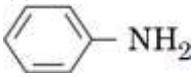
1. **(a)** It is preferred for polymers and proteins because the measurements are taken at room temperature and the magnitude of the pressure is large enough to be measured accurately even for very dilute solutions.
2. **(c)** At high altitudes, the partial pressure of oxygen is less than at sea level. This leads to lower concentrations of oxygen in the blood and tissues, a condition known as anoxia.
3. **(d)** In a cell representation, the anode (oxidation) is written on the left and the cathode (reduction) on the right. Zinc is being oxidized ($Zn \rightarrow Zn^{2+}$) and silver is being reduced ($Ag^{+} \rightarrow Ag$).
4. **(c)** For a reaction to be spontaneous, the change in Gibbs free energy (ΔG) must be negative, and the cell potential (E^{*}_{cell}) must be positive.
5. **(c)** A catalyst provides an alternative reaction pathway with a lower activation energy (E_a), thereby increasing the rate of the reaction. It does not affect thermodynamic properties like $\Delta H, \Delta G$, or ΔS.
6. **(c)** The reaction between Hydrogen and Chlorine over water in the presence of sunlight ($h\nu$) is a zero-order reaction because the rate is determined by the intensity of light rather than the concentration of the reactants.
7. **(b)** The most common oxidation state of lanthanoids is +3 .
8. **(c)** Exchange of ion inside and outside coordination sphere gives ionisation isomerism.
   $[Co(SO_4)(NH_3)_5]Br$ and $[Co(Br)(NH_3)_5]SO_4$
9. **(b)** Alkyl fluorides are best prepared by Swarts reaction.
10. **(a)** Lucas reagent reaction:
    $R-OH + HCl \xrightarrow{ZnCl_2} RCl + H_2O$
    Reactivity order:
    $3^{\circ} > 2^{\circ} > 1^{\circ}$
11. **(b)** This is Hofmann bromamide reaction:
    $CH_3CONH_2 \xrightarrow{Br_2/NaOH} CH_3NH_2$
12. **(c)** In aniline, lone pair on nitrogen is delocalized into benzene ring, so it is least basic.
    
13. **(c)** Amylose part of starch contains:
    $C_1 - C_4 \alpha$-glycosidic linkage
14. **(c)** α-helix is a structure found in proteins/polypeptides.
15. **(b)**• Assertion (A): True $-NH_2$ is an o,p-directing group due to +R effect.
    • Reason (R): True - Aniline does not undergo Friedel-Crafts reaction.
    • But R does not explain A .
    So, Both A and R are true, but R is not the correct explanation.
16. **(c)** • Assertion (A): True - Acetylation decreases activation and prevents polysubstitution, giving mainly monosubstituted product.
    • Reason (R): False $-NHCOCH_3$ is less activating than $-NH_2$.
17. **(a)** $H_2 + Br_2 \rightarrow 2HBr$
    • A: True
    • R: True
    • Molecularity $= 2$ because two reactant molecules are involved.
    R correctly explains A.
    So, Both A and R are true, but R is the correct explanation.
18. **(a)** Low spin tetrahedral complexes
    • A: True
    • R: True
    • In tetrahedral complexes, $\Delta_t < P$, so electrons remain unpaired → high spin complexes form.
    R correctly explains A.
    So, Both A and R are true, but R is the correct explanation.
19. Henry's Law
    Henry's law states that:
    $p = k_H x$
    where

• p = partial pressure of gas
• x = mole fraction of gas in liquid
• k_H = Henry's constant
Application:
Used in manufacture of soda water and soft drinks.

20. **(A)** Electrolyte A is weak because its molar conductivity increases greatly (25 times) on dilution ionisation. Electrolyte B is strong because its molar conductivity increases only slightly (1.5 times).
Graph:
• Strong electrolyte → gradual increase in Λ_m with dilution.
• Weak electrolyte → sharp increase in Λ_m with dilution.

