CHEMISTRY

Time Allowed : 3 Hours   *Maximum Marks : 70*

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 1 mark. There is no internal choice in this section.

1. The solubility of common salt is 36.0 g in 100 g of water at 20 °C. If systems, I, II and III contain 40.0, 36.0 and 20.0 g of the salt added to 100.0 g of water in each case, the vapour pressures would be in the order
    (a) I < II < III   (b) I > II > III   (c) I = II > III   (d) I = II < III

2. The coordination number and the oxidation state of the element E in the complex $[E(en)_2(C_2O_4)]NO_2$ (where *en* is ethylenediamine) are respectively
    (a) 6 and +3   (b) 6 and +2   (c) 4 and +2   (d) 4 and +3

3. In a transition series, with the increase in atomic number, the paramagnetism
    (a) increases gradually
    (b) decreases gradually
    (c) first increases to a maximum and then decreases
    (d) first decreases to a minimum and then increases.

4. Magnetic moment 2.83 B.M. is given by which of the following ions?
    (At. nos. Ti = 22, Cr = 24, Mn = 25, Ni = 28)
    (a) Ti^{3+} (b) Ni^{2+}
    (c) Cr^{3+} (d) Mn^{2+}

5. The amino acid which is not optically active is
    (a) lactic acid   (b) serine
    (c) alanine   (d) glycine.

6. The cell reaction of the given cell : $Cu_{(s)} \mid Cu^{2+}_{(aq)} \parallel Hg^{2+}_{(aq)} \mid Hg_{(l)}$ is
    (a) $Hg + Cu^{2+} \rightarrow Hg^{2+} + Cu$ (b) $Hg + Cu^{2+} \rightarrow Cu^+ + Hg^+$
    (c) $Cu + Hg \rightarrow CuHg$ (d) $Cu + Hg^{2+} \rightarrow Cu^{2+} + Hg$

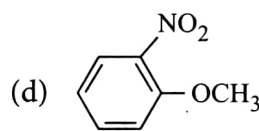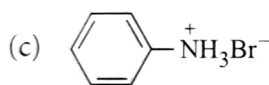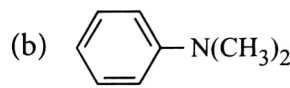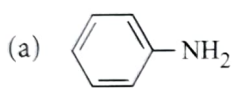7. Match the column I and column II and mark the appropriate choice.

Column I		Column II	
(A)	CH_3CHCl_2	(i)	Vinyl halide
(B)	CH_2ClCH_2Cl	(ii)	Alkylidene halide
(C)	$CHCl=CH_2$	(iii)	Alkylene dihalide
(D)	$ClCH_2-CH=CH_2$	(iv)	Allyl halide

(a) (A) → (i), (B) → (ii), (C) → (iv), (D) → (iii)
(b) (A) → (ii), (B) → (iii), (C) → (i), (D) → (iv)
(c) (A) → (iii), (B) → (iv), (C) → (ii), (D) → (i)
(d) (A) → (iv), (B) → (i), (C) → (iii), (D) → (ii)

8. Which of the following is most reactive towards aqueous NaOH?
(a) C_6H_5Br
(b) $C_6H_5CH_2Br$
(c) C_6H_5F
(d) ClC_6H_4Br

9. End product (A) of the following sequence of reaction is

$$\text{[benzene]}-NO_2 \xrightarrow[\text{30\% HCl}]{\text{Fe}} \xrightarrow{Na_2CO_3} \xrightarrow[\text{CH}_3\text{Br}]{\text{excess}} A$$

(a) [benzene]$-NH_2$

(b) [benzene]$-N(CH_3)_2$

(c) [benzene]$-\overset{+}{N}H_3Br^-$

(d) [benzene with] NO_2, $-OCH_3$
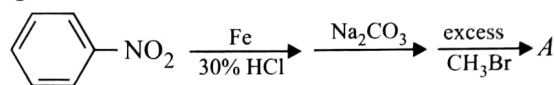
10. A quantity of iodine was reacted with a large excess of propanone and dilute acid. The equation for the reaction was

$$I_2 + CH_3COCH_3 \xrightarrow{[H^+]} ICH_2COCH_3 + HI$$
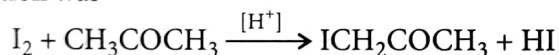
The concentration of iodine in the reaction mixture was recorded at regular time intervals and the result is shown in figure.
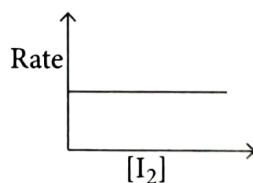
Which one of the following conclusions can be made from this graph?
(a) The rate of reaction is directly proportional to $[I_2]$.
(b) The rate of reaction is inversely proportional to $[I_2]$.
(c) The rate of reaction is independent of $[I_2]$.
(d) The rate of reaction is independent of $[H^+]$.

11. Gadolinium belongs to 4f series. Its atomic number is 64. Which of the following is the correct electronic configuration of gadolinium?
(a) $[Xe]\, 4f^9 5s^1$
(b) $[Xe]\, 4f^7 5d^1 6s^2$
(c) $[Xe]\, 4f^6 5d^2 6s^2$
(d) $[Xe]\, 4f^8 6d^2$

12. What is the correct electronic configuration of the central atom in $K_4[Fe(CN)_6]$ based on crystal field theory?
(a) $e^4 t_2^2$
(b) $t_{2g}^4 e_g^2$
(c) $t_{2g}^6 e_g^0$
(d) $e^3 t_2^3$

13. **Assertion (A)** : Solubility of proteins is minimum at the isoelectric point.
    Reason (R) : At isoelectric point, protein molecule behaves as a zwitter ion.
    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)** : The pressure exerted by a liquid at a given temperature is called its vapour pressure.
    Reason (R) : If a non-volatile solute is added to a solvent to give a solution, the vapour pressure of the solution is found to be greater than the vapour pressure of the pure solvent.
    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)** : CH_3OCH_3 and C_2H_5OH has comparable molecular weight but boiling point of C_2H_5OH is more than dimethyl ether.
    Reason (R) : C_2H_5OH 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.

