

CHEMISTRY

Time Allowed : 3 Hours

Maximum Marks : 70

General Instructions :

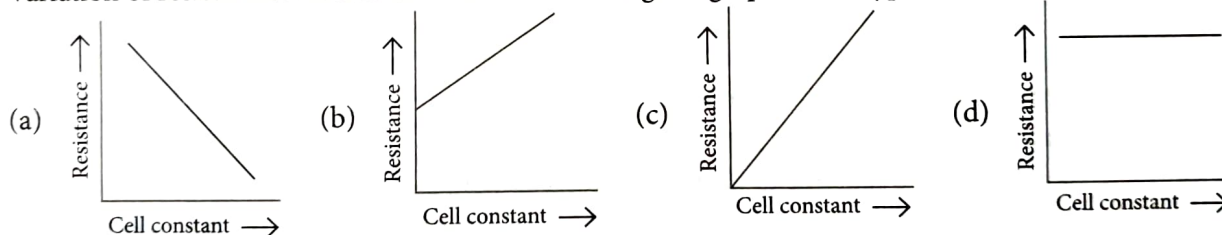
Read the following instructions carefully.

- There are 33 questions in this question paper with internal choice.
- SECTION A consists of 16 multiple-choice questions carrying 1 mark each.
- SECTION B consists of 5 short answer questions carrying 2 marks each.
- SECTION C consists of 7 short answer questions carrying 3 marks each.
- SECTION D consists of 2 case-based questions carrying 4 marks each.
- SECTION E consists of 3 long answer questions carrying 5 marks each.
- All questions are compulsory.
- Use of log tables and calculators is not allowed.

SECTION A

The following questions are multiple-choice questions with one correct answer. Each question carries 1 mark. There is no internal choice in this section.

1. Variation of resistance with increase in cell constant gives graph of the type

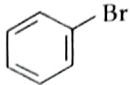


2. Match the reactions given in column I with the type of reaction mentioned in column II and mark the appropriate choice.

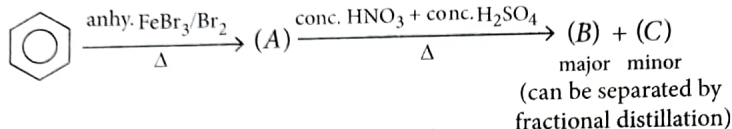
Column I		Column II	
(A)	$\text{CH}_3-\underset{\text{Br}}{\text{CH}}-\underset{\text{CH}_3}{\text{CH}}-\text{CH}_3 + \text{C}_2\text{H}_5\text{ONa} \longrightarrow \text{CH}_3\text{CH}_2-\overset{\text{OC}_2\text{H}_5}{\underset{\text{CH}_3}{\text{C}}}-\text{CH}_3$	(i)	β -elimination
(B)	$\text{CH}_3\text{CH}_2\text{Br} \xrightarrow{\text{AgOH}} \text{CH}_3\text{CH}_2\text{OH}$	(ii)	$\text{S}_{\text{N}}1$ nucleophilic substitution
(C)	$\text{CH}_3\text{CH}=\text{CH}_2 + \text{HBr} \xrightarrow{\text{Peroxide}} \text{CH}_3\text{CH}_2\text{CH}_2\text{Br}$	(iii)	$\text{S}_{\text{N}}2$ nucleophilic substitution
(D)	$\text{CH}_3-\text{CH}_2\text{Br} + \text{alc. KOH} \longrightarrow \text{CH}_2=\text{CH}_2$	(iv)	Kharasch effect

- (A) \rightarrow (iv), (B) \rightarrow (i), (C) \rightarrow (ii), (D) \rightarrow (iii)
- (A) \rightarrow (ii), (B) \rightarrow (iii), (C) \rightarrow (iv), (D) \rightarrow (i)
- (A) \rightarrow (i), (B) \rightarrow (ii), (C) \rightarrow (iv), (D) \rightarrow (iii)
- (A) \rightarrow (iii), (B) \rightarrow (i), (C) \rightarrow (ii), (D) \rightarrow (iv)

3. Which is not a pyrimidine base?
- (a) Uracil (b) Thymine
(c) Cytosine (d) Guanine

4. The final product of the following reaction is  $\xrightarrow[\text{(iii) H}_2\text{O}]{\text{(i) Mg, (ii) CO}_2}$
- (a) benzaldehyde (b) benzene
(c) benzoic acid (d) phenol.

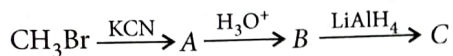
5. The final products B and C formed in the following sequence of reactions,



are respectively

- (a) both bromobenzene
(b) *o*-bromonitrobenzene and *p*-bromonitrobenzene
(c) *m*-bromonitrobenzene and *p*-bromonitrobenzene
(d) *p*-bromonitrobenzene and *o*-bromonitrobenzene.
6. Arrange the oxides of manganese according to increasing acidic strength.
- (a) $\text{MnO} < \text{Mn}_3\text{O}_4 < \text{Mn}_2\text{O}_3 < \text{MnO}_2 < \text{Mn}_2\text{O}_7$
(b) $\text{Mn}_2\text{O}_7 < \text{MnO}_2 < \text{Mn}_2\text{O}_3 < \text{Mn}_3\text{O}_4 < \text{MnO}$
(c) $\text{MnO}_2 < \text{Mn}_2\text{O}_7 < \text{Mn}_3\text{O}_4 < \text{Mn}_2\text{O}_3 < \text{MnO}$
(d) $\text{Mn}_3\text{O}_4 < \text{Mn}_2\text{O}_3 < \text{Mn}_2\text{O}_7 < \text{MnO}_2 < \text{MnO}$
7. Which of the following statements is in accordance with the Arrhenius equation?
- (a) Rate of a reaction decrease with increase in temperature.
(b) Rate of reaction does not change with increase in activation energy.
(c) Rate constant decreases exponentially with increase in temperature.
(d) Rate of a reaction increases with decrease in activation energy.
8. An organic compound 'A' having molecular formula, $\text{C}_2\text{H}_3\text{N}$ on reduction gave another compound 'B'. Upon treatment with nitrous acid 'B' gave ethyl alcohol. On warming with chloroform and alcoholic KOH, 'B' forms an offensive smelling compound 'C'. The compound 'C' is
- (a) $\text{CH}_3\text{CH}_2\text{NH}_2$ (b) $\text{CH}_3\text{CH}_2\text{N}\equiv\text{C}$
(c) $\text{CH}_3\text{C}\equiv\text{N}$ (d) $\text{CH}_3\text{CH}_2\text{OH}$
9. Consider the following set of reactions :
- $$\text{C}_6\text{H}_6 \xrightarrow[350\text{ K}]{\text{H}_2\text{SO}_4} \text{A} \xrightarrow[\text{H}^+/\text{H}_2\text{O}]{\text{Alkali}} \text{B} \xrightarrow[\text{H}_2\text{O}]{\text{Br}_2} \text{C}$$
- The final product, C is
- (a) *o*-bromophenol (b) *p*-bromophenol
(c) *m*-bromophenol (d) 2, 4, 6-tribromophenol.
10. The rate constant of n^{th} order reaction has units
- (a) $\text{L}^{1-n} \text{mol}^{n-1} \text{s}^{-1}$ (b) $\text{mol}^{1-n} \text{L}^{1-n} \text{s}^{-1}$
(c) $\text{mol}^{1-n} \text{L}^{n-1} \text{s}^{-1}$ (d) none of these.