OR

(B) Given:
$R = 5.55 \times 10^3 \Omega$
Diameter $= 1$ cm
$r = 0.5$ cm
Length:
$l = 50$ cm
Area:
$A = \pi r^2 = \pi(0.5)^2 = 0.785\ \text{cm}^2$
Conductivity:
$\kappa = \frac{l}{RA}$
$\kappa = \frac{50}{(5.55 \times 10^3)(0.785)}$
$\kappa \approx 1.15 \times 10^{-2} \Omega^{-1}\ \text{cm}^{-1}$
$1.15 \times 10^{-2} \Omega^{-1}\ \text{cm}^{-1}$

21. Complete the following equations:
(A) $2MnO_4^- + 5NO_2^- + 6H^+ \rightarrow 2Mn^{2+} + 5NO_3^- + 3H_2O$
(B) $Cr_2O_7^{2-} + 14H^+ + 6e^- \rightarrow 2Cr^{3+} + 7H_2O$

22. Identify ' A ' and ' B ' in the reactions:
(A)• A: 2-chloropropane $(CH_3 - CHCl - CH_3)$
• B: 2-isocyanopropane ($CH_3 - CH(NC) - CH_3$)
(B)• A: Prop-1-ene $(CH_3CH = CH_2)$ - Elimination reaction
• B: 2-bromopropane $(CH_3CHBrCH_3)$ - Markovnikov addition

23. **(A)** Account for the following:
(i) Phenol vs Alcohol acidity: Phenol is more acidic because the phenoxide ion formed after losing a proton is stabilized by resonance, whereas the alkoxide ion from alcohol is destabilized by the $+I$ effect of alkyl groups.
(ii) Boiling point vs Branching: As branching increases, the surface area decreases, which leads to weaker Van der Waals forces, thereby decreasing the boiling point.

OR

(B) **(i)** Mechanism (Ethanol to Ethene):
(1) Protonation: $C_2H_5OH + H^+ \rightarrow C_2H_5OH_2^+$
(2) Formation of carbocation: $CH_3CH_2OH_2^+ \rightarrow CH_3CH_2^+ + H_2O$ (Slow step)
(3) Elimination of proton: $CH_3CH_2^+ \rightarrow CH_2 = CH_2 + H^+$
(ii) Reimer-Tiemann Reaction:
$C_6H_5OH + CHCl_3 + 3NaOH \xrightarrow{343\ K} C_6H_4(OH)CHO + 3NaCl + 2H_2O$
(Phenol forms Salicylaldehyde)

24. Explain briefly:
(A) Carbylamine reaction: Aliphatic or aromatic primary amines react with chloroform and ethanolic KOH to form foul-smelling isocyanides (carbylamines).
(B) Gabriel phthalimide synthesis: A method used for the preparation of primary aliphatic amines by reacting phthalimide with KOH, followed by an alkyl halide and subsequent hydrolysis.

25. **(A)** D-glucose straight chain reaction:

Heating D-glucose with Hydroiodic acid (HI) for a long time gives n-hexane, showing that all six carbons are linked in a straight chain.

$C_6H_{12}O_6 \xrightarrow{HI,\Delta} CH_3CH_2CH_2CH_2CH_2CH_3$

(B) Protein linkage:

The linkage responsible for the formation of proteins is the Peptide linkage (-CONH -).

26. **(A)** Ideal solution vs Non-ideal solution

Ideal Solution	Non-ideal Solution
Obeys Raoult's law	Does not obey Raoult's law
$\Delta H_{mix} = 0$	$\Delta H_{mix} \neq 0$
$\Delta V_{mix} = 0$	$\Delta V_{mix} \neq 0$
Intermolecular forces are similar	Intermolecular forces are different

(B) Given:

• Urea $= 30$ g

• Water $= 846$ g

• Vapour pressure of pure water $P^0 = 23.8$ mmHg

Moles of water:

$$n_{water} = \frac{846}{18} = 47$$

Moles of urea:

$$n_{urca} = \frac{30}{60} = 0.5$$

Mole fraction of water:

$$X_{water} = \frac{47}{47 + 0.5} = \frac{47}{47.5} = 0.989$$

Vapour pressure:.

