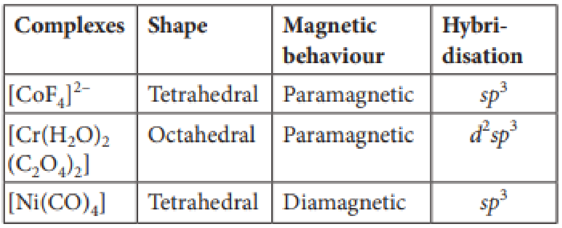
27. For the complex [Fe(en)2Cl2], Cl, (en = ethylene diamine), identify (i) the oxidation number of iron, (ii) the hybrid orbitals and the shape of the complex, (iii) the magnetic behaviour of the complex,

Ans: (i) [Fe(en)2Cl2]Cl x + 0 × 2 + (–1) × 2 + (–1) × 1 = 0 \ x = 3 Oxidation number of iron = 3

(ii) d2 sp3 hybridisation and octahedral shape.

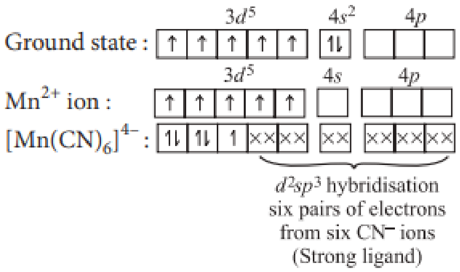
(iii) Paramagnetic due to presence of one unpaired electron.

28. Compare the following complexes with respect to their shape, magnetic behaviour and the hybrid orbitals involved : (i) [CoF4] 2- (ii) [Cr(H2O)2(C2O4)2]– (iii) [Ni(CO)4] (Atomic number : Co = 27, Cr = 24, Ni = 28)



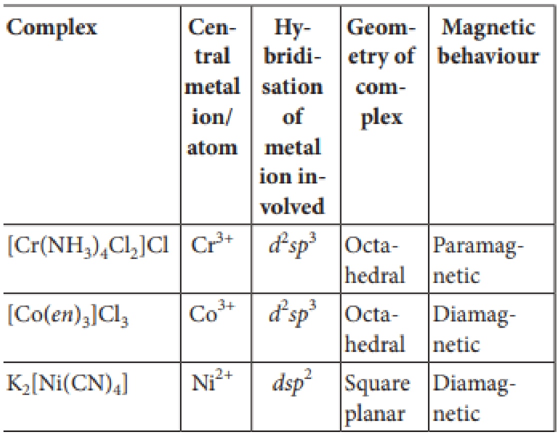
Complexes	Shape	Magnetic behaviour	Hybri-disation
$[CoF_4]^{2-}$	Tetrahedral	Paramagnetic	sp^3
$[Cr(H_2O)_2(C_2O_4)_2]$	Octahedral	Paramagnetic	d^2sp^3
$[Ni(CO)_4]$	Tetrahedral	Diamagnetic	sp^3

29. Write the IUPAC name, deduce the geometry and magnetic behaviour of the complex $K_4[Mn(CN)6]$. [Atomic no. of Mn = 25]



IUPAC name : Potassium hexacyanomanganate (II)
Geometry : Octahedral
No. of unpaired electrons, $n = 1$
Magnetic behaviour : paramagnetic.

30. Write the state of hybridization, the shape and the magnetic behaviour of the following complex entities : (i) $[Cr(NH_3)_4Cl_2]Cl$ (ii) $[Co(en)_3]Cl_3$ (iii) $K_2[Ni(CN)_4]$



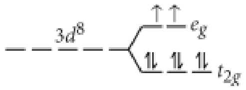
Complex	**Central metal ion/ atom**	**Hybridisation of metal ion involved**	**Geometry of complex**	**Magnetic behaviour**
$[Cr(NH_3)_4Cl_2]Cl$	Cr^{3+}	d^2sp^3	Octahedral	Paramagnetic
$[Co(en)_3]Cl_3$	Co^{3+}	d^2sp^3	Octahedral	Diamagnetic
$K_2[Ni(CN)_4]$	Ni^{2+}	dsp^2	Square planar	Diamagnetic

31. How is the stability of a co-ordination compound in solution decided? How is the dissociation constant of a complex defined?

Ans: The stability of a complex in solution refers to the degree of association between the two species involved in the state of equilibrium. The magnitude of the equilibrium constant for the association, quantitatively expresses the stability. The instability constant or dissociation constant of coordination compound is defined as the reciprocal of the formation constant.

32. Explain the following : (i) Low spin octahedral complexes of nickel are not known. (ii) The p-complexes are known for transition elements only. (iii) CO is a stronger ligand than NH3 for many metals.

Ans: (i) Nickel forms octahedral complexes mainly in +2 oxidation state which has 3d8 configuration. In presence of strong field ligand also it has two unpaired electrons in e_g orbital.



Hence, it does not form low spin octahedral complexes.

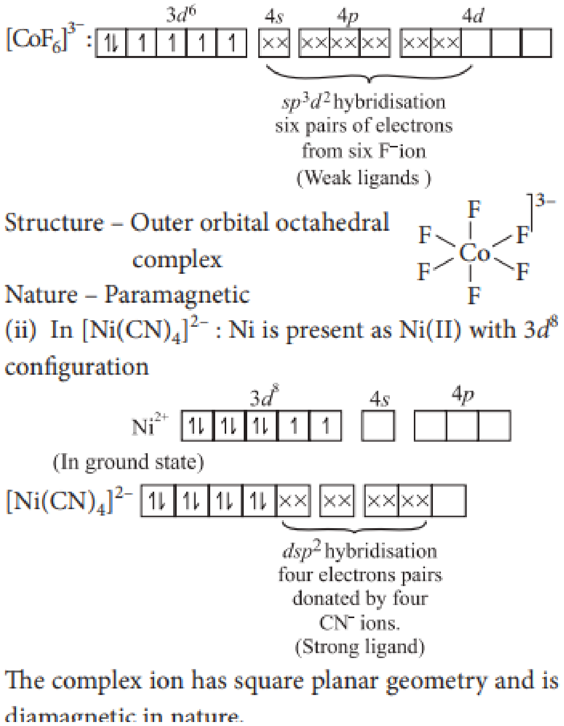
(ii) the transition metals/ions have empty d orbitals into which the electron pairs can be donated by ligands containing p electrons. For example: $CH_2= CH_2$ and C_6H_6, $C_5H_5^-$.

(iii) Co is stronger ligand than NH3 because CO has vacant molecular orbitals with which it can form p-bond with metal through back donation.

33. (i) Write down the IUPAC name of the following complex. [Cr (en)3]Cl3 (ii) Write the formula for the following complex. Potassium trioxalato chromate (III)

Ans: Tris(ethylenediammine)chromium(III) chloride (ii) K3[Cr(ox)3]

34. Write the hybridization and shape of the following complexes: (i) [CoF6] 3– (ii) [Ni(CN)4] 2



sp^3d^2 hybridisation
six pairs of electrons
from six F^- ion
(Weak ligands)

Structure – Outer orbital octahedral complex

Nature – Paramagnetic

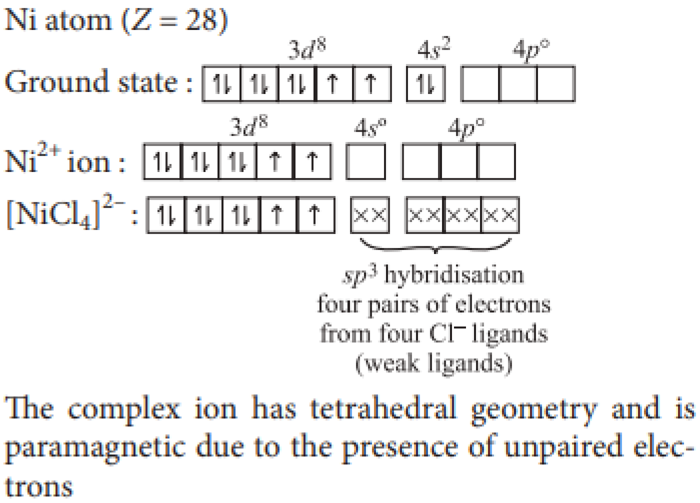
(ii) In $[Ni(CN)_4]^{2-}$: Ni is present as Ni(II) with $3d^8$ configuration

dsp^2 hybridisation
four electrons pairs
donated by four
CN^- ions.
(Strong ligand)

The complex ion has square planar geometry and is diamagnetic in nature.

35. For the complex [NiCl4] 2–, write (i) the IUPAC name (ii) the hybridization type (iii) the shape of the complex. (Atomic no. of Ni = 28)

(i) Tetrachloridonickelate(II) ion


Ni atom (Z = 28)

sp^3 hybridisation
four pairs of electrons
from four Cl^- ligands
(weak ligands)

The complex ion has tetrahedral geometry and is paramagnetic due to the presence of unpaired electrons

SECTION D:

(4MARKS)

CASE BASED QUESTIONS:

36. **Read the given passage and answer the questions that follow:**

Complex compounds play an important role in our daily life. Werner's theory of complex compounds says every metal atom or ion has primary valency (oxidation state) which is satisfied by –vely charged ions, ionisable where secondary valency (coordination number) is nonionisable, satisfied by ligands (+ve, –ve, neutral) but having lone pair. Primary valency is nondirectional, secondary valency is directional. Complex compounds are name according to IUPAC system. Valence bond theory helps in determining shapes of complexes based on hybridisation, magnetic properties, outer or inner orbital complex. Complex show ionisation, linkage, solvate and coordination isomerism also called structural isomerism. Some of them also show stereoisomerism i.e. geometrical and optical isomerism. Ambidentate ligand are essential to show linkage isomerism. Polydentate ligands form more stable complexes then unidentate ligands. There are called chelating agents. EDTA is used to treat lead poisoning, cis-platin as anticancer agents. Vitamin B12 is complex of cobalt. Haemoglobin, oxygen carrier is complex of Fe2+ and chlorophyll essential for photosynthesis is complex of Mg2+.

(a) What is the oxidation state of Ni in $[Ni(CO)_4]$?

Ans. Zero

(b) One mole of CrCl3 . 6H2O reacts with excess of AgNO3 to yield 2 mole of AgCl. Write formula of complex. Write IUPAC name also.

Ans. $[Cr(H2O)5Cl]Cl_2 . H_2O$, pentaaquachloridochromium (III) chloride.

(c) Out Cis – $[Pt(en)_2 Cl2]$ 2+ and trans [Pt(en)2Cl2] 2+ which one shows optical isomerism?

Ans. Cis – [Pt(en)2 Cl2] 2+ shows optical isomerism.

(d) Name the hexadentate ligand used for treatment of lead poisoning.

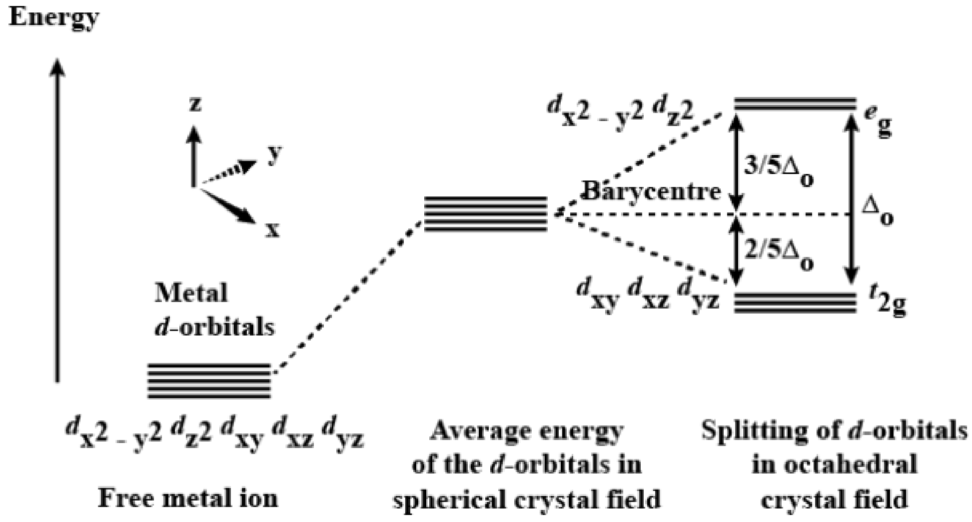
Ans. EDTA4– (ethylenediamine tetraacetate)

(e) What is hybridisation of [CoF6] 3–? [Co = 27] Give its shape and magnetic properties.

Ans. Sp3 d 2 , octahedral, paramagnetic. (f) What type of isomerism is shown by [Cr(H2O)6] Cl3 and [Cr(H2O)5 Cl] Cl2 .H2O?

Ans. Solvate isomerism.

37. Observe the diagram of splitting of d-orbitals in octahedral field and answer the questions based on the diagrams and related studied concepts.



(a) What is crystal field splitting anergy?

Ans. The energy difference between the two sets of d-orbitals is called crystal field splitting energy denoted by Δ0.

(b) Arrange the following complex ions in the increasing order of Crystal field splitting energy $[CrCl_6]^{3-}$, $[CrCN_6]^{3-}$, $[Cr(NH_3)_6]^{3+}$

(c) Ans. $[CrCl_6]^{3-}$, $[Cr(NH_3)_6]^{3+}$, $[CrCl_6]^{3-}$

(d) What is relationship between Δ0 (CFSE) and strength of ligand?

Ans. Greater the Δ0(CFSE), more will be strength of ligand

(e) What is electronic configuration of d5 ion if Δ 0< P?

Ans. $t^2g^3\ eg^2$

38. **Read the following paragraph and answer the questions.**

In 1823, Werner put forth this theory to describe the structure and formation of complex compounds or coordination compounds. It is because of this theory that he got the Nobel prize and is known as the father of coordination chemistry. According to his theory The central metals of coordination compounds exhibit two types of valencies, primary valency and secondary valency. The primary valencies are ionizable. These are written outside the coordination sphere. These are nondirectional and do not give any geometry to complex compound. The secondary valency of metals is either by negative ions or neutral molecules or both. In modern terminology it represents the coordination number of the metal. Secondary valencies are written inside the coordination sphere. These are directional in nature and give definite geometry to the complex. These are non-ionisable.

(a)A coordination compound CrCl3.4H2O precipitates silver chloride when treated with silver nitrate. The molar conductance of its solution corresponds to a total of 2 ions. Write the structural formula of the complex.

Ans. [Co(H2O)4Cl2]Cl

(b)The increasing order of conductivity of the following complexes in their solutions [Co(NH3)3Cl3] , [Co(NH3)6]Cl3 ,[Co (NH3)4Cl2]Cl

Ans. [Co(NH3)3Cl3], ,[Co (NH3)4Cl2]Cl, [Co(NH3)6Cl3

(c)Write the correct formula for the following coordination compound CrCl3.6H2O with 3 chloride ions precipitated as AgCl.

Ans.[Cr(H2O)6]Cl3

(f) How many ions are produced from the complex [Co(NH3)5Cl]Cl2 in solution ? Ans.3

39. **Read the following paragraph and answer the questions.**

Valence bond theory considers the bonding between metal and the ligands as purely covalent. On the other hand the crystal field theory considers the bond to be ionic purely arising from electrostatic interactions between the metal ion and the ligands. In coordination compounds the interaction between the metal ion and the ligands causes the 5 d orbitals to split up. This is called crystal field splitting and the energy difference between the two sets of orbitals is called crystal field splitting energy. CFSE depends upon the nature of the ligand.

(a)Write the electronic configuration of [CoF6] 3- on the basis of crystal field theory Ans. Co3+ has (d 6) ; t2g 4 eg 2 configuration

(b)Arrange the following complex ions in the increasing order of crystal field splitting energy $[CrCl_6]_{3-}$, [Cr(CN)6] 3- ,[Cr(NH3)6] 3+ Ans. $[CrCl_6]_{3-}$, [Cr(NH3)6] 3+,[Cr(CN)6] 3

(dCAmong the ligands ,NH3 ,en and CO which ligand is having the highest field strength ?

Ans.CO

(d)What will be the increasing order for the wave lengths of absorption in the visible region of the following : [Ni (NO2)6] 4- , [Ni (NH3)6] 2+,[Ni (H2O)6] 2+

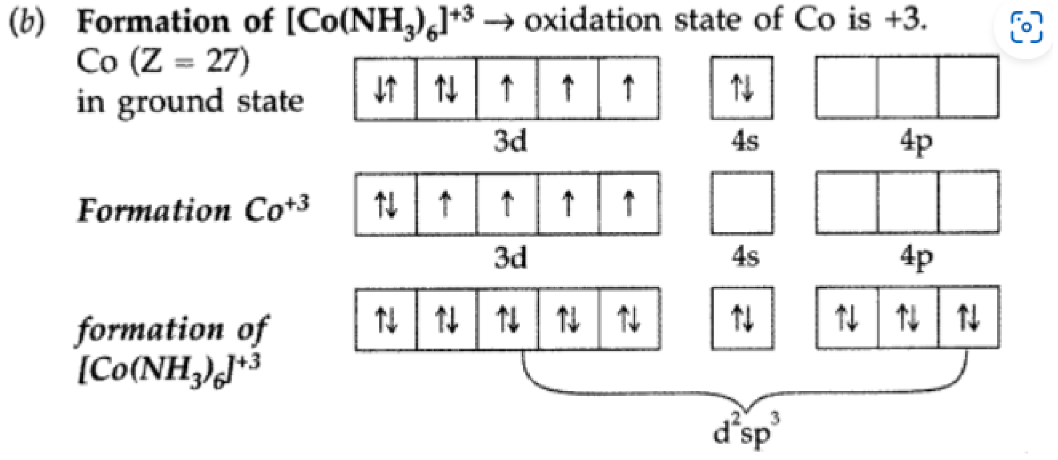
Ans. [Ni (H2O)6] 2+, [Ni (NH3)6] 2+, [Ni (NO2)6] 4-

SECTION E

(5 MARKS)

40. (a) Give two examples of coordination compounds used in industries.
(b) Using valence bond theory, explain the geometry and magnetic behavior of $[Co(NH_3)_6]^{3+}$
(At. no. of Co = 27)

Ans: (a) Examples:
(i) Pure Ni can be obtained from $Ni(CO)_4$
(ii) Gold and Ag are extracted by the use of complex formation like $Na[Ag(CN)_2]$.



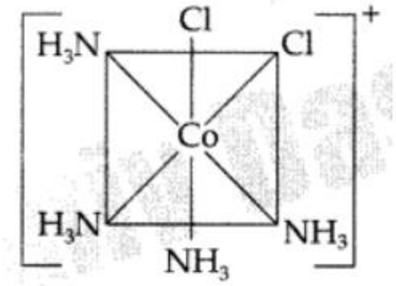
(b) **Formation of $[Co(NH_3)_6]^{+3}$ → oxidation state of Co is +3.**

41. (a) How is a double salt different from a complex?
(b) Write IUPAC names of the following:
(i) $K_3[Fe(C_2O_4)_3]$
(ii) $[Pt(NH_3)_6]Cl_4$.
(c) Draw the structure of cis isomer of $[CO(NH_3)_4Cl_2]^+$

Ans: (a) Double salt dissociates completely into its constituent ions in their aqueous solution.
Example : $KCl.MgCl_2.6H_2O$ dissociates into K^+, Cl^-, Mg^{2+} and H_2O
Complex does not dissociate into its constituent ions.
Example : $K_4[Fe(CN)_6] \rightarrow 4K^+ + Fe(CN)_6]^{4-}$

(b) (i) $K_3[Fe(C_2O_4)_3]$ IUPAC name : Potassium trioxalatoferrate (III)
(ii) $[Pt(NH_3)_6]Cl_4$ IUPAC name : Hexaammine Platinum (IV) chloride

(c) Structure of cis isomer of $[CO(NH_3)_4Cl_2]^+$



42. When a coordination compound $CrCl_3.6H_2O$ is mixed with $AgNO_3$ solution, 3 moles of AgCl are precipitated per mole of the compound. Write :

(i) Structural formula of the complex

(ii) IUPAC name of the complex

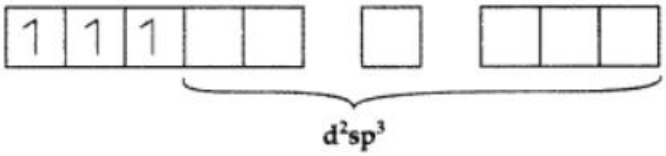
(iii) Magnetic and spin behaviour of the complex

$$CrCl_3.6H_2O + AgNO_3 \longrightarrow [Cr(H_2O)_6]^{3+} + \underset{\text{3 moles of AgCl}}{3AgCl}$$

(*i*) $[Cr(H_2O)_6]^{3+} Cl_3^-$

(*ii*) IUPAC name : Hexaaquachromium (III) chloride

(*iii*) E.C. of $Cr^{3+} = 3d^3 4s^0 4p^0$; unpaired electrons = 3



Inner orbital complex so it is low spin complex.

Since 3 unpaired electrons are present, it is paramagnetic in nature.

43. (i) What type of isomerism is shown by the complex $[Co(NH_3)_6][Cr(CN)_6]$?

(ii) Why a solution of $[Ni(H_2O)_6]^{2+}$ is green while a solution of $[Ni(CN)_4]^{2-}$ is colourless? (At. no. of Ni = 28)

(iii) Write the IUPAC name of the following complex: $[CO(NH_3)_5(CO_3)]Cl$.

Ans: (i) Coordination isomerism

(ii) $[Ni(H_2O)_6]^{2+}$ is an outer orbital complex due to weak field ligand H_2O and the presence of unpaired electrons undergoes d—d transition by absorbing red light and shows green colour while $[Ni(CN)_4]^{2-}$ is an inner orbital complex and has no unpaired electrons hence colourless.

(iii) Pentaamminecarbonatocobalt (III) Chloride***

COORDINATION COMPOUNDS (2ND HALF)

Section A

- **Section A - 1 Mark's MCQ (15)**
- **Section B - 2 Mark's questions (10)**
- **Section C - 3 Mark's questions (10)**
- **Section D - 4 Mark's case study based questions (4)**
- **Section E - 5 Mark's questions (4)**

MCQ carrying 1 mark each

Q.1. The crystal field splitting energy for octahedral (Δo) and tetrahedral (Δt) complexes is related as -

a) $\Delta t = 2/9\Delta o$ b) $\Delta t = 5\backslash 9\Delta o$ c) $\Delta t = 4/9\Delta o$ d) $\Delta t = 2\Delta o$

Q.2. What are the number of unpaired electrons in the square planer $[Pt(CN)4]2-$ ion?

a) 0 b) 1 c) 4 d)6

Q.3. Magnetic nature and spin of $[Co(NH3)6]3+$ is -

a) Paramagnetic, High spin complex b) Diamagnetic, low spin complex

c) Paramagnetic, low spin complex d) Diamagnetic, high spin complex

Q.4. What was the term proposed by Werner for the number of groups bound directly to the metal ion in a coordination complex?

a) Primary valence

b) Secondary valence

c) Oxidation number

d) Polyhedra

Q.5. Werner postulated that octahedral, tetrahedral and square planar geometrical shapes are more common in coordination compounds of ________

a) alkali metals

b) lanthanides

c) actinides

d) transition metals

Q.6. What is the sum of the oxidation number of cobalt in $[Co(H2O)(CN)(en)2]2+$and $[CoBr2(en)2]+$?

a) +3

b) +4

c) +5

d) +6

Q.7. Hybridisation of [Ni(CN)4]2- is

(a) dsp2

(b) d2sp2

(c) sp3

(d) d2sp3

Q.8. Which of the following is true for the formation of stable bonds according to valence bond theory?

(a) Greater overlapping between atomic orbitals

(b) Close proximity between two atoms

(c) Pairing of electrons having opposite spins

(d) All of the above

Q.9. A coordination complex’s core atom/ion is also known as ________

a) Bronsted-Lowry acid

b) Lewis base

c) Lewis acid

d) Bronsted-Lowry base

Q.10. Which of the following d orbitals take part in the octahedral complex with d2sp3 hybridisation?

(a) dxy, dyz

(b) dxz, dx2−y2

(c) dx2−y2, dz2

(d) dz2, dxz

Q.11. The correct increasing order of splitting power of ligands according to spectrochemical series is

(a) Cl– < OH– < CN–

(b) Cl– < CN– < OH–

(c) OH– < Cl– < CN–

(d) OH– < CN– < Cl–

Q.12. Which of the following is paramagnetic?

(a) [CoBr]42-

(b) Mo(Co)6

(c) [Pt(en)Cl2]

(d) [Co(NH3)6]3+

Q.13. Hardness of water is estimated by simple titration with which compound?

a) Na2(EDTA)

b) Fe(EDTA)

c) Mg(EDTA)

d) Co(EDTA)

Q.14. Haemoglobin is a complex compound of which metal ion?

a) Fe3+

b) Fe2+

c) Co2+

d) Co3+

Q.15. The complex ion [Ag(S2O3)2]3- is associated with which field?

a) Electroplating

b) Medicine

c) Water treatment

d) Photography

Section - B

Q.16. Write the hybridization and shape of the following complexes -

i) [CoF6]3-   ii) [Ni(CN)4]2-

Q.17. Why crystal field splitting energy more in case of octahedral complexes as compared to tetrahedral complexes?

Q.18. Explain crystal field splitting in an octahedral complex.

Q.19. Explain the term spectrochemical series.

Q.20. Using valence bond approach, explain the magnatic character of [Co(NH3)6]3+ ion. (At. No. Of Co = 27)

Q.21. Write the hybridization and shape of the complex [NiCl4]2-.

Q.22. Differentiate between weak field and strong field ligand.

Q.23. Why are low spin tetrahedral complexes not formed?

Q.24. Why are different colours observed in Octahedral and tetrahedral complexes for the same metal and same ligands?

Q.25. CuSO4.5H2O is blue in colour while CuSO4 is colourless. Why?

Section - C

Q.26. Using valence bond theory, explain the following in relation to the complexes given below:

[Mn(CN)6]3-, [Co(NH3)6]3+, [Cr(H2O)6]3+

(i) Type of hybridisation.

(ii) Inner or outer orbital complex.

(iii) Magnetic behaviour.

Q.27. NH_3 acts as complexing agent but NH_4^+ does not, explain.

Q.28. $Fe(H_2O)6]^{3-}$ is strongly paramagnetic whereas [Ni(NH3)6]2+

weakly paramagnetic. Explain.

Q.29. Name the central metal atom/ion present in -Chlorophyll, Haemoglobin, Vitamin B-12.

Q.30.Write the limitations of Valence Bond Theory.

Q.31. (i) Low spin octahedral complexes of nickel are not known.

(ii) The π-complexes are known for transition elements only.

Q.32. What is meant by crystal field splitting energy? On the basis of crystal field theory, write the electronic configuration of d4 in terms of t2g and eg in an octahedral field when

(i) $\Delta 0 > P$

(ii) $\Delta 0 < P$

Q.33. Discuss the nature of bonding in metal carbonyl.

Q.34. State and describe the factors which govern stability of complexes.

Q.35. Discuss briefly giving an example in each case the role of coordination compound in

(1) biological systems (2) medicinal chemistry (3) analytical chemistry

Section - D

Q.36. Read the passage given below and answer the following questions:

To explain bonding in coordination compounds various theories were proposed. One of the important theory was valence bond theory. According to that, the central metal ion in the complex makes available a number of empty orbitals for the formation ofcoordination bonds with suitable ligands. The appropriate atomic orbitals of the metal hybridise to give a set of equivalent orbitals of definite geometry. The d-orbitals involved in the hybridisation may be either inner d-orbitals i.e., (n - 1) d or outer d-orbitals i.e., nd. For example, CO3+ forms both inner orbital and outer orbital complexes, with ammonia it forms [Co(NH3)6]3+ and with fluorine it forms [CoF6]3- complex ion.

The following questions are multiple choice questions. Choose the most appropriate answer:

(i) Which of the following is not true for [CoF6]3- ?

(a) It is paramagnetic. (b) It has coordination number of 6.

(c) It is outer orbital complex . (d) It involves d2sp3 hybridisation.

(ii) Which of the following is true for [Co(NH3)6]3+ ?

(a) It is an octahedral, dimagnetic and outer orbital complex.

(b) It is an octahedral, paramagnetic and outer orbital complex.

(c) It is an octahedral, paramagnetic and inner orbital complex.

(d) It is an octahedral, dimagnetic and inner orbital complex.

(iii) The paramagnetism of [CoF6]3- is due to

(a) 3 electrons (b) 4 electrons (c) 2 electrons (d) 2 electrons

(iv) Which of the following is an inner orbital or low spin complex?

(a) [Ni(H2O)6]3+

(b)[FeF6]3−

(c) [Co(CN)6]3−

(d) [NiCl4]2−

Q.37. Valence bond theory considers the bonding between the metal ion and the ligands as purely covalent. On the other hand, crystal field theory considers the metal-ligand bond to be ionic arising from electrostatic interaction between the metal ion and the ligands. In coordination compounds, the interaction between the ligand and the metal ion causes the five d-orbitals to split-up. This is called crystal field splitting and the energy difference between the two sets of energy level is called crystal field splitting energy. The crystal field splitting energy (Δo) depends upon the nature of the ligand. The actual configuration of complexes is divided by the relative values of Δo and P (pairing energy)

If Δo < P, then complex will be high spin.

If Δo > P, then complex will be low spin.

The following questions are multiple choice questions. Choose the most appropriate answer :

(i) Which of the following ligand has lowest Δo value?

(a) CN- (b) CO (c) F- (d) NH3

(ii) The crystal field splitting energy for octahedral (Δo) and tetrahedral (Δt) complex is related as

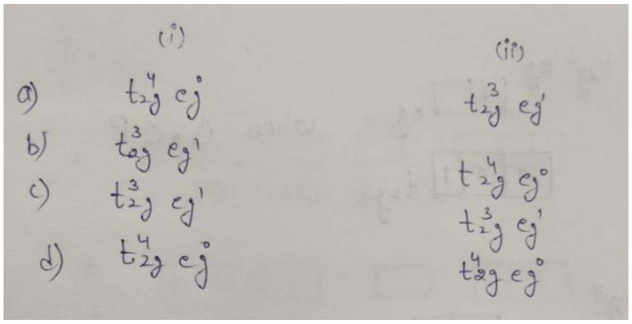
(a) Δt=1/2Δo

(b) Δt=4/9Δo

(c) Δt=3/5Δo

(d) Δt=2/5Δo

(iii) On the basis of crystal field theory, the electronic configuration of d4 in two situations: (i) Δo > P and (ii) Δo< P are



	(i)	(ii)
a)	$t_{2g}^4 e_g^0$	$t_{2g}^3 e_g^1$
b)	$t_{2g}^3 e_g^1$	$t_{2g}^4 e_g^0$
c)	$t_{2g}^3 e_g^1$	$t_{2g}^3 e_g^1$
d)	$t_{2g}^4 e_g^0$	$t_{2g}^4 e_g^0$

(iv) Using crystal field theory, calculate magnetic moment of central metal ion of [FeF6]4-.

(a) 1.79 B.M. (b) 2.83 B.M. (c) 3.85 B.M. (d) 4.9 B.M.

Q.38. balance bond theory describe the bonding in complexes in terms of co-ordinate covalent bonds resulting from overlap filled ligand orbitals with vacant metal hybrid orbitals. The theory explain magnetic behaviour and geometrical shape of coordination compounds. Magnetic moment of a complex can be determined experimentally and theoretically by using spin only formula.

Magnetic momentum √n(n+2)BM (n is no. Of unpaired electrons)

(i) write the state of hybridization, shape and the magnetic behaviour of the [Cr(H2O)2(C2O4)2]-.

(ii) Why s orbital does not show preference to any direction.

(III) why is [CoF6]3- is paramagnetic but [Co(NH3)6]3+ is diamagnetic in nature?

(IV) Describe the type of hybridization, shape and magnetic property of [Co(NH3)4Cl2]Cl.

Q.39. coordination compound plays many important role in animals and plants they are essential in the storage and transport of oxygen, as electron transfer agents as catalysts and in photosynthesis. White range of application in daily life takes place through formation of complexes photo photographic fixing qualitative and quantitative analysis purification of water, metallurgical extraction are some specific worth mentioning.

(I) Exalic acid is commonly used

(A)To make medicines

(B) To remove rust and stains

(C)as a thinner or in polishing the wooden material

(D)all of the above

(Ii) Ziegler- NATA catalyst is used to convert

(A) ethylene

(b) ethyne

(c) ethanal

(d)ethanol

(III) calcium dihydrogen salt of EDTA is used as an antidote for lead poisoning because

(A) excess EDTA remove Ca2+ ions from body

(b) calcium ions co-ordinates with Lead in the body

(c) excess EDTA will not remove Ca2+ ions from body

(d) b and C

(IV) cis - platin, stands for

(A) cis - diamminechloroplatinum (II)

(b) cis - dichloridodiammineplatinum(I)

(c) cis - dimethyldichloridoplantinum (II)

(d)bcis - dichloridodiammineplatinum (II)

Section - E

Q.40. Using valence bond theory, explain the following in relation to the complexes given below:

[Mn(CN)6]3-, [Co(NH3)6]3+, [FeCl6]4-

(i) Type of hybridisation.

(ii) Inner or outer orbital complex.

(iii) Magnetic behaviour.

(iv) Spin only magnetic moment value.

Q.41. Explain Werner's theory of coordinate compounds with suitable examples?

Q.42. What is crystal field splitting? Explain crystal field splitting in tetrahedral complexes.

Q.43. a) Explain why [Fe(HO)6]3+ has a magnetic moment value of 5.92 BM whereas [Fe(CN)6]3- has a value of only 1.74 BM.

b) Why do compounds having similar geometry have different magnetic moments?

MCQ answer key

Q.1. c)

Q.2. a)

Q.3. b)

Q.4. b)

Q.5. d)

Q.6. d)

Q.7. a)

Q.8. d)

Q.9. c)

Q.10. c)

Q.11. a)

Q.12. a)

Q.13. a)

Q.14. b)

Q.15. d)

Section - B Answer key

Q.16. i) In [CoF6]3- cobalt is in+3 O.S.. F- is a weak field ligand. It does not cause pairing.

Therefore cobalt undergoes sp3d2 hybridization and have octahedral geometry.

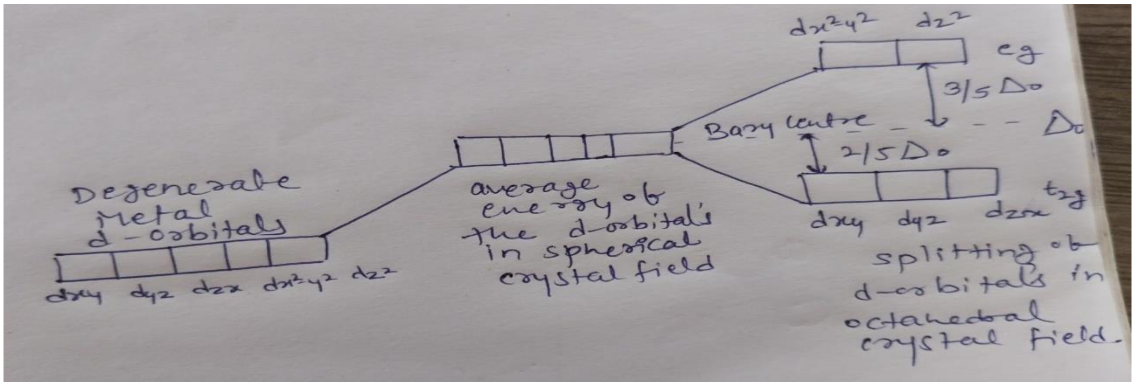
ii) In [Ni(CN)4]2- Ni is in+2 O. S. and has the electronic configuration 3d84s0. As CN- is strong field ligand it causes pairing of electrons resulting one 3d orbital empty, with one 4s and two 4p it gives dsp2 hybridization. And shape is square planer.

Q.17. Crystal field splitting energy in Octahedral complexes is more than in tetrahedral complexes, because -

i) in Octahedral complexes there are 6 ligand which face repulsion from valence electrons of central metal atom. But only 4 ligand in tetrahedral complexes.

ii) Also because in Octahedral complexes 2 ligands approach Central metal atom along the direction of 2 d orbitals (dx2-y2, dz2). But in tetrahedral complexes all ligands approach the central metal atom between the axes not along any axes with d orbitals.

Q.18. Crystal field splitting in Octahedral field -In free transition metal ion all d orbitals are equal in energy called degenerate orbitals. But as soon as ligand approaches the central metal ion, repulsion between electron's of central metal ion and electron's of ligand causes splitting of 5 degenerate d orbitals into two sets of orbitals. eg orbitals with 2 orbitals are high in energy and t2g with 3 orbitals low in energy as follows

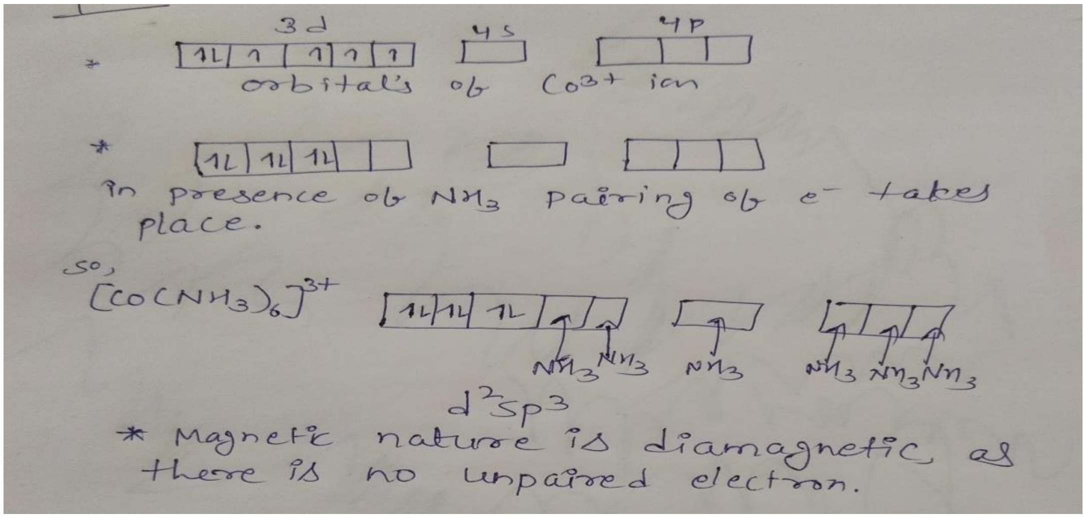


Q.19. Spectrochemical series - The arrangement of ligands in the order of increasing field strength or increasing crystal field splitting energy values is known as spectrochemical series.

Br-, Cl-,SCN-,F-, OH-, H2O, NH3, en, CN- , CO

Q.20. In [Co(NH3)6]3+ ion O.S. of Co is +3

hybridization in presence of NH3 is strong field ligand



* orbital's of Co3+ ion

* In presence of NH3 pairing of e⁻ takes place.

So, [Co(NH3)6]3+

* Magnetic nature is diamagnetic as there is no unpaired electron.

Q.22. Weak field ligand - the ligand which have small value of crystal field splitting energy (Δo). For these ligands Δo<P, (p is pairing energy). These ligands produce high spin complexes.

Strong field ligand - the ligand which have large value of crystal field splitting energy and also, Δo>P. These ligands produce low spin complexes.

Q.23. For tetrahedral complexes, the crystal field splitting energy is smaller than pairing energy, so pairing doesn't take place and high spin complexes are formed instead of low spin.

Q.24. Δt=(4/9)Δo

So, a higher wavelength of light is absorbed in octahedral complexes than tetrahedral complexes for same metal and ligands. Thus, different colours are observed.

Q.25. Water acts as a ligand in CuSO4.5H2O, causing crystal field splitting. As a result, in CuSO4.5H2O, a d—d transition is possible and coloured. Crystal field splitting is impossible in anhydrous CuSO4 due to the lack of water (ligand), hence there is no colour.

Section - C

Q.26. [Mn(CN)6]3-

(i) Type of hybridisation = d2sp3 hybridisation

(ii) Inner or outer orbital complex = Inner orbital complex because (n-1)d – orbitals are used.

(iii) Magnetic behaviour = Paramagnetic, as two unpaired electrons are present.

[Co(NH3)6]3+

(i) Type of hybridisation = d2sp3 hybridisation

(ii) Inner or outer orbital complex = Inner orbital complex (as(n-1)d-orbitals take part.)

(iii) Magnetic behaviour = Diamagnetic (as three paired electrons are present.)

[Cr(H2O)6]3+

(i) Type of hybridisation = d2sp3 hybridisation

(ii) Inner or outer orbital complex = Inner orbital complex as(n-1)d-orbitals take part.)

(iii) Magnetic behaviour = Paramagnetic (as three unpaired electrons are present.)

Q.27. Because ammonia only has one lone pair of electrons, it can accept electrons from coordination complexes. Ammonia is transformed into an ion called ammonium, which lacks a lone pair to donate and form complexes. As a result, whereas ammonia can be an excellent ligand, the ammonium ion does not form complexes.

Q.28. The ligand NH3 is neither a strong field ligand nor a weak field ligand in the [Ni(NH3)6]2+ complex ion. It is, in fact, a weak strong field ligand. However, because the crystal field stabilisation energy is smaller than the pairing energy, the ligand NH3 acts as a weak field ligand in the [Ni(NH3)6]2+ ion. As a result, the electronic configuration under the effect of an octahedral crystal field is t2 g6eg2. The complex has two unpaired electrons, according to the aforementioned electrical structure. As a result, the [Ni(NH3)6]2+ complex is weakly paramagnetic.

In the complex [Fe(H2O)6]3+ the oxidation state of Fe is +3, having the structure 3 d5. Water (H2O) is a weak ligand, and 3 d electrons do not couple up in its presence. The sp3d2 hybridization results in an outer orbital octahedral complex with 5 unpaired electrons. As a result, it is very paramagnetic.

Q.29. The central metal ion in the structure of chlorophyll is magnesium.

The central metal ion in the structure of haemoglobin is iron.

The central metal ion in the structure of vitamin B-12 is cobalt.

Q.30. The limitations of valence bond theory are:

(i) VBT fails in explaining the tetravalency of carbon.

(ii) The geometries of ammonia, water, methane, etc cannot be properly explained by this theory.

(iii) Bond angles of molecules such as carbon dioxide, water, ammonia, etc could not properly be given by VBT.

(iv) VBT does not explain the magnetic properties of complex

Q.31. (i) The electronic configuration of Ni is [Ar] 3d8 4s2 which shows that it can only form two types of complexes i.e. square planar (dsp2) in presence of strong ligand and tetrahedral (sp3) in presence of weak ligand. There are four empty orbitals in Ni while octahedral complexes require six empty orbitals.

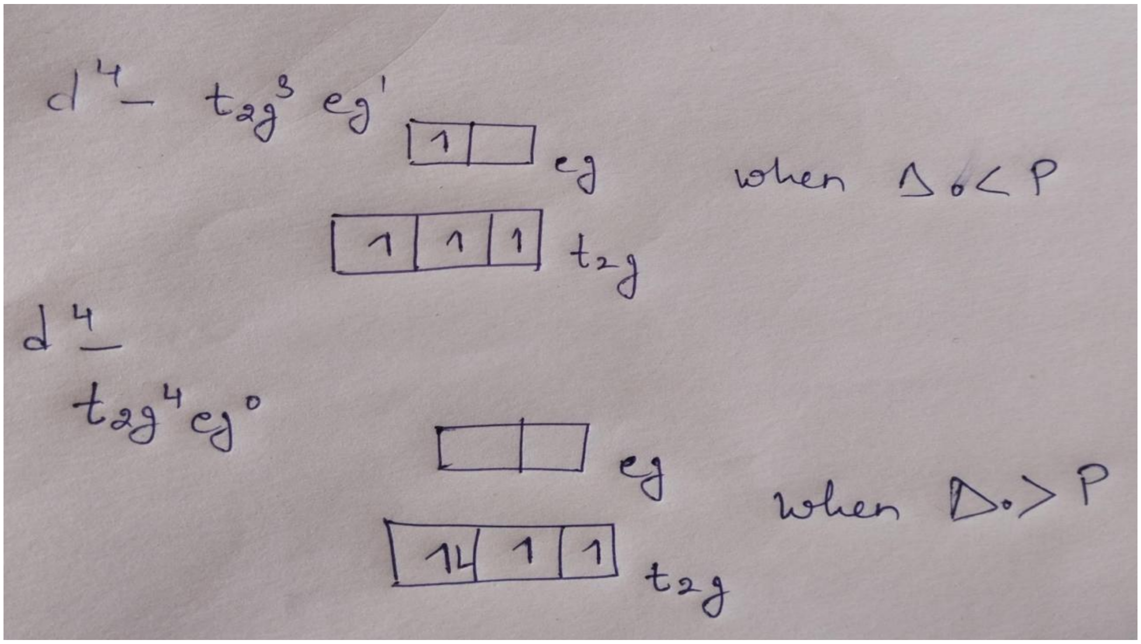
(ii) Due to presence of empty d-orbitals in transition metals, they can accept electron pairs from ligands containing π electrons and hence can form ic-bonding complexes.

Q.32. d-orbital is degenerate which split into two levels eg and t2g in the presence of ligands. This splitting is due to the presence of ligands. This is called the crystal-field splitting and the energy difference between the two levels (eg and t2g) is called the crystal-field splitting energy, Δ0 Electrons are singly filled in the t2g energy levels first and the remaining electrons are filled based on the crystal field splitting energy and pairing energy.

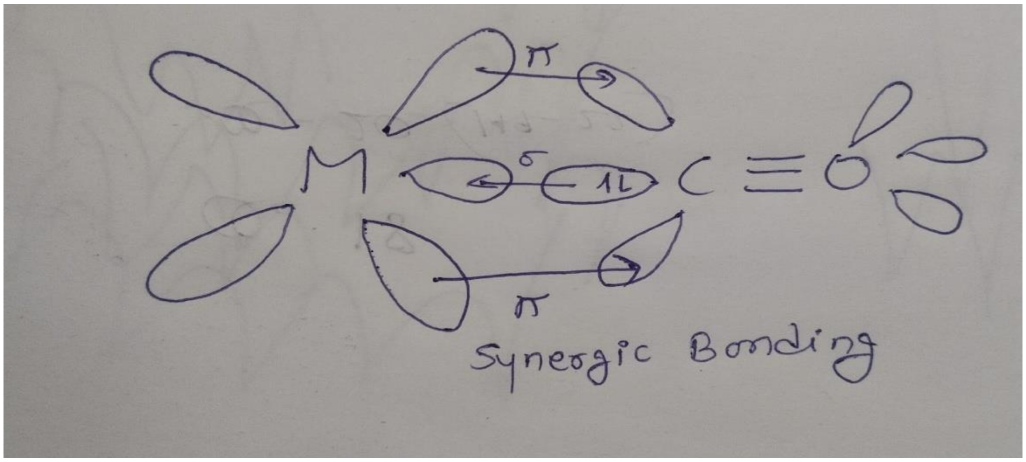
Filling up of the remainig electrons takes place in two ways.

(i) If the CFSE (Δ0) is greater than that of the pairing energy (p), electrons will be filled in the 'eg' orbitals.

(ii) If the CFSE (Δ0) is lesser than that of the pairing energy (p), electrons will be paired up in the t2g energy levels.



Q.33. The metal carbon bond in metal carbonyl have both sigma and pi character. The metal carbon sigma bond is formed by the donation of lone pair of electrons of the carbonyl carbon to a vacant orbital of the metal. The metal carbon pi bond is formed by the donation of a pair of electrons from a filled d orbital of metal into the vacant antibonding pi molecular orbitals of carbon monoxide. The metal to ligand bonding creates a synergic effect which strengthen the bond between CO and the metal.



Q.34. I) Charge on the central metal ion - greater the charge, greater is the stability of complex.

II) Nature of the metal ion- group 3-6 form more stable complexes.

III) Basic nature of the ligands.

IV) presence of chelate rings increases the stability of complex.

V) Multidentate cyclic ligands without any steric effect increases the stability of complex further.

Q.35. Biological systems -

(A) hemoglobin the oxygen carrier in blood is a complex of Fe2+ with porphyrin.

(B) the pigment chlorophyll in plants responsible for photosynthesis is a complex of Mg2+ with porphyrin.

(C) vitamin B12 is a complex of Cobalt.

Medicinal chemistry

(A) the platinum complex cis platin is used in the treatment of cancer.

(B) the excess of copper and iron present in animal system are removed by the chelating ligands.

Analytical chemistry

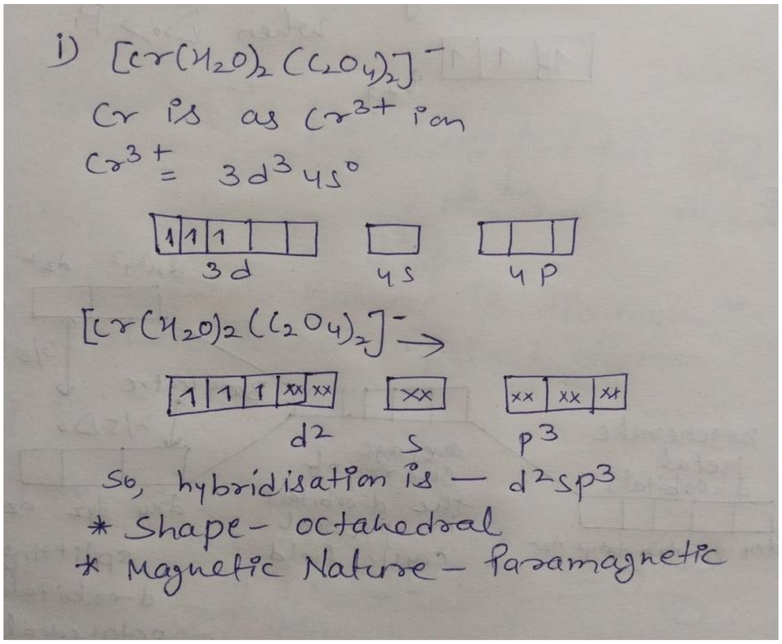
(A) detection of Cu2+ is based on the formation of a blue Tetra Ammine copper (II) ion.

(B) Ni2+ is detected by the formation of red complex with dimethyl glyoxime.

Q.36. (i) d (ii) d (III) b (iv) c

Q.37. (i) c (ii) b (III) a (iv) d

Q.38.



i) $[Cr(H_2O)_2(C_2O_4)_2]^-$

Cr is as Cr^{3+} ion

$Cr^{3+} = 3d^3 4s^0$

$[Cr(H_2O)_2(C_2O_4)_2]^- \rightarrow$

So, hybridisation is — d^2sp^3

* Shape- octahedral

* Magnetic Nature – Paramagnetic

(ii) The s orbital is spherically symmetric in shape so it does not show preference to any direction. It is the same from all the directions

(III) In [CoF6]3- unpaired electrons are present in sp3d2 configuration but in [Co(NH3)6]3+ all electrons are paired in d2sp3 configuration.

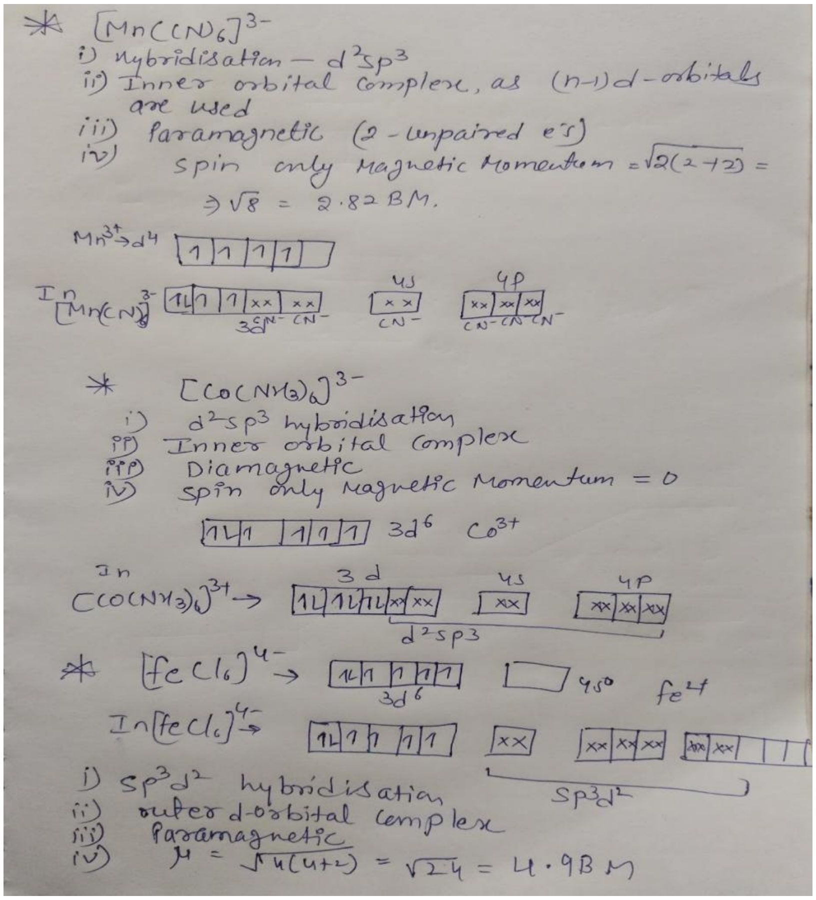
(IV) Hybridisation - d2sp3

Shape - Octahedral

Magnetic nature - Diamagnetic

Q.39. (I) b (ii) a (III) c (iv) d

Q.40.



* $[Mn(CN)_6]^{3-}$

i) hybridisation — d^2sp^3

ii) Inner orbital complex, as (n-1)d-orbitals are used

iii) Paramagnetic (2 - unpaired e's)

iv) spin only Magnetic Momentum = $\sqrt{2(2+2)}$ = $\Rightarrow \sqrt{8}$ = 2.82 BM.

$Mn^{3+} \to d^4$

In $[Mn(CN)_6]^{3-}$

* $[Co(NH_3)_6]^{3-}$

i) d^2sp^3 hybridisation

ii) Inner orbital complex

iii) Diamagnetic

iv) spin only Magnetic Momentum = 0

$3d^6$ Co^{3+}

In $[Co(NH_3)_6]^{3+} \to$

* $[FeCl_6]^{4-} \to$

In $[FeCl_6]^{4-} \to$

i) sp^3d^2 hybridisation

ii) outer d-orbital complex

iii) Paramagnetic

iv) $\mu = \sqrt{4(4+2)} = \sqrt{24} = 4.9$ BM

Q.41. 1) Several metals have two types of valence:

i) Primary valence or principal valence or ionisable valence. It is designated by solid line. It corresponds to oxidation number of the metal ion.

ii) Secondary valence or auxiliary valence or subsidiary valence or residual valence or non ionisable valence. It is designated by dotted line. It correspond to coordination number.

2) Every metal has tendency to satisfy both valences.

3) Every metal has fixed number of secondary valence

4) The primary valences are non-rigid and non-directional. The secondary valences are directional in nature. The secondary valence is always directed towards fixed position in space.

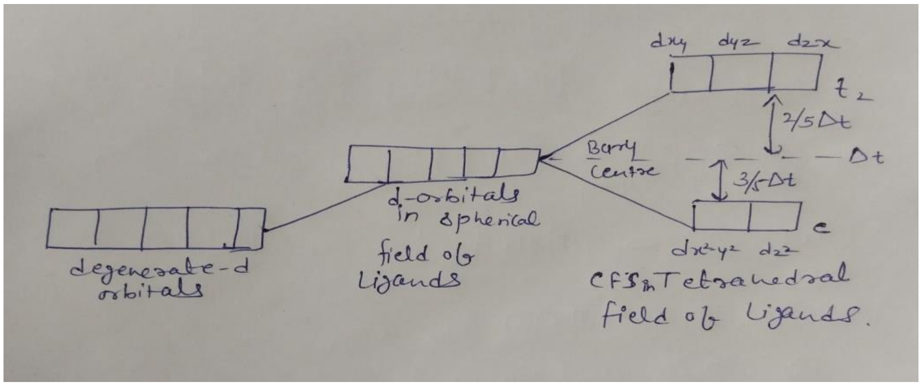
5) There are two spheres around the central metal ion. The inner sphere is the coordination sphere and the outer sphere is the ionization sphere.

6) Groups present in inner sphere are firmly attached to the metal ion and cannot be easily separated. The groups present in the ionization sphere are loosely bound and can be separated as ions on dissolving the complex in suitable solvent.

For example, in the complex PtCl4, the primary as well as secondary valencies of Pt metal are 4 each.

Q.42. Crystal field splitting - splitting of 5 degenerate d-orbitals into different set of orbitals in presence of ligands because of repulsion between the electrons of ligands and valence electrons of central metal atom.

Crystal field splitting in tetrahedral complexes -



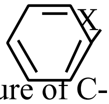
Q.43. a) [Fe(CN)6]3– involves d2sp3 hybridisation with one unpaired electron and [Fe(H2O)6]3+ involves sp3d2 hybridisation with five unpaired electrons. This difference is due to the presence of strong ligand CN– and weak ligand H2O in these complexes.

b) The presence of weak and strong field ligands in complexes is the reason for this. For example, [CoF6]3- and [Co(NH3)6]3+ are paramagnetic and diamagnetic respectively, because F is a weak field ligand and NH3 is a strong field ligand while both have similar geometry. Because F is a weak field ligand and NH3 is a strong field ligand, the complex will have a low magnetic moment if CFSE is high, and vice versa.

CHAPTER- HALOALKANES AND HALOARENES

TOPIC- HALOARENES :

ARYL HALIDES/HALOARENES :- The compound in which the halogen atom is bonded to an sp^2 hybridised carbon atom of an aromatic ring is called haloarenes .



• Nature of C-X bond: X is more electronegative than carbon. So, the C-X bond is polarized with C having a partial positive charge and X having a partial negative charge.carbon halogen bond length increases from C-F to C-I .consequently carbon -halogen bond enthalpy decreases from C-F to C-I .

$-\dot{C}^{\delta\dagger}\text{--}X^{\delta-}$

SUBSTITUTION REACTIONS:- two types

i) Nucleophilic Substitution :- it involves the replacement of an atom or group of atoms by a nucleophile (electron rich species)

$A\text{-}B + Nu^- \rightarrow A\text{-}Nu + B^-$

It is of two types:-

a) Unimolecular nucleophilic substitution reaction (SN1)

b) Bimolecular nucleophilic substitution reaction (SN2 2)

a) Unimolecular substitution reaction (SN1):- (i) it involves two steps

(ii) in this retention/Racemization of configuration take place.
(iii) unimolecular and all are first order.

Mechanism:-

(step1) formation of carbocation.

(Step2)Attack of nucleophile on carbocation Cl – (front/rear end)

Order of reactivity: $3^0 > 2^0 > 1^0$ (Because 3^0 carbocation is more stable)

(b) Bimolecular Nucleophilic Substitution SN2:-

(i)it involves onestep.

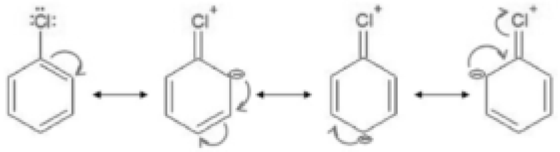
(ii)in this inversion of configuration takes place.

(iii)Bimolecular mechanism: -in this nucleophile attacks from the backside Where halogen atom is attached. It facilitates the departure of leaving halide group. Order of reactivity:-$1^0 > 2^0 > 3^0$ (Because of less steric hindrancein 1^0 alkylhlide)

. Nucleophilic substitution:-

Aryl halides are extremely less reactive towards nucleophilic substitution reactions due to the following reasons:

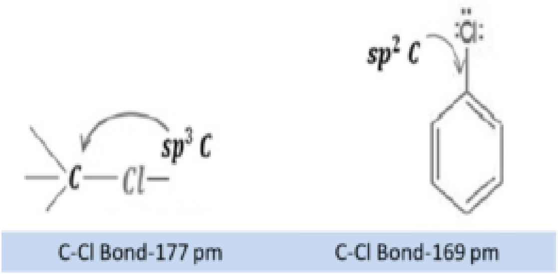
(i) Resonance effect : In haloarenes, the electron pairs on halogen atom are in conjugation with p-electrons of the ring and the following resonating structures are possible.



Example of Resonance Effect

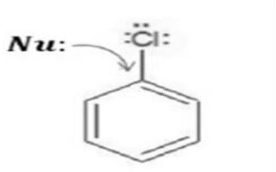
C—Cl bond acquires a partial double bond character due to resonance. As a result, the bond cleavage in haloarene is difficult than haloalkane and therefore, they are less reactive towards nucleophilic substitution reaction.

(ii) Difference in hybridisation of carbon atom in C—X bond: Since it is difficult to break a shorter bond than a longer bond, therefore, haloarenes are less reactive than haloalkanes towards nucleophilic substitution reaction.



Difference in Hybridization of Carbon Atom in C-X Bond

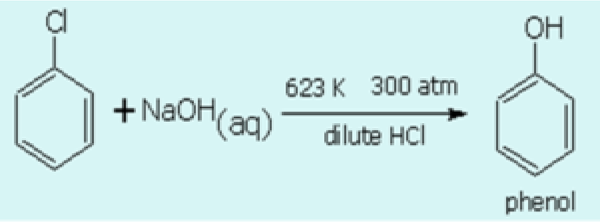
(iii) Instability of phenyl cation



Electronic Repulsion

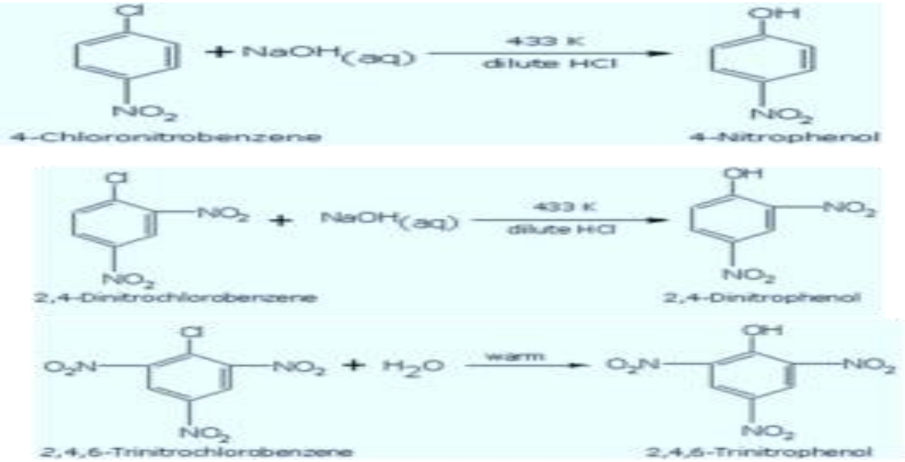
We know that haloarenes are generally unreactive or less reactive towards nucleophilic substitution Below example will further help to understand how certain haloarenes are reactive towards nucleophilic substitution reaction in certain drastic conditions.

Replacement by Hydroxyl Members



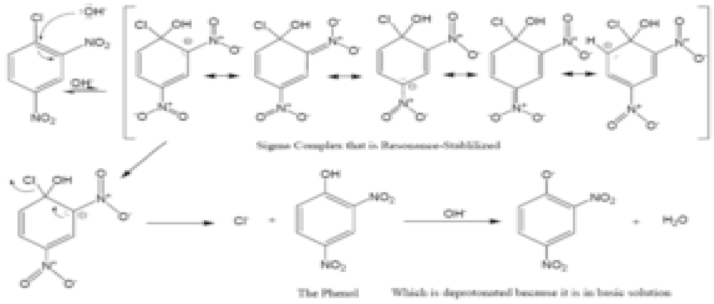
Replacement by Hydroxyl Member

However, if an electron withdrawing group such as $-NO_2$ is present in the ortho, para, and both ortho- and para- positions then the reactivity of the reaction increases in much lesser drastic conditions.



Increase of Reactivity Based on Position

Mechanism of Aromatic Nucleophilic Substitution Reaction:-



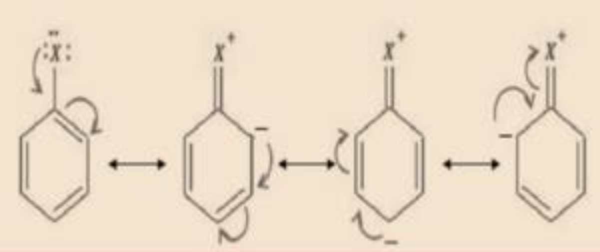
Mechanism of Nucleophilic Substitution Reaction

II. Electrophilic Substitution Reactions

An electrophile means an electron seeking species. Haloarenes will undergo the usual benzene ring reactions such as nitration, halogenation, Friedel-Crafts reactions and sulphonation.

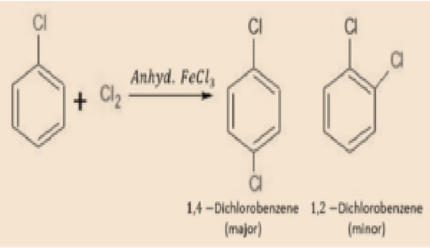
The +M effect will result in the concentration of electron density at ortho −and para −positions.

However, electrophilic substitution reactions with respect to the haloarene reactions are slow in comparison to benzene reactions. This is because the halogen group present in haloarenes are deactivating because of the –I effect. Hence, electrons withdraw from the benzene ring.

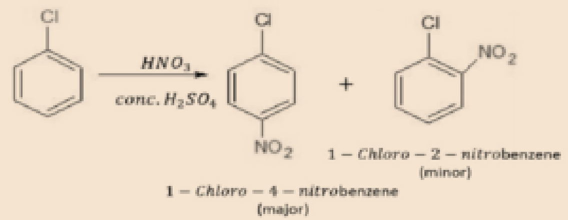


Electrophilic Substitution Reaction

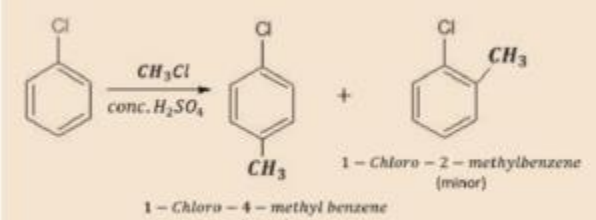
Sulphonation



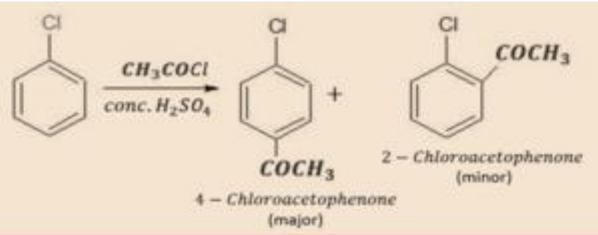
Halogenation Reaction



Nitration

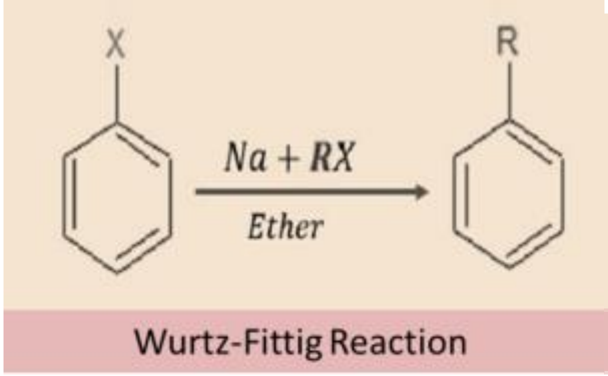


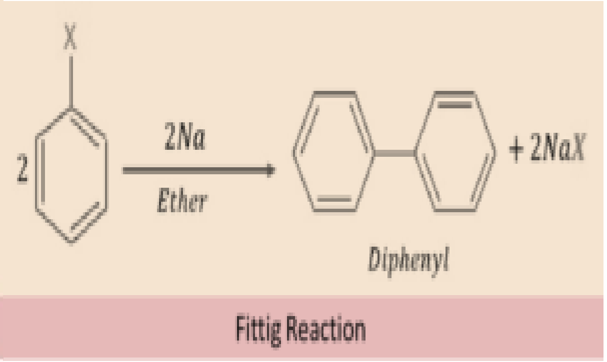
Friedel-Crafts Alkylation Reactions



Friedel-Crafts Acylation Reaction

III. Reactions with Metals

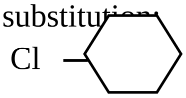


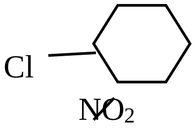


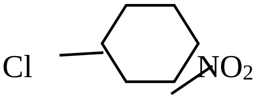
QUESTION BANK

MULTIPLE CHOICE QUESTIONS

1. Arrange the following compounds in increasing order of rate of reaction towards nucleophilic substitution:







(a) i < ii < iii (b) i < iii < ii (c) ii < i < iii (d) iii < ii < I

2. Aryl halides are less reactive toward nucleophilic substitution reaction than alkyl halides due to-
   (a) the formation of stable carbocation
   (b) Partial double bond character due to resonance
   (c) longer carbon-halogen bond
   (d) sp3 hybridised carbon attached to halogen

3. A mono haloarene is an example of __________
   a) aliphatic halogen compound
   b) side-chain substituted aryl halide
   c) alkyl halide
   d) aromatic halogen compound

4. Chlorobenzene reacts with alkyl chloride in the presence of sodium metal gives

a. tolvene b. xylene c. benzyl chloride d. phenol

5. Reaction of C_6H_5Br with aqueous sodium hydroxide follows _____ .

a. SN1 B. SN2 C. any of the above two depending upon the temperature of reaction

d. Saytzeff rule

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

a.electrophilic elimination reaction.

b.electrophilic substitution reaction.
c. nucleophillic substitution reaction.
d.free radical addition reaction

7. As the stability of carbocation formed in the first step of S_N1 reaction increases, the rate of the reaction _________
a) increases
b) decreases
c) remains same
d) may increase or decrease

8 . In haloarene compounds, halogen combines with carbon having which hybridisation?

(a) sp^2
(b) sp^3
(c) Sp
(d) dsp^2

9. In haloalkane, carbon in C-X bond possesses which partial electric charge ?
(a) Chargeless
(b) Positive
(c) Negative
(d) Anionic

10. On which of the following factors the stability of carbocation depends ?
(a) Resonance
(b) Temperature
(c) Trasition state
(d) Reaction rate

Answer 1. B,2 b,3.b,4-c,5-a,6-b,7-a,8-a,9-b,10-a.

Assertion reason

11. Assertion : p-Nitrophenol is more acidic than phenol

. Reason : Nitro group helps in the stabilization of the phenoxide ion by dispersal of negative charge due to resonance

12. Assertion (A): Boiling points of alkyl halides decreases in the order : RI>RBr>BCl>RF
Reason (R) : Attractions get stronger as the molecules get bigger in size.

13.Assertion : Inversion of configuration is observed in SN^2 Raction

Reason:- the reaction proceeds with the formation of carbocation.

14.Assertion –p-methoxy phenol is a stronger acid than p-nitrophenol

Reason:-Methoxy group shows +I effect where as nitro group shows –I effect .

15. Assertion: In mono haloarenes, further electrophilic substitution occurs at ortho and para positions.
Reason: Halogen atom is a ring deactivator.
Answer-(11-a,12-a,13-b,14-a,15-a)
Short answer type.

16. Discuss the role of Lewis acids in the preparation of aryl bromides and chlorides in the dark..

17. Although chlorine is an electron withdrawing group, yet it is *ortho*-, *para*- directing in electrophilic aromatic substitution reaction.give reason.

18. Out of C6H5 Cl and C6H5CH2-Cl,which one is more reactive towards SN1 reactions ?

19. Out of chlorobenzene and cyclohexyl chloride which one is more reactivity towards nucleophilic substitution reaction and why?

20. Give reason: The presence of –NO2 group at ortho or para position increases the reactivity of haloarenes towards nucleophilic substitution reactions.

21. What happen when? (i) Chlorobenzene is treated with $Cl2 / FeCl3$.

22Of the two bromoderivatives, C6H5CH(CH_3)Br andWhich C6H5CH(C6H5)Br which one is more reactive in SN1 substitution reaction and why?

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

24. Cyanide ion acts as an ambident nucleophile. From which end it acts as a stronger nucleophile in aqueous medium ? Give reason for your answer.

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

Answers:

Ans.16-Lewis acids are species that lack electrons. They are the ones who cause halogen molecules to undergo heterolytic fission. Lewis acid's function is to form an electrophile. The electrophile produces aryl bromides and chlorides by attacking the electron-rich benzene ring. Lewis acid's function is to form an electrophile. The electrophile produces aryl bromides and chlorides by attacking the electron-rich benzene ring.
Aryl bromides and chlorides can be prepared in the presence of Lewis acid catalysts (iron or iron chloride) from the electrophilic substitution of arenes with bromine and chlorine respectively.

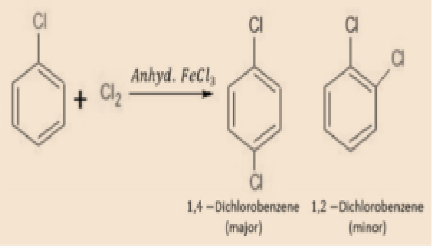
Answer17:- In Chlorobenzene, Cl imparts both electron withdrawing inductive (-I) effect and electron releasing resonance (+R) effect.

answer 18.-The rate of SN1 reaction depends upon the stability of carbocation intermediate formed during the reaction. Hence C6H5CH2Cl will react faster due to the resonance stabilisation of carbocation

ANSWER-19. Cyclohexyl chloride is more reactive towards nucleophilic substitution reaction because C—Cl bond strength is less in cyclohexyl chloride than chlorobenzene.

ANS 20..The presence of nitro group at ortho or para position increases the reactivity of haloarenes towards nucleophilic substitution because − N O 2 group, being an electron-withdrawing group decreases the electron density over the benzene ring.

Ans.21.



Halogenation Reaction

ANS.22.The carbocation obtained from II is more stabilised through resonance compared to that obtained from I. Therefore, C6H5CH(C6H5)Br is more reactive in SN1 substitution

Ans23. Iodination reactions are reversible in nature. To carry out the reaction in the forward direction, HI formed during iodination is removed by oxidation.HIO_4 is used as an oxidising agent.

Ans 24.. It acts as a stronger nucleophile from the carbon end because it will lead to the formation of C- C bond which is more stable (bond between two similar atoms) than C-N bond

Answer25:The melting point of p-dibromobenzene is higher than that of the other two compounds. This is due to the symmetry of p-dibromobenzene, which allows the molecule to fit into the crystal lattice more easily. As a result, breaking the bonds between the molecules demands a higher temperature, resulting in a higher melting poin

Short answer type :- (3 MARKS)

26. Which of the compounds will react faster in S_N1 reaction with the "OH" ion?
CH_3-CH_2-Cl or C_6H_5-CH_2-Cl

27. Write the structure of the product when chlorobenzene is treated with methyl chloride in the presence of sodium metal and dry ether.