16. **Assertion (A)** : Transition metals are good catalysts.
    Reason (R) : V_2O_5 or Pt is used in the preparation of H_2SO_4 by Contact process.
    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. Why are alkyl halides generally not prepared in the laboratory by free radical halogenation of alkanes?

18. Two solutes X and Y in equal amounts are dissolved separately in 10 moles of solvent C. If X molecule is heavier than Y molecule, which solution will have larger relative lowering of vapour pressure?

19. Explain the following observations **(any 2)** :
    (a) In aqueous solution, the K_b order is $Me_2NH > MeNH_2 > Me_3N$.
    (b) Tertiary amines do not undergo acylation reaction.
    (c) Higher aliphatic amines are insoluble in water.

20. A reaction is of second order with respect to its reactant. How will its reaction rate be affected if the concentration of the reactant is (i) doubled (ii) reduced to half ?

21. What is the difference between a nucleoside and nucleotide?
    OR
    (a) What is the cause of denaturation?
    (b) What is the effect of denaturation on the structure of protein?

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. (a) Name two disaccharides which are reducing sugar.
    (b) How is glucose and galactose linked in lactose?
    (c) Name the components of starch.

23. Write reactions and conditions for the following conversions :
    (a) 2-Propanone into 2-methyl-2-propanol
    (b) *n*-Propyl alcohol into *n*-hexane

24. Compound '*A*' with molecular formula C_4H_9Br is treated with aqueous KOH solution. The rate of this reaction depends upon the concentration of the compound '*A*' only. When another optically active isomer '*B*' of this compound was treated with aqueous KOH solution, the rate of reaction was found to be dependent on concentration of compound '*B*' and KOH both.
    (a) Write down the structural formula of both compounds '*A*' and '*B*'.
    (b) Out of these two compounds, which one will be converted to the product with inverted configuration.

25. A solution of glucose in water is labelled as 20% (*w/w*). The density of the solution is 1.20 g mL^{-1}. Calculate
    (a) molality
    (b) molarity and
    (c) mole fraction of each component in solution.

26. (a) Name the products obtained when an amide containing three carbon atoms is
        (i) reduced by $LiAlH_4$
        (ii) treated with Br_2 + KOH.
    (b) *p*-Methoxyaniline is a stronger base than aniline but *p*-nitroaniline is a weaker base than aniline. Give reason.

27. $FeSO_4$ solution mixed with $(NH_4)_2SO_4$ solution in 1:1 molar ratio gives the test of Fe^{2+} ion but $CuSO_4$ solution mixed with aqueous ammonia in 1 : 4 molar ratio does not give the test of Cu^{2+} ion. **Explain why?**

28. Explain why electrolysis of an aqueous solution of NaCl gives H_2 at cathode and Cl_2 at anode.
    $E^{\circ}_{Na^+/Na} = -2.71\text{V}, \; E^{\circ}_{H_2O/H_2} = -0.83 \text{ V}$
    $E^{\circ}_{Cl_2/Cl^-} = +1.36 \text{ V}, \; E^{\circ}_{2H^+/H_2O} = +1.23 \text{ V}$

OR

The resistance of a conductivity cell when filled with 0.05 M solution of an electrolyte *X* is 100 ohms at 40 °C. The same conductivity cell filled with 0.01 M solution of an electrolyte *Y* has a resistance of 50 ohms. The conductivity of 0.05 M solution of electrolyte *X* is $1.0 \times 10^{-4} \text{ S cm}^{-1}$.
Calculate :
(a) Cell constant
(b) Conductivity of 0.01 (M) *Y* solution
(c) Molar conductance of 0.01 (M) *Y*

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. A nucleophile attacks the electrophilic carbon atom of a carbonyl compound from a direction perpendicular to the plane of sp^2 hybridised orbital of carbonyl carbon. The hybridisation of carbon changes from sp^2 to sp^3 in this process and a tetrahedral alkoxide intermediate is produced.

This intermediate captures a proton from the reaction medium to give the electrically neutral product. The net result is addition of Nu^- and H^+ across the carbon oxygen double bond.

Nucleophile attacks from the top face

Planar   Tetrahedral intermediate   Addition product
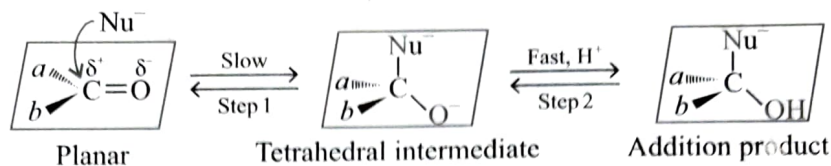
Answer the following questions :

(a) Aldehydes are more reactive than ketones towards nucleophiles. Why?

(b) What is the role of dry HCl in the addition of alcohol to carbonyl group?

OR

Benzaldehyde is less reactive than acetaldehyde towards nucleophilic substitution reaction. Why?

(c) The reaction of carbonyl compound with pure HCN is very slow and becomes fast in presence of a base. Given reason.

30. The quantitative relationship between rate constant of a reaction and temperature proposed by Arrhenius is known as arrhenius equation.

The rate constant of a reaction at any given temperature T is given by Arrhenius equation

$$k = Ae^{-E_a/RT} \qquad \text{...(i)}$$

where, k = Rate constant of a reaction

A = Arrhenius factor or frequency factor. Its value is constant for a particular reaction.

E_a = Activation energy (Joules/mole)

R = Gas constant.

Taking logarithm of equation (i)

$$\ln k = \ln A - \frac{E_a}{RT} \quad \text{or} \quad \ln k = \frac{-E_a}{R}\left(\frac{1}{T}\right) + \ln A$$

Answer the following questions :

(a) Define activation energy of a reaction. What is the effect of adding a catalyst on it?