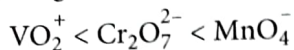
11. In the following sequence of reactions,



The end product C is

- (a) methane (b) ethyl alcohol
(c) acetone (d) acetaldehyde.

12. Following order is observed in oxidising power of certain ions:



The reason for this increasing order of oxidising power is

- (a) increasing stability of the lower species to which they are reduced
(b) increasing stability of the higher species to which they are oxidised
(c) increasing stability of the higher species to which they are reduced
(d) increasing stability of the lower species to which they are oxidised.

13. **Assertion (A)** : CH_3OCH_3 and $\text{C}_2\text{H}_5\text{OH}$ has comparable molecular weight but boiling point of $\text{C}_2\text{H}_5\text{OH}$ is more than dimethyl ether.

Reason (R) : $\text{C}_2\text{H}_5\text{OH}$ forms intermolecular H-bonding while CH_3OCH_3 forms intramolecular H-bonding.
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 (A)** : *p*-Chlorobenzoic acid is stronger acid than benzoic acid.

Reason (R) : Chlorine in aromatic compound has electron donating resonance (+R)-effect as well as -I effect.
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.

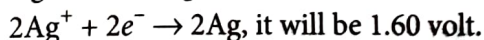
15. **Assertion (A)** : A solution of sucrose in water is dextrorotatory but on hydrolysis in presence of little hydrochloric acid, it becomes laevorotatory.

Reason (R) : Sucrose on hydrolysis gives unequal amounts of glucose and fructose as a result of which change in sign of rotation is observed.

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 (A)** : If standard reduction potential for the reaction,



Reason (R) : If concentration of Ag^+ ions is doubled, the standard electrode potential remains same.

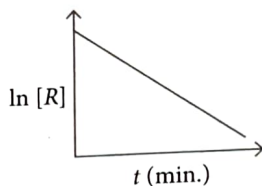
Select the most appropriate answer from the options given below:

- (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 two questions. The following questions are very short answer type and carry 2 marks each.

17. For a certain chemical reaction, variation in the concentration, $\ln[R]$ vs time (min.) plot is shown below:



For this reaction

- What is the order of the reaction?
- Give the relationship between k and $t_{1/2}$ of this reaction.

OR

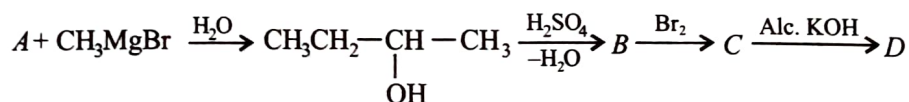
Write expression for rate constant of a zero order reaction and explain the terms involved. What is the unit of rate constant of a zero order reaction?

- What are the sign of ΔH and ΔV for a solution with positive deviation from ideal behaviour?
 - Osmotic pressure of 1 M KCl solution is higher than 1 M urea solution. Why?
- Why ethyl iodide undergoes S_N2 reaction faster than ethyl bromide?
 - Arrange each set of compounds in order of increasing boiling points.
Bromomethane, bromoform, chloromethane, dibromomethane.
- How will you convert the following (any 2) :
 - Aniline to chlorobenzene
 - Nitrobenzene to phenol
 - Aniline to benzoic acid
- Name two fat soluble vitamins, their sources and the diseases caused due to their deficiency in diet.
 - Write Haworth structure of α - and β -D-(-)-fructose.

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.

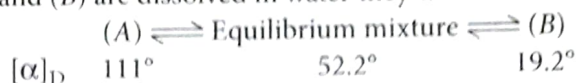
- The magnetic moment of a transition metal ion is found to be 3.87 BM. How many number of unpaired electrons are present in it ?
 - Cu(I) compounds undergo disproportionation reaction in aqueous solution. Why?
- Out of HCl and NaCl, which do you expect will have greater value for Λ_m° and why?
 - Write Nernst equation and explain the terms involved.
 - Define the terms specific conductance and molar conductivity.
- Convert aniline to :
 - Phenyl isocyanide
 - Benzonitrile
 - Sulphanilic acid
- Write the structural formulae of A, B, C and D in the following sequence of reactions.



- Give the plausible explanation for the following :
 - Glucose does not give 2,4-DNP test.
 - Starch and cellulose both contain glucose unit as monomer, yet they are structurally different.

OR

An optically active compound having molecular formula, $C_6H_{12}O_6$ is found in two isomeric forms (A) and (B) in nature. When (A) and (B) are dissolved in water they show the following equilibrium :



- (a) What are such isomers called?
 (b) Can they be called enantiomers? Justify your answer.
 (c) Draw the cyclic structure of isomer (A).
27. (a) Define the following terms :
 (i) Enantiomers (ii) Racemic mixture
 (b) Why is chlorobenzene resistant to nucleophilic substitution reaction ?
28. For the reaction : $2NO_{(g)} + Cl_{2(g)} \longrightarrow 2NOCl_{(g)}$ the following data were collected. All the measurements were taken at 263 K.

Exp. No.	Initial [NO](M)	Initial [Cl ₂] (M)	Initial rate of disapp. of Cl ₂ (M/min)
1.	0.15	0.15	0.60
2.	0.15	0.30	1.20
3.	0.30	0.15	2.40
4.	0.25	0.25	?