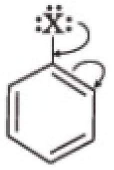
28. C-Cl bond length in chlorobenzene is shorter than C -- Cl bond length in CH_3−Cl.

29. Explain as to why haloarenes are much less reactive than haloalkenes towards nucleophilic substitution reactions.

30. Haloarenes are less reactive than haloalkanes?explain

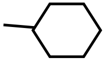
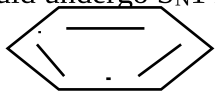
31. Why can aryl halides not be prepared by reaction of phenol with HCl in the presence of $ZnCl_2$?

32. Draw other resonance structures related to the following structure and find out whether the functional group present in the molecule is ortho, para directing or meta directing..



.

33. Which of the following compounds would undergo S_N1 reaction faster and why?

CH_2Cl  CH_2Cl — 

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

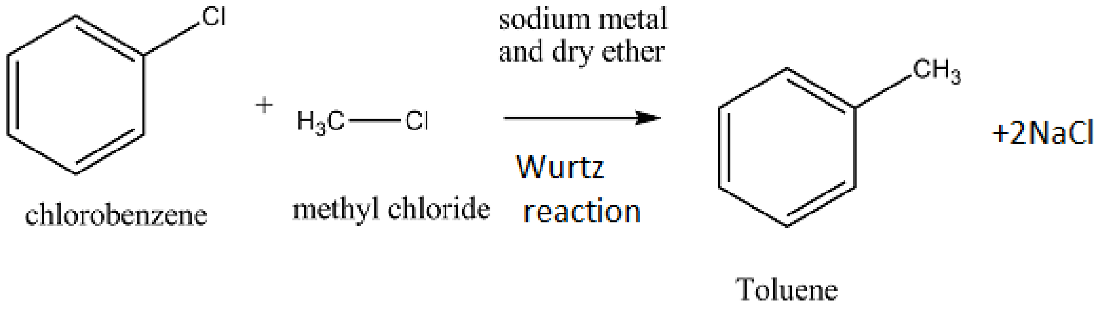
35. Discuss the nature of C-X bond in the haloarenes.

Answers:

Answer26: In the rate-determining phase of the S_N1 reaction, a carbocation intermediate is initially generated. The benzyl carbocation is resonance stabilised in benzyl chloride.

In the case of ethyl chloride or chloroethane, however, the $CH_3CH_2^+$ carbocation can only have a hyper-conjugation effect. It is less stable in comparison. As a result, in the S_N1 reaction, benzyl chloride reacts faster with the OH ion than ethyl chloride.

ANSWER.27



answer**28** Electrons on Cl in chlorobenzene take part in resonance with the benzene ring. This creates a partial double bond character between C and Cl. This does not happen in methyl chloride. A double bond is shorter than single bond.

ANS29. Haloarenes are less reactive than haloalkanes towards nucleophilic substitution due to the following reasons :

(i) Resonance effect : Due to resonance with benzene ring, there is partial double bond character in C-Cl bond. Bond cleave in haloarenes is difficult compared to that in haloalkanes.

(ii) Difference in hybridisation of carbon atom in C-X bond : Carbon attached to halogen in haloalkanes is sp3 hybridised while that in haloarene is sp2 hybridised. sp2 hybridised carbon is more electronegative because of greater s character, it holds the electrons more tightly, giving less charge to halogen.

(iii) It is difficult for electron rich nucleophiles to approach electron rich benzene ring in haloarenes.

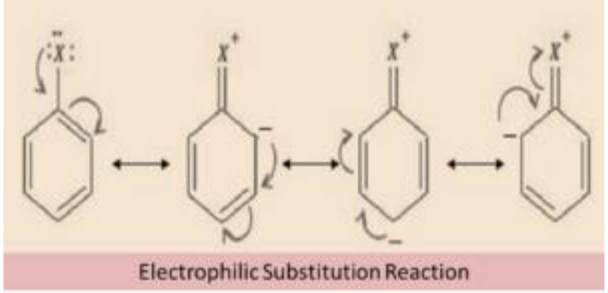
Answer30:Polarity of the carbon-halogen bond- As we all know, the higher the polarity, the higher the reactivity. The dipole moment of the C-X bond in haloarenes is less than that of the haloalkane (for example, the dipole moment for C-X in haloalkane is 2.0-2.2D while the dipole moment for chlorobenzene is 1.7D), hence the higher the polarity of the haloalkane, the more reactive it is.Haloarenes are in the sp^2 hybridisation state, whereas haloalkanes are in the sp^3 hybridisation state. Because the bond length in the sp^2 hybridisation is shorter than in the sp^3 hybridisation, the bond generated by the haloarenes is stronger than the haloalkane bond. so the haloarenes are less reactive.

The electron of the benzene ring is in combination with the electron pair of the halogen in the haloarenes, resulting in resonance stabilisation. As a result of the resonance hybrid nature of haloarenes, the C-X bond possesses a partial double bond character, making the haloarene more stable and less reactive.

Answer31: When an alkyl halide is formed, a carbocation is formed, which then interacts with HCl to generate an alkyl halide.

However, in order for aryl halide to react with HCl in the presence of $ZnCl_2$, phenyl carbocation formation must occur, which is impossible because it is a highly unstable structure that never occurs in its free state. As a result, no aryl halide is generated.

ANSWER.32 Resonance in halobenzene.



Because electron density is higher at ortho and para locations, the functional groups contained in these compounds are ortho-para directed.

Answer33: Compound (B) Undergoes S_N1 reaction faster than (A) because in case of (B), the carbocation formed after the loss of Cl^- is stabilised by resonance, whereas, no such stabilisation is possible in the carbocation obtained from (A)
Answer34: Allyl chloride has a high reactivity because the carbocation generated by hydrolysis is stabilised by resonance, whereas n-propyl chloride has no such stabilisation.Because n-propyl chloride does not undergo ionisation to form n-propyl carbocation, allyl chloride is more easily hydrolyzed than n-propyl chloride

Answer35: The carbon of benzene is linked to the halogen in haloarenes. The electronegativity of halogen is higher than that of the benzene ring's sp2 hybridised carbon. As a result, the C- X bond is a polar bond. Aside from that, the halogen atom's lone pair of electrons are engaged in the benzene ring's resonance. As a result, this C- X bond now has a partial bond character.Haloarenes' C-X bond is less polar than haloalkanes' C-X bond. The fact that the dipole moment of chlorobenzene (= 1.69 D) is slightly lower than that of CH_3CI (= 1.83 D) supports this.

Case study based question:-
36. **Read the passage given below and answer the following questions:**

Nucleophilic substitution reactions are of two types; substitution nucleophilic bimolecular (S_N2) and substitution nucleophilic unimolecular (S_N1) depending on molecules taking part in determining the rate of reaction. Reactivity of alkyl halide towards S_N1 and S_N2 reactions depends on various factors such as steric hindrance, stability of intermediate or transition state and polarity of solvent. S_N2 reaction mechanism is favoured mostly by primary alkyl halide or transition state and polarity of solvent, S_N2 reaction mechanism is favoured mostly by primary alkyl halide then secondary and then tertiary. This order is reversed in case of SN1 reactions.

The following questions are multiple choice question. Choose the most appropriate answer:
(i) Which of the following is most reactive towards nucleophilic substitution reaction?
(a) C_6H_5Cl
(b) $CH_2=CHCl$
(c) $ClCH_2CH=CH_2$
(d) $CH_3CH=CHCl$
(ii) Isopropyl chloride undergoes hydrolysis by
(a) S_N1 mechanism

(b) S_N2 mechanism
(c) S_N1 and S_N2 mechanism
(d) neither S_N1 nor S_N2 mechanism

(iii) The most reactive nucleophile among the following is
(a) CH_3O-
(b) C_6H_5O-
(c) $(CH_3)_2CHO$-
(d) $(CH_3)_3CO$-

(iv) Tertiary alkyl halides are practically inert to substitution by S_N2 mechanism because of
(a) insolubility
(b) instability
(c) inductive effect
(d) steric hindrance

OR

Which of the following is the correct order of decreasing S_N2 reactivity?
(a) $RCH_2X > R_2CHX > R_3CX$
(b) $R_3CX > R_2CHX > RCH_2X$
(c) $R_2CHX > R_3CX > RCH_2X$
(d) $RCH_2X > R_3CX > R_2CHX$

37. Larger the number of alkyl groups at alpha-carbon atom, more is the steric hindrance and hence lesser the reactivity towards SN2 mechanism.halogen acids, phosphorus halides or thionyl chloride. Thionyl chloride is preferred because in this reaction alkyl halide is formed along with gases SO_2 and HCl. The two gaseous products are escapable, hence, the reaction gives pure alkyl halides. The reactions of primary and secondary alcohols with HCl require the presence of a catalyst, $ZnCl_2$. With tertiary alcohols, the reaction is conducted by simply shaking the alcohol with concentrated HCl at room temperature. Constant boiling with HBr (48%) is used for preparing alkyl bromide. Good yields of R- I may be obtained by heating alcohols with sodium or potassium iodide in 95%orthophosphoric acid. The order of reactivity of alcohols with a given haloacid is 3◦>2◦>1◦ . Phosphorus tribromide and triiodide are usually generated in situ (produced in the reaction mixture) by the reaction of red phosphorus with bromine and iodine respectively.

A.Name the reagents that can be used for halogenation of alcohols.
B. Which catalyst is required when we prepare halogen compounds using concentrated HCI?
C. H ow are PBr3 and PI3 prepared for halogenating the hydroxyl group of alcohols ?
D. Give the reactivity order of alcohols in halogenation using a haloacid

38. **READ THE PASSAGE GIVEN BELOW AND ANSWER THE FOLLOWING QUESTIONS:**

ALKYL/ARYL HALIDES MAY BE CLASSIFIED AS MONO, DI OR POLYHALOGEN COMPOUNDS DEPENDING ON ONE, TWO OR MORE HALOGEN ATOMS IN THEIR STRUCTURES. ALKYL HALIDES ARE PREPARED BY FREE RADICAL HALOGENATION OF ALKANES, ADDITION OF HALOGEN ACIDS TO ALKENES AND REPLACEMENT OF –OH GROUP OF ALCOHOLS WITH HALOGENS USING PHOSPHORUS HALIDES, THIONYL CHLORIDE OR HALOGEN ACIDS. ARYL HALIDES ARE PREPARED BY ELECTROPHILIC SUBSTITUTION TO ARENES.

Q. NAME THE MAJOR MONOHALO PRODUCT OF THE FOLLOWING REACTION:

C 6H11OH † $SOCl_2$ ---□

2. **Aryl halides are formed by arenens through**
   (a) nucleophillic substitution (b) electrophillic substitution
   © elimination reaction (d) none
3. formation of haloarenes from benzene takes place through -------------

39. **Read the passage given below and answer the following questions:**

Aryl halides are extremely less reactive towards nucleophilic substitution reactions due to the following reasons:

(i) In haloarenes, the electron pairs on halogen atom are in conjugation with π-electrons of the ring.

(ii) In haloalkane, the carbon atom attached to halogen is sp^3 hybridised while in case of haloarene, the carbon atom attached to halogen is sp^2 -hybridised.

(iii) In case of haloarenes, the phenyl cation formed as a result of self-ionisation will not be stabilised by resonance.

Q.(a) Which of the following alkyl halides will undergoes S_N1 reaction most readily?

- A.$(CH_3)_3C$—F

● B.$(CH_3)_3C$—Cl

○ C.$(CH_3)_3C$—Br

○ D.$(CH_3)_3C$—I

○ **Q. (b)Reaction of $C_6H_5CH_2Br$ with aqueous sodium hydroxide follows _______.**

- A.S_N1 mechanism

● B.S_N2 mechanism

○ C.Any of the above two depending upon the temperature of reaction

○ D Saytzeff rule.

○ **Q.(c) A primary alkyl halide would prefer to undergo ________.**

- A.S_N1 reaction ○
- B.S_N2 reaction

○ C.α-Elimination

● D.Racemisation

Answers36(i) (c) Allylic chlorides are most reactive.
(ii) c
(iii) a
(iv) d
or
(a)

Ans.37 A. Concentrated halogen acid, phosphorus halides and thionyl chloride.
B.$ZnCl_2$
C. These are obtained in situ by the reaction between red phosphorus and the halogen.
D.$3^0>2^0>1^0$

Answer 38.(i) Answer- chlorocyclohexane(ii) b(iii)halogenations

Answer 39. (A) $(CH)_3$C-I being a tertiary alkyl halide will most readily undergo S_N1 reaction.
(B) C_6H_5-CH_2 is stable cation so favours the progress of reaction by S_N1 mechanism

(C)SN2 reaction

Long answer type question:-
40. why aryl halides are less reactive in nucleophillic substitution?give reason

41.complete following reactions
(a)chlorobenzene to biphenyl
(B)chlorobenzene to 2-acetophenone
(c)chlorobenzene to tolvene
d)chlorobenzene to 1,2-dichlorobenzene
e)chlorobenzene to 1-chlro-2-nitrobenzene

42.(a)complete following reaction;-
C6H5Br-----Mg(dry ether)--□A------CO2/H30$^+$-□B-------PCl5---□c

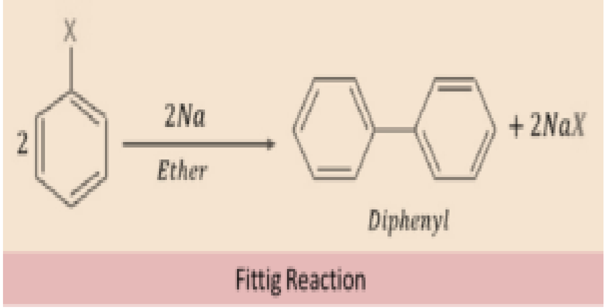
42 b) Chlorobenzene and Benzyl chloride

43.Although chlorine is an electron withdrawing group,it is ortho-para directing in an electrophillic aromatic substitution reaction ,explain.
Answer40: Because of the following reasons, aryl halides are less reactive in nucleophilic substitution reactions.

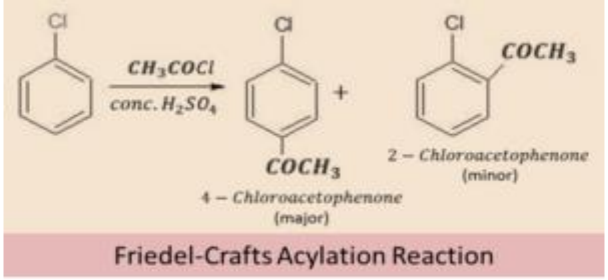
- The lone pair of electrons on the halogen are in resonance with the benzene ring in haloarenes. As a result, the C-Cl bond gains a partial double bond character, which strengthens the bond. As a result, they have a lower reactivity to nucleophilic substitution reactions.

- The carbon atom linked to the halogen is sp^2 hybridised in haloarenes. Compared to sp^3 hybridised carbon, sp^2 hybridised carbon is more electronegative. In haloarenes, the sp^2-hybridised carbon can retain the electron pair of the C-X bond more tightly, making the C-CI link shorter than the C-Cl bond in haloalkanes.
- Because a shorter bond is more difficult to break than a longer connection, haloarenes are less reactive than haloarenes.
- The phenyl cation will not be stabilised by resonance in haloarenes, hence the S_N1 mechanism is ruled out (iv) Because the nucleaphile and electron-rich arenes repel each other, aryl halides are less reactive than alkyl halides.

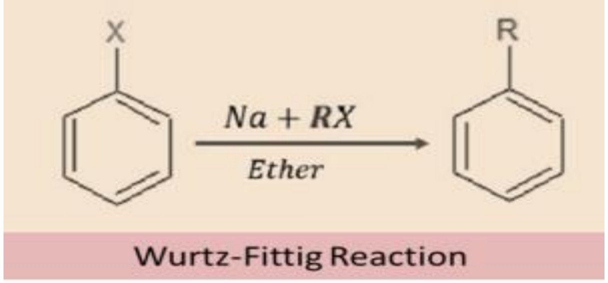
When an electron withdrawing group (NO_2) is present at the ortho and para positions, the reactivity of aryl halides can be increased. The presence of this electron withdrawing group at the above-mentioned location causes the benzene ring to lose electron density. As a result, the nucleophile will have an easier time attacking. Carbocation is produced as a result of resonance. The electron density is clearly higher at the ortho and para locations. As a result, the presence of EWG facilitates nucleophilic at ortho and para locations but not at metaL.



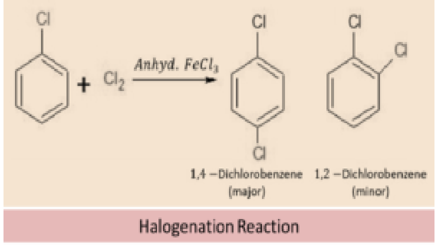
Ans.41 (i) Chlorobenzene to biphenyl
(ii) Chlorobenzene to 2-chloroacetophenone



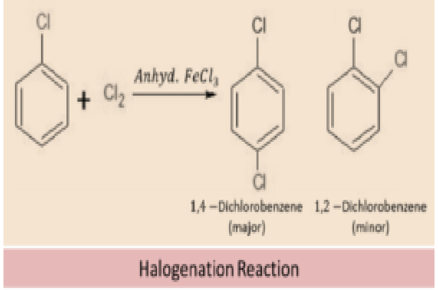
(iii) chlrobenzene to tolvene



(iv) chlrorbenzene to 1,2- dichlorobenzene



(v)chlorobenzene to 1-chloro-2-nitrobenzene



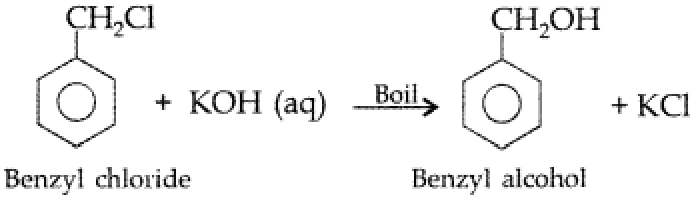
ANSWER 42 (a) C6H5Br-----Mg(dry ether)--□A------CO2/H30$^+$-□B-------PCl5---□c

$$C_6H_5Br \xrightarrow[\text{dry ether}]{Mg} \underset{\textbf{(A)}}{C_6H_5MgBr} \xrightarrow[(b)\ H_3O^-]{(a)\ CO_2} \underset{\textbf{(B)}}{C_6H_5COOH} \xrightarrow{PCl_5} \underset{\textbf{(C)}}{C_6H_5COCl}$$

A = Phenylmagnesium bromide
B = Benzoic acid
C = Benzoyl chloride

.

ANSWER 42(b) Chlorobenzene and Benzyl chloride: Benzyl chloride is more reactive than chlorobenzene towards nucleophillic substitution reactions, therefore, benzyl chloride on boiling with aqueous KOH produces benzyl alcohol and KCI.



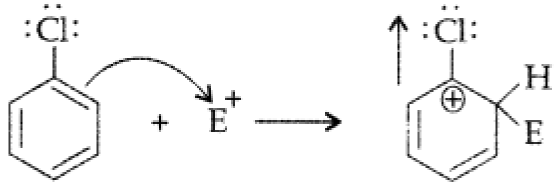
The reaction mixture on acidification with dil. HNO_3 followed by treatment with $AgNO_3$ solution produces white ppt. of AgCl due to formation of KCl

$$KCl + AgNO_3 \longrightarrow \underset{\text{white ppt.}}{AgCl\downarrow} + KNO_3$$

But chlorobenzene does not undergo hydrolysis under these mild conditions to give phenol and KCl.

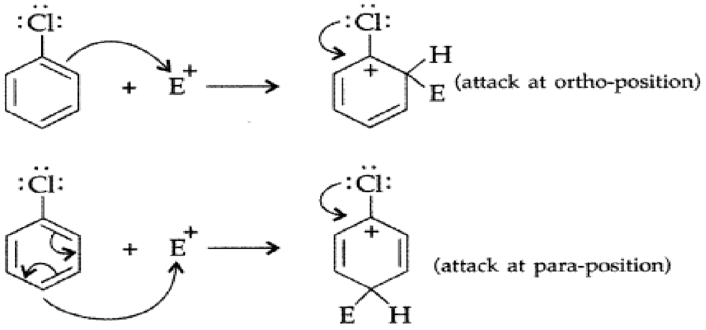
Answer 43: Chlorine withdraws electrons through inductive effect and releases through resonance. Although

Cl shows -1 effect but through resonance, Cl tends to stabilize the intermediate carbocation and the effect is more pronounced at ortho and para positions.



Inductive effect destabilises intermediate carbocation

This can also be explained diagramatically as:



(Resonance effect stabilises the intermediate carbocation)

ASSIGNMENT WORK

CLASS XII

TOPIC: Uses and environmental effects of - dichloromethane, trichloromethane, tetrachloromethane, iodoform, freons, DDT.

SECTION A

1.The IUPAC name of chloroform is –

a) Chloromethane b) Dichloromethane

c) Trichloromethane d) Carbon tetrachloride

2. The chloro compound which can be used as fire extinguisher is—

a) $CHCl_3$ b) CH_3Cl

c) $COCl_2$ d) CCl_4

3. Exposure to lower levels of a compound in air can lead to slightly impaired hearing and vision. Identify the compound—

a) Chloroform b) Chloromethane

c) Carbon tetrachloride d) Methylene chloride

4. Which among the following is true—

a) Freon does not initiate radical chain reactions in stratosphere.

b) Iodoform initiate radical chain reactions in stratosphere.

c) Freon initiate radical chain reactions in stratosphere.

d) Chloroform initiate radical chain reactions in stratosphere.

5. The antiseptic properties of iodoform is due to which of the following—

a) Liberation of iodine b) Colour of ioform

c) Smell of iodoform d) None of the above

6. Which of the following is not a use of methylene chloride?

a) Paint removal b) Propellant in aerosols

c) Metal cleaning d) Antiseptic

7. The oxidation of trichloromethane results in the formation of a poisonous gas called ________---

a) carbon monoxide b) carbonyl chloride

c) hydrogen sulphide d) phosphine

8. Which of the following is not a freon?

a) CCl_3F b) CCl_2F_2

c) CBr_2F_2 d) $CClF_3$

9. Freon 12 is manufactured from the Swarts reaction of which compound?

a) Dichloromethane b) Trichloromethane

c) Tetrachloromethane d) Dichlorodifluoromethane

10. Which of the following is not a characteristic of $CHClF_2$?

a) Non-toxic b) Non-flammable

c) Non-corrosive d) Non-liquefiable

11. Which of the following is not a harmful effect of DDT?

a) It is non-biodegradable b) Cannot be metabolized by animals

c) Highly toxic towards fish d) Causes air pollution

12. Which of the following is not a use of carbon tetrachloride?

a) Manufacturing of refrigerants b) Manufacturing of pharmaceuticals

c) Degreasing agent d) Insecticide

13. Which of the following is used as refrigerant—

a) CCl_2F_2 b) CCl_4

c) CF_4 d) Acetone

14. Full form of DDT—

a) 1,1,- trichloro-2.2-bis(p-chlorophenyl) ethane

b) 1,1-dichloro-2.2-diphenyl trimethylethane.

c) 1,1-dichloro-2.2-diphenyl trichloroethane

d) none of the above

15. Which are the harmful effects of methylene chloride—

a) skin burning b) dizziness, nausea, tingling

c) impaired hearing and vision d) all of these.

SECTION B

1.Give one use of the following—

A) Freon -12 b)DDT

2.Why is chloroform kept in dark bottles?

3.Why are freons used as coolants in air conditioners?

4. At room temperature ethyl chloride is gas whereas ethyl iodide is liquid .Explain?

5.What are the uses of chloromethane?

6.What are the environmental effects of dichloromethane?

7.What are the medicinal uses of iodoform?

8.What are the important polyhalogen compounds?

9.What are the harmful effects of polyhalogen compounds?

10.Why fluorine does not form polyhalide?

SECTION C

1.Give uses of the following—

a) Freon-12 b) DDT c) Chloroform

2. Describe the uses of chloroform in the medical field and industry.

3. Explain the role of carbon tetrachloride in fire extinguishers and its use as a solvent.

4.What are the applications of chlorofluorocarbons in various industries?

5.Discuss the environmental impact of CFCs on the ozone layer.

6.How does CCl_4 contribute to environmental pollution and health hazards?

7.Describe the role of iodoform in the manufacture of disinfectants.

8.Discuss the impact of iodoform on human health and the environment when released into water bodies.

9.What are the primary uses of dichloromethane in industry and research?

10.Discuss the health hazards associated with prolonged exposure to DDT.

SECTION D

1.Case 1-Industrial use of Carbon Tetrachloride

An industrial facility uses carbon tetrachloride as a solvent in its cleaning processes. Recently there have been concerns about the health and environmental impacts of CCl_4.

a) What is the primary use of carbon tetrachloride in industries?

b) What health hazards can be seen with exposure to carbon tetrachloride?

c) Suggest alternative solvents that could be used to reduce the hazards of CCl_4.

2.Case 2—Environmental concerns with chlorofluorocarbons

A country is evaluating the use of CFCs in refrigeration and aerosol products due to their environmental impact particularly on the ozone layer.

a) Discuss the health consequencies of increased UV radiation due to ozone layer depletion.

b) What alternatives to CFCs can be used in refrigeration and aerosol products to mitigate environmental impact?

C) How CFCs contribute to ozone layer depletion?

3. Case 3—Agricultural use of DDT

A farming community has been using DDT extensively to control pests on their crops. Recently concerns have been raised about the potential environmental and health impacts of DDT.

a) What were the benefits of using DDT in agriculture?

b) Discuss the environmental consequencies of extensive DDT use in agriculture.

c) What are the health risks associated with indoor exposure to DDT?

4.Case 4—Iodoform in medical use

A small clinic uses Iodoform to treat wounds and infections. Recently the clinic has faced issues regarding the safety and effectiveness of iodoform.

a) Discuss the antiseptic properties of iodoform .

b) What are the side effects of the use of iodoform?

c) What can be safer alternatives to iodoform for wound treatment?

SECTION E

1.Discuss the industrial uses and environmental effects of CFCs.
2. Describe the applications of DDT and its effects on the environment.
3. Outline the uses of chloroform and its impact on the environment and human health.
4. Describe the uses of iodoform (CHI3) and its environmental and health effects.
5. Describe the properties, industrial uses , environmental and health impacts of dichloromethane.

ANSWER KEY

SECTION A

1. c
2. d
3. d
4. c
5. a
6. d
7. b
8. c
9. c
10. d
11. d
12. d
13. a
14. a
15. D

SECTION B

1.a) Freon-12, also known as dichlorodifluoromethane (CCl_2F_2), was commonly used as a refrigerant in older refrigeration and air conditioning systems. Its primary use was in household refrigerators, freezers, and automotive air conditioning units.

b) One use of DDT (dichlorodiphenyltrichloroethane) was as an insecticide to control malaria, typhus, and other insect-borne diseases. It was particularly effective in combating mosquitoes.

2. Chloroform is kept in dark bottles to prevent it from undergoing photodegradation. When exposed to light, chloroform can slowly decompose into phosgene, a highly toxic and corrosive gas. Therefore, storing chloroform in dark bottles helps to minimize this decomposition reaction and maintain its stability and safety over time.

3. Freons, such as Freon-12 (dichlorodifluoromethane) and other similar compounds, were historically used as coolants in air conditioners and refrigeration systems for several reasons:

a.Efficient Heat Transfer: Freons have excellent heat transfer properties, which means they can effectively absorb heat from the surrounding environment (such as inside a refrigerator or room) when they evaporate.

b.Chemical Stability: Freons are chemically stable under normal operating conditions, which allows them to cycle through the refrigeration system without breaking down easily.

c.Non-Flammable: Freons are non-flammable, which enhances their safety in case of leaks or malfunctions within the refrigeration system.

d.Low Toxicity: Most Freons have low toxicity levels when used in controlled environments, making them relatively safe for use in household and commercial applications.

4. The difference in physical state (gas versus liquid) of ethyl chloride and ethyl iodide at room temperature is primarily due to differences in their molecular structures and intermolecular forces. Ethyl chloridehas a smaller molecular size and lower molecular mass(64.5 g/mol) compared to ethyl iodide(155.0 g/mol). Ethyl chloride molecules are held together primarily by weaker van der Waals forces and dipole-dipole interactions.allowing ethyl chloride to exist as a gas at room temperature. In contrast, ethyl iodide molecules are larger and heavier, and they experience stronger van der Waals forces (including London dispersion forces) due to the larger and more polarizable iodine atom. These stronger intermolecular forces lead to greater molecular cohesion and stability, causing ethyl iodide to exist as a liquid at room temperature.

5. Chloromethane, also known as methyl chloride (CH_3Cl), has several industrial and commercial uses:
a) Chemical Intermediate: Chloromethane is used as a chemical intermediate in the production of various chemicals, including silicones, methyl cellulose, and quaternary ammonium compounds.

b) Solvent: It is used as a solvent in industrial applications, particularly in the production of pharmaceuticals and pesticides.

c) Refrigerant: Chloromethane has been used as a refrigerant in the past, although its use has diminished due to environmental concerns.

d) Methylating Agent: It is used as a methylating agent in organic synthesis, where it can introduce methyl groups into molecules.

e) Extractive Agent: Chloromethane is used in the extraction of oils, resins, and waxes from natural products.

f) Aerosol Propellant: It has been used as a propellant in aerosol products, although this use is less common today due to environmental regulations.

g) Laboratory Reagent: Chloromethane is used in laboratories as a reagent for various chemical reactions and processes

6. Dichloromethane (DCM), also known as methylene chloride, has several environmental effects:

a) Air Quality: DCM is volatile and is used as a solvent. In the atmosphere, it contributes to photochemical smog formation. Breathing in high concentrations of DCM vapor can cause respiratory irritation and central nervous system effects in humans.

b) Water Quality: DCM is moderately soluble in water and can contaminate groundwater and surface water through industrial discharges, improper disposal, and spills. In aquatic environments, DCM can accumulate in sediments and organisms.

c) Ozone Depletion: While DCM itself does not deplete the ozone layer directly, it can break down in the atmosphere to release chlorine atoms. These chlorine atoms can then participate in reactions that contribute to ozone depletion. However, DCM's ozone-depleting potential is much lower compared to CFCs and halons.

d) Global Warming Potential: It contributes to global warming as a greenhouse gas. Its impact is much less than substances like carbon dioxide or methane.

e) Ecological Impact: DCM can be toxic to aquatic organisms, especially in high concentrations. Chronic exposure to low levels of DCM can also impact aquatic ecosystems.

7. Iodoform (CHI3) has limited direct medicinal uses today due to its toxicity and potential for systemic absorption leading to adverse effects. However, historically, iodoform was used in medicine for several purposes:

a) Antiseptic: Iodoform was used as an antiseptic due to its ability to release iodine slowly. It was applied to wounds and surgical incisions to prevent infection.

b) Dressing: It was used as a component in medicated dressings for wounds.

c) Packing Material: Iodoform-soaked gauze or other materials were used as packing material in surgical cavities to promote healing and prevent infection.
d) Topical Antifungal: In dermatology, iodoform was sometimes used in combination with other ingredients as a topical treatment for fungal infections.

8. Polyhalogen compounds are chemical compounds that contain more than one halogen atom per molecule. Some important polyhalogen compounds include:
a) Dichlorodifluoromethane (Freon-12, CCl_2F_2): Historically used as a refrigerant and propellant, but phased out due to its ozone-depleting properties.
b) Carbon Tetrachloride (CCl_4): Used in the past as a solvent and fire extinguisher, but its use has declined due to its toxicity and environmental concerns.
c) Dichloromethane (Methylene chloride, CH_2Cl_2): Used as a solvent in various industrial processes and as a paint stripper. It is volatile and can contribute to air pollution..
d) Trichlorofluoromethane (Freon-11, CCl_3F): Used as a refrigerant and propellant, but also phased out due to ozone depletion.
e) Chloroform ($CHCl_3$): Historically used as an anesthetic and solvent. It has been largely replaced due to its toxicity and potential health risks.

9.Polyhalogen compounds can have significant harmful effects on human health and the environment due to their Toxicity,Environmental Persistence,Ozone layer Depletion,.Contribution to Climate Change,Groundwater Contamination.

10. The combination of fluorine's strong bonding tendencies, high electronegativity, small atomic size, and high reactivity limits its ability to form stable polyhalide compounds compared to other halogens. While there are a few examples of fluorine-containing polyhalides under specific conditions, they are generally less common and less stable than polyhalides involving other halogens.

SECTION C

1.a)Freon-12 (Dichlorodifluoromethane, CCl_2F_2): Freon-12 was commonly used as a refrigerant in household refrigerators and air conditioning systems due to its effective heat transfer properties. It helped in maintaining cool temperatures inside appliances and ensuring efficient cooling.
b).DDT (Dichloro-diphenyl-trichloroethane): DDT was widely used as an insecticide to control diseases such as malaria and typhus by targeting mosquitoes and other disease-carrying insects.

c).Chloroform ($CHCl_3$): Chloroform was used as an anesthetic agent in medical procedures. It was valued for its ability to induce temporary unconsciousness during surgical operations before the development of more modern anesthetics.

2. Chloroform ($CHCl_3$) has had various uses in both the medical field and industry, though many of these applications have decreased or been discontinued due to its toxicity and potential health risks.

Medical Uses:

a) Anesthetic: Chloroform was used as a general anesthetic in surgery. It was administered by inhalation to induce unconsciousness and loss of sensation during surgical procedures.

b) Labor Analgesia: Chloroform was sometimes used for pain relief during labor and childbirth.

Industrial Uses:

a) Solvent: Chloroform was used extensively as a solvent in various industrial processes, as it can dissolve a wide range of substances, including fats, oils, resins, and alkaloids.

b) Production of Pharmaceuticals: Chloroform was used in the production of some pharmaceuticals, particularly for extracting and purifying active ingredients from plant materials or chemical synthesis processes.

3. Carbon tetrachloride (CCl_4) has been used in fire extinguishers and as a solvent, although its use has declined significantly due to health and environmental concerns.

Role in Fire Extinguishers:

a) Chemical Fire Extinguisher: Carbon tetrachloride was used in fire extinguishers for extinguishing small fires in homes, offices, and industrial settings.

b) Mechanism of Action: When sprayed onto a fire, carbon tetrachloride vaporizes quickly and displaces oxygen near the flames, effectively smothering the fire. It also inhibits the chemical reactions that sustain combustion.

c) Safety Concerns: Despite its effectiveness, the use of carbon tetrachloride in fire extinguishers declined due to safety concerns. Carbon tetrachloride vapor is toxic when inhaled, and exposure can lead to serious health effects, including liver damage, kidney damage, and neurological problems. Inhalation of carbon tetrachloride vapor in firefighting situations posed significant risks to firefighters and bystanders.

Use as a Solvent:

a) Industrial Solvent: Carbon tetrachloride was widely used as a solvent in various industrial processes, particularly for cleaning and degreasing metal parts, as well as in the production of certain chemicals.

b) Chemical Reactions: It was also used as a solvent for chemical reactions, especially in laboratories and chemical manufacturing processes where a non-polar solvent was required.

4. Chlorofluorocarbons (CFCs) have chemical stability, non-flammability, and low toxicity. However, their use reduced or phased out due to their detrimental effects on the ozone layer.

1. Refrigeration and Air Conditioning:
   - CFCs, such as CFC-12 (dichlorodifluoromethane) and CFC-11 (trichlorofluoromethane), were widely used as refrigerants in air conditioning units, refrigerators, and freezers. They have thermodynamic properties and stability.
2. Foam Blowing Agents:
   - CFCs were used as blowing agents in the production of foam insulation and packaging materials. They helped create lightweight and insulating foams used in construction, appliances, and packaging.
3. Propellants:
   - CFCs were used as propellants in aerosol cans for products such as hairsprays, deodorants, and insecticides. They allowed these products to be dispensed as fine mists or sprays.
4. Solvents:
   - Some CFCs were used as solvents in industrial cleaning applications, particularly in electronics manufacturing and precision cleaning processes due to their chemical stability and low flammability.

5. Chlorofluorocarbons (CFCs) have had a profound and detrimental impact on the ozone layer in the Earth's stratosphere.

Mechanism of Ozone Depletion:

1. Release into the Atmosphere:
   - CFCs are stable compounds that were widely used in refrigeration, air conditioning, foam blowing agents, aerosol propellants, and other industrial applications. When released into the atmosphere through leaks, improper disposal, or during use, CFCs eventually reach the stratosphere.
2. Breakdown and Release of Chlorine:
   - In the stratosphere, CFC molecules are broken down by ultraviolet (UV) radiation from the sun. This breakdown releases chlorine atoms (Cl•) from the CFC molecules.
3. Reaction with Ozone (O3):
   - Chlorine atoms are highly reactive and can catalytically destroy ozone (O3) molecules. A single chlorine atom can destroy thousands of ozone molecules in a chain reaction:
     - $Cl\bullet + O_3 \rightarrow ClO\bullet + O_2$

    - ClO• + O → Cl• + O_2
  - The net result is a reduction in the amount of ozone in the stratosphere, leading to the formation of an ozone hole or thinning of the ozone layer.

Environmental Impact:

1. Increased UV Radiation:
   - Ozone depletion allows more harmful ultraviolet-B (UV-B) and ultraviolet-C (UV-C) radiation to reach the Earth's surface. UV radiation is known to cause skin cancer, cataracts, and immune suppression in humans. It can also harm marine ecosystems, including phytoplankton, which form the base of the marine food chain.
2. Climate Change:
   - The stratospheric ozone layer plays a role in regulating the Earth's temperature. Ozone depletion can indirectly affect climate by altering atmospheric circulation patterns and influencing the distribution of greenhouse gases in the atmosphere.
3. Effects on Plants and Animals:
   - Increased UV radiation can damage plant tissues, leading to reduced crop yields and changes in plant ecosystems. It can also harm aquatic organisms, such as fish larvae and amphibians, that are sensitive to UV exposure.
   -

6. Carbon tetrachloride (CCl_4) contributes to environmental pollution and poses significant health hazards .

Environmental Pollution:

1. Air Pollution:
   - CCl_4 can be released into the atmosphere during industrial processes, improper disposal, or accidental spills and can contribute to air pollution.
   - CCl_4 is a volatile organic compound contributing to the formation of ground-level ozone (smog) and other secondary pollutants.
2. Ozone Depletion:

CCl_4 can break down in the upper atmosphere (stratosphere) to release chlorine atoms. These chlorine atoms can catalytically destroy ozone molecules, contributing to ozone depletion.

3. Greenhouse Gas:
   - CCl_4 is classified as a greenhouse gas leading to potential climate change impacts.
4. Groundwater Contamination:
   - CCl_4 is highly soluble in water and can contaminate groundwater if released into the environment.

Health Hazards:

1. Toxicity:
    - CCl4 is toxic to humans and animals. Inhalation of CCl4 can lead to acute health effects, including headache, dizziness, nausea, liver and kidney damage, and central nervous system depression.
    - Long-term exposure to CCl4 cause liver disease, kidney disease, and neurological disorders.
2. Carcinogenicity:

CCl4 may be carcinogenic to humans. Long-term exposure to CCl4 has been associated with an increased risk of developing liver cancer.

3. Reproductive and Developmental Effects:
    - Exposure to CCl4 has been linked to reproductive and developmental toxicity in animals. It may interfere with reproductive function and fetal development in humans.

7.Iodoform (CHI3) has played a role in the manufacture of disinfectants, primarily due to its antiseptic properties.

Antiseptic Properties:

1. Antimicrobial Activity:
    - Iodoform possesses broad-spectrum antimicrobial activity. It is effective against bacteria, fungi, and some viruses.
    - Its mechanism of action involves releasing iodine slowly when in contact with moisture, which acts as a potent germicide.
2. Wound Healing:
    - Iodoform has been used in disinfectant formulations for wound care. It helps prevent infections in cuts, abrasions, and surgical wounds by killing or inhibiting the growth of microorganisms.

8. Iodoform (CHI3) can have significant impacts on human health and the environment if released into water bodies.

Human Health Impact:

1. Toxicity:
    - Iodoform is considered toxic if ingested, inhaled, or absorbed through the skin in significant quantities. Acute exposure can cause irritation to the respiratory system and skin, nausea, vomiting, and headache.
    - Chronic exposure to iodoform may lead to more serious health effects, including liver and kidney damage, central nervous system effects, and potential reproductive or developmental toxicity.
2. Bioaccumulation:
    - While iodoform itself does not bioaccumulate significantly in aquatic organisms, its breakdown products and metabolites may accumulate in organisms over time, potentially affecting higher trophic levels in aquatic food chains.

Environmental Impact:

1. Persistence and Transformation:
    - Iodoform can persist in water bodies for a period due to its stability. It may undergo slow degradation, releasing iodine ions into the aquatic environment. These iodine ions can have ecological effects, although they are generally less harmful than the parent compound.
2. Ecological Effects:
    - Direct exposure to iodoform can be toxic to aquatic organisms, such as fish and invertebrates, particularly in high concentrations. It may interfere with their respiratory and metabolic processes.

- Indirect effects may occur through the disruption of aquatic ecosystems, impacting biodiversity and ecosystem functions.

9. Dichloromethane (CH_2Cl_2), also known as methylene chloride, is a versatile solvent with several primary uses in both industry and research settings. Here are its main applications:

Industrial Uses:

1. Paint and Coating Removal:
    - Dichloromethane is widely used as a solvent for removing paint, varnish, and other coatings from surfaces. Its ability to dissolve a wide range of organic compounds makes it effective for stripping paint from metals, plastics, and wood.
2. Adhesive Production:
    - In the manufacturing of adhesives , dichloromethane serves as a solvent to dissolve and mix various ingredients. It helps achieve desired viscosity and ensures uniform application and bonding properties.
3. Extraction Solvent:
    - Dichloromethane is used as an extraction solvent in the pharmaceutical, food, and fragrance industries. It can extract compounds from natural products and botanicals, such as flavors, fragrances, and active pharmaceutical ingredients (APIs).
4. Chemical Synthesis:
    - It is employed in chemical synthesis processes, particularly for reactions where a highly polar or non-polar solvent is required. Dichloromethane's properties make it suitable for facilitating reactions and separating reaction products.

Research Uses:

1. Laboratory Solvent:
    - Dichloromethane is widely used as a solvent in laboratory research across various scientific disciplines, including chemistry, biochemistry, and environmental science. It is valued for its ability to dissolve both polar and non-polar compounds, facilitating the preparation and analysis of samples.
2. Chromatography:
    - In chromatographic techniques, such as thin-layer chromatography (TLC) and liquid chromatography (LC), dichloromethane is used as a mobile phase solvent or in preparing solvent mixtures. It aids in separating and analyzing components of complex mixtures.
3. Spectroscopy:
    - In spectroscopic analyses, dichloromethane can serve as a solvent for preparing samples for infrared spectroscopy (IR), nuclear magnetic resonance (NMR), and mass spectrometry (MS). Its low volatility and compatibility with analytical instruments make it useful in sample preparation

10. DDT (Dichloro-diphenyl-trichloroethane) is a pesticide. Here are the health hazards associated with prolonged exposure to DDT:

Health Hazards:

1. Carcinogenicity:
    - Prolonged exposure to DDT has been associated with an increased risk of certain cancers, including liver cancer and breast cancer.
2. Endocrine Disruption:

- DDT is an endocrine disruptor. It can disrupt normal hormone function and potentially lead to reproductive and developmental effects.
- Exposure to DDT during critical periods of fetal development or early childhood may impact neurological development and reproductive health later in life.

3. Liver Toxicity:
    - DDT and its metabolites can accumulate in the liver, where they can cause toxicity and impair liver function over time. This can lead to liver damage and other related health issues.
4. Developmental Effects:
    - Prenatal exposure to DDT leads to developmental effects in children, including low birth weight, premature birth, and developmental delays.
    - Childhood exposure to DDT has cognitive deficits and behavioral disorders.
5. Immune System Effects:

DDT exposure may suppress the immune system, making individuals more susceptible to infections and other immune-related disorders

SECTION D

1.a) Carbon tetrachloride was used as a solvent and precursor chemical.
b) Exposure to carbon tetrachloride poses significant health risks, particularly to the liver, kidneys, central nervous system, and reproductive system.
c) 1,1,1-Trichloroethane (TCA), Dichloromethane, Tetrahydrofuran, Ethyl Acetate, Isopropyl Alcohol, Acetone.

2.a) Skin Cancer, Cataracts and Eye Damage, Immune Suppression, Premature Aging of the Skin, Impact on Marine Life, Disruption of Ecosystems.
b) Alternatives to CFCs in refrigeration and aerosol products include HCFCs (phasing out), HFCs (low GWP versions), natural refrigerants, hydrocarbons, and environmentally friendly propellants like DME.
c) CFCs contribute to ozone layer depletion by releasing chlorine atoms in the stratosphere, which catalytically destroy ozone molecules. This process results in a reduction of the ozone layer's protective capacity, leading to increased UV radiation exposure and associated environmental and health impacts.

- 3.a) DDT was highly effective in killing a wide range of insect pests that threatened agricultural crops. It helped to significantly reduce crop damage and increase agricultural yields by eliminating pests like mosquitoes, flies, and agricultural pests such as beetles and caterpillars.

b) Bioaccumulation and Biomagnification, Impact on Wildlife, Loss of Biodiversity, Resistance Development.
c)Indoor exposure to DDT is generally low, potential health risks such as respiratory irritation, skin reactions, acute toxicity, and long-term health effects remain a concern.

4.a) Iodoform's antiseptic properties stem from its ability to release iodine, which effectively kills a wide range of microorganisms.
b) While iodoform remains a valuable antiseptic in certain medical contexts, its use requires careful management due to potential side effects such as iodine toxicity, allergic reactions, tissue staining, and delayed wound healing.

c) Betadine, Chlorhexidine Gluconate, Silver-based Dressings, Hypochlorous Acid, Honey-based Dressings.

SECTION E

1. Chlorofluorocarbons (CFCs) have industrial applications due to their stability, non-flammability, and low toxicity.

Industrial Uses of CFCs:

1. Refrigeration and Air Conditioning:
   - CFCs, such as CFC-12 (dichlorodifluoromethane), were commonly used as refrigerants in air conditioning systems, refrigerators, and freezers. They provided efficient cooling properties and were non-corrosive to equipment.
2. Foam Blowing Agents:
   - CFCs were used as blowing agents in the production of foam materials, such as expanded polystyrene (EPS) and polyurethane foams. They enabled the formation of lightweight and insulating foam products used in construction, packaging, and furniture.
3. Solvents:
   - Some CFCs, like CFC-113 (trichlorotrifluoroethane), were used as solvents in various industrial processes, including cleaning electronic components and degreasing metals. Their stability and non-flammability made them suitable for precision cleaning applications.
4. Aerosol Propellants:
   - CFCs served as propellants in aerosol products, such as sprays for cosmetics, insecticides, and household cleaners. They provided a consistent and reliable mechanism for dispensing products from pressurized containers.

Environmental Effects of CFCs:

1. Ozone Depletion:
   - CFCs are significant contributors to ozone layer depletion in the stratosphere. When released into the atmosphere, CFC molecules can reach the stratosphere, where they break down under ultraviolet (UV) radiation, releasing chlorine atoms. These chlorine atoms catalytically destroy ozone molecules (O3), reducing the ozone layer's ability to protect against harmful UV radiation.
2. Global Warming Potential (GWP):
   - CFCs and their breakdown products, known as halocarbons, have high global warming potentials (GWPs). They are potent greenhouse gases that trap heat in the Earth's atmosphere, contributing to global climate change.

2. DDT (dichlorodiphenyltrichloroethane) has been used for various applications primarily as an insecticide.

Applications of DDT:

1. Agricultural Pest Control:
   - DDT was extensively used in agriculture to control pests such as mosquitoes, flies, beetles, and caterpillars. It helped reduce crop damage and increase agricultural yields by eliminating insect pests that threatened crops.
2. Public Health:

- DDT played a crucial role in public health programs to combat vector-borne diseases such as malaria, typhus, and yellow fever. It was used to spray indoor surfaces (indoor residual spraying) to kill mosquitoes that transmit malaria, reducing disease transmission in endemic regions.

3. Livestock and Household Pest Control:
   - DDT was used to control pests in livestock farming and for domestic purposes, including controlling pests in homes and gardens.
4. Industrial Uses:
   - DDT was also used in industrial settings, such as controlling pests in warehouses and food processing facilities, due to its effectiveness and persistence.

Environmental Effects of DDT:

1. Persistence and Bioaccumulation:
   - DDT is highly persistent in the environment, meaning it breaks down very slowly. Once released into the environment through agricultural runoff, air drift from spraying, or improper disposal, DDT can persist in soil, water, and sediment for many years.
   - DDT bioaccumulates in the fatty tissues of organisms. It accumulates as it moves up the food chain, resulting in higher concentrations in predators at the top of the food web, such as birds of prey and fish-eating mammals.
2. Impact on Wildlife:
   - Birds: DDT's most notorious impact was on bird populations, such as eagles, hawks, and falcons. It caused thinning of eggshells, leading to reproductive failures and population declines. This effect was notably observed in populations of bald eagles and peregrine falcons.
   - Fish and Aquatic Life: DDT contamination in water bodies affected aquatic ecosystems, with potential harm to fish and other aquatic organisms. DDT's persistence in sediments and its accumulation in fish tissue posed risks to aquatic biodiversity.
3. Endocrine Disruption and Health Effects:
   - DDT is an endocrine disruptor, meaning it can interfere with hormonal systems in animals and humans. Exposure to DDT has been associated with reproductive and developmental effects in wildlife, including reduced fertility, altered reproductive behaviors, and developmental abnormalities in offspring.
   - Human health effects of DDT exposure include potential risks of cancer (e.g., breast cancer) and impacts on neurological development and immune function, although direct evidence in humans is debated and often associated with historical exposures

3. Chloroform ($CHCl_3$) has historically been used for various purposes due to its properties as a volatile liquid with a sweet odor. Its uses, environmental impact, and effects on human health are detailed below:

Uses of Chloroform:

1. Anesthetic:
   - Chloroform was historically used as a general anesthetic in medical and surgical procedures. It induced a state of unconsciousness and muscle relaxation, allowing for surgical interventions.
2. Solvent:
   - Chloroform has been used as a solvent in various industrial processes, particularly for extracting compounds from organic materials and as a solvent in the production of pharmaceuticals and chemicals.
3. Intermediate in Chemical Synthesis:

- It serves as an intermediate in the production of other chemicals, such as fluorocarbons and refrigerants. Historically, it was also used in the synthesis of dyes, pesticides, and pharmaceuticals.

4. Historical Uses:
   - Chloroform has been used as ingredient in cough syrups and other medicinal formulations.

1. Health Effects of Exposure:
   - Acute Exposure: Inhalation or ingestion of chloroform vapors can cause dizziness, nausea, headache, and central nervous system depression. High concentrations or prolonged exposure can lead to respiratory depression, liver and kidney damage, and even death.
   - Chronic Exposure: Long-term exposure to chloroform has been associated with liver and kidney toxicity, as well as potential carcinogenic effects. Animal studies suggest it may cause tumors in the liver and other organs.
2. Occupational Hazards:
   - Workers in industries where chloroform is used may face occupational exposure risks, particularly through inhalation and dermal contact. Occupational safety measures, such as ventilation and personal protective equipment, are essential to minimize exposure.

Environmental Impact:

1. Persistence and Bioaccumulation:
   - Chloroform is moderately persistent in the environment and can enter water bodies through industrial discharges, wastewater, and runoff from landfills. It can accumulate in aquatic organisms and bioaccumulate in the food chain.
2. Aquatic Toxicity:
   - Chloroform's presence in water bodies can be toxic to aquatic organisms, affecting fish and other aquatic life forms. Chronic exposure to chloroform may disrupt aquatic ecosystems and biodiversity.
3. Air Pollution:
   - Chloroform can contribute to air pollution when released into the atmosphere, particularly from industrial sources. It can react with other compounds in the atmosphere to form potentially harmful by-products.

4. Iodoform (CHI_3) is a chemical compound that has been used for various purposes, primarily in medical and minor industrial applications. Its uses, as well as its environmental and health effects, are discussed below:

Uses of Iodoform:

1. Antiseptic:
   - Iodoform has been used as an antiseptic agent in wound care. It was particularly valued in the past for its ability to prevent and treat infections in surgical wounds, abscesses, and other skin lesions.
   - It works by slowly releasing iodine when applied to wounds. Iodine is a potent antimicrobial agent that kills a wide range of bacteria, fungi, and some viruses, thereby promoting wound healing.
2. Dental Applications:
   - In dentistry, iodoform is used in combination with other materials (such as calcium hydroxide) as an intra-canal dressing in root canal therapy. It helps disinfect the root canal system and promote healing.
3. Veterinary Medicine:
   - Iodoform has also been used in veterinary medicine for similar purposes as in human medicine, particularly in wound management and as a component in certain veterinary preparations.

Environmental and Health Effects:

1. Environmental Impact:
   - Iodoform is considered to have low environmental persistence and is not known to bioaccumulate significantly in the environment. Its environmental impact is therefore generally minimal compared to persistent organic pollutants.
   - However, disposal of large quantities of iodoform or its residues should be done according to regulatory guidelines to prevent potential environmental contamination.
2. Health Effects:
   - Topical Use: When applied topically, iodoform is generally considered safe and effective for short-term use in wound care. It may cause mild irritation or allergic reactions in some individuals, particularly those sensitive to iodine.
   - Systemic Effects: Prolonged or extensive exposure to iodoform, especially through inhalation or ingestion, can lead to systemic effects such as iodine toxicity. Symptoms may include nausea, vomiting, abdominal pain, and in severe cases, thyroid dysfunction.
   - Occupational Exposure: Healthcare workers and individuals handling iodoform in industrial settings should follow appropriate safety measures to minimize exposure risks, including ventilation and personal protective equipment.

5. Dichloromethane (DCM), also known as methylene chloride, is a versatile chemical compound with several industrial applications. Its properties, uses, and environmental and health impacts are detailed below:

Industrial Uses of Dichloromethane:

1. Solvent:
   - Dichloromethane is widely used as a solvent in various industrial applications, particularly in paint stripping, adhesive formulations, metal cleaning, and as a process solvent in pharmaceutical manufacturing.
   - Its ability to dissolve a wide range of organic compounds makes it valuable in extraction processes, such as caffeine extraction from coffee beans and decaffeination of tea.
2. Chemical Synthesis:
   - It serves as a reagent in chemical synthesis for producing pharmaceuticals, agrochemicals, and other specialty chemicals.
   - Dichloromethane is involved in the production of fluorocarbons, which are used in refrigerants and propellants, although its use in this context has decreased due to environmental concerns.
3. Aerosol Propellant:
   - In the past, dichloromethane was used as a propellant in aerosol products, including paints, adhesives, and insecticides. However, its use in consumer aerosols has declined due to regulatory restrictions.

Environmental Impacts of Dichloromethane:

1. Air Pollution:
   - Dichloromethane can contribute to air pollution when released into the atmosphere, particularly from industrial processes and solvent applications. It is volatile and can evaporate easily, leading to its presence in ambient air.
   - It has a short atmospheric lifetime, primarily decomposing through reaction with hydroxyl radicals in the atmosphere.
2. Water Contamination:

- While dichloromethane has low solubility in water, accidental spills or improper disposal can lead to contamination of water bodies. It can persist in aquatic environments and potentially impact aquatic organisms.

3. Ozone Depletion:
   - Dichloromethane has negligible ozone-depleting potential (ODP) compared to other chlorinated solvents like CFCs. Its environmental impact primarily relates to its contribution to volatile organic compound (VOC) emissions and associated secondary pollution.

Health Impacts of Dichloromethane:

1. Acute Exposure:
   - Inhalation or skin exposure to dichloromethane vapor can cause irritation of the respiratory tract, eyes, and skin. Symptoms may include dizziness, headache, nausea, and in severe cases, central nervous system depression.
   - Acute exposure to high concentrations can lead to respiratory failure, cardiac arrhythmias, and unconsciousness.
2. Chronic Exposure:
   - Long-term occupational exposure to dichloromethane has been associated with liver toxicity, kidney damage, and potentially increased risk of certain cancers, such as liver cancer.
   - Regulatory agencies, such as the Occupational Safety and Health Administration (OSHA) in the United States, have set exposure limits to protect workers from these health risks.

CHAPTER 7: ALCOHOLS

MULTIPLE -CHOICE QUESTIONS WITH ONE CORRECT ANSWER

QUESTIONS

1- To get carboxylic acids directly from alcohol, which of the following oxidising agents is used?
a) Alkaline $KMnO_4$
b) Aqueous $KMnO_4$
c) Acidified $KMnO_4$
d) Anhydrous CrO_3

2- Dehydration of alcohol to ethers is catalysed by
(a) cone. H2SO4 at 413 K
(b) Hot NaOH
(c) Hot HBr
(d) Hot HNO3

3- Which of the following processes does not result in the production of alcohol?
a) Acid catalysed hydration of alkenes
b) Free radical halogenation of alkanes
c) Reduction of aldehydes
d) Hydroboration-oxidation of alkenes

4- The conversion of trialkyl borane to an alcohol does not require which of the following?
a) Sodium hydroxide
b) Water
c) Diborane
d) Hydrogen peroxide

5- Which of the following alcohols is not polyhydric?
a) Propylene glycol
b) Ethylene glycol
c) Cyclohexanol
d) Benzene-1,2-diol

6- Amongst the following alcohols which would react fastest with conc. HCl and $ZnCl_2$?
(a) pentan-1-ol
(b) 2-methyl butan-1-ol
(c) pentan-2-ol
(d) 2-methyl butan-2-ol

7- Amongst the following alcohols which would react fastest with conc. HCl and $ZnCl_2$?
(a) pentan-1-ol

(b) 2-methyl butan-1-ol
(c) pentan-2-ol
(d) 2-methyl butan-2-ol

8- Rate of dehydration of alcohols follows the order:
(a) 2° > 1° > CH_3OH > 3°
(b) 3° > 2° > 1° > CH_3OH
(c) 2° > 3° > 1° > CH_3OH
(d) CH_3OH > 1° > 2° > 3°

9- Which of the following is a secondary alcohol?
(a) 2-methylbutan-2-ol
(b) 3-methylbutan-1-ol
(c) 2-methylbutan-1-ol
(d) 3- methylbutan-2-ol

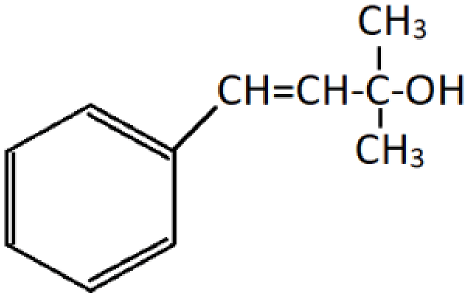
10- Which of the following is used for denaturation of commercial alcohol?
(a) Copper sulphate
(b) Pyridine
(c) Methyl alcohol
(d) All of the above

11- Which of the following is true regarding polyhydric alcohols?
a) It should have one or more OH groups
b) It should have two or more OH groups
c) It should have three or more OH groups
d) It should have more than four OH groups

12- Which of the following types of alcohol contain a bond between sp^2 hybridised carbon and OH group?
a) Primary allylic alcohols
b) Secondary allylic alcohols
c) Tertiary allylic alcohols
d) Vinylic alcohols

13- Which of the following terms does not describe $CH_2=CH-CH_2OH$?
a) Primary
b) Monohydric
c) Allylic
d) Vinylic

14- Choose the most suitable classification for the shown compound?



a) Secondary alcohol
b) Allylic alcohol
c) Dihydric alcohol
d) Benzylic alcohol

15- Dehydration of alcohol is an example of
a. addition reaction
b. elimination reaction
c. substitution reaction
d. redox reaction

ANSWERS

1- C

2- A

3- B

4- C

5- C

6- D

7- A

8- B

9- D

10- D

11- B

12- D

13- D

14- B

15- B

SHORT ANSWERS QUESTIONS- 2 MARKS EACH

QUESTIONS

1- Name the factors responsible for the solubility of alcohols in water.

2- Suggest a reagent for the following conversion.

3- Describe the Hydroboration oxidation of alkanes.

4- Alcohols have higher boiling points than ethers of comparable molecular masses. What is the reason for this?

5- Phenols are more acidic than alcohols. Explain.

6- Name the chemical test commonly used to distinguish between the following pairs of compounds.

1. n-Propyl alcohol and isopropyl alcohol.
2. Methanol and ethanol

7. Of the two hydroxy organic compounds ROH and R'OH, the first one is basic and other is acidic in behaviour. How is R different from R'?

8- How would you obtain ethane-1, 2-diol from ethanol?

9- Draw the structures of the isomers of alcohols with the molecular formula $C_4H_{10}O$. Which of these will exhibit optical activity?

10- Alcohols are more soluble in water than the hydrocarbons of relative molecular masses. Explain Why?

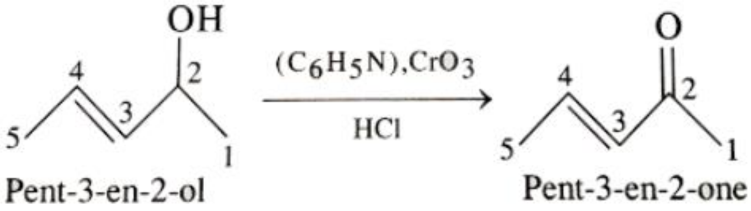
ANSWERS

1- A) Hydrogen bonds – Because of their propensity to create hydrogen bonds with water molecules or intermolecular hydrogen bonding, alcohols are soluble in water.

B) Size of the alkyl or aryl groups – The solubility of alcohols in water diminishes as the size of the alkyl or aryl groups grows larger. The presence of intermolecular hydrogen bonding between alcohol molecules makes low molecular mass alcohols liquid in water.

C) Molecular mass of the Alcohols – It reduces the effect of the polar character of the –OH group of alcohol with an increase in the alkyl group of alcohol or in the case of large molecular mass alcohols. As a result, as the molecular size of an alcohol increases, its solubility drops, therefore alcohols with lower molecular masses are more soluble than alcohols with larger molecular masses.

2- The given reactant is $H_3C-CH=CH-CH(OH)-CH_3$. It is a secondary alcohol. Secondary alcohol gives ketone when oxidised by CrO_3 or pyridinium chlorochromate without carrying out oxidation at the double bond.



3- Hydroboration Oxidation of Alkanes: This is a two-step process to produce alcohol from alkenes. This method follows the Anti-Markovnikov rule as the hydrogen atom dissociated from BH3 or BHR2 attaches itself to the most substituted carbon present in the double bond of alkene and the boron atom attaches itself to the least substituted carbon.

4- The presence of the intermolecular hydrogen bond makes the boiling points of alcohols high whereas this type of bond is not present in ethers. Therefore, alcohols have higher boiling points than ethers of comparable molecular masses.

5- The acidic nature of phenol and alcohol depends on their reactivity towards the ionisation reaction of the O−H bond. The ionisation reaction of alcohols can be expressed by the following equation:

$H2O + R-OH$ (alcohol) $\leftrightharpoons H3O+ + R-O-$(alkoxide)

The tendency of alkyl to release electrons destabilises the alkoxide ion of alcohol. Therefore, alcohols never ionise in water.

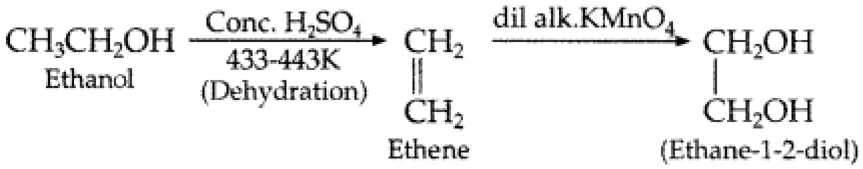
However, the phenoxide ion produced by the ionisation of phenol in water is stabilised through delocalisation of the negative charge produced in the aqueous solution of phenol. Hence, phenol shows more acidic nature by completing the ionisation process.

6- 1. n-Propyl alcohol and isopropyl alcohol can be distinguished by the Lucas Test.

2. Methanol and ethanol can be distinguished by the Iodoform Test.

7- When R = alkyl, ROH behaves as a bronsted base and when R’ = aryl, R’OH behaves as a bronsted acid.

8-



9- There are four isomers of alcohols with the molecular formula $C_4H_{10}O$.

- Butanol
- 2- Methyl propanol
- 2-methyl propan-2-ol
- Butan-2-ol

Out of the four isomers mentioned above, Butan-2-ol will show optical activity and exist in two optically active forms.

10- Alcohols are more soluble in water than the hydrocarbons of equivalent molecular masses because alcohols form a hydrogen bond with water molecules and break the existing hydrogen bonds of water molecules. Thus, they are soluble in water. In contrast, hydrocarbon cannot form hydrogen bonds with water molecules. Thus, they are insoluble in water.

SHORT ANSWER QUESTIONS- 3 MARKS EACH

QUESTIONS

1-_Differentiate between alcohol and phenol.

2- Name the factors responsible for the solubility of alcohols in water.

3- Illustrate the following reactions giving a chemical equation for each:
(i) Kolbe’s reaction
(ii) Williamsons synthesis of an ether

4- How are the following conversions carried out?
(i) Propene to propan-2-ol
(ii) Ethylmagnesium chloride to propan-1-ol.

5- Explain the mechanism of acid catalysed hydration of an alkene to form corresponding alcohol.

6- Explain the mechanism of following reaction:

$$2CH_3-CH_2-OH \xrightarrow[413K]{H^+} CH_3CH_2-\overset{\cdot\cdot}{\underset{\cdot\cdot}{O}}-CH_2-CH_3+H_2O$$

7- How will you convert:
(i) Propene to Propane-1-ol?
(ii) Ehtanal to Propan-2-ol

8- Write the mechanism of the following reaction

$$CH_3CH_2OH \xrightarrow{HBr} CH_3CH_2Br + H_2O$$

9- How are the following conversions carried out?
(i) Propene to Propan-2-ol
(ii) Ethyl chloride to Ethanal

10- Explain the mechanism of dehydration steps of ethanol : (Comptt. Delhi 2015)

$$CH_3CH_2OH \xrightarrow[443K]{H^+} CH_2 = CH_2 + H_2O$$

ANSWERS-

1-

Difference Between Alcohol and Phenol	
Alcohol	Phenol
The alcohols are a class of organic compounds that hold at least one hydroxyl functional group that is attached to a carbon atom.	Phenols, on the other hand, are organic compounds consisting of a hydroxyl group which is attached to an aromatic system of hydrocarbons (arene).
Alcohols usually feature the hydroxyl group attached to aliphatic hydrocarbons.	Phenols usually contain aromatic hydrocarbons.
In comparison to phenol, alcohols are known to be less acidic.	Phenols are relatively more acidic in nature and should, therefore, be diluted before usage.
In terms of usage, alcohol is the main ingredient in alcoholic beverages. They are also used in ink, pharma, ink and many other industries.	Phenols are mainly used in medicinal products as antiseptic agents.
Alcohols are mostly colourless, and they usually exist in the liquid state.	Phenols are colourless solids that usually exist as crystals at STP.
Alcohols show no impact or reaction during tests as they are mostly neutral.	Phenol can change litmus paper red as they are acidic in nature.

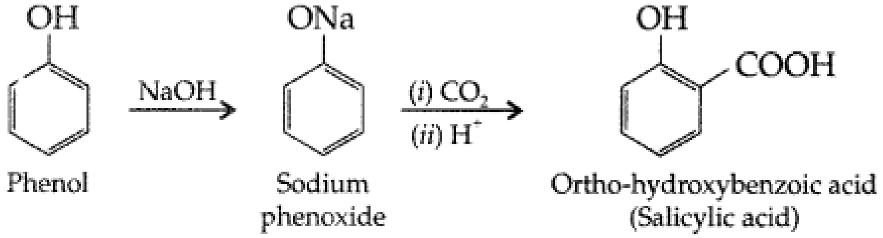
2- A)Hydrogen bonds – Because of their propensity to create hydrogen bonds with water molecules or intermolecular hydrogen bonding, alcohols are soluble in water.

B) Size of the alkyl or aryl groups – The solubility of alcohols in water diminishes as the size of the alkyl or aryl groups grows larger. The presence of intermolecular hydrogen bonding between alcohol molecules makes low molecular mass alcohols liquid in water.

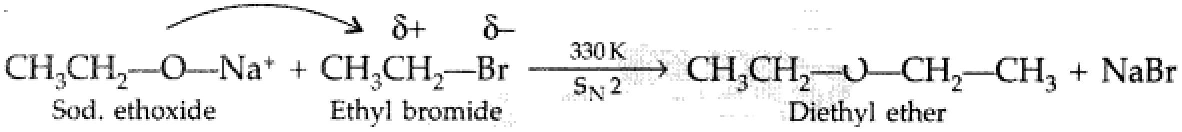
C) Molecular mass of the Alcohols

– It reduces the effect of the polar character of the –OH group of alcohol with an increase in the alkyl group of alcohol or in the case of large molecular mass alcohols. As a result, as the molecular size of an alcohol increases, its solubility drops, therefore alcohols with lower molecular masses are more soluble than alcohols with larger molecular masses.