(b) It has been found that for a chemical reaction with rise in temperature by 10°, the rate constant is

    (i) nearly doubled   (ii) nearly tripled

    (iii) increases 5 times   (iv) increases 4 times.

(c) A reaction proceeds five times more at 60°C as it does at 30°C. Estimate energy of activation.

    (i) 45.7   (ii) 34.6

    (iii) 10.75   (iv) 13.4

OR

The rate constant of a first order reaction increases from 2×10^{-2} to 4×10^{-2} when the temperature changes from 300 K to 310 K. Calculate the energy of activation (E_a).

($\log 2 = 0.301$, $\log 3 = 0.4771$, $\log 4 = 0.6021$)

    (i) 53.59   (ii) 57.4

    (iii) 63.5   (iv) 11.2

SECTION E

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

31. (a) Give reason for the following :

    (i) Propanol has higher boiling point than that of the hydrocarbon butane.

    (ii) Preparation of ether by acid dehydration of secondary and tertiary alcohols is not a suitable method.

Chemistry

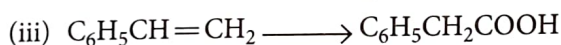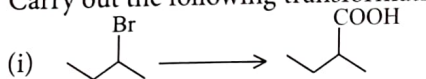(b) Complete each synthesis by giving missing starting materials, reagents or products (**any 2**) :

(i)

(ii)

(iii)
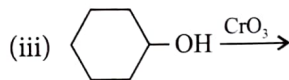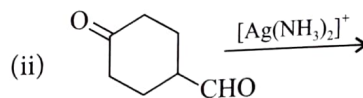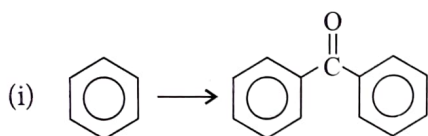
OR

(a) What happens when
  (i) Ethyl alcohol reacts with red P and Br_2?
  (ii) Ethanol is heated with conc. H_2SO_4 at 443 K?

(b) Carry out the following transformations.

(i)

(ii) $HC\equiv CH \longrightarrow$

(iii) $C_6H_5CH=CH_2 \longrightarrow C_6H_5CH_2COOH$

32. (a) Explain the structure of $[NiCl_4]^{2-}$ on the basis of V.B.T.

   (b) Mention any three processes where transition metals act as catalysts.

   (c) The outer electronic configuration of two members of the lanthanoids are as follows :
   $4f^1\,5d^1\,6s^2$ and $4f^7\,5d^0\,6s^2$.
   What are their atomic numbers? Predict the oxidation states exhibited by these elements in their compounds.
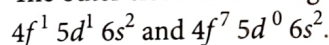
OR

(a) Name the following coordination compounds and draw their structures :
  (i) $[CoCl_2(en)_2]Cl$
  (ii) $[Pt(NH_3)_2Cl(NO_2)]$
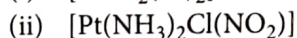
(b) Explain :
  (i) Why is europium (II) more stable than cerium (II)?
  (ii) Why is +3 oxidation state of gadolinium ($Z = 64$) and lutetium ($Z = 71$) especially stable?

33. (a) Give reason : Conductivity of CH_3COOH decreases on dilution.

   (b) Calculate e.m.f and ΔG for the cell : $Mg_{(s)} \mid Mg^{2+}$ (0.001 M) $\parallel Cu^{2+}$ (0.0001 M) $\mid Cu_{(s)}$
   $E^\circ_{(Mg^{2+}/Mg)} = -2\cdot37$ V, $E^\circ_{(Cu^{2+}/Cu)} = +0.34$ V
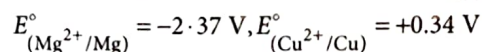
OR

(a) The E° values in respect of electrodes of chromium ($Z = 24$), manganese ($Z = 25$) and iron ($Z = 26$) are: $Cr^{3+}/Cr^{2+} = -0.4$ V ; $Mn^{3+}/Mn^{2+} = +1.5$ V ; $Fe^{3+}/Fe^{2+} = 0.8$ V. On the basis of the above information compare the feasibilities of further oxidation of their + 2 oxidation states.

(b) Calculate standard electrode potential for the half-cell $Fe^{3+} + 3e^- \rightleftharpoons Fe$ from the following data :
$Fe^{3+} + e^- \rightleftharpoons Fe^{2+}$; $E^\circ = 0.77$ V
$Fe^{2+} + 2e^- \rightleftharpoons Fe$; $E^\circ = -0.44$ V
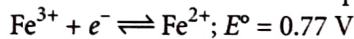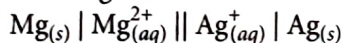
(c) For the given cell
$Mg_{(s)} \mid Mg^{2+}_{(aq)} \parallel Ag^+_{(aq)} \mid Ag_{(s)}$
Write Nernst equation to calculate the cell potential of the above cell.

1. **(d):** I is supersaturated, II is saturated and III is unsaturated solution. In solution I and II, amount of dissolved substance is same.

2. **(a):** In the given complex $[E(en)_2(C_2O_4)]^+NO_2^-$ ethylenediamine is a bidentate ligand and $(C_2O_4^{2-})$ i.e., oxalate ion is also bidentate ligand. Therefore, coordination number of the complex is 6 i.e., it is an octahedral complex.
Oxidation number of E in the given complex is
$x + 2 \times 0 + 1 \times (-2) = +1 \Rightarrow x = +3$

3. **(c):** In transition series, paramagnetism first increases due to increase in the number of unpaired electrons. After Mn, number of unpaired electrons decreases. So, paramagnetism decreases.

4. **(b):** Magnetic moment is given by
$\mu = \sqrt{n(n+2)}$ B.M. [where n = no. of unpaired electrons]
When $n = 2$, then $\mu = 2.83$ B.M.
For Ti^{3+} $(3d^1)$, $n = 1$; Cr^{3+} $(3d^3)$, $n = 3$
Ni^{2+} $(3d^8)$, $n = 2$; Mn^{2+} $(3d^5)$, $n = 5$
Hence, Ni^{2+} has two unpaired electrons, with magnetic moment 2.83 B.M.