- (a) Write the expression for rate law.
 (b) Calculate the value of rate constant and specify its units.

SECTION D

The following questions are case-based questions. Each question has an internal choice and carries 4 (2+1+1) marks each. Read the passage carefully and answer the questions that follow.

29. Metal carbonyl is an example of coordination compounds in which carbon monoxide (CO) acts as ligand. These are also called homoleptic carbonyls. These compounds contain both σ and π character. Some carbonyls have metal-metal bonds. The reactivity of metal carbonyls is due to (i) the metal centre and (ii) the CO ligands. CO is capable of accepting an appreciable amount of electron density from the metal atom into their empty π or π^* orbitals. These types of ligands are called π -acceptor or π -acid ligands. These interactions increases the Δ_o value.
- (a) Which of the following can be reduced easily? Explain.
 $V(CO)_6$, $[Co(CO)_4]^-$, $Mo(CO)_6$, $Fe(CO)_5$
- (b) Out of $[Cr(CO)_6]$ and $[V(CO)_6]^-$, which has the lowest C - O bond order?

OR

What is the oxidation state of cobalt in $K[Co(CO)_4]$?

- (c) What is shape of deca carbonyl manganese ?
30. Kohlrausch's law states that, limiting molar conductivity *i.e.*, molar conductivity at infinite dilution on an electrolyte is the sum of ionic conductivities of cations and anions, each multiplied with the number of ions present in one formula unit of the electrolyte. We can say that each ion makes a definite contribution to the total molar conductivity of an electrolyte irrespective of the nature of the other ion. *e.g.*, for A_xB_y ,
 $\Lambda_m^\circ = x\lambda_{A^{x+}}^\circ + y\lambda_{B^{y-}}^\circ$; λ_m° for NaCl = $\lambda_{Na^+}^\circ + \lambda_{Cl^-}^\circ$
- (a) Calculate the degree of dissociation of acetic acid at 298 K, given that :
 $\Lambda_m(CH_3COOH) = 11.7 \text{ S cm}^2 \text{ mol}^{-1}$; $\Lambda_m(CH_3COO^-) = 49.9 \text{ S cm}^2 \text{ mol}^{-1}$; $\Lambda_m(H^+) = 349.1 \text{ S cm}^2 \text{ mol}^{-1}$
- (b) $\Lambda_{ClCH_2COONa}^\circ = 224 \text{ ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}$, $\Lambda_{NaCl}^\circ = 38.2 \text{ ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}$, $\Lambda_{HCl}^\circ = 203 \text{ ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}$,
 What is the value of Λ_{ClCH_2COOH} in $\text{ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}$?
- (i) 888.8 (ii) 388.8
 (iii) 204.2 (iv) 402.6

- (c) λ_m° for NH_4Cl , NaOH and NaCl are 130, 248 and $126.5 \text{ ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}$ respectively. The λ_m° of NH_4OH will be
- | | |
|-----------|------------|
| (i) 251.5 | (ii) 244.5 |
| (iii) 130 | (iv) 504.5 |

OR

What is the SI unit of conductivity?

- | | |
|----------------------|------------------------|
| (i) S m | (ii) S m^{-1} |
| (iii) S m^2 | (iv) S m^{-2} |

SECTION E

The following questions are long answer types and carry 5 marks each. All questions have an internal choice.

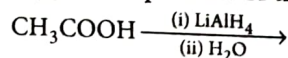
31. (a) Compare qualitatively the first and second ionisation potentials of copper and zinc. Explain the observation.
- (b) Deduce the structure of $[\text{NiCl}_4]^{2-}$ and $[\text{Ni}(\text{CN})_4]^{2-}$ considering the hybridisation of the metal ion. Calculate the magnetic moment (spin only) of the species.

OR

- (a) What happens when :
- (i) aqueous ammonia is added dropwise to a solution of copper sulphate till it is in excess.
 - (ii) CrCl_3 solution is treated with sodium hydroxide and then with hydrogen peroxide.
- (b) Nickel chloride, when treated with dimethylglyoxime in presence of ammonium hydroxide, a bright red precipitate is obtained. Answer the following.
- (i) Draw the structure of the complex showing H-bonds.
 - (ii) Give oxidation state of nickel and its hybridisation.
 - (iii) Predict the magnetic behaviour of the complex.
32. (a) Which type of deviation is shown by the solution formed by mixing cyclohexane and ethanol?
- (b) 18 g of glucose, $\text{C}_6\text{H}_{12}\text{O}_6$ is dissolved in 1 kg of water in a saucepan. At what temperature will the water boil? K_b for water is $0.52 \text{ K kg mol}^{-1}$.
- (c) A and B liquids on mixing produced a warm solution. Which type of deviation is there and why?

OR

- (a) Why is camphor preferred as a solvent in determination of depression in freezing point (ΔT_f)?
 - (b) Aquatic species are more comfortable in cold water rather than in warm water. Why?
 - (c) A 10% solution (by mass) of sucrose in water has freezing point of 269.15 K. Calculate the freezing point of 10% glucose in water, if freezing point of pure water is 273.15 K.
(Given : Molar mass of sucrose = 342 g mol^{-1} , molar mass of glucose = 180 g mol^{-1})
33. (a) Write the reaction and IUPAC name of the product formed when 2-methylpropanal (*iso*-butyraldehyde) is treated with ethyl magnesium bromide followed by hydrolysis.
- (b) (i) A mixture of *tert*-butyl alcohol and ethyl alcohol gives a good yield of a single ether. What ether is this likely to be? How do you account for this good yield?
- (ii) Suggest the product of the following reaction :



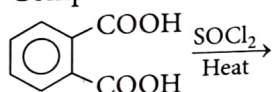
OR

- (a) A hydrocarbon (A) with molecular formula C_5H_{10} on ozonolysis gives two products (B) and (C). Both (B) and (C) give a yellow precipitate when heated with iodine in presence of NaOH while only (B) gives a silver mirror on reaction with Tollens' reagent.
- (i) Identify (A), (B) and (C).
 - (ii) Write the reaction of B with Tollens' reagent.
- (b) Illustrate with examples the limitations of Williamson's synthesis for the preparation of certain types of ethers.