3- (i) Kolbe's reaction: Phenol reacts with CO_2 in presence of sodium hydroxide (NaOH) at 4 – 7 Atm and 390 – 410 K giving salicylic acid

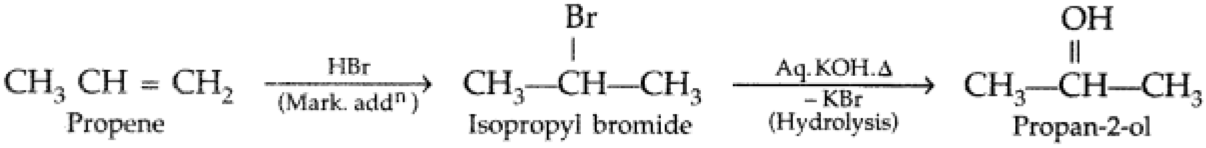


(ii) Williamsons synthesis of an ether: The reaction involves the nucleophilic substitution of the halide ion from the alkyl halide by the alkoxide ion by S_N2 mechanism.
Example:



$$\underset{\text{Sod. ethoxide}}{CH_3CH_2{-}O{-}Na^+} + \underset{\text{Ethyl bromide}}{CH_3\overset{\delta+}{CH_2}{-}\overset{\delta-}{Br}} \xrightarrow[S_N2]{330\,K} \underset{\text{Diethyl ether}}{CH_3CH_2{-}O{-}CH_2{-}CH_3} + NaBr$$

4- (i) Propene to propan-2-ol

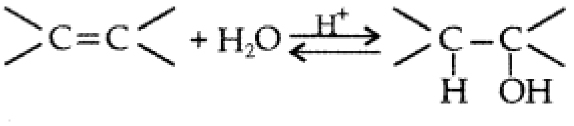


$$\underset{\text{Propene}}{CH_3\,CH=CH_2} \xrightarrow[\text{(Mark. add}^n)]{HBr} \underset{\text{Isopropyl bromide}}{CH_3{-}\overset{\overset{\displaystyle Br}{|}}{C}H{-}CH_3} \xrightarrow[\substack{-KBr\\ \text{(Hydrolysis)}}]{\text{Aq. KOH.}\Delta} \underset{\text{Propan-2-ol}}{CH_3{-}\overset{\overset{\displaystyle OH}{||}}{C}H{-}CH_3}$$

(ii) Ethylmagnesium chloride to propan-1-ol

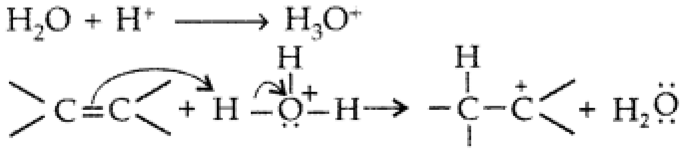
$$\underset{\text{Ethyl Magnesium chloride}}{CH_3CH_2MgCl} \xrightarrow[\text{(Grignard Rx}^n)]{HCHO} \underset{\text{Addition product}}{[CH_3CH_2CH_2OMgCl]} \xrightarrow{H^+/H_2O} \underset{\text{Propan-1-ol}}{CH_3CH_2CH_2OH} + Mg(OH)Cl$$

5- Acid catalysed hydration: Alkenes react with water in the presence of acid as catalyst to form alcohols

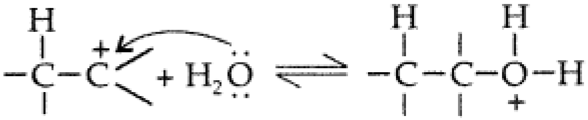


Mechanism: It involves three steps:

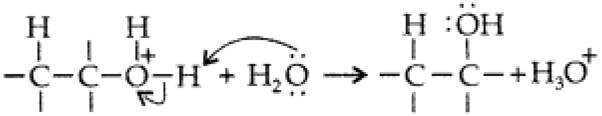
(i) Protonation of alkene to form carbocation by electrophilic attack of H_3O^+



(*ii*) Nucleophilic attack of water on carbocation



(*iii*) Deprotonation to form an alcohol

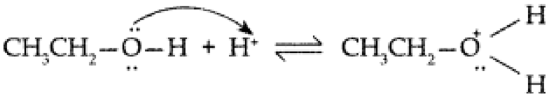


6-

$$2CH_3-CH_2-OH \xrightarrow[413K]{H^+} CH_3CH_2-\ddot{O}-CH_2-CH_3+H_2O$$

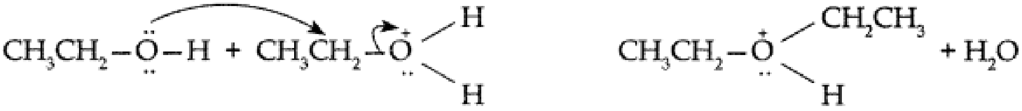
Excess

Mechanism: ***Step 1:*** Protonation of alcohol

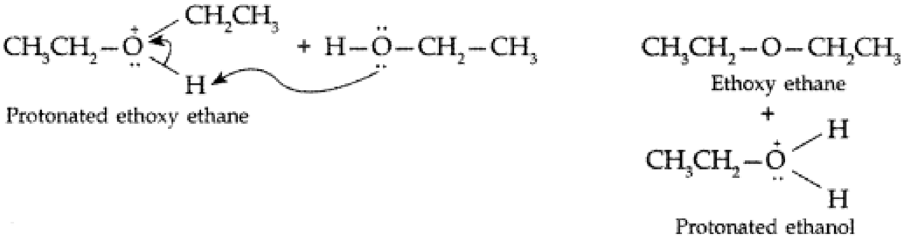


Protonated ethanol
(oxonium salt)

Step 2: Nucleophillic attack by unprotonated alcohol molecule on protonated alcohol molecule



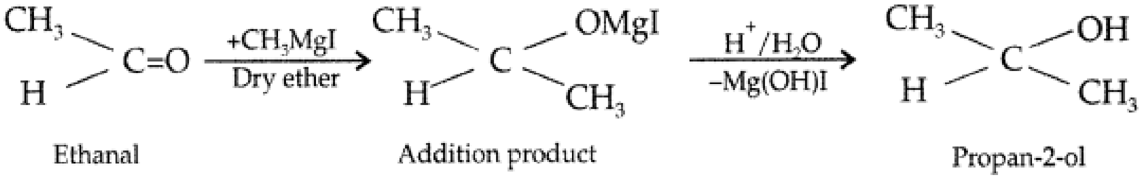
Step 3: Loss of a portion to form ethoxy ethane



7-

$$\underset{}{CH_3CH{=}CH_2} \xrightarrow[\text{(Anti-Mark addn.)}]{\text{HBr/Peroxide}} \underset{\text{1-Bromopropane}}{CH_3CH_2CH_2Br} \xrightarrow[\Delta\ \text{(Hydrolysis)}]{\text{Aq. KOH}} \underset{\text{Propan-1-ol}}{CH_3CH_2CH_2OH}$$

(*ii*) Ehtanal to Propan-2-ol



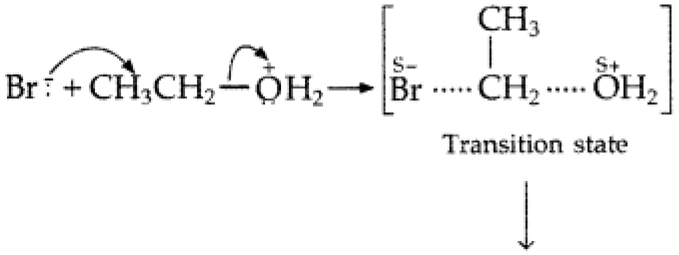
8-

(*a*) $$CH_3CH_2-OH + HBr \xrightarrow[\text{Reflux}]{\text{Conc.}H_2SO_4} \underset{\text{Bromo ethane}}{CH_3CH_2-Br} + H_2O$$

Mechanism : S_N2 mechanism

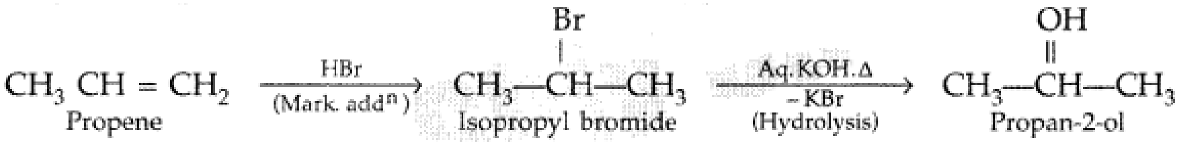
(*i*) $$CH_3CH_2-\ddot{O}H + H^+ \rightleftharpoons \underset{\text{Protonated 1° alcohol}}{CH_3CH_2-\overset{+}{\ddot{O}}H_2}$$

(*ii*)



$$\underset{\text{Bromoethane}}{Br-CH_2-CH_3 + H_2O}$$

9-(i) Propene to propan-2-ol

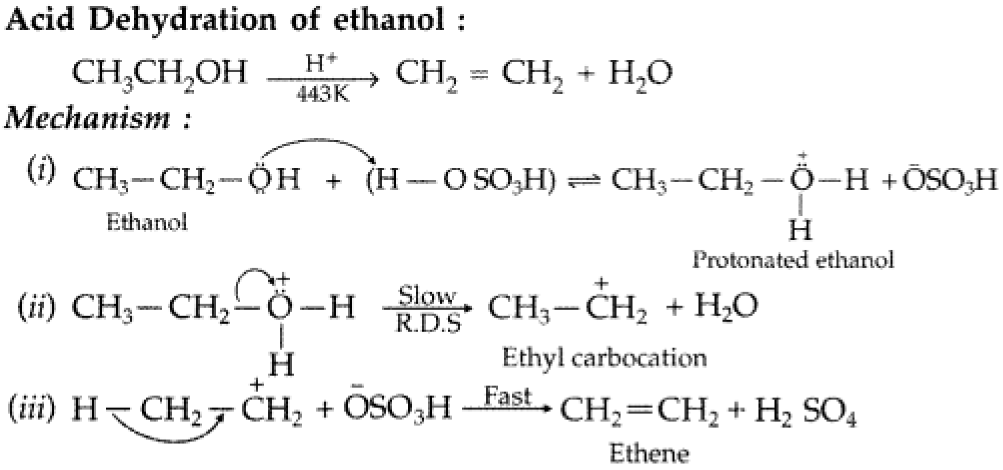


$$\underset{\text{Propene}}{CH_3\ CH=CH_2} \xrightarrow[\text{(Mark. add}^n\text{)}]{\text{HBr}} \underset{\text{Isopropyl bromide}}{CH_3-\overset{Br}{CH}-CH_3} \xrightarrow[\substack{-\text{KBr}\\ \text{(Hydrolysis)}}]{\text{Aq.KOH.}\Delta} \underset{\text{Propan-2-ol}}{CH_3-\overset{OH}{CH}-CH_3}$$

(*ii*) **Ethyl chloride to ethanal**

$$\underset{\text{Ethyl chloride}}{CH_3CH_2Cl} \xrightarrow{\text{Aq.KOH}} \underset{\text{Ethanol}}{CH_3CH_2OH} \xrightarrow{\text{Cu / 573K}} \underset{\text{Ethanal}}{CH_3CHO}$$

10-



$$CH_3CH_2OH \xrightarrow[443K]{H^+} CH_2 = CH_2 + H_2O$$

LONG ANSWER QUESTIONS- 5 MARKS EACH

QUESTIONS

1-Write the mechanism of the reaction of HI with methoxybenzene.
2- (a) Name the starting material used in the industrial preparation of phenol.

(b) Write a complete reaction for the bromination of phenol in an aqueous and non-aqueous medium.

(c) Explain why Lewis acid is not required in the bromination of phenol?

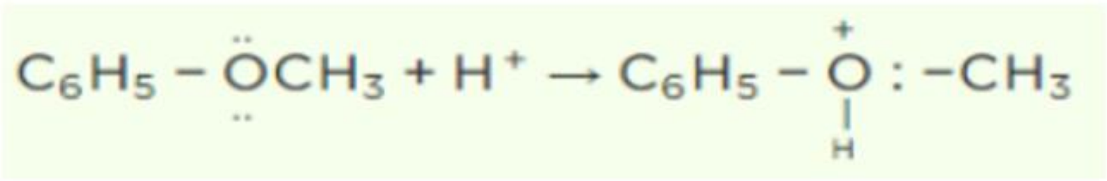
3- Explain a process in which a biocatalyst is used in industrial preparation of a compound known to you.

4- Why is phenol more acidic than ethanol?

ANSWERS

1- In case of alkyl aryl ethers, the products are always phenol and an alkyl halide because due to resonance C_6H_5-O bond has a partial double bond character. The mechanism is given below.

Mechanism Protonation of anisole gives methyl phenyl oxonium ion.

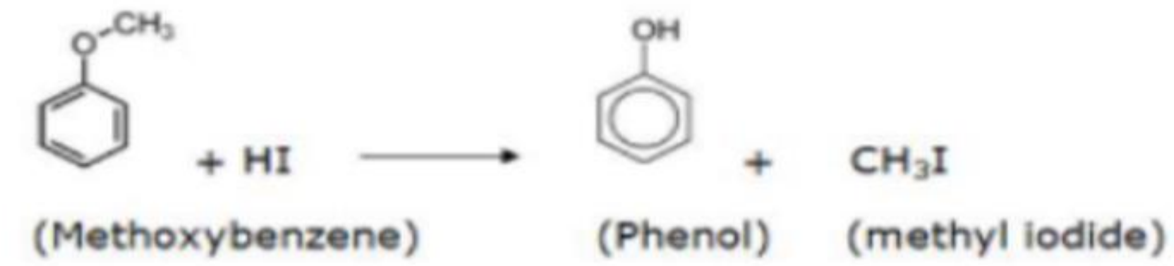


$$C_6H_5 - \ddot{O}CH_3 + H^+ \rightarrow C_6H_5 - \overset{+}{O}(H) : -CH_3$$

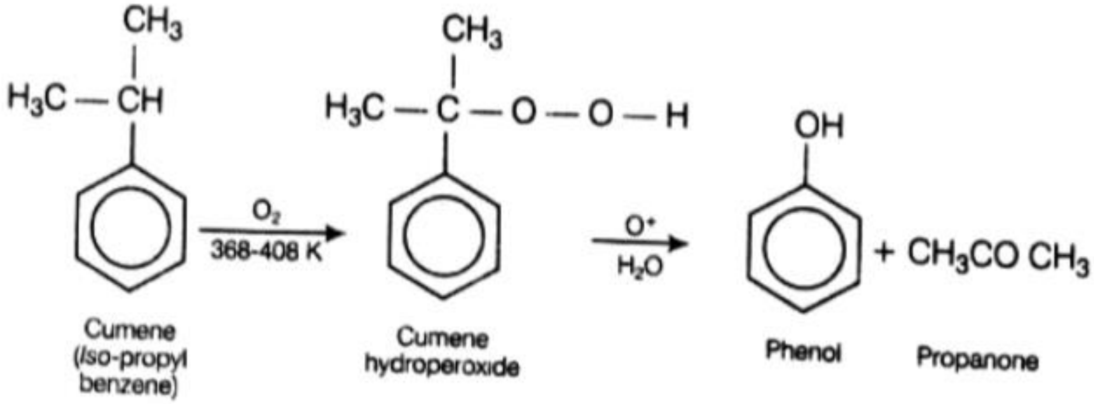
In this ion, the bond between O−CH_3 is weaker than the bond between

$O-C_6H_5$ which has a partial double bond character. This partial double bond character is due to the resonance between the lone pair of electrons on the O -atom and the sp^2 hybridised carbon atom of the phenyl group. Therefore, an attack by I^- ion exclusively breaks the weaker

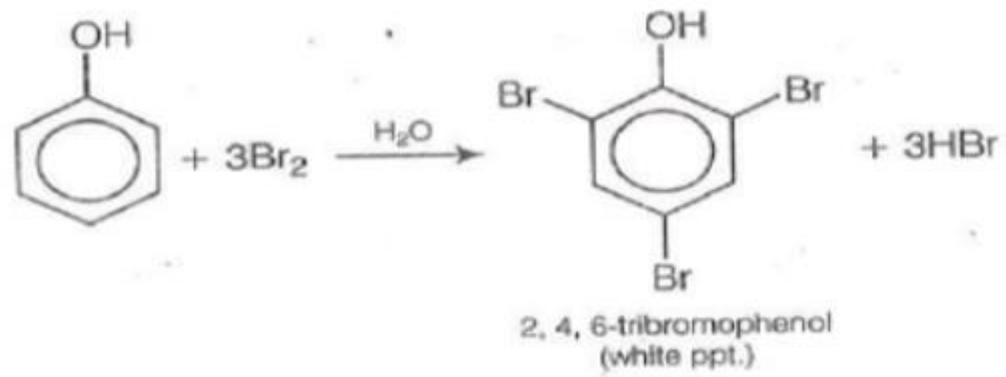
$O-CH_3$ bond, forming methyl iodide and phenol.

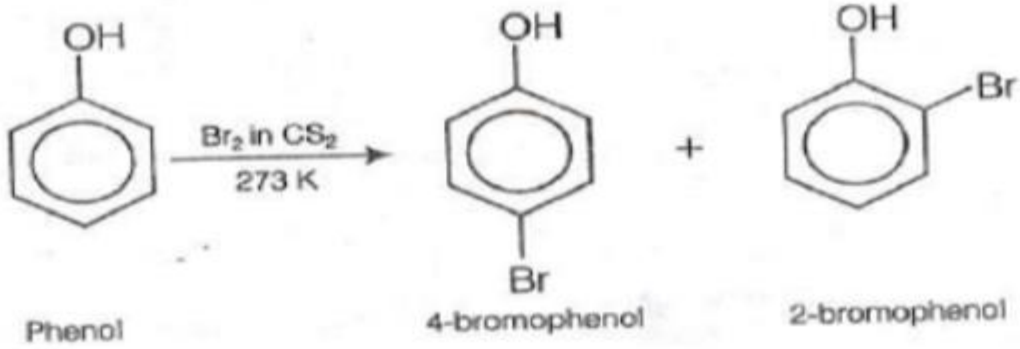


2- (a) The starting material used in the industrial preparation of phenol is cumene.



(b) Phenols when treated with bromine water give polyhalogen derivatives in which all the hydrogen atoms present at ortho and para positions with respect to the -OH group are replaced by bromine atoms.

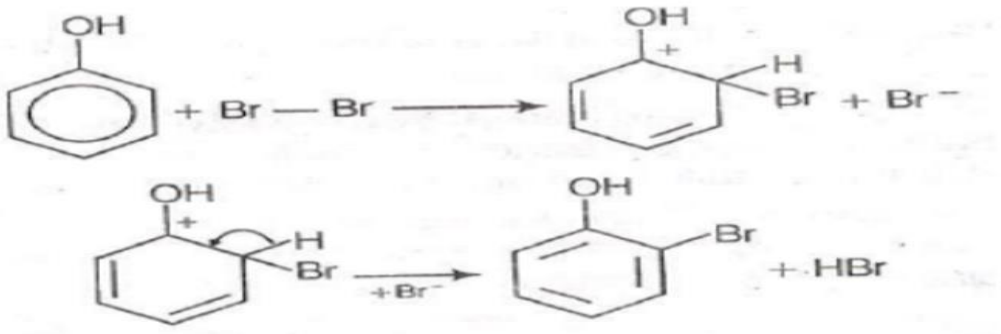




In an aqueous solution, phenol ionises to form phenoxide ions. This ion activates the benzene ring to a very large extent and hence the substitution of halogen takes place at all three positions.

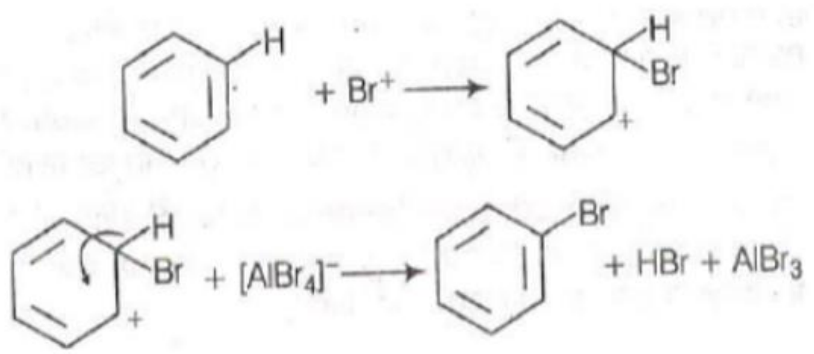
(c) In bromination of benzene, Lewis acid is used to polarise Br_2 to form the reactive electrophile, Br^+. In case of phenol, Lewis acid is not required because the O-atom of phenol itself polarises the Br_2 molecule to form Br^+ ions. further, the +R-effect of OH group makes phenol highly activated towards electrophilic substitution reactions.

Mechanism of bromination of phenol**.**



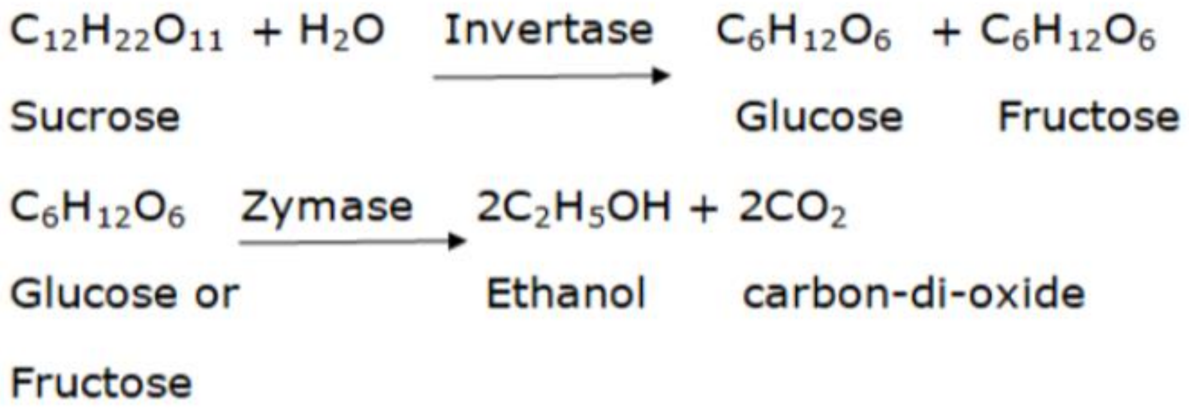
Mechanism of bromination of benzene:

$AlBr_3 + Br{-}Br \rightarrow [AlBr_4]^- + Br^+$



3- Biocatalysts are enzymes. These biocatalysts (enzymes) are utilised in the production of ethanol in industry. Ethanol is made by fermenting molasses, a dark brown coloured syrup left behind after sugar crystallisation that still contains around 40% sugar.

Fermentation is the process of breaking down big molecules into smaller ones in the presence of enzymes. Yeast is the source of these enzymes. The numerous reactions that occur during carbohydrate fermentation are listed below.



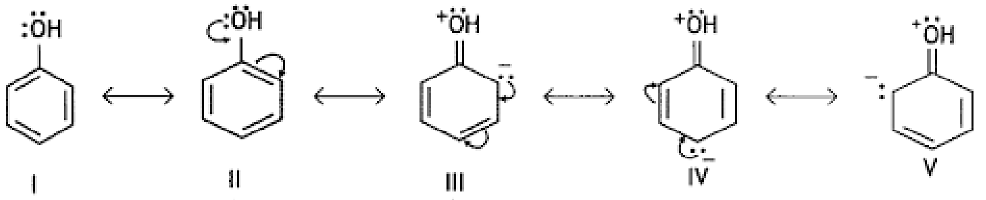
$$\underset{\text{Sucrose}}{C_{12}H_{22}O_{11}} + H_2O \xrightarrow{\text{Invertase}} \underset{\text{Glucose}}{C_6H_{12}O_6} + \underset{\text{Fructose}}{C_6H_{12}O_6}$$

$$\underset{\text{Glucose or Fructose}}{C_6H_{12}O_6} \xrightarrow{\text{Zymase}} \underset{\text{Ethanol}}{2C_2H_5OH} + \underset{\text{carbon-di-oxide}}{2CO_2}$$

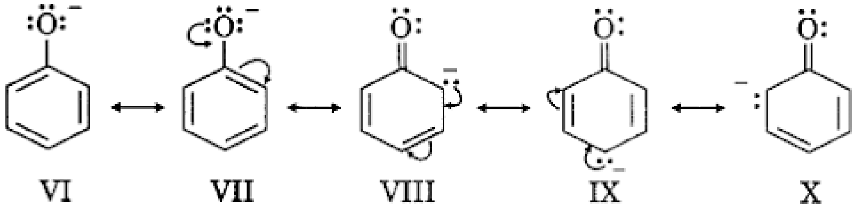
Grapes are used to make wine because they contain sugars and yeast. The amount of sugar in grapes increases as they ripen, and yeast forms on the outer peel. When the sugar and enzyme in the grapes come into touch, fermentation begins. Fermentation occurs in anaerobic conditions, that is, without the presence of oxygen. During fermentation, CO_2 gas is produced.

Once the percentage of alcohol generated exceeds 14 percent, the action of zymase is blocked. If air is introduced into the fermenting mixture, oxygen oxidises ethanol to ethanoic acid, destroying the flavour of alcoholic beverages.

4- Phenols are more acidic than alcohols because phenoxide **ions** are more stable than ethoxide ions. phenols as compared to alcohols can be explained based on resonance. (Resonance is a way of describing delocalized electron within certain molecules or polyatomic ions where the bond cannot be expressed with the help of the lewis formula) . Phenol based on resonance can be expressed by the following structure



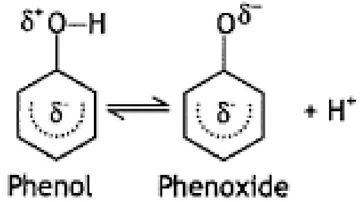
The three structure of Phenol has a positive charge on the oxygen of the -OH group. This oxygen attracts the electron pairs of the O-H bond strongly towards itself, which weakens their bond and therefore facilitates the release of w. the phenoxide ion in resonance is stabilized as the following



We observe that both phenol and phenoxide ions are stabilised by resonance.

Now if we observe the structure the phenoxide ion is more stabilized than phenol. In phenol three contributing structures have both positive and negative charges, therefore, these nuclei are unstable. On the other hand, there is no structure for the phenoxide ion which requires separation thus, the resonance hybrid of phenol is less than phenoxide ion and the reaction is very much in favour of the phenoxide ion. Therefore the phenol is more acidic.

On the other hand, the case with alcohols is a bit different neither alcohol nor the alkoxide ion is stabilised by resonance.



Phenoxide ion is more resonance stabilised.

$R{-}O{-}H \rightleftharpoons R{-}O^- + H^+$

No resonance

No resonance stabilisation for alcohol or alkoxide ion.

Thus, phenols are more acidic than alcohol.

TOPIC – PHENOLS – (nomenclature, method of preparation, physical and chemical properties, acidic nature of phenol, electrophilic substitution reaction, uses of phenols**)**

SECTION A

Multiple-Choice Questions (MCQs):

1. Which of the following is not a property of phenols?

   A. They are more acidic than alcohols.

   B. They react with sodium hydroxide to form salts.

   C. They have a characteristic aromatic odor.

   D. They are highly soluble in water.

   Answer: D. They are highly soluble in water.

2. Phenol reacts with bromine water to give:

   A. 2,4,6-tribromophenol

   B. 2,4,6-tribromobenzene

   C. 2,4-dibromophenol

   D. 2,4-dibromobenzene

   Answer: A. 2,4,6-tribromophenol

3. The reaction of phenol with chloroform in the presence of sodium hydroxide gives:

   A. Salicylic acid

   B. Benzyl chloride

   C. Chlorobenzene

   D. Phenyl acetate

   Answer: C. Chlorobenzene

4. Which of the following is a characteristic test for phenol?

   A. Ferric chloride test

B. Tollen's reagent test

C. Fehling's test

D. Benedict's test

Answer: A. Ferric chloride test

5. Phenol can be distinguished from alcohol by:

A. Reaction with sodium bicarbonate

B. Reaction with sodium metal

C. Reaction with Lucas reagent

D. Reaction with bromine water

Answer: D. Reaction with bromine water

6. The compound formed when phenol reacts with acetyl chloride is:

A. Phenyl acetate

B. Salicylic acid

C. Phenyl chloride

D. Acetophenone

Answer: A. Phenyl acetate

7. Which of the following statements about phenols is true?

A. They are weaker acids than alcohols.

B. They form strong hydrogen bonds with water molecules.

C. They are typically less reactive towards electrophilic aromatic substitution reactions.

D. They do not undergo oxidation reactions easily.

Answer: B. They form strong hydrogen bonds with water molecules.

Assertion-Reason Questions:

8. **Assertion-Reason 1: Assertion (A):** Phenol is more acidic than alcohols. **Reason (R):** The negative charge in the phenoxide ion is delocalized over the aromatic ring, stabilizing it.

   Answer: A is true, R is the correct explanation of A.

9. **Assertion-Reason 2: Assertion (A):** Phenol gives a violet coloration with ferric chloride solution. **Reason (R):** This coloration is due to the formation of a complex between ferric ions and the aromatic ring of phenol.

   Answer: A is true, R is the correct explanation of A.

10. **Assertion-Reason 3: Assertion (A):** Phenol does not undergo nucleophilic substitution reactions easily. **Reason (R):** The lone pair of electrons on the oxygen atom in phenol is involved in resonance stabilization.

    Answer: A is true, but R is not the correct explanation of A.

SECTION B

SHORT ANSWER TYPE QUESTIONS (2 MARKS)

1. Explain why phenol is more acidic than alcohols. Compare the acidity of phenol with that of methanol and justify your answer.
2. Discuss the chemical reactions of phenol with bromine water and with chloroform in the presence of sodium hydroxide. Write balanced chemical equations for these reactions.
3. How does phenol react with ferric chloride? Explain the color change observed and write the chemical equation for the reaction.
4. Describe the preparation of phenol from benzene. Outline the major steps involved and the catalyst used in the process.
5. Explain why phenols do not undergo nucleophilic substitution reactions easily compared to alkyl halides. Provide a structural explanation based on the nature of the phenoxide ion.
6. Discuss the electrophilic substitution reactions of phenol. Illustrate with an example of one such reaction and explain the mechanism involved.
7. Write the IUPAC name of phenol and draw its structure. Discuss the resonance stabilization of the phenoxide ion and its significance in acidity.
8. Compare the solubility of phenol in water with that of alcohols. Explain the reason behind the difference in solubility based on their chemical structures.
9. Compare the acidic strengths of phenol, p-nitrophenol, and p-methylphenol. Provide a brief explanation for the order of acidity.
10. Describe the preparation of salicylic acid from phenol. Outline the steps involved, including any reagents and conditions required for the conversion

SECTION C

SHORT ANSWER TYPE QUESTIONS (3 MARKS)

1. Explain the preparation of phenol from benzene using the Dow's process. Discuss the role of concentrated sulfuric acid and the catalyst involved in this process. Write the balanced chemical equation for the reaction.
2. Describe the mechanism of electrophilic aromatic substitution in phenol. Use a specific example, such as nitration or bromination, to illustrate the process. Include any relevant intermediates and the role of the hydroxyl group.
3. Discuss the structural differences between phenol and alcohols that contribute to the differences in their physical properties, such as boiling point and solubility. Explain how these structural features influence their reactivity.
4. Compare and contrast the reactions of phenol with bromine water and with chlorine in the presence of sodium hydroxide. Highlight the products formed in each reaction and explain the differences in their chemical pathways.
5. Explain the acidic nature of phenol in terms of its molecular structure and resonance stabilization of the phenoxide ion. Compare the acidity of phenol with that of carboxylic acids, providing reasons for their relative acidities.
6. Discuss the role of phenol in the manufacture of important industrial chemicals. Provide examples of specific compounds or products derived from phenol and describe their industrial applications.
7. Explain how phenol reacts differently with acetyl chloride compared to typical alcohols. Outline the reaction mechanism involved in the formation of phenyl acetate and discuss the conditions under which this reaction occurs.
8. Describe the chemical tests used to identify the presence of phenol in a given sample. Include the principles behind each test and how they distinguish phenol from similar compounds.
9. Discuss the environmental impact of phenol and its derivatives. Highlight both positive and negative aspects, considering factors such as toxicity, biodegradability, and regulatory measures.
10. Explain the biological significance of phenols in plants and animals. Discuss their roles as secondary metabolites in plant defense mechanisms and their therapeutic applications in medicine.

SECTION D

CASE BASED QUESTIONS (4 MARKS)

Case Study:1

Phenol, also known as carbolic acid, is a significant organic compound with various industrial and medicinal applications. Its chemical properties allow it to undergo several reactions, making it a valuable chemical in multiple processes. A student conducted an experiment where phenol was reacted with bromine water, and the product formed was a white precipitate of 2,4,6-tribromophenol. The student also tested the acidic nature of phenol by comparing its reaction with sodium hydroxide to that of ethanol.

Questions:

1. Identify the product formed when phenol reacts with bromine water. (1 mark)
2. Explain why phenol is more acidic than ethanol. (1 mark)
3. Write the balanced chemical equations for the reaction of phenol with bromine water and for the reaction of phenol with sodium hydroxide. Explain the observations in each case. (2 marks)

Case Study:2

A chemistry class conducted an experiment to compare the acidic nature of phenol and acetic acid by titrating both with a strong base, sodium hydroxide (NaOH). They observed that phenol required more NaOH to neutralize compared to an equivalent amount of acetic acid. The students also tested the reactions of phenol and ethanol with NaOH to compare their acidic strengths.

Questions:

1. Why does phenol require more NaOH to neutralize compared to acetic acid? (1 mark)
2. Write the balanced chemical equation for the reaction between phenol and sodium hydroxide. (1 mark)
3. Compare the acidic strengths of phenol and ethanol by describing their reactions with sodium hydroxide. (2 marks)

Case Study:3

In an organic chemistry lab, students observed the nitration of phenol using dilute nitric acid. They noted the formation of two major products: ortho-nitrophenol and para-nitrophenol. They also performed the bromination of phenol with bromine water and observed the formation of a white precipitate.

Questions:

1. What are the two major products formed during the nitration of phenol with dilute nitric acid? (1 mark)
2. Write the balanced chemical equation for the bromination of phenol with bromine water. (1 mark)
3. Explain why phenol undergoes electrophilic substitution reactions more readily than benzene. (2 marks)

Case Study:4

A group of students studied the physical and chemical properties of phenol. They noted that phenol is a white crystalline solid with a distinct odor and slightly soluble in water. In a separate experiment, they reacted phenol with zinc dust, which resulted in the formation of benzene.

Questions:

1. What are the physical properties of phenol observed by the students? (1 mark)
2. Write the balanced chemical equation for the reaction of phenol with zinc dust. (1 mark)

3. Describe the significance of phenol's chemical property observed in the reaction with zinc dust. (2 marks)

SECTION E

LONG ANSWER TYPE QUESTION (5 MARKS)

1. Discuss the acidic nature of phenols. Compare it with the acidity of alcohols and carboxylic acids. Why is phenol more acidic than cyclohexanol?
2. Describe the electrophilic aromatic substitution reactions of phenol. Explain why phenol undergoes these reactions more readily than benzene. Include the nitration and bromination of phenol in your explanation.
3. Explain the mechanism of the Reimer-Tiemann reaction for the preparation of salicylaldehyde from phenol.
4. Describe the physical properties and uses of phenol. Highlight any two specific uses and explain why phenol is suitable for these applications.

QUESTIONS ON ETHERS

MULTIPLE CHOICE QUESTIONS(1 Marks)

1. Ethers may be used as solvents because they react only with which of the following reactants?
a) Oxidising agent
b) Bases
c) Acids
d) Reducing agents

2 It's called ether when the alkyl groups connected to either side of the oxygen atom in an ether are different.
a) mixed
b) symmetrical
c) simple
d) diethyl

3. Which of the following is the most suitable requirement for the dehydration of ethanol to form an ether?
a) Sulphuric acid at 413K
b) Sulphuric acid at 443K
c) Sodium hydroxide at 413K
d) Sodium hydroxide at 443K

4 Which of the following is not favourable for the proper dehydration of alcohol to form ether?
a) Good temperature control during reaction
b) Excess of alcohol
c) Presence of protic acids
d) Presence of bulky alkyl groups in the alcohol

5. What is the major product formed when ethanol is dehydrated with concentrated H_2SO_4 at 413K?
a) Ethene
b) Methoxymethane
c) Methoxyethane
d) Ethoxyethane.

6. Sodium methoxide on heating with bromoethane gives __________
a) methoxymethane
b) methoxyethane
c) ethoxyethane
d) diethyl ether

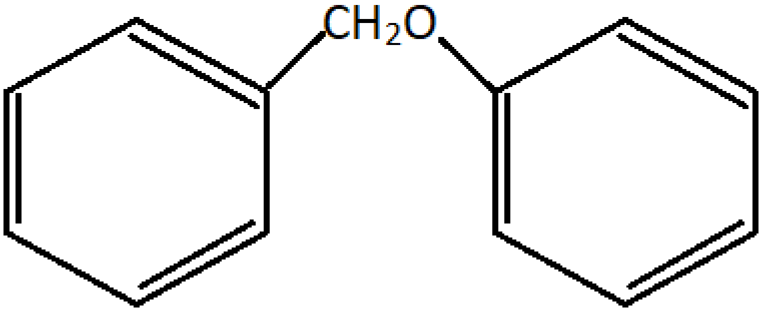
7. The reaction between tert-Butyl chloride and sodium ethoxide gives _______
a) tert-Butyl ethyl ether
b) tert-Butyl methyl ether
c) 2-Methylprop-1-ene
d) butane

8. The boiling point of ethers is ______ the boiling point of alcohols of comparable molecular mass.
a) lower than
b) similar to
c) little higher than
d) much higher than

9. Which of the following is the least reactive functional group?
a) Alcohols
b) Ethers
c) Aldehydes
d) Ketones

10. 10. One molecule of dialkyl ether produces how many molecules of alkyl halides with excess of halogen acid?
a) 1
b) 2
c) 3
d) 4

11. What product(s) are formed when the shown ether is heated with hydrogen iodide?



a) $(C_6H_5)CH_2I$ and $(C_6H_5)OH$

b) $(C_6H_5)CH_2OH$ and $(C_6H_5)I$
c) $(C_6H_5)CH_2OH$ and $(C_6H_5)CH_2I$
d) $(C_6H_5)OH$ and $(C_6H_5)I$

12. What is the major product of bromination of anisole in ethanoic acid?
a) o-Dibromobenzene
b) p-Dibromobenzene
c) o-Bromoanisole
d) p-Bromoanisole

13. . Identify the major product of Friedel-Crafts acylation of anisole with ethanoyl chloride?
a) 2-Methoxytoluene
b) 4-Methoxytoluene
c) 2-Methoxyacetophenone
d) 4-Methoxyacetophenone

14. 4-Nitroanisole is obtained as the major product when anisole reacts with _____
a) concentrated H_2SO_4
b) concentrated HNO_3
c) mixture of concentrated H_2SO_4 and HNO_3
d) mixture of dilute H_2SO_4 and HNO_3

15. Ethers are linear molecules with zero dipole moment.
a) True
b) False

ANSWERS

1.c
2.a
3.a
4 .d
5. d
6 b
7. C
8. A
9. B
10.b
11.a
12.d
13.d
14 c
15.b

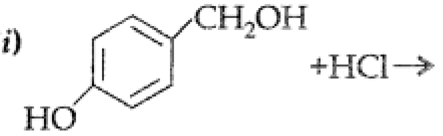
SHORT ANSWER QUESTIONS (2 MARKS)

1.Write equation of the nitration of anisole.

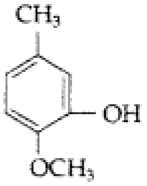
2.Complete the following reaction equations: (Delhi 2009)

(i)

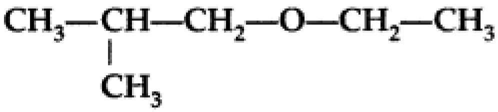
(ii)



3. Write IUPAC name of the following



4. Write the IUPAC name of given compound: (All India 2015)



$$CH_3-\underset{\displaystyle CH_3}{\underset{|}{CH}}-CH_2-O-CH_2-CH_3$$

5. Explain why is O=C=O nonpolar while R-O-R is polar.

6. Why is the C-O-H bond angle in alcohols slightly less than the tetrahedral angle whereas the C-O-C bond angle ether is slightly greater?

7. Explain why alcohols and ethers of comparable molecular mass have different boiling points?

8. What happens when benzene diazonium chloride is heated with water?

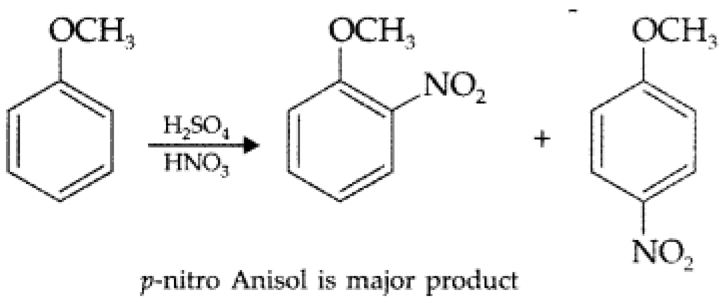
9. Suggest a reagent for the following conversion.

10. . Why are ethers used as a solvent?

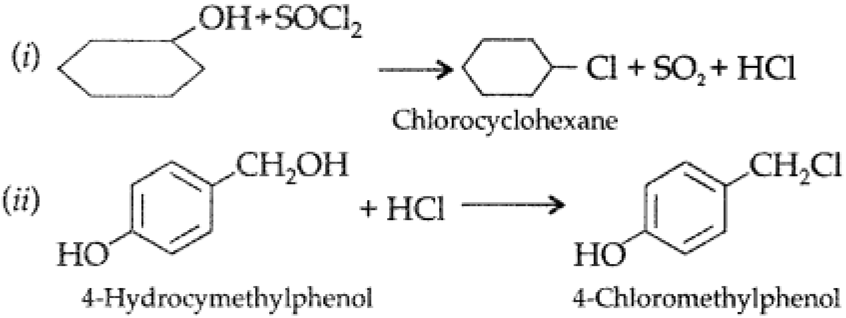
.

ANSWERS

1.



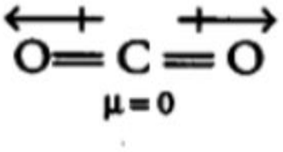
2.



3. IUPAC name : 2-Methoxy-5-methyl phenol

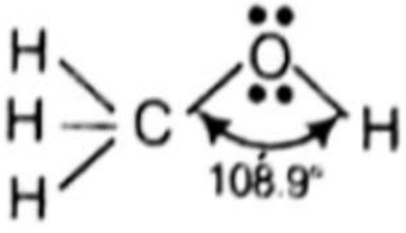
4. IUPAC name : 1-Ethoxy-2-methylpropane

5. The dipole moments of the two C=O bonds are exactly equal and opposite, making O=C=O nonpolar. As a result, they cancel each other out, resulting in a net dipole moment of zero for O=C=O. Because the form of this compound is non-linear, the net dipole moment of R—O—R is not equal to zero, and hence R—O—R is polar in nature.

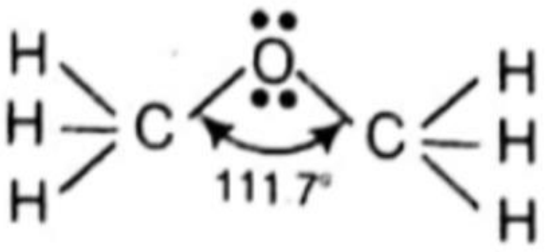


6. The bond angle in C−:O:−H in alcohols is slightly less than tetrahedral angle (108.9). It is due to the repulsion between the unshared electron pairs of oxygen. In alcohols, two lone pairs of electrons are present. Therefore, there is comparatively more repulsion and less bond angle.

The C-O-C bond angle (111.7◦) in ether is slightly greater than the tetrahedral angle due to the repulsive interaction between the two bulky (- R) groups.



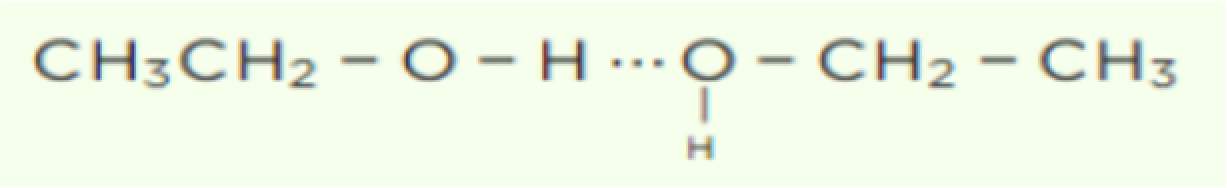
Methanol



Methoxymethane

7. Because the ethers have a low polarity, they do not display any intermolecular hydrogen bonding.

Because breaking weak dipole-dipole forces in ethers requires less energy than breaking strong hydrogen bonds in alcohol.

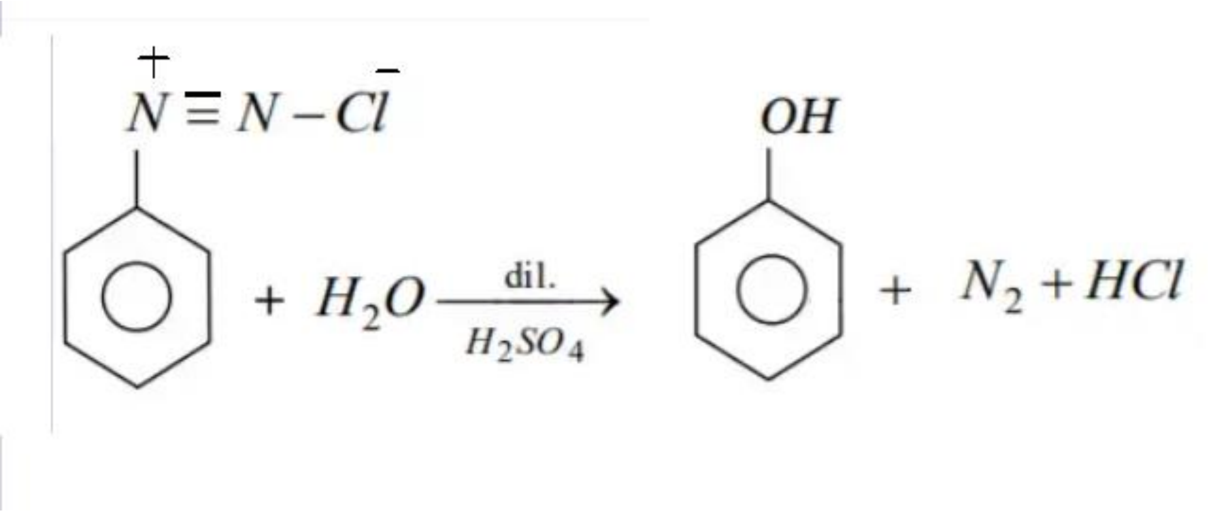


$$CH_3CH_2-O-H\cdots\underset{\underset{H}{|}}{O}-CH_2-CH_3$$

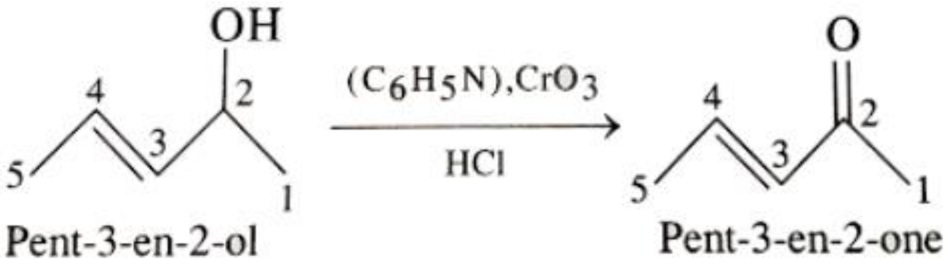
Hydrogen Bond in alcohols.

As a result, ethers have low boiling points, which are lower than isomeric alcohols and nearly equal to alkanes of comparable molecular weights. Alcohols and ethers have vastly different boiling points due to the presence of hydrogen bonding in alcohols.

8. The phenol is formed. When benzene diazonium chloride is heated with water, it produces phenol as well as nitrogen gas and hydrochloric acid as by-products.



9. The given reactant is $H_3C-CH=CH-CH(OH)-CH_3$. It is a secondary alcohol. Secondary alcohol gives ketone when oxidised by CrO_3 or pyridinium chlorochromate without carrying out oxidation at the double bond.



10. They are primarily used as good solvents because of their high volatility, slow chemical reactivity, and ability to accept the hydrogen bond.

SHORT ANSWER QUESTION (3 MARKS)

1. llustrate the following reactions giving a chemical equation for each :
   (i) Kolbe’s reaction
   (ii) Williamsons synthesis of an ether

2.Explain the following reactions with an example for each :
(i) Reimer-Tiemann reaction
(ii) Friedel-Crafts reaction.

3. Explain the following giving one example for each :
(i) Reimer-Tiemann reaction.
(ii) Friedel-Craft’s acetylation of anisole.

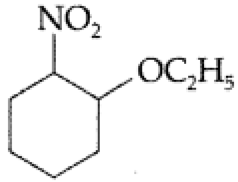
4. Explain the following observations :
(i) The boiling point of ethanol is higher than that of methoxymethane.
(ii) Phenol is more acidic than ethanol.
(iii) o- and p-nitrophenols are more acidic than phenol.

5, How would you convert the following :
(i) Phenol to benzoquinone

(ii) Propanone to 2-methylpropan-2-ol
(iii) Propene to propan-2-ol

6. (a) Give a seperate chemical test to distinguish between the following pairs of compounds:
(i) Ethanol and Phenol (ii) 2-Pentanol and 3-Pentanol
(b) Explain Kolbe's reaction with the help of suitable example.

7. (a) How would you obtain the following :
(i) 2-methylpentan-2-ol from 2-methyl-1-pentene
(ii) Acetophenone from phenol
(b) Write IUPAC name of the following :



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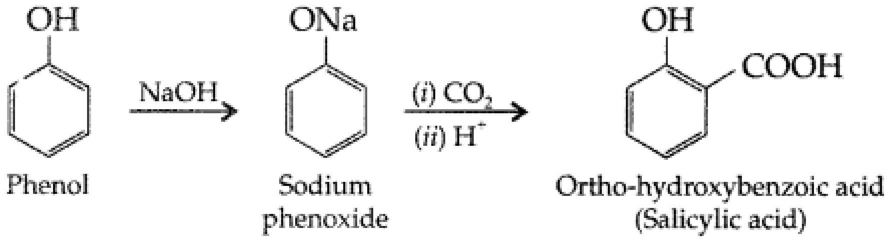
8. a) Give mechanism of preparation of ethoxy ethane from ethanol.
(b) How is toluene obtained from phenol?

9. How are the following conversions carried out?
(i) Propene → 4 Propan-2-ol
(ii) Ethylmagnesium chloride → 4 Propan-l-ol
(iii) Benzyl chloride → Benzyl alcohol

10.. How do you convert the following :
(i) Phenol to anisole
(ii) Propan-2-ol to 2-methylpropan-2-ol
(iii) Aniline to phenol

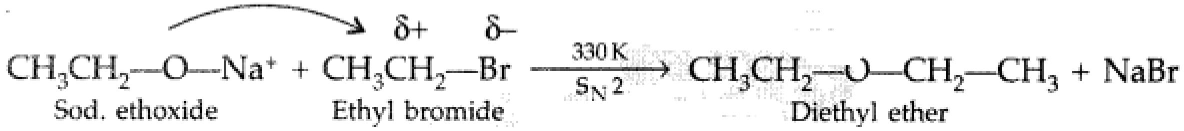
ANSWERS

1.(i) Kolbe's reaction : Phenol reacts with CO_2 in presence of sodium hydroxide (NaOH) at 4 – 7 Atm and 390 – 410 K giving salicylic acid



(ii) Williamsons synthesis of an ether : The reaction involves the nucleophilic substitution of the halide ion from the alkyl halide by the alkoxide ion by S_N2 mechanism.

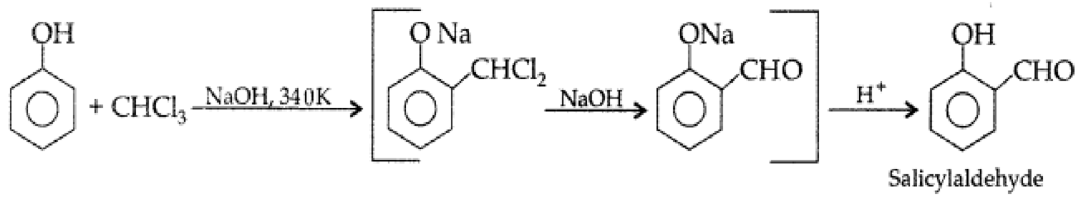
Example :



2. Answer:

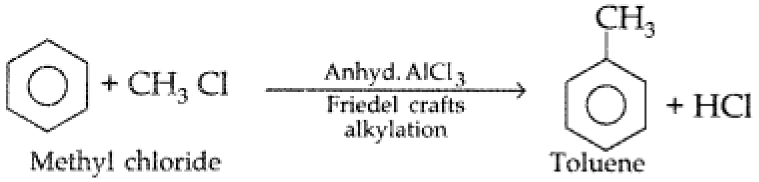
(i) Reimer-Tiemann reaction : Treatment of phenol with $CHCl_3$ in presence of aqueous NaOH at 340K followed by hydrolysis gives salicylaldehyde.

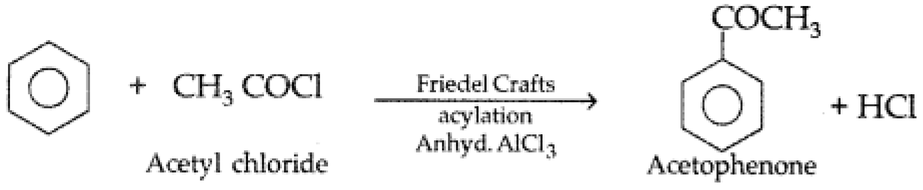
Example :



(ii) Friedel-Crafts reaction : This reaction is used for introducing an alkyl or an acyl group into an aromatic compound in presence of Lewis acid catalyst ($AlCl_3$)

Example:

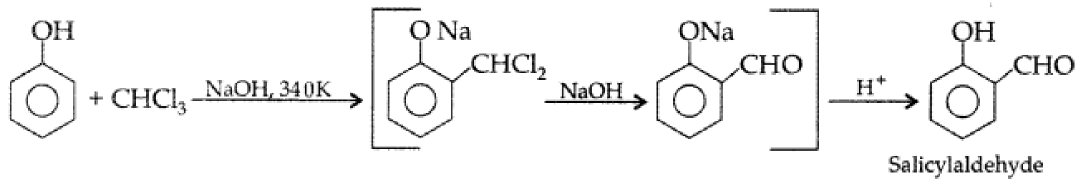




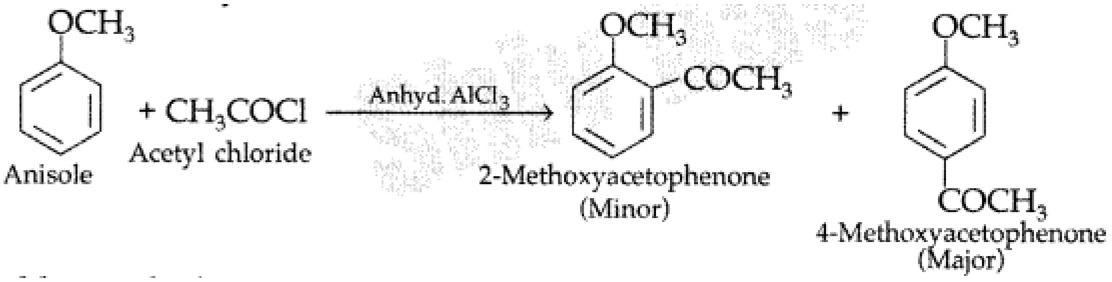
3. Answer:

(i) Reimer-Tiemann reaction : Treatment of phenol with $CHCl_3$ in presence of aqueous NaOH at 340K followed by hydrolysis gives salicylaldehyde.

Example :



(ii) Friedel-Craft's acetylation of anisole :



4. Answer:

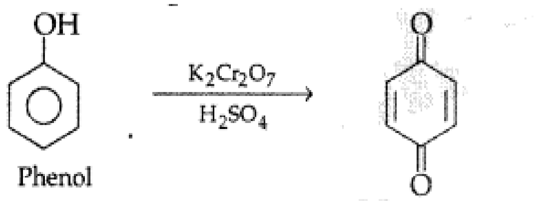
(i) Due to presence of intermolecular H-bonding, associated molecules are formed, hence ethanol has high boiling point while methoxymethane does not have intermolecular H-bonding.

(ii) Phenol on losing H^+ ion forms phenoxide ion, and ethanol on losing H^+ ion forms ethoxide ion. Phenoxide ion is more stable than ethoxide ion as phenoxide ion exists in resonance structure. Due to this phenol is more acidic than ethanol.

(iii) Both o- and p-nitrophenols contain the NO_2 group which is an electron withdrawing group. Due to -R and -I effect of the $-NO_2$ group, electron density in the OH bond of substituted phenol decreases and hence the loss of proton becomes easy and therefore more acidic

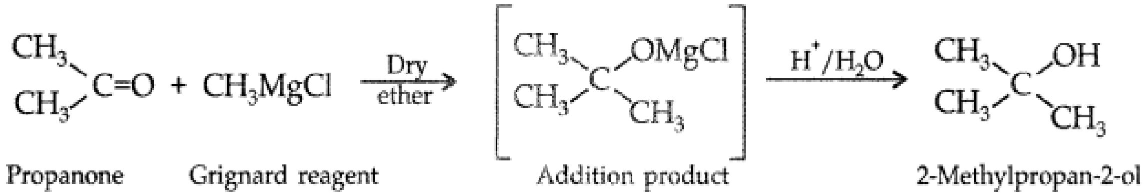
5. Answer:

(i) Phenol to benzoquinone

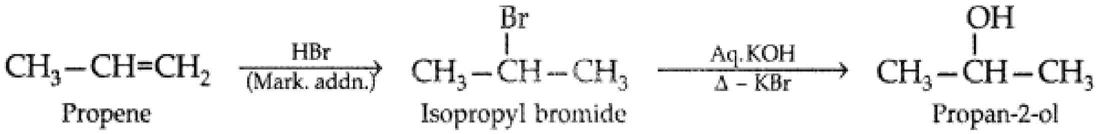


P-Benzoquinone

(*ii*) Propanone to 2-methylpropan-2-ol



(*iii*) Propene to propan-2-ol



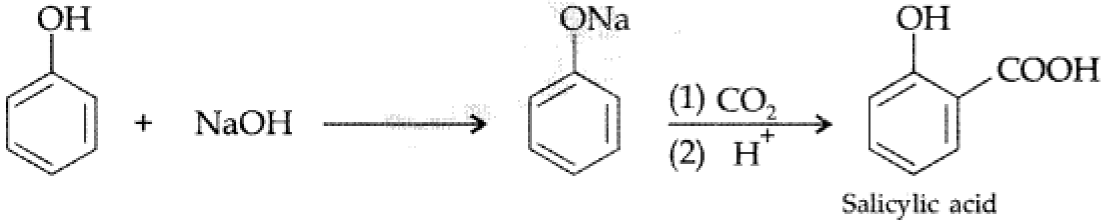
$$CH_3-CH{=}CH_2 \xrightarrow[\text{(Mark. addn.)}]{HBr} CH_3-\overset{\overset{\displaystyle Br}{|}}{C}H-CH_3 \xrightarrow[\Delta\ -\ KBr]{Aq.KOH} CH_3-\overset{\overset{\displaystyle OH}{|}}{C}H-CH_3$$

6. Answer:

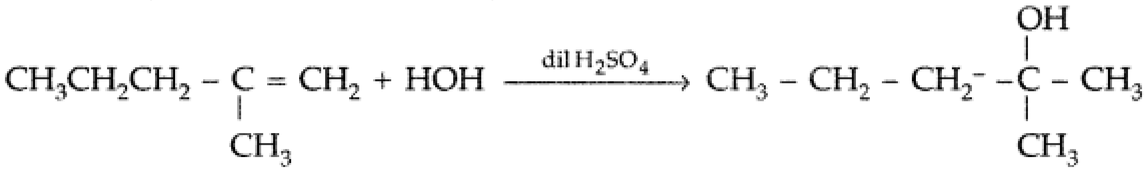
(a) (i) Ethanol on reacting with I_2 in NaOH gives yellow ppt of iodoform whereas phenol does not respond to this test.

(ii) 2-Pentanol on reacting with I_2 in NaOH gives yellow ppt of iodoform whereas 3-pentanol does not respond to this test.

(b) Kolbe's reaction : Phenol reacts with NaOH to give sodium phenoxide which on reaction with CO_2 in acid gives salicylic acid.

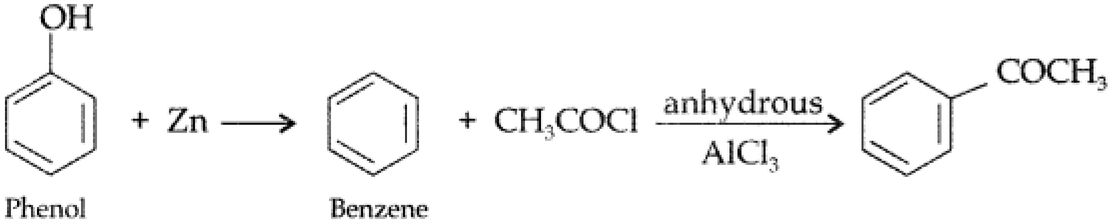


7. (a) (i) 2-Methylpentan-2-ol from 2-methyl-1-pentene



$$CH_3CH_2CH_2-\underset{\displaystyle CH_3}{\underset{|}{C}}=CH_2+HOH\xrightarrow{\text{dil }H_2SO_4}CH_3-CH_2-CH_2^{-}-\overset{\displaystyle OH}{\overset{|}{\underset{\displaystyle CH_3}{\underset{|}{C}}}}-CH_3$$

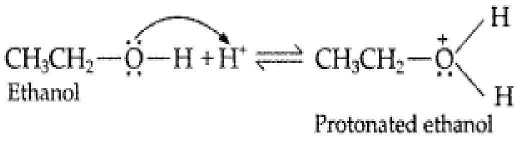
(*ii*) **Acetophenone from phenol**



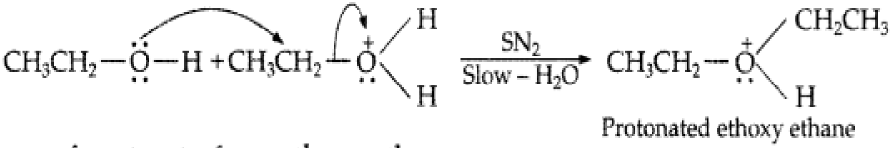
(b) IUPAC name : 1 -ethoxy-2-nitrocyclohexane.

8. (a) Mechanism of formation of ethoxy ethane

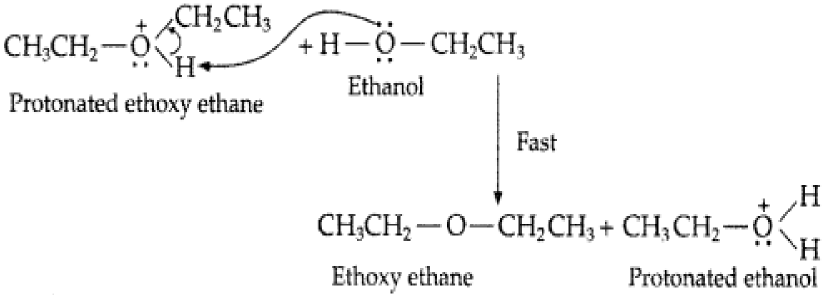
Step 1 : Protonation of ethanol



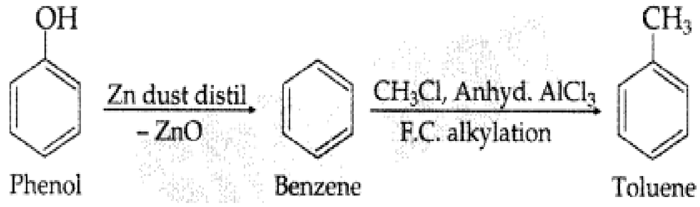
Step 2 : Nucleophillic attack by unprotonated alcohol molecule on protonated alcohol molecule



Step 3 : Loss of proton to form ethoxy ethane

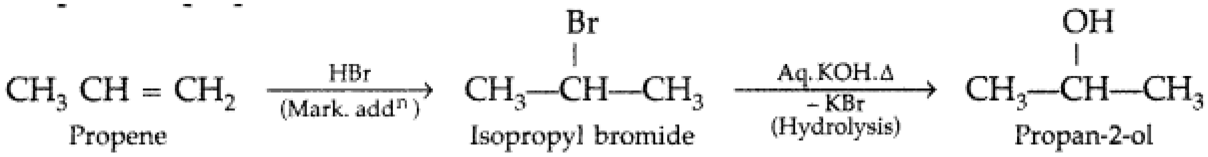


(*b*) **Toluene from Phenol**



9. Answer:

(i) Propene to propan-2-ol

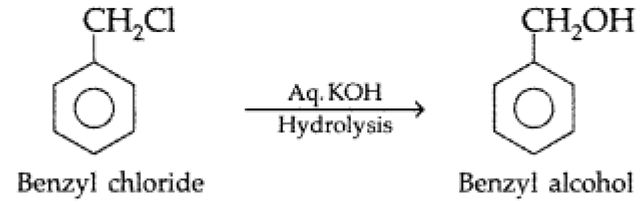


$$CH_3\,CH=CH_2 \xrightarrow[\text{(Mark. add}^n)]{HBr} CH_3-\overset{\overset{Br}{|}}{CH}-CH_3 \xrightarrow[\substack{-\,KBr \\ \text{(Hydrolysis)}}]{Aq.\,KOH.\Delta} CH_3-\overset{\overset{OH}{|}}{CH}-CH_3$$

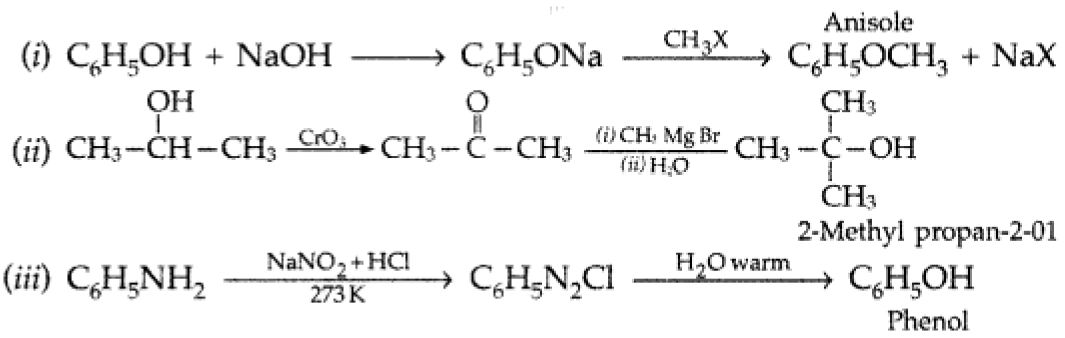
(ii) Ethylmagnesium chloride to propan-1-ol

$$\underset{\text{Ethyl Magnesium chloride}}{CH_3CH_2MgCl} \xrightarrow[\text{(Grignard Rx}^n)]{HCHO} \underset{\text{Addition product}}{[CH_3CH_2CH_2OMgCl]} \xrightarrow{H^+/H_2O} \underset{\text{Propan-1-ol}}{CH_3CH_2CH_2OH} + Mg(OH)Cl$$

(iii) Benzyl chloride → Benzyl alcohol



10.Answer:



$$(i)\ C_6H_5OH + NaOH \longrightarrow C_6H_5ONa \xrightarrow{CH_3X} \overset{\text{Anisole}}{C_6H_5OCH_3} + NaX$$

$$(ii)\ CH_3-\overset{OH}{\overset{|}{C}H}-CH_3 \xrightarrow{CrO_3} CH_3-\overset{O}{\overset{\|}{C}}-CH_3 \xrightarrow[(ii)\ H_2O]{(i)\ CH_3MgBr} CH_3-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-OH$$

2-Methyl propan-2-01

$$(iii)\ C_6H_5NH_2 \xrightarrow[273\,K]{NaNO_2+HCl} C_6H_5N_2Cl \xrightarrow{H_2O\ \text{warm}} C_6H_5OH$$

Phenol

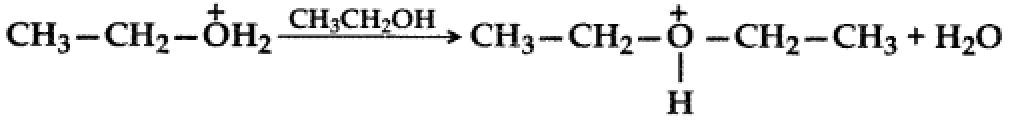
LONG ANSWER QUESTIONS (5 MARKS)

1.Write the mechanism of the following reaction:

$$2CH_3CH_2OH \xrightarrow[413\ K]{Conc.\ H_2SO_4} CH_3CH_2—O—CH_2—CH_3$$

2. a) What happens when CH_3—O—CH<sub3 is heated with HI?
(b) Explain mechanism for hydration of acid catalyzed ethene :
CH2 = CH2 + HzO ⟶H+CH3—CH,—OH

3. Write the formula of reagents used in the following reactions:
(i) Bromination of phenol to 2,4,6-tribromophenol
(ii) Hydroboration of propene and then oxidation to propanol.
(b) Arrange the following compound groups in the increasing order of their property indicated:
(i) p-nitrophenol, ethanol, phenol (acidic character)
(ii) Propanol, Propane, Propanal (boiling point)
(c) Write the mechanism (using curved arrow notation) of the following reaction:



$$CH_3-CH_2-\overset{+}{O}H_2 \xrightarrow{CH_3CH_2OH} CH_3-CH_2-\underset{\underset{H}{|}}{\overset{+}{O}}-CH_2-CH_3 + H_2O$$

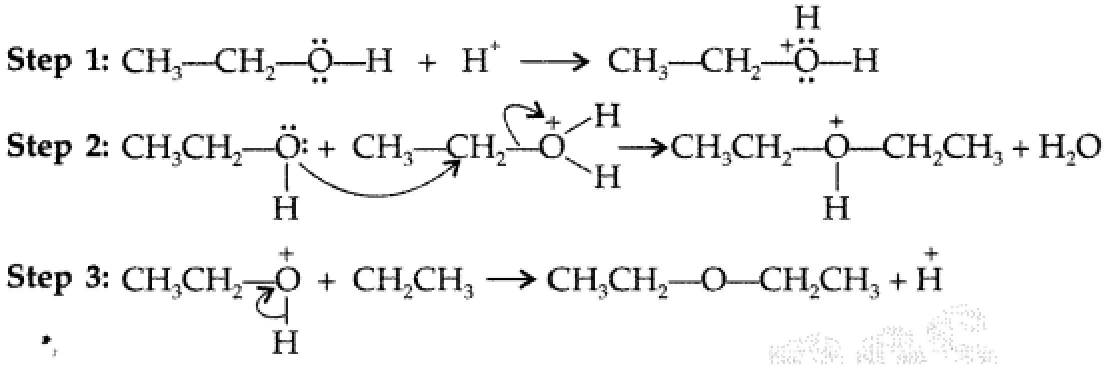
4. . (a) Name the starting material used in the industrial preparation of phenol.

(b) Write a complete reaction for the bromination of phenol in an aqueous and non-aqueous medium.

(c) Explain why Lewis acid is not required in the bromination of phenol?

ANSWERS

1. Answer:
Mechanism:

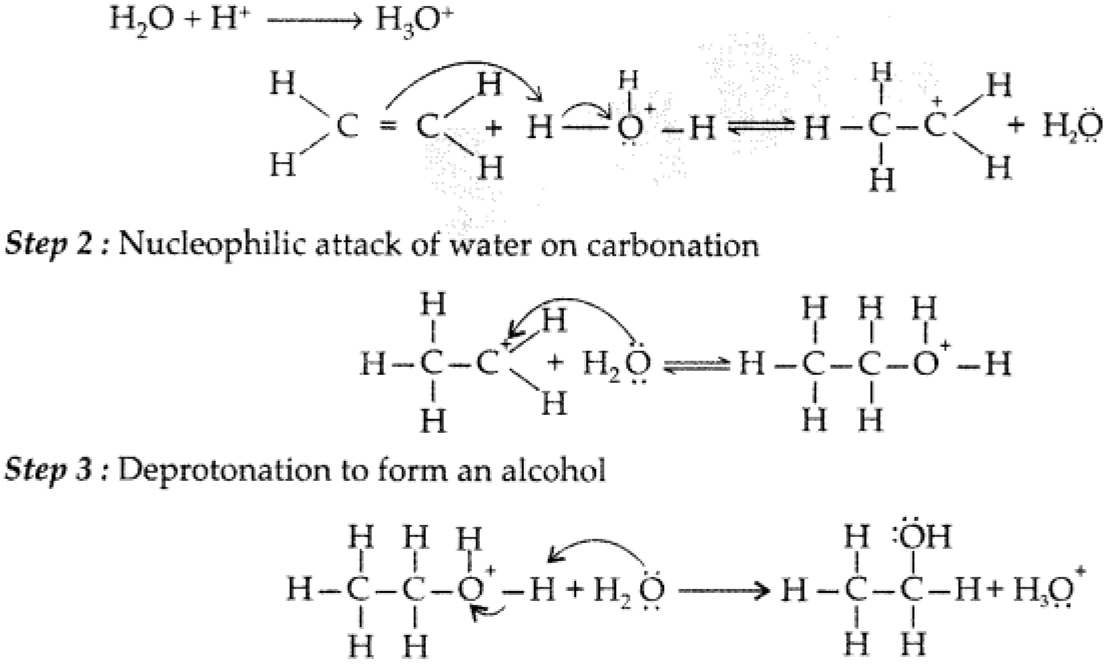


2.Answer:
(a) Methyl Iodide (CH_3I) and Methanol (CH_3OH) are formed when $CH_3—O—CH_3$ is heated with HI.

$CH_3—O—CH_3 + HI \longrightarrow CH_3I + CH_3OH$

Dimethyl ether Methyl Iodide Methanol

(b) Acid catalysed hydration : Alkenes react with water in the presence of acid as catalyst to form alcohols.
Mechanism : It involves the following three steps :
Step 1: Protonation of alkene to form carbocation by electrophilic attack of H_3O^+.

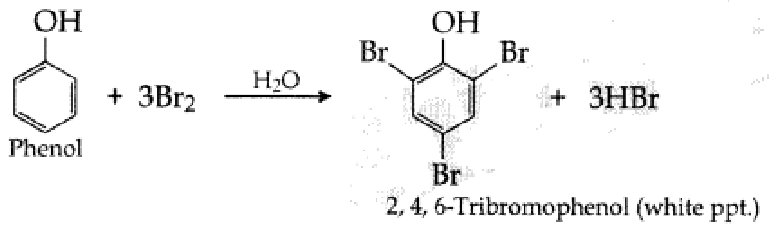


Step 2 : Nucleophilic attack of water on carbonation

Step 3 : Deprotonation to form an alcohol

.

(a) (i) Br_2/H_2O

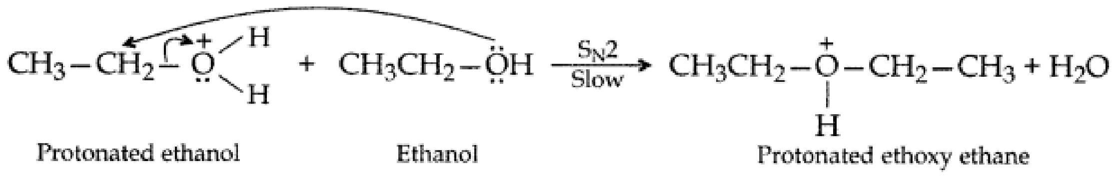


(ii) B_2H_6, H_2O_2 and OH^-

$$\underset{\text{Propene}}{CH_3{-}CH = CH_2} \xrightarrow[(b)\ H_2O_2/OH^-]{(a)\ BH_3/THF} \underset{\text{Propanol}}{CH_3CH_2CH_2OH}$$

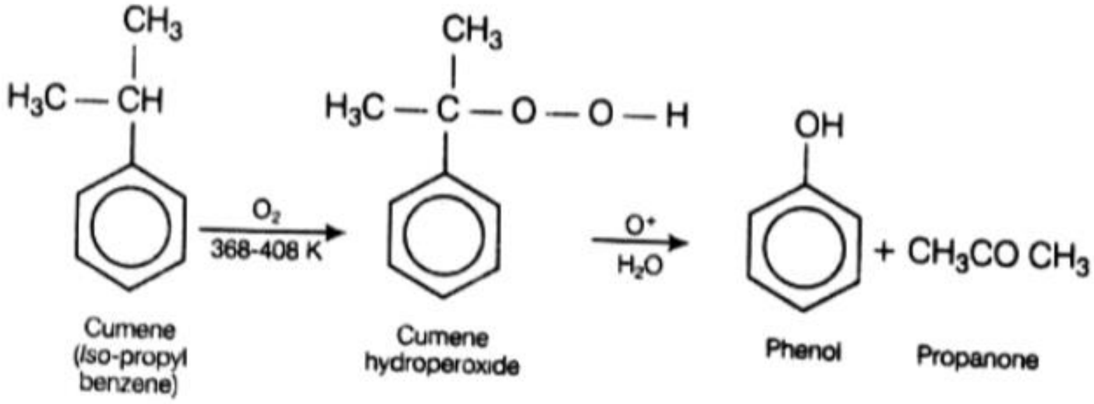
(b) (i) p-nitrophenol > Phenol > Ethanol *(Acidic character)*
(ii) Propanol > Propanal > Propane *(Boiling point)*

(c)

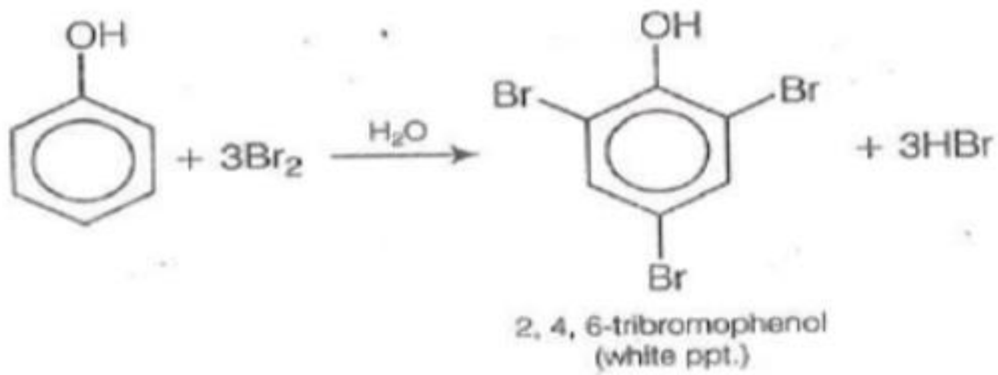


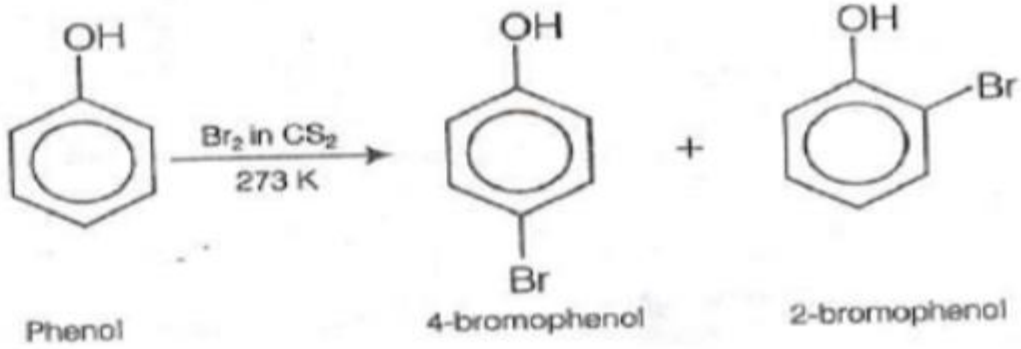
3.Answer

4. (a) The starting material used in the industrial preparation of phenol is cumene.