5. **(d)**

6. **(d):** Cell reaction : $Cu + Hg^{2+} \rightarrow Cu^{2+} + Hg$

7. **(b)**

8. **(b):** Aromatic halides are less reactive than alkyl or aryl alkyl halides. Hence, $C_6H_5CH_2Br$ is the most reactive towards aqueous NaOH.

9. **(b):**
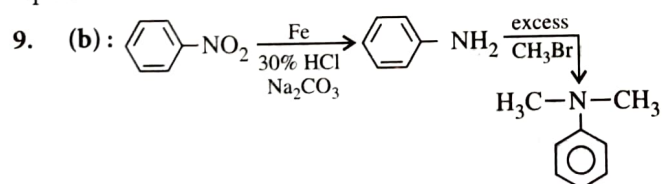
10. **(c)**   **11.** **(b)**

12. **(c):** In $K_4[Fe(CN)_6]$ complex, Fe is in +2 oxidation state.
As CN^- is a strong field ligand, it causes pairing of electrons therefore, electronic configuration of Fe^{2+} in $K_4[Fe(CN)_6]$ is $t_{2g}^6 e_g^0$.

13. **(a):** At isoelectric point, protein molecules behave as zwitter ions and hence, do not move toward any electrode or act as neutral molecules. This reduces their solubility to minimum and thus, helps in their separation and purification.

14. **(c):** The vapour pressure of solution is found to be lower than the vapour pressure of pure solvent. In the solution, the surface has both solute and solvent molecules, thereby the number of solvent molecules gets reduced at the surface, consequently, the number of solvent molecules escaping from the surface is correspondingly reduced and this results in the decrease of vapour pressure.

15. **(c):** Due to the presence of hydroxyl group(–OH), there is extensive hydrogen bonding between the ethanol molecules (C_2H_5OH). 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.

16. **(b):** Due to large surface area and variable valencies, transition metals form intermediate activated complexes easily, hence they are used as good catalysts.

17. Free radical halogenation of alkanes is not a suitable method to obtain an alkyl halide because
(i) it gives a mixture of isomeric monohalogenated products whose boiling points are so close that their separation is difficult.
(ii) polyhalogenation may also occur making the product mixture more complex and hence, difficult to separate.

18. Molar mass of Y is less than that of X, therefore, for the same mass of X and Y, moles of Y will be more than the moles of X. Thus, mole fraction of Y will be more than that of X. Hence, relative lowering of vapour pressure will be larger in case of Y.

19. **(a)** In alkyl amines, a combination of +I effect of alkyl groups, steric factors and H-bonding factors determine the stability of ammonium cations in aqueous solution. All these factors are favourable for 2° amines and for smaller alkyl group, stability due to hydrogen bonding predominates over the stability due to +I effect. Consequently, we get the given K_b order :
$$Me_2NH > MeNH_2 > Me_3N$$
(b) Tertiary amines do not undergo acylation reaction because they do not contain any H-atom on the nitrogen atom.
(c) Lower aliphatic amines are soluble in water because they can form hydrogen bonds with water molecules. Effect of small hydrophobic alkyl part is negligible where as higher aliphatic amines are insoluble in water.
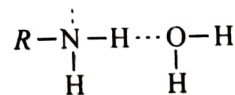
20. Let the concentration of the reactant be $[A] = a$
Given : Order of reaction = 2
so rate of reaction $= k [A]^2 = ka^2$ ...(1)
(i) Given that concentration of the reactant is doubled
So, $[A] = 2a$,
Putting the value in equation (1) we get
New rate of reaction, $R_1 = k(2a)^2 = 4ka^2$
Hence, rate of reaction will increased to 4 times.
(ii) Given that concentration of the reactant is reduced to half

So, $[A] = (1/2)a$

Putting the value in equation (1), we get

New rate of reaction $R_2 = k((1/2)a)^2 = (1/4)ka^2$

Hence, rate of reaction will reduce to 1/4 times.

21. Nucleoside contains pentose sugar, and nitrogenous base whereas nucleotide contains pentose sugar, nitrogenous base as well as phosphate group.

Nucleoside = Base + Sugar
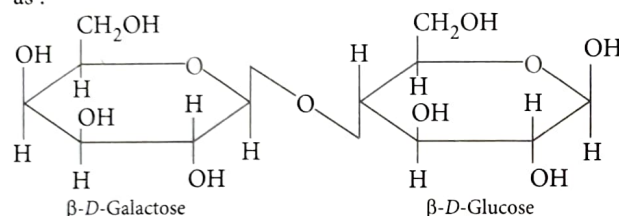
Nucleotide = Base + Sugar + Phosphate

OR

(a) Change in pH or temperature breaks the H-bonding, sulphide linkages etc. and cause denaturation.

(b) During denaturation, 2° and 3° structures are destroyed but 1° structure remains intact.

22. (a) Maltose and lactose are reducing disaccharides.

(b) In lactose, C-1 of galactose is linked with C-4 of glucose as :

β-D-Galactose   β-D-Glucose

(c) Amylose and amylopectin are the components of starch.

23. (a) 2-Propanone is treated with Grignard reagent, (CH_3MgBr) and the product is hydrolysed.