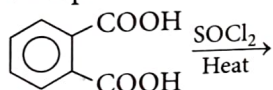
- (b) On the basis of E° values, O_2 gas should be liberated at anode but it is Cl_2 gas which is liberated in the electrolysis of aqueous NaCl. Give reason.

OR

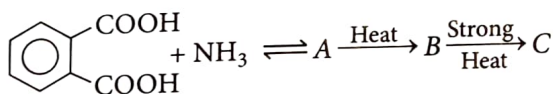
- (a) A steady current of 2 amperes was passed through two electrolytic cells X and Y connected in series containing electrolytes $FeSO_4$ and $ZnSO_4$ until 2.8 g of Fe is deposited at the cathode of cell X. How long did the current flow? Calculate the mass of Zn deposited at the cathode of cell Y. (Molar mass : Fe = 56 g mol⁻¹, Zn = 65.3 g mol⁻¹, 1 F = 96500 C mol⁻¹)
- (b) Why does silver nitrate solution becomes bluish when copper rod is placed in it?
33. (a) Give a chemical test to distinguish between the following :



- (b) Complete the following reaction :



- (c) Identify A, B and C in the following sequence:



OR

- (a) Give a chemical test to distinguish between ethanal and ethanoic acid.
- (b) Why is the α -hydrogen of aldehydes and ketones acidic in nature?
- (c) An organic compound 'A' with molecular formula $C_4H_8O_2$ undergoes acid hydrolysis to form two compounds 'B' and 'C'. Oxidation of C with acidified potassium permanganate also produces 'B'. Sodium salt of 'B' on heating with soda lime gives methane.
- (i) Identify 'A', 'B' and 'C'.
- (ii) Out of 'B' and 'C', which will have higher boiling point? Give reason.

1. (c): We know that the electrical resistance of electrolytic solutions is directly proportional to its length (l) and inversely proportional to its area of cross-section (A)

$$\text{i.e., } R \propto \frac{l}{A} \Rightarrow R = \rho \frac{l}{A}$$

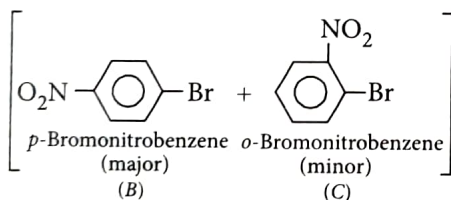
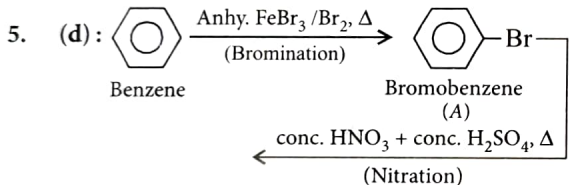
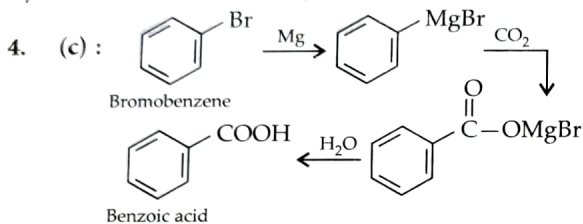
Comparing with $y = mx + c$.

The graph of R vs (l/A) will be a straight line starting from the origin with slope ρ .

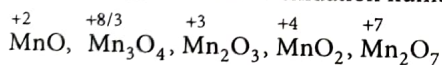
2. (b)

3. (d): Purines: Adenine (A) and Guanine (G)

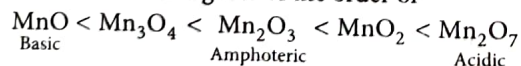
Pyrimidines: Uracil (U), Thymine (T) and Cytosine (C)



6. (a): Acidic strength of oxides of transition metals increases with increase in oxidation number.

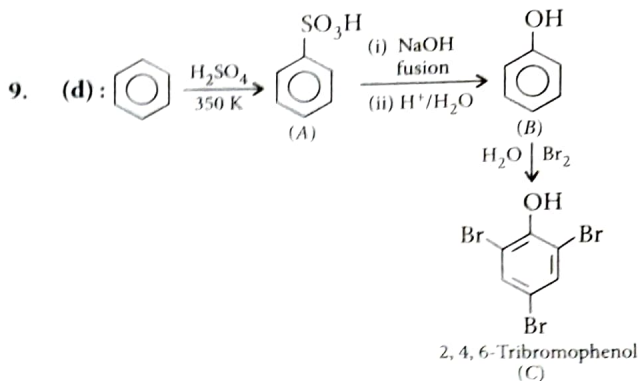
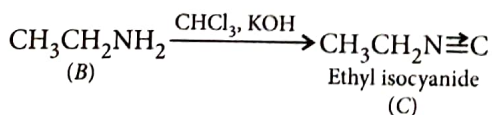
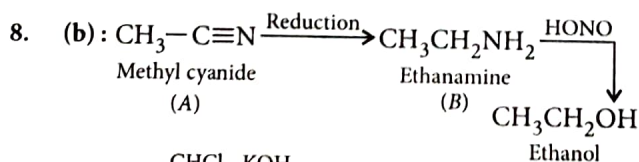


Hence acidic strength is of the order of



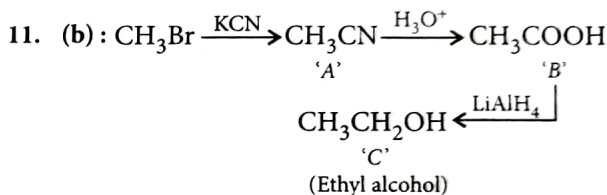
7. (d): According to Arrhenius equation, $k = Ae^{-E_a/RT}$

On increasing temperature and decreasing activation energy (E_a), rate of reaction increases.



10. (c): For n^{th} order reaction; $r = k[A]^n$

$$\therefore k = \frac{r}{[A]^n} = \frac{\text{mol L}^{-1} \text{s}^{-1}}{(\text{mol L}^{-1})^n} = \text{mol}^{1-n} \text{L}^{n-1} \text{s}^{-1}$$



12. (a): The increasing order of oxidising power is due to increasing stability of the lower species to which they are reduced.