(b) Phenols when treated with bromine water give polyhalogen derivatives in which all the hydrogen atoms present at ortho and para positions with respect to the -OH group are replaced by bromine atoms.

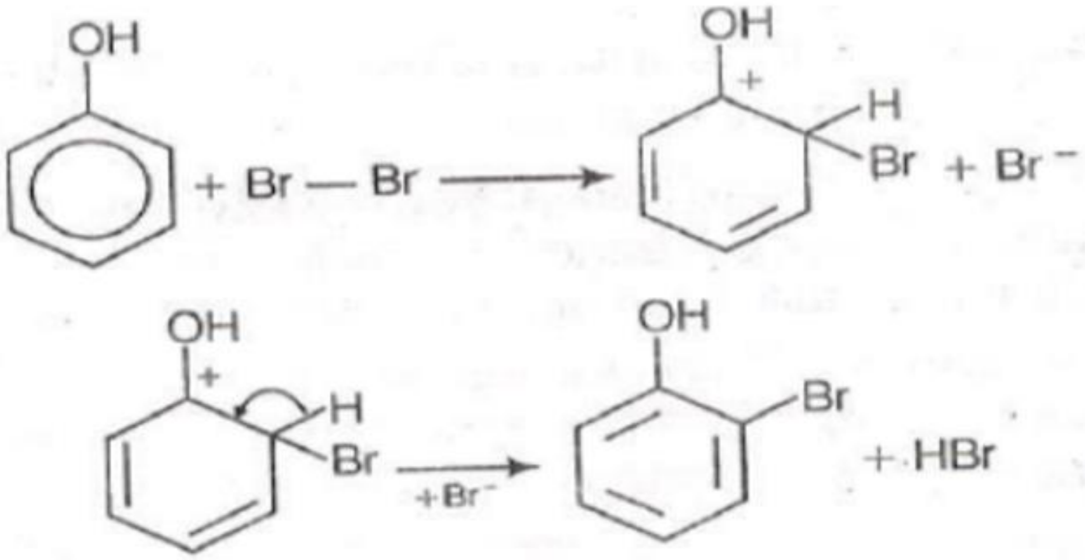




In an aqueous solution, phenol ionises to form phenoxide ions. This ion activates the benzene ring to a very large extent and hence the substitution of halogen takes place at all three positions.

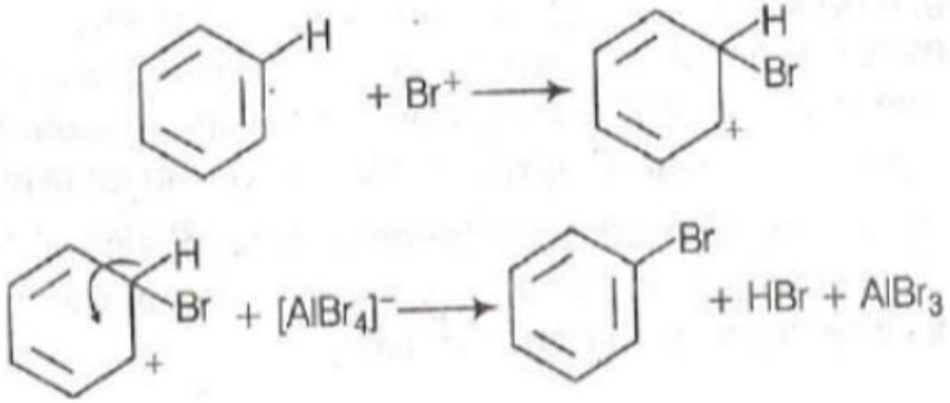
(c) In bromination of benzene, Lewis acid is used to polarise Br_2 to form the reactive electrophile, Br^+. In case of phenol, Lewis acid is not required because the O-atom of phenol itself polarises the Br_2 molecule to form Br^+ ions. further, the +R-effect of OH group makes phenol highly activated towards electrophilic substitution reactions.

Mechanism of bromination of phenol.



Mechanism of bromination of benzene:

$$AlBr_3 + Br{-}Br \rightarrow [AlBr_4]^- + Br^+$$



CASE-BASED QUESTIONS(4 MARKS)

Read the passage given below and answer the following questions:

1.A compound (X) containing C, H and O is unreactive towards sodium. It also does not react with Schiff's reagent. On refluxing with an excess of hydroiodic acid, (X) yields only one organic product (Y). On hydrolysis, (Y) yields a new compound (Z) which can be converted into (Y) by reaction with red phosphorous and iodine. The compound (Z) on oxidation with potassium permanganate gives a carboxylic acid. The equivalent weight of this acid is 60.

The following questions are multiple choice question. Choose the most appropriate answer:

i) The compound (X) is an
(a) acid
(b) aldehyde
(c) alcohol
(d) ether

(ii) The IUPAC name of the acid formed is
(a) methanoic acid
(b) ethanoic acid
(c) propanoic acid
(d) butanoic acid

(iii) Compound (Y) is
(a) ethyl iodide
(b) methyl iodide
(c) propyl iodide
(d) mixture of (a) and (b)

or

Compound (Z) is
(a) methanol
(b) ethanol
(c) propanol
(d) butanol

(iv) Compound (X) on treatment with excess of Cl_2 in presence of light gives
(a) α-chlorodiethyl ether
(b) α, α'-dichlorodiethyl ether
(c) perchlorodiethyl ether
(d) none of these

2. Alcohols play a very important role in our daily life. Ordinary spirit used as an antiseptic contains methanol. Ethanol is present in cough syrups, tonics, wine, beer, and whisky, Sugar, starch, cellulose are carbohydrates that also contain a large number —OH groups. Phenol is also an antiseptic in low concentration (0.2%) whereas a 2% solution of phenol is used as a disinfectant. The fragrance of rose is due to citronellol (unsaturated alcohol). Phenol is used for the preparation of many useful compounds like aspirin, methyl salicylate (Iodex), and phenyl salicylate (salol) used as an intestinal antiseptic.

(a) How is phenol prepared from cumene? What is the advantage of this method?
(b) How is phenol converted into salicylic acid?

(c) Convert phenol to picric acid.

(d) Distinguish between phenol and benzyl alcohol?.
(e) Why does phenol turn pink after long-standing?.

3. Read the passage given below and answer the following questions:
The reaction of phenol with aqueous sodium hydroxide indicates that phenols are stronger acids than alcohols and water. Due to the higher electronegativity of sp^2 hybridized carbon of phenol to which –OH is attached, electron density decreases on oxygen. This increases the polarity of the O–H bond and results in an increase in ionization of phenols than that of alcohols. Now let us examine the stabilities of alkoxide and phenoxide ions. In alkoxide ion, the negative charge is localized on oxygen while in phenoxide ion, the charge is delocalized. The delocalisation of negative charge makes phenoxide ions more stable and favours the ionization of phenol.

1. Phenol is less acidic than_________.
(A) Ethanol (B) o-nitrophenol (C) o-methylphenol (D) o-methoxy phenol
2. Which of the following is most acidic?
(A) Benzyl alcohol (B) Cyclohexanol (C) Phenol (D) m-Chlorophenol
3. Phenol can be distinguished from ethanol by the reaction with _____
(A) Br_2/water (B) Na (C) Glycerol (D) All of the above

4. An organic compound (A) having molecular formula C6H6O gives a characteristic color with an aqueous $FeCl_3$ solution. (A) on treatment with CO_2 and NaOH at 400 K under pressure gives (B), which on acidification gives a compound (C). The compound (C) reacts with acetyl chloride to give (D) which is a popular pain killer.

i) Compound (A) is

a) 2-hexanol	(b) dimethyl ether	(c) phenol	(d) 2-methyl pentanol.

ii) Number of carbon atoms in compound (D) is

(a) 7	(b) 6	(c) 8	(d) 9

(iii) The conversion of compound (A) to (C) is known as

a) Reimer- Tiemann reaction	(b) Kolbe’s reaction	(c) Schmidt reaction	(d) Swarts reaction

iv) Compound (A) on heating with compound (C) in presence of $POCl_3$ gives a compound (D) which is used
(a) in perfumery as a flavoring agent

(b) as an antipyretic

(c) as an analgesic

(d) as an intestinal antiseptic.

ANSWERS

1 (i) d
(ii) b
(iii) a
or
b
(iv) c

2. (a). Phenol is industrially prepared by the ‘Dow’s Process‘.
   This process involves the following steps:
   (i) Cumene is oxidized in presence of air at 400K in the presence of a metal catalyst to form cumene hydroperoxide.
   (ii) In the second step cumene hydroperoxide is treated with dilute sulphuric acid at 350K. It causes hydrolysis and forms phenol and acetone.

(b). Phenol is converted to salicylic acid by using Kolbe’s reaction. In this reaction the carboxyl group can be introduced directly into a phenol nucleus by passing carbon dioxide over the heated sodium phenoxide was first observed by Kolbe. Substitution occurs predominantly in the ortho position.

(c). It can be converted using the following reaction

(d). Add neutral $FeCl_3$. Phenol gives violet colour whereas benzyl alcohol does not

(e). It is due to oxidation

3 Ans 1. (B)
Explanation: Phenol is less acidic than o-nitrophenol as the electron-withdrawing ($-NO_2$) group increases the acidity of phenols
Ans 2. (D)

Explanation: m-chlorophenol is most acidic as the electron-withdrawing (−Cl) group increases the acidity of phenols
Ans 3. (A)
Explanation: Phenol decolorizes bromine water to form a white precipitate of 2,4,6-tribromophenol whereas ethanol does not precipitate.

4.(i)c

(ii)d

(iii)b

(iv)d

QUESTIONS ON ETHERS

MULTIPLE CHOICE QUESTIONS(1 Marks)

1. Ethers may be used as solvents because they react only with which of the following reactants?
a) Oxidising agent
b) Bases
c) Acids
d) Reducing agents

2 It's called ether when the alkyl groups connected to either side of the oxygen atom in an ether are different.
a) mixed
b) symmetrical
c) simple
d) diethyl

3. Which of the following is the most suitable requirement for the dehydration of ethanol to form an ether?
a) Sulphuric acid at 413K
b) Sulphuric acid at 443K
c) Sodium hydroxide at 413K
d) Sodium hydroxide at 443K

4 Which of the following is not favourable for the proper dehydration of alcohol to form ether?
a) Good temperature control during reaction
b) Excess of alcohol
c) Presence of protic acids
d) Presence of bulky alkyl groups in the alcohol

5. What is the major product formed when ethanol is dehydrated with concentrated H_2SO_4 at 413K?
a) Ethene
b) Methoxymethane
c) Methoxyethane
d) Ethoxyethane.

6. Sodium methoxide on heating with bromoethane gives __________
a) methoxymethane
b) methoxyethane
c) ethoxyethane
d) diethyl ether

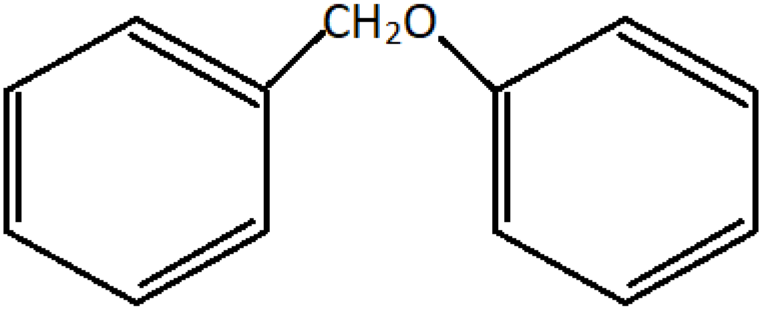
7. The reaction between tert-Butyl chloride and sodium ethoxide gives _______
a) tert-Butyl ethyl ether
b) tert-Butyl methyl ether
c) 2-Methylprop-1-ene
d) butane

8. The boiling point of ethers is ______ the boiling point of alcohols of comparable molecular mass.
a) lower than
b) similar to
c) little higher than
d) much higher than

9. Which of the following is the least reactive functional group?
a) Alcohols
b) Ethers
c) Aldehydes
d) Ketones

10. 10. One molecule of dialkyl ether produces how many molecules of alkyl halides with excess of halogen acid?
a) 1
b) 2
c) 3
d) 4

11. What product(s) are formed when the shown ether is heated with hydrogen iodide?



a) $(C_6H_5)CH_2I$ and $(C_6H_5)OH$

b) $(C_6H_5)CH_2OH$ and $(C_6H_5)I$
c) $(C_6H_5)CH_2OH$ and $(C_6H_5)CH_2I$
d) $(C_6H_5)OH$ and $(C_6H_5)I$

12. What is the major product of bromination of anisole in ethanoic acid?
a) o-Dibromobenzene
b) p-Dibromobenzene
c) o-Bromoanisole
d) p-Bromoanisole

13. . Identify the major product of Friedel-Crafts acylation of anisole with ethanoyl chloride?
a) 2-Methoxytoluene
b) 4-Methoxytoluene
c) 2-Methoxyacetophenone
d) 4-Methoxyacetophenone

14. 4-Nitroanisole is obtained as the major product when anisole reacts with _____
a) concentrated H_2SO_4
b) concentrated HNO_3
c) mixture of concentrated H_2SO_4 and HNO_3
d) mixture of dilute H_2SO_4 and HNO_3

15. Ethers are linear molecules with zero dipole moment.
a) True
b) False

ANSWERS

1.c
2.a
3.a
4 .d
5. d
6 b
7. C
8. A
9. B
10.b
11.a
12.d
13.d
14 c
15.b

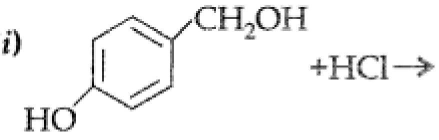
SHORT ANSWER QUESTIONS (2 MARKS)

1.Write equation of the nitration of anisole.

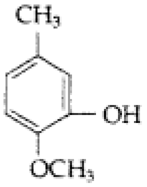
2.Complete the following reaction equations : (Delhi 2009)

(i)

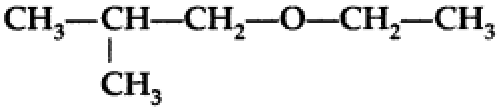
(ii)



3. Write IUPAC name of the following



4. Write the IUPAC name of given compound: (All India 2015)



$$CH_3-\underset{\underset{CH_3}{|}}{CH}-CH_2-O-CH_2-CH_3$$

5. Explain why is O=C=O nonpolar while R-O-R is polar.

6. Why is the C-O-H bond angle in alcohols slightly less than the tetrahedral angle whereas the C-O-C bond angle ether is slightly greater?

7. Explain why alcohols and ethers of comparable molecular mass have different boiling points?

8. What happens when benzene diazonium chloride is heated with water?

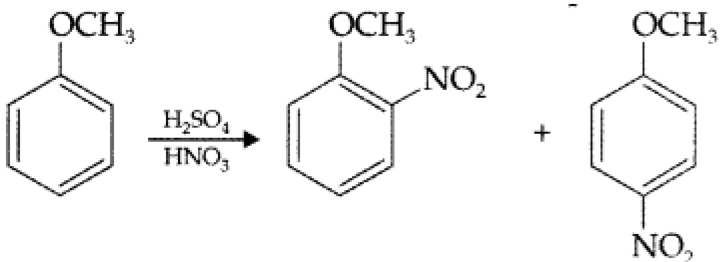
9. Suggest a reagent for the following conversion.

10. . Why are ethers used as a solvent?

.

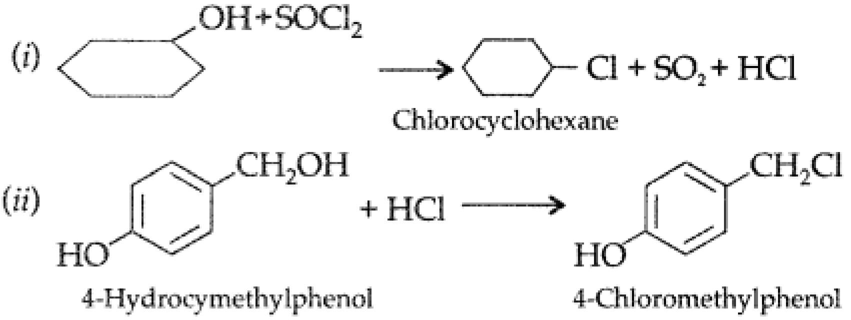
ANSWERS

1.



p-nitro Anisol is major product

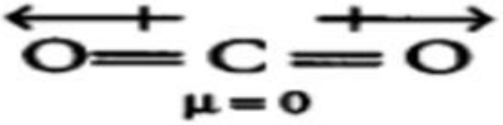
2.

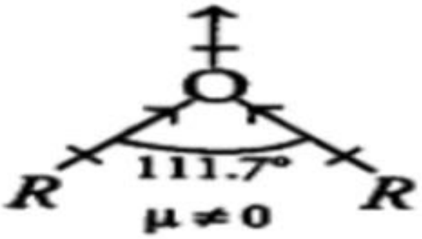


3. IUPAC name : 2-Methoxy-5-methyl phenol

4. IUPAC name : 1-Ethoxy-2-methylpropane

5. The dipole moments of the two C=O bonds are exactly equal and opposite, making O=C=O nonpolar. As a result, they cancel each other out, resulting in a net dipole moment of zero for O=C=O. Because the form of this compound is non-linear, the net dipole moment of R—O—R is not equal to zero, and hence R—O—R is polar in nature.

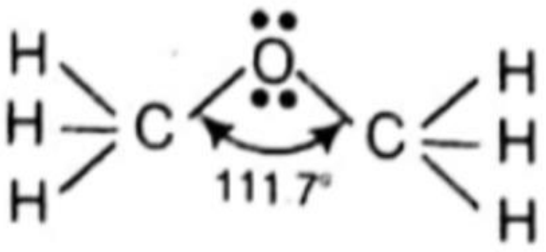




6. The bond angle in C−:O:−H in alcohols is slightly less than tetrahedral angle (108.9). It is due to the repulsion between the unshared electron pairs of oxygen. In alcohols, two lone pairs of electrons are present. Therefore, there is comparatively more repulsion and less bond angle.

The C-O-C bond angle (111.7◦) in ether is slightly greater than the tetrahedral angle due to the repulsive interaction between the two bulky (- R) groups.

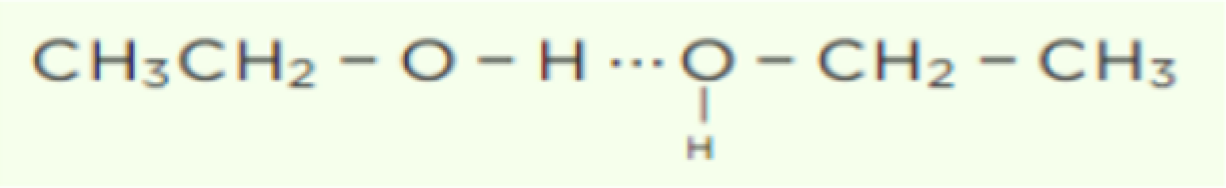
Methanol



Methoxymethane

7. Because the ethers have a low polarity, they do not display any intermolecular hydrogen bonding.

Because breaking weak dipole-dipole forces in ethers requires less energy than breaking strong hydrogen bonds in alcohol.

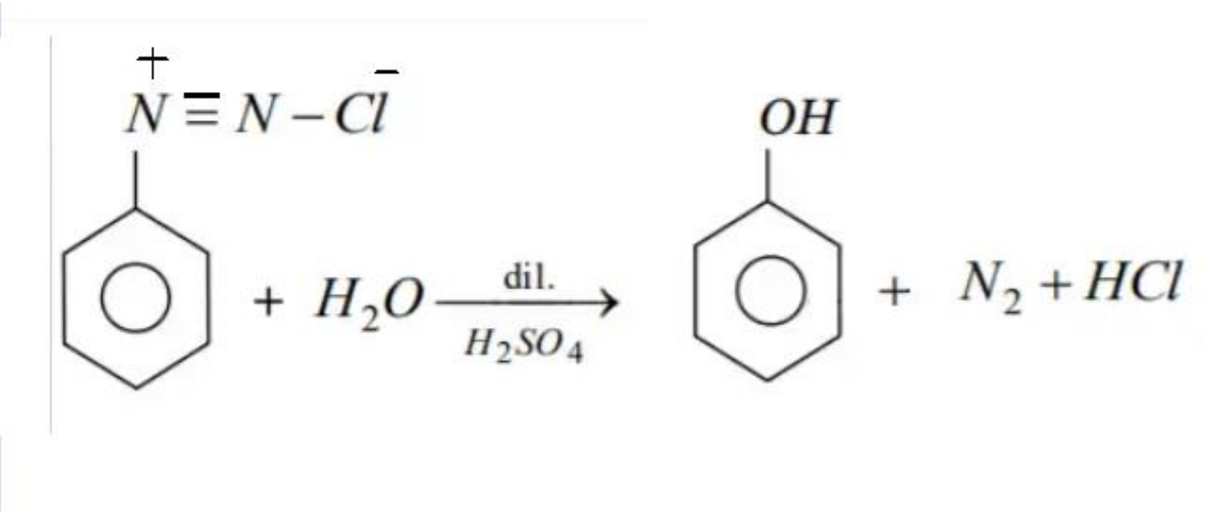


$$CH_3CH_2-O-H\cdots\underset{\displaystyle H}{\underset{|}{O}}-CH_2-CH_3$$

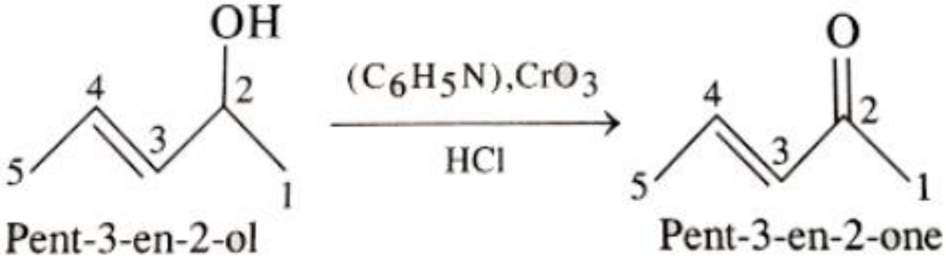
Hydrogen Bond in alcohols.

As a result, ethers have low boiling points, which are lower than isomeric alcohols and nearly equal to alkanes of comparable molecular weights. Alcohols and ethers have vastly different boiling points due to the presence of hydrogen bonding in alcohols.

8. The phenol is formed. When benzene diazonium chloride is heated with water, it produces phenol as well as nitrogen gas and hydrochloric acid as by-products.



9. The given reactant is $H_3C-CH=CH-CH(OH)-CH_3$. It is a secondary alcohol. Secondary alcohol gives ketone when oxidised by CrO_3 or pyridinium chlorochromate without carrying out oxidation at the double bond.



10. They are primarily used as good solvents because of their high volatility, slow chemical reactivity, and ability to accept the hydrogen bond.

SHORT ANSWER QUESTION (3 MARKS)

1. llustrate the following reactions giving a chemical equation for each :
   (i) Kolbe's reaction
   (ii) Williamsons synthesis of an ether

2.Explain the following reactions with an example for each :
(i) Reimer-Tiemann reaction
(ii) Friedel-Crafts reaction.

3. Explain the following giving one example for each :
(i) Reimer-Tiemann reaction.
(ii) Friedel-Craft's acetylation of anisole.

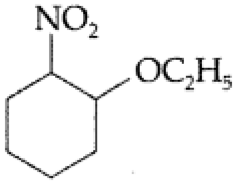
4. Explain the following observations :
(i) The boiling point of ethanol is higher than that of methoxymethane.
(ii) Phenol is more acidic than ethanol.
(iii) o- and p-nitrophenols are more acidic than phenol.

5, How would you convert the following :
(i) Phenol to benzoquinone
(ii) Propanone to 2-methylpropan-2-ol

(iii) Propene to propan-2-ol

6. (a) Give a seperate chemical test to distinguish between the following pairs of compounds:
(i) Ethanol and Phenol (ii) 2-Pentanol and 3-Pentanol
(b) Explain Kolbe’s reaction with the help of suitable example.

7. (a) How would you obtain the following :
(i) 2-methylpentan-2-ol from 2-methyl-1-pentene
(ii) Acetophenone from phenol
(b) Write IUPAC name of the following :



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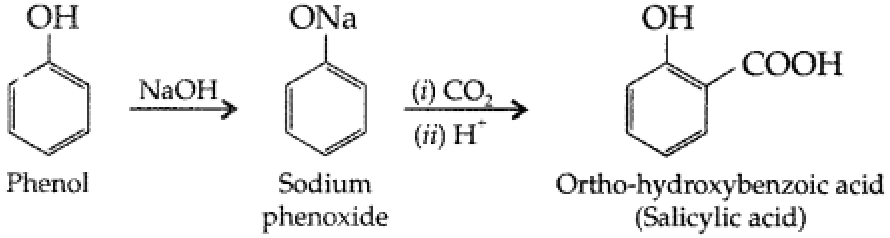
8. a) Give mechanism of preparation of ethoxy ethane from ethanol.
(b) How is toluene obtained from phenol?

9. How are the following conversions carried out?
(i) Propene → 4 Propan-2-ol
(ii) Ethylmagnesium chloride → 4 Propan-l-ol
(iii) Benzyl chloride → Benzyl alcohol

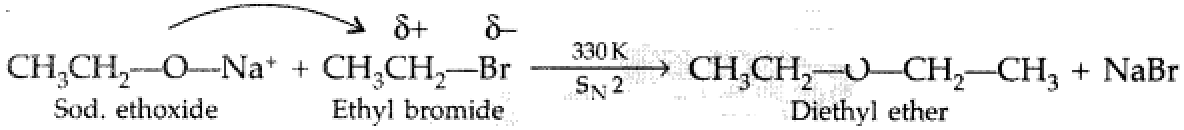
10.. How do you convert the following :
(i) Phenol to anisole
(ii) Propan-2-ol to 2-methylpropan-2-ol
(iii) Aniline to phenol

ANSWERS

1.(i) Kolbe's reaction : Phenol reacts with CO_2 in presence of sodium hydroxide (NaOH) at 4 – 7 Atm and 390 – 410 K giving salicylic acid

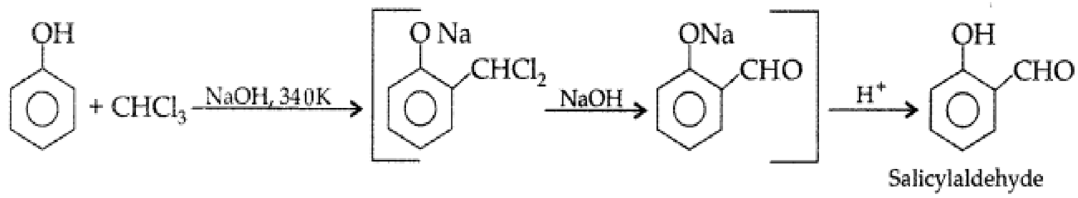


(ii) Williamsons synthesis of an ether : The reaction involves the nucleophilic substitution of the halide ion from the alkyl halide by the alkoxide ion by S_N2 mechanism.
Example :

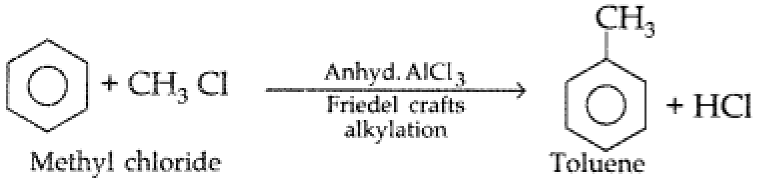


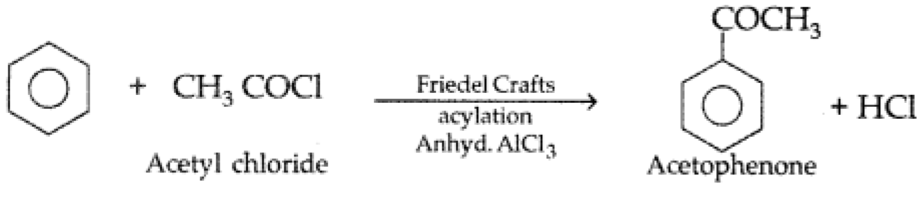
2. Answer:
(i) Reimer-Tiemann reaction : Treatment of phenol with $CHCl_3$ in presence of aqueous NaOH at 340K followed by hydrolysis gives salicylaldehyde.

Example :



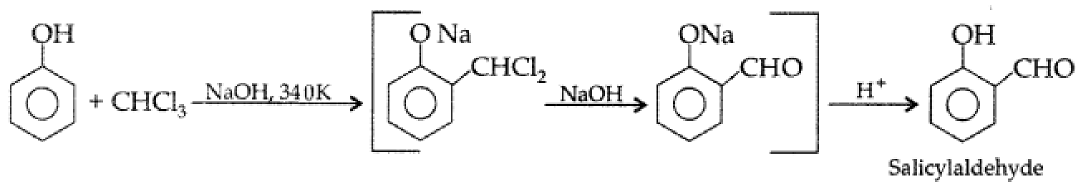
(ii) Friedel-Crafts reaction : This reaction is used for introducing an alkyl or an acyl group into an aromatic compound in presence of Lewis acid catalyst ($AlCl_3$)
Example:



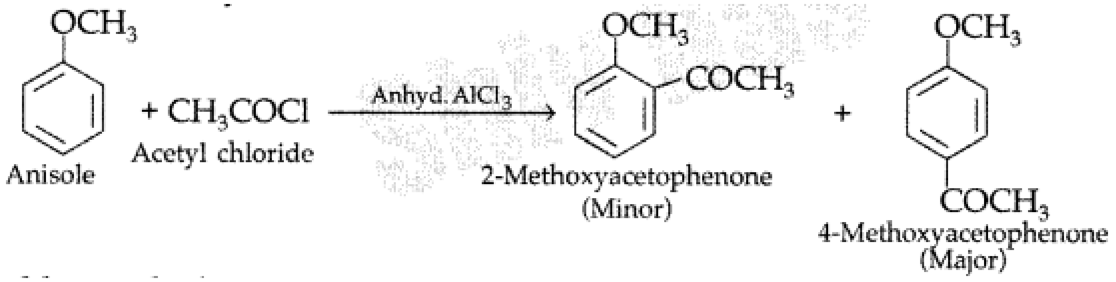


3. Answer:
(i) Reimer-Tiemann reaction : Treatment of phenol with $CHCl_3$ in presence of aqueous NaOH at 340K followed by hydrolysis gives salicylaldehyde.

Example :



(ii) Friedel-Craft's acetylation of anisole :



4. Answer:

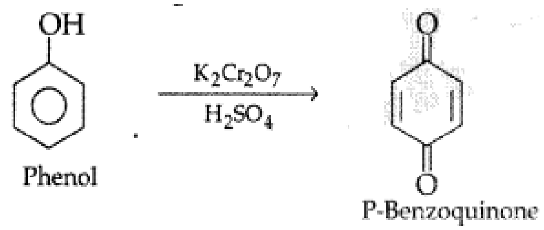
(i) Due to presence of intermolecular H-bonding, associated molecules are formed, hence ethanol has high boiling point while methoxymethane does not have intermolecular H-bonding.

(ii) Phenol on losing H^+ ion forms phenoxide ion, and ethanol on losing H^+ ion forms ethoxide ion. Phenoxide ion is more stable than ethoxide ion as phenoxide ion exists in resonance structure. Due to this phenol is more acidic than ethanol.

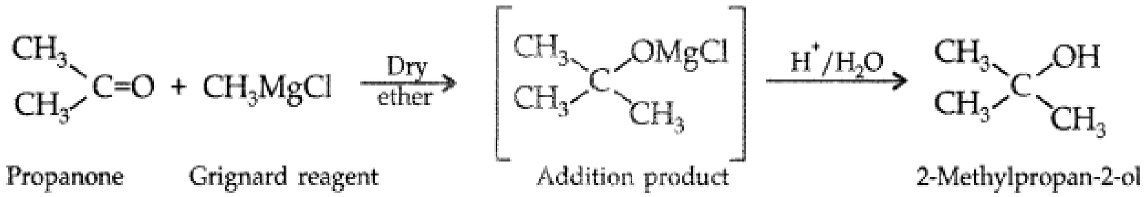
(iii) Both o- and p-nitrophenols contain the NO_2 group which is an electron withdrawing group. Due to -R and -I effect of the $-NO_2$ group, electron density in the OH bond of substituted phenol decreases and hence the loss of proton becomes easy and therefore more acidic

5. Answer:

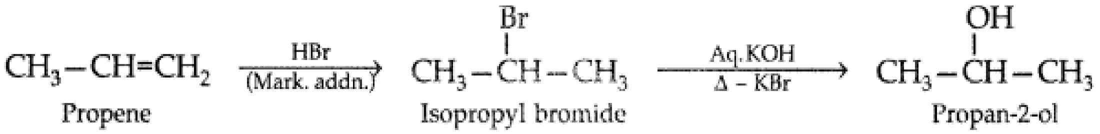
(i) Phenol to benzoquinone



(*ii*) Propanone to 2-methylpropan-2-ol



(*iii*) Propene to propan-2-ol

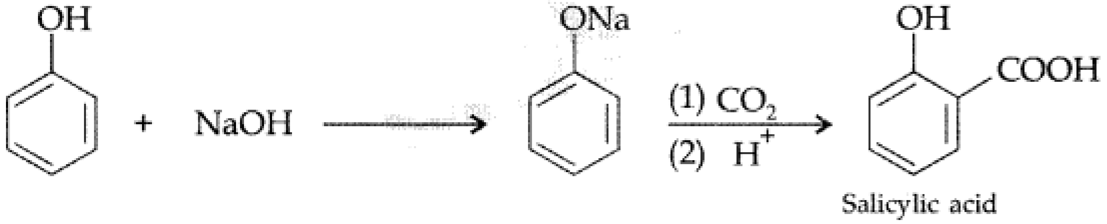


6. Answer:

(a) (i) Ethanol on reacting with I_2 in NaOH gives yellow ppt of iodoform whereas phenol does not respond to this test.

(ii) 2-Pentanol on reacting with I_2 in NaOH gives yellow ppt of iodoform whereas 3-pentanol does not respond to this test.

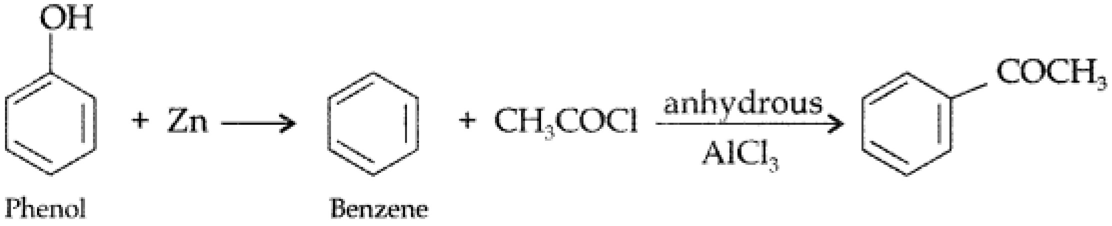
(b) Kolbe’s reaction : Phenol reacts with NaOH to give sodium phenoxide which on reaction with CO_2 in acid gives salicylic acid.



7. (a) (i) 2-Methylpentan-2-ol from 2-methyl-1-pentene

$$CH_3CH_2CH_2-\underset{CH_3}{\underset{|}{C}}=CH_2+HOH\xrightarrow{\text{dil}\,H_2SO_4}CH_3-CH_2-CH_2^{-}-\overset{OH}{\overset{|}{\underset{CH_3}{\underset{|}{C}}}}-CH_3$$

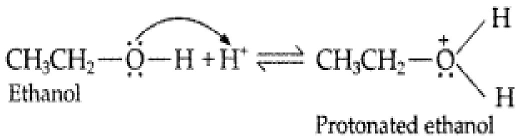
(*ii*) Acetophenone from phenol



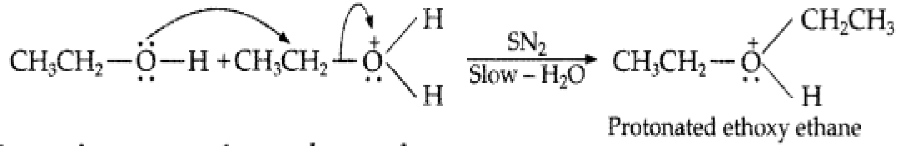
(b) IUPAC name : 1 -ethoxy-2-nitrocyclohexane.

8. (a) Mechanism of formation of ethoxy ethane

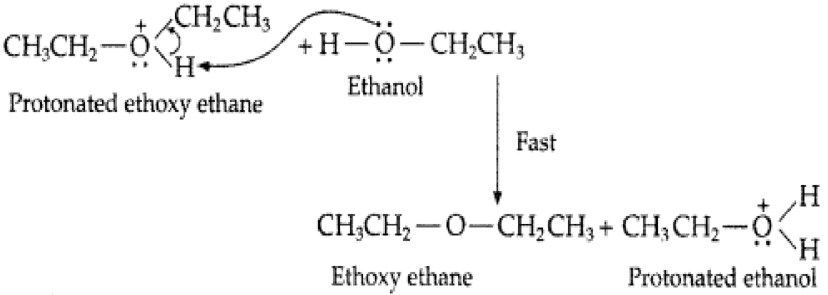
Step 1 : Protonation of ethanol



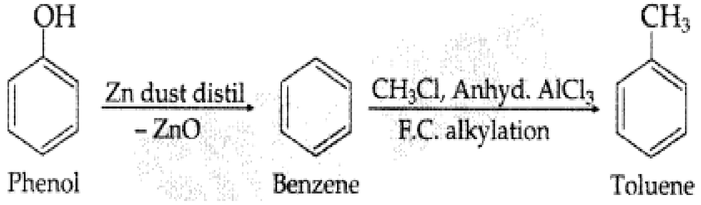
Step 2 : Nucleophillic attack by unprotonated alcohol molecule on protonated alcohol molecule



Step 3 : Loss of proton to form ethoxy ethane

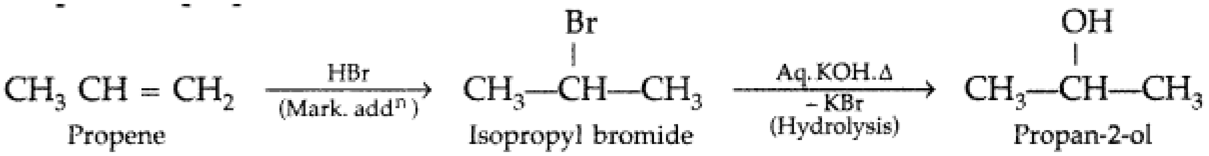


(*b*) **Toluene from Phenol**



9. Answer:

(i) Propene to propan-2-ol

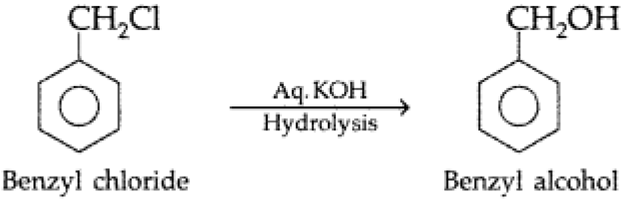


$$\underset{\text{Propene}}{CH_3\,CH = CH_2} \xrightarrow[\text{(Mark. add}^n\text{)}]{HBr} \underset{\text{Isopropyl bromide}}{CH_3-\overset{\overset{\displaystyle Br}{|}}{CH}-CH_3} \xrightarrow[\substack{-\,KBr\\ \text{(Hydrolysis)}}]{\text{Aq. KOH}.\Delta} \underset{\text{Propan-2-ol}}{CH_3-\overset{\overset{\displaystyle OH}{|}}{CH}-CH_3}$$

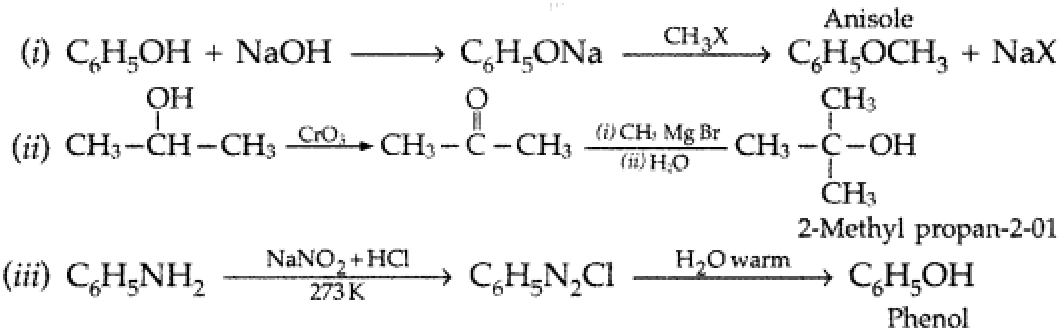
(ii) Ethylmagnesium chloride to propan-1-ol

$$\underset{\text{Ethyl Magnesium chloride}}{CH_3CH_2MgCl} \xrightarrow[\text{(Grignard Rx}^n\text{)}]{HCHO} \underset{\text{Addition product}}{[CH_3CH_2CH_2OMgCl]} \xrightarrow{H^+/H_2O} \underset{\text{Propan-1-ol}}{CH_3CH_2CH_2OH} + Mg(OH)Cl$$

(iii) Benzyl chloride → Benzyl alcohol



10.Answer:



$$(i)\ C_6H_5OH + NaOH \longrightarrow C_6H_5ONa \xrightarrow{CH_3X} \overset{\text{Anisole}}{C_6H_5OCH_3} + NaX$$

$$(ii)\ CH_3-\overset{OH}{\overset{|}{C}H}-CH_3 \xrightarrow{CrO_3} CH_3-\overset{O}{\overset{\|}{C}}-CH_3 \xrightarrow[(ii)\,H_2O]{(i)\,CH_3MgBr} CH_3-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-OH$$

2-Methyl propan-2-01

$$(iii)\ C_6H_5NH_2 \xrightarrow[273\,K]{NaNO_2+HCl} C_6H_5N_2Cl \xrightarrow{H_2O\ \text{warm}} \underset{\text{Phenol}}{C_6H_5OH}$$

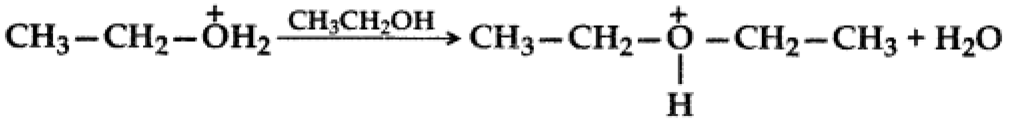
LONG ANSWER QUESTIONS (5 MARKS)

1.Write the mechanism of the following reaction:

$$2CH_3CH_2OH \xrightarrow[413\,K]{\text{Conc. } H_2SO_4} CH_3CH_2—O—CH_2—CH_3$$

2. a) What happens when CH_3—O—CH<sub3 is heated with HI?
(b) Explain mechanism for hydration of acid catalyzed ethene :
CH2 = CH2 + HzO ⟶H+CH3—CH,—OH

3. Write the formula of reagents used in the following reactions:
(i) Bromination of phenol to 2,4,6-tribromophenol
(ii) Hydroboration of propene and then oxidation to propanol.
(b) Arrange the following compound groups in the increasing order of their property indicated:
(i) p-nitrophenol, ethanol, phenol (acidic character)
(ii) Propanol, Propane, Propanal (boiling point)
(c) Write the mechanism (using curved arrow notation) of the following reaction:



$$CH_3-CH_2-\overset{+}{O}H_2 \xrightarrow{CH_3CH_2OH} CH_3-CH_2-\underset{\underset{H}{|}}{\overset{+}{O}}-CH_2-CH_3 + H_2O$$

4. . (a) Name the starting material used in the industrial preparation of phenol.

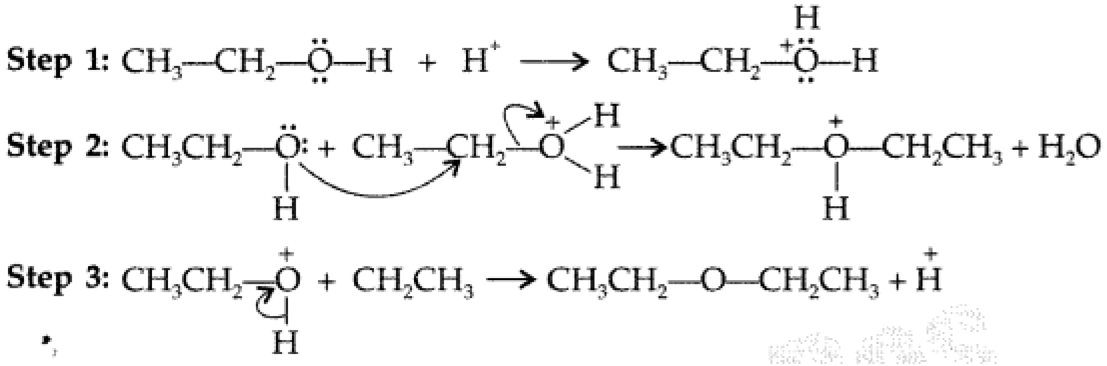
(b) Write a complete reaction for the bromination of phenol in an aqueous and non-aqueous medium.

(c) Explain why Lewis acid is not required in the bromination of phenol?

ANSWERS

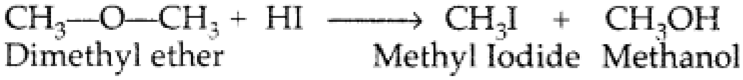
1. Answer:

Mechanism:



2.Answer:

(a) Methyl Iodide (CH_3I) and Methanol (CH_3OH) are formed when CH_3—O—CH_3 is heated with HI.

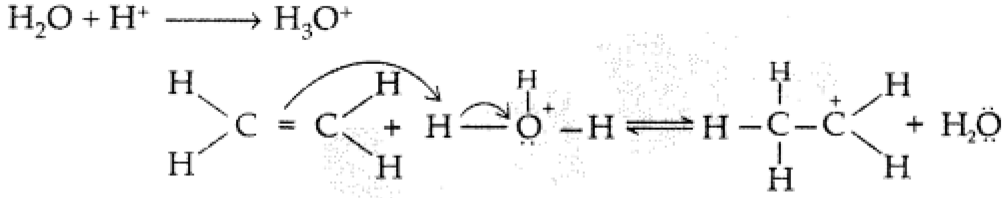


$$CH_3—O—CH_3 + HI \longrightarrow CH_3I + CH_3OH$$

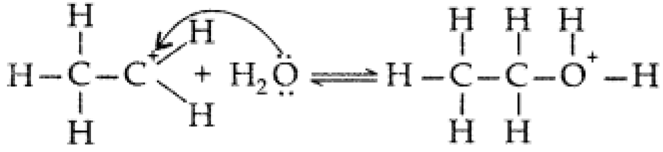
(b) Acid catalysed hydration : Alkenes react with water in the presence of acid as catalyst to form alcohols.

Mechanism : It involves the following three steps :

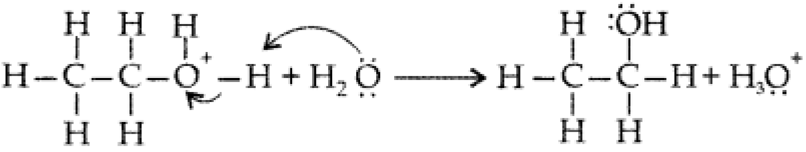
Step 1: Protonation of alkene to form carbocation by electrophilic attack of H_3O^+.



Step 2 : Nucleophilic attack of water on carbonation



Step 3 : Deprotonation to form an alcohol



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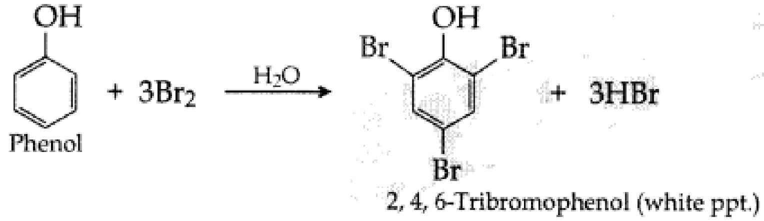
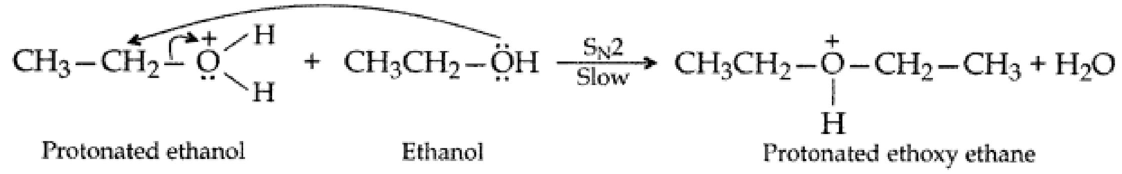
(*a*) (*i*) Br_2/H_2O



(*ii*) B_2H_6, H_2O_2 and OH^-

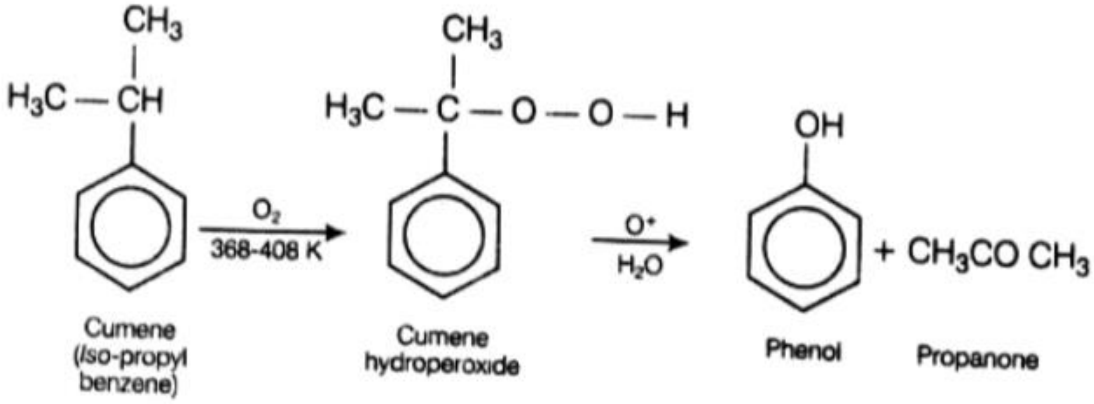
$$\underset{\text{Propene}}{CH_3{-}CH=CH_2} \xrightarrow[(b)\ H_2O_2/OH^-]{(a)\ BH_3/THF} \underset{\text{Propanol}}{CH_3CH_2CH_2OH}$$

(*b*) (*i*) p-nitrophenol > Phenol > Ethanol *(Acidic character)*
(*ii*) Propanol > Propanal > Propane *(Boiling point)*

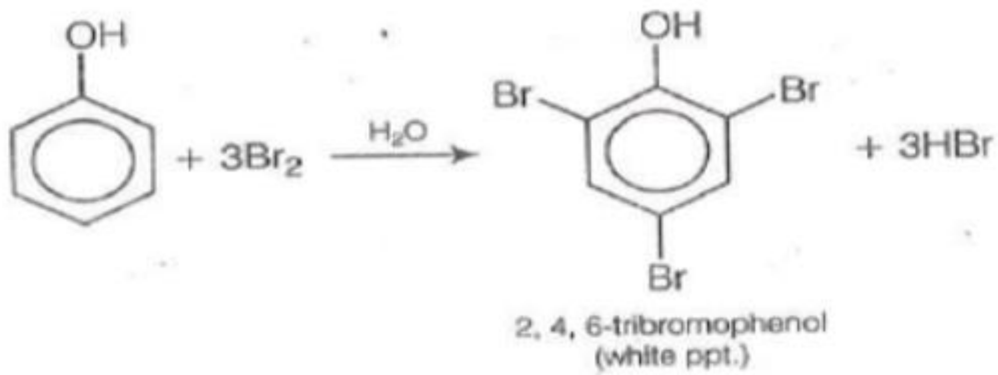
(*c*)


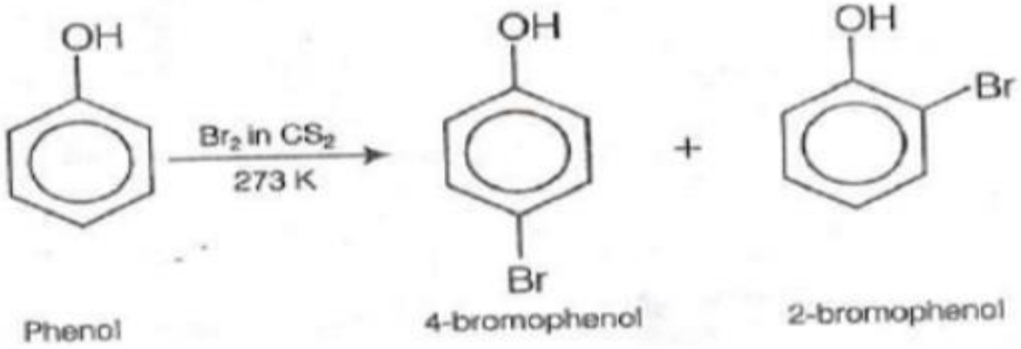
3.Answer

4. (a) The starting material used in the industrial preparation of phenol is cumene.



(b) Phenols when treated with bromine water give polyhalogen derivatives in which all the hydrogen atoms present at ortho and para positions with respect to the -OH group are replaced by bromine atoms.

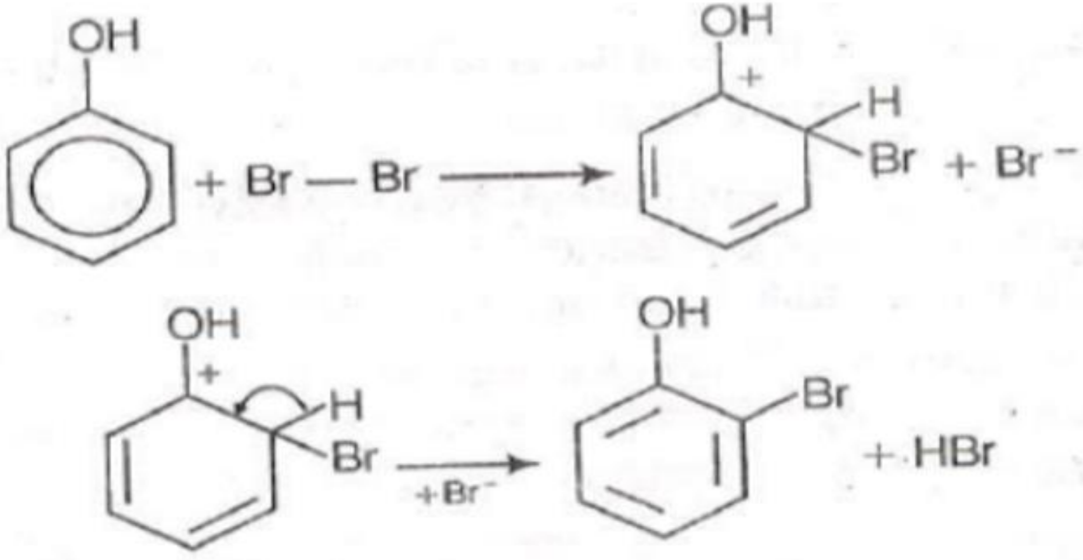




In an aqueous solution, phenol ionises to form phenoxide ions. This ion activates the benzene ring to a very large extent and hence the substitution of halogen takes place at all three positions.

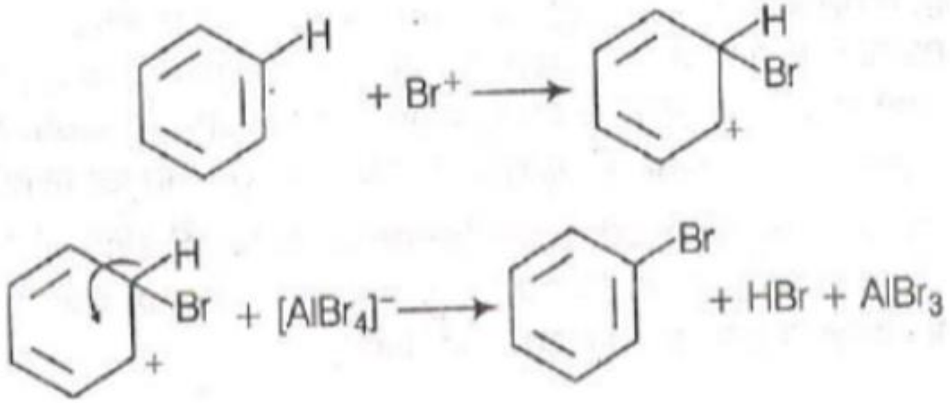
(c) In bromination of benzene, Lewis acid is used to polarise Br_2 to form the reactive electrophile, Br^+. In case of phenol, Lewis acid is not required because the O-atom of phenol itself polarises the Br_2 molecule to form Br^+ ions. further, the +R-effect of OH group makes phenol highly activated towards electrophilic substitution reactions.

Mechanism of bromination of phenol.



Mechanism of bromination of benzene:

$$AlBr_3 + Br{-}Br \rightarrow [AlBr_4]^- + Br^+$$



CASE-BASED QUESTIONS(4 MARKS)

Read the passage given below and answer the following questions:

1.A compound (X) containing C, H and O is unreactive towards sodium. It also does not react with Schiff's reagent. On refluxing with an excess of hydroiodic acid, (X) yields only one organic product (Y). On hydrolysis, (Y) yields a new compound (Z) which can be converted into (Y) by reaction with red phosphorous and iodine. The compound (Z) on oxidation with potassium permanganate gives a carboxylic acid. The equivalent weight of this acid is 60.

The following questions are multiple choice question. Choose the most appropriate answer:

i) The compound (X) is an
(a) acid
(b) aldehyde
(c) alcohol
(d) ether

(ii) The IUPAC name of the acid formed is
(a) methanoic acid
(b) ethanoic acid
(c) propanoic acid
(d) butanoic acid

(iii) Compound (Y) is
(a) ethyl iodide
(b) methyl iodide
(c) propyl iodide
(d) mixture of (a) and (b)

or

Compound (Z) is
(a) methanol
(b) ethanol
(c) propanol
(d) butanol

(iv) Compound (X) on treatment with excess of Cl_2 in presence of light gives
(a) α-chlorodiethyl ether
(b) α, α'-dichlorodiethyl ether

(c) perchlorodiethyl ether
(d) none of these

2. Alcohols play a very important role in our daily life. Ordinary spirit used as an antiseptic contains methanol. Ethanol is present in cough syrups, tonics, wine, beer, and whisky, Sugar, starch, cellulose are carbohydrates that also contain a large number —OH groups. Phenol is also an antiseptic in low concentration (0.2%) whereas a 2% solution of phenol is used as a disinfectant. The fragrance of rose is due to citronellol (unsaturated alcohol). Phenol is used for the preparation of many useful compounds like aspirin, methyl salicylate (Iodex), and phenyl salicylate (salol) used as an intestinal antiseptic.

(a) How is phenol prepared from cumene? What is the advantage of this method?
(b) How is phenol converted into salicylic acid?

(c) Convert phenol to picric acid.

(d) Distinguish between phenol and benzyl alcohol?.
(e) Why does phenol turn pink after long-standing?.

3. Read the passage given below and answer the following questions:
The reaction of phenol with aqueous sodium hydroxide indicates that phenols are stronger acids than alcohols and water. Due to the higher electronegativity of sp^2 hybridized carbon of phenol to which –OH is attached, electron density decreases on oxygen. This increases the polarity of the O–H bond and results in an increase in ionization of phenols than that of alcohols. Now let us examine the stabilities of alkoxide and phenoxide ions. In alkoxide ion, the negative charge is localized on oxygen while in phenoxide ion, the charge is delocalized. The delocalisation of negative charge makes phenoxide ions more stable and favours the ionization of phenol.

1. Phenol is less acidic than_________.
(A) Ethanol (B) o-nitrophenol (C) o-methylphenol (D) o-methoxy phenol
2. Which of the following is most acidic?
(A) Benzyl alcohol (B) Cyclohexanol (C) Phenol (D) m-Chlorophenol
3. Phenol can be distinguished from ethanol by the reaction with _____
(A) Br_2/water (B) Na (C) Glycerol (D) All of the above

4. An organic compound (A) having molecular formula C6H6O gives a characteristic color with an aqueous $FeCl_3$ solution. (A) on treatment with CO_2 and NaOH at 400 K under pressure gives (B), which on acidification gives a compound (C). The compound (C) reacts with acetyl chloride to give (D) which is a popular pain killer.

i) Compound (A) is

a) 2-hexanol	(b) dimethyl ether	(c) phenol	(d) 2-methyl pentanol.

ii) Number of carbon atoms in compound (D) is

(a) 7	(b) 6	(c) 8	(d) 9

(iii) The conversion of compound (A) to (C) is known as

a) Reimer- Tiemann reaction	(b) Kolbe's reaction	(c) Schmidt reaction	(d) Swarts reaction

iv) Compound (A) on heating with compound (C) in presence of $POCl_3$ gives a compound (D) which is used
(a) in perfumery as a flavoring agent

(b) as an antipyretic

(c) as an analgesic

(d) as an intestinal antiseptic.

ANSWERS

1 (i) d
(ii) b
(iii) a
or
b
(iv) c

2. (a). Phenol is industrially prepared by the 'Dow's Process'.
This process involves the following steps:
(i) Cumene is oxidized in presence of air at 400K in the presence of a metal catalyst to form cumene hydroperoxide.
(ii) In the second step cumene hydroperoxide is treated with dilute sulphuric acid at 350K. It causes hydrolysis and forms phenol and acetone.

(b). Phenol is converted to salicylic acid by using Kolbe's reaction. In this reaction the carboxyl group can be introduced directly into a phenol nucleus by passing carbon dioxide over the heated sodium phenoxide was first observed by Kolbe. Substitution occurs predominantly in the ortho position.

(c). It can be converted using the following reaction

(d). Add neutral $FeCl_3$. Phenol gives violet colour whereas benzyl alcohol does not

(e). It is due to oxidation

3 Ans 1. (B)
Explanation: Phenol is less acidic than o-nitrophenol as the electron-withdrawing (−NO_2) group increases the acidity of phenols
Ans 2. (D)
Explanation: m-chlorophenol is most acidic as the electron-withdrawing (−Cl) group increases the acidity of phenols
Ans 3. (A)
Explanation: Phenol decolorizes bromine water to form a white precipitate of 2,4,6-tribromophenol whereas ethanol does not precipitate.

4.(i)c

(ii)d

(iii)b

(iv)d

CHAPTER: ALDEHYDES, KETONES AND CARBOXYLIC ACIDS

TOPIC: CARBOXYLIC ACIDS

MULTIPLE CHOICE QUESTIONS (1 MARK EACH)

1. What is the correct order of boiling points of the following?
(A) $HCOOH > CH_3COOH > C_2H_5COOH$
(B) $C_2H_5COOH > CH_3COOH > HCOOH$
(C) $HCOOH > C_2H_5COOH > CH_3COOH$
(D) $CH_3COOH > HCOOH > C_2H_5COOH$

2. Esterification of carboxylic acids is a/an __________ reaction.

(A) irreversible
(B) nucleophilic addition
(C) electrophilic substitution
(D) nucleophilic substitution

3. α-Hydroxypropanoic acid can be prepared from ethanal by following the steps given in the sequence
(A) Treat with HCN followed by acidic hydrolysis
(B) Treat with NaHSO3 followed by reaction with Na2CO3
(C) Treat with H2SO4 followed by hydrolysis
(D) Treat with K2Cr2O7 in presence of sulphuric acid

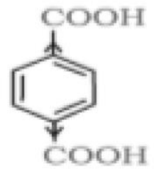
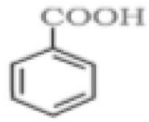
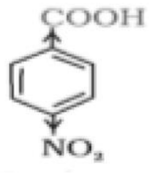
4. An organic compound A upon reacting with NH_3 gives B. On heating B gives C. C in presence of KOH reacts with Br_2 to given $CH_3CH_2NH_2$. A is
(A) CH_3COOH
(B) $CH_3CH_2CH_2COOH$
(C) CH_3 $CH(CH_3)$ COOH
(D) CH_3CH_2COOH

5. What is the IUPAC name of the given compound- (CH3)2CHCOOH
(A) Dimethylethanoic acid
(B) 3,3-Dimethylethanoic acid
(C) 2-Methylpropanoic acid
(D) Butanoic acid

6. Which of the following test is for carboxylic acid?
1. Litmus test
2. Ester test
3. Sodium bicarbonate test
4. m-dinitrobenzene test
(A) Only 1 & 3
(B) Only 2 & 3

(C) Only 1,2,3
(D) 1,2,3,4

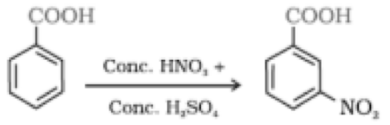
7. What is the correct sequence of decreasing acidic character?

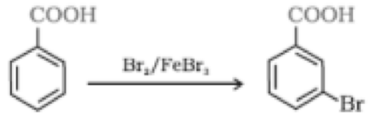




(A) (i)> (ii) > (iii)
(B) (ii)> (i) > (iii)
(C) (iii)> (ii) > (i)
(D) (ii) > (i) > (iii)

8. Which of the following statement is not true about the acidic nature of carboxylic acids.
(A) Smaller the pKa value, stronger is the acid.
(B) The presence of electron donating group on the phenyl of aromatic carboxylic acid increases their acidity.
(C) The presence of electron withdrawing group on the phenyl ring of aromatic carboxylic acid increases their acidity.
(D) Carboxylic acids are weaker than mineral acids

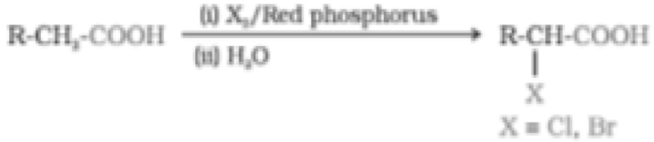
9. Ramesh learnt about the following reactions. Which statement about these reactions is correct





(A) Aromatic carboxylic acids undergo electrophilic substitution reactions
(B) The carboxyl group acts as a deactivating group.
(C) The carboxyl group acts as a meta-directing group.
(D) All of these statements are correct.

10. The following reaction is



$$\text{R-CH}_2\text{-COOH} \xrightarrow[\text{(ii) } H_2O]{\text{(i) } X_2\text{/Red phosphorus}} \underset{\substack{| \\ X}}{\text{R-CH-COOH}}$$

X = Cl, Br

(A) b) Kolbe electrolysis
(B) Friedel Crafts reaction
(C) Hell Volhard Zelinsky reaction
(D) Clemmensen reduction

11. Which among following is commonly used food preservative?
(A) Sodium benzoate
(B) Sodium ethanoate

(C) Sodium methanoate
(D) Silver benzoate

ASSERTION REASON QUESTIONS

In the following questions a statement of Assertion (A) followed by a statement of Reason (R) is given. Choose the correct answer out of the following choices.

(A) Assertion and Reason both are correct statements and Reason is correct explanation for Assertion.
(B) Assertion and Reason both are correct statements but Reason is not correct explanation for Assertion.
(C) Assertion is correct statement but Reason is wrong statement.
(D) Assertion is wrong statement but Reason is correct statement.

12. **Assertion (A):** (CH3)3C-COOH does not undergo Hell Volhard Zelinsky reaction reaction.
Reason (R): It does not have any α- hydrogen

13. **Assertion (A):** Benzoic acid has higher pka value than phenol.
Reason (R): Conjugate base of phenol is less stable than benzoic acid.

14. **Assertion (A):** Carboxylic acid exists as dimer in gas phase.
Reason (R): Strong intermolecular hydrogen bonding in carboxylic acid.

15 **Assertion (A):** Benzoic acid does not undergo Friedel Craft reaction.
Reason (R): Caboxylic carbon is less electrophilic than carbonyl carbon.

Answers of MCQs

1. (B) $C_2H_5COOH > CH_3COOH > HCOOH$
2. (D) nucleophilic substitution
3. (A) Treat with HCN followed by acidic hydrolysis
4. *(d)* CH3CH2COOH
5. (C) 2-Methylpropanoic acid
6. (C) Only 1,2,3
7. (C) (iii)> (ii) > (i)
8. (C) The presence of electron withdrawing group on the phenyl of aromatic carboxylic acid increases their acidity.
9. (D) All of these statements are correct
10. (C) Hell Volhard Zelinsky reaction
11. (A) Sodium benzoate

12. (A)
13. (D)
14. (A)
15. (D)

VERY SHORT ANSWER QUESTIONS (2 MARKS EACH)

16. Which acid of the pair shown here would you expect to be stronger? CH_3COOH or FCH_2COOH . Why?

17. Give reasons :
(i) Electrophilic substitution in Benzoic acid takes place at meta position.
(ii) Carboxylic acids do not give characteristic reactions of carbonyl group

18. (a) Arrange the following compounds in an increasing order of their indicated property :
(i) Benzoic acid, 4-Nitrobenzoic acid, 3,4-Dinitrobenzoic acid, 4- Methoxybenzoic acid (acid strength)
(ii) $CH_3CH_2CH(Br)COOH$, $CH_3CH(Br)CH_2COOH$, $(CH_3)_2CHCOOH$, $CH_3CH_2CH_2COOH$ (acid strength)

19.Distinguish between the following pairs of compounds:
(i) acetic acid and formic acid
(ii) phenol and benzoic acid

20. Do the following conversions in not more than two steps:
(i) Benzoic acid to benzaldehyde
(ii) Ethyl benzene to Benzoic acid

21. Carry out the following conversions :
(i) P-nitrotoluene to 2-bromobenzoic acid
(ii) Propanoic acid to acetic acid

22 Write equations for the following reactions.
(i) Kolbe’s electrolysis
(ii) Hell Volhard Zelinsky reaction

23(i) During preparation of esters from a carboxylic acid and an alcohol in the presence of acid catalyst water or ester formed should be removed as soon as it is formed.
(ii) Write chemical equation for the above reaction.

24 (i) Why is the boiling point of an acid anhydride higher than the acidfrom which it isderived?
(ii) PCC cannot oxidise methanol to methanoic acid and while $KMnO_4$ can?

Q.25 Give reasons:
(i) Most aromatic acids are solids while acetic acid and others of this series are liquids. Explain why?
(ii) acyl chorides have lower boling point than corresponding acids?

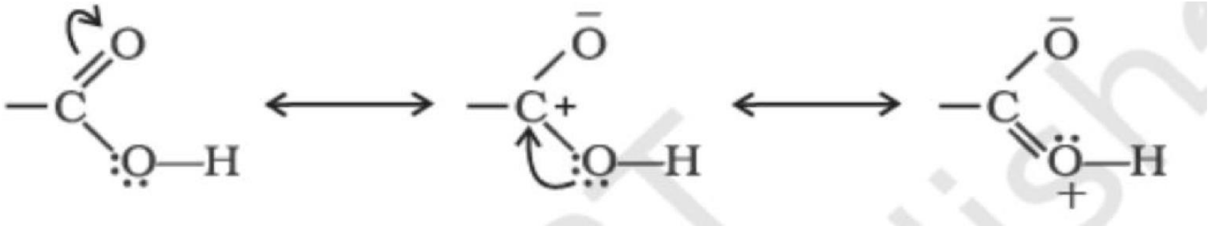
ANSWERS

16. FCH_2COOH .

Reason: Due to lesser electron density in the O — H bond and greater stability of FCH_2COO^- ion over CH_3COO^- ion FCH_2COOH is a stronger acid than CH_3COOH.

17. (i) The benzene ring of benzoic acid undergoes electrophilic substitution reaction such as nitration, sulphonation etc. Since the — COOH group in benzene is an electron withdrawing group, therefore it is meta directing group.

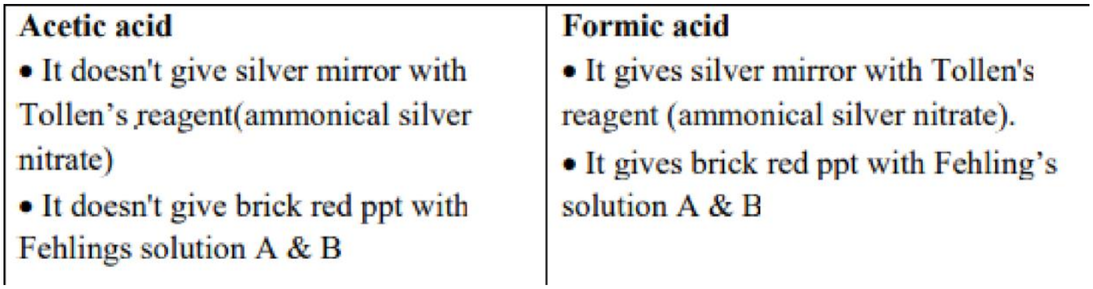
(ii) The carboxylic carbon is less electrophilic than carbonyl carbon because of the possible resonance structure.



18. (i) 4-Methoxy benzoic acid < Benzoic acid < 4-Nitrobenzoic acid < 3, 4- Dinitrobenzoic acid.
The order is due to increasing -I effect

(ii) $(CH_3)_2CHCOOH$, <$CH_3CH_2CH_2COOH$ <CH_3CH (Br) CH_2COOH <CH_3CH_2CH (Br) COOH
The above order is due to –I effect,with decrease of distance and decrease of +I effect.