2-Methyl-2-propanol
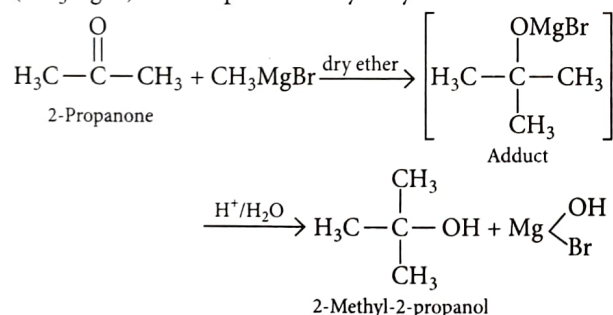
(b) $CH_3CH_2CH_2OH + PCl_5 \longrightarrow CH_3CH_2CH_2Cl +$

n-Propyl alcohol $\qquad\qquad POCl_3 + HCl$

$2CH_3CH_2CH_2Cl + 2Na \xrightarrow[\text{ether}]{\text{Dry}}$

1-Chloropropane

$\qquad\qquad CH_3CH_2CH_2CH_2CH_2CH_3 + HCl$

n-Hexane

24. (a) As the rate of reaction depends upon the concentration of compound '*A*' (C_4H_9Br) only therefore, the reaction is proceeded by S_N1 mechanism and the given compound will be tertiary alkyl halide, *i.e.*, 2-bromo-2-methylpropane and the structure of (*A*) is $(CH_3)_3CBr$. Optically active isomer of '*A*' is 2-bromobutane (*B*) and its structural formula is $CH_3CH_2\overset{*}{C}H(Br)CH_3$.

(b) The rate of reaction of compound '*B*' depends on both the concentration of compound '*B*' and KOH. Hence, the reaction follow S_N2 mechanism. In S_N2 reaction, nucleophile attack from the backside, therefore the product of hydrolysis will have opposite configuration.

(B)   Transition state

Inverted product
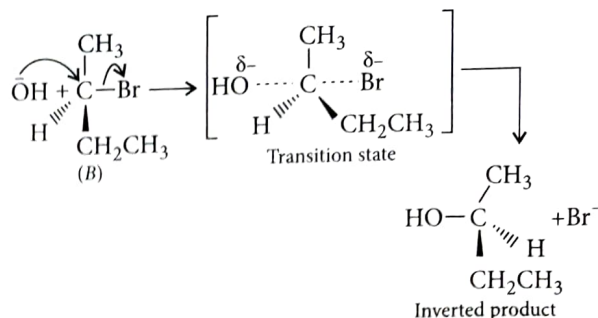
25. (a) 20% (*w/w*) solution of glucose means that 20 g of glucose is present in 100 g of solution or in 80 g of water.

$$\text{Molality} = \frac{\text{Moles of solute}}{\text{Mass of solvent in g}} \times 1000$$

$$\text{Moles of glucose} = \frac{20}{180} = 0.1111 \text{ mol}$$

Mass of solvent (water) = 80 g

$$\therefore \quad \text{Molality} = \frac{0.1111}{80} \times 1000 = 1.388 \text{ m}$$

(b) $$\text{Molarity} = \frac{\text{Moles of solute}}{\text{Volume of solution}} \times 1000$$

Moles of glucose = 0.1111 mol

$$\text{Volume of solution} = \frac{\text{Mass}}{\text{Density}} = \frac{100}{1.20} = 83.3 \text{ mL}$$

$$\therefore \quad \text{Molarity} = \frac{0.1111}{83.3} \times 1000 = 1.333 \text{ M}$$
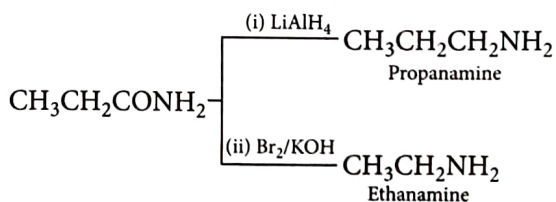
(c) Moles of glucose = 0.1111 mol

$$\text{Moles of water} = \frac{90}{18} = 5.0 \text{ mol}$$

Total moles = 5.0 + 0.1111 = 5.1111

$$\text{Mole fraction of glucose} = \frac{0.1111}{5.1111} = 0.022$$

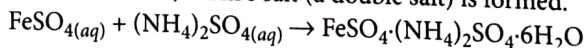$$\text{Mole fraction of water} = \frac{5.0}{5.1111} = 0.978$$

26. (a) The amide containing three carbon atoms is propanamide $(CH_3CH_2CONH_2)$. The reactions are

(i) LiAlH$_4$ $\longrightarrow CH_3CH_2CH_2NH_2$

Propanamine

$CH_3CH_2CONH_2$

(ii) Br$_2$/KOH $\longrightarrow CH_3CH_2NH_2$

Ethanamine
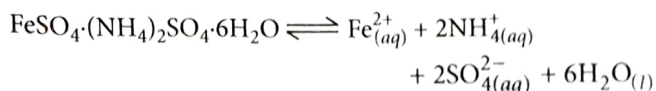
(b) Methoxy $(-OCH_3)$ group is electron-releasing group due to +R effect. Therefore, it increases the electron density on the N-atom of the $-NH_2$ groups. This makes *p*-methoxyaniline a stronger base than aniline. On the other hand, nitro group $(-NO_2)$ is electron-withdrawing group. This reduces the electron density on the N-atom. As a result, *p*-nitroaniline is a weaker base than aniline.

27. When $FeSO_4$ and $(NH_4)_2SO_4$ solutions are mixed in 1 : 1 molar ratio, Mohr's salt (a double salt) is formed.

$$FeSO_{4(aq)} + (NH_4)_2SO_{4(aq)} \rightarrow FeSO_4 \cdot (NH_4)_2SO_4 \cdot 6H_2O$$

$$FeSO_4 \cdot (NH_4)_2SO_4 \cdot 6H_2O \rightleftharpoons Fe^{2+}_{(aq)} + 2NH^+_{4(aq)}$$
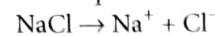$$+ 2SO^{2-}_{4(aq)} + 6H_2O_{(l)}$$

Because Fe^{2+} ions are formed on dissolution of Mohr's salt, its aqueous solution gives the test of Fe^{2+} ions.