13. (c): Due to the presence of hydroxyl group (-OH), there is extensive hydrogen bonding between the ethanol molecules ($\text{C}_2\text{H}_5\text{OH}$). But there is no such hydrogen bonding in dimethyl ether (due to absence of -OH group). So, boiling point of dimethyl ether is much lower than ethanol.

14. (b): Chlorine has both +R effect and -I effect but -I effect outweighs +R effect. -I effect of chlorine atom disperses the -ve charge on the benzoate anion and thus, makes *p*-chlorobenzoate anion more stable. As a result, *p*-chlorobenzoic acid is a stronger acid than benzoic acid.

15. (c): Sucrose on hydrolysis gives equal amount of glucose and fructose. Since glucose has less positive and fructose has more negative magnitude of rotation, therefore change in sign of rotation is observed.

16. (d): Standard reduction potential of an electrode has a fixed value.

17. (a) Reaction is of first order.

(b) For a first order reaction, $t_{1/2} = \frac{0.693}{k}$

OR

Expression for rate constant of a zero order reaction is

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

where $[R]_0$ is the initial concentration, $[R]$ is the final concentration and t is time.

k = proportionality constant called rate constant of reaction.

Unit of rate constant for zero order reaction can be determined by,

$$k = \frac{\text{Rate}}{[A]^x [B]^y}$$

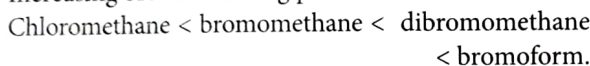
x and y are zero for zero order reaction. or $k = \text{mol L}^{-1} \text{s}^{-1}$

18. (a) $\Delta H_{\text{mixing}} = +ve$, $\Delta V_{\text{mixing}} = +ve$

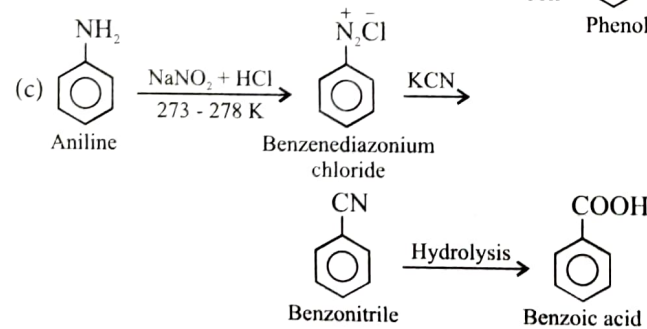
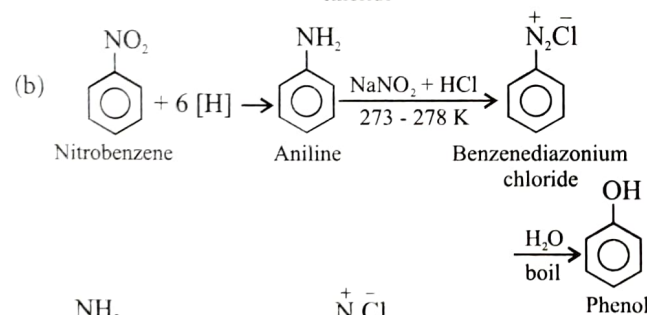
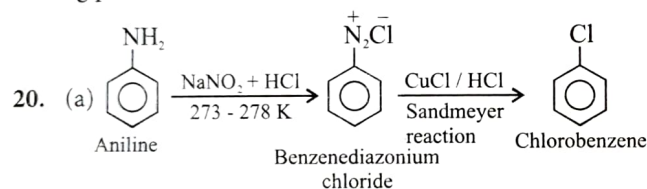
(b) KCl is an electrolyte, it undergoes dissociation in solution, hence number of particles increases. Urea is non-electrolyte.

19. (a) Iodide is a better leaving group because of its larger size than bromide, therefore, ethyl iodide undergoes S_N2 reaction faster than ethyl bromide.

(b) Increasing order of boiling points :

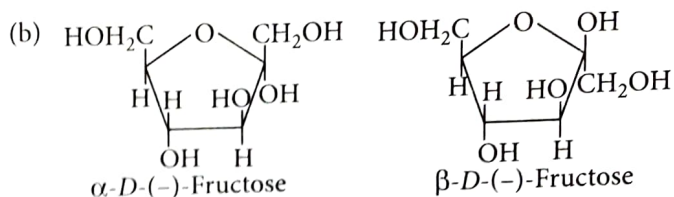


Boiling point increases with increasing molecular mass.



21. (a) Fat soluble vitamins are vitamins A and D.

Name of vitamins	Sources	Deficiency diseases
Vitamin A	Fish liver oil, carrots, butter, milk	Night blindness
Vitamin D	Fish and egg yolk	Rickets and osteomalacia



22. (a) Magnetic moment, $\mu_{\text{eff}} = 3.87$ B.M. corresponds to the number of unpaired electrons, $n = 3$ by applying the formula.

$$\mu_{\text{eff}} = \sqrt{n(n+2)} \text{ B.M.}$$

For $n = 1$, $\mu = 1.73$ B.M., for $n = 2$, $\mu = 2.83$ B.M.

For $n = 3$, $\mu = 3.87$ B.M. and so on.

(b) Cu(I) compounds are unstable in aqueous solution hence undergo disproportionation to yield more stable Cu^{2+} .



23. (a) HCl. Because H^+ ions are smaller than Na^+ ions and hence H^+ ions have greater ionic mobility than Na^+ ions.

(b) For a redox reaction,

$$E_{\text{cell}} = E_{\text{cell}}^{\circ} - \frac{0.0591}{n} \log \frac{[\text{Oxidised state}]}{[\text{Reduced state}]}$$

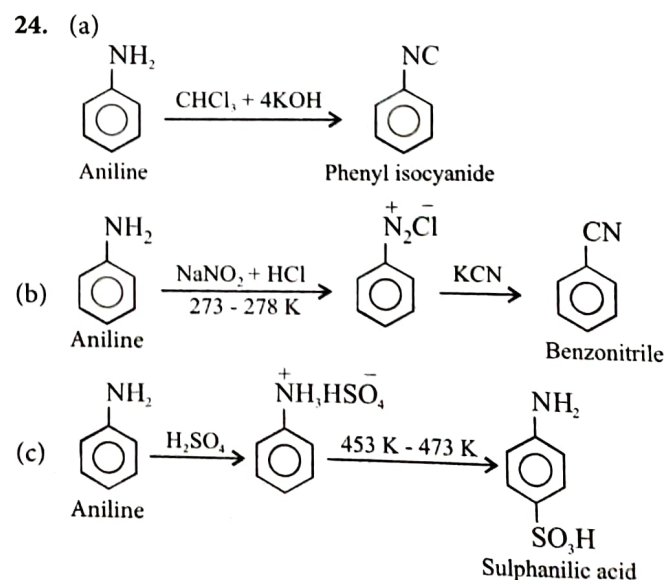
n = number of electrons involved, E_{cell}° is the standard electrode potential of cell, E_{cell} is electrode potential under operating condition.