19.(i)

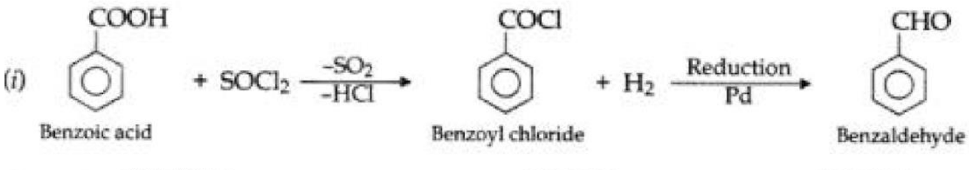


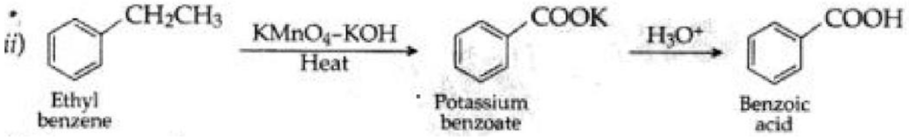
Acetic acid	**Formic acid**
• It doesn't give silver mirror with Tollen's reagent(ammonical silver nitrate) • It doesn't give brick red ppt with Fehlings solution A & B	• It gives silver mirror with Tollen's reagent (ammonical silver nitrate). • It gives brick red ppt with Fehling's solution A & B

(ii)

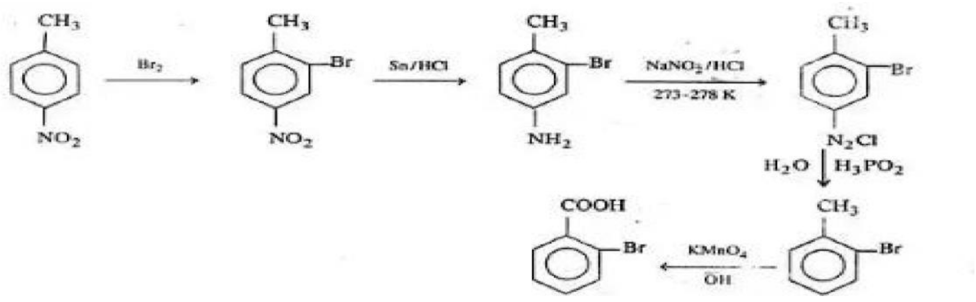
Phenol	Benzoic acid
No effervescence of CO_2 with $NaHCO_3$	Gives effervescence of CO_2 with $NaHCO_3$
Gives violet colour with $FeCl_3$	Does not give violet colour with $FeCl_3$

20.

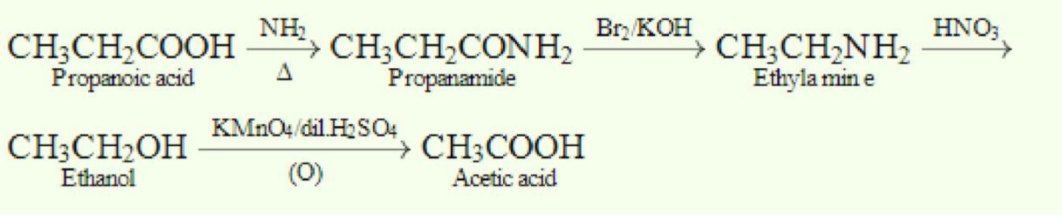




21. (i)



(ii)



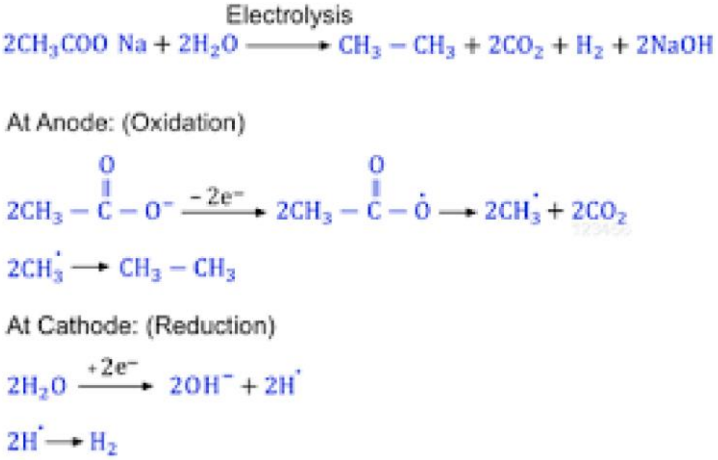
$$CH_3CH_2COOH \xrightarrow[\Delta]{NH_3} CH_3CH_2CONH_2 \xrightarrow{Br_2/KOH} CH_3CH_2NH_2 \xrightarrow{HNO_3}$$

Propanoic acid, Propanamide, Ethyla min e

$$CH_3CH_2OH \xrightarrow[(O)]{KMnO_4/dil.H_2SO_4} CH_3COOH$$

Ethanol, Acetic acid

22. (i) Kolbe's electrolysis :Alkali metal salts of carboxylic acids also undergo decarboxylation on electrolysis of their aqueous solutions and form hydrocarbons having twice the number of carbon atoms present in the alkyl group of the acid.



$$2CH_3COO\ Na + 2H_2O \xrightarrow{\text{Electrolysis}} CH_3-CH_3 + 2CO_2 + H_2 + 2NaOH$$

At Anode: (Oxidation)

$$2CH_3-\overset{O}{\overset{\|}{C}}-O^- \xrightarrow{-2e^-} 2CH_3-\overset{O}{\overset{\|}{C}}-\dot{O} \longrightarrow 2\dot{C}H_3 + 2CO_2$$

$$2\dot{C}H_3 \longrightarrow CH_3-CH_3$$

At Cathode: (Reduction)

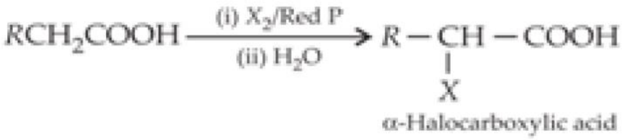
$$2H_2O \xrightarrow{+2e^-} 2OH^- + 2H^{\cdot}$$

$$2H^{\cdot} \longrightarrow H_2$$

(ii) H

Carboxylic acids having an alpha hydrogen are halogenated at the alpha position on treatment with chlorine or bromine in the presence of small amount of red phosphorus to give alpha-halocarboxylic acids.

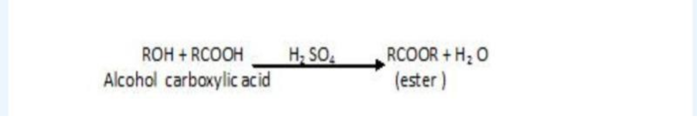
Hell—Volhard—Zelinsky reaction :



$$RCH_2COOH \xrightarrow[\text{(ii) } H_2O]{\text{(i) } X_2/\text{Red P}} R-\underset{X}{\underset{|}{CH}}-COOH$$

α-Halocarboxylic acid

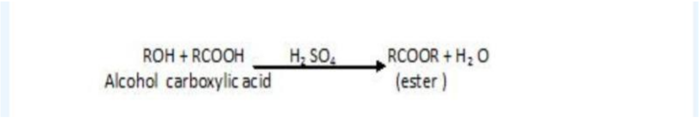
23.(i) The formation of esters from a carboxylic acid and an alcohol in the presence of acid catelyst is a reversible reaction.



$$ROH + RCOOH \xrightarrow{H_2SO_4} RCOOR + H_2O$$

Alcohol carboxylic acid (ester)

To shift the equilibrium in forward direction, the water or ester formed should be removed as fast as it is formed.

(ii) 

$$ROH + RCOOH \xrightarrow{H_2SO_4} RCOOR + H_2O$$

Alcohol carboxylic acid (ester)

24. (i) Acid anhydrides are bigger in size than corresponding acids have moresurface area more van der Waals. Force of attraction hence have higher boiling point.
(ii) Ans. This is because PCC is a mild oxidising agent and can oxide methanol to methanal only.
While KMNO4 being strong oxidising agent oxidises it to methanoic acid.

25.(i) Aromatic acids have higher molecular weight,
More van-der waals force of attracrtion as compared to aliphalic acids They are solids.
(ii) Acyl chlorides are not associated with intermolecular H-bonding
They have lower boiling point.

SHORT ANSWER QUESTIONS(3 MARKS EACH)

26. An organic compound A has the molecular formula $C_8H_{16}O_2$. It gets hydrolysed with dilute sulphuric acid and gives a carboxylic acid B and an alcohol C. Oxidation of C with chromic acid also produced B. C on dehydration reaction gives but-1-ene. Write equations for the reactions involved.

27. Arrange the following acid in increasing order of the property as indicated: (any three)
(i) Benzoic acid, 4-nitrobenzoic acid, Phenol, 4-methoxybenzoic acid (pKa value)
(ii) CH3CH2CH(Br)COOH, CH3CH(Br)CH2COOH, (CH3)2CHCOOH, CH3CH2CH2COOH (acid strength)
(iii) HCOOH, F-CH2-COOH, C6H5COOH , NO2-CH2COOH, CH3COOH (Ka value)

28,.How will you prepare the following compounds from benzene? You may use any inorganic reagent and any organic reagent having not more than one carbon atom.

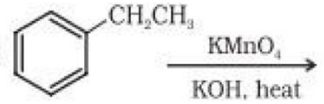
(i) m-Nitro Benzoic Acid
(ii) p-Nitrobenzoic Acid
(iii) Phenylacetic Acid

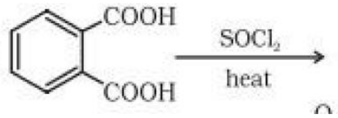
29. How will you bring about the following conversions in not more than two steps?

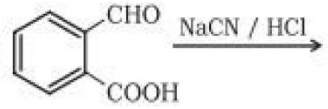
Benzoic acid to Benzaldehyde

Benazaldehyde to α-Hydroxyphenylacetic acid
(viii) Benzoic acid to m- Nitrobenzyl alcohol?

30. Complete each synthesis by giving missing starting material, reagent or products.







31(A) Name the following compounds according to IUPAC system of nomenclature:
(CH3)3CCH2COOH

(B) Draw the structures of the following compounds.

(i) 3-Bromo-4-phenylpentanoic acid
(ii) Hex-2-en-4-ynoic acid.

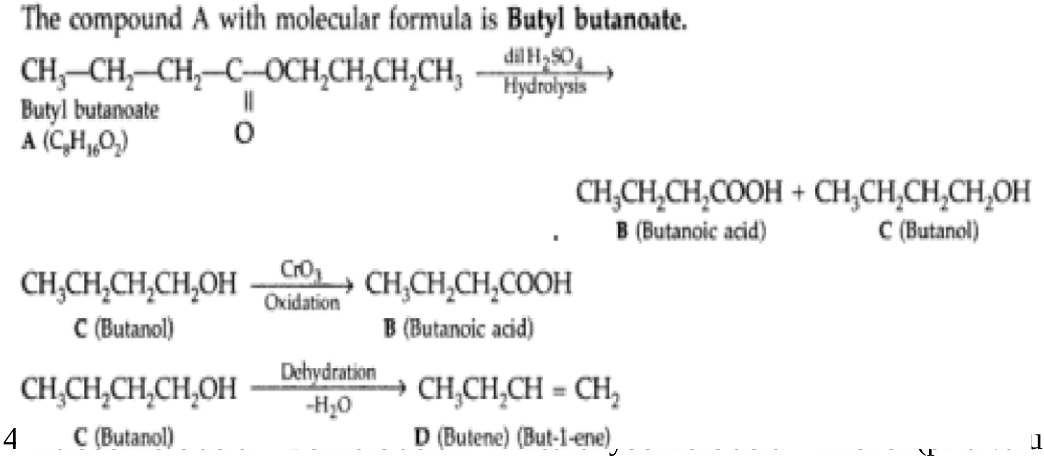
32 An aromatic compound A on treatment with aqueous ammonia and heating forms compound B which on heating with Br_2 and KOH forms a compound C of molecular formula C_6H_7N .Identify A,B,C .

33 A. Name the products formed when
(i) Monocarboxylic acids react with alcohols or phenol in the presence of an acid catalyst
(ii) HCN undergoes hydrolysis

B. Arrange the following componds in increasing order of boiling point
Butanol, Ethoxy-ethane , n-butane , Propanoic acid , Butanal

ANSWERS

26.



The compound A with molecular formula is **Butyl butanoate.**

$$\underset{\substack{\text{Butyl butanoate}\\ \text{A } (C_8H_{16}O_2)}}{CH_3{-}CH_2{-}CH_2{-}\overset{\displaystyle O}{\overset{\|}{C}}{-}OCH_2CH_2CH_2CH_3} \xrightarrow[\text{Hydrolysis}]{\text{dil } H_2SO_4} \underset{\text{B (Butanoic acid)}}{CH_3CH_2CH_2COOH} + \underset{\text{C (Butanol)}}{CH_3CH_2CH_2CH_2OH}$$

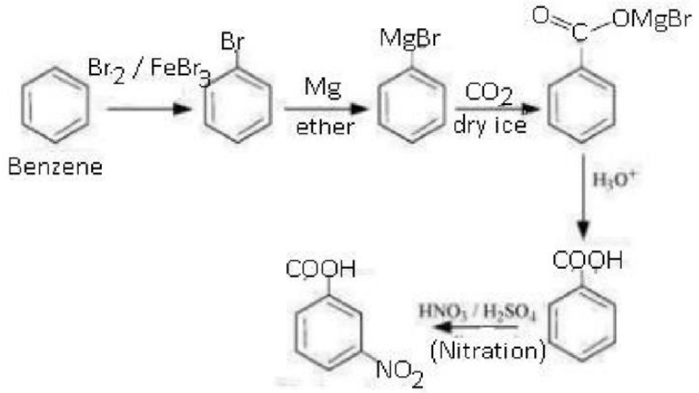
$$\underset{\text{C (Butanol)}}{CH_3CH_2CH_2CH_2OH} \xrightarrow[\text{Oxidation}]{CrO_3} \underset{\text{B (Butanoic acid)}}{CH_3CH_2CH_2COOH}$$

$$\underset{\text{C (Butanol)}}{CH_3CH_2CH_2CH_2OH} \xrightarrow[-H_2O]{\text{Dehydration}} \underset{\text{D (Butene) (But-1-ene)}}{CH_3CH_2CH = CH_2}$$

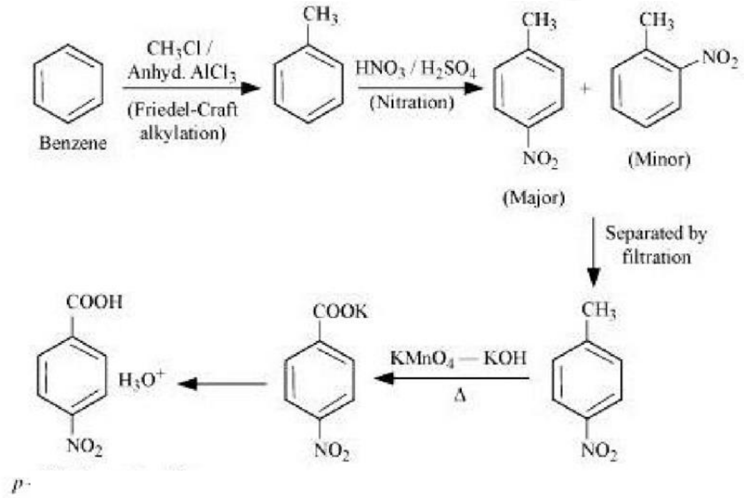
27. (i) 4 [illegible] ue)
(ii)CH3CH2CH2COOH < (CH3)2CHCOOH < CH3CH(Br)CH2COOH < CH3CH2CH(Br)COOH

(iii) CH3COOH < C6H5COOH < HCOOH < F-CH2COOH < O2NCH2COOH

28.(i)



(ii)



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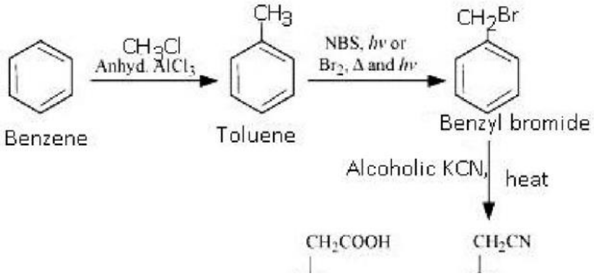
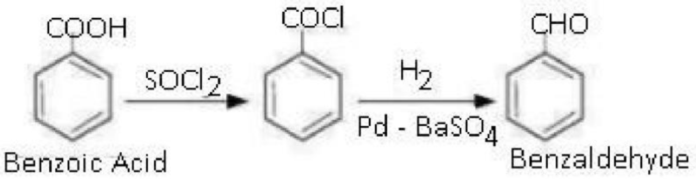
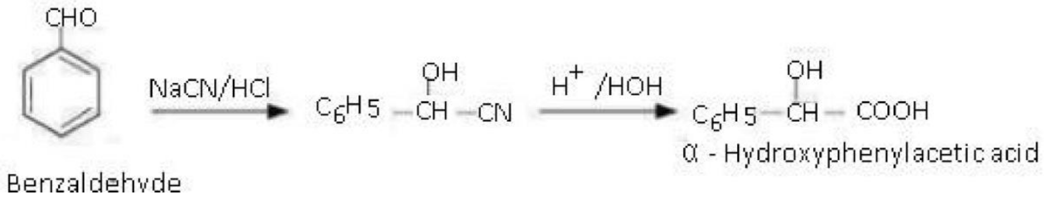


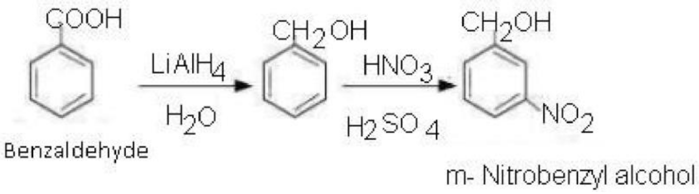
29. (i)



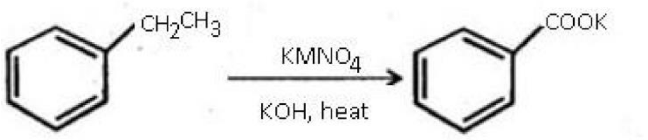
(ii)



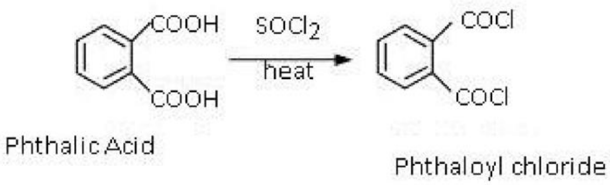
(iii)



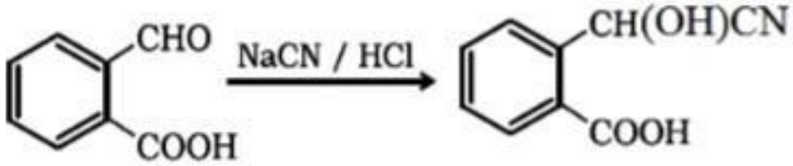
30. (i)



(ii)

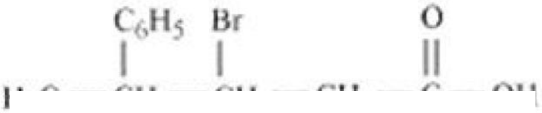


(iii)

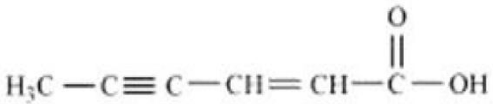


31. (A) (C

B (i)



(ii)

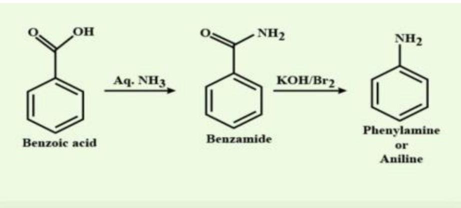


$H_3C-C\equiv C-CH=CH-\overset{\overset{\displaystyle O}{\|}}{C}-OH$

32.The aromatic compound A is benzoic acid C6H5COOH.

On treatment with aqueous ammonia and heating forms compound B, which is benzamide, C6H5CONH2.

Benzamide on heating with bromine and KOH forms a compound C of molecular formula C which is aniline C6H5NH2.



33 .A(i) Esters
(ii) Formic acid
B. n-butane < Ethoxy ethane < butanal < butanol < propanoic acid

LONG ANSWER QUESTIONS (5 MARKS EACH)

34.A. Give reasons:
(i) Why pH of reaction should be carefully controlled while preparing ammonia derivatives of carbonyl compound?
(ii)Although phenoxide ion has more number of resonating structures than carboxylate ion, carboxylic acid is a stronger acid than phenol.

B. Give simple chemical test to distinguish the following pair of compounds
(i) Phenol and Benzoic acid
(ii) Benzoic acid and Ethyl benzoate
C. How will you convert acetaldehyde to: But-2-en-oic acid

35. An organic compound with the molecular formula C9H10O forms 2, 4-DNP derivative, reduces Tollens' reagent and undergoes Cannizzaro reaction. On vigorous oxidation, it gives 1, 2-benzenedicarboxylic acid. Identify the compound.
Explain with the help of suitable equations, how do you reach the answer.

36. Give the structures of A, B, and C in the following reactions:
a) CH3COOH NH3 A Br2,/ KOH B CHCl3, alc. KOH C
2. Write the IUPAC nomenclature of
(i) (CH3)2C=CH-COOH.
(ii) (CH3)2CHCOOH

37. Answer the following questions.
(i)For which functional derivative of carboxylic acids, acidic hydrolysis is the fastest?
(ii)Name the class of compounds formed on decarboxylation of sodium benzoate on heating with soda lime?
(iii)Name the reagent used to replace the –OH group of an alcohol or the – COOH group of a carboxylic acid by – Cl.
(iv)Which of the following acids has the smallest dissociation constant?
(A) CH3CHFCOOH
(B) FCH2CH2COOH
(C) BrCH2CH2COOH
(D) CH3CHBrCOOH
(v) Which of the following is the strongest acid?
(A) CH3COOH

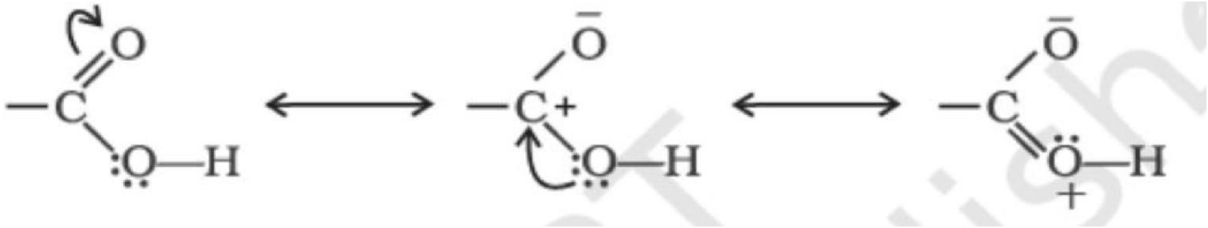
(B) HCOOH
(C) CH3CH2COOH
(D) C6H5COOH

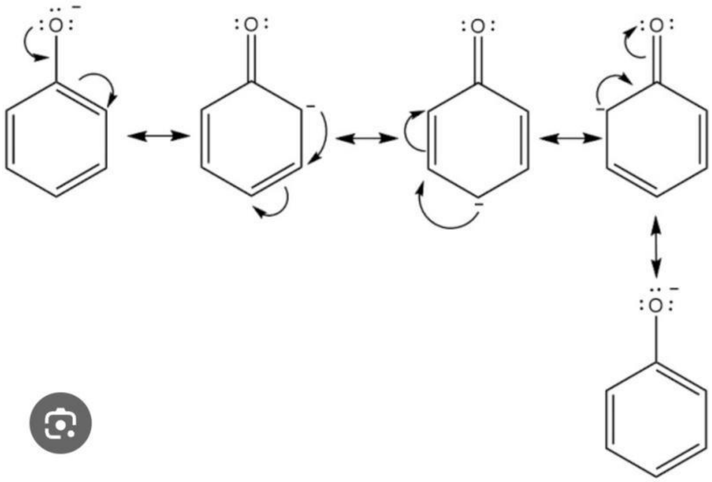
ANSWERS

34.(i) In strongly acidic medium ammonia derivatives being basic will react with acids and will not react with carbonyl compound. In basic mesium, OH will attack carbonyl group.
Thus, pH of a reaction should be carefully controlled.

(ii) Carboxylic acid is a stronger acid than phenol because
(a) The release of a proton from carboxylic acids is much easier than from phenols

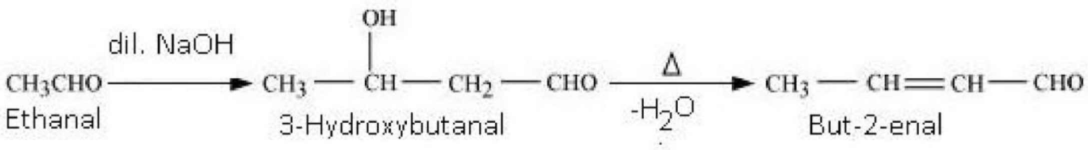
(b) In the resonating structure of phenol and carboxylic acid, the negative charge on the carboxylate ion is delocalised over two oxygen atoms while in phenol they are localized on one oxygen atom.



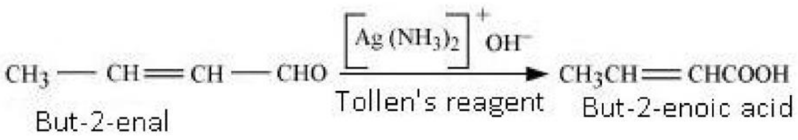


B(i) Phenol reacts with neutral FeCl 3 to form an iron-phenol complex giving violet colouration.

But benzoic acid reacts with neutral FeCl 3 to give a buff coloured ppt. of ferric benzoate.
(ii) Sodium bicarbonate test:
Acids react with NaHCO3 to produce brisk effervescence due to the evolution of CO2 gas.
Benzoic acid being an acid responds to this test, but ethylbenzoate does not.
C. (ii) On treatment with dilute alkali, ethanal gives 3-hydroxybutanal which on heating produces but-2-enal.

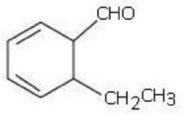


When treated with Tollen’s reagent, But-2-enal produces but-2-enoic acid.

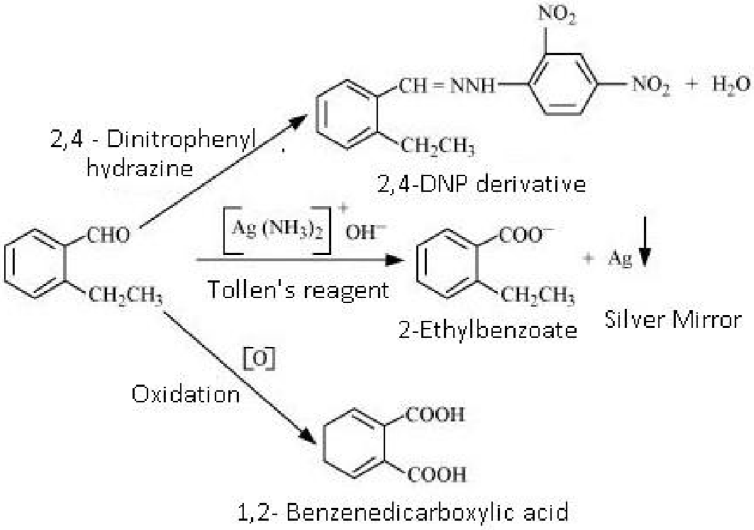


35. It is given that the compound (with molecular formula C9H10O) forms 2, 4-DNP derivative and reduces Tollen's reagent. Therefore, the given compound must be an aldehyde. Again, the compound undergoes Cannizzaro reaction and on oxidation gives 1, 2-benzenedicarboxylic acid. Therefore, the -CHO group is directly attached to a benzene ring and this benzaldehyde is ortho-substituted.

Hence, the compound is 2-et



2-Ethylbenzaldehyde



36. a. A- Ethanamide(CH3C

B- Methanamine (CH3NH2)

C- Methyl isocyanide (CH3NC)

2. 3- Methyl but-2-en-oic acid.

(C) 2-Methylpropanoic acid

37.(i) Acid chlorides

(ii) Benzene

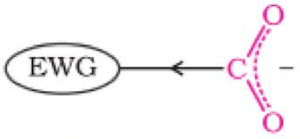
(iii)Phosphorus pentachloride

(iv) BrCH2Ch2COOH

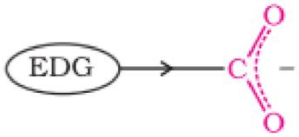
(v)HCOOH

CASE BASED QUESTIONS (4 MARKS EACH)

38. Read the passage given below and answer the following questions:
Effect of substituents on the acidity of carboxylic acids:
Substituents may affect the stability of the conjugate base and thus, also affect the acidity of the carboxylic acids. Electron withdrawing groups increase the acidity of carboxylic acids by stabilising the conjugate base through delocalisation of the negative charge by inductive and/or resonance effects. Conversely, electron donating groups decrease the acidity by destabilising the conjugate base.



Electron withdrawing group (EWG) stabilises the carboxylate anion and strengthens the acid



Electron donating group (EDG) destabilises the carboxylate anion and weakens the acid

1. Arrange the following compound in increasing order of their acid character-

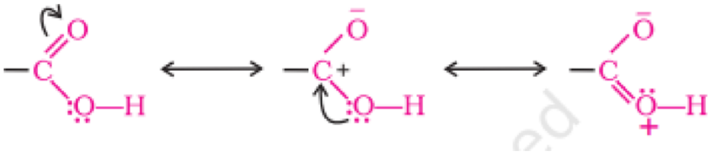
FCH2COOH, O2N-CH2-COOH, CH3COOH, HCOOH

1. Write the conjugate base of acetic acid.
2. Consider the given statement-

‘Direct attachment of groups such as phenyl or vinyl to the carboxylic acid, increases the acidity of corresponding carboxylic acid.’
Is it correct statement? Justify your answer.

“OR”

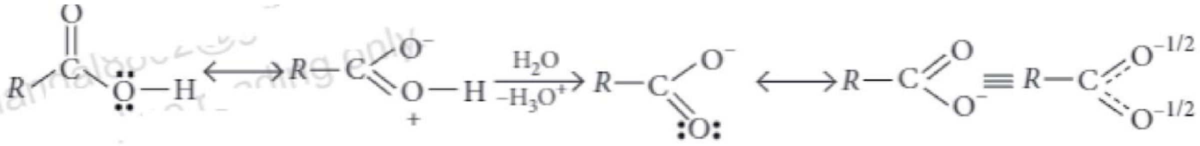
The resonance structures A, B and C; of the carboxylic acid group are shown below, which of them is the most stable and why



39. Read the passage given below and answer the following questions.
Carboxylic acids dissociate in water to give carboxylate ion and hydronium ion.
RCOOH + H2O →$RCOO^-$ + $H3O^+$

The acidity of carbonxl group is due to the positive charge on oxygen atom which liberates proton. The

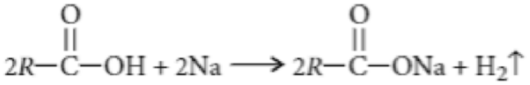
carboxylate ion formed is resonance stabilized.



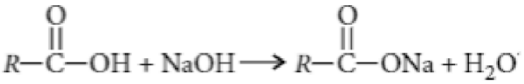
Carboxylic acids are stronger acids than phenols. Electron withdrawing groups increase the acidity of carboxylic acids by stabilizing the conjugate base by delocalization of negative charge by inductive and/or resonance effects. Electron donating groups decrease the acidity by destabilizing the conjugate base.

Now answer the following questions by choosing the most appropriate answer.

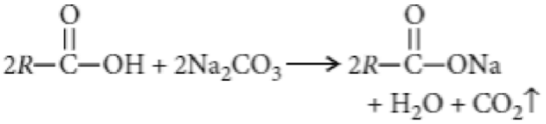
(i) which of the following reactions is showing the acidic property of carboxylic acids?

(a) 

$2R-\overset{\overset{O}{\|}}{C}-OH + 2Na \longrightarrow 2R-\overset{\overset{O}{\|}}{C}-ONa + H_2\uparrow$

(b) 

$R-\overset{\overset{O}{\|}}{C}-OH + NaOH \longrightarrow R-\overset{\overset{O}{\|}}{C}-ONa + H_2O$

(c) 

$2R-\overset{\overset{O}{\|}}{C}-OH + 2Na_2CO_3 \longrightarrow 2R-\overset{\overset{O}{\|}}{C}-ONa + H_2O + CO_2\uparrow$

(d) All of these.

(ii) Which of the following is the correct order of acidic strength?

(a) $CF_3COOH > CHCl_2COOH > HCOOH > C_6H_5CH_2COOH > CH_3COOH$

(b) $CH_3COOH > HCOOH > CF_3COOH > CHCl_2COOH > C_6H_5CH_2COOH$

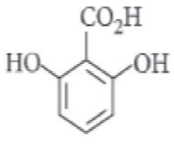
(c) $HCOOH > C_6H_5CH_2COOH > CF_3COOH > CHCl_2COOH > CH_3COOH$

(d) $CF_3COOH > CH_3COOH > HCOOH > CHCl_2COOH > C_6H_5CH_2COOH$

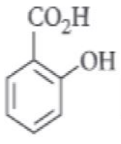
(iii) Which of the following acids has the smallest dissociation constant?

(a) $CH_3CHFCOOH$ (b) FCH_2CH_2COOH (c) $BrCH_2CH_2COOH$ (d) $CH_3CHBrCOOH$

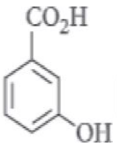
(iv) The correct order of acidity for the following compounds is



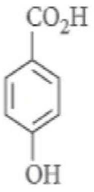
I



II



III



IV

(a) I > II > III > IV (b) III > I > II > IV (c) III > IV > II > I (d) I > III > IV> II

ANSWERS

1. **38.** CH3COOH < HCOOH < FCH2COOH < O2N-CH2-COOH
2. CH3COO- or ‘Acetate ion’.
3. Yes, statement is correct. This is because of greater electronegativity of sp2 hybridised carbon to which carboxyl carbon is attached.

“OR”

The structure (C) is most stable. This is because structure (C) has all the atoms with a complete octet or duplet, in case of hydrogen.

39.(i) (d) carboxylic acids form sodium salts with all, i.e alkali metals, NaOH and Na2CO3 and removes the acidic proton from the carboxylic acid.

(ii) (a) In general, greater the +I effect of the group attached to the carboxylic group lesser will be the acidic strength and greater the –I effect of the group, greater will be the acidic strength. As the number of halogen atoms increases, acidic strength increases.

(iii) (c) Stronger –I group attached closer to –COOH group makes the acid stronger and acid has larger dissociation constant. –Br shows poor –I effect and also far away from –COOH group. Therefore, BrCH2CH2COOH has the smallest dissociation constant.
(iv) (a)

CHAPTER 9: AMINES

Topics to be covered: Nomenclature, classification, structure, method of preparation, physical and chemical properties, uses, identification of primary, secondary, and tertiary amines.

Amines are derivatives of ammonia, obtained by displacement of one, two or all three H atoms by an alkyl or aryl groups.

e.g. methylamine CH_3-NH_2
Aniline C_6H_5-NH_2
Dimethyl amine CH_3-NH-CH_3

Classification of Amines

Depending upon the number of hydrogen atoms replaced by alkyl or aryl groups in the ammonia molecule, Amines are classified as primary, secondary and tertiary.

Primary Amines

If one hydrogen atom of ammonia is replaced by R or Ar, we get RNH_2 or $ArNH_2$

Example: Methylamine, Ethylamine, Aniline,

Secondary Amines

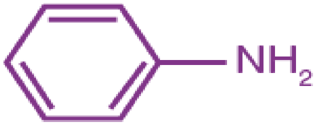
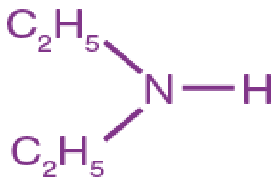
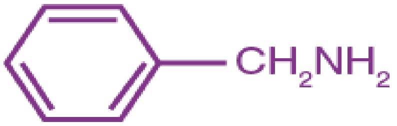
If two hydrogen atoms of ammonia or one hydrogen atom of R-NH_2 are replaced by another alkyl/aryl(R') group we get R-NH-R or Ar-NH-Ar a secondary amine.

Example: Dimethylamine

Tertiary Amines

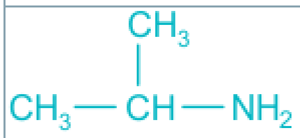
If three hydrogen atoms of ammonia or one hydrogen atom of R- NH2$NH2$ are replaced by another alkyl/aryl(R') group we get R3N or Ar3N, a tertiary amine.

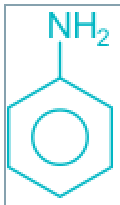
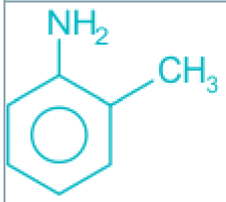
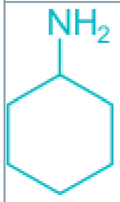
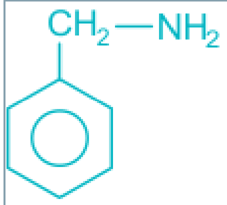
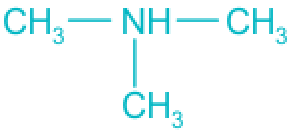
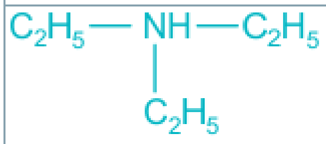
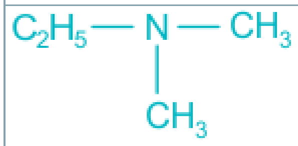
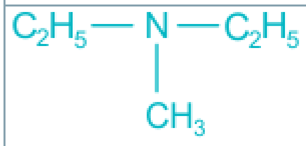
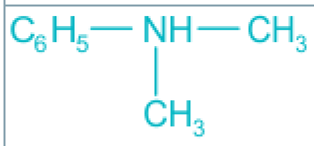
e.g Trimethyl amine

Methylamine	CH_3NH_2	Trimethylamine	$(CH_3)_3N$
Ethylamine	$C_2H_5NH_2$	Aniline	
Diethylamine		Benzylamine	

IUPAC Names

- In this method, the aliphatic amines are called alkanamines. The name of the amine is obtained by replacing the suffix ‘e’ with the name of the parent alkane by amine. The position of the amino group is indicated by the lowest possible number.
- If more than one amino group is present at a different position in parents, their numbers are indicated by suitable prefix like di, tri, etc. added before amine. The position amino group is indicated by the lowest possible number.
- If more than one amino groups are present at a different position in parents change their numbers are indicated by suitable prefix like
- di, tri, etc. added before amine. The letter ‘e’ in the suffix of the alkane is retained.
- In secondary and tertiary amines the largest alkyl group is considered as parent alkane and other alkyl groups as N substituents.
- In aryl amines, the suffix ‘e’ of the arene is replaced by ‘amine’.
- In arylamines, the suffix ‘e’ of the arene is replaced by ‘amine’.

Amines	Common Names	IUPAC
 $CH_3-\overset{CH_3}{\overset{\vert}{C}H}-NH_2$	isopropylamine	Propan-2-amine
$H_2N-CH_2-CH_2-NH_2$	ethylenediamine	Ethan-1,2-diamine
$H_2N-{}^{1}CH_2-{}^{2}CH={}^{3}CH_2$	allylamine	Prop-2-en-1-amine

	aniline/ phenylamine	Aniline or Benzenamine
	o-toluidine	2-Aminotoulene
	cyclohexylamine	Cycloheaxanamine
	benzylamine	Phenylmethanamine
$CH_3-NH-CH_3$	dimethylamine	N-Methylmethanamine
$CH_3-CH_2-NH-CH_3$	ethylmethylamine	N-Methylethanamine
$C_6H_5-NH-C_6H_5$	diphenylamine	N-Phenylaniline or N-Phenyl benzenamine
 $CH_3-\underset{\underset{CH_3}{\vert}}{NH}-CH_3$	trimethylamine	N, N- Dimethylmethanamine
 $C_2H_5-\underset{\underset{C_2H_5}{\vert}}{NH}-C_2H_5$	triethylamine	N, N- Diethylethanamine
 $C_2H_5-\underset{\underset{CH_3}{\vert}}{N}-CH_3$	ethyldimethylamine	N, N- Dimethylethanamine
 $C_2H_5-\underset{\underset{CH_3}{\vert}}{N}-C_2H_5$	dimethylamine	N-Ethyl-N-methylethanamine
 $C_6H_5-\underset{\underset{CH_3}{\vert}}{NH}-CH_3$	N, N- Dimethylamine	N, N- Dimethylaniline or N, N- Dimethylbenzenamine

Preparation of Amines:

(i) By reduction of nitro compounds: Nitro compounds can be catalytically reduced by passing hydrogen gas in presence of Raney Ni, finely divided Pt or Pd as catalyst at room temperature.

a) $R-NO_2+3H_2 \xrightarrow{Ni,Pt \text{ or pd}} R-NH_2+2H_2O$

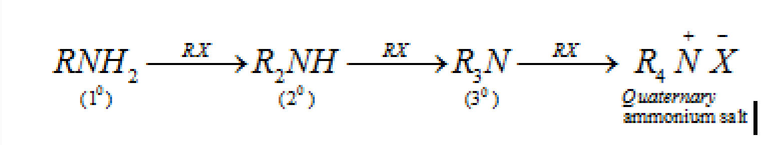
b) $Ar-NO_2+3H_2 \xrightarrow{Ni,\text{ Pt or pd}} Ar-NH_2+2H_2O$

Nitro compounds can also be reduced with active metals such as Fe, Sn, Zn etc. with conc. HCl.

a) $R-NO_2+3H_2 \xrightarrow{Sn/HCl \text{ or Fe/HCl}} R-NH_2+2H_2O$

b) $Ar-NO_2+3H_2 \xrightarrow{Sn/HCl \text{ or Fe/HCl}} Ar-NH_2+2H_2O$

(ii) **By Hoffmann's method (Ammonolysis of alkyl halides):** Reaction of alkyl halides with an ethanolic solution of ammonia in a sealed tube at 373 K forms a mixture of primary, secondary and tertiary amine and finally quarternary ammonium salt. Process of cleavage of C-X bond by ammonia is called ammonolysis.



$$\underset{(1^0)}{RNH_2} \xrightarrow{RX} \underset{(2^0)}{R_2NH} \xrightarrow{RX} \underset{(3^0)}{R_3N} \xrightarrow{RX} \underset{\substack{\text{Quaternary} \\ \text{ammonium salt}}}{R_4\overset{+}{N}\overset{-}{X}}$$

- The free amine can be obtained from the ammonium salt by treatment with a strong base:
  a) $NH_3+RX \rightarrow RNH_3{}^+X^- \xrightarrow{NaOH} \underset{(1^0 a\min e)}{RNH_2} + H_2O + Na^+X^-$
  b) $RNH_2+RX \rightarrow R_2NH_2{}^+X^- \xrightarrow{NaOH} \underset{(2^0 a\min e)}{R_2NH} + H_2O + Na^+X^-$
  c) $R_2NH+RX \rightarrow R_3NH^+X^- \xrightarrow{NaOH} \underset{(3^0 a\min e)}{R_3N} + H_2O + Na^+X^-$
- Order of reactivity of halides is: RI>RBr>RCl
- Larger the size of halogen atom easier is the cleavage of R-X bond
- Limitations of Hoffmann's method: Method gives mixture of amines which are difficult to separate in a laboratory.
- Methods to get only one product by Hoffmann's method:

(i) When ammonia is taken in excess primary amine is formed as main product

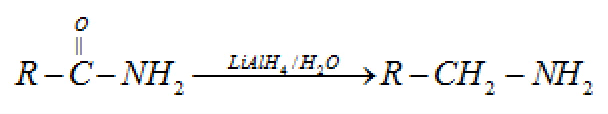
(ii) When alkyl halide is used in excess quarternary ammonium salt is formed as main product.

Method is not suitable for preparation of aryl amines because aryl amines are relatively less reactive than alkyl halides towards nucleophilic substitution reactions.

(iii) By reduction of nitriles: Nitriles can be reduced to amines using H_2 / Ni , $LiAlH_4$ or Na(Hg) / C_2H_5 OH

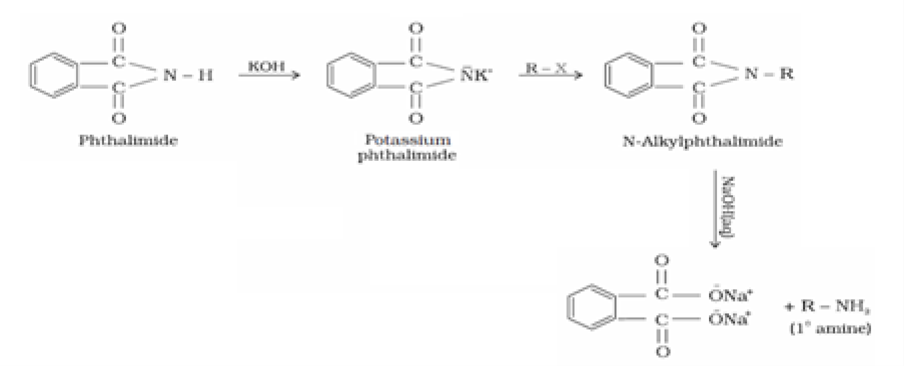
$$R-C\equiv N \xrightarrow{\substack{H_2/Ni \\ Or \\ Na(Hg)/C_2H_5OH \\ Or \\ LiAlH_4}} R-CH_2-NH_2$$

(iv) By reduction of amides: Amides are reduced to corresponding amines by LiAlH4



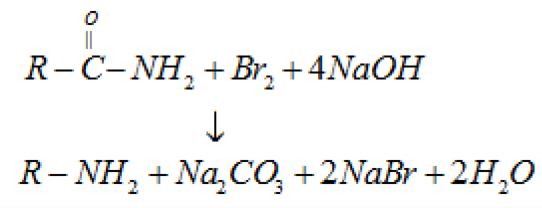
$$R-\overset{\overset{O}{\|}}{C}-NH_2 \xrightarrow{LiAlH_4/H_2O} R-CH_2-NH_2$$

(v) By Gabriel phthalimide synthesis: Gabriel synthesis is used for the preparation of primary amines. When phthalimide is treated with ethanolic potassium hydroxide, it forms potassium salt of phthalimide which on heating further with alkyl halide followed by alkaline hydrolysis produces the corresponding primary amine.



Aromatic primary amines cannot be prepared by this method because aryl halides do not undergo nucleophilic substitution with potassium phthalimide.

(vi) By Hoffmann bromamide degradation reaction: Primary amines can be prepared from amides by treatment with Br_2 and KOH. Amine contains one carbon atom less than the parent amide.



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

Physical Properties of Amines:

(i) Solubility: Lower aliphatic amine is soluble in water because they can form hydrogen bonding with water. Solubility decreases with increases in molar mass of amines due to increase in size of hydrophobic group

(ii) Boiling points: Among the isomeric amines primary and secondary amines have high boiling point because they can form hydrogen bonding. Tertiary amine cannot form hydrogen bonding due to the absence of hydrogen atom available for hydrogen bond formation. Hence order of boiling of isomeric amines is Primary>Secondary> Tertiary

Chemical properties of Amines:

(a) Basic character of amines: Amines have an unshared pair of electrons on nitrogen atom due to which they behave as Lewis base. Basic character of amines can be better understood in terms of their K_b and pK_b values

$$R-NH_2+H_2O \Leftrightarrow R-\overset{+}{N}H_3+\overset{-}{O}H$$

$$K=\frac{[R-\overset{+}{N}H_3][\overset{-}{O}H]}{[R-NH_2][H_2O]}$$

Or $K[H_2O] = \frac{[R-\overset{+}{N}H_3][\overset{-}{O}H]}{[R-NH_2]}$

$$K_b = \frac{[R-\overset{+}{N}H_3][\overset{-}{O}H]}{[R-NH_2]}$$

$$pK_b = -\log K_b$$

Greater K_b value or smaller pK_b indicates base is strong.

(b) Comparison of basic strength of aliphatic amines and ammonia: Aliphatic amines are stronger bases than ammonia due to +I effect of alkyl groups leading to high electron density on the nitrogen atom.

(c) Comparison of basic strength of primary, secondary and tertiary amines

(i) The order of basicity of amines in the gaseous phase follows the expected order on the basis of +I effect: tertiary amine > secondary amine > primary amine > NH_3

(ii) In aqueous solution it is observed that tertiary amines are less basic than either primary or secondary amines. This can be explained on basis of following factors:

a) Solvation effect: Greater is the stability of the substituted ammonium cation formed, stronger is the corresponding amine as a base. Tertiary ammonium ion is less hydrated than secondary ammonium ion which is less hydrated than primary amine. Thus tertiary amines have fewer tendencies to form ammonium ion and consequently are least basic.

On the basis of solvation effect order of basicity of aliphatic amines should be primary amine>secondary amine>tertiary amine.

b) Steric factor: As the crowding of alkyl group increases from primary to tertiary amine hinderance to hydrogen bonding increases which eventually decreases the basic strength. Thus there is a subtle interplay of the inductive effect, solvation effect and steric hinderance of the alkyl group which decides the basic strength of alkyl amines in the aqueous state.

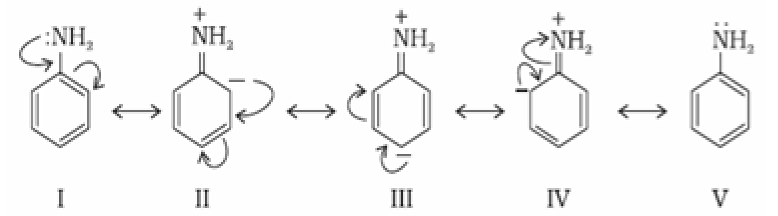
When the alkyl group is small like CH_3 there is no steric hindrance to hydrogen bonding. In this case order of basicity in aqueous medium is

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

When alkyl group is ethyl group order of basicity in aqueous medium is

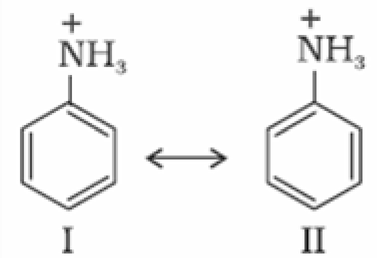
$$(C_2H_5)_2NH > (C_2H_5)_3N > C_2H_5NH_2 > NH_3$$

c) Comparison of basic strength of aryl amines and alkylamines: Generally aryl amines are considerably less basic than alkyl amines .Taking an example of aniline and ethylamine it is observed that ethyl amine is more basic than aniline. In aniline –NH2 group is directly attached to benzene ring. Hence unshared pair of electron on nitrogen is less available for protonation because of resonance. Below mentioned are resonating structures of aniline.



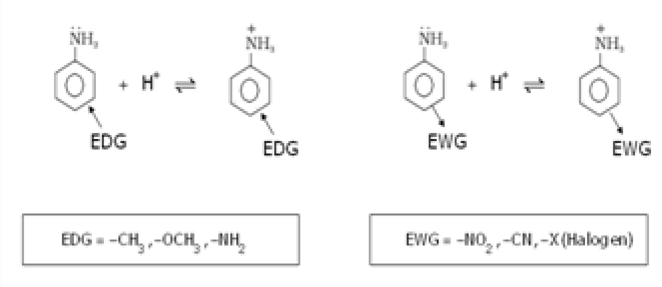
In the above resonating structures there is a positive charge on nitrogen atom making the lone pair less available for protonation. Hence aniline is less basic than ethyl amine which has no resonating structures. Less basicity of aniline can also be explained by comparing the relative stability of aniline and anilinium ion obtained by accepting a proton. Greater the number of resonating structures, greater is the stability of that species.

Aniline is resonance hybrid of five resonating structures whereas anilinium ion has only two resonating structures.



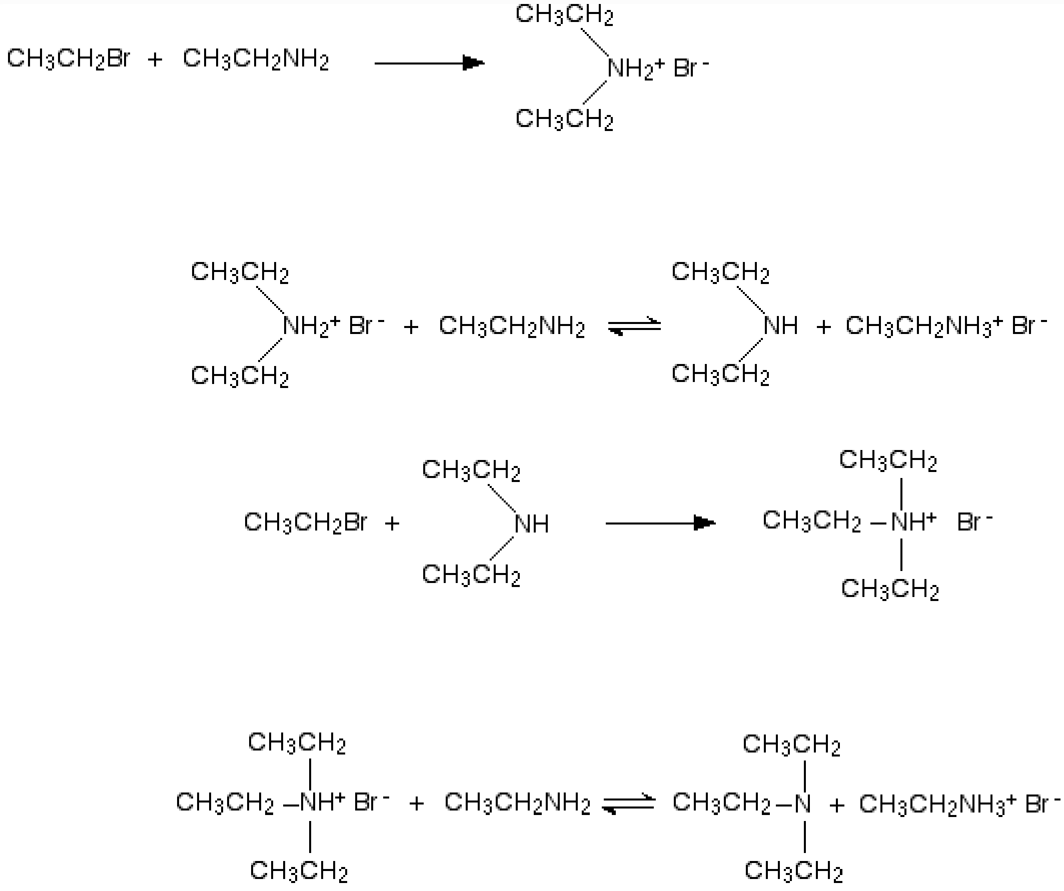
Thus aniline has less tendency to accept a proton to form anilinium ion.

d) Effect of substituent on basic character of amines: Electron donating or electron releasing group/groups (EDG) increases basic strength while electron withdrawing (EWG) decreases basic strength.



- Reactions of amines:

1. **Alkylation**: The amines react with alkyl halides to form substituted amines.



$$CH_3CH_2Br + CH_3CH_2NH_2 \longrightarrow (CH_3CH_2)_2NH_2^+\,Br^-$$

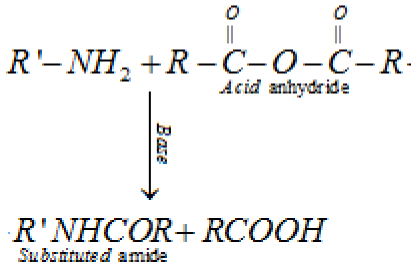
$$(CH_3CH_2)_2NH_2^+\,Br^- + CH_3CH_2NH_2 \rightleftharpoons (CH_3CH_2)_2NH + CH_3CH_2NH_3^+\,Br^-$$

$$CH_3CH_2Br + (CH_3CH_2)_2NH \longrightarrow (CH_3CH_2)_3NH^+\,Br^-$$

$$(CH_3CH_2)_3NH^+\,Br^- + CH_3CH_2NH_2 \rightleftharpoons (CH_3CH_2)_3N + CH_3CH_2NH_3^+\,Br^-$$

2. **Acylation Reaction:** Aliphatic and aromatic primary and secondary amines (which contain replaceable hydrogen atoms) react with acid chlorides, anhydrides and esters to form substituted amide. Process of introducing an acyl group (R-CO-) into the molecule is called acylation. The reaction is carried out in the presence of a stronger base than the amine, like pyridine, which removes HCl formed and shifts the equilibrium to the product side.

$$R-NH_2 + \underset{\text{Acid chloride}}{RCOCl} \xrightarrow{Base} \underset{\text{Substituted amide}}{RNHCOR} + HCl$$



$$\begin{tikzcd} R'-NH_2 + \underset{\text{Acid anhydride}}{R-\overset{O}{\overset{\|}{C}}-O-\overset{O}{\overset{\|}{C}}-R} \arrow[d, "Base"] \\ \underset{\text{Substituted amide}}{R'NHCOR} + RCOOH \end{tikzcd}$$

$$R_2NH + RCOCl \xrightarrow{Base} R_2NCOR + HCl$$

Since tertiary amine do not contain replaceable hydrogen atom they do not undergo acylation reaction.

3. **Carbylamine reaction:** Only aliphatic and aromatic primary amines on heating with chloroform and ethanolic potassium hydroxide form isocyanides or carbylamine.

   Secondary and tertiary amines do not give the above test.

$$\begin{tikzcd} R-NH_2 + CHCl_3 + 3KOH \arrow[d, "Heat"] \\ R-NC + 3KCl + 3H_2O \end{tikzcd}$$

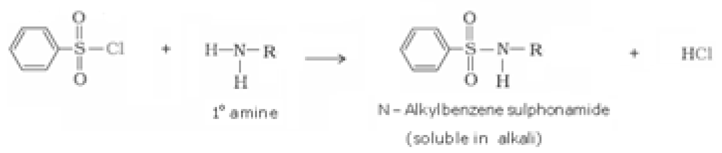
4. **Reaction of primary amine with nitrous acid:**
   (i) Primary aliphatic amine on reaction with nitrous acid (HNO_2) forms aliphatic diazoniumsalt which decomposes to form alcohol and evolve nitrogen.

$$\begin{tikzcd} R-NH_2 + HNO_2 \arrow[d, "NaNO_2+HCl"] \\ {[R-N_2Cl]} \arrow[d, "H_2O"] \\ ROH + N_2 + HCl \end{tikzcd}$$

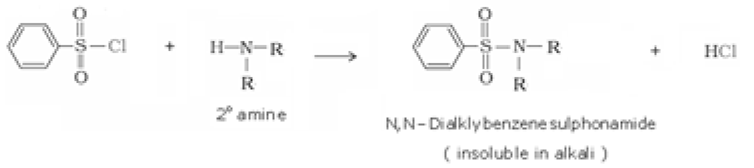
(ii) Primary aromatic amines react with nitrous acid (HNO2) in cold (273-278 K) to form diazonium salt.

$$\underset{\text{Aniline}}{C_6H_5-NH_2} \xrightarrow{NaNO_2+2HCl/273-278K} \underset{\text{Benzenediazonium chloride}}{C_6H_5-\overset{+}{N}_2\overset{-}{Cl}} + NaCl + 2H_2O$$

5. **Reaction with benzene sulphonyl chloride:**Hinsberg's reagent-Benzenesulphonyl chloride (C6H5SO2Cl) reacts with primary and secondary amines to form sulphonamides.



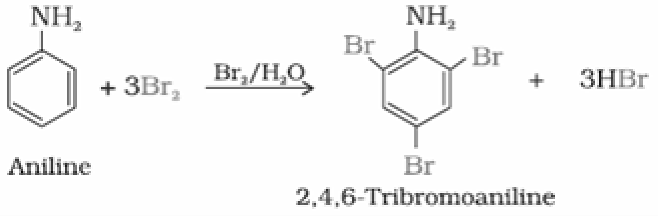
The hydrogen attached to nitrogen in sulphonamide formed by primary amine is strongly acidic due to the presence of strong electron withdrawing sulphonyl group. Hence, it is soluble in alkali.



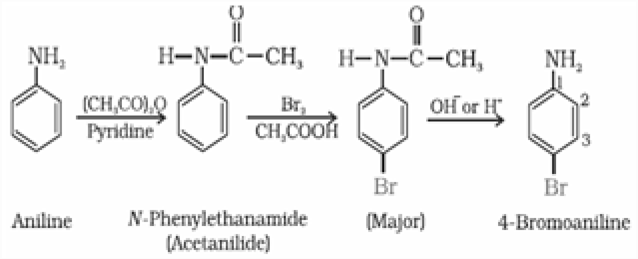
Since sulphonamide formed by secondary amine does not contain any hydrogen atom attached to nitrogen atom, so it is not acidic. Hence it is insoluble in alkali.

Ring substitution in aromatic amine: Aniline is more reactive than benzeneand undergoes electrophilic substitution reaction preferably at ortho and para position.

(i) Bromination: Aniline reacts with bromine water at room temperature to give a white precipitate of 2, 4, 6-tribromoaniline

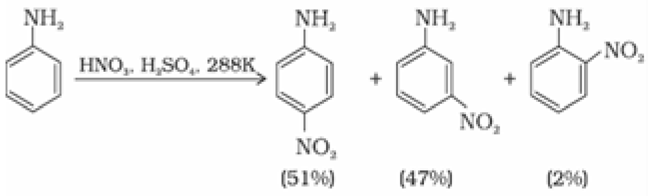


In order to stop reaction at monosubstitution activating effect of –NH2 group is reduced by acetylation. This prevents di and tri substituted products. Acetyl group is removed by hydrolysis.



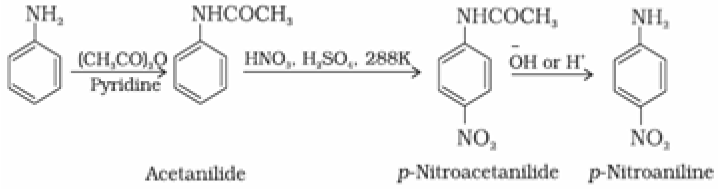
(ii) Nitration:

(a) Under strongly acidic medium aniline gets protonated to form anilinium ion, which is deactivating group and is meta directing. Hence minitroaniline is also formed in 47% along with ortho and para products.

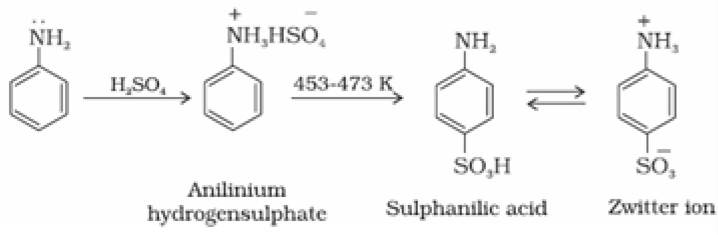


Aromatic amines cannot be nitrated directly because HNO3 being a strong oxidising agent oxidises it forming black mass.

(b) Nitration by protecting the –NH_2 group by acetylation reaction with acetic anhydride:



iii) Sulphonation: Aniline reacts with conc. H_2SO_4 to form aniliniumhydrogensulphate which on heating with sulphuric acid at 453-473K produces p-aminobenzenesulphonic acid, commonly known as sulphanilic acid, as the major product.



Uses of Amines:

1. Aliphatic amines of low molecular mass are used as solvents.
2. Amines are also used as intermediates in drug manufacturing and as a reagent in organic synthesis.
3. Aromatic amines are used for the manufacture of polymers, dyes and as a intermediates for rubber industry.
4. Aromatic amines are converted to arene diazonium salts which are used to prepare variety of aromatic compounds.

Identification of primary, secondary and Tertiary Amines:

S.No	Reactions	Primary Amines	Secondary Amines	Tertiary Amines
1	Action with Nitrous Acid ($NaNO_2$ + HCl)	N_2 is released with the formation of alcohols.	No gas released	No gas released
2	Carbylamine test ($CHCl_3$ + alc. KOH)	Give foul smelling carbylamine.	No reaction	No reaction
3	Acylation	Forms amides	Forms amide	No reaction
4	Heinsberg's test	Gives clear solution which on acidification gives insoluble material	Gives insoluble material which is not affected by acid	No reaction
5	Azo dye test	Give coloured dye	No reaction	No reaction

Topic: Diazonium salts: Preparation, chemical reactions and importance in synthetic organic chemistry.

SECTION A

1. Which of the following will be most stable diazonium salt $RN^+_2X^-$?

a) $CH_3CH_2N^+_2X^-$ b) $C_6H_5N^+_2X^-$ C) $CH_3N^+_2X^-$ d) $C_6H_5CH_2N^+_2X^-$

2. Coupling generally occurs at the ______ position with respect to the hydroxyl or the amino group.

a) Ortho b) Meta c) Para d) anywhere

3. Sandmeyer's reaction is a type of reaction involving

a) Displacement of nitrogen b) Retention of diazo group

c) Both A and B d) None of the above

4. Conversion of benzene diazonium chloride to chlorobenzene is an example of which of the following reaction?

a) Claisen b) Friedal-craft

c) Wurtz d) Sandmeyer

5. Diazotisation is a process of conversion of which substance into diazonium salts?

a) Primary aromatic amines b) Secondary aromatic amines

c) Primary aliphatic amines d) Secondary aliphatic amines

6. Identify the correct name of : $Ar\text{-}N_2^+Cl^-$

a) Benzene azonium chloride b) Benzene diazonium chloride
c) cyclohexane diazonium chloride d) Aniline diazonium chloride

7. If the temperature of the diazonium salt solution is allowed to rise upto 283 K , what happens to the salt?

a) It gets converted to the ketone b) it gets oxidised to acid
c) its gets dehydrated d) it gets hydrolysed to phenol

8. Coupling reactions of aryldiazonium salts with phenols or arylamines give rise to the formation of:

a) Azo dyes b) Aniline c) Benzene d) Aryl halides

9. The colours of p-Hydroxyazobenzene and p-Aminoazobenzene are

a) Red, Yellow b) Blue, Orange
c) Orange, Yellow d) Red, Orange

10. Chlorine is introduced in the benzene ring by treating the diazonium salt solution with HCl in the presence of copper powder. This is referred as

a) Sandmeyer reaction b) Gatterman reaction
c) Diazotisation d) None of these

11. Which of the following statement is not correct about benzenediazonium chloride

a) Colourless b) Crystalline
c) Stable in cold d) Stable in dry state

12. Choose the correct statement about arenediazonium salts

i) Stable for short time in solution
ii) Stable for short time in dry state
iii) Stable at low temperatures
iv) Stable due to resonance

a) I,ii,iii b) i,ii,iv
c) i,iii,iv d) ii,iii,iv

13. Which of the following can not be prepared by Sandmeyer’s reaction?

a) Chlorobenzene b) Bromobenzene
c) Iodobenzene d) All of these

14. Which of the following compound will not undergo azo coupling reaction with benzene diazonium chloride?

a) Aniline b) Phenol
c) Anisole d) Nitrobenzene.

15. When benzene diazonium chloride reacts with phenol, it forms a dye. This reaction is called

a) Diazotisation reaction b) Coupling reaction
c) Condensation reaction d) Acetylation reaction

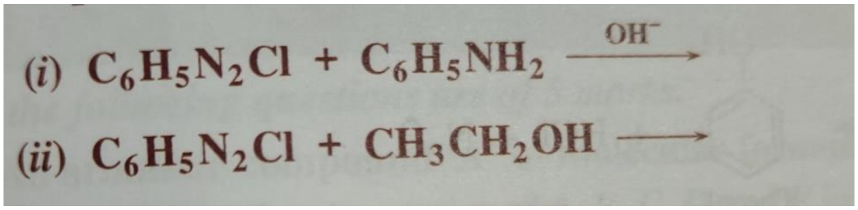
ANSWERS OF SECTION A

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

5. A
6. B
7. D
8. A
9. C
10. B
11. D
12. C
13. C
14. D
15. C

SECTION B

1. Differentiate between benzenediazonium chloride and benzenediazonium fluoroborate on the basis of their solubility and stability.
2. Explain Coupling reaction with one example.
3. Coupling reaction occurs at which position and which type of substitution takes place in it.
4. How will you convert benzene diazonium chloride to phenol?
5. Why diazonium salts of aromatic amines are more stable than those of aliphatic amines?
6. Write a short note on Diazotization reaction.
7. Complete the chemical reaction:

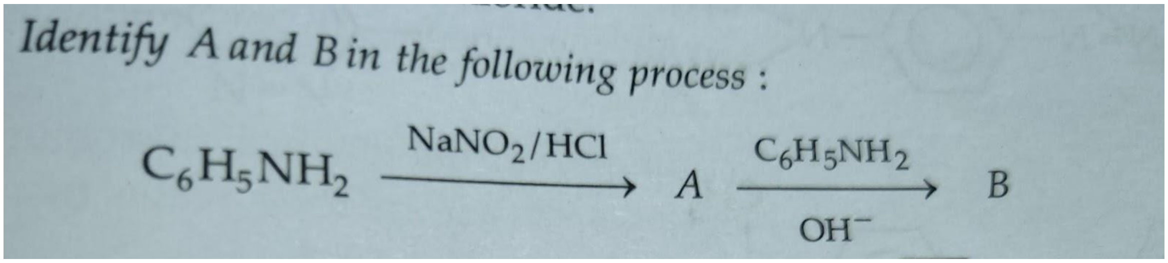


(i) $C_6H_5N_2Cl + C_6H_5NH_2 \xrightarrow{OH^-}$

(ii) $C_6H_5N_2Cl + CH_3CH_2OH \longrightarrow$

8. Convert Benzene diazonium chloride to nitrobenze.

9.



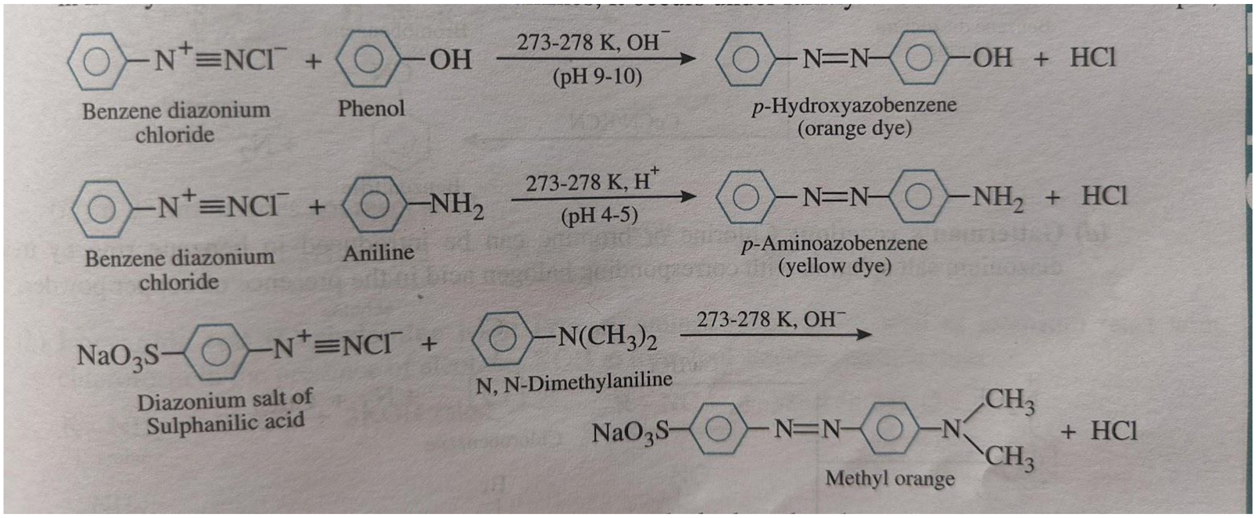
Identify A and B in the following process :

$$C_6H_5NH_2 \xrightarrow{NaNO_2/HCl} A \xrightarrow[OH^-]{C_6H_5NH_2} B$$

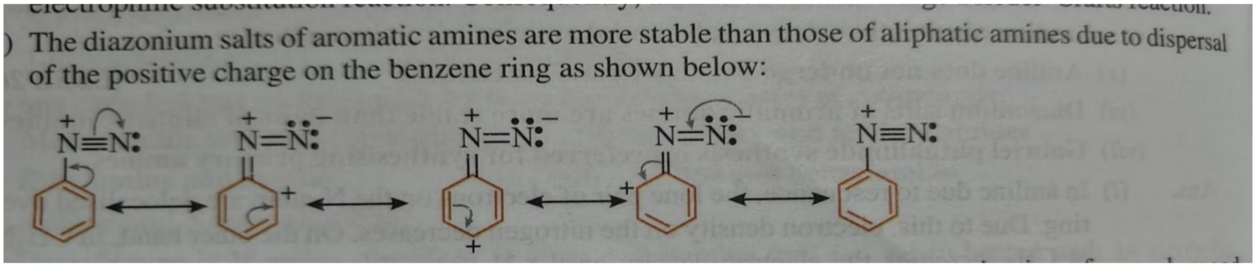
10. Under what reaction conditions (acidic/basic) the coupling reaction of aryldiazonium chloride with aniline is carried out?

ANSWERS OF SECTION B

1. i) benzenediazonium chloride is soluble in water but benzenediazonium fluoroborate is water insoluble.
   ii) benzenediazonium chloride is stable at low temperature, however it reacts with water when warmed. benzenediazonium fluoroborate is stable at room temperature.
2. Coupling reaction: The reaction of diazonium salts with phenols and aromatic amines to form azo compounds of the general formula, Ar-N=N-Ar is called coupling reaction.
   Any one example from the following:

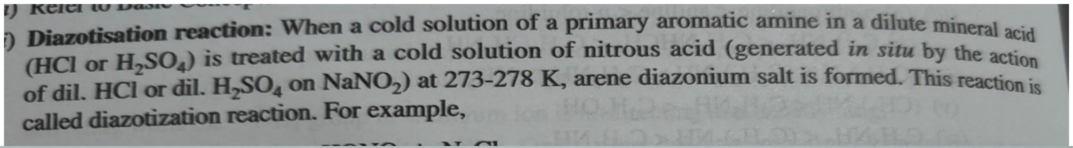


3. Coupling generally occurs at the p- position, wrt the hydroxyl or the amino group, if free, otherwise it takes place at the o-position. The mechanism is of electrophilic substitution where the diazonium ion is electrophile.
4. Benzene diazonium chloride + water—--boil—---> Phenol + HCl + N_2
5.