$P = X_{water}\, P^0$

$P = 0.989 \times 23.8$

$P \approx 23.5$ mmHg

27. Main products formed

(A)

$CH_3Cl \xrightarrow{NaI/\ Aectone} CH_3I$

(Product methyl iodide)

(B)

2,4, 6-trinitrochlorobenzene $\xrightarrow{hydrolysis}$ 2,4,6-trinitrophenol

(Product picric acid)

(C)

$CH_3CH_2CH_2CH_2Cl \xrightarrow{alc.\ KOH} CH_3CH_2CH = CH_2$

(Product but-1-ene)

28. Conversions (Any three)

(A) Phenol → Picric acid

$C_6H_5OH \xrightarrow{conc.\ HNO_3/\ conc.\ H_2SO_4}$ 2, 4, 6-trinitrophenol

(B) Propanone - 2-Methylpropan-2-ol

$CH_3COCH_3 \xrightarrow{CH_3MgBr} (CH_3)_3COMgBr \xrightarrow{H_3O^+} (CH_3)_3COH$

(C) Phenol → Anisole

$C_6H_5OH \xrightarrow{NaOH} C_6H_5ONa$

$C_6H_5ONa \xrightarrow{CH_3I} C_6H_5OCH_3$
(Anisole)

(D) Propene → Propan-1-ol

$CH_3CH = CH_2 \xrightarrow{BH_3/THF} \xrightarrow{H_2O_2/OH^-} CH_3CH_2CH_2OH$
(Propan-1-ol)

29. (A) (i) Carboxyl group in benzoic acid is meta directing

• $COOH$ group is electron withdrawing ($-I$ and $-M$ effect), so it decreases electron density at ortho and para positions. Hence electrophilic substitution occurs mainly at meta position.

(ii) Sodium bisulphite is used for purification of aldehydes and ketones

Aldehydes and ketones form crystalline bisulphite addition compounds with $NaHSO_3$, which can be separated and decomposed to obtain pure compound.

(iii) Carboxylic acids do not give characteristic reactions of carbonyl group

Due to resonance, the carbonyl carbon in carboxylic acids becomes less electrophilic, so they do not show nucleophilic addition reactions of carbonyl group.

OR

(B) Given:

$A(C_3H_8O) \xrightarrow{C_{u,573K}} B$

B does not reduce Fehling solution ⇒ B is ketone.

B gives iodoform test ⇒ contains CH_3CO - group.

Therefore:

$B = CH_3COCH_3$
(Propanone)

Hence.

$A = CH_3CHOHCH_3$
(Propan-2-ol)

Iodoform formed:

$C = CHI_3$
(Yellow ppt.)

30. (A) Hydrolysis products

(i) Lactose

Lactose $\xrightarrow{h_{pdrolysis}}$ Glucose + Galactose

(ii) Maltose

Maltose $\xrightarrow{h_{padrolysis}}$ Glucose + Glucose

(B) Difference between starch and cellulose

• Starch: contains α-glucose units linked by $\alpha(1 \rightarrow 4)$ glycosidic bonds.

• Cellulose: contains β-glucose units linked by $\beta(1 \rightarrow 4)$ glycosidic bonds.

31. (i) The average rate of reaction is the change in concentration of reactants or products divided by the time interval over which that change occurs $\left(r_{avg} = \frac{\Delta[C]}{\Delta t}\right)$

(ii) Two factors that affect the rate of reaction are:

• Concentration of reactants: Increasing concentration generally increases the rate.

• Temperature: Increasing temperature usually speeds up the reaction. (Other factors include catalysts and surface area).

(iii)

(1) For a zero-order reaction: The rate of reaction remains constant and is independent of the concentration of the reactants.

(2) Unit of k: $molL^{-1}\ s^{-1}$ (or Ms^{-1}).

OR

(iii) (1) Order of the reaction: The sum of the powers of the concentrations in the rate law.

Order $= \frac{1}{2} + 1 = 1.5$ (or $3/2$).

(2) Pseudo first order reaction: A reaction that is higher-order according to the stoichiometry but behaves as a first-order reaction due to one reactant being in large excess.

Example: Acid-catalyzed hydrolysis of ethyl acetate. Water is in such large excess that its concentration change is negligible.

$CH_3COOC_2H_5 + H_2O \xrightarrow{H^+} CH_3COOH + C_2H_5OH$

32. **(i)**Since $PtCl_2 \cdot 2NH_3$ does not react with $AgNO_3$, no free Cl^-ion is present outside the coordination sphere.