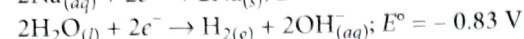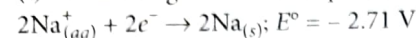When $CuSO_4$ is mixed with ammonia, following reaction occurs :

$$CuSO_{4(aq)} + 4NH_{3(aq)} \rightarrow [Cu(NH_3)_4]SO_4$$
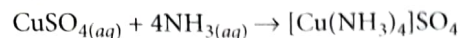
This complex does not produce Cu^{2+} ion, so the solution of $CuSO_4$ and NH_3 does not give the test of Cu^{2+} ion.

28. Aqueous NaCl ionises as

$$NaCl \rightarrow Na^+ + Cl^-$$

(i) Following reactions are possible at cathode,

$$2Na^+_{(aq)} + 2e^- \rightarrow 2Na_{(s)}; \ E° = -2.71 \text{ V}$$
$$2H_2O_{(l)} + 2e^- \rightarrow H_{2(g)} + 2OH^-_{(aq)}; \ E° = -0.83 \text{ V}$$

The reaction with higher $E°$ value will take place, hence H_2 is produced at cathode.

(ii) Following reactions may take place at anode,

$$2Cl^-_{(aq)} \rightarrow Cl_{2(g)} + 2e^-; \ E° = 1.36 \text{ V}$$
$$H_2O_{(l)} \rightarrow \frac{1}{2}O_{2(g)} + 2H^+ + 2e^-, \ E° = 1.23 \text{ V}$$
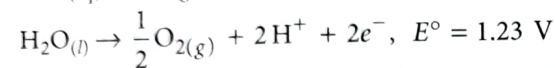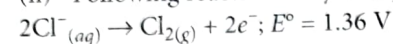
The reaction with lower $E°$ value will take place, but due to overvoltage, Cl_2 is liberated at anode.

OR

(a) For electrolyte X

Molarity $M = 0.05$, $R = 100$ ohm, $\kappa = 1.0 \times 10^{-4}$ S cm^{-1}

Cell constant, $G = \kappa \times R$

or $G = 1.0 \times 10^{-4}$ S cm$^{-1} \times 100$ ohm $= 1.0 \times 10^{-2}$ cm^{-1}

(b) For electrolyte Y

Molarity, $M = 0.01$, Resistance, $R = 50$ ohm,

Conductivity $\kappa = ?$

Using formula, $\kappa = G \cdot \dfrac{1}{R}$

or, $\kappa = 1.0 \times 10^{-2}$ cm$^{-1} \times \dfrac{1}{50 \text{ ohm}}$

$= 2 \times 10^{-4}$ ohm^{-1} cm^{-1}

(c) Molar conductance, $\Lambda_m = \dfrac{\kappa \times 1000}{M}$

or, $\Lambda_m = \dfrac{2 \times 10^{-4} \text{ ohm}^{-1} \text{ cm}^{-1} \times 10^3 \text{ cm}^3 \text{ L}^{-1}}{0.01 \text{ mol L}^{-1}}$

or, $\Lambda_m = 20$ ohm^{-1} cm^2 mol^{-1}

29. (a) Ketones are less reactive than aldehydes towards nucleophilic addition reactions because :

(i) The two electron releasing alkyl groups decrease the magnitude of positive charge on carbonyl carbon and make it less susceptible to nucleophilic attack.

$$\underset{R}{\overset{R}{>}}C=O \qquad \underset{H}{\overset{R}{>}}C=O$$
$$\text{Ketone} \qquad\qquad \text{Aldehyde}$$
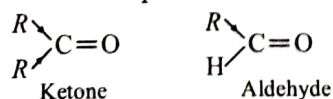
(ii) The two bulkier alkyl groups hinder the approach of the nucleophile to the carbonyl carbon. This is called steric factor.

(b) Dry hydrogen chloride protonates the oxygen atom of carbonyl compound thereby increasing the electrophilicity of the carbonyl carbon and facilitates the nucleophilic attack by the alcohol molecule.

OR

+R effect of benzene ring in benzaldehyde decreases electrophilicity on the carbonyl carbon, the ease of attack of the nucleophiles in benzaldehyde decreases. Also due to greater steric factor in benzaldehyde it is less reactive.
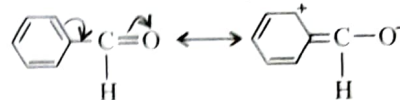
(c) With pure HCN reaction occurs very slowly because it is a weak nucleophile. With base it produces CN^- ion which is a strong nucleophile and readily adds to the carbonyl compound.

$$HCN + \overline{O}H \longrightarrow H_2O + CN^-$$
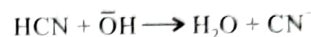
30. (a) The minimum extra energy which must be supplied to the reactants to enable them to cross over the potential energy barrier between reactants and products is called activation energy. It is denoted by E_a.

$$E_a = E_T - E_R$$
$$[E_T = \text{Threshold energy, } E_R = \text{Energy of reactants}]$$

A catalyst lowers the activation energy (E_a) by providing an alternate pathway reaction mechanism.

(b) (i)

(c) (iii) : As $2.303 \log \dfrac{k_2}{k_1} = \dfrac{E_a}{R}\left(\dfrac{T_2 - T_1}{T_2 T_1}\right)$

Here, $T_2 = 60 + 273 = 333$ K, $T_1 = 30 + 273 = 303$ K

$R = 1.987 \times 10^{-3}$ kcal $\qquad E_a = ?$

As $r = k[A]^n$ $\qquad\qquad$ (at a temperature T)

Hence $\dfrac{r_2}{r_1} = \dfrac{k_2}{k_1}$ $\qquad$ (at temperature T_2 and T_1)

but $\dfrac{r_2}{r_1} = 5$ (Given) $\qquad \therefore \ \dfrac{k_2}{k_1} = 5$

$\therefore \quad 2.303 \log_{10} 5 = \dfrac{E_a}{1.987 \times 10^{-3}}\left[\dfrac{333-303}{333 \times 303}\right]$