(c) Specific conductance : It is the conductance due to ions present in 1 cm^3 of electrolytic solution.

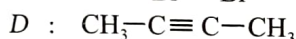
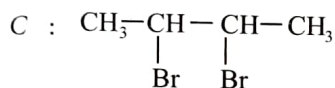
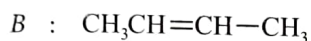
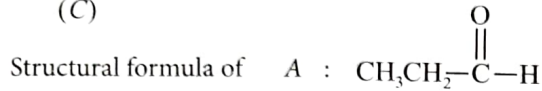
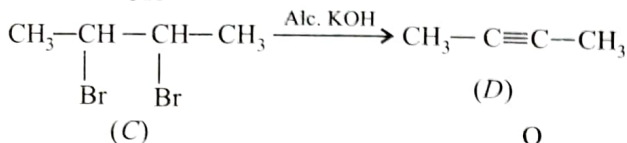
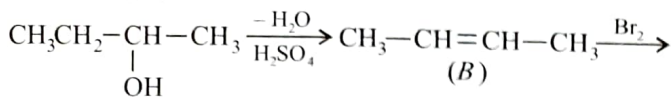
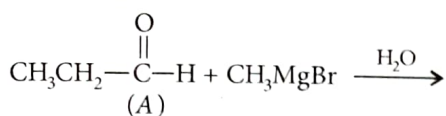
Molar Conductivity : Molar conductivity of a solution at a volume V is the conductance of all the ions produced from one mole of the electrolyte dissolved in $V \text{ cm}^3$ of the solution when the electrodes are one cm apart and the area of the electrodes is so large that the whole solution is contained between them.

$$\Lambda_m = \kappa V$$

Its units are $\text{S cm}^2 \text{ mol}^{-1}$.



25. The given reaction will be as :



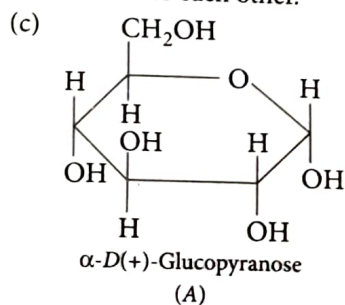
26. (a) Actually, glucose exists in the cyclic hemiacetal form with only a small amount (< 0.05%) of the open chain form. Since, the concentration of the open chain form is low and its reaction with 2,4-DNP is reversible, therefore, formation of 2,4-DNP derivative cannot disturb the equilibrium to regenerate more of the open chain form from the cyclic hemiacetal form and hence, does not give this test.

(b) The basic structural difference between starch and cellulose is of linkage between the glucose units. In starch, there is α -D-glycosidic linkage. Both the components of starch-amylose and amylopectin are polymers of α -D-glucose. On the other hand, cellulose is a linear polymer of β -D-glucose in which C₁ of one glucose unit is connected to C₄ of the other through β -D-glycosidic linkage.

OR

(a) These are called anomers.

(b) No, they are not enantiomers because this pair of stereoisomers are superimposable to each other except at C₁. Configuration of these isomers differ at C₁ hence they are anomers to each other.

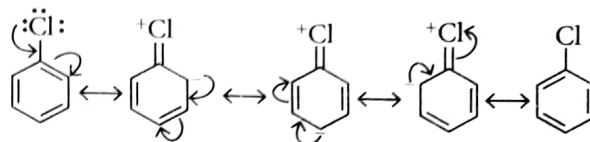


27. (a) (i) The stereoisomers related to each other as non-superimposable mirror images are called enantiomers.

(ii) A mixture containing two enantiomers in equal proportions will have zero optical rotation as the rotation due to one isomer will be cancelled by the rotation due to other isomer. Such a mixture is known as racemic mixture.

(b) Haloarenes are much less reactive than haloalkanes towards nucleophilic substitution reactions due to the following reasons.

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



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, are less reactive towards nucleophilic substitution reaction.

(ii) In haloarenes, halogen is attached to sp^2 -hybridised carbon while in haloalkanes, halogen is attached to sp^3 -hybridised carbon.

28. Given reaction : $2\text{NO}_{(g)} + \text{Cl}_{2(g)} \longrightarrow 2\text{NOCl}_{(g)}$

Exp. No.	Initial [NO] (M)	Initial [Cl ₂] (M)	Initial rate of disapp. 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) Let rate of this reaction $r = k[\text{NO}]^m[\text{Cl}_2]^n$

$$\text{then } \frac{r_1}{r_2} = \frac{0.60}{1.20} = \frac{k(0.15)^m(0.15)^n}{k(0.15)^m(0.30)^n}$$

$$\text{or } \frac{1}{2} = \left(\frac{1}{2}\right)^n \Rightarrow n=1$$

$$\text{Again from } \frac{r_2}{r_3} = \frac{1.20}{2.40} = \frac{k(0.15)^m(0.30)^1}{k(0.30)^m(0.15)^1}$$

$$\text{or } \frac{1}{2} = \left(\frac{1}{2}\right)^m \cdot \frac{2}{1} \text{ or } \frac{1}{4} = \left(\frac{1}{2}\right)^m \Rightarrow m=2$$

Hence, expression for rate law is

$$r = k[\text{NO}]^2 [\text{Cl}_2]^1$$

(b) Substituting the values in experiment (1), $0.60 \text{ M min}^{-1} = k(0.15 \text{ M})^2 (0.15 \text{ M})^1$

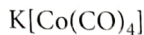
$$\text{or } k = \frac{0.60 \text{ M min}^{-1}}{0.0225 \times 0.15 \text{ M}^3} = 177.77 \text{ M}^{-2} \text{ min}^{-1}$$

29. (a) $\text{V}(\text{CO})_6$ can be easily reduced to $[\text{V}(\text{CO})_6]^-$.