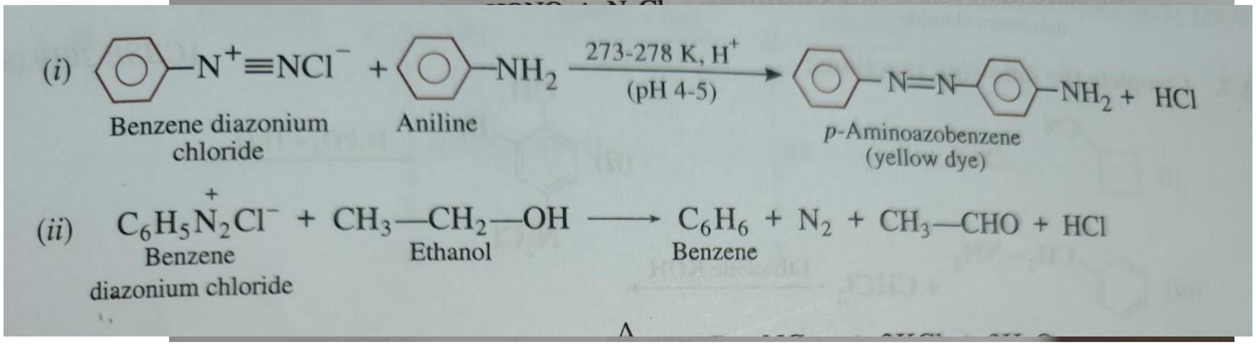


The diazonium salts of aromatic amines are more stable than those of aliphatic amines due to dispersal of the positive charge on the benzene ring as shown below:

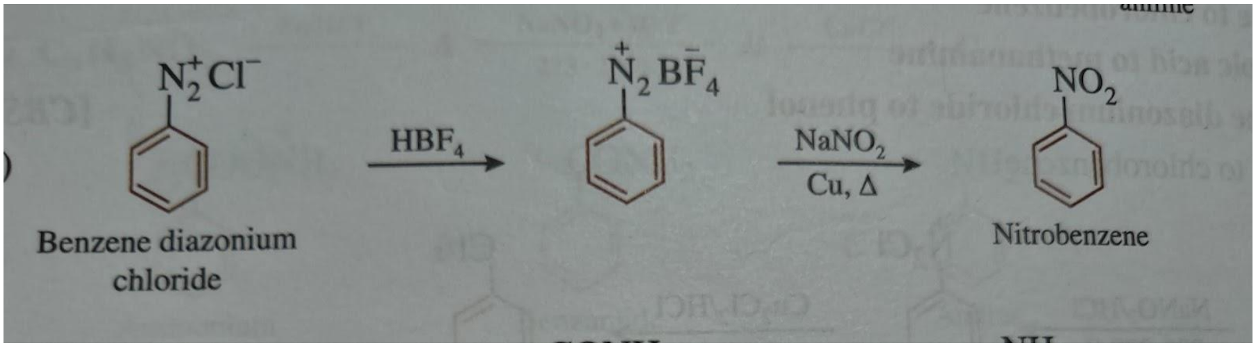
6.
7.



(i) **Diazotisation reaction:** When a cold solution of a primary aromatic amine in a dilute mineral acid (HCl or H_2SO_4) is treated with a cold solution of nitrous acid (generated *in situ* by the action of dil. HCl or dil. H_2SO_4 on $NaNO_2$) at 273-278 K, arene diazonium salt is formed. This reaction is called diazotization reaction. For example,



$$C_6H_5\overset{+}{N}_2Cl^- + CH_3-CH_2-OH \longrightarrow C_6H_6 + N_2 + CH_3-CHO + HCl$$



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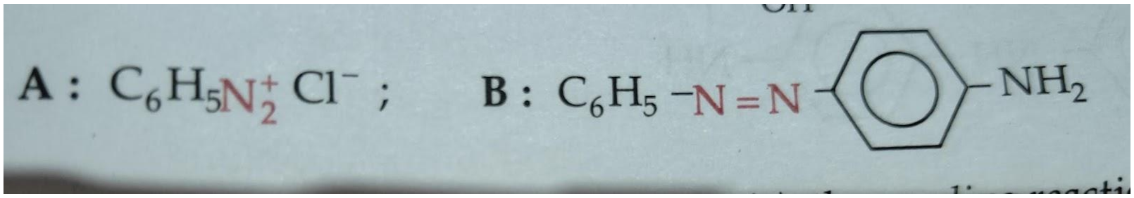
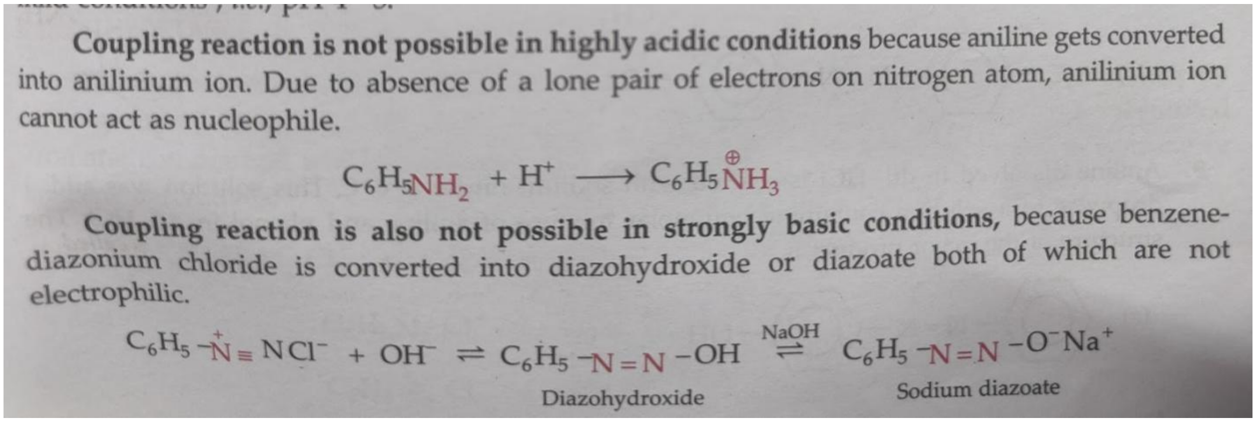


9.

10. The coupling reaction of aryldiazonium chloride with aniline is carried out under mild conditions; i.e. pH 4-5.



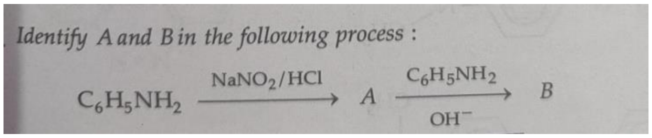
Coupling reaction is not possible in highly acidic conditions because aniline gets converted into anilinium ion. Due to absence of a lone pair of electrons on nitrogen atom, anilinium ion cannot act as nucleophile.

$$C_6H_5NH_2 + H^+ \longrightarrow C_6H_5\overset{\oplus}{N}H_3$$

Coupling reaction is also not possible in strongly basic conditions, because benzene-diazonium chloride is converted into diazohydroxide or diazoate both of which are not electrophilic.

$$C_6H_5-\overset{+}{N}\equiv NCl^- + OH^- \rightleftharpoons \underset{\text{Diazohydroxide}}{C_6H_5-N=N-OH} \overset{NaOH}{\rightleftharpoons} \underset{\text{Sodium diazoate}}{C_6H_5-N=N-O^-Na^+}$$

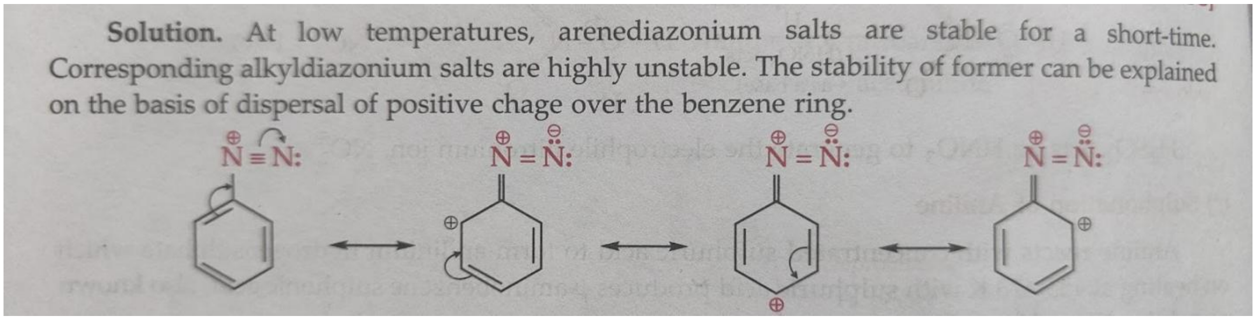
SECTION C

1. Enlist any 3 physical properties of diazonium salts.
2. i) How benzene is synthesised from diazonium salts?
   ii) Complete the following reactions:
   a) $C_6H_5N_2Cl$+ CH_3CH_2OH —-------->
   b) $C_6H_5N_2Cl$+ H_3PO_2+ H_20 —---------------------->
3. i) Why arenediazonium salts are more stable than alkyl diazonium salts?
   ii) What do you mean by diazotisation?
4. Explain the importance of diazonium salts in synthesis of Aromatic compounds.
5. i) why benzenediazonium chloride is not stored and is used immediately after its preparation?
   ii) Explain Sandmeyer and Gattermann reactions.
6. Show the synthesis of iodobenzene and nitrobenzene from arenediazonium chloride.
7. Explain the Mechanism of Diazonium coupling reaction.
8. I) 
   Identify A and B in the following process :
   $$C_6H_5NH_2 \xrightarrow{NaNO_2/HCl} A \xrightarrow[OH^-]{C_6H_5NH_2} B$$
   II) Under what reaction conditions (acidic/basic) the coupling reaction of aryldiazonium chloride with aniline is carried out?
9. How will you convert benzene diazonium chloride to phenol, iodobenzene and nitrobenzene?
10. Explain Coupling reaction. Coupling reaction occurs at which position and which type of substitution takes place in it.

ANSWERS OF SECTION C

1. i) Colour: They are colorless crystalline solids.
   ii) Solubility: benzenediazonium chloride is soluble in water but benzenediazonium fluoroborate is water insoluble.
   iii) Stability: benzenediazonium chloride is stable at low temperature , however it reacts with water when warmed. benzenediazonium fluoroborate is stable at room temperature.
2. i) Diazonium salts are reduced to arenes by mild reducing agents like ethanol or phosphoric acid (or hypo-phosphorous acid H_3PO_2)
   ii) The diazo group is replaced by hydrogen in these reactions.

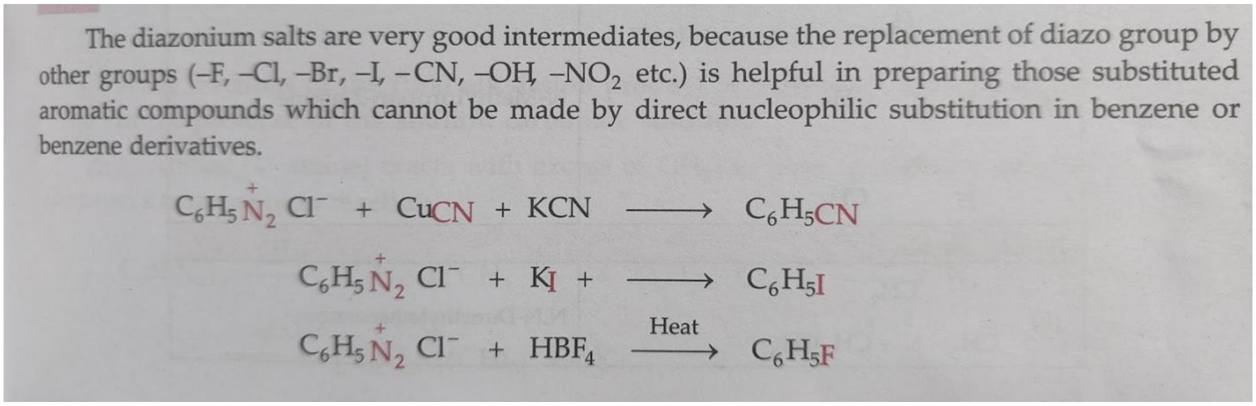
3. i)



Solution. At low temperatures, arenediazonium salts are stable for a short-time. Corresponding alkyldiazonium salts are highly unstable. The stability of former can be explained on the basis of dispersal of positive chage over the benzene ring.

ii) Diazotisation is a process of conversion of primary aromatic amines into diazonium salts.

4.



The diazonium salts are very good intermediates, because the replacement of diazo group by other groups (–F, –Cl, –Br, –I, –CN, –OH, –NO$_2$ etc.) is helpful in preparing those substituted aromatic compounds which cannot be made by direct nucleophilic substitution in benzene or benzene derivatives.

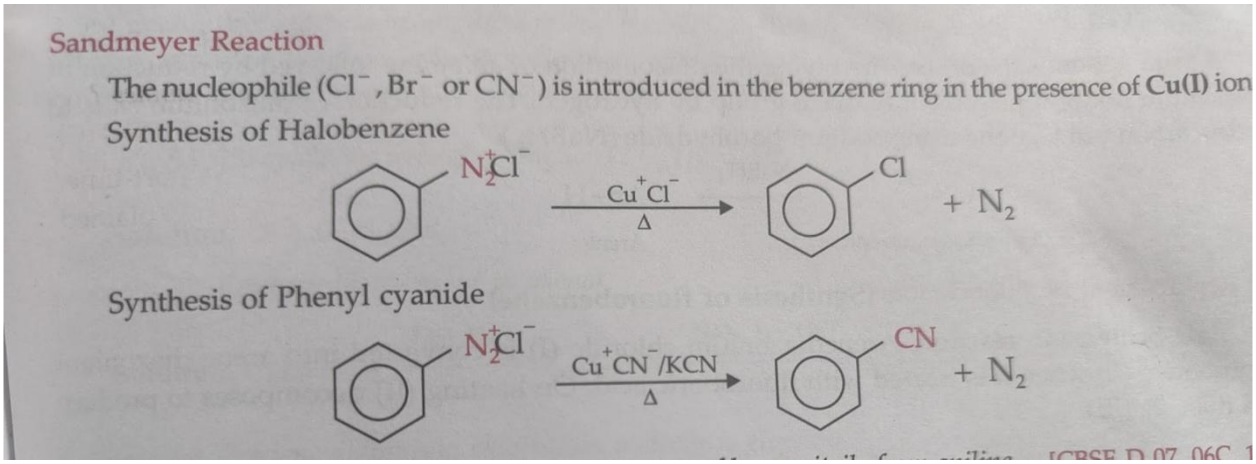
$$C_6H_5\overset{+}{N}_2\ Cl^- + CuCN + KCN \longrightarrow C_6H_5CN$$

$$C_6H_5\overset{+}{N}_2\ Cl^- + KI + \longrightarrow C_6H_5I$$

$$C_6H_5\overset{+}{N}_2\ Cl^- + HBF_4 \xrightarrow{\text{Heat}} C_6H_5F$$

5. i) Arenediazonium salts are not very stable, so they are not stored. They need to be used immediately after their preparation.

ii)

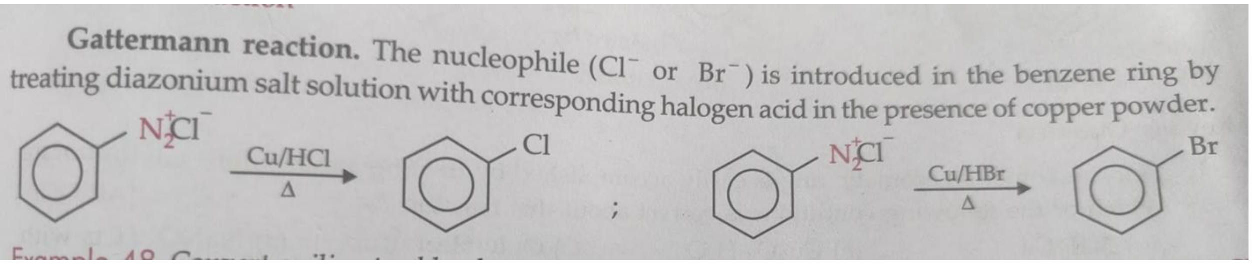


Sandmeyer Reaction

The nucleophile (Cl$^-$, Br$^-$ or CN$^-$) is introduced in the benzene ring in the presence of **Cu(I)** ion

Synthesis of Halobenzene

Synthesis of Phenyl cyanide

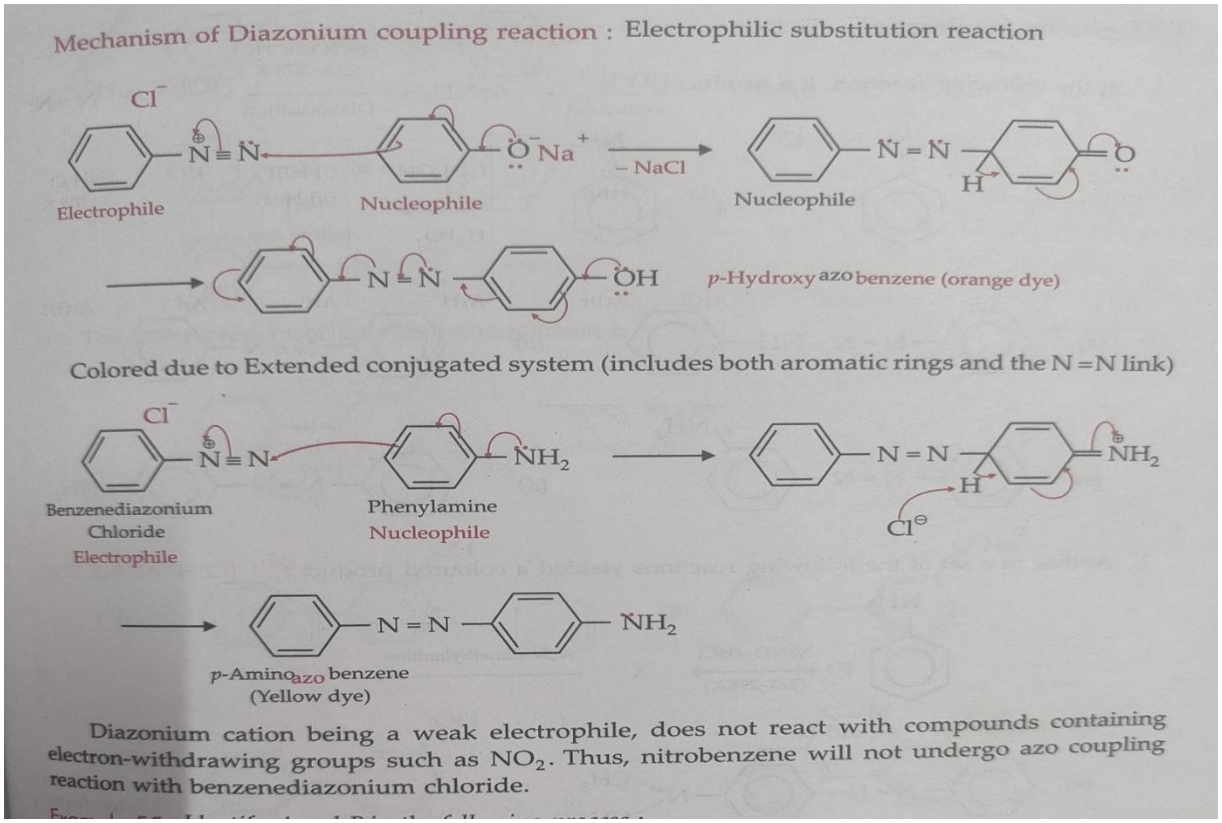


Gattermann reaction. The nucleophile (Cl$^-$ or Br$^-$) is introduced in the benzene ring by treating diazonium salt solution with corresponding halogen acid in the presence of copper powder.

6. $Ar\text{-}N_2Cl + KI \longrightarrow Ar\text{-}I + KCl + N_2$

$Ar\text{-}N_2Cl + HBF_4 \longrightarrow Ar\text{-}N_2BF_4 \xrightarrow{NaNO_2,\ Cu,\ Heat} Ar\text{-}NO_2 + NaBF_4 + N_2$

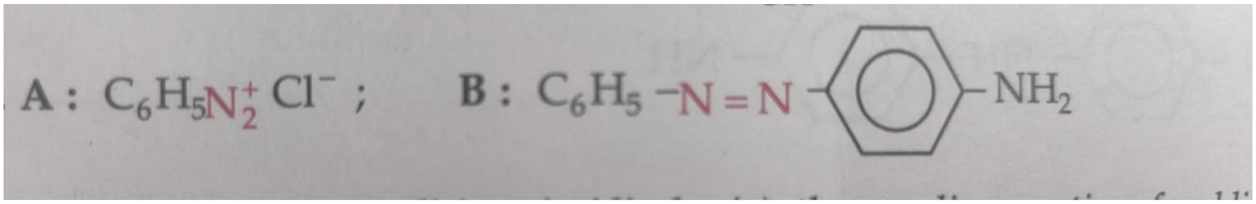
7.



Mechanism of Diazonium coupling reaction : Electrophilic substitution reaction

Colored due to Extended conjugated system (includes both aromatic rings and the N =N link)

Diazonium cation being a weak electrophile, does not react with compounds containing electron-withdrawing groups such as NO_2. Thus, nitrobenzene will not undergo azo coupling reaction with benzenediazonium chloride.

8. 

A : $C_6H_5N_2^+Cl^-$; B : $C_6H_5-N=N-$

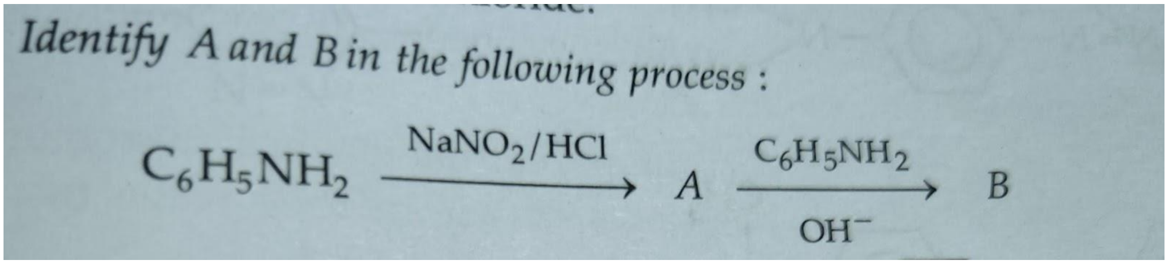
ii)

The coupling reaction of aryldiazonium chloride with aniline is carried out under mild conditions; i.e. pH 4-5.

9. Benzene diazonium chloride + water—--boil—---> Phenol + HCl + N_2
   Ar-N_2Cl + KI —> Ar-I + KCl + N_2
   Ar-N_2Cl + HBF_4 —> Ar-N_2BF_4——--$NaNO_2$, Cu, Heat—->Ar-NO_2 + $NaBF_4$ + N_2
10. Coupling reaction: The reaction of diazonium salts with phenols and aromatic amines to form azo compounds of the general formula , Ar-N=N-Ar is called coupling reaction.
    Coupling generally occurs at the p- position, wrt the hydroxyl or the amino group, if free, otherwise it takes place at the o-position. The mechanism is of electrophilic substitution where the diazonium ion is electrophile.

SECTION- D

1. a) According to solubility and stability differentiate between benzenediazonium chloride and benzenediazonium fluoroborate.

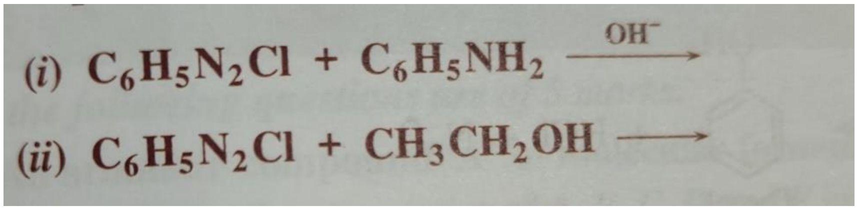
b) 

Identify A and B in the following process :

$$C_6H_5NH_2 \xrightarrow{NaNO_2/HCl} A \xrightarrow[OH^-]{C_6H_5NH_2} B$$

2. Explain Coupling reaction with one example. Coupling reaction occurs at which position and which type of substitution takes place in it.
3. i) How will you convert benzene diazonium chloride to a) phenol b) nitrobenze.?

   ii) Complete the chemical reaction:



(i) $C_6H_5N_2Cl + C_6H_5NH_2 \xrightarrow{OH^-}$

(ii) $C_6H_5N_2Cl + CH_3CH_2OH \longrightarrow$

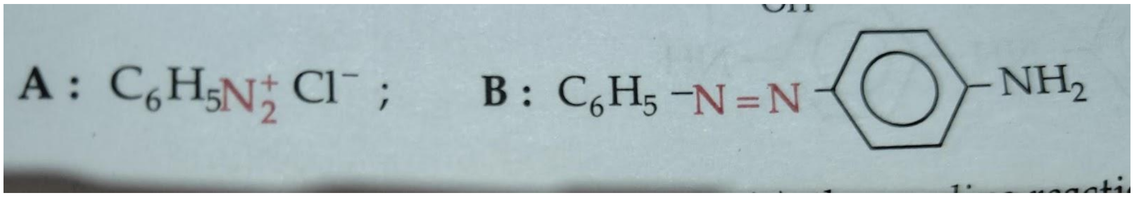
4. a) Write a short note on Diazotization reaction. Why diazonium salts of aromatic amines are more stable than those of aliphatic amines?

   b) Under what reaction conditions (acidic/basic) the coupling reaction of aryldiazonium chloride with aniline is carried out?

ANSWERS OF SECTION D

1. a) i) benzenediazonium chloride is soluble in water but benzenediazonium fluoroborate is water insoluble.

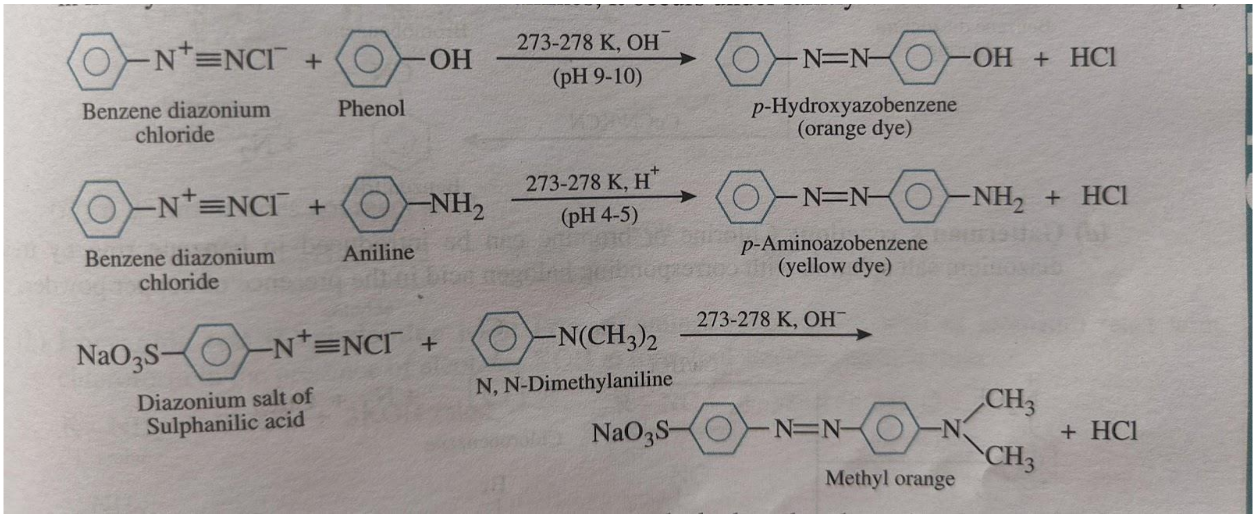
ii) benzenediazonium chloride is stable at low temperature , however it reacts with water when warmed. benzenediazonium fluoroborate is stable at room temperature.

b) 

A : $C_6H_5N_2^+Cl^-$; B : $C_6H_5-N=N-$

2. Coupling reaction: The reaction of diazonium salts with phenols and aromatic amines to form azo compounds of the general formula , Ar-N=N-Ar is called coupling reaction.

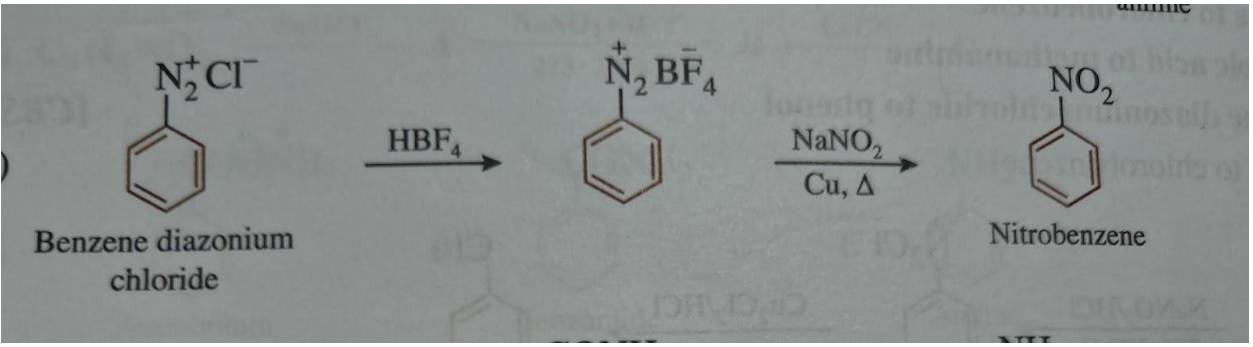
Any one example from the following:



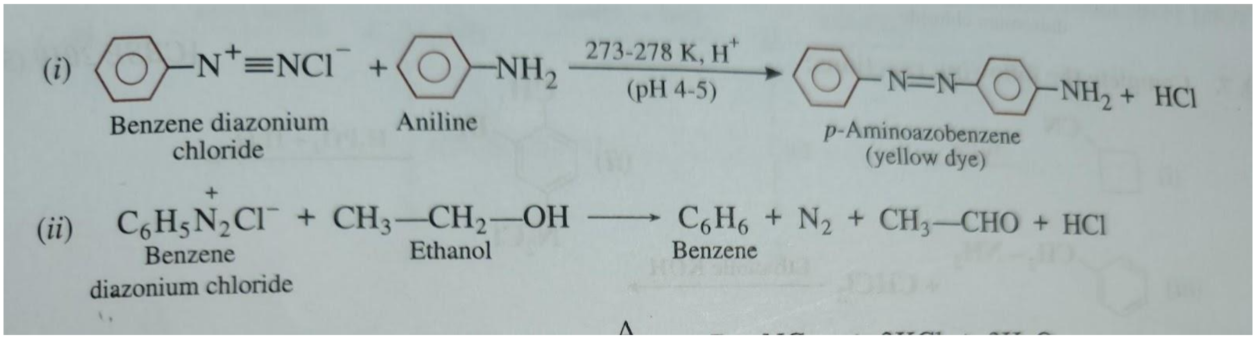
Coupling generally occurs at the p- position, wrt the hydroxyl or the amino group, if free, otherwise it takes place at the o-position. The mechanism is of electrophilic substitution where the diazonium ion is electrophile.

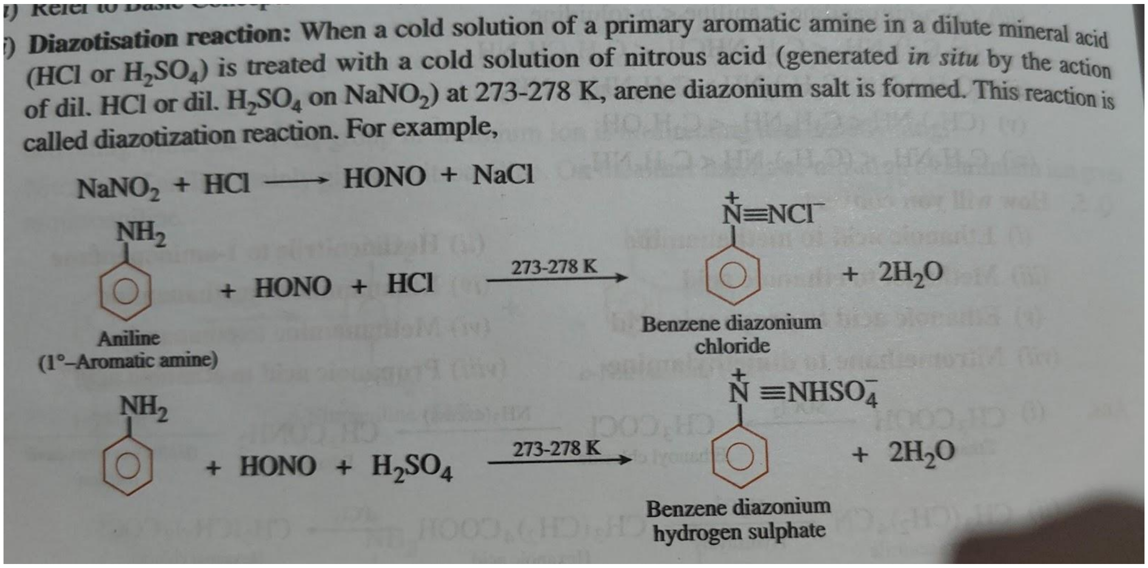
3. i) a) Benzene diazonium chloride + water——-boil——--> Phenol + HCl + N_2

i) b)



ii)



11. 4. a) 

Diazotisation reaction: When a cold solution of a primary aromatic amine in a dilute mineral acid (HCl or H_2SO_4) is treated with a cold solution of nitrous acid (generated *in situ* by the action of dil. HCl or dil. H_2SO_4 on $NaNO_2$) at 273-278 K, arene diazonium salt is formed. This reaction is called diazotization reaction. For example,

$$NaNO_2 + HCl \longrightarrow HONO + NaCl$$

NH_2 + HONO + HCl $\xrightarrow{273\text{-}278\ K}$ $\overset{+}{N}\equiv NCl^-$ + $2H_2O$

Aniline (1°–Aromatic amine)

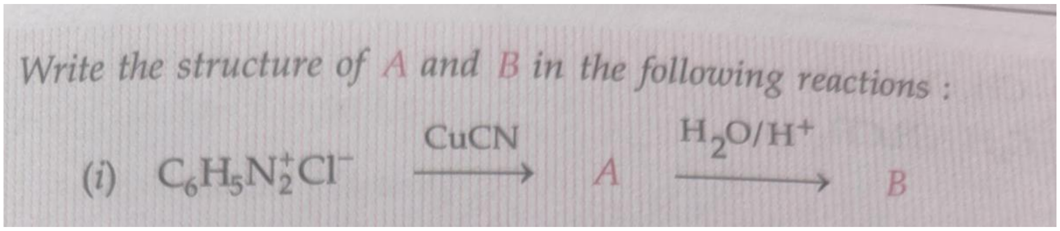
Benzene diazonium chloride

NH_2 + HONO + H_2SO_4 $\xrightarrow{273\text{-}278\ K}$ $\overset{+}{N}\equiv NHSO_4^-$ + $2H_2O$

Benzene diazonium hydrogen sulphate

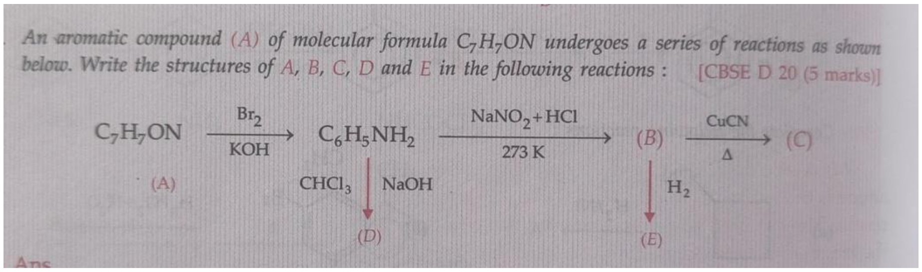
b) The coupling reaction of aryldiazonium chloride with aniline is carried out under mild conditions; i.e. pH 4-5.

SECTION E

1. a) What is Gomberg reaction?
   b) Which test will you use to distinguish between Aniline and Benzylamine?
   c) 

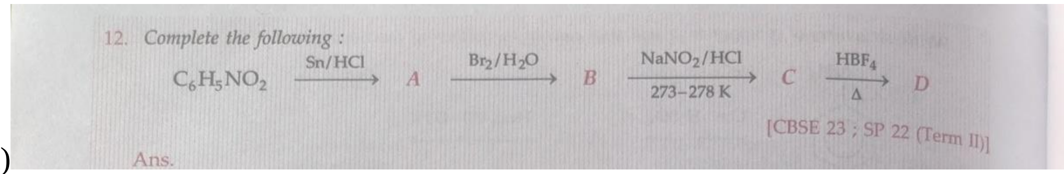
Write the structure of A and B in the following reactions :

(*i*) $C_6H_5N_2^+Cl^- \xrightarrow{CuCN} A \xrightarrow{H_2O/H^+} B$

2. 

An aromatic compound (A) of molecular formula C_7H_7ON undergoes a series of reactions as shown below. Write the structures of A, B, C, D and E in the following reactions : [CBSE D 20 (5 marks)]

$$\begin{tikzcd}
\underset{(A)}{C_7H_7ON} \arrow[r, "Br_2", "KOH"'] & C_6H_5NH_2 \arrow[r, "NaNO_2+HCl", "273\ K"'] \arrow[d, "CHCl_3"', "NaOH"] & (B) \arrow[r, "CuCN", "\Delta"'] \arrow[d, "H_2"] & (C) \\
 & (D) & (E) &
\end{tikzcd}$$

3. A) 

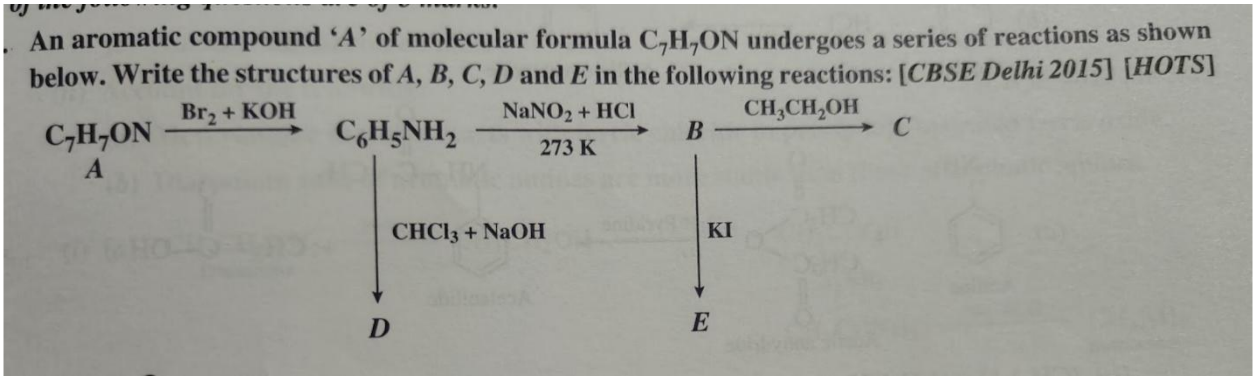
12. *Complete the following :*

$$C_6H_5NO_2 \xrightarrow{Sn/HCl} A \xrightarrow{Br_2/H_2O} B \xrightarrow[273\text{–}278\ K]{NaNO_2/HCl} C \xrightarrow[\Delta]{HBF_4} D$$

[CBSE 23 ; SP 22 (Term II)]

Ans.

B) Which type of solids are diazonium salts?

4. 

An aromatic compound 'A' of molecular formula C_7H_7ON undergoes a series of reactions as shown below. Write the structures of *A, B, C, D* and *E* in the following reactions: [*CBSE Delhi 2015*] [*HOTS*]

$$\begin{tikzcd}
\underset{A}{C_7H_7ON} \arrow[r, "Br_2 + KOH"] & C_6H_5NH_2 \arrow[r, "NaNO_2 + HCl", "273\ K"'] \arrow[d, "CHCl_3 + NaOH"] & B \arrow[r, "CH_3CH_2OH"] \arrow[d, "KI"] & C \\
 & D & E &
\end{tikzcd}$$

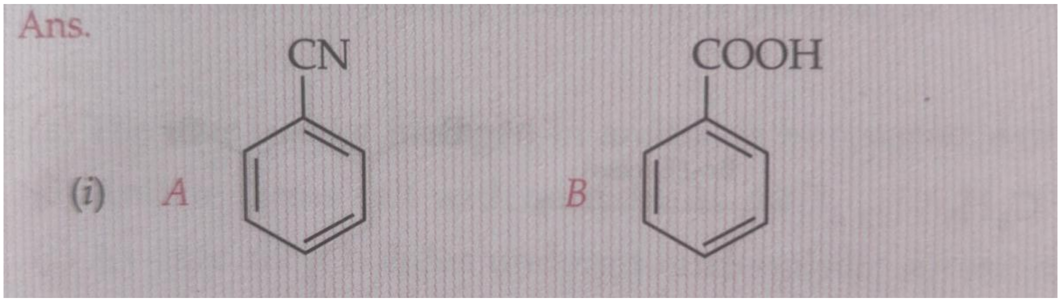
ANSWERS OF SECTION E

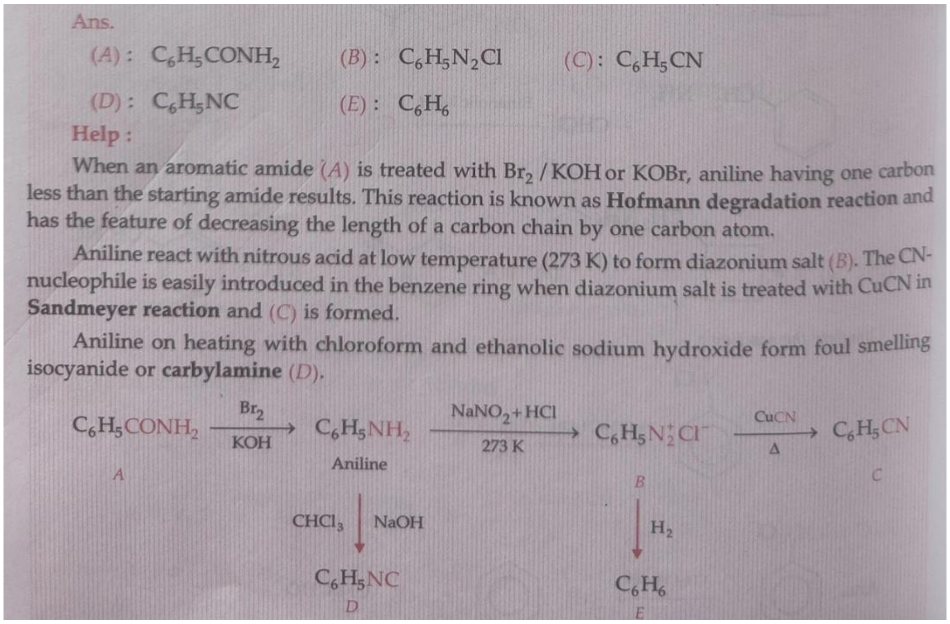
1. a) In Gomberg reaction, Diazonium salts are reduced to arenes by mild reducing agents like ethanol or phosphinic acid.

   b) Azo dye test: Dissolve the organic amine in HCl , cool it and then add cold aqueous solution of $NaNO_2$ and then add solution of beta naphthol.

   Aniline forms a brilliant orange red dye.

   Benzylamine does not form dye.

   c) 

2. 

Ans.

(*A*) : $C_6H_5CONH_2$ (*B*) : $C_6H_5N_2Cl$ (*C*) : C_6H_5CN

(*D*) : C_6H_5NC (*E*) : C_6H_6

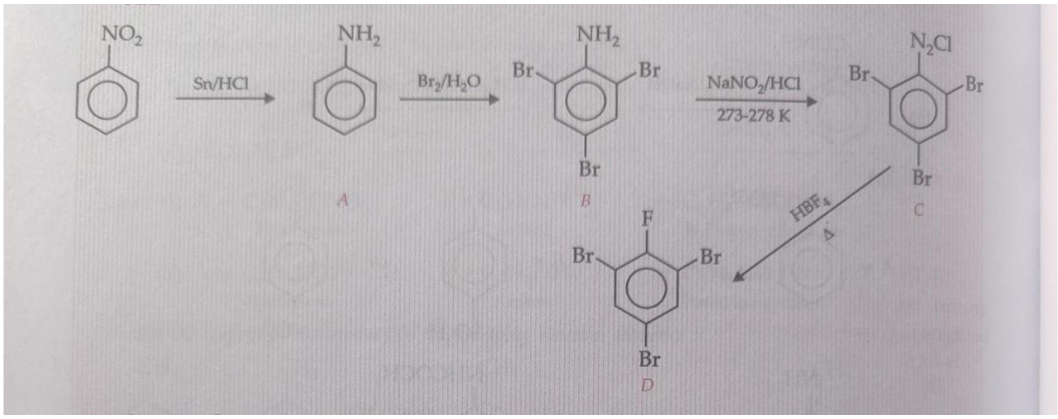
Help :

When an aromatic amide (*A*) is treated with Br_2 / KOH or KOBr, aniline having one carbon less than the starting amide results. This reaction is known as **Hofmann degradation reaction** and has the feature of decreasing the length of a carbon chain by one carbon atom.

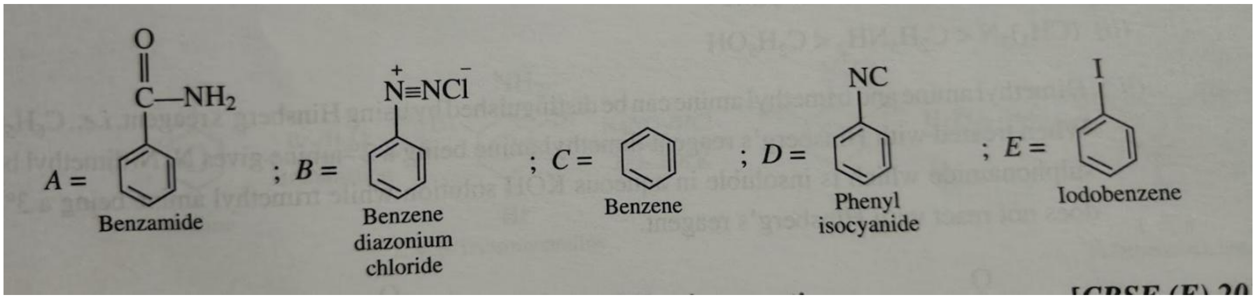
Aniline react with nitrous acid at low temperature (273 K) to form diazonium salt (*B*). The CN- nucleophile is easily introduced in the benzene ring when diazonium salt is treated with CuCN in **Sandmeyer reaction** and (*C*) is formed.

Aniline on heating with chloroform and ethanolic sodium hydroxide form foul smelling isocyanide or **carbylamine** (*D*).

$$\begin{tikzcd}
\underset{A}{C_6H_5CONH_2} \arrow[r, "Br_2", "KOH"'] & \underset{\text{Aniline}}{C_6H_5NH_2} \arrow[r, "NaNO_2+HCl", "273\ K"'] \arrow[d, "CHCl_3"', "NaOH"] & \underset{B}{C_6H_5N_2^+Cl^-} \arrow[r, "CuCN", "\Delta"'] \arrow[d, "H_2"] & \underset{C}{C_6H_5CN} \\
 & \underset{D}{C_6H_5NC} & \underset{E}{C_6H_6} &
\end{tikzcd}$$

3. A) 

   B) They are crystalline solids.

4. 

CHAPTER10 : BIOMOLECULES

SECTION A

All the following questions are of MCQ and has 1 mark each

1. Sucrose (cane sugar) is a disaccharide. One molecule of sucrose on hydrolysis gives _________.

(i) 2 molecules of glucose

(ii) 2 molecules of glucose + 1 molecule of fructose

(iii) 1 molecule of glucose + 1 molecule of fructose

(iv) 2 molecules of fructose

2. Which of the following polymer is stored in the liver of animals?

(i) Amylose

(ii) Cellulose

(iii) Amylopectin

(iv) Glycogen

3. Glycogen is a branched-chain polymer of α-D-glucose units in which the chain is formed by C1—C4 glycosidic linkage, whereas branching occurs by the formation of C1-C6 glycosidic linkage. The structure of glycogen is similar to__________.

(i) Amylose

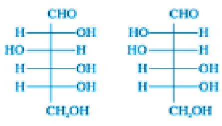
(ii) Amylopectin

(iii) Cellulose

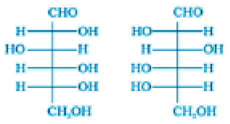
(iv) Glucose

4. Which of the following pairs represents anomers?

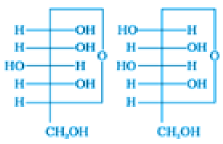
A.



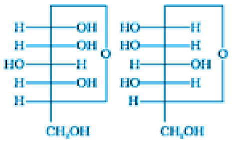
B.



C.

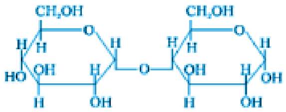


D.

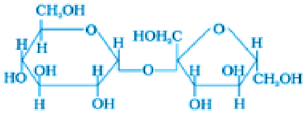


5. n disaccharides, if the reducing groups of monosaccharides, i.e. aldehydic or ketonic groups, are bonded, these are non-reducing sugars. Which of the following disaccharide is a non-reducing sugar?

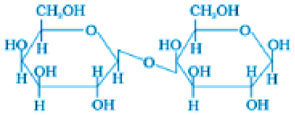
A.



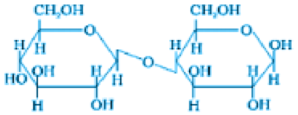
B.



C.



D.



6. Which of the following statements is not true about glucose?

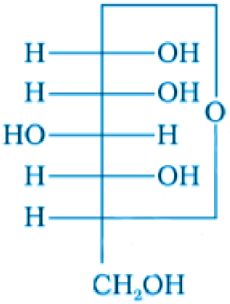
(i) It is an aldohexose.

(ii) On heating with HI, it forms n-hexane.

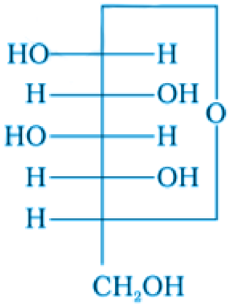
(iii) It is present in furanose form.

(iv) It does not give 2,4-DNP test.

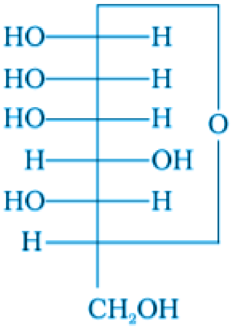
7. Three cyclic structures of monosaccharides are given below, which of these are anomers.



(I)



(II)



(III)

(i) I and II

(ii) II and III

(iii) I and III

(iv) III is anomer of I and II

8. Which of the following reactions of glucose can be explained only by its cyclic structure?

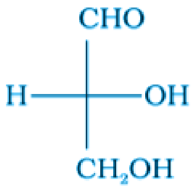
(i) Glucose forms pentaacetate.

(ii) Glucose reacts with hydroxylamine to form an oxime.

(iii) Pentaacetate of glucose does not react with hydroxylamine.

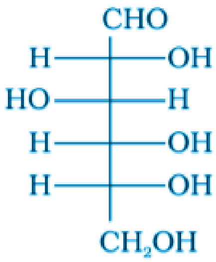
(iv) Glucose is oxidised by nitric acid to gluconic acid.

9. Optical rotations of some compounds, along with their structures, are given below. Which of them has a D configuration?



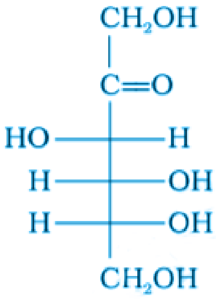
(+) rotation

(I)



(+) rotation

(II)



(–) rotation

(III)

(i) I, II, III

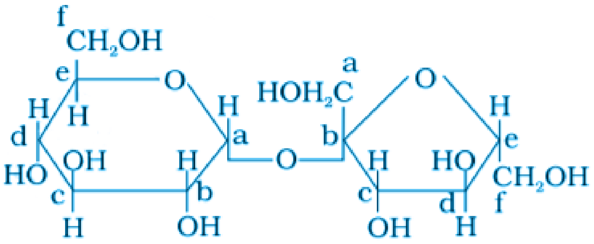
(ii) II, III

(iii) I, II

(iv) III

10. Structure of a disaccharide formed by glucose and fructose is given below.

Identify anomeric carbon atoms in monosaccharide units.



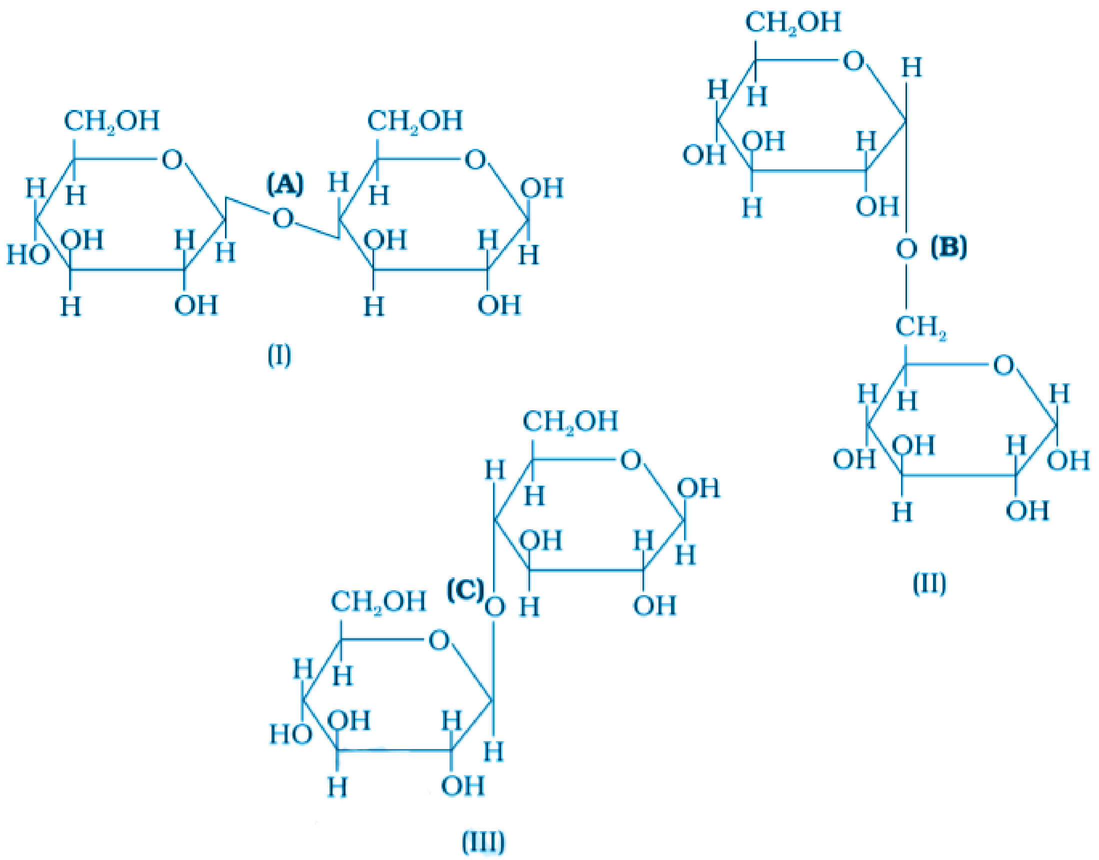
(i) ‘a’ carbon of glucose and ‘a’ carbon of fructose.

(ii) ‘a’ carbon of glucose and ‘e’ carbon of fructose.

(iii) ‘a’ carbon of glucose and ‘b’ carbon of fructose.

(iv) ‘f’ carbon of glucose and ‘f ’ carbon of fructose.

11. Three structures are given below in which two glucose units are linked. Which of these linkages between glucose, units are between C1 and C4 and which linkages are between C1 and C6?



(i) (A) is between C1 and C4, (B) and (C) is between C1 and C6

(ii) (A) and (B) are between C1 and C4, (C) is between C1 and C6

(iii) (A) and (C) is between C1 and C4, (B) is between C1 and C6

(iv) (A) and (C) is between C1 and C6, (B) is between C1 and C4

12. Carbohydrates are classified on the basis of their behaviour on hydrolysis

and also as reducing or non-reducing sugar. Sucrose is a __________.

(i) monosaccharide

(ii) disaccharide

(iii) reducing sugar

(iv) non-reducing sugar

13. Which of the following carbohydrates are branched polymer of glucose?

(i) Amylose

(ii) Amylopectin

(iii) Cellulose

(iv) Glycogen

14. Which of the following monosaccharides are present as five-membered cyclic structure (furanose structure)?

(i) Ribose

(ii) Glucose

(iii) Fructose

(iv) Galactose

15. Which of the following statements about starch is incorrect?

(a) It gives blue colour with iodine

(b) It is a polymer of α-D-glucose

(c) It is a reducing carbohydrate

(d) It consists of branched chains

Solution:

1. (iii) .
2. Iv
3. Ii
4. C
5. B
6. Iii
7. I
8. Iii
9. I
10. Iii
11. Iii
12. Option (ii) and (iv)
13. Option (i) and (iv)
14. Option (i) and (iii)

15. c

SECTION B

All the following questions contain short answers questions and has 2 marks each

1. Classify the following into monosaccharides and disaccharides.
   Ribose, 2-deoxyribose, maltose, galactose, fructose and lactose.
2. Name the sugar present in milk. How many monosaccharide units are present in it? What are such oligosaccharides called?
3. How do you explain the presence of all the six carbon atoms in glucose in a straight chain?
4. Name the linkage connecting monosaccharide units in polysaccharides.
5. Under what conditions is glucose converted to gluconic and saccharic acid?

6. Aldopentoses named as ribose and 2-deoxyribose are found in nucleic acids. What is their relative configuration?

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

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

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

10. Write two main functions of carbohydrates in plants.

Solution

1. Ribose, 2-deoxyribose, galactose, fructose - monosaccharides
   Maltose and lactose - disaccharides.
2. The sugar present in milk is lactose. Lactose contains two monosaccharides, glucose and galactose.

   Oligosaccharides containing two monosaccharide units are called disaccharides.
3. When glucose is heated for a prolonged time with HI, it forms n-hexane, suggesting that all the six carbon atoms are linked in a straight chain.
4. The monosaccharide units in polysaccharides are linked by glycosidic bonds. A glycosidic linkage is when an oxide linkage is formed between two monosaccharide units with the loss of a water molecule.
5. Glucose is converted to gluconic acid, which is a six-carbon carboxylic acid, on treatment with a mild oxidizing agent like Br2 water. Glucose is converted to saccharic acid, which is a dicarboxylic acid, on treatment with nitric acid.
6. The configuration of both the aldopentoses is D-configuration. Ribose is named β-D-ribose, and 2-deoxyribose is β-D-2-deoxyribose.

7. Sucrose is also known as invert sugar. It is a naturally occurring sugar derived from sugarcane and sugarbeet. The hydrolysis of sucrose brings about a change in the sign of rotation, from Dextro (+) to laevo (–), and thus the product is named as invert sugar.
8. During the curdling of milk, which is caused due to bacteria, the sugar present in milk lactose is converted to lactic acid.
9. Glucose can be treated with bromine water, which undergoes mild oxidation to give the carboxylic acid gluconic acid, which confirms the presence of an aldehyde group.
10. The two main functions of carbohydrates in a plant are as follows:

    (a) Polysaccharides like starch act as storage molecules.

    (b) Cellulose is used to build the cell wall, and it is a polysaccharide.

SECTION C (Each question carries 3 marks)

1. What happens when D-glucose is treated with the following reagents?

    (i)HI (ii) Bromine water (iii) HNO_3

2. Enumerate the reactions of D-glucose which cannot be explained by its open chain structure.
3. Sucrose is dextrorotatory, but the mixture obtained after hydrolysis is laevorotatory. Explain.
4. What do you understand by the term glycosidic linkage?
5. What is the basic structural difference between starch and cellulose?
6. Write down the structures and names of the products formed when D-glucose is treated with
    (i) Hydroxylamine
    (ii) Acetic anhydride
7. Define the following terms :
    (i) Glycosidic linkage
    (ii) Invert sugar
    (iii) Oligosaccharides
8. **How many types of carbohydrates are there? Mention their names.**
9. **Write a reaction which shows that all the carbon atoms in glucose are linked in a straight chain.**
10. (i)**Write the structure of the product obtained when glucose is oxidised with nitric acid.**

(ii)What is meant by 'reducing sugars'?

SOLUTION

1. (i) when glucose is treated with HI, it forms n-hexane.

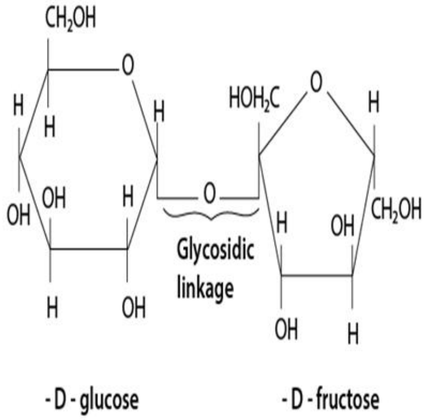
    (ii) when glucose is treated with Bromine water, gluconic acid is formed.

(iii) when glucose is treated with nitric acid, Saccharic acid is formed.

2. (i) Despite having aldehyde group, glucose does not give Schiff test and 2,4-DNP test.
   (ii)Glucose does not react with sodium hydrogen bisulphite to form addition product.

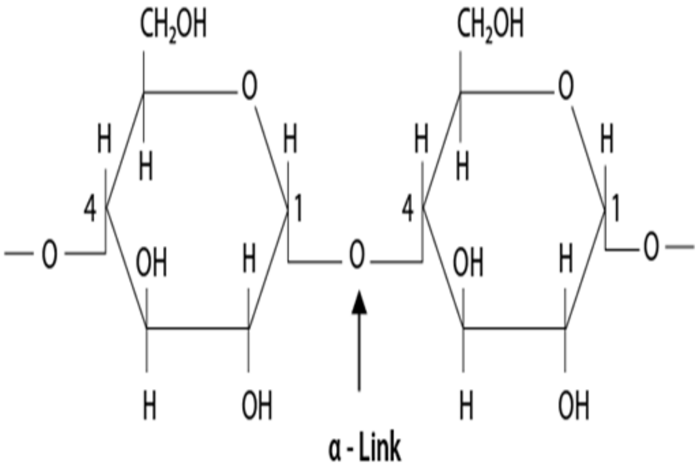
(iii)The pentaacetate of glucose does not react with hydroxyl amine showing the absence of free -CHO group.

3. Sucrose is dextrorotatory in its aqueous solution and rotates plane-polarized light entering the solution 66.5° to the right. When sucrose is hydrolysed with dilute acids or invertase enzyme, it gives two products in equimolar concentration, dextrorotatory D-(+)-glucose and laevorotatory D-(-)-fructose. Thus, hydrolysis of sucrose brings about a change in the sign of rotation, from Dextro (+) to laevo (–). So the hydrolysed mixture is laevorotatory.
4. The linkage which forms by the loss of water between two monosaccharide units through an oxygen atom is known as glycosidic linkage. For example, in a sucrose molecule, two monosaccharide units,α-glucose and β – fructose, are joined together by a glycosidic linkage.



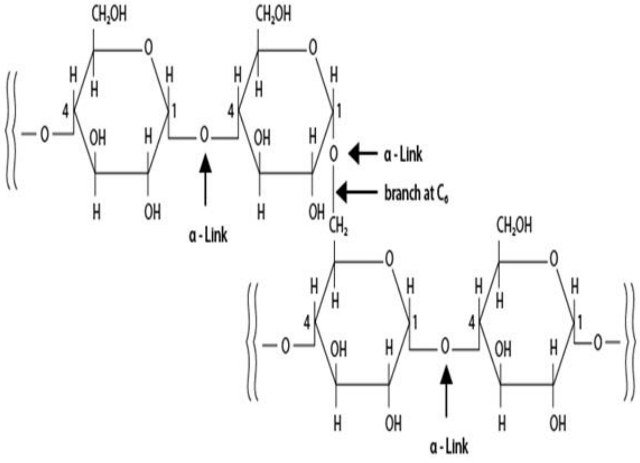
Sucrose

5. Starch consists of two components – amylopectin and amylose. Amylose have a longer linear chain of α– D −(+)−glucose units joined by C1−C4 glycosidic linkage (α-link).



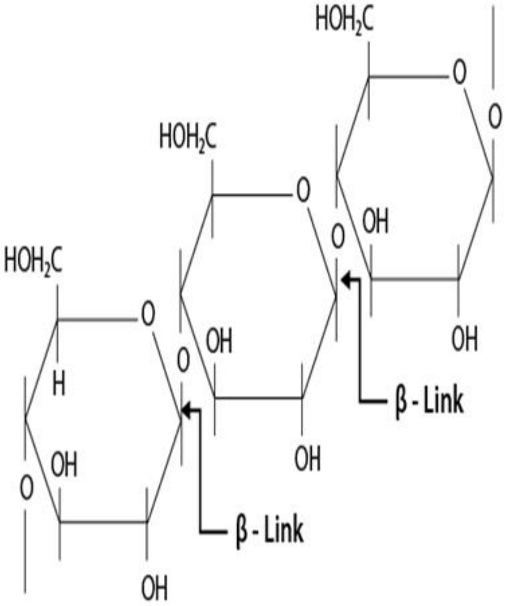
Amylose

While amylopectin is a branched-chain polymer of α-D-glucose units, in which the chain is formed by C1−C4 glycosidic linkage, and the branching occurs by C1−C6 glycosidic linkage.

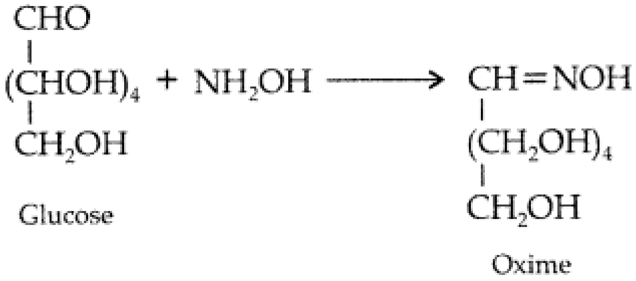


Amylopectin

The cellulose is a straight-chain polysaccharide of β– D-glucose units joined by C1−C4 glycosidic linkage (β– link).

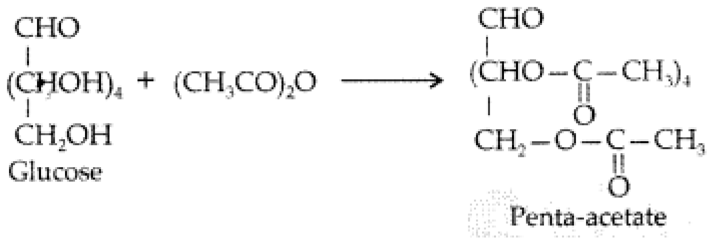


6. (i) D-glucose reacts with hydroxylamine to form oxime.



$$\begin{matrix}\text{CHO} \\ | \\ (\text{CHOH})_4 \\ | \\ \text{CH}_2\text{OH}\end{matrix} + \text{NH}_2\text{OH} \longrightarrow \begin{matrix}\text{CH}=\text{NOH} \\ | \\ (\text{CH}_2\text{OH})_4 \\ | \\ \text{CH}_2\text{OH}\end{matrix}$$

(ii) D-glucose reacts with acetic anhydride to give penta-acetate.



7. i) Glycosidic linkage : The two monosaccharide units are joined together through an etheral or oxide linkage formed by loss of a molecule of water. Such a linkage between two monosaccharide units through oxygen atom is called glycosidic linkage

   (ii) Invert sugar : An equimolar mixture of glucose and fructose obtained by hydrolysis of sucrose in presence of an acid such as dil. HC1 or the enzyme invertase or sucrase is called invert sugar.

   (iii) Oligosaccharides : Those carbohydrates which on hydrolysis give 2-10 molecules of monosaccharides are called oligosaccharides.
   Example : sucrose, maltose.

8. Carbohydrates can be divided into four categories based on the presence of a certain number of sugar molecules, namely, monosaccharides, disaccharides, oligosaccharides, and polysaccharides. These categories can be further divided in the following manner:

1. Monosaccharides (having one sugar molecule)
    1. Glucose
    2. Fructose
    3. Galactose
2. Disaccharides (having two sugar molecules)
    1. Sucrose
    2. Lactose
    3. Maltose
2. Oligosaccharides (having three sugar molecules)
    1. Raffinose
    2. Stachyose
2. Polysaccharides (having four sugar molecules)
    1. Starch
    2. Glycogen
    3. Cellulose

9. On prolonged heating with HI, it forms n-hexane, shows that all the six carbon atoms are linked in a straight chain :

10.(i)

(ii)Reducing sugar contains aldehydic or ketonic group in the hemiacetal and hemiketal forms and can reduce Tollen’s reagent or Fehlmg’s solution.

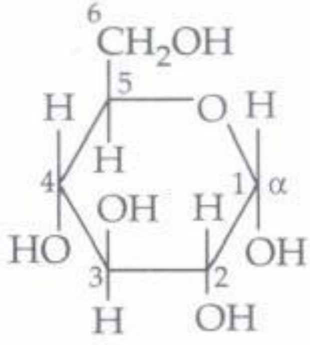
SECTION D CASE STUDY QUESTIONS (Each question carries 4 marks)

Read the passage given below and answer the following questions:
Pentose and hexose undergo intramolecular hemiacetal or hemiketal formation due to combination of the -OH group with the carbonyl group. The actual structure is either of five or six membered ring containing an oxygen atom. In the free state all pentoses and hexoses exist in pyranose form (resembling pyran). However, in the combined state some of them exist as five membered cyclic structures, called furanose (resembling furan).

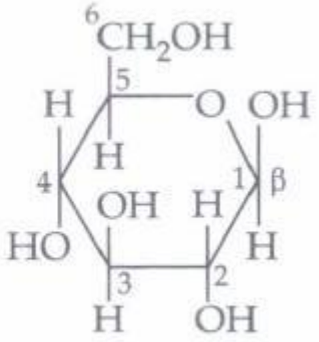
Pyran

Furan

The cyclic structure of glucose is represented by Haworth structure:



α-D-(+)-Glucopyranose

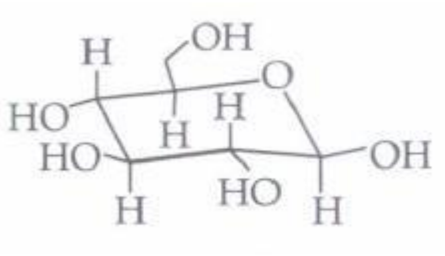


β-D-(+)-Glucopyranose

αα and ββ -D-glucose have different configuration at anomeric (C-l) carbon atom, hence are called anomers and the C-l carbon atom is called anomeric carbon (glycosidic carbon).
The six membered cyclic structure of glucose is called pyranose structure.
The following questions are multiple choice questions. Choose the most appropriate answer:
(i) αα -D(+)-glucose and ββ -D(+)glucose are

(a)	(b)	(c)	(d)
enantiomers	conformers	epimers	anomers

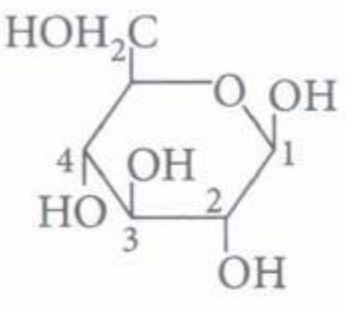
(ii) The following carbohydrate is



(a) a ketohexose (b) an aldohexose

(c) an αα-furanose (d) an αα-pyranose

(iii) In the following structure,



anomeric carbon is

(a) C-l (b) C-2 (c) C-3 (d) C-4

(iv) The term anomers of glucose refers to

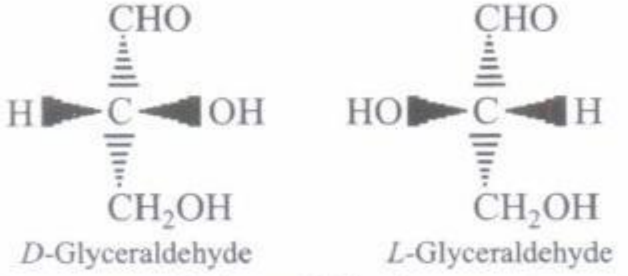
(a) isomers of glucose that differ in configurations at carbons one and four (C-l and C-4)

(b) a mixture of (D)-glucose and (L)-glucose

(c) enantiomers of glucose

(d) isomers of glucose that differ in configuration at carbon one (C-l).

2.Read the passage given below and answer the following questions:
Carbohydrates can exist in either of two conformations, as determined by the orientation of the hydroxyl group about the asymmetric carbon farthest from the carbonyl.



D-Glyceraldehyde L-Glyceraldehyde

(Structures of glyceraldehyde enantiomers)

By convention, a monosaccharide is said to have D-configuration if the hydroxyl group attached to the

asymmetric carbon atom adjacent to the - CH2OH group is on the right hand side irrespective of the positions of the other hydroxyl groups. On the other hand, the molecule is assigned L-configuration if the - OH group attached to the carbon adjacent to the - CH2OH group is on the left hand side.
The following questions are multiple choice questions. Choose the most appropriate answer:
(i) D-Glyceraldehyde and L-Glyc~raldehyde are

(a) epimers (b) enantiomers

(c) anomers (d) conformational diasteriomers

(ii) Which of the following monosaccharides, is the majority found in the human body?

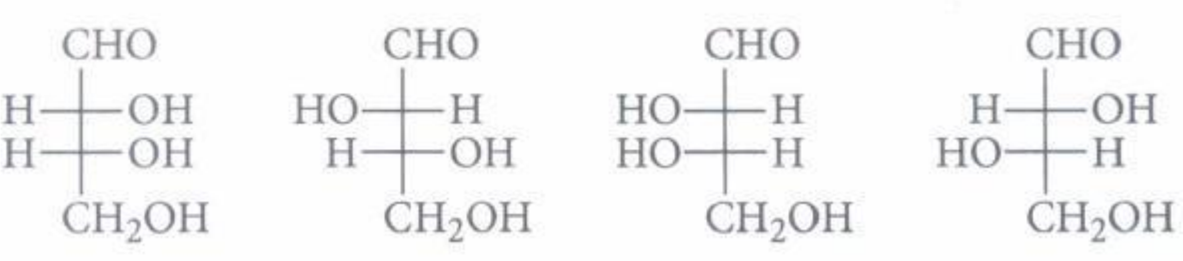
(a) D-type (b) L-type (c) Both of these (d) None of these

(iii) Monosaccharides contain

(a) always six carbon atoms(b) always five carbon atoms

(c) always four carbon atoms (d) may contain 3 to 7 carbon atoms

(iv) The correct corresponding order of names of four aldoses with configuration given below



respectively, is

(a) L-erythrose, L-threose, L-erythrose, D-threose

(b) D-threose, D-erythrose, L-tl?repse, L-erythrose

(c) L-erythrose, L-threose, D-erythrose, D-threose

(d) D-erythrose, D-threose, L-erythrose, L-threose.