$\therefore \quad E_a = 10.757$ kcal mol^{-1}

OR

(i) : Given, $T_1 = 300$ K, $T_2 = 310$ K

$k_1 = 2 \times 10^{-2}, k_2 = 4 \times 10^{-2}, \ E_a = ?$

Using Arrhenius equation,

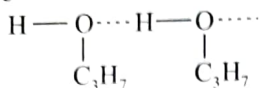$$\log \dfrac{k_2}{k_1} = \dfrac{E_a}{2.303R}\left[\dfrac{1}{T_1} - \dfrac{1}{T_2}\right]$$

or $\log \dfrac{4 \times 10^{-2}}{2 \times 10^{-2}} = \dfrac{E_a}{2.303 \times 8.314}\left[\dfrac{1}{300} - \dfrac{1}{310}\right]$

or $\log 2 = \dfrac{E_a}{2.303 \times 8.314} \times \left[\dfrac{310-300}{310 \times 300}\right]$

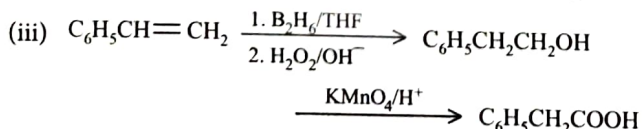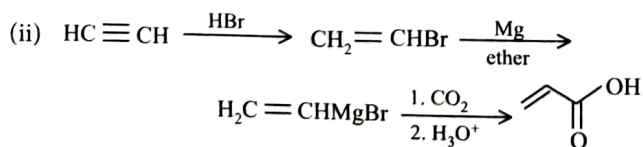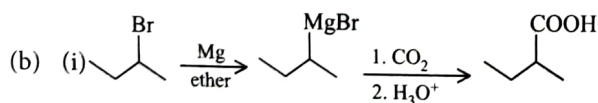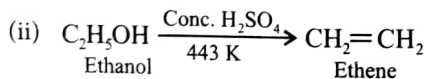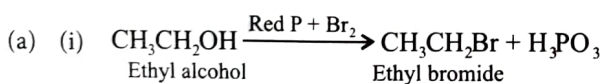or $E_a = \dfrac{0.301 \times 2.303 \times 8.314 \times 310 \times 300}{10}$
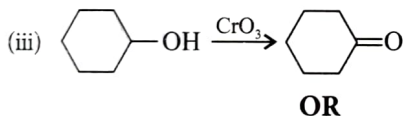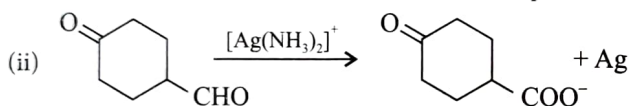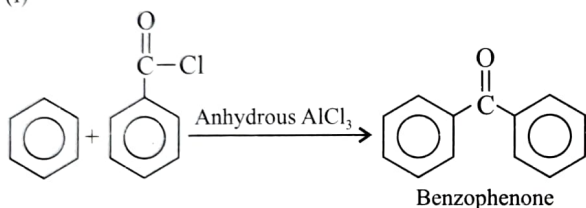
$= 53598 \text{ J} = 53.598 \text{ kJ mol}^{-1}$

31. (a) (i) The molecules of butane are held together by weak van der Waals' forces of attraction while those of propanol are held together by stronger intermolecular hydrogen bonding.

$$H-O\cdots H-O\cdots$$
$$\quad\ |\qquad\quad |$$
$$\quad C_3H_7\qquad C_3H_7$$

(ii) Acid dehydration of 2° and 3° alcohol gives alkenes rather than ethers. Due to steric hindrance the nucleophilic attack by the alcohol molecule on the protonated alcohol molecule does not occur. The protonated 2° and 3° alcohols lose a molecules of water to form stable 2° and 3° carbocations.

(b) (i)

Benzophenone

(ii)

(iii)

OR

(a) (i) $\underset{\text{Ethyl alcohol}}{CH_3CH_2OH} \xrightarrow{\text{Red P + Br}_2} \underset{\text{Ethyl bromide}}{CH_3CH_2Br} + H_3PO_3$

(ii) $\underset{\text{Ethanol}}{C_2H_5OH} \xrightarrow[443\ K]{\text{Conc. H}_2SO_4} \underset{\text{Ethene}}{CH_2{=}CH_2}$

(b) (i)

(ii) $HC{\equiv}CH \xrightarrow{\text{HBr}} CH_2{=}CHBr \xrightarrow[\text{ether}]{\text{Mg}}$

$H_2C{=}CHMgBr \xrightarrow[2.\ H_3O^+]{1.\ CO_2}$

(iii) $C_6H_5CH{=}CH_2 \xrightarrow[2.\ H_2O_2/OH^-]{1.\ B_2H_6/THF} C_6H_5CH_2CH_2OH$

$\xrightarrow{\text{KMnO}_4/H^+} C_6H_5CH_2COOH$

32. (a) In $[NiCl_4]^{2-}$, Ni is in +2 oxidation state and has $3d^8$ outer electronic configuration.
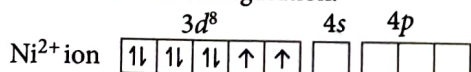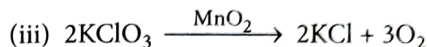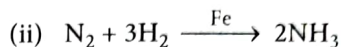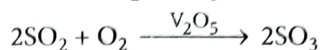

Under the influence of weak field ligand :
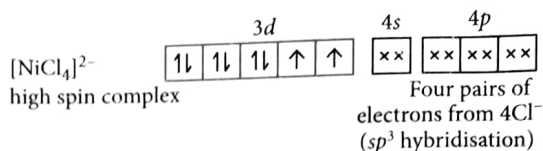
It is sp^3 hybridised hence, structure is tetrahedral.
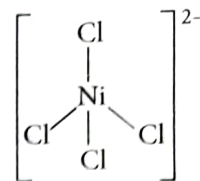
(b) (i) Vanadium (V) oxide V_2O_5 in contact process for oxidation of SO_2 to SO_3

$$2SO_2 + O_2 \xrightarrow{V_2O_5} 2SO_3$$

(ii) $N_2 + 3H_2 \xrightarrow{\text{Fe}} 2NH_3$

(iii) $2KClO_3 \xrightarrow{\text{MnO}_2} 2KCl + 3O_2$

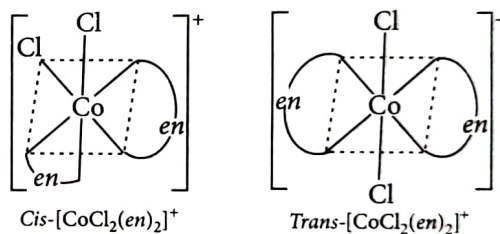**(c)** The configuration $4f^1 5d^1 6s^2$ corresponds to Ce(Z = 58).