$\text{V}(\text{CO})_6$ has a total of 17 bonding electrons, hence it is very reactive and unstable. $[\text{V}(\text{CO})_6]^-$ on the other hand has complete set of 18 bonding electrons as an electron is added into the bonding orbital when $\text{V}(\text{CO})_6$ gets reduced to $[\text{V}(\text{CO})_6]^-$. All others have 18 bonding electrons.

(b) In $[\text{V}(\text{CO})_6]^-$, the anionic carbonyl complex can delocalise more electron density to antibonding π -orbital ($d\pi$ - $p\pi$ back bonding) of CO and thus lowers the bond order.

OR



$+1 + (x) + 4(0) = 0$ or $x = -1$

(c) $\text{Mn}_2(\text{CO})_{10}$ is made up of two square pyramidal $\text{Mn}(\text{CO})_5$ units joined by Mn - Mn bond.

30. (a) Degree of dissociation, $\alpha = \frac{\Lambda_m}{\Lambda_m^\circ}$
 $= \frac{11.7 \text{ S cm}^2 \text{ mol}^{-1}}{(49.9 + 349.1) \text{ S cm}^2 \text{ mol}^{-1}} = \frac{11.7}{399} = 3 \times 10^{-2}$

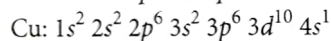
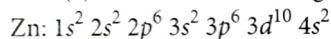
(b) (ii): $\Lambda_{\text{CICH}_2\text{COOH}}^\circ = \Lambda_{\text{CICH}_2\text{COONa}}^\circ + \Lambda_{\text{HCl}}^\circ - \Lambda_{\text{NaCl}}^\circ$
 $224 + 203 - 38.2 = 388.8 \text{ ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}$

(c) (i): $\Lambda_{m(\text{NH}_4\text{OH})}^\circ = \Lambda_{m(\text{NH}_4\text{Cl})}^\circ + \Lambda_{m(\text{NaOH})}^\circ - \Lambda_{m(\text{NaCl})}^\circ$
 $= 130 + 248 - 126.5 = 251.5 \text{ ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}$

OR

(ii): SI units of conductivity is S m^{-1}

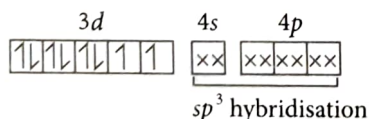
31. (a) The electronic configuration of Zn and Cu are:



From the above configuration it is clear that first ionisation energy of Zn is greater than that of Cu (because of $4s^2$ and $4s^1$ configuration of Zn and Cu respectively). More energy is needed to remove an electron of $4s^2$ than that of $4s^1$.

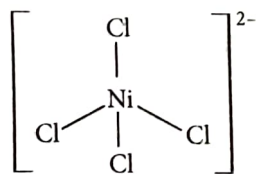
The second I.E. of Cu is higher than that of Zn because for Cu^{2+} the configuration is $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10}$ and for Zn^+ the configuration is $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^1$, it is easier to remove $4s^1$ electron of Zn^+ than a $3d$ -electron from $3d^{10}$ (stable configuration).

(b) Cl^- is a weak field ligand and so it is not in a position to pair the electrons in Ni^{2+} , so in $[\text{NiCl}_4]^{2-}$ we have



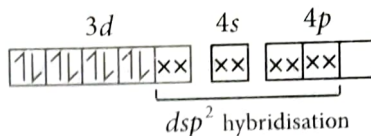
$[\text{Ni}^{2+}$ is $3d^8$]

Because of sp^3 hybridisation, it is tetrahedral.

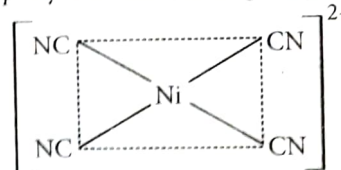


Magnetic moment of $[\text{NiCl}_4]^{2-} = \sqrt{2(2+2)} \quad [\because n=2]$
 $= \sqrt{2 \times 4} = \sqrt{8}$ or 2.83 B.M.

In $[\text{Ni}(\text{CN})_4]^{2-}$, CN^- is a strong field ligand and in this case pairing of electrons occurs in Ni^{2+} .

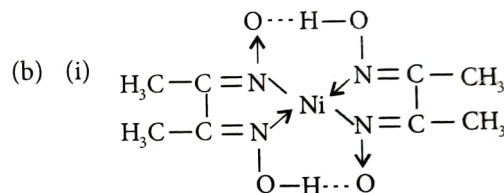
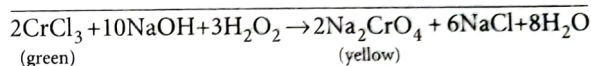
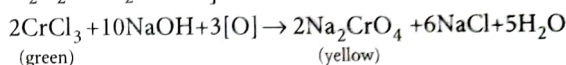
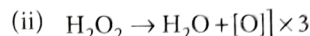
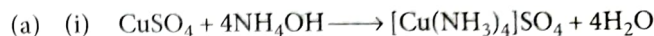


Because of dsp^2 hybridisation it is square planar.



Magnetic moment of $[\text{Ni}(\text{CN})_4]^{2-}$
 $= \sqrt{0(0+2)} = 0.0 \text{ B.M.} \quad [\because n=0]$

OR



Bis(dimethylglyoximate)nickel(II)

(ii) Charge on Ni in the complex is +2. Hybridisation involved is dsp^2 .

(iii) Since, in Ni^{2+} , there is no unpaired electron, so the complex is diamagnetic.

32. (a) Hydrogen bonds exist among the molecules of ethanol (i.e., strong forces). When cyclohexane is added to ethanol, the cyclohexane molecule will come in between the ethanol molecules and disturb the hydrogen bondings. The forces between ethanol and cyclohexane will be weaker than the H-bonding, hence there will be positive deviation.

(b) $\Delta T_b = K_b \times \frac{W_B}{M_B} \times \frac{1000}{W_A}$

Given : Mol. wt. of glucose, $W_B = 18 \text{ g}$

Mol. wt. of glucose, $M_B = 180 \text{ g}$

Wt. of solvent = 1 kg = 1000 g, $K_b = 0.52 \text{ K kg mol}^{-1}$

$\Delta T_b = 0.52 \times \frac{18}{180} \times \frac{1000}{1000} = 0.052 \text{ K}$

The boiling point of water will become

$373.15 + 0.052 = 373.202 \text{ K}$.