3.Carbohydrates are polyhydroxy aldehydes and ketones and those compounds which on hydrolysis give such compounds are also carbohydrates. The carbohydrates which are not hydrolysed are called monosaccharides. Monosaccharides with aldehydic group are called aldose and those which free ketonic groups are called ketose. Carbohydrates are optically active. Number of optical isomers = 2n
Where n = number of asymmetric carbons. Carbohydrates are mainly synthesised by plants during photosynthesis.
The monosaccharides give the characteristic reactions of alcohols and carbonyl group (aldehydes and ketones). It has been found that these monosaccharides exist in the form of cyclic structures. In cyclization,

the -OH groups (generally C5 or C4 in aldohexoses and C5 or C6 in ketohexoses) combine with the aldehyde or keto group. As a result, cyclic structures of five or six membered rings containing one oxygen atom are formed, e.g., glucose forms a ring structure. Glucose contains one aldehyde group, one 1o alcoholic group and four 2o alcoholic groups in its open chain structure.
The following questions are multiple choice questions. Choose the most appropriate answer:
(i) First member of ketos sugar is

(a)	(b)	(c)	(d)
ketotriose	ketotetrose	ketopentose	ketohexose

(ii) In CH2OHCHOHCHOHCHOHCHOHCHO, the number of optical isomers will be

(a) 16 (b) 8 (c) 32 (d) 4

(iii) Some statements are given below:
1. Glucose is aldohexose.
2. Naturally occurring glucose is dextrorotatory.
3. Glucose contains three, chiral centres.
4. Glucose contains one 1o alcoholic group and four 2o alcoholic groups.
Among the above, correct statements are

(a) 1 and 2 only (b) 3 and 4 only

(c) 1,2 and 4 only (d) 1,2,3 and 4

(iv) Which of the following reactions of glucose can be explained only by its cyclic structure?

(a) Glucose forms cyanohydrin with HCN

(b) Glucose reacts with hydroxylamine to form an oxime

(c) Pentaacetate of glucose does not react with hydroxylamine

(d) Glucose is oxidised by nitric acid to gluconic acid .

4. Glucose is known as dextrose because it occurs in nature as the optically active dextrorotatory isomer. It is essential constituent of human blood. The blood normally contains 65 to 110 mg of glucose per 100 mL (hence named Blood sugar). The level may be much higher in diabetic persons. The urine of diabetic persons also contain considerable amount of glucose. In combined form, it occurs in cane sugar and polysaccharides such as starch and cellulose.
Glucose has an aldehyde group (-CHO), one primary alcoholic group (-CH2OH) and four secondary alcoholic groups (-CHOH) in their structure. Due to the presence five hydroxyl groups (-OH), glucose acetylation. Glucose also undergoes oxidation with mild oxidising agents like bromine water as well as with strong oxidising agents like nitric acid. Since glucose is readily oxidised, it acts as a strong reducing agent and reduces Tollen's reagent and Fehling solution. Glucose exists in two crystalline forms: αα -D-glucose and ββ -Dglucose undergoes If either of the two forms is dissolved in water and allowed to stand, the specific rotation of the solution changes gradually, until a constant value is obtained. This change is called mutarotation.
In these questions (i-iv), a statement of assertion followed by a statement of reason is given. Choose the

correct answer out of the following choices.
(a) Assertion and reason both are correct statements and reason is correct explanation for assertion.
(b) Assertion and reason both are correct statements but reason is not correct explanation for assertion.
(c) Assertion is correct statement but reason is wrong statement.
(d) Assertion is wrong statement but reason is correct statement.

(i) Assertion: A diabetic person carries a packet of glucose with him always.
Reason: Glucose increases the blood sugar level almost instantaneously.

(ii) Assertion: On oxidation with nitric acid, glucose as well as gluconic acid both yield saccharic acid.
Reason: The pentaacetate of glucose does not react with hydroxylamine indicating the absence of free -CHO group.

(iii) Assertion: Glucose reacts with acetyl chloride to form pentaacetyl glucose.
Reason: The formation of pentaacetyl derivative confirms the presence of five -OH groups in glucose.

(iv) Assertion: A certain compound gives negative test with ninhydrin and positive test with Benedict's solution, the compound is an amino acid.
Reason: Glucose is a monosaccharide.

SECTION E (Each question carries 5 marks)

1. (i) Which one of the following is a polysaccharide:
Starch, Maltose, Fructose, Glucose?
(ii) Write the structural difference between starch and cellulose.
(iii)Draw pyranose structure of glucose.
(iv)What is meant by ‘reducing sugars’? (1+1+1+2=5)

2. (I)What are monosaccharides?
(ii)Write the structure of the product obtained when glucose is oxidised with nitric acid.
(iii)Write a reaction which shows that all the carbon atoms in glucose are linked in a straight chain. (1+2+2=5)

3.(I)What are the expected products of hydrolysis of lactose ?
(ii)What is essentially the difference between a-form of glucose and p-form of glucose? Explain. (2+3=5)

4.(I)Explain what is meant by a glycosidic linkage.

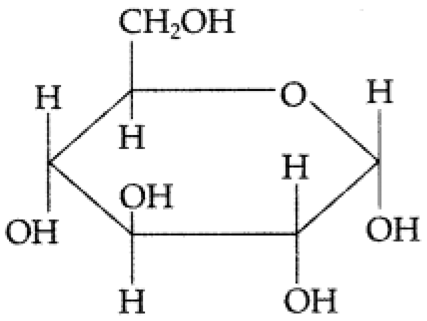
(ii)Write down the structures and names of the products formed when D-glucose is treated with
(i) Hydroxylamine
(ii) Acetic anhydride. (2+3=5)

SOLUTIONS

1.(I) Starch is a polysaccharide.

(i) Starch contains the β-D-glucose as its monomer units while cellulose contains β-D- glucose as its monomer units.

(ii) Pyranose structure of glucose



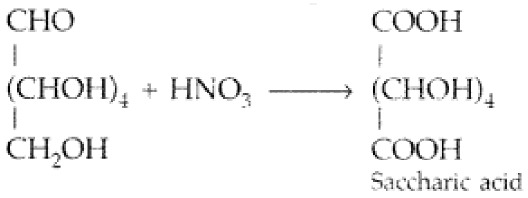
(iii) Reducing sugar contains aldehydic or ketonic group in the hemiacetal and hemiketal forms and can reduce

Tollen's reagent or Fehlmg's solution.

2(I)These are the simplest carbohydrates which cannot be hydrolysed to smaller molecules. Their general formula is (CH2O)n where n = 3 – 7

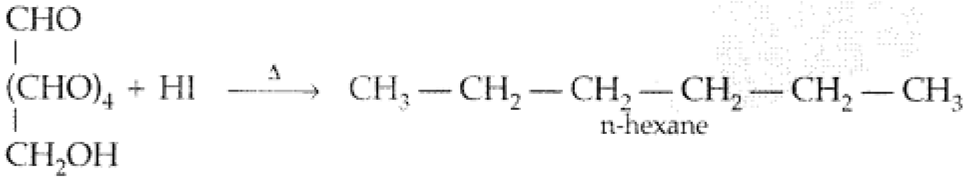
Example : glucose, fructose etc.

(ii)



$$\begin{matrix}CHO\\|\\(CHOH)_4\\|\\CH_2OH\end{matrix} + HNO_3 \longrightarrow \underset{\text{Saccharic acid}}{\begin{matrix}COOH\\|\\(CHOH)_4\\|\\COOH\end{matrix}}$$

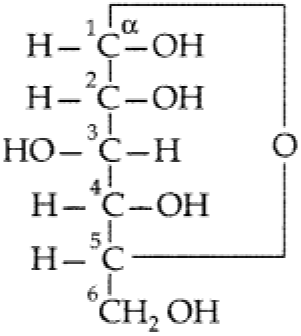
(iv) On prolonged heating with HI, it forms n-hexane, shows that all the six carbon atoms are linked in a straight chain :

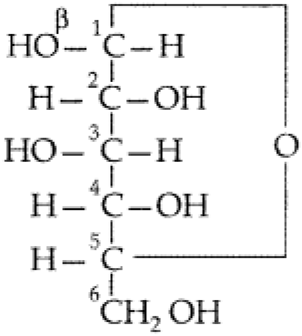


$$\begin{matrix}CHO\\|\\(CHO)_4\\|\\CH_2OH\end{matrix} + HI \xrightarrow{\Delta} \underset{\text{n-hexane}}{CH_3-CH_2-CH_2-CH_2-CH_2-CH_3}$$

3. (I)On hydrolysis, lactose gives P-D-galactose and p-D-glucose.

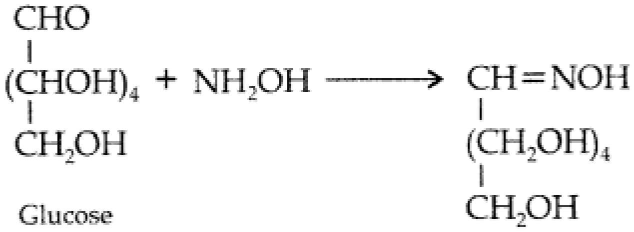
(ii)In a-α-glucose, the OH group at C1 is towards right while in p-D-glucose, the OH group at C1 is towards left.


α-D-glucose or
α-D-glucopyranose


β-D-glucose or
β-D-glucopyranose

4.(I)Glycosidic linkage : The two monosaccharide units are joined together through an etheral or oxide linkage formed by loss of a molecule of water. Such a linkage between two monosaccharide units through oxygen atom is called glycosidic linkage.

(ii)i) D-glucose reacts with hydroxylamine to form oxime.

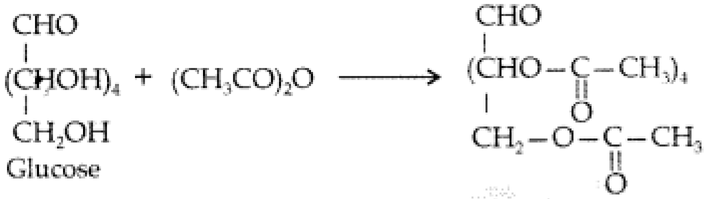


$$\begin{array}{c}CHO\\ |\\ (CHOH)_4\\ |\\ CH_2OH\end{array} + NH_2OH \longrightarrow \begin{array}{c}CH{=}NOH\\ |\\ (CH_2OH)_4\\ |\\ CH_2OH\end{array}$$

Glucose

Oxime

(ii) D-glucose reacts with acetic anhydride to give penta-acetate.



$$\begin{array}{c}CHO\\ |\\ (CHOH)_4\\ |\\ CH_2OH\end{array} + (CH_3CO)_2O \longrightarrow \begin{array}{l}CHO\\ |\\ (CHO-\underset{\overset{\|}{O}}{C}-CH_3)_4\\ |\\ CH_2-O-\underset{\overset{\|}{O}}{C}-CH_3\end{array}$$

Glucose

Penta-acetate

CHAPTER10: BIOMOLECULES

SUB-TOPIC-ENZYMES, HORMONES, VITAMINS-CLASSIFICATIONS AND FUNCTIONS, NUCLEIC ACIDS- DNA AND RNA.

I.MCQ

1.Which of the following B group vitamins can be stored in our body?

(i) Vitamin B1
(ii) Vitamin B2
(iii) Vitamin B6
(iv) Vitamin B12

2.In DNA, the complementary bases are

(i) adenine and thymine; guanine and cytosine.

(ii) adenine and thymine; guanine and uracil.

(iii) adenine and guanine; thymine and cytosine.

(v) uracil and adenine; cytosine and guanine.

3. Nucleic acids are the polymers of **______________**.

(i) Nucleosides

(ii) Nucleotides

(iii) Bases

(iv) Sugars

4.Dinucleotide is obtained by joining two nucleotides together by phosphodiester linkage. Between which carbon atoms of pentose sugars of nucleotides are Are these linkages present?

(i) 5′ and 3′

(ii) 1′ and 5′

(iii) 5′ and 5′

(iv) 3′ and 3′Solution.

5. Which of the following bases is not present in DNA?

(i) Adenine

(ii) Thymine

(iii) Cytosine

(iv) Uracil.

6. DNA and RNA contain four bases each. Which of the following bases is not present in RNA?

(i) Adenine

(ii) Uracil

(iii) Thymine

(iv) Cytosine

7. Which of the following bases is not present in DNA?

(i) Adenine

(ii) Thymine

(iii) Cytosine

(iv) Uracil

8. Which of the following acids is a vitamin?

(i) Aspartic acid

(ii) Ascorbic acid

(iii) Adipic acid

(iv) Saccharic acid

9. Which of the following terms are correct about enzymes?

(i) Proteins

(ii) Dinucleotides

(iii) Nucleic acids

(iv) Biocatalysts

10.Which sugar is present in RNA?

(i) Glucose

(ii) Fructose

(iii) D-Ribose

(iv) D-2-Deoxyribose

11. Vitamin A is

(i) Retinol

(ii) Ascorbic acid

(iii) Thiamine

(iv) Calciferol

12. Nucleotides are joined together by

(i) Glycosidic linkage

(ii) Peptide linkage

(iii) Hydrogen bonding

(iv) Phosphodiester linkage

13.Scurvy is caused due to deficiency of

(i) Vitamin B1

(ii) Vitamin B2

(iii) Ascorbic acid

(iv) Glutamic acid

14. Which among the following is a water-soluble vitamin?

(i) Vitamin C

(ii) Vitamin D

(iii) Vitamin A

(iv) Vitamin E

15. Which of the following are purine bases?

(i) Guanine

(ii) Adenine

(iii) Thymine

(iv) Uracil

ANS-1. (iv) Vitamin B12

2. (i) adenine and thymine; guanine and cytosine.

3. (ii) Nucleotides

4. (i) 5′ and 3′

5. (iv) Uracil.

6. (iii) Thymine

7. (iv) Uracil

8. (ii) Thymine

9. (i) and (iv)

10. (iv) D-2-Deoxyribose

11. (i) Retinol

12. (iv) Phosphodiester linkage

13. (iii) Ascorbic acid

14. (i) Vitamin C

15. (i) Guanine and (ii) Adenine

II.SHORT ANS TYPE QUESTIONS-2M EACH.

1. Why must vitamin C be supplied regularly in the diet?
2. The activation energy for the acid-catalysed hydrolysis of sucrose is 6.22 kJ mol–1, while the activation energy is only 2.15 kJ mol–1 when hydrolysis is catalyzed by the enzyme sucrase. Explain.
3. Structures of glycine and alanine are given below. Show the peptide linkage in glycylalanine.
4. Which moieties of nucleosides are involved in the formation of phosphodiester linkages present in dinucleotides? What does the word diester in the name of linkage indicate? Which acid is involved in the formation of this linkage?
5. How do enzymes help a substrate to be attacked by the reagent effectively?
6. Draw structures of glycine and alanine . Show the peptide linkage in glycylalanine.
7. Write the structures of fragments produced on complete hydrolysis of DNA. How are they linked in DNA molecule? Draw a diagram to show pairing of nucleotide bases in double helix of DNA.

ANS-

1.Vitamin C is a water-soluble vitamin, and hence the excess is excreted regularly from the body. Since it cannot be stored in the body, vitamin C must be supplied regularly in the diet.

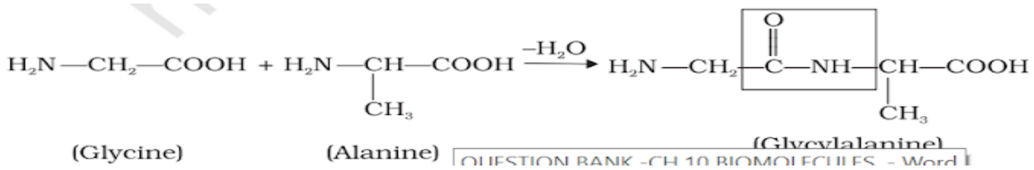
2. Mainly the enzymes are biocatalysts which provide an alternative path to reduce the reaction activation energy. Using the enzyme sucrase, the hydrolysis of sucrose is much faster than conventional acidic hydrolysis.

3. The hydroxyl group of glycine is linked to the amine group of alanine by peptide (-CONH) linkage to form glycylalanine.

4. Phosphoric acid is involved in the formation of phosphodiester linkage. The word ‘diester’ in this linkage indicates that two −OH groups of phosphoric acid are involved in forming two ester linkages. In the formation of dinucleotides, the 3−OH group of the pentose sugar of one nucleotide unit and the 5−OH group of the pentose sugar of the other nucleotide unit are involved in generating the phosphodiester linkage.

5. The active site of enzymes holds the substrate molecule in a suitable position to be attacked by the reagent effectively.

6.



$$H_2N{-}CH_2{-}COOH + H_2N{-}\underset{\displaystyle CH_3}{\underset{|}{CH}}{-}COOH \xrightarrow{-H_2O} H_2N{-}CH_2{-}\boxed{\overset{\displaystyle O}{\overset{\|}{C}}{-}NH}{-}\underset{\displaystyle CH_3}{\underset{|}{CH}}{-}COOH$$

III.SHORT ANS TYPE QUESTIONS-3M EACH

1.How are vitamins classified? Name the vitamin responsible for the coagulation of blood.

2. Why are Vitamin A and Vitamin C essential to us? Give their important sources.

3. What are nucleic acids? Mention their two important functions.

4. What is the difference between a nucleoside and a nucleotide?

5. The two strands in DNA are not identical but complementary. Explain.

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

7. What are the different types of RNA found in the cell?

ANSWERS

1. We can classify vitamins on the basis of solubility in water or fat into two categories.

(a) Water-soluble vitamins: Vitamins which are soluble in water come in the category.

For example, B group vitamins ($B1, B2, B12, etc.$) and vitamin C.

(b) Fat-soluble vitamins: Those vitamins which are soluble only in fat, not in the water, come under this group. For example, Vitamins A, D, E, and K.

However, biotin or Vitamin H is neither soluble in water nor in fat.

The vitamin which is responsible for the coagulation of blood is Vitamin K.

2.These two vitamins are essential to us because the deficiency of these two vitamins causes us harmful diseases like xerophthalmia (which hardens the cornea of the eye) and night blindness. While the deficiency of Vitamin C causes scurvy (bleeding gums).

The sources of these two vitamins are given below:

Vitamin A: Carrots, fish liver oil, milk and butter.

Vitamin C: Amla, citrus fruits and green leafy vegetables.

3.It is a molecule which is found as one of the constituents of chromosomes which is found in the nuclei of all living cells.

Nucleic acid can be categorised into two categories: ribonucleic acid (RNA) and deoxyribonucleic acid (DNA).

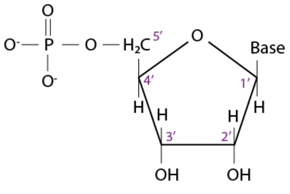
Nucleic acids are long-chain polymers of nucleotides, so they are also known as polynucleotides.

(i) It is responsible for heredity. In heredity, there is a transfer of inherent characters from one generation to another. This process is held by the DNA.

(ii) The protein cell synthesis is held by nucleic acid (both RNA and DNA). Protein synthesis is majorly done by the various RNA molecules in a cell, while DNA contains the message for the synthesis of a specific protein.

4.A nucleotide is formed by the combination of all three basic components of nucleic acids, i.e. base, pentose sugar, and phosphoric acid).

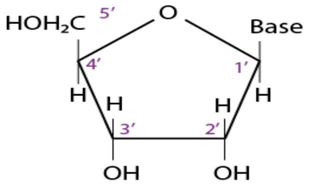
Therefore, Nucleotide = Base + Sugar + Phosphoric acid



Structure of nucleotide

On the other hand, a nucleoside is formed by the attachment of a base to the 1’ position of the sugar.

Nucleoside = Sugar + Base



Structure of nucleoside

5.In the helical structure of DNA, the hydrogen bond holds the two strands between specific pairs of bases. Adenine forms a hydrogen bond with thymine, while cytosine forms a hydrogen bond with guanine. As a result, the two strands act as complementary to each other.

6.The difference between DNA and RNA, on the basis of their functions, is as follows:

DNA		**RNA**	
1	DNA is the chemical basis of heredity.	1	RNA is not responsible for heredity.

DNA		**RNA**	
1	The sugar moiety in DNA molecules is β -D-2 deoxyribose.	**1**	The sugar moiety in RNA molecules is β -D-ribose.
2	Bases are Adenine(A), Guanine(G), Cytosine(C) and Thymine(T).	**2**	The bases are Adenine(A), Guanine(G), Cytosine(C), and Uracil(U).
3	The helical structure of DNA is double-stranded.	**3**	The helical structure of RNA is single-stranded.

7.(i) Messenger RNA (m-RNA)

(ii) Ribosomal RNA (r-RNA)

(iii) Transfer RNA (t-RNA)

IV.CASE BASED QUESTION. (4 MARKS EACH)

1.When a protein in its native form, is subjected to physical changes like change in temperature or chemical changes like change in pH, the hydrogen bonds are disturbed. Due to this, globules unfold and helix gets uncoiled and protein loses its biological activity. This is called denaturation of protein. The denaturation causes change in secondary and tertiary structures but primary structures remain intact. Examples of denaturation of protein are coagulation of egg white on boiling, curdling of milk, formation of cheese when an acid is added to milk.

(a)Define native protein?

(b) All α-amino acids are optically active except one α-amino acid. Give named of it.

(c)Write the difference between globular protein and fibrous protein with one example.

OR

(c)State the difference between essential and non-essential amino acids with one example.

2.The activity of an enzyme can be affected by a change in the conditions which can alter the tertiary structure of the protein. These include temperature, pH, and change in substrate concentration or binding of specific chemicals that regulate its activity. Enzymes generally function in a narrow range of temperature and PH. Each enzyme shows its highest activity at a particular temperature and pH called the optimum temperature and optimum PH. Activity declines both below and above the optimum value. Low temperature preserves the enzyme in a temporarily inactive state whereas high temperature destroys enzymatic activity because proteins are denatured by heat. Concentration of Substrate With the increase in substrate concentration, the velocity of the enzymatic reaction rises at first. The reaction ultimately reaches a maximum velocity (Vmax) which is not exceeded by any further rise in concentration of the substrate. This is because the enzyme molecules are fewer than the substrate molecules and after saturation of these molecules, there are no free enzyme molecules to bind with the additional substrate molecules.

(a) Name a chemical compound or molecule which is responsible for decrease or stop the enzyme activity by binding to an enzyme?

(b) Give reason – why most of the enzymes get destroyed above optimum temperature?

(c) Explain the relation between substrate concentration and enzymatic activity?

OR

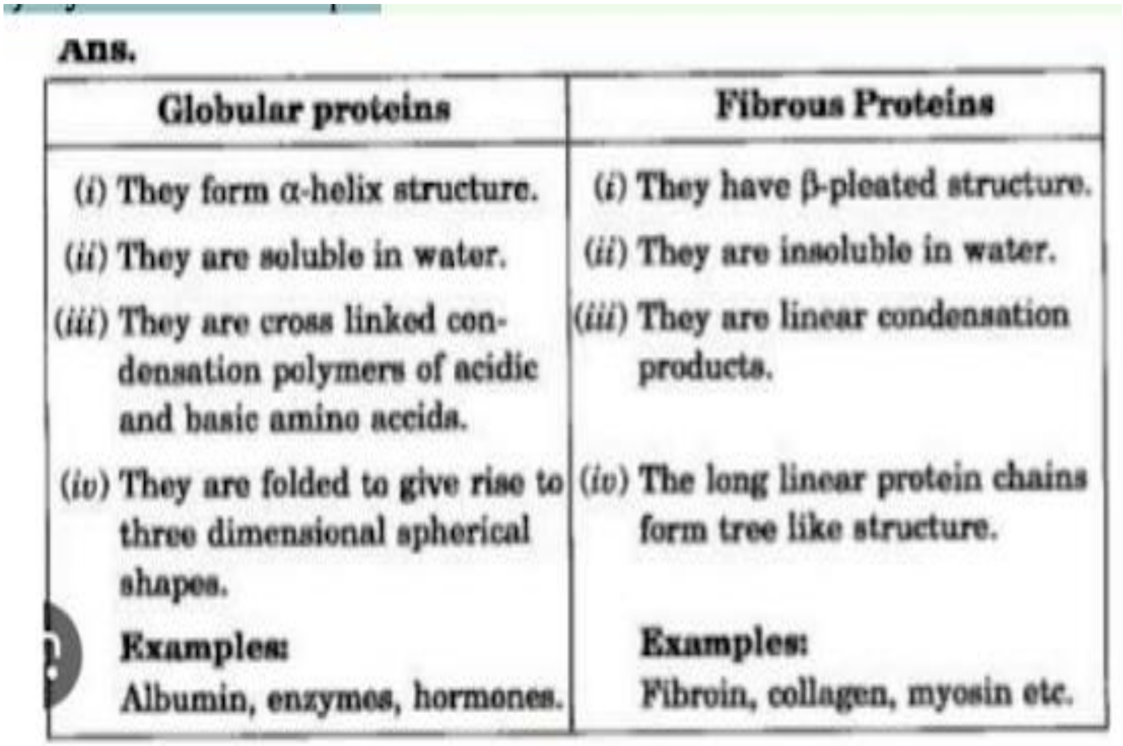
(c) What are co-enzyme and co-factor.

ANS.

1. (a)Protein found in a biological system with a unique three-dimensional structure and biological activity is called a native protein.

b) glycine

(c)any one with example



Ans.

Globular proteins	Fibrous Proteins
(*i*) They form α-helix structure.	(*i*) They have β-pleated structure.
(*ii*) They are soluble in water.	(*ii*) They are insoluble in water.
(*iii*) They are cross linked condensation polymers of acidic and basic amino accids.	(*iii*) They are linear condensation products.
(*iv*) They are folded to give rise to three dimensional spherical shapes.	(*iv*) The long linear protein chains form tree like structure.
Examples: Albumin, enzymes, hormones.	**Examples:** Fibroin, collagen, myosin etc.

(c) Nonessential amino acids can be made by the body, while essential amino acids cannot be made by the body so you must get them from your diet. You must have all of the amino acids so your body can build the wide variety of proteins it needs. Protein is needed for the repair, growth and maintenance of the cells.any one exemple of essential and nonessential aminoacid.

2.

a) Inhibitor

(b) Enzymes are composed of one or several polypeptide chains. Almost all enzymes are protein. High temperature condition destroys enzymatic activity because proteins are denatured by heat.

(c) Concentration of Substrate With the increase in substrate concentration, the velocity of the enzymatic reaction rises at first. The reaction ultimately reaches a maximum velocity (Vmax) which is not exceeded by any further rise in concentration of the substrate. This is because the enzyme molecules are fewer than the substrate molecules and after saturation of these molecules, there are no free enzyme molecules to bind with the additional substrate molecules.

OR

Cofactors are non-protein chemical compounds which are termed helper molecules. .Cofactors are of 2 types, one with inorganic and other organic, where the organic ones are called as coenzymes and they are of 2 types, based on bond, if bond is permanent, it is prosthetic group, if the bond is temporary, it is substrate. Coenzymes are small organic molecules that bind to the enzymes, assisting the function of the enzyme.

TOPIC: PROTEINS

SECTION A - MULTIPLE CHOICE QUESTIONS (1 MARK)

1. Proteins are found to have two different types of secondary structures namely α-helix and β-pleated sheet structure, α-helix structure of protein is stabilized by
(a) peptide bonds (b) van der Waals forces (c) hydrogen bonds (d) dipole-dipole interactions

2. Each polypeptide in a protein has amino acids linked with each other in a specific sequence. This sequence of amino acids is said to be
(a) Primary structure of proteins (b) secondary structure of proteins
(c) tertiary structure of proteins (d) quaternary structure of proteins

3. Which of the following is not a function of proteins in living organisms?
A) Storage of genetic information B) Enzymatic catalysis
C) Structural support D) Transport of molecules

4. Protein is a polymer made of
(a) carbohydrates (b) amino acids (c) nucleic acids (d) carboxylic acids

5. The specific sequence of amino acids in a polypeptide chain is known as
(a) Primary structure of proteins (b) Secondary structure of proteins
(c)Tertiary structure of proteins (d) Quaternary structure of proteins

6. Which of the following is an example of globular protein
(a) Insulin (b) Keratin (c) Myosin (d) Pectin

7. The building blocks of proteins are:
a) glucose b) glycerol c) fats d) amino acids

8. In the following questions a statement of Assertion(A) is followed by a statement of Reason(R).Select the most appropriate answer from the options given below:
(a) Both A and R are true and R is the correct explanation ofA

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

(c) Ais true but R is false.

(d) A is false but R is true.

Assertion:- Insulin is a globular protein.
Reason:-Globular Proteins are water insoluble because of hydrophilic part

9. The primary structure of a protein refers to:
A) The sequence of amino acids
B) The three-dimensional arrangement of the polypeptide chain
C) The arrangement of multiple polypeptide chains
D) The formation of disulfide bonds

10. Which of the following amino acids is polar and uncharged?
A) Alanine B) Glycine C) Serine D) Valine

11. Which level of protein structure is primarily determined by hydrogen bonds between backbone atoms?
A) Primary structure B) Secondary structure C) Tertiary structure D) Quaternary structure

12. An alpha helix and a beta sheet are examples of:
A) Primary structure B) Secondary structure C) Tertiary structure D) Quaternary structure

13. Which of the following is an example of a fibrous protein?
A) Insulin B) Myoglobin C) Collagen D) Hemoglobin

14. Which of the following is not classified as proteins:
a) Enzymes b) Antibodies c) Hormones d) Antigen

15. Which of the following is a non-polar amino acids:
a) Alanine b) Arginine c) lysine d) Serine

ANSWERS:
1. a
2. a
3. a
4. b
5. a
6. a
7. d
8. c
9. a
10. c
11. b
12. b

13. c
14. d
15. a

SECTION B- SHORT ANSWER (2 MARK)

1. Describe what you understand by primary structure and secondary structure of proteins?

2. Distinguish between insulin and keratin.

3. Give one example of
(a) A fibrous protein (b) A globular protein

4. Classify the following as globular or fibrous proteins.
(i) Keratin (ii) Myosin (iii) Insulin (iv) Hemoglobin

5. Name four types of intermolecular forces which stabilize structure of proteins.

6. What are essential and non-essential amino acids? Give one example of each type.

7. Mention the type of linkage responsible for the formation of the following :
(i) Primary structure of proteins (ii) Cross-linkage of polypeptide chains
(iii) a-helix formation (iv) b-sheet structure

8. Answer the following :
(i) What type of linkage is responsible for the primary structure of proteins?
(ii) Name the location where protein synthesis occurs in our body.

9. Where does the water present in the egg go after boiling the egg?

10. Explain what is meant by a peptide linkage.

ANSWERS:

1. Primary structure of proteins : Proteins may have one or more polypeptide chains. Each polypeptide in a protein has amino acids linked with each other in a specific sequence which is known as primary structure of protein.

Secondary structure of proteins : The conformation which the polypeptide chains assume as a result of hydrogen bonding is called the secondary structure of the protein.

2. Insulin is a lobular protein and keratin is fibrous protein

3. Fibrous protein–Keratins and Myosin
Globular protein–Insulin and Hemoglobin.

4. Fibrous proteins are structural proteins that are made up of long and narrow strands (they are something) example: keratin and myosin.
Globular proteins are more compact and rounded in form, and they have a functional purpose (they do something) example: insulin and haemoglobin.

5. Hydrogen bonds, disulphide connections, van der Waals, and electrostatic forces of attraction are the primary factors that stabilize the secondary and tertiary structures of proteins.

6. Essential amino acids : Amino acids which the body cannot synthesize are called essential amino acids. Example : Valine, leucine etc. Therefore they must be supplied in diet.

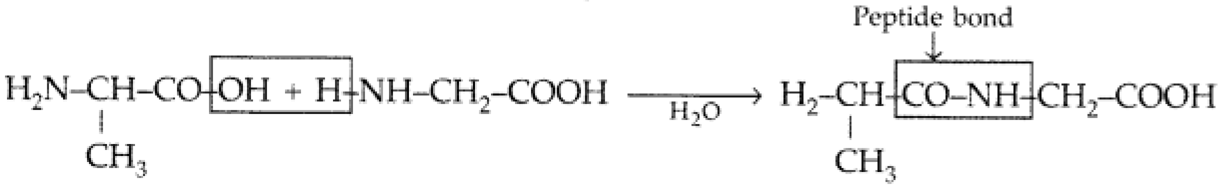
Non-essential amino acids : Amino acids which the body can synthesize are called non-essential amino acids. Therefore, they may or may not be present in diet.
Example : Glycine, alanine etc.

7. Peptide linkage, hydrogen bonding

8. peptide linkage & proteins are formed in ribosomes of cell.

9. In an egg, denaturation of protein is the coagulation of albumin present in the white of an egg. When an egg is boiled in water, the globular proteins present in it change to a rubber like insoluble mass which absorbs all the water present in the egg by making hydrogen bond with it.

10. Peptide linkage: A peptide linkage is an amide linkage formed between – COOH group of one α-amino acid and NH_2 group of the other a-amino acid by loss of a molecule of water.



$$H_2N-\underset{\underset{CH_3}{|}}{CH}-CO\boxed{OH + H}NH-CH_2-COOH \xrightarrow[H_2O]{} H_2-\underset{\underset{CH_3}{|}}{CH}\overset{\overset{\text{Peptide bond}}{\downarrow}}{\boxed{CO-NH}}CH_2-COOH$$

SECTION C- SHORT ANSWER (3 MARK)

1. Define the following terms as related to proteins : (i) Peptide linkage (ii) Primary structure (iii) Denaturation

2. Write difference between tertiary and quartenary structure with diagram.

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

4. Amino acids may be acidic, alkaline or neutral, How does this happen?

5. Describe zwitter ion in detail.

6. Compare and contrast denaturation and coagulation of proteins.

7. State difference between globular and fibrous proteins.

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

9. Protein found in a biological system with a unique three-dimensional structure and biological activity is called a native protein. Protein denaturation occurs when a protein in its native form is subjected to a physical change like a change in temperature or a chemical change like a change in pH. Explain the cause.

10. Amino acid show amphoteric behavior. Give reason.

ANSWERS:

1. Peptide linkage: A peptide linkage is an amide linkage formed between – COOH group of one α-amino acid and NH_2 group of the other a-amino acid by loss of a molecule of water.

Primary Structure: The primary structure of a protein refers to the linear sequence of amino acids linked by peptide bonds.

Denaturation: Denaturation is the disruption of a protein's secondary, tertiary, or quaternary structure, resulting in the loss of its biological activity. It can be caused by heat, pH extremes, organic solvents, or mechanical agitation. Example: Cooking of egg whites causes denaturation of the albumin protein.

2. Tertiary Structure: Tertiary structure refers to the overall three-dimensional shape of a protein. It is stabilized by interactions between amino acid side chains (hydrophobic interactions, hydrogen bonds, disulfide bonds, etc.).

Quaternary Structure:- Quaternary structure refers to the arrangement of multiple protein subunits (polypeptide chains) in a multi-subunit complex. It involves interactions between different polypeptide chains (subunits).

3. When the egg white is boiled, the soluble globular protein albumin is converted into insoluble fibrous protein. During this denaturation, (i) biological activity is lost and (ii) secondary and tertiary structures of

albumin protein are destroyed while the primary structure (representing the sequence of amino acids) remains intact.

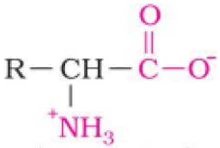
4. Amino acids can be broadly classified into three classes i.e. acidic, alkaline and neutral amino acids depending on the number of —NH_2 group and — COOH group.

Acidic amino acids : Those a-amino acids such as aspartic acid, asparagine and glutamic acid which contain two -COOH groups and one -NH_2 group are called acidic amino acids.

Alkaline or Basic amino acids : Those a-amino acids such as lysine, arginine and histidine which contain two -NH_2 groups and one -COOH group, are called basic amino acids.

Neutral amino acids : Those a-amino acids such as glycine, alanine, valine etc. which contain one -NH_2 and one – COOH group, are called neutral amino acids.

5. Amino acids contain amino and carboxylic acid group, 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.This is neutral but contains both positive and negative charges



$R-\underset{\overset{|}{^{+}NH_3}}{CH}-\overset{\overset{O}{||}}{C}-O^-$

(Zwitter ion)

6. Denaturation: Denaturation is the disruption of a protein's secondary, tertiary, or quaternary structure, resulting in the loss of its biological activity. It can be caused by heat, pH extremes, organic solvents, or mechanical agitation. Example: Cooking of egg whites causes denaturation of the albumin protein.

Coagulation: Coagulation refers specifically to the irreversible aggregation of denatured protein molecules, leading to the formation of a solid or gel-like mass. Example: Formation of curd from milk involves coagulation of casein proteins under acidic conditions.

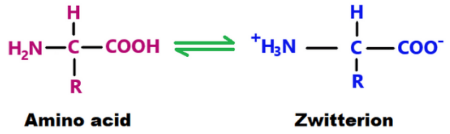
7.

S.NO.	**Globular Protein**	**Fibrous Protein**
1	they form α-helix structure	they have β-pleated structure
2	They are water soluble.	they are water insoluble
3	They involve H bonding.	they have strong intermolecular forces of attraction

8. Amino acids behave like salts rather than simple amines or carboxylic acids due to the presence of both acidic (-COOH) and basic (-NH_2) groups. In solution, the -COOH group can lose a proton, and an amine group can accept a proton, giving rise to a dipolar ion called the Zwitter ion.

9. Due to physical and chemical changes, hydrogen bonds in proteins are disturbed. Due to this, globules unfold, and, the helix gets uncoiled, the protein loses its biological activity. This is known as the denaturation of proteins.

10. Due to presence of carboxylic acid and amino group in the same molecule or due to formation of zwitter ion or dipolar ion, amino acid show amphoteric behavior.



SECTION D- CASE BASED QUESTIONS (4 MARK)

1. Protein found in a biological system with a unique three-dimensional structure and biological activity is called a native protein. Protein denaturation occurs when a protein in its native form is subjected to a physical change like a change in temperature or a chemical change like a change in pH..α Helix is a secondary structure of proteins formed by twisting the polypeptide chain into right-handed screw-like structures.
i) Explain the cause of denaturation.
ii) Which type of interactions is responsible for making the α -helix structure stable?
iii) Which structure of proteins remains intact during the denaturation process?
iv) What type of structure is α -helix and β-pleated structures of proteins?

2. The Amino acids, which are required in our body but can't be synthesized by our body are called essential amino acids. Amino acids can be classified as alpha, beta, gamma, delta, and so on, depending upon the relative position of the amino group concerning the carboxyl group.

i) What are alpha amino acids?
ii) Which type of amino acids forms the polypeptide chain in proteins?
iii) Give any two examples of alpha amino acids.
iv) What are non-essential amino acids?

ANSWERS:
1. i) Due to physical and chemical changes, hydrogen bonds in proteins are disturbed. Due to this, globules unfold, and, the helix gets uncoiled, the protein loses its biological activity. This is known as the denaturation of proteins.

ii) In α helix, a polypeptide chain is stabilised by forming hydrogen bonds between the −NH− group of amino acids in one turn with the >C−O groups of amino acids belonging to adjacent turn.
iii) Primary structure remains intact during the denaturation process.
iv) Secondary structures

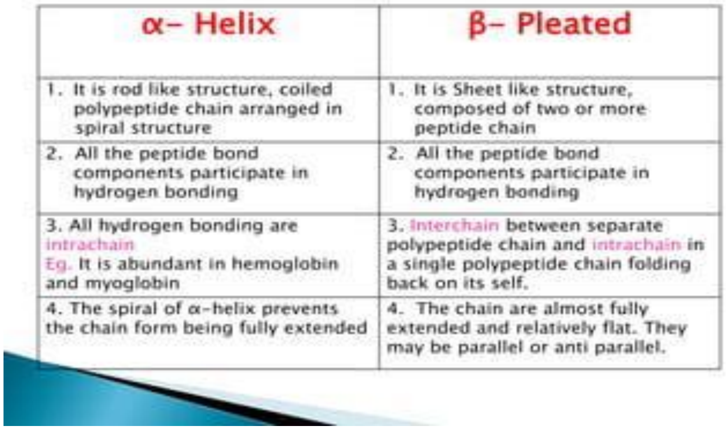
2. i) The α-amino acids are the amino acids whose one carbon contains both the amino group (NH_2) and carboxyl group (COOH). Such type of carbon is called α-carbon. Thus, the amino acid that contains an α-carbon is called an α-amino acid.
ii) α amino acid forms a polypeptide chain by eliminating water molecules.

SECTION E- LONG ANSWER (5 MARK)

1. Explain the terms primary and secondary structure of proteins. What is the difference between the alpha-helix and beta-pleated sheet structure of proteins?
2. Differentiate between fibrous proteins and globular proteins. What is meant by the denaturation of a protein?
3. Explain tertiary structure of Protein.
4. Explain the primary, secondary, tertiary, and quaternary structures of proteins.

ANSWERS:

1. Protein primary structure is the linear sequence of amino acids in a peptide or protein. In contrast, Secondary structure refers to regular, recurring arrangements in the space of adjacent amino acid residues in a polypeptide chain. It is maintained by hydrogen bonds between amide hydrogens and carbonyl oxygens of the peptide backbone. The major secondary structures are α-helices and β-structures.



α– Helix	β– Pleated
1. It is rod like structure, coiled polypeptide chain arranged in spiral structure	1. It is Sheet like structure, composed of two or more peptide chain
2. All the peptide bond components participate in hydrogen bonding	2. All the peptide bond components participate in hydrogen bonding
3. All hydrogen bonding are intrachain Eg. It is abundant in hemoglobin and myoglobin	3. Interchain between separate polypeptide chain and intrachain in a single polypeptide chain folding back on its self.
4. The spiral of α–helix prevents the chain form being fully extended	4. The chain are almost fully extended and relatively flat. They may be parallel or anti parallel.

2.

Globular Proteins	Fibrous Proteins
1. Globular proteins have almost spheroidal shape due to folding of the polypeptide chain.	1. Polypeptide chains of fibrous proteins consist of thread like molecules which tend to lie side by side to form fibres.
2. Globular proteins are soluble in water.	2. Fibrous proteins are insoluble in water.
3. Globular proteins are sensitive to small changes of temperature and pH. Therefore they undergo denaturation on heating or on treatment with acids/bases	3. Fibrous proteins are stable to moderate changes of temperature and pH.
4. They possess biological activity that's why they act as enzymes.	4. They do not have any biological activity but serve as chief structural material of animal tissues.
Example: Maltase, invertase etc., hormones (insulin) antibodies, transport agents (haemoglobin), etc.	Example: Keratin in skin, hair, nails and wool, collagen in tendons, fibroin in silk etc.

Denaturation of protein : Due to coagulation of globular protein under the influence of change in temperature, change in pH etc., the native shape of the protein is destroyed and biological activity is lost and the formed protein is called denaturated proteins and the phenomenon is denaturation.

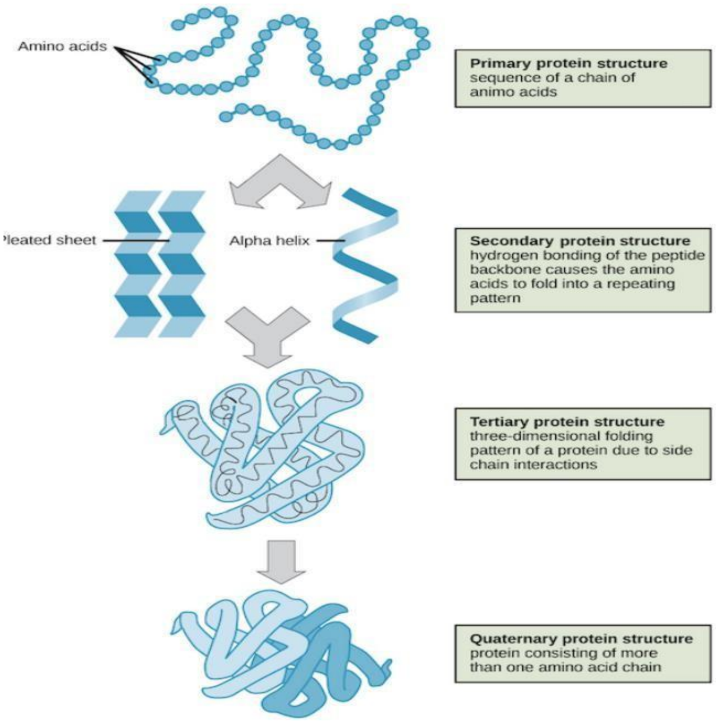
3. Tertiary structure of proteins: The tertiary structure of proteins represents overall folding of the polypeptide chains i.e., further folding of the secondary structure. It gives rise to two major molecular shapes viz. fibrous and globular. The main forces which stabilize the 2° and 3° structures of proteins are hydrogen bonds, disulphide linkages, van der Waals and electrostatic force of attraction. Explanation with diagram.

4. Primary Structure: The primary structure of a protein refers to the linear sequence of amino acids linked by peptide bonds.

Secondary Structure: Secondary structure refers to the local folded structures that form within a polypeptide chain. The two main types are alpha helices and beta sheets, stabilized by hydrogen bonds between backbone atoms.

Tertiary Structure: Tertiary structure refers to the overall three-dimensional shape of a protein. It is stabilized by interactions between amino acid side chains (hydrophobic interactions, hydrogen bonds, disulfide bonds, etc.).

Quaternary Structure:- Quaternary structure refers to the arrangement of multiple protein subunits (polypeptide chains) in a multi-subunit complex. It involves interactions between different polypeptide chains (subunits).


Amino acids
Primary protein structure
sequence of a chain of animo acids
Pleated sheet
Alpha helix
Secondary protein structure
hydrogen bonding of the peptide backbone causes the amino acids to fold into a repeating pattern
Tertiary protein structure
three-dimensional folding pattern of a protein due to side chain interactions
Quaternary protein structure
protein consisting of more than one amino acid chain

SAMPLE PAPER SESSION: 2024-25

SUBJECT:
CHEMISTRY
THEORY CLASS-XII

MM: 70 **Time:3 Hours**

General Instructions:

Read the following instructions carefully.

a) There are **33** questions in this question paper with internal choice.
b) SECTION A consists of 16 multiple-choice questions carrying 1 mark each.
c) SECTION B consists of 5 very short answer questions carrying 2 marks each.
d) SECTION C consists of 7 short answer questions carrying 3 marks each.
e) SECTION D consists of 2 case-based questions carrying 4 marks each.
f) SECTION E consists of 3 long answer questions carrying 5 marks each.
g) All questions are compulsory.
h) Use of log tables and calculator is not allowed.

SECTION A

The following questions are multiple – choice questions with one correct answer. Each question carries 1 mark. There is no internal choice in this section.

Q1. Which of the following statement is not true about glucose?

(a) It is an aldohexose (b) On heating with HI it forms n-hexane

(c) It is present in furanose form (d)It does not give 2,4-D N P test

Q2. The position of Br in the compound CH3=CHC(Br)(CH3)2 can be classified as

(a) Allyl (b) Aryl (c) Vinyl
(d) Secondary

Q3. Methylamine react with HNO2 to form

(a) CH3-O-N=O (b) CH3OH (c) (C2H5)2NH (d) C6H5NHC6H5

Q4. Addition of water to alkynes occur in acidic medium in the presence of Hg^{2+} ions as catalyst. Which of the following product will be formed on addition of water to but-1-yne under these conditions?

(a) CH3-CH2CH2CHO (b) CH3CH2COCH3

(c) CH3CH2COOH + CO2 (d) CH3COOH + HCO

Q5. The acid formed when propyl magnesium bromide is treated with CO2 is

(a) C3H7COOH (b) C2H5COOH

(c) Both (a) & (b) (d)

None of these

Q6. Which of the following set of ions exhibit specific colours:

(a) Sc^{3+}, Ti^{4+}, Mn^{3+} (b) Sc^{3+}, Zn^{2+}, Ni^{2+}

(c) V^{3+}, $V2^{+}$, Fe^{3+} (d) Ti^{3+}, Ti^{4+}, Ni^{2+}

Q7. Actinoids exhibit greater number of oxidation states than lanthanoids. The main reason being

(a) More energy difference between 5f & 6d than between 4f & 5f orbitals.

(b) 4f – orbitals are more diffused than the 5f- orbitals.

(c) Lesser energy difference between 5f and 6d than between 4f and 5d orbitals.

(d) More reactive nature of actinoids than the Lanthanoids.

Q8. The rate of a gaseous reaction is given by the expression, rate= k[A] [B]. If volume of the reaction vessel is suddenly reduced to ¼ of the initial volume, the reaction rate related to original rate will be

(a) 1/16 (b) 1/8 (c) 8 (d) 16

Q9. Match the following and choose the correct option.

Column-1	Column-2
(i) Half life of Ist order reaction	A. Order = 1
(ii) $k.[A]^{1/2}\,[B]^{1/2}$	B. Molecularity = 1
(iii) Zero order reaction	C. 0.693/k
(iv) NH4NO2→ N2 + 2H2O	D. k = [R]0 –[R]/t

(a) (i) – A, (ii) – D, (iii) – C, (iv) – B (b) (i) – B, (ii) – A, (iii) – C, (iv) – D

(c) (i) – A, (ii) – C, (iii) – D, (iv) – B (d) (i) –C, (ii) – A, (iii) – D, (iv) – B

Q10. Monochlorination of toluene in sunlight followed by hydrolysis with aq. NaOH gives.

(a) o-cresol (b) m-cresol

(c) 2,4 –Dihydroxy toluene (d) Benzyl alcohol

Q11. Phenol is less acidic than

(a) ethanol (b) o-nitrophenol

(c) o-methyl phenol (d) o-methoxy phenol

Q12. The correct IUPAC name for CH2=CHCH2NHCH3 is

(a) Allyl methylamine (b) 2- amino-pent-4-ene

(c) 4-amino pent-1-ene (d) N-methyl prop-2-en-1amine

Q13. Given below are two statements labelled as Assertion (A) and Reason (R)

Assertion (A): The two strands of DNA are complementary to each other.

Reason (R): The hydrogen bonds are formed between specific base pairs.

(a) Both A and R are true and R is the correct explanation of A.
(b) Both A and R are true and R is not the correct explanation of A.
(c) A is true but R is false.
(d) A is false but R is true.

Q14. Given below are two statements labelled as Assertion (A) and Reason (R)

Assertion (A): Reactivity of ketone is more than aldehyde towards nucleophilic addition.

Reason (R): Carbonyl carbon of ketone is less electrophilic as compared to aldehydes.

(a) Both A and R are true and R is the correct explanation of A.
(b) Both A and R are true and R is not the correct explanation of A.
(c) A is true but R is false.
(d) A is false but R is true.

Q15. Given below are two statements labelled as Assertion (A) and Reason (R)

Assertion (A): In Lucas test, 3 alcohols react immediately.

Reason (R): A mixture of anhyd ZnCl2 and conc. HCl is Lucas reagent.

(a) Both A and R are true and R is the correct explanation of A.
(b) Both A and R are true and R is not the correct explanation of A.
(c) A is true but R is false.
(d) A is false but R is true.

Q16. Given below are two statements labelled as Assertion (A) and Reason (R) Assertion (A) : Electrolysis of NaCl solution gives chlorine at anode instead of O2.

Reason (R) : Formation of oxygen at anode requires over voltage

(a) Both A and R are true and R is the correct explanation of A.
(b) Both A and R are true and R is not the correct explanation of A.
(c) A is true but R is false.
(d) A is false but R is true.

SECTION B

Q17. The rate constant for first order decomposition of N2O5 is given by the following equation:

Log k = 23.6 – 2 x 10^4 k/T

Calculate Ea for this reaction [R =8.314$JK^{-1}mol^{-}$

OR

For the reaction

2N2O5 (g) → 4NO2 (g) + O2 (g)

Calculate the rate of reaction if rate of disappearance of N2O5 (g) is 1.4 x 10^{-3} ms^{-1}

Q18 (a) What is the difference between native protein and denatured protein.

(b) Write the name of vitamin responsible for coagulation of blood.

Q19. (a) Why is osmotic pressure of 1M NaCl higher than 1M glucose solution?

(b) Blood cells are isotonic with 0.9 % sodium chloride solution. What happens if we place blood cells in a solution containing: i) 1.2 % NaCl solution ii) 0.4% NaCl solution.

Q20. Among all the isomers of C4H9Br, identify

(a) the one isomer which is optically active

(b) the one isomer which is highly reactive towards SN^2 reaction.

Q21. Convert the following

(a) Benzoic acid to Benzaldehyde

(b) Ethanol to 3- hydroxyl butanal

SECTION C

Q22. An alkene ‘A’ (C5H10) on ozonolysis gives a mixture of two compounds ‘B’ and ‘C’. Compound ‘B’ gives positive Fehling’s test and also reacts with iodine and NaOH solution. Compound ‘C’ does not give Fehling’s test but forms iodoform. Identify ‘A’, ‘B’ and ‘C’ giving suitable explanation and write reactions of ozonolysis and iodoform formation.

Q23. In a coordination entity, the electronic configuration of central metal ion is $t2g^3eg^1$

(a) Is the coordination compound high spin or low spin. Identify the nature of ligand.

(b) Draw crystal field splitting diagram for the above complex.

Q24. Conductivity of 2.5 x 10^{-4} M Methanoic acid is 5.25 x 10^{-5} Scm^{-1}. Calculate its molar conductivity and degree of dissociation. (Given λ°(H+) = 349.5 $Scm^2mol^{-1}$and λ°(HCOO-) = 50.5 Scm^2mol^{-1}.

Q25. (a) A non-reducing disaccharide ‘A’ on hydrolysis with dilute acids gives an equimolar mixture of D-(+) glucose and D-(-) fructose.

$$A + H_2O \overset{HCl}{\rightarrow\rightarrow} C_6H_{12}O_6 + C_6H_{12}O_6$$

Identify A. What is the mixture of D- (+) glucose and D- (-) fructose called?

(b) What is the difference between

(i) α – form of glucose and β-form of glucose.

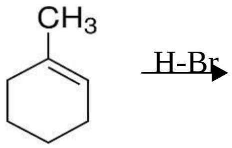
(ii) Nucleoside and Nucleotide

Q26. (a) Give reason for the following

(i) aryl halides are less reactive towards nucleophilic substitution reaction.

(ii) Thionyl chloride method is preferred for preparing alkyl chloride from alcohol.

(b) Write the major product



Q27. (a) Give equation for the following and write name of the reaction.

(i) Sodium t-butoxide is treated with CH_3Cl.

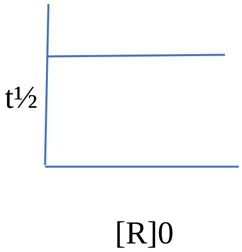
(ii) Treating phenol with chloroform in the presence of aq. NaOH

(b) How will you distinguish between Phenol and ethanol?

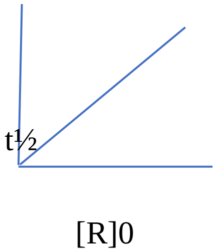
Q28. (a) A first order reaction is 75% completed in 40 min. Calculate t½.

(c) Predict order of reaction

(i)



(ii)



Given log 2 = 0.3010 log 4 = 0.6021

SECTION D

Read the following paragraph and answer the question that follows:

Q29. In coordination compounds, metals show two types of linkages, primary and secondary. Primary valencies are ionisable and are satisfied by negatively charged ions. Secondary valencies are non-ionisable and are satisfied by neutral or negative ions having lone pair of electrons. Primary valencies are non-directional while secondary valencies decide the shape of the complexes.

(a) When a coordination compound CrCl3.6H2O is mixed with AgNO3, 2 moles of AgCl are precipitated. Write structure of the compound.

(b) What is secondary valency of [Co (en)3 $]^{3+}$

(c)- (i) Write formula of Iron (III) hexa cyanido ferrate (II)

(ii) Write the IUPAC name [Co (H2O) (CN) (en)2$]^{2+}$

OR

Write hybridization and magnetic behavior of [Ni (CN)4$]^{2-}$

Q30. Read the following paragraph and answer the question that follows:

Amines are usually formed from nitro compounds, halides, amides, imides, etc. They exhibit hydrogen bonding which influences their physical properties. In alkyl amines a combination of electron releasing, steric and hydrogen bonding factors influence the stability of the substituted ammonium cations in protic polar solvents and thus affect the basic nature of amines. In aromatic amines, electron releasing and withdrawing groups, respectively increase and decrease their basic character. Influence of the number of hydrogen atoms at nitrogen atom on the type of reactions and nature of products is responsible for identification and distinction between primary, secondary and tertiary amines. Presence of amino group in aromatic ring enhances reactivity of the aromatic amines. Aryl diazonium salts provide advantageous methods for producing aryl halides, cyanides, phenols and arenes by reductive removal of the diazo group.

Answer the following questions:

(a) Arrange the following in the increasing order of their pkb, values in aqueous solution: C2H5NH2, (C2H5)2NH, (C2H5)3N

(b) Aniline on nitration gives a substantial amount of m-nitroaniline, though amino group is o/p directing. why?

(c) An aromatic compound ‘A’ of molecular ‘Formula C7H6O2 on treatment with aqueous ammonia and heating forms compound ‘B’. Compound B’ on heating with Br2 and aqueous KOH gives a compound ‘C’ of molecular formula C6H7N.

Write the structures of A, B and C.

SECTION E

Q31) (a) Represent the cell in which following reaction takes place:

$2Al (s) + 3Ni^{2+} (0.1M) \qquad > 2Al^{3+}(0.01M) + 3Ni(s)$

Calculate emf of cell if E^0 cell = 1.41 V

(a) How does molar conductivity increase with increase in concentration for strong and weak electrolyte? How can you obtain limiting molar conductivity for weak electrolyte.

(b) Name the cell which:

(i) was used in Apollo Space programme. (ii) is suitable for hearing aids and watches.

Q32) (a) In the ions: Mn^{3+}, V^{3+},Cr^{3+}, Ti^{4+}

(i) Which ion is most stable in aqueous solution?

(ii) Which ion is colourless?

(iii) Which ion is strongest oxidizing agent?

(iv) Which ion has highest magnetic moment?

(b) Account for the following:

(i) Orange colour of dichromate ion changes to yellow in alkaline medium.

(ii) E^0 (Mn^{2+}/Mn) value highly negative as compared to other elements.

(iii) Transition metals show variable oxidation state.

OR

(a) How does Potassium dichromate reacts with:

(i) Iron(II) ions (ii) Oxalic acid

(b) Name oxo metal anion of the transition metal in which metal exhibits the oxidation state equal to group number.

(c) Account for the following:

(i) Scandium is regarded as transition element but zinc is not.

(ii) Zr and Hf have almost similar radii.

Q33) (a)Define the following terms: (i) Azeotropes (ii) Molal elevation Constant

(b) A solution containing 15 g Urea (Molar mass = 60 g/mol) per litre of solution in water is isotonic with a solution of glucose in water. Calculate the mass of glucose present in one litre of solution.

OR

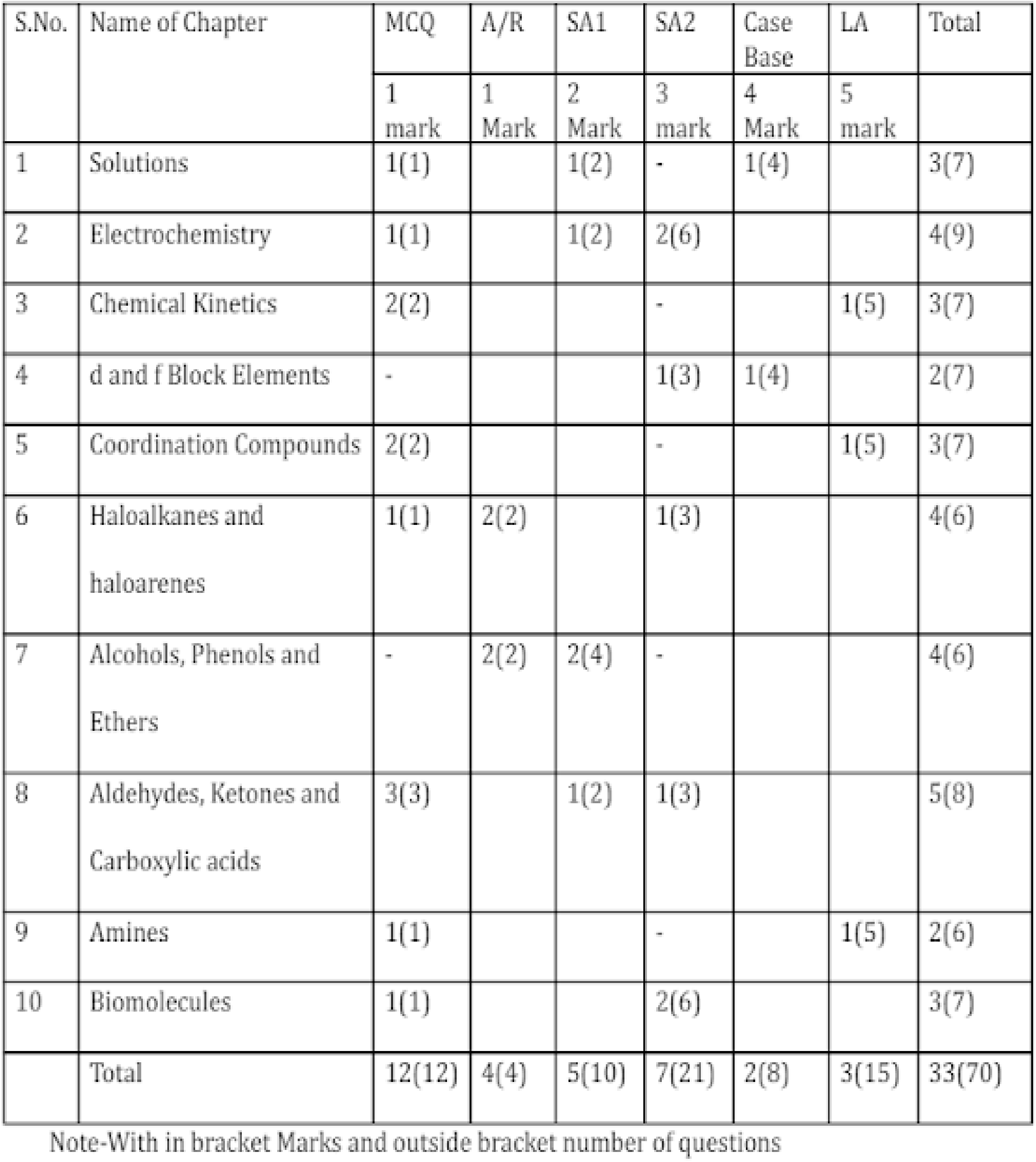
(a) On mixing liquid A and liquid B volume of resulting solution decreases. What type of deviation from Raoult’s law is shown by the mixture.

(b) Which colligative property is considered best for determining molar mass of proteins.

(c) A solution of glucose (M = 180 g/mol) in water has a boiling point of 100.20 ^{0}C. Calculate the freezing point of same solution. Molar constant for water **Kf** and **Kb** are **1.86 K kg mol^{-1}** and **0.512K kg mol^{-1}** respectively

SAMPLE PAPER

BLUE PRINT 0F SAMPLE PAPER 3 (CHEMISTRY)



S.No.	Name of Chapter	MCQ	A/R	SA1	SA2	Case Base	LA	Total
		1 mark	1 Mark	2 Mark	3 mark	4 Mark	5 mark	
1	Solutions	1(1)		1(2)	-	1(4)		3(7)
2	Electrochemistry	1(1)		1(2)	2(6)			4(9)
3	Chemical Kinetics	2(2)			-		1(5)	3(7)
4	d and f Block Elements	-			1(3)	1(4)		2(7)
5	Coordination Compounds	2(2)			-		1(5)	3(7)
6	Haloalkanes and haloarenes	1(1)	2(2)		1(3)			4(6)
7	Alcohols, Phenols and Ethers	-	2(2)	2(4)	-			4(6)
8	Aldehydes, Ketones and Carboxylic acids	3(3)		1(2)	1(3)			5(8)
9	Amines	1(1)			-		1(5)	2(6)
10	Biomolecules	1(1)			2(6)			3(7)
	Total	12(12)	4(4)	5(10)	7(21)	2(8)	3(15)	33(70)

Note-With in bracket Marks and outside bracket number of questions

SAMPLE PAPER (2024 -25)

CHEMISTRY THEORY (043)

Max. Marks: 70 **Time**: 3 hours

General Instructions:

Read the following instructions carefully.

(a) There are 33 questions in this question paper with internal choice.

(b) SECTION A consists of 16 multiple -choice questions carrying 1 mark each.

(c) SECTION B consists of 5 short answer questions carrying 2 marks each.

(d) SECTION C consists of 7 short answer questions carrying 3 marks each.

(e) SECTION D consists of 2 case - based questions carrying 4 marks each.

(f) SECTION E consists of 3 long answer questions carrying 5 marks each.

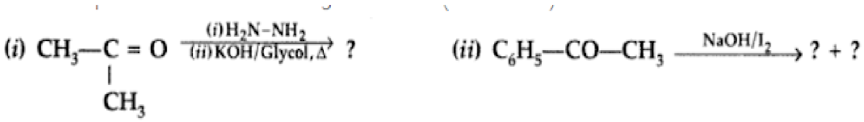
(g) All questions are compulsory.

(h) Use of log tables and calculators is not allowed.