$[Pt(NH_3)_2Cl_2]$

(ii) In $[Co(en)_3]^{3+}$, ethylenediamine (en) is bidentate.

$3 \times 2 = 6$

Secondary valency $= 6$

(iii)(1) Formula of Iron(III) hexacyanidoferrate(II)

$Fe_4[Fe(CN)_6]_3$

(2) IUPAC name of $[Co(NH_3)_5Cl]Cl_2$

Pentaamminechloridocobalt(III) chloride

OR

(iii) For $[Ni(CN)_4]^2$

Ni atomic number $= 28$

$Ni^{2+}: 3d^8$

$CN^-$is strong field ligand - pairing occurs.

Hybridisation:

dsp^2

Shape:

Square planar

Magnetic behaviour:

All electrons are paired.

Diamagnetic

33. **(A) (i)** Kohlrausch's law

At infinite dilution, the limiting molar conductivity of an electrolyte is equal to the sum of limiting molar conductivities of cations and anions.

For acetic acid:

$\Lambda_m^\circ(CH_3COOH) = \Lambda_m^\circ(HCl) + \Lambda_m^\circ(CH_3COONa) - \Lambda_m^\circ(NaCl)$

(ii) Reaction:

$Ni(s) + 2Ag^+(aq) \rightharpoonup Ni^{2+}(aq) + 2Ag(s)$

Cell emf

$E^\circ_{ecll} = E^\circ_{eathode} - E^\circ_{anode}$

$= 0.80 - (-0.25) = 1.05\ V$

Maximum work

$w_{max} = nFE^\circ_{cell}$

Here $n = 2$

$w_{max} = 2 \times 96500 \times 1.05$

$2.03 \times 10^5\ J\ mol^{-1}$

Calculation of $\log K_c$

$E^\circ_{cell} = \frac{0.0591}{n}\log K_c$

$1.05 = \frac{0.0591}{2}\log K_c$

$\log K_c = \frac{2 \times 1.05}{0.0591}$

$\log K_c \approx 35.5$

OR

(B) (i) Faraday's first law

The mass of a substance deposited during electrolysis is directly proportional to the quantity of electricity passed.

For:

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

1 mol Cu requires 2 mol electrons.

2 Faraday

(ii) Cell:

$Mg|Mg^{2+}(0.1M)||Cu^{2+}(0.01M)|Cu$
Given:
$E^{\circ}_{\text{cell}} = 2.71\ \text{V}$
Reaction:
$\text{Mg} + \text{Cu}^{2+} \rightarrow \text{Mg}^{2+} + \text{Cu}$
$n = 2$
Reaction quotient:
$$Q = \frac{[Mg^{2+}]}{[Cu^{2+}]} = \frac{0.1}{0.01} = 10$$
Using Nernst equation:
$$E_{\text{cell}} = E^{\circ}_{\text{cell}} - \frac{0.0591}{n}\log Q$$
$$E_{\text{cell}} = 2.71 - \frac{0.0591}{2}\log 10$$
$$= 2.71 - 0.02955$$
$E_{\text{cell}} \approx 2.68\ \text{V}$

34. **(i)**Manganese shows highest oxidation state +7 because it has maximum number of unpaired electrons due to configuration:
$3d^5 4s^2$
Thus all 7 electrons can participate in bonding.
(ii) Transition metals are good catalysts because they show variable oxidation states and form intermediate complexes during reactions.
(iii)$\text{Cr}^{2+}(d^4)$ easily loses one electron to form stable $\text{Cr}^{3+}(d^3)$, hence it acts as reducing agent. $Mn^{3+}(d^4)$ easily gains one electron to form stable $Mn^{2+}(d^5)$, hence it acts as oxidising agent.
(iv) Zn has lowest enthalpy of atomization because of completely filled $3d^{10}$ configuration, resulting in weak metallic bonding.
(v)Cu^4 is unstable in aqueous solution because it undergoes disproportionation:
$2\text{Cu} + \text{Cu}^{2+} + \text{Cu}$
since Cu^{2+} is more stable than Cu^{+}.