(c) Negative type of deviation is present. In negative deviation the solute-solute ($A-A$) interaction and solvent-solvent ($B-B$) interaction will be weaker than solute-solvent ($A-B$) interaction. Since, the new forces are stronger, therefore, the heat is evolved and solution becomes warm.

OR

(a) Camphor has very high molal depression constant ($K_f = 39.70 \text{ K kg mol}^{-1}$) therefore, depression in freezing point will be large even when small quantity of a solute is added. This would be easily measurable even by an ordinary thermometer.

(b) Aquatic species need dissolved oxygen for breathing. As the solubility of gas, e.g., O_2 decreases with rise in temperature, less oxygen is available in warm water. Hence, they feel more comfortable in cold water as more dissolved oxygen is available.

(c) Molality (m) of sucrose solution

$$= \frac{w \times 1000}{M \times \text{Mass of solvent}} = \frac{10}{342} \times \frac{1000}{90} = 0.325 \text{ m}$$

$$\Delta T_f \text{ for sucrose solution} = T_f^\circ - T_f = (273.15 - 269.15)$$

$$\Delta T_f = 4 \text{ K}$$

$$\therefore \Delta T_f = K_f \times m$$

$$\therefore K_f = \frac{\Delta T_f}{m} = \frac{4 \text{ K}}{0.325 \text{ m}} = 12.308 \text{ K/m}$$

$$\text{Molality of glucose solution} = \frac{10}{180} \times \frac{1000}{90} = 0.617 \text{ m}$$

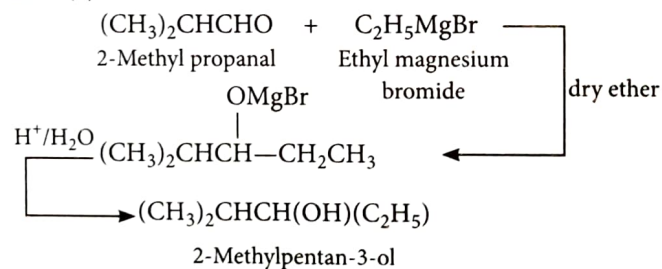
$$\Delta T_f = K_f \times m$$

$$\therefore \Delta T_f = 12.308 \text{ K/m} \times 0.617 \text{ m} = 7.6 \text{ K}$$

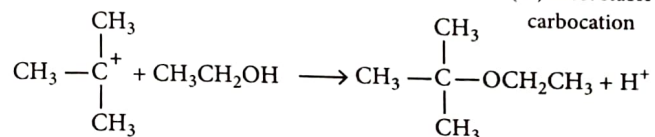
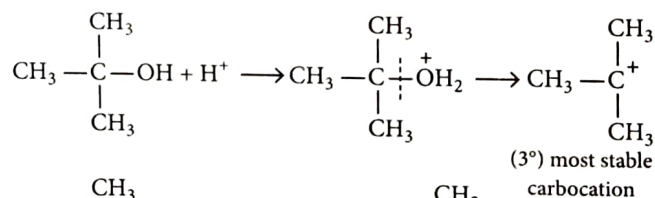
\therefore Freezing point of glucose solution,

$$T_f^\circ - \Delta T_f = (273.15 - 7.60) \text{ K} = 265.55 \text{ K}$$

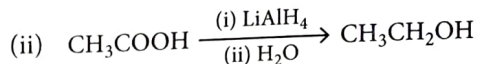
33. (a)



(b) (i)



Since, protonated 3° alcohol (*tert*-butyl alcohol) can make most stable carbocation, hence this leads to the single ether in good quantity.

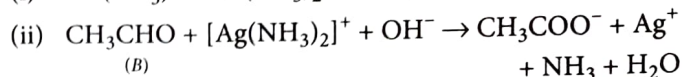


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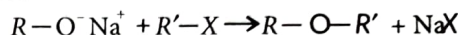
(a) *A* is an alkene while '*B*' gives silver mirror test so, *B* is an aldehyde with $-\text{CH}_3$ group.

As '*C*' gives yellow precipitate so, *C* is a methyl ketone.

(i) *A* : $(\text{CH}_3)\text{CH}=\text{C}(\text{CH}_3)_2$; *B* : CH_3CHO ; *C* : $\text{O}=\text{C}(\text{CH}_3)_2$

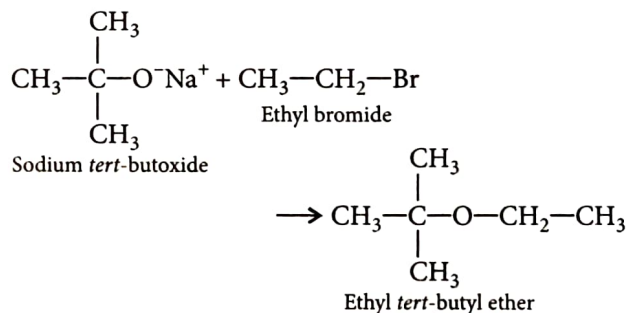


(b) In Williamson's synthesis, an alkyl halide is treated with sodium or potassium salt of an alcohol or phenol to give ethers.

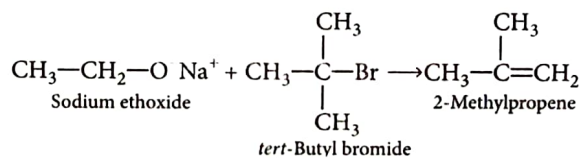


The reaction involves the nucleophilic substitution of the halogen atom by an alkoxide ion. For the preparation of aliphatic ethers by this method, the alkyl halides used should be primary because secondary or tertiary alkyl halides may undergo elimination to form alkenes due to strongly basic nature of alkoxides.

For example, if ethyl *tert*-butyl ether is to be prepared, then better yields are obtained by reactions of ethyl bromide with sodium *tert*-butoxide.



But if the reaction between sodium ethoxide and *tert*-butyl bromide is carried out then 2-methylpropene is obtained as the major product.



Another limitation is in the preparation of aliphatic-aromatic ethers where the reaction proceeds by the treatment of sodium phenoxide with alkyl halide.