SECTION – A

1	Which of the following aqueous solutions should have the highest boiling point? (a) 1.0 M Glucose (b) 1.0 M Na_2SO_4 (c) 1.0 M KCl (d) 1.0 M Urea	1
2	How much electricity required to get 1 mole 'Al' from $AlCl_3$ solution ? (a 3F (b) 2F (c)1 F (d)3 A (ampere))	1
3	A reaction's rate constant is $k=3.28 \times 10^{-4}$ s^{-1}. Determine the reaction's order. (a) First order (b)Second order (c) Third order(d) Fourth order	1
4	In the formation of $S0_2$ by contact process; $2SO_2 + O_2 \rightarrow 2SO_3$, the rate of reaction was measured as $-d[O_2]dt = 2.5 \times 10^{-4}$ mol $L^{-1}s^{-1}$. at The rate of formation of of $S0_3$ will be (a) -5.0×10^{-4} mol $L^{-1}s^{-1}$ (b) -1.25×10^{-4} mol $L^{-1}s^{-1}$ (c) 3.75×10^{-4} mol $L^{-1}s^{-1}$ (d) 5.00×10^{-4} mol $L^{-1}s^{-1}$	1
5	How many donor atoms can $EDTA^{4-}$ ligand bind through? a) 2 b) 4 c) 6 d) 8	1
6	Identify the correct naming for $K_2[PdCl_4]$. a)Potassium tetrachlorinepalladium(II)(b)Potassium tetrachlorinepalladate(II) c) Potassium tetrachloridopalladium(II)(d)Potassium tetrachloridopalladate(II)	1
7	A chemical compound carrying a molecular formula of C_3H_7Cl can have _______ possibilities of structural isomers. a)Four b)Two c)Nine d)Seven	1
8	Conversion of propyne to acetone requires three important reagents. Identify which of the following is not one of the three? a) Water b) Zinc dust c) H_2SO_4 d) $HgSO_4$	1

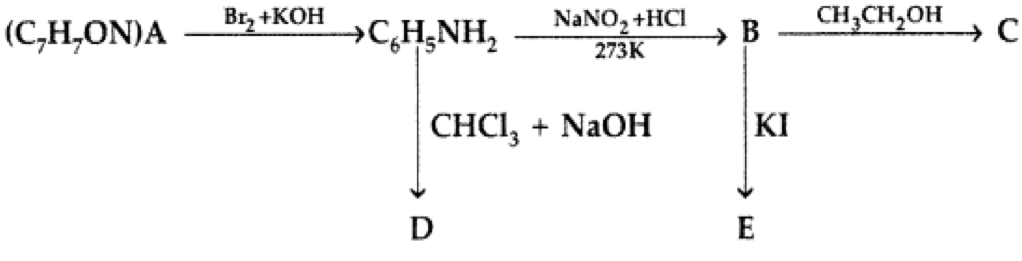
9	What is the correct order of reactivity towards nucleophilic addition? a) Benzaldehyde > Benzophenone > Acetophenone b) Benzophenone > Benzaldehyde > Acetophenone c) Acetophenone > Benzaldehyde > Benzophenone d) Benzaldehyde > Acetophenone > Benzophenone	1
10	In a set of the given reactions, acetic acid yielded a product C $CH_3COOH + PCl_5 \rightarrow A \xrightarrow[anh.\ AlCl_3]{C_6H_6} B \xrightarrow[ether]{C_2H_5MgBr}$ What would be product C? a) $CH_3{-}C{-}C_2H_5(OH)C_6H_5$ b) $CH_3CH(OH)C_2H_5$ c) $CH_3COC_6H_5$ d) $CH_3CH(OH)C_6H_5$	1
11	What is the order of quantities of all isomers of nitroaniline formed on the reaction of aniline with nitric acid and sulphuric acid at 288K? a) ortho > meta > para b) para > ortho > meta c) para > meta > ortho d) meta > para > ortho	1
12	Identify the complementary strand of the DNA primary structure ATGCCGATC. a) AUGCCGAUC b) TACGGCTAG c) UACGGCUAG d) GATCGGCAT	1
13	In the Following questions(13 to 16) a statement of Assertion(A) is followed by a statement of Reason(R). Select the most appropriate answer from the options given below: (a) Both A and R are true and R is the correct explanation of A (b) Both A and R are true but R is not the correct explanation of A. (c) A is true but R is false. (d) A is false but R is true. **Assertion:** Boiling point of alkyl halides increases with increase in molecular weight. **Reason**: Boiling point of alkyl halides is in the order RI > RBr > RCI >RF	1
14	**Assertion**: Electron withdrawing groups in aryl halides decrease the reactivity towards nucleophilic substitution. **Reason**: 2, 4-Dinitrochlorobenzene is more reactive than chlorobenzene.	1

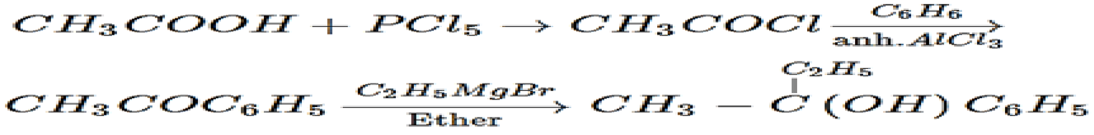
15	**Assertion** : Aromatic aldehydes and formaldehyde undergo Cannizzaro reaction. **Reason** : Aromatic aldehydes are almost as reactive as formaldehyde.	1
16	**Assertion:** Compounds containing- CHO group are easily oxidized to corresponding carboxylic acids. **Reason:** Carboxylic acids can be reduced to alcohols by treatment with $LiAlH_4$	1
	SECTION -B	
17	Predict the products of the following reactions :  (i) $CH_3-\underset{\underset{CH_3}{\vert}}{C}=O \xrightarrow[(ii)\,KOH/Glycol,\Delta]{(i)\,H_2N-NH_2} ?$ (ii) $C_6H_5-CO-CH_3 \xrightarrow{NaOH/I_2} ? + ?$	2
18	An aqueous solution of sodium chloride freezes below 273 K. Explain the lowering in freezing points of water with the help of a suitable diagram	2
19	The conductivity of 0.20 M solution of KCl at 298 K is 0.025 S cm^{-1}. Calculate its molar conductivity. OR The standard electrode potential for Daniell cell is 1.1 V. Calculate the standard Gibbs energy for the cell reaction. (F = 96,500 C mol^{-1})	2
20	Give a separate chemical test to distinguish between the following pairs of compounds: (i) Ethanol and Phenol (ii) 2-Pentanol and 3-Pentanol	2
21	How are the following conversions carried out? (i) Benzyl chloride to benzyl alcohol, (ii) Methyl magnesium bromide to 2-methylpropan-2-ol.	2
	SECTION -C	
22	Account for the following: (i) The C – Cl bond length in chlorobenzene is shorter than that in CH_3 – Cl. (ii) Chloroform is stored in closed dark brown bottles. (iii) p-dichlorobenzene have a higher m.p. than its o- and m-isomers.	3

23	Explain the following observations: (i) Copper atom has completely filled d orbitals ($3d^{10}$) in its ground state, yet it is regarded as a transition element. (ii) Cr^{2+} is a stronger reducing agent than Fe^{2+} in aqueous solutions. (iii) Silver atom has completely filled d-orbitals ($4d^{10}$) in its ground state, yet it is regarded as a transition element.	3
24	(a) Following reactions occur at cathode during the electrolysis of aqueous silver chloride solution: $Ag^+(aq) + e^{-1}$ ————> Ag(s) E° = +0.80 V $H^+(aq) + e^{-1}$ ————> $1/2H_2(g)$ E° = 0.00 V On the basis of their standard reduction electrode potential (E°) values, which reaction is feasible at the cathode and why? (b) Define limiting molar conductivity. Why conductivity of an electrolyte solution decreases with the decrease in concentration?	3
25	Calculate the emf of the following cell at 25 °C: Zn | Zn^{2+} (0.001 M) | | H^+(0.01 M) | H_2(g) (1 bar) | Pt(s)	3
26	(i) Which one of the following is a polysaccharide: Starch, Maltose, Fructose, Glucose? (ii) What one difference between a-helix and P-pleated sheet structure of protein. (iii) Write the name of the disease caused by the deficiency of Vitamin B_{12}.	3
27	(i) Deficiency of which vitamin causes scurvy? (ii) What type of linkage is responsible for the formation of proteins? (iii) Write the product formed when glucose is treated with HI.	3
28	) How would you bring about the following conversions : (i) Propanone to Propene (ii) Benzoic acid to Benzaldehyde (iii) Bromobenzene to 1-phenylethanol	3
	SECTION -D	

29	Read the passage given below and answer the following case-based questions: Boiling point or freezing point of liquid solution would be affected by the dissolved solids in the liquid phase. A soluble solid in solution has the effect of raising its boiling point and depressing its freezing point. The addition of non-volatile substances to a solvent decreases the vapour pressure and the added solute particles affect the formation of pure solvent crystals. According to many researches the decrease in freezing point directly correlated to the concentration of solutes dissolved in the solvent. This phenomenon is expressed as freezing point depression and it is useful for several applications such as freeze concentration of liquid food and to find the mass of an unknown solute in the solution. Freeze concentration is a high-quality liquid food concentration method where is removed by forming ice crystals. This is done by cooling the liquid food below the freezing point of the solution. The freezing point depression is referred as a colligative property and it is proportional to the concentration of the solution (m), along with vapour pressure relative lowering, boiling point elevation, and osmotic pressure. These are physical characteristics of solutions that depend only on the identity of the solvent and the concentration of the solute. The characters are not depending on the solute's identity. (a) What is the relation between vapour pressure of solid and liquid states of particular substance at freezing point? (b)Why freezing point of 0.1m solution of acetic acid in benzene is less than freezing point of 0.01m solution? (c) Out of the following 0.10 m aqueous solutions, which one will exhibit the largest Freezing point depression KCl, $C_6H_{12}O_6$, $Al_2(SO_4)_3$, K_2SO_4 OR (c) If K_f for water is 1.86 o C/m, explain why 1m NaCl in water does not have a freezing point equal to- (a) -1.86 ^oC (b) -3.72^oC	4

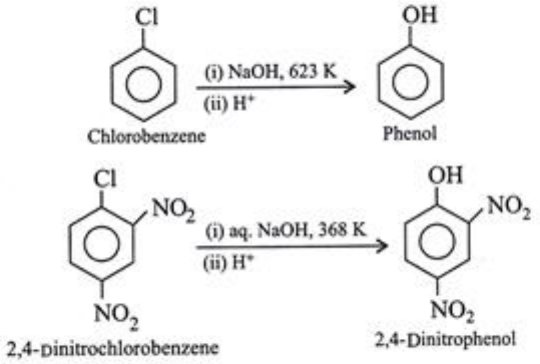
30	**Read the passage given below and answer the following questions:** The f-block elements are those in which the differentiating electron enters the (n - 2) f orbital. There are two series of f-block elements corresponding to filling of 4f and 5f-orbitals. The series of 4f- orbitals is called lanthanides. Lanthanides show different oxidation states depending upon stability of f^0, f^7 and f^{14} configurations, though the most common oxidation states is +3. There is a regular decrease in size of lanthanides ions with increase in atomic number which is known as lanthanide contraction. **The following questions are multiple choice questions. Choose the most appropriate answer:** (i) The atomic numbers of three lanthanide elements X, Y and Z are 65, 68 and 70 respectively, their Ln^{3+} electronic configuration is a) $4f^8$, $4f^{11}$, $4f^{13}$ b) $4f^{11}$, $4f^8$, $4f^{13}$ c) $4f^o$, $4f^2$, $4f^{11}$ d) $4f^3$, $4f^7$, $4f^9$ (ii) Lanthanide contraction is observed in a) Gd b)At c)Xe d)Te (iii) Name a member of the lanthanoid series which is well known to exhibit +4 oxidation state. a) Cerium (Z = 58) b) Europium (Z = 63) c)) Lanthanum (Z = 57) d) Gadolinium (Z = 64) (iv) Identify the incorrect statement among the following. a) Lanthanoid contraction is the accumulation of successive shrinkages b) The different radii of Zr and Hf due to consequence of the lanthanoid contraction c) Shielding power of 4f electrons is quite weak. d) There is a decrease in the radii of the atoms or ions as one proceeds from La to Lu.	4
	SECTION -E	

31	(a) A reaction is second order in A and first order in B. (i) Write the differential rate equation, (ii) How is the rate affected on increasing the concentration of A three times? (iii) How is the rate affected when the concentrations of both A and B are doubled? (b) A first order reaction takes 40 minutes for 30% decomposition. Calculate $t_{1/2}$ for this reaction. (Given log 1.428 = 0.1548)	3+ 2
32	(a) How is a double salt different from a complex? (b) Write IUPAC names of the following : (i) $K_3[Fe(C_2O_4)_3]$ (ii) $[Pt(NH_3)_6]Cl_4$. (c) Draw the structure of cis isomer of $[CO(NH_3)_4Cl_2]^+$ OR (i) Write the IUPAC name of the complex $[Cr(NH_3)_4Cl_2]Cl$ (ii) What type of isomerism is exhibited by the complex $\{Co(en)_3]^{3+}$? (en = ethane-1, 2-diamine) (iii) Why is $[NiCl_4]^{2-}$ paramagnetic but $[Ni(CO)_4]$ is diamagnetic? (At. nos. : Cr = 24, Co = 27, Ni = 28)	**2+** **2+** **1** **1+** **1+** **3**
33	a) How would you convert---- (i) Aniline to nitrobenzene (ii) Aniline to iodobenzene b) Complete the following chemical equations : (*i*) $C_6H_5N_2Cl + C_6H_5NH_2 \xrightarrow{OH^-}$ (*ii*) $C_6H_5N_2Cl + CH_3CH_2OH \longrightarrow$ (*iii*) $RNH_2 + CHCl_3 + KOH \longrightarrow$ OR An aromatic compound "A' of molecular formula $C_7H_{27}ON$ undergoes a series of reactions as shown below. Write the names and structures of A, B, C, D and E in the following reactions : 	2+ 3

	MARKING SCHEME SAMPLE PAPER SET 3	
1	(b) 1.0 M Na_2SO_4	1
2	(a)3F	1
3	a)first order Explanation: Given that k= $3.28 \times 10^{-4} s^{-1}$ The standard formula for calculating rate constant units is k=$(mol\ L^{-1})^{1-n} s^{-1}$, where n is the order of the reaction. For $(mol\ L^{-1})^{1-n}$s-1 to become s-1, the value of n must be 1. As a result, k=$3.28 \times 10^{-4} s^{-1}$ denotes a first order reaction.	1
4	(d)	1
5	(c) Explanation: $EDTA^{4-}$ is a hexadentate ligand which can bind through two nitrogen and four oxygen atoms to a central metal ion, giving it a total of 2 + 4 = 6 donor atoms.	1
6	(d) Explanation: Since Cl is an anionic ligand, it ends in -o, hence chlorido. Also, the complex ion is anionic, and the metal must end with the suffix -ate, hence palladate.	1
7	(b) Two **Explanation:** Structural isomers are molecules whose atoms are rearranged in a new pattern within the molecular formula. The compound with the molecular formula C_3H_7Cl is known to be n-propyl chloride. This compound can have two structural isomers, namely 1-chloropropane and 2-chloropropane	1
8	(b) Explanation: Addition of water to propyne in the presence of H_2SO_4 and $HgSO_4$ gives acetone. Zinc dust is an important reagent in the ozonolysis of alkenes.	1
9	(d) Explanation: Generally, the aromatic carbonyl compounds are less reactive than corresponding aliphatic compounds. From benzaldehyde to acetophenone to benzophenone, the number of electron releasing groups increases and the magnitude of positive charge on carbonyl carbon reduces, hence decreasing its reactivity towards nucleophile attack.	1
10	(a) Explanation: In a set of the given reactions, acetic acid yielded a product C is CH_3−C-C_2H_5(OH)C_6H_5.  $CH_3COOH + PCl_5 \rightarrow CH_3COCl \xrightarrow[\text{anh.} AlCl_3]{C_6H_6}$ $CH_3COC_6H_5 \xrightarrow[\text{Ether}]{C_2H_5MgBr} CH_3 - \overset{C_2H_5}{\overset{\mid}{C}}(OH)C_6H_5$	1

<table>
<tr><td>11</td><td>(c)
Explanation: Nitration of aniline produces nitro derivatives. Under controlled conditions, aniline is protonated (by strong acidic medium) to form anilinium ion, which is meta directing. Therefore, apart from p-nitroaniline (51%) and o-nitroaniline (2%), a significant amount of m-nitroaniline (47%) is also formed.</td><td>1</td></tr>
<tr><td>12</td><td>b
Explanation: DNA does not contain uracil. Since adenine (A) pairs only with thymine (T) and cytosine (C) pairs with guanine (G), complementary strand will be TACGGCTAG.</td><td>1</td></tr>
<tr><td>13</td><td>(b)
Explanation: Greater the molecular mass, stronger the van der Waals' forces of attraction and hence higher is the melting point/boiling point</td><td>1</td></tr>
<tr><td>14</td><td>(d)

Explanation: Halobenzenes become reactive to nucleophilic substitution reactions when electron withdrawing group (nitro, cyano) are present at ortholpara position. This is evident from the milder conditions required for hydrolysis in 2,4-dinitrochlorobenzene than chlorobenzene.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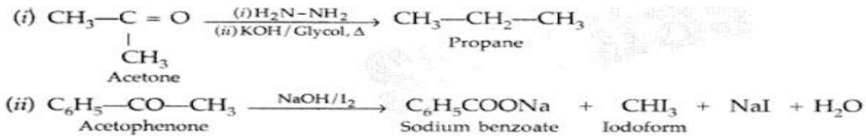
<tr><td>15</td><td>(c)</td><td>1</td></tr>
<tr><td>16</td><td>(b)</td><td>1</td></tr>
<tr><td></td><td>SECTION –B</td><td></td></tr>
<tr><td>17</td><td>
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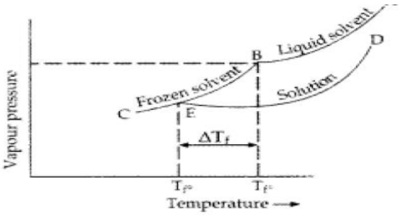
<tr><td>18</td><td>An aqueous solution of sodium chloride freezes below 273 K because vapour pressure of the solution is less than that of the pure solvent.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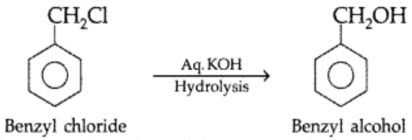
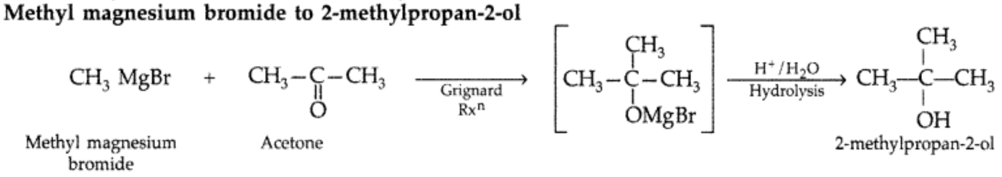
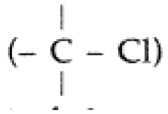
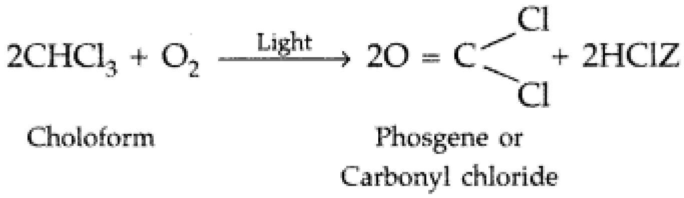
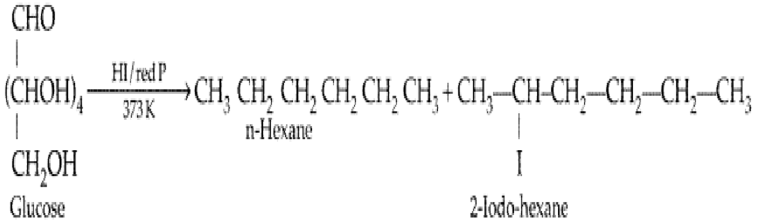
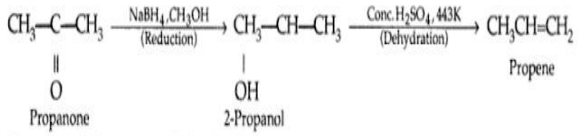
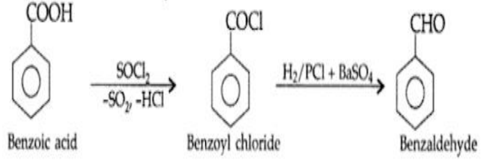
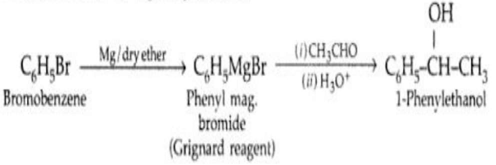
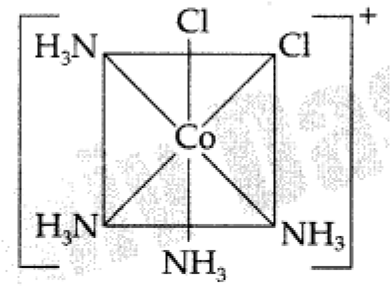
19	Molar conductivity Λ_m = 1000×κM Given : K = 0.025 S cm^{-1}, M = 0.20 M Hence, Λ_m = 0.025×10000.20 ∴ Λ_m = 125 S cm^2 mol^{-1} OR Given : E° = 1.1V, F = 96,500 C mol^{-5}, n = 2 $Zn + Cu^2 \rightleftharpoons Cu + Zn^{2+}$ Using ΔG° = -nFE° = -2 × 96500 × 1.1 = 212,300 CV mol^{-1}	2
20	Phenol gives a violet colouration with $FeCl3$ solution while ethanol does not. $3C6H5OH$Phenol+$FeCl3$→$(C6H5O)Fe$Violet colouration+$3HCl$ $C2H5OH$+$FeCl3$→ No violet colouration ii)On adding I_2 and NaOH, 2-pentanol will give yellow precipitate of iodoform whereas 3-pentanol will not give yellow precipitate.	2
21	(i) Benzyl chloride to benzyl alcohol  (*ii*) **Methyl magnesium bromide to 2-methylpropan-2-ol**  	2
	SECTION-C	

22	(i) In haloalkanes, the halogen atom is attached  $(-\overset{\vert}{\underset{\vert}{C}}-Cl)$ to sp^3-hybridized carbon while in haloarenes it is attached to sp^2 -hybridized carbon whose size is smaller than sp^3 orbital carbon. Therefore C – Cl bond in chloro-benzene is shorter than alkyl chloride. (ii) $CHCl_3$ is stored in dark coloured bottles to cut off light because $CHCl_3$is slowly oxidised by air in presence of light to form an extremely poisonous gas, carbonyl chloride, popularly known as phosgene.  (iii) (a) p-isomers are comparetively more symmetrical and fit closely in the crystal lattice, thus require more heat to break these strong forces of attraction. Therefore higher melting point than o- and m-isomers.	1 + 1 + 1
23	(i) Copper atom has completely filled d orbitals (3d^{10}) in its ground state, yet it is regarded as a transition element due to incompletely filled d-orbital in its ionic states i.e. Cu^{2+} (3d^9). (ii) The highest oxidation state for Cr is +6, therefore it can loose 3 more electrons, whereas Fe needs to loose only 1 electron to achieve its highest oxidation state of +3. Thus, Cr^{3+} is more reducing than Fe^{2+}. (iii) Because silver has incomplete d-orbital (4d^9) in its +2 oxidation state, hence it is a transition element.	1 + 1 + 1
24	(*a*) $E^\circ_{Cell} = E^\circ_{Ag^+/Ag} - E^\circ_{H^+/\frac{1}{2}H_2}$ $= +0.80 - 0.00 = +0.80\ V$ $\frac{1}{2}H_2 + Ag^+ \longrightarrow H^+(aq) + Ag(s)$ This reaction is feasible because E°_{Cell} is +ve. Therefore, ΔG will be –ve, since $\Delta G^\circ = -nE^\circ F$. (b) Limiting molar conductivity is the maximum conductivity when solution is infinitely dilute, such that on further dilution there is no increase in Am. Conductivity decreases with decrease in concentration because number of ions per unit volume decrease.	1 + 2

25	$Zn(s) \longrightarrow Zn^{2+}(aq) + 2e^-$ $2H^+(aq) + 2e^- \longrightarrow H_2(g)$ $Zn(s) + 2H^+(aq) \longrightarrow Zn^{2+}(aq) + H_2(g)$ $n = 2$ Now, $E_{cell} = E^\circ_{cell} - \frac{0.0591}{n} \log \frac{[Zn^{2+}]}{[H^+]^2}$ $= (E^\circ_{H^+/H_2} - E^\circ_{Zn^{2+}/Zn}) - \frac{0.0591}{2} \log \frac{10^{-3}}{[10^{-2}]^2}$ $= [0 - (-0.76\ V)] - \frac{0.0591}{2} \log 10$ $\therefore \quad E_{cell} = +0.76\ V - 0.0295 = 0.7305\ V$	3
26	(i) Starch is a polysaccharide. (ii) α-Helix structure : The polypeptide chains are held together (stabilized) by intramolecular H-bonding. β-Pleated sheet structure : The two neighbouring polypeptide chains are held together by intermolecular , H-bonding. (iii) Disease caused by the deficiency of Vitamin B_{12} is Pernicious anaemia.	1 + 1 + 1
27	i) Vitamin C causes scurvy. (ii) Peptide linkages are responsible for the formation of proteins. (iii) Glucose is treated with HI --- 	1 + 1 + 1
28	i) (i) **Propanone to Propene**  (ii) **Benzoic acid to Benzaldehyde** *(Rosenmund reduction)* :  ii) **Bromobenzene to 1-phenylethanol** 	

	SECTION –D	
29	(a)Equal (b)Depression in FP in 0.1m solution is more than 0.01 solution so FP of first is less.(change in freezing point is directly proportional to molality) (c)$Al_2(SO4)_3$ OR a) as there are 2 moles of ions per mol of NaCl b) degree of ionisation is not 100% at freezing point due to stronger interactions for 1m solution	1 + 1 + 2
30	**(i) (a):**Terbium (65), $4f^8$; Dysprosium (Dy), $4f^9$; Ytterbium (Yb), $4f^{13}$. **(ii) (a)** **(iii) (a)** **(iv) (b):** The almost identical radii of Zr (160 pm) and Hf(159 pm), a consequence of lanthanoid contraction.	1 + 1 + 1 + 1
	SECTION – E	
31	) (a) (i) Differential rate equation : $dx/dt = K [A]^2[B]$ (ii) When concentration of A is increased to three times, the rate of reaction becomes 9 times $r = K[3A]^2B \therefore r = 9KA^2B$ i.e. = 9 times (iii) $r = K[2A]^2[2B] \therefore r = 8KA^2B$ i.e. = 8 times (b) Given : Time, t = 40 minutes, t =? Let a = 100, $\therefore$ x = 30% of 100 = 30 Using the formula : $t = \frac{2.303}{K} \log \frac{a}{a-x}$ or $40 = \frac{2.303}{K} \log \frac{100}{100-30}$ or $K = \frac{2.303}{40} \log \frac{100}{70}$ or $K = \frac{2.303}{40} (\log 10 - \log 7)$ or $K = \frac{2.303}{40} (1 - 0.8451)$ or $K = \frac{2.303}{40} \times 0.1549$ or $K = \frac{0.3567}{40} = 0.0089$ min $\therefore t_{1/2} = \frac{0.693}{K} = \frac{0.693}{0.0089} = \mathbf{77.86\ min.}$	

32	(a) Double salt dissociates completely into its constituent ions in their aqueous solution. Example : $KCl.MgCl_2.6H_2O$ dissociates into K^+, Cl^-, Mg^{2+} and H_2O Complex does not dissociate into its constituent ions. Example : $K_4[Fe(CN)_6] \rightarrow 4K^+ + Fe(CN)_6]^{4-}$ (b) (i) $K_3[Fe(C_2O_4)_3]$ IUPAC name : Potassium trioxalatoferrate (III) (ii) $[Pt(NH_3)_6]Cl_4$ IUPAC name : Hexaammine Platinum (IV) chloride (c) Structure of cis isomer of $[CO(NH_3)_4Cl_2]^+$ 	2+ 2+ 1
	OR (i) IUPAC name : Tetraammine dichlorido chromium (III) chloride (ii) Optical isomerism is exhibited by the complex $[Co(en)_3]^{3+}$ (iii) In $[NiCl_4]^{2-}$, Ni^{2+} has $3d^84s^0$ configuration and due to weak ligand i.e. Cl^-, electrons cannot pair up hence show paramagnetism while in $[Ni(CO)_4]$, Ni is in zero oxidation state with $3d^84s^2$ configuration and the 4s electrons are used up in pairing of 3d electrons as carbonyl ligand is strong hence diamagnetic.	1+ 1+ 3

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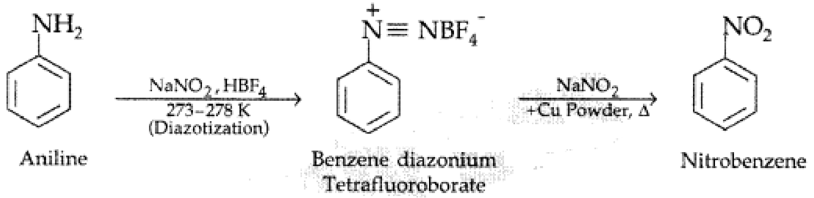
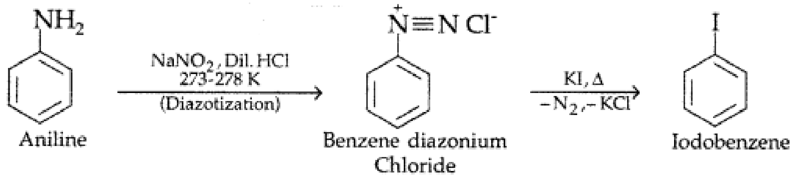
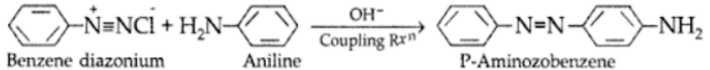
a) (i) Aniline to nitrobenzene



(*ii*) Aniline to iodobenzene



(*i*)



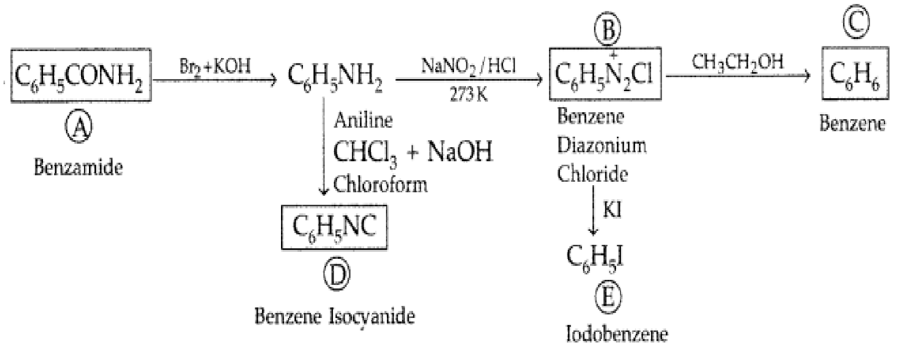
Benzene diazonium chloride Aniline P-Aminozobenzene

(*ii*) $\underset{\text{Benzene diazonium chloride}}{C_6H_5N_2Cl} + \underset{\text{Ethanol}}{CH_3CH_2OH} \xrightarrow{\text{Reduction}} \underset{\text{Benzene}}{C_6H_6} + \underset{\text{Ethanal}}{CH_3CHO} + N_2 + HCl$

(*iii*) $\underset{1^\circ\text{ Amine}}{RNH_2} + \underset{\text{Chloroform}}{CHCl_3} + 3KOH \xrightarrow[\text{Carbylamine reaction}]{\Delta} \underset{\text{Alkyl isocyanide (offensive smell)}}{R{-}N \rightleftarrows C} + 3KCl + 3H_2O$

b)

OR



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SAMPLE QUESTION PAPER -4

Class XII **Chemistry**

Time: 3 Hours. **Max. Marks: 70**

General Instructions:

1. There are 33 questions in this question paper with internal choice.
2. SECTION A consists of 16 multiple-choice questions carrying 1 mark each.
3. SECTION B consists of 5 very short answer questions carrying 2 marks each.
4. SECTION C consists of 7 short answer questions carrying 3 marks each.
5. SECTION D consists of 2 case-based questions carrying 4 marks each.
6. SECTION E consists of 3 long answer questions carrying 5 marks each.
7. All questions are compulsory.
8. Use of log tables and calculators is not allowed.

SECTION - A

1.For non-electrolyte solute the value of Van’t Hoff factor is

(a) 0 (b) 1 (c) >1 (d) <1

2.Charge carried by 1 mole of electrons is

(a) 6.023×10^{23} coulomb
(b) 1.6×10^{-19} coulomb
(c) 9.65×10^{4} coulomb
(d) 6.28×10^{19} coulomb

3.The difference between the electrode potentials of two electrodes when no current is drawn through the cell is called

(a) Cell potential.
(b) Cell emf
(c) Potential difference.
(d) Cell voltage

4. In the reaction, A + 2B -> 6C + 2D, if the initial rate – d [A]/dt at t = 0 is 2.6×10^{-2} M sec^{-1} will be the value of – d [B]/dt at t = 0?

(a) 8.5×10^{-2}M sec^{-1}
(b) 5.2×10^{-2} M sec^{-1}
(c)2.5×10^{-2} M sec^{-1}
(d)7.5×10^{-2} M sec^{-1}

5.Which of the following lanthanoids show +2 oxidation state besides the characteristic oxidation state +3 of lanthanoids?

(a) Ce (b) Eu (c) Yb (d) Ho

6.The magnetic moment is associated with its spin angular momentum and orbital angular momentum. Spin only magnetic moment value of Cr^{3+}ion is

(a) 2.87 B.M.
(b) 3.87 B.M.

(c) 3.47B.M
(d) 3.57B.M

7.The compounds $[Co(SO_4)(NH_3)_5]Br$ and $[Co(SO_4)(NH_3)_5]Cl$
(a) Linkage isomerism
(b) Ionisation isomerism
(c) No isomerism
(d) Coordination isomerism

8.The formula of the complex tris(ethylenediamine)cobalt(III) sulphate is
(a) $[Co(en)_3]SO_4$
(c)$[Co(en)_3]_2(SO_4)_3$
(b)$[Co(en)_3]SO_4]$
(d)$[Co(en)_3]](SO_4)_3$

9.Which reagent will you use for the following reaction?
$CH_3CH_2CH_2CH_3 \rightarrow CH_3CH_2CH_2CH_2Cl + CH_3CH_2CHClCH_3$
(a) Cl_2/UV light
(b) $NaCl + H_2SO_4$
(c) Cl_2 gas in presence of Fe in dark
(d) Cl_2 gas in dark

10. Phenol is less acidic than
(a) Ethanol
(b) o-nitrophenol
(c) o-methylphenol
(d) o-methoxyphenol

11 Which out of the following reactions need α-H atom to get started?
(a) Etard reaction
(b) Cannizaro's reaction
(c) Aldol condensation
(d) HVZ reaction

12 Hoffmann Bromamide Degradation reaction is shown by
(a) $ArNH_2$
(b) $ArCONH_2$
(c) $ArNO_2$
(d) $ArCH_2NH_2$

In the Following questions a statement of Assertion(A) is followed by a statement of Reason(R). Select the most appropriate answer from the options given below:
(a) Both A and R are true and R is the correct explanation of A
(b) Both A and R are true but R is not the correct explanation of A.
(c) A is true but R is false.
(d) A is false but R is true.

13.Assertion(A) :Benzoic acid does not undergo Friedel-Crafts reaction.

Reason(R): carboxyl group is deactivating and the catalyst aluminium chloride (Lewis acid) gets bonded to the carboxyl group.

14.Assertion(A) : Benzaldehyde is more reactive in nucleophilic addition reactions than propanal.

Reason(R): The polarity of the carbonyl group attached to benzene ring is reduced in benzaldehyde due to resonance.

15.Assertion(A) : Acetanilide is more basic than aniline.

Reason(R): Acetylation of aniline results in decrease of electron density on nitrogen.

16.Assertion(A) : Hoffmann's bromamide reaction is given by primary amines.

Reason(R): Primary amines are more basic than secondary amines.

SECTION B

This section contains 5 questions with internal choice in one question. The following questions are very short answer type and carry 2 marks each.

17. Name the cell which

(a) was used in Apollo space programme.

(b) is suitable for hearing aid and watches.

(c) is used in automobiles and inverters.

(d) is used in transistors.

18. Complete the following chemical equations

(a) $MnO^{4-} + S^{2}O_3^{2-} + H_2O$ ____________

(b) Cr2 O7 2- + Sn^{2+} + H+ ______________

19.(a) What type of isomerism is shown by the complex $[Cr(H_2O)_6]Cl_3$?

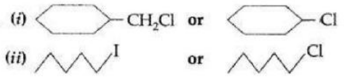
(b)On the basis of CFT , write the electronic configuration for d^4 ion if $\Delta_0 > P$

Or

(a) Using IUPAC norms write the systematic name of the $[Co(en)_3]^{3+}$

(b) Draw the structures of optical isomers of: $[Cr(C_2O_4)_3]^{3-}$

20. Which one in the following pairs of substances undergoes SN^2 substitution reaction faster and why?



21. Explain the following terms:

(a) Reducing sugar

(b) Polypeptides

SECTION C

This section contains 7 questions with internal choice in one question. The following questions are short answer type and carry 3 marks each

22. An aqueous solution freezes at 272.4 K while pure water freezes at 273 K. Determin

(i) Molality of solution.

(ii) Boiling point of solution

Given: K_f = 1.86 K Kg mol-1 , K_b = 0.512 K Kg Mol^{-1}

23. Give reasons

(a) Measurement of osmotic pressure method is preferred for the determination of molar masses of Macromolecules such as proteins and polymers.

(b) Aquatic animals are more comfortable in cold water than in warm water.

(c) Red blood cells shrink when placed in saline water but swell in distilled water.

24. Calculate the emf of the cell in which the following reaction takes place:

$$Ni_{(s)} + 2Ag^{+}(0.002M) \rightarrow Ni^{2+}(0.160M) + 2Ag_{(s)}$$

Given that $E^{0}_{cell} = 1.05\ V$

25. Accounts for the following

(a)Cu^{2+}salts are coloured while Zn^{2+} are white

(b) E^0 value for the Mn^{3+} / Mn^{2+} couple is much more positive than that for Cr^{3+} /Cr^{2+} .

(c) There is a gradual decrease in the size of atoms with increasing atomic number in the series of Lanthanoids.

Or

Describe the preparation of potassium permanganate. How does the acidified permanganate solution react with oxalic acid? Write the ionic equations for the reactions.

26. Give reasons :

(a)n-Butyl bromide has higher boiling point than t-butyl bromide.

(b)Racemic mixture is optically inactive.

(c) Which one of the following compounds is more easily hydrolyzed by KOH and why?

$CH_3CHClCH_2CH_3$ or $CH_3\ CH_2\ CH_2\ Cl$

27. (a) Write the chemical equations involved in the following name reactions:

(i) Clemmensen reduction

(ii) Cannizzaro reaction

(b) Distinguish between following pair of compounds CH_3CHO and $C_6\ H_5$ -CHO

28. (a) Deficiency of which vitamin causes night-blindness?

(b) Name the base that is found in nucleotides of RNA only.

(c) Glucose on reaction with HI gives n-hexane. What does it suggest about the structure of glucose?

SECTION D

The following questions are case -based questions. Each question has an internal choice and carries 4 (1+1+2) marks each. Read the passage carefully and answer the questions that follow.

29. Read the following passage and answer questions given below:

A secondary cell after use can be recharged by passing current through it in the opposite direction so that it can be used again. A good secondary cell can undergo a large number of discharging and charging cycles. The most important secondary cell is the lead storage battery commonly used in automobiles and inverters. It consists of a lead anode and a grid of lead packed with lead dioxide (PbO_2) as cathode. A 38 % solution of sulphuric acid is used as electrolyte (density=1.294 g mL^{-1}.The battery holds 3.5 L of the acid. During the discharge of the battery, the density of H_2 g mL^{-1} (20% H_2 SO_4 by mass).

a. Write the reaction taking place at the cathode when the battery is in use.

b. How much electricity (in Coulombs) is required to carry out the reduction of one mole of PbO_2

c. The anodic half cell of Lead-Acid Battery is recharged using electricity of 0.05 Faraday. What amount in gram of $PbSO_4$

? is electrolyzed during the process? The molar mass of $PbSO_4$= 303 g mol^{-1}

OR

Write reactions at cathode and anode during recharging of lead storage cell.

30. When a protein in its native form, is subjected to physical changes like change in temperature or chemical changes 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 protein.

The denaturation causes change in secondary and tertiary structures but primary structures remain intact. Examples of denaturation of protein are coagulation of egg white on boiling, curdling of milk, formation of cheese when an acid is added to milk. (i)Which structure of proteins are unaffected with denaturation of protein?

(ii) All α-amino acids are optically active except one α-amino acid. Give named of it. (iii)Write the difference between globular protein and fibrous protein with one example.

SECTION E

The following questions are long answer type and carry five marks each.

All questions have internal choice.

31.Attempt any five of following

(a)Which transition metal of 3d -series has positive E^o (M^{2+}/M) value.

(b) Out of Cr^{3+} , Mn^{3+} , which is stronger oxidising agent and why?

(c)Name a member of lanthanoid series which is well sure to exhibit +4 oxidation state.

(d)What happen potassium chromate is acidified $2CrO_4^2$

$^-$(e)$KMnO_4$----heat---□

(f)Cu^{2+} , is more stable than cu^{+1} in aqueous solution, why?

(g) Enthalpy of atomisation of transition element is very high. assign the reason?

32. (a) Illustrate the following name reactions by giving example:

(i) Cannizzaro’s reaction

(ii) Clemmensen reduction

(b) An organic compound A contains 69.77% carbon, 11.63% hydrogen and rest oxygen. The molecular mass of the compound is 86. It does not reduce Tollens’s reagent but forms an addition compound with sodium hydrogen sulphite and gives positive iodoform test. On vigorous oxidation it gives ethanoic and propanoic acids. Derive the possible structure of compound A.

OR

32.(a) An organic compound (A) having molecular formula C_4 H_8O gives orange red precipitate with 2,4-DNP reagent. It does not reduce Tollens' reagent but gives yellow precipitate of iodoform on heating with NaOH and I_2. Compound (A) on reduction with $NaBH_4$ gives compound (B) which undergoes dehydration reaction on heating with conc. H_2SO_4 to form compound (C). Compound (C) on Ozonolysis gives two molecules of ethanal. Identify (A), (B) and (C) and write their structures. Write the reactions of compound (A) with

(i) NaOH/I_2 and (ii) NaBH4 .

(b) Write the products formed when acetone reacts with the following reagent

(i) phenyl hydrazine

(ii) acetone heated with Dilute NaOH

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

(b)What value of k is predicted for the rate constant by Arrhenius equation if temperature is infinite? is this value physically responsible?

(c) Why does equilibrium constant not change with presence of a catalyst?

Or

(a) Rate constant k of a reaction varies with temperature according to the equation $\log k = \log A - E_a/2.303RT$; where E_a is the energy of activation for the reaction. When a graph is plotted for log k vs 1/T a straight line with a slope −6670K is obtained. The activation energy for this reaction will be? ($R=8.314\ JK^{-1}mol^{-1}$)

(b)What is fraction of molecule having energy equal to or greater than activation energy? What is the quantity called?

(c) An exothermic reaction A converts into B has an activation energy 17 kJmol-1 of A. The heat of reaction is 40 kJ. Calculate the activation energy for the reverse reaction from B to A.

MARKING SCHEME:

1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16
b	c	b	b	b	b	c	c	a	b	c	b	a	d	d	c

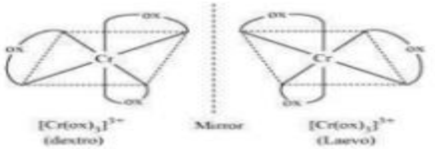
17.(a) Fuel Cell (b) Mercury cell (c) Lead storage battery (d) Dry cell

18. (a) $8MnO_4^- + 3S_2O_3^{2-} + H_2O \longrightarrow 8MnO_2 + 6SO_4^{2-}$ ·
(b) $Cr_2O_7^{2-} + 3Sn^{2+} + 14\ H^+ \longrightarrow 2Cr^{3+} + 3Sn^{4+} +$

19. (a) Hydrate isomerism.
(b) $\Delta_0 > P$ so $t2g^4 e_g^0$

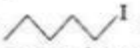
Or

(a) Tris(ethan-1,2-diammine)cobalt(III) ion
(b)



20.

(*i*)  CH_2Cl is a primary halide and therefore undergoes S_N2 reaction faster.

(*ii*)  : As iodine is a better leaving group because of its large size, therefore undergoes S_N2 reaction faster.

21. (a) Sugars which reduce with tollen's reagent and Fehling solutions are called reducing sugars. Eg. Glucose.

(b)Polypeptides : They are formed when several molecules of a-amino acids are joined together by peptide bonds.

22.(i) ΔT_f = m Therefore m = ΔT_f K_f / K_f = 0.6/1.86 = 0.32mol / Kg

(ii) ΔT_b = m = 0.512 x 0.32 = 0.164 Therefore Tb Kb (1)

(iii) ΔP = P0 .m.MA= 23.756 x 0.32 x 0.018 = 0.137 mm Hg. (1)

23. (a) The osmotic pressure can be measured at room temperature and its magnitude is large even for very dilute solution. (1)

(b) At higher temperature the solubility of oxygen get decreased in water (1)

(c) Because exosmosis will occur when kept saline water while endosmosis will occur when kept in distilled water.

24. Applying Nernst equation we have:
Ecell = 0.914V

25.(a) Cu^{2+} have unpaired electron while Zn^{2+}

(b) The large positive E° value for Mn^{3+} does not have unpaired electron /Mn^{2+} shows that Mn^{2+} stable half-filled configuration ($3d^{5)}$. Therefore the 3rd and Mn^{3+} is much more stable than Mn^{+3} ½ (1)

due to ionisation energy ofMn will be very high is unstable and can be easily reduced to Mn^{2+} small i.e. Cr^{3+} can also be reduced to Cr^{2+} but less easily. Thus Cr^{3+}

(c) This is due to lanthanoid contraction

26.(a) n-Butyl bromide has higher boiling point than t-butyl bromide because it has larger surface area.

(b) Rotation due to one enantiomer is cancelled by another enantiomer

(c) Refer NCERT

27.Refer NCERT

28.(i) Vitamin A causes night blindness.

(ii) Uracil is found in nucleotide ofRNA only.

(iii) It suggests the open /straight chain structure of glucose.

29.a).PbO_2 (s) + $SO_4{}^{2-}$ (aq) + $4H^+$ (aq) + 2e– → $PbSO_4$(s) + $2H_2$0

b. 2 F = 2 × 96500 = 193000 C

c. 2 Faraday of electricity = 303 gm $PbSO_4$ 0.05F= 0.05/2*303=7.6 gm

OR

Recharge reaction of cell: It changes the direction of electrode reaction. $PbSO_4$ accumulated at cathode gets reduced to Pb. At cathode: $PbSO_4$(s) +2e– → Pb(s) + SO_4

At anode: $PbSO_4$ gets oxidised to PbO_2

$PbSO_4$ (s) + $2H_2O$→PbO_2 (s) + $4H^+$(aq) + $SO_4{}^{2-}$ + 2e-

Overall reaction $PbSO_4$ (s) + $2H_2$ O(l) → Pb(s) +PbO_2(s) + $2H_2SO_4$

30.(i)Primary protein structure (ii)glycine (iii)Any one difference with one example

Or

(iii) Any one difference with one example

31.(a)copper

(b) Mn^{3+}, Due to $3d^5$ half field configuration (c)Ce

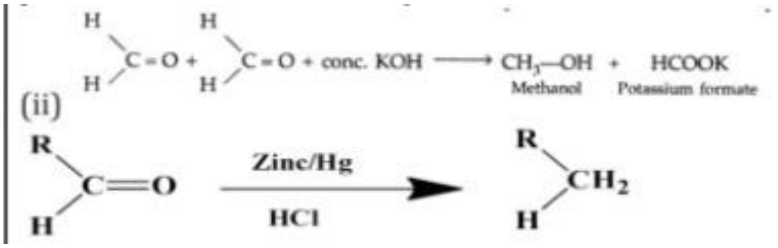
(d)Potassium dichromate is formed

(e)$KMnO_4$----heat---□ K_2 MnO_4 +MnO_2 +O_2

(f)Second ionisation enthalpy of copper compensate with hydration enthalpy of Cu^{2+}

(g)Transition metal have large number of unpaired electron forms stronger metal metal bonding

32.(a) (i) Cannizzaro's reaction: Aldehydes, which do not have an alpha-hydrogen atom undergo self-oxidation and reduction on treatment with cone, alkali and produce alcohol and carboxylic acid salt.

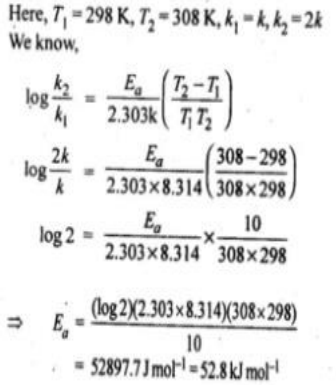


(b)An organic compound contains 69.77% C, 11.63% H and rest O. The molecular mass of the compound is 86.

Empirical formula mass =5×12+10×1+1×16=86. It is equal to molecular formula mass. Hence, molecular formula is same as empirical formula. It does not reduce Tollens reagent. Hence, it is not an aldehyde It forms an addition compound with sodium hydrogen sulphite. Hence, it contains carbonyl group. It give positive iodoform test. Hence, it is a methyl ketone On vigorous oxidation it gives ethanoic and propanoic acid.

Hence, it is 2-pentanone.

33.(a)



Here, $T_1 = 298$ K, $T_2 = 308$ K, $k_1 = k$, $k_2 = 2k$

We know,

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

$$\log\frac{2k}{k} = \frac{E_a}{2.303 \times 8.314}\left(\frac{308 - 298}{308 \times 298}\right)$$

$$\log 2 = \frac{E_a}{2.303 \times 8.314} \times \frac{10}{308 \times 298}$$

$$\Rightarrow \quad E_a = \frac{(\log 2)(2.303 \times 8.314)(308 \times 298)}{10}$$

$$= 52897.7\ \text{J mol}^{-1} = 52.8\ \text{kJ mol}^{-1}$$

(b)if temperature is infinite k = A so that Ea = 0, this will not feasible (c) Catalyst increase the rate of forward and backward reaction to the same extent. therefore, equilibrium attain quickly but the position equilibrium does not change.

OR

(a) Slope of the line = $-E_a/2.303R = -6670$K

E_a = Slope x 2.303 x 8.314

Ea =2.303×8.314(JK−1mol−1

= 127711.4 Jmol−1) × 6670K =127.71 kJmol−1

(b) fraction of molecule having energy equal to or greater than activation energy is equal to e-Ea /RT at temp T. It is called Boltzmann factor. (c) A ----□ B E_a=17 kJ Since the reaction is exothermic, the energy of product is less than that of reactant, hence B-□ A Ea (reverse)=Ea(forward) + ΔE;

Ea (reverse)=17 +40=57 kJ

SAMPLE PAPER (2024 -25)

CHEMISTRY THEORY (043)

Max. Marks:70 Time: 3 hours

General Instructions:

Read the following instructions carefully.

(a) There are 33 questions in this question paper with internal choice.

(b) SECTION A consists of 16 multiple -choice questions carrying 1 mark each.

(c) SECTION B consists of 5 short answer questions carrying 2 marks each.

(d) SECTION C consists of 7 short answer questions carrying 3 marks each.

(e) SECTION D consists of 2 case - based questions carrying 4 marks each.

(f) SECTION E consists of 3 long answer questions carrying 5 marks each.

(g) All questions are compulsory.

(h) Use of log tables and calculators is not allowed

SECTION A

The following questions are multiple -choice questions with one correct answer. Each question carries 1mark. There is no internal choice in this section.

1. In the reaction $2A + B \rightarrow A_2B$, order of reaction is two with respect to A and one with respect to B, if the concentration of A is doubled and that of B is halved, then the rate of the reaction will
   a) decrease 2 times
   b) increase 4 times
   c) increase 2 times
   d) remain the same

2. Which of the following statement is true?
   a) molecularity of reaction can be zero or a fraction.
   b) molecularity has no meaning for complex reactions.
   c) molecularity of a reaction is an experimental quantity
   d) reactions with the molecularity three are very rare but are fast.

3. Which of the following statements about a lead storage cell (or a lead-acid battery) is false?

a) It is a primary cell
b) The cathode is made up of lead (IV) oxide
c) The anode is made up of lead
d) The electrolyte used is an aqueous solution of Sulphuric acid

4. $KMnO_4$ acts as an oxidising agent in alkaline medium. when alkaline $KMnO_4$ is treated with KI, iodide ion is oxidised to.......

a) I_2
b) IO^-
c) IO_3^-
d) IO_4^-

5. Generally transition elements form coloured salts due to the presence of unpaired electron. which of the following compounds are coloured in solid state.

a) Ag_2SO_4
b) CuF_2
c) ZnF_2
d) Cu_2Cl_2

6. Determine which of the following statements about VBT is inaccurate.

a) It does not explain the colour of coordination compounds

b) It can distinguish between strong and weak ligands

c) It does not explain the kinetic stabilities of coordination compounds

d) It is unreliable in the prediction of geometries of 4-coordinate complexes

7. The core atom of which of the following biologically significant coordination molecules is magnesium?

a) Vitamin B12

b) Haemoglobin

c) Chlorophyll

d) Carboxypeptidase-A

8. When only two hydrogen atoms are attached to the nitrogen of an amine, it is classified as a ________
amine.

a) primary
b) secondary
c) aliphatic
d) aromatic

9. Which of the following is an arylalkyl amine?
a) $C_6H_5NHC_6H_5$
b) $C_6H_5NH_2$
c) $(C_6H_5CH_2)NH$
d) $(C_6H_5)_3N$

10. Find out correct order of acidic strength among the following:

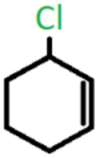
a) Ethanol>Water>Phenol

b) Ethanol<Water<Phenol

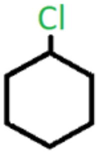
c) Water<Ethanol<Phenol

d) Phenol>ethanol=Water

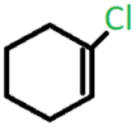
11. Which of the following compounds contains an allylic carbon?



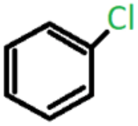
A



B



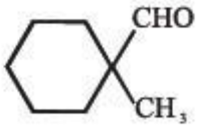
C

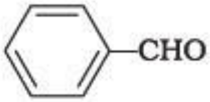


D

a) A
b) B
c) C
d) D

12. Cannizzaro’s reaction is not given by _____________.

(i)


(ii)


(iii) H CHO
(iv) CH_3CHO

13. Given below are two statements labelled as Assertion (A) and Reason (R)

Assertion (A): During electrolysis of aqueous copper sulphate solution using copper electrodes hydrogen gas is released at the cathode.

Reason (R): The electrode potential of Cu2+ /Cu is greater than that of H +/H 2

Select the most appropriate answer from the options given below:

(a) Both A and R are true and R is the correct explanation of A
(b) Both A and R are true but R is not the correct explanation of A.
(c) A is true but R is false.
(d) A is false but R is true.

14. **Assertion :** In Lucas test, 3º alcohols react immediately.
Reason : An equimolar mixture of anhyd. $ZnCl_2$ and conc. HCl is called Lucas reagent.

Select the most appropriate answer from the options given below:

(a) Both A and R are true and R is the correct explanation of A
(b) Both A and R are true but R is not the correct explanation of A.
(c) A is true but R is false.
(d) A is false but R is true.

15. **Assertion :** D(+)– Glucose is dextrorotatory in nature.
Reason : ‘D’ represents its dextrorotatory nature.

Select the most appropriate answer from the options given below:

(a) Both A and R are true and R is the correct explanation of A
(b) Both A and R are true but R is not the correct explanation of A.
(c) A is true but R is false.
(d) A is false but R is true

16. **Assertion :** Aniline does not undergo Friedel-Crafts reaction.
Reason : –NH2 group of aniline reacts with AlCl3 (Lewis acid) to give acid-base reaction.

Select the most appropriate answer from the options given below:

(a) Both A and R are true and R is the correct explanation of A
(b) Both A and R are true but R is not the correct explanation of A.
(c) A is true but R is false.
(d) A is false but R is true.

SECTION B

This section contains 5 questions with internal choice in one question. The following questions are very short answer type and carry 2 marks each.

17. a. Radioactive decay follows first - order kinetics. The initial amount of two radioactive elements X and Y is 1 gm each. What will be the ratio of X and Y after two days if their half-lives are 12 hours and 16 hours respectively?

    b. The hypothetical reaction P + Q R is half order w.r.t 'P' and zero order w.r.t 'Q'. What is the unit of rate constant for this reaction?

18. Indicate the types of isomerism exhibited by the following complexes and draw the structures for these isomers:
    i. K $[Cr(H_2O)_2(C_2O_4)_2$
    ii. $[Co(en)_3]Cl_3$
    iii. $[Co(NH_3)_5(NO_2)](NO_3)_2$
    iv. $[Pt(NH_3)(H_2O)Cl_2]$

19. Halo alkanes react with KCN to form alkyl cyanides as main product while AgCN forms isocyanides as the chief product. Explain.

20. Arrange the following compounds in increasing order of their property as indicated:
    i. Acetaldehyde, Acetone, Di-tert-butyl ketone, Methyl tert-butyl ketone (reactivity towards HCN)
    ii. $CH_3CH_2CH(Br)COOH$, $CH_3CH(Br)CH_2COOH$, $(CH_3)_2CHCOOH$, $CH_3CH_2CH_2COOH$ (acid strength)

21. What happens when D-glucose is treated with the following reagents?

    (i) HI (ii) Bromine water

OR

(a) DNA fingerprinting is used to determine paternity of an individual. Which property of DNA helps in the procedure?

(b) What structural change will occur when a native protein is subjected to change in pH?

SECTION C

22. (a) Can we construct an electrochemical cell with two half-cells composed of ZnSO4 solution and zinc electrodes? Explain your answer.

(b) Calculate the λ0m for Cl- ion from the data given below:

Λ^0_m $MgCl_2$ = 258.6 $Scm^2mol^{-1}$and λ^0_m Mg^{2+} = 106 Scm^2mol^{-1}

(c) The cell constant of a conductivity cell is 0.146 cm-1. What is the conductivity of 0.01 M solution of an electrolyte at 298 K, if the resistance of the cell is 1000 ohm.

23. 3.9 g of benzoic acid dissolved in 49 g of benzene shows a depression in freezing point of 1.62 K. Calculate the van't Hoff factor and predict the nature of solute (associated or dissociated).(Given: Molar mass of benzoic acid = 122 g mol^{-1}, K_f for benzene = 4.9 K kg mol^{-1})

24. Nitrogen pentoxide decomposes according to equation :
$2N_2O_5(g) \rightarrow 4\ NO_2(g) + O_2(g)$.
This first order reaction was allowed to proceed at 40°C and the data below were collected :

[N_2OJ (M)	**Time (min)**
0.400	0.00
0.289	20.0`
0.209	40.0`
0.151	60.0`
0.109	80.0

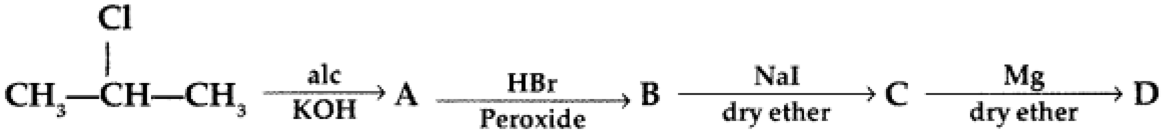
(a) Calculate the rate constant. Include units with your answer.
(b) What will be the concentration of N_2O_5 after 100 minutes?
(c) Calculate the initial rate of reaction.

25. Giving a suitable example for each, explain the following :
(i) Crystal field splitting
(ii) Linkage isomerism
(iii) Ambidentate ligand

OR

(a) Write the formula for the following coordination compound Bis(ethane-1,2-diamine) dihydroxidochromium(III) chloride
(b) Does ionization isomer for the following compound exist? Justify your answer. $Hg[Co(SCN)_4]$
(c) Is the central metal atom in coordination complexes a Lewis acid or a Lewis base? Explain.

26. (a) Write the structural formula of A, B, C and D in the following sequence of reaction:



$$CH_3-\overset{\overset{\large Cl}{|}}{C}H-CH_3 \xrightarrow[KOH]{alc} A \xrightarrow[Peroxide]{HBr} B \xrightarrow[dry\ ether]{NaI} C \xrightarrow[dry\ ether]{Mg} D$$

(b) Illustrate Sandmeyer's reaction with the help of a suitable example.

27. How would you convert the following :
(i) Phenol to benzoquinone
(ii) Propanone to 2-methylpropan-2-ol
(iii) Propene to propan-2-ol

28. State reasons for the following :
(i) pK_b value for aniline is more than that for methylamine.
(ii) Ethylamine is soluble in water whereas aniline is not soluble in water.
(iii) Primary amines have higher boiling points than tertiary amines.

SECTION D

The following questions are case -based questions. Each question has an internal choice and carries 4 (1+1+2) marks each. Read the passage carefully and answer the questions that follow.

29. Read the paragraph carefully and give answers of the questions followed

Boiling point or freezing point of liquid solution would be affected by the dissolved solids in the liquid phase. A soluble solid in solution has the effect of raising its boiling point and depressing its freezing point. The addition of non-volatile substances to a solvent decreases the vapour pressure and the added solute particles affect the formation of pure solvent crystals According to many researches the decrease in freezing point directly correlated to the concentration of solutes dissolved in the solvent. This phenomenon is expressed as freezing point depression and it is useful for several applications such as freeze concentration of liquid food and to find the molar mass of an unknown solute in the solution. Freeze concentration is a high-quality liquid food concentration method where water is removed by forming ice crystals, this is done by cooling the liquid food below the freezing point of the solution. The freezing point depression is referred as a colligative property and it is proportional to the molar concentration of the solution (m), along with vapour pressure lowering boiling point elevation, and osmotic pressure. These are physical characteristics of solutions that depend only on the identity of the solvent and the concentration of the solute. The characters are not depending on the solute's identity. (Source: Jayawardena, J. A. E. C., Vanniarachchi, M. P. G., & Wansapala, M. A. J.(2017). Freezing point depression of different Sucrose solutions and coconut water)

Answer the following questions

a. Four samples BaCl2, NaCl, ZnCl2 and AICI3 of 0.5 M are being boiled Which of the among will show highest elevation in boiling point?

b. How does sprinkling of salt help in clearing the snow-covered roads in hilly areas?

c. The freezing point of nitrobenzene is 278.8 K. When 2.8 g of an unknown substance is dissolved in 100 g of nitrobenzene, the freezing point of solution is found 276.8 K. If the freezing point depression of nitrobenzene is 8.0 K kg mol^{-1}, what is the molar mass of unknown substance? [Kf=8 KKgmol^{-1}for nitrobenzene]

OR

C.A solution prepared by dissolving 2g of oil of wintergreen (methyl salicylate) in 100.0 g of benzene has a boiling point of 80. 31° C. Determine the molar mass of this compound. (B.P. of benzene - 80.10°C and Kb for benzene 2.520 C kg mol-1)

30. Read the paragraph carefully and give answers of the questions followed

Vitamins are vital for life. A, D, E, K are fat soluble vitamins whereas B1, B2, B3, B5, B6, B7, B9, C are water soluble vitamins. Vitamin A helps in improving eye sight. Vitamin C prevents scurvy and increases immunity. Vitamin D helps in strong bones and teeth. Our requirement of vitamin D is 15mcg. We get vitamin D from sunlight, eggs, dairy products, orange, oats and mushroom etc. Citrus fruits contain vitamin. Carrot contains vitamin A. We should include chick pea flour in our diet to prevent inflammation. It has phytonutrients and fibres which have anti-inflammatory properties. It prevents accumulation of fats. It contains Fe, Cu, Mg, fibre, K which are essential to control our wait. It increases our immune system. It contains proteins, amino acids, Mg, vitamin B and P. Pomegranates are good source of vitamin C which our body needs to make collagen. It is rich source of B-complex, vitamin B5 folates pyridoxine and vitamin K. It contains essential minerals like Ca, Cu, Mg and Mn. Pomegranates are rich source of insoluble fibres which help us keep fuller for longer time and regulate bowel function.

Answer the following questions:

a) Why should vitamin B and C must be taken regularly in diet?

b) Which vitamin deficiency causes pernicious anaemia? Is it fat or water soluble?

c) i) What is meant by vitamin B-complex?

ii) What is deficiency decease and source of vitamin E

OR

c) i) Which vitamin deficiency leads to bleeding for long time? What is its source?

ii) What is the role of fibre in our body?

SECTION E

The following questions are long answer type and carry 5 marks each. All questions have an internal choice.

31. Attempt any five of the following:

(a) Which of the following ions will have a magnetic moment value of 1.73 BM.

Sc^{3+}, Ti^{3+}, Ti^{2+}, Cu^{2+}, Zn^{2+}

(b) In order to protect iron from corrosion, which one will you prefer as a sacrificial electrode, Ni or Zn? Why? (Given standard electrode potentials of Ni, Fe and Zn are -0.25 V, -0.44 V and -0.76 V respectively.)

(c) The second ionization enthalpies of chromium and manganese are 1592 and 1509 kJ/mol respectively. Explain the lower value of Mn.

(d) Give two similarities in the properties of Sc and Zn.

(e) What is actinoid contraction? What causes actinoid contraction?

(f) The transition metals and their compounds act as good catalysts. Give reason

(g) Write the ionic equation for reaction of KI with acidified $KMnO_4$.

32. Describe the following:

- (i) Aldol Condensation
- (ii) Cannizzaro Reaction
- (iii) Clemmensen Reduction
- (iv) Rosenmund Reduction
- (v) Hell Volhard Zelinsky Reaction

33. (a) Define the following terms :

(i) Molar conductivity (Λ_m)

(ii) Secondary batteries

(iii) Fuel cell

(b) State the following laws :

(i) Faraday first law of electrolysis

(ii) Kohlrausch's law of independent migration of ions

OR

(a) What type of a battery is the lead storage battery? Write the anode and the cathode reactions and the overall reaction occurring in a lead storage battery when current is drawn from it

(b) In the button cell, widely used in watches, the following reaction takes place

$Zn_{(s)} + Ag_2O_{(s)} \rightarrow Zn^{2+}_{(aq)} + 2Ag_{(s)} + 2OH^{-}O_{(aq)}$

Determine E^0 and ΔG^0 for the reaction.

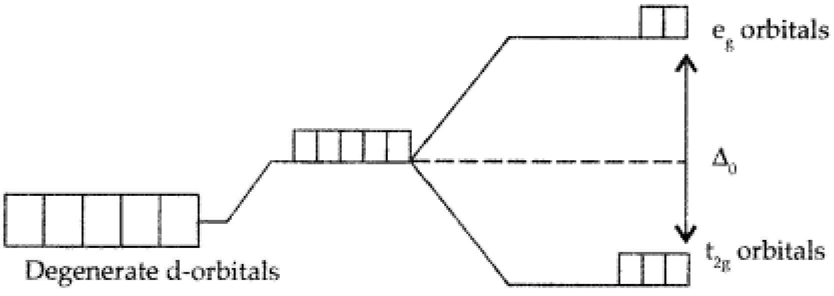
(Given $E^0 Ag^+/Ag = +0.80V$, $E^0 Zn^{2+}/Zn = -0.76$ V)

	SOLUTION
Q.NO.	**ANSWER**
1.	(c) increase 2 times
2.	(a) molecularity of reaction can be zero or a fraction.
3.	(a) It is a primary cell
4.	(c) IO_3^-
5.	(b) CuF_2
6.	(a) It can distinguish between strong and weak ligands
7.	(c) Chlorophyll
8.	(a) primary
9.	(c) $(C_6H_5CH_2)NH$
10.	(a) Ethanol<Water<Phenol
11.	(a) A
12.	(d) CH_3CHO
13.	(d) A is false but R is true
14.	(b) Both A and R are true but R is not the correct explanation of A.
15.	(c) A is true but R is false.
16.	(a) Both A and R are true and R is the correct explanation of A

17.	(a) for first order reaction half-life of X = 12 hours 2 days = 48 hours means 4 half lives , amount of X left = 1/16 of initial value half life of Y = 16 hours (½) 2 days = 48 hours means 3 half lives, amount left = 1/8 of initial value Ratio of X:Y = 1:2 (½) (b) b. $mol^{1/2}L^{-1/2}s^{-1}$ as Rate = k $[P]^{1/2}$
18.	I. Both geometrical (cis and trans) and optical isomers for cis. II. Two optical isomers III. Geometrical, ionization and linkage isomers. IV. Geometrical (cis and trans)
19.	1 . KCN is predominantly ionic and provides cyanide ions in solution. Although both carbon and nitrogen atoms are in a position to donate electron pairs, the attack takes place mainly through carbon atom and not through nitrogen atom since C—C bond is more stable than C—N bond. 2 . AgCN is mainly covalent in nature and nitrogen is free to donate electron pair forming isocyanides as the main product.
20.	(i) Acetaldehyde > Acetone > Methyl tert-butyl ketone > Di-tert-butyl ketone (ii) (CH3)2CHCOOH < CH3CH2CH2COOH < CH3 CH (Br) CH2 COOH < CH3CH2CH (Br) COOH
21.	(i) when glucose is treated with HI, it forms n-hexane. (ii) when glucose is treated with Bromine water, gluconic acid is formed. OR (a) Replication A sequence of bases on DNA is unique for a person and is the genetic material transferred to the individual from the parent which helps in the determination of paternity. (1) (b) During denaturation secondary and tertiary structures are destroyed but the primary structure remains intact. (1)
22.	(a) Yes, if the concentration of ZnSO4 in the two half-cell is different, the electrode potential will be different making the cell possible. (b) $\Lambda^0m\ (MgCl_2) = \lambda\ 0m\ (Mg^{2+}) + 2\ \lambda\ 0m\ (Cl^-)$ 258.6 = 106 + 2 λ ^{0}m (Cl-) λ ^{0}m (Cl^-) = 76.3 Scm2mol–1 (c) cell constant G* = k x R k= G*/R = 0.146/ 1000 = 1.46 x 10^{-4} Scm^{-1}

23.	$\Delta T_f = i K_f \times \frac{W_B}{M_B} \times \frac{1000}{W_A}$ ⇒ $1.62 = i \times 4.9 \times \frac{3.9}{122} \times \frac{1000}{49}$ ⇒ $i = \frac{1.62 \times 122 \times 49}{4.9 \times 3.9 \times 1000} = \frac{162 \times 122 \times 10 \times 10}{100 \times 39 \times 1000}$ ⇒ $i = \frac{19764}{39000} = 0.507$ The solute is associated because $i < 1$.
24.	(a) K = 2.303*t*log[A0][A] Substituting the values, we get $K = \frac{2.303}{20} \log \frac{0.400}{0.289}$ or $K = \frac{2.303}{20} \log 1.3840$ or $K = 0.11515 \log 1.3840$ ∴ **$K = 0.0163 \text{ min}^{-1}$** (*b*) $K = \frac{2.303}{t} \log \frac{[A_0]}{[A]}$ ∴ $0.0163 = \frac{2.303}{100} \log \frac{0.400}{[A]}$ or $\log \frac{0.400}{[A]} = \frac{0.0163 \times 100}{2.303}$ or $\log \frac{0.400}{[A]} = 7.0777$ ∴ **$[A] = 0.078 \text{ M}$** (*c*) Initial Rate, $R = K [N_2O_5]$ $= 0.0163 \text{ min}^{-1} (0.400 \text{ M})$ **$= 0.00652 \text{ M min}^{-1}$**

25. Crystal field splitting: It is the splitting of the degenerate energy levels due to the presence of ligands. When ligand approaches a transition metal ion, the degenerate d-orbitals split into two sets, one with lower energy and the other with higher energy. This is known as crystal field splitting and the difference between the lower energy set and higher energy set is known as crystal field splitting energy (CFSE)



Splitting of d-orbitals in an octahedral complex

Example : $3d^5$ of Mn^{2+}

(ii) Linkage isomerism: When more than one atom in an ambidentate ligand is linked with central metal ion to form two types of complexes, then the formed isomers are called linkage isomers and the phenomenon is called linkage isomerism.

$[Cr(H_2O)_5(NCS)]^{2+}$ Pentaaquathiocyanate chromium (III) ion

$[Cr(H_2O)_5(NCS)]^{2+}$

Pentaaquaisothiocyanate chromium (III) ion

(iii) Ambidentate ligand: The monodentate ligands with more than one coordinating atoms is known as ambidentate ligand. Monodentate ligands have only one atom capable of binding to a central metal atom or ion. For example, the nitrate ion NO_2^- can bind to the central metal atom/ion at either the nitrogen atom or one of the oxygen atoms.

Example : — SCN thiocyanate, — NCS isothiocyanate

OR

(a) $[Cr(en)_2(OH)_2]Cl$ or $[Cr(H_2NCH_2CH_2NH_2)_2(OH)_2]Cl$ (1)

(b) No, ionization isomers are possible by exchange of ligand with counter ion only and not by exchange of central metal ion. (1)

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<td>(c) The central atom is electron pair acceptor so it is a Lewis acid. (1)</td>
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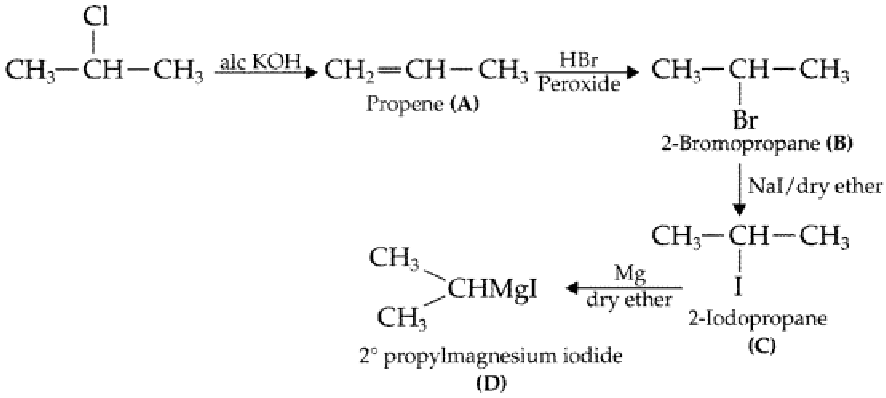
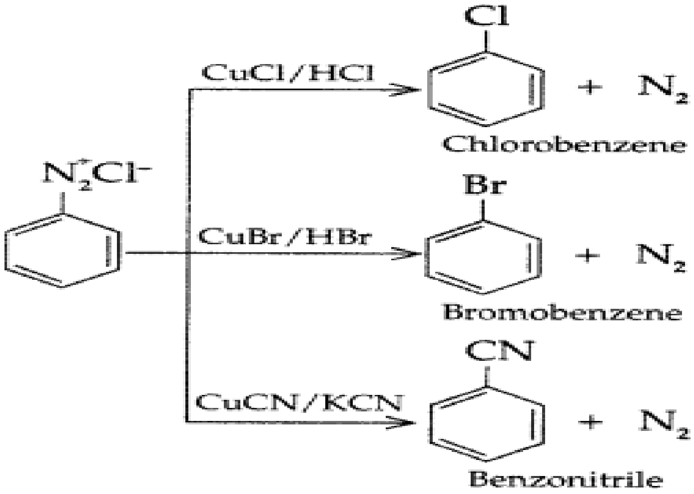
(*a*)



(b) Sandmeyer's reaction: The substitution of diazo group of benzene diazonium chloride by Chloro, Bromo and Cyano group with the help of solution of CuCl dissolved in HC1, CuBr/HBr and CuCN/KCN respectively is known as Sandmeyer's reaction.



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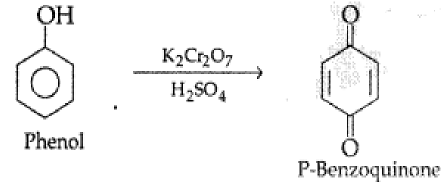
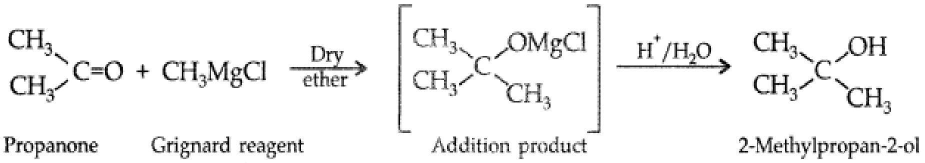
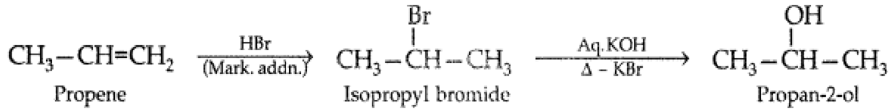
27.	(i) Phenol to benzoquinone  **(*ii*) Propanone to 2-methylpropan-2-ol**  **(*iii*) Propene to propan-2-ol** 
28.	(i) Higher the pK_b value, lower will be the basicity therefore aniline is less basic than methylamine because the lone pair of electrons on nitrogen atom gets delocalized over the benzene ring are unavailable for protonation due to resonance in aniline which is absent in case of alkylamine. (ii) Ethylamine is soluble in water due to its capability to form H-bonds with water while aniline is insoluble in water due to larger hydrocarbon part which tends to retard the formation of H-bonds. (iii) Due to presence of two H-atoms on N-atom of primary amines, they undergo extensive intermolecular H-bonding while tertiary amines due to the absence of a H-atom on the N-atom, do not undergo H- bonding. As a result, primary amines have higher boiling points than 3° amines.
29.	a. AlCl3 b. By depression of freezing point (it lowers freezing point of water less than 0 c. ΔTf = i kf m 2=1x 8 x (2.8/Mb)x1000/100 =8x2.8x10/Mb Mb=8x28/2=8x14=112g/mol **OR** ΔTb = i kb m 0.21= 1x 2.52x2x1000/100xMb Mb= 2.52x2x10/0.21=240 g/mol

30.	a) It is because vitamin B and C are water soluble and excreted through urine. So it should be taken regularly. b) Vitamin B12. It is neither fat nor water soluble c) i) It consists of vitamin B1, B2, B3, B5, B6, B7, B9 and B12. ii) Vitamin E deficiency leads to dry skin and loss of reproductive power. Its source is oils like cotton seed oil. **OR** c) i) Vitamin K. It is present in green leafy vegetables. ii) Fiber helps in digestion and helps to reduce weight.
31.	(a) Both Ti3+ and Cu2+ have 1 unpaired electron, so the magnetic moment for both will be 1.73 BM (b) Zn, it has a more negative electrode potential so will corrode itself in place of iron. (c) Mn+ has 3d54s1 configuration and configuration of Cr+ is 3d5, therefore, ionisation enthalpy of Mn+ is lower than Cr+. (d) Sc and Zn both form colourless compound and are diamagnetic. (e) The decrease in the atomic and ionic radii with increase in atomic number of actinoids due to poor shielding effect of 5f electron. (f) their ability to adopt multiple oxidation states and to form complexes (any correct reason) (g)$2MnO_4{-}{+}16H^{+}+10I^{-}\rightarrow 2Mn^{2+}+8H_2O+5I_2$
32.	Correct definition with one example in each case.

33.

(a) (i) Molar conductivity Λ_m): Molar conductivity can be defined as the conductance of the volume V of electrolytic solution kept between two electrodes of a conducting cell at distance of unit length but having area of cross section large enough to accomodate sufficient volume of solution that contains one mole of the electrolyte.

$\Lambda_m = KV$

(ii) Secondary batteries: Those cells which can be recharged on passing electric current through them in opposite direction and can be used again are called secondary batteries, e.g. Lead-acid storage cell.

(iii) Fuel cell : Galvanic cells that are designed to convert the chemical energy of combustion of fuels like hydrogen, methane etc. into electrical energy are called fuel cells, e.g. $H_2 - O_2$ fuel cell

(b) (i) Faraday first law of electrolysis : According to this law the mass of the substance deposited or liberated at any electrode during electrolysis is directly proportional to the quantity of charge passed through the electrolyte.

$\omega \propto Q$ ($\because Q = I \times t$)

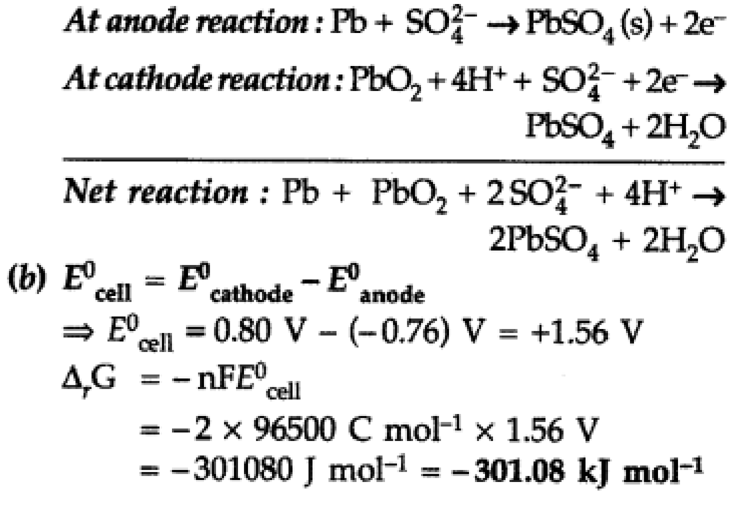
$\omega = = ZIt$

(ii) Kohlrausch's law of independent migration of ions : According to this law limiting molar conductivity of an electrolyte can be represented as the sum of the limiting ionic conductivities of the cation and the anion each multiplied with the number of ions present in one formula unit of electrolyte.

$\Lambda^o m$ for $A xB y = x\lambda^o_+ + y\lambda^o_-$

OR

It is a secondary cell.



At anode reaction : $Pb + SO_4^{2-} \rightarrow PbSO_4(s) + 2e^-$

At cathode reaction : $PbO_2 + 4H^+ + SO_4^{2-} + 2e^- \rightarrow PbSO_4 + 2H_2O$

Net reaction : $Pb + PbO_2 + 2SO_4^{2-} + 4H^+ \rightarrow 2PbSO_4 + 2H_2O$

(*b*) $E^0_{cell} = E^0_{cathode} - E^0_{anode}$

$\Rightarrow E^0_{cell} = 0.80\ V - (-0.76)\ V = +1.56\ V$

$\Delta_r G = -nFE^0_{cell}$

$= -2 \times 96500\ C\ mol^{-1} \times 1.56\ V$

$= -301080\ J\ mol^{-1} = \mathbf{-301.08\ kJ\ mol^{-1}}$