35. **(A) (i)** Conversions
(1) Ethanol → But-2-en-1-al
$$\text{CH}_3\text{CH}_2\text{OH} \xrightarrow{\text{PCC}} \text{CH}_3\text{CHO}$$
$$2\text{CH}_3\text{CHO} \xrightarrow{\text{dil.NaOH}} \text{CH}_3\text{CH} = \text{CHCHO}$$
(But-2-en-1-al)
(2) Propanoic acid → 2-chloropropanoic acid
$$\text{CH}_3\text{CH}_2\text{COOH} \xrightarrow{\text{Cl}_2/\text{redP}} \text{CH}_3\text{CHClCOOH}$$
(Hell-Volhard-Zelinsky reaction)
(ii) Given:
• $A = C_5H_{10}$
• On ozonolysis gives B and C
• B gives Fehling and iodoform test ⇒ $B = CH_3\text{CHO}$ (ethanal)
• C gives iodoform but not Fehling ⇒ ketone with CH_3CO
$\text{C} = \text{CH}_3\text{COCH}_2\text{CH}_3$
(Butan-2-one)
Hence alkene:
$A = \text{CH}_3\text{CH} = \text{C}(\text{CH}_3)\text{CH}_2\text{CH}_3$
(3-methylpent-2-ene)

OR

(B) (i) Distinguish
(1) $\text{CH}_3\text{COCH}_2\text{CH}_3$ and $\text{CH}_3\text{CH}_2\text{CH}_2\text{CHO}$
Use Fehling's solution:
• Aldehyde gives red ppt.
• Ketone does not react.
(2) Ethanal and Ethanoic acid

Use sodium bicarbonate:
• Ethanoic acid gives brisk effervescence of CO_2
• Ethanal does not react.
(ii) Oxime of acetone
$(CH_3)_2C = NOH$
(iii) Identify A to D
$CH_3COOH \xrightarrow{PCl_3} A$
$A = CH_3COCl$
(Acetyl chloride)
$A \xrightarrow{H_2/Pd-BaSO_4} B$
$B = CH_3CHO$
(Ethanal)
$B \xrightarrow[(t)H_3O^+]{(t)CH_3MBr^3} C$
$C = CH_3CH(OH)CH_3$
(Propan-2-ol)
$B \xrightarrow{LtAlH_4} D$
$D = CH_3CH_2OH$
(Ethanol)

36. (c) Alkyl halide + alcoholic KOH gives alkene by elimination of HX , so it is dehydrohalogenation.

37. (b) In $[Fe(CO)_5]$, CO is a neutral ligand.
Let oxidation state of $Fe = x$
$x + 5(0) = 0$
$x = 0$

38. (c) Strongest base:
Basic strength depends on availability of lone pair on N .
(a) Aniline → lone pair delocalized in benzene ring
(b) p-Toluidine → CH_3 donates electrons, increases basicity
(c) Benzylamine ($C_6H_5CH_2NH_2$) → lone pair not conjugated with ring, most available
(d) Nitro group decreases basicity strongly

39. (b) For first order reaction:
$\ln[R] = \ln[R_0] - kt$
Slope of $\ln[R]$ vs time graph $= -k$

40. (b) α-helix is a structural feature of proteins/polypeptides.

41. (a) Racemisation occurs through planar carbocation intermediate in S_N1 reaction.

42. (c) Henry's constant K_H increases with increase in temperature because solubility of gases decreases at higher temperature.

43. (a) Molar conductivity increases on dilution.
Lowest concentration = highest molar conductivity.

44. (a) The reactivity of primary halides is in the order, $-CH_3 > CH_3CH_2 -> CH_3CH_2CH_2 -$ and the tendency of alkyl halides to undergo ellimination is $3° > 2° > 1°$. Hence, for better yield, the alkyl halide should be primary and alkoxide should be secondary or tertiary.

45. (a) Reactivity in nucleophilic addition decreases with increasing alkyl groups due to +1 effect and steric hindrance.
$HCHO > CH_3CHO > CH_3COCH_3 > CH_3COC_2H_5$

46. (c) Aldol condensation requires at least one α-hydrogen.
(a) CH_3CHO → has $\alpha - H$
(b) Cyclohexane carbaldehyde → has $\alpha - H$
(c) Benzaldehyde (C_6H_5CHO) → no α-H
(d) CH_3COCH_3 → has α-H

47. (b) For reaction:
$3A \rightarrow 2B$

$$\text{Rate} = -\frac{1}{3}\frac{d[A]}{dt} = +\frac{1}{2}\frac{d[B]}{dt}$$

So,

$$+\frac{d[B]}{dt} = -\frac{2}{3}\frac{d[A]}{dt}$$

48. (d) Transition metals show catalytic activity mainly due to variable oxidation states.