It exhibits oxidation states $Ce^{3+}(4f^1)$ and Ce^{4+} $(4f^0)$.
The configuration $4f^7 5d^0 6s^2$ corresponds to Eu (Z = 63).
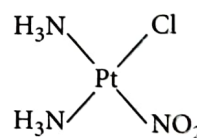It exhibits oxidation states $Eu^{2+}(4f^7)$ and Eu^{3+} $(4f^6)$.

OR

(a) (i) Dichlorido*bis*(ethane-1, 2-diamine)cobalt(III) chloride.

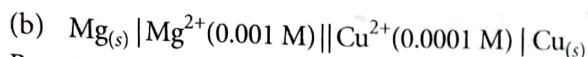$Cis\text{-}[CoCl_2(en)_2]^+$ $Trans\text{-}[CoCl_2(en)_2]^+$
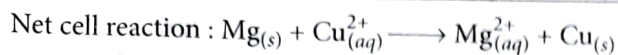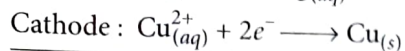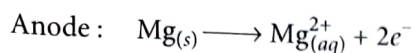
(ii) Diamminechloridonitrito-N-platinum(II)

(b) (i) Europium (II) has electronic configuration $[Xe]4f^7 5d^0$ while cerium (II) has electronic configuration $[Xe]4f^1 5d^1$. In Eu^{2+}, 4f subshell is half filled and 5d-subshell is empty. Since half filled and completely filled electronic configurations are more stable, hence Eu^{2+} ion is more stable than Ce^{2+}.

(ii) This is because gadolinium in +3 state has half filled 4f-subshell $(4f^7)$ and lutetium in +3 state has completely filled 4f-subshell which are very stable configurations.

33. (a) Conductivity of CH_3COOH (weak electrolyte) decreases with dilution because the number of current carrying particles i.e., ions present per cm^3 of the solution becomes less and less on dilution.

(b) $Mg_{(s)} | Mg^{2+}(0.001 \text{ M}) || Cu^{2+}(0.0001 \text{ M}) | Cu_{(s)}$

Reactions :

Anode : $Mg_{(s)} \longrightarrow Mg^{2+}_{(aq)} + 2e^-$

Cathode : $Cu^{2+}_{(aq)} + 2e^- \longrightarrow Cu_{(s)}$

Net cell reaction : $Mg_{(s)} + Cu^{2+}_{(aq)} \longrightarrow Mg^{2+}_{(aq)} + Cu_{(s)}$

$\therefore \quad n = 2$

Using Nernst equation :

$$E_{cell} = E^\circ_{cell} - \frac{2.303RT}{nF} \log \frac{[Mg^{2+}]}{[Cu^{2+}]}$$

For the given cell

$E^\circ_{cell} = E^\circ_{cathode} - E^\circ_{anode} = E^\circ_{Cu2+/Cu} - E^\circ_{Mg2+/Mg}$

$= 0.34 \text{ V} - (-2.37 \text{ V}) = 2.71 \text{ V}$

Given, $[Mg^{2+}] = 0.001 \text{ M}, [Cu^{2+}] = 0.0001 \text{ M}$

Putting in Nernst equation at 298 K

$E_{cell} = 2.71 \text{ V} - \frac{0.059}{2} \log \frac{0.001}{0.0001}$
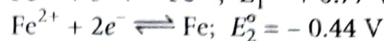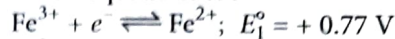
$E_{cell} = 2.71 - 0.0295 \log 10 = 2.68 \text{ V}$

$\Delta_r G = -nFE_{cell} = -2 \times 96500 \text{ C mol}^{-1} \times 2.68$

$= -517,240 \text{ J mol}^{-1} = -517.24 \text{ kJ mol}^{-1}$

OR

(a) From electrode potential data it is obvious that +2 oxidation state of Mn is more stable than +2 oxidation state of Fe which in turn is more stable than +2 oxidation state of Cr, so the order of feasibility of further oxidation of +2 oxidation state is $Cr^{2+} > Fe^{2+} > Mn^{2+}$.

(b) Given equations are

$Fe^{3+} + e^- \rightleftharpoons Fe^{2+}; \quad E^\circ_1 = +0.77 \text{ V}$

$Fe^{2+} + 2e^- \rightleftharpoons Fe; \quad E^\circ_2 = -0.44 \text{ V}$

The desired equation is

$Fe^{3+} + 3e^- \rightleftharpoons Fe; \quad E^\circ_3 = ?$

The desired equation is obtained by adding above two equations.

Therefore, $E^\circ_3 = \dfrac{n_1 E^\circ_1 + n_2 E^\circ_2}{n_3}$

or, $E^\circ_3 = \dfrac{1 \times 0.77 \text{ V} + 2 \times (-0.44 \text{ V})}{3}$

$= \dfrac{-0.11}{3} = -0.036 \text{ V}$

(c) $E_{cell} = E^\circ_{cell} - \dfrac{2.303 \, RT}{nF} \log \dfrac{[Mg^{2+}_{(aq)}]}{[Ag^+_{(aq)}]^2}$

[Here $n = 2$]

☺☺☺