49. (b) Let the complex be:

$[PtCl_2(en)_2]^x$

• en (ethane-1,2-diamine) is neutral

• $Cl^- = -1$ each

• Pt oxidation state $= +4$

So charge on complex:

$+4 - 2 = +2$

Therefore two nitrate ions are needed outside the coordination sphere.

Formula:

$[PtCl_2(en)_2](NO_3)_2$

50. (c) Osmotic pressure

• Assertion (A): Osmotic pressure is a colligative property → True.

• Reason (R): Osmotic pressure is proportional to molality → False.

Osmotic pressure is proportional to molarity ($\pi = CRT$), not molality.

A is true, R is false.

51. (a) Conductivity vs concentration

• Assertion (A): Conductivity decreases with decrease in concentration → True.

• Reason (R): Number of ions per unit volume decreases on dilution → True.

• R correctly explains A.

Both A and R are true, and R is the correct explanation of A.

52. (d) Copper as transition element

• Assertion (A): Copper is a non-transition element → False.

• Reason (R): Copper has completely filled d-orbitals in ground state → True ($3d^{10}4s^1$).

But transition element definition: forms ions with incomplete d-orbitals. Cu^{2*} has 3 d^9 → transition element.

A is false, R is true.

53. (a) Nucleophilic substitution

• Assertion (A): Nucleophilic substitution of iodoethane is easier than chloroethane → True.

• Reason (R): Bond enthalpy of $C - I$ is less than $C - Cl$ → True.

• R correctly explains A.

Both A and R are true, and R is the correct explanation of A.

54. For an ideal solution:

$P_{total} = X_X P_X^\circ + X_Y P_Y^\circ$

Equal moles $\Rightarrow X_X = X_Y = \frac{1}{2}$

$$P_{total} = \frac{1}{2}(120) + \frac{1}{2}(160)$$

$= 60 + 80 = 140$ mmHg

• 140 mm Hg

55. (A) (i) Mercury cell delivers constant potential because:

The overall reaction does not involve any ion whose concentration changes during discharge, so cell potential remains constant.

(ii) DC is not used in conductance measurement because:

Direct current causes electrolysis and polarization of electrodes, which changes resistance and gives inaccurate results.

OR

(B) Fuel Cell:

A fuel cell is an electrochemical cell that converts chemical energy of a fuel directly into electrical energy.

Example:

Hydrogen-oxygen fuel cell.

Advantages over primary and secondary cells:

• Continuous supply of electricity as long as fuel is supplied.
• Higher efficiency.
• Environment friendly (water formed as product).
• No need for recharging.

56. **(A)** For second order reaction:

Rate $\propto [A]^2$

If concentration becomes 3[A].

New rate $= (3)^2 = 9$

Rate becomes 9 times.

(B) Pseudo first order reaction:

A reaction which is actually of higher order but behaves as first order because one reactant is pre: large excess.

Example:

$CH_3COOC_2H_5 + H_2O \rightarrow CH_3COOH + C_2H_5OH$

Water is taken in excess.

57. **(A)** **(i)** $[Co(NH_3)_5(ONO)]^{24}$

ONO = nitrito-O ligand

Oxidation state of Co:

$x + 0 - 1 = +2 \Rightarrow x = +3$

Name:

Pentaammine nitrito-O cobalt(III) ion

(ii) $K_2[NiCl_4]$

Oxidation state of Ni:

$x + 4(-1) = -2 \Rightarrow x = +2$

Name:

Potassium tetrarchloridonickelate(II)

OR

(B) **(i)** Chelate complex:

A complex in which a multidentate ligand forms ring structure with the metal ion.

Example:

$[Cu(en)_2]^{2+}$

(ii) Heteroleptic complex:

A complex containing different kinds of ligands.

Example:

$[Co(NH_3)_4Cl_2]^+$

58. **(A)** Reimer-Tiemann reaction

$C_6H_5OH + CHCl_3 + 3NaOH \rightarrow o - HOC_6H_4CHO + 3NaCl + 2H_2O$

(Phenol gives salicylaldehyde)

(B) Acetylation of salicylic acid

Salicylic acid $+ (CH_3CO)_2O \xrightarrow{H_2SO_4}$ Aspirin $+ CH_3COOH$

$C_7H_6O_3 + (CH_3CO)_2O \rightarrow C_9H_8O_4 + CH_3COOH$

59. **(A)** $CH_3CN \rightarrow CH_3COCH_3$

$CH_3CN \xrightarrow{CH_3Mg_9Br}$ imine complex $\xrightarrow{H_3O^+} CH_3COCH_3$

(B) $C_6H_5COOH \rightarrow C_6H_6$

$C_6H_5COOH \xrightarrow{NaOH} C_6H_5COONa$

$C_6H_5COONa \xrightarrow[\text{soda lime}]{} C_6H_6$

60. Two differences between DNA and RNA

DNA	RNA
Contains deoxyribose sugar	Contains ribose sugar
Contains thymine	Contains uracil

61. **(A) (i)** Mechanism of formation of diethyl ether

Reaction:

$$2CH_3CH_2OH \xrightarrow[413\ K]{H^+} CH_3CH_2 - O - CH_2CH_3 + H_2O$$

Step 1 : Protonation of ethanol

$$CH_3CH_2OH + H^+ \rightarrow CH_3CH_2OH_2^+$$

Step 2 : Nucleophilic attack by another ethanol molecule

$$CH_3CH_2OH + CH_3CH_2OH_2^+ \rightarrow CH_3CH_2 - O^+H - CH_2CH_3 + H_2O$$

Step 3 : Deprotonation

$$CH_3CH_2 - O^+H - CH_2CH_3 \rightarrow CH_3CH_2 - O - CH_2CH_3 + H^+$$

(ii) Reason

• o-Nitrophenol shows intramolecular hydrogen bonding, so molecules are less associated and become steam volatile.

• p-Nitrophenol shows intermolecular hydrogen bonding, causing stronger association and higher boiling point; hence not steam volatile.

OR

(B) (i) Anisole $+CH_3Cl/AlCl_3$

Friedel-Crafts alkylation occurs.

$C_6H_5OCH_3 + CH_3Cl \xrightarrow{AlCl_3}$ o - and p-methylanisole

(ii) Oxidation of phenol with $Na_2Cr_2O_7/H^+$

$$C_6H_5OH \xrightarrow{Na_2Cr_2O_7/H^+} \text{p-Benzoquinone}$$

(iii) $(CH_3)_3COH \xrightarrow{Cu,sTaK} (CH_3)_2C = CH_2 + H_2O$

Tert-butyl alcohol undergoes dehydration to give 2-methylpropene.

62. **(A)** Isomer of C_5H_{10} giving only one monochloro product:

Cyclopentane

All hydrogens are equivalent.

(B) Increasing order of S_N2 reactivity:

2-Bromo-2-methylbutane < 2-Bromopentane < 1-Bromopentane

$(3° < 2° < 1°)$

(C) p-Dichlorobenzene is more symmetrical than ortho and meta isomers, so its molecules pack more efficiently in crystal lattice, giving higher melting point.

(D) Step 1: Formation of Grignard reagent

$$\text{Bromocyclobutane} \xrightarrow[\text{dry ether}]{Mg} \text{Cyclobutyl magnesium bromide}$$

So,

A = Cyclobutyl magnesium bromide

Step 2: Hydrolysis

$$\text{Cyclobutyl magnesium bromide} + H_2O \rightarrow \text{Cyclobutane}$$

So,

B = Cyclobutane

63. For first order reaction:

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

At 300K :

$$k_1 = \frac{0.693}{30} = 0.0231\ min^{-1}$$

At 320K :

$$k_2 = \frac{0.693}{10} = 0.0693\ min^{-1}$$

$$\frac{k_2}{k_1} = 3$$

Using Arrhenius equation:

$$\log\frac{k_2}{k_1} = \frac{E_a}{2.303R}\left(\frac{T_2 - T_1}{T_1T_2}\right)$$
$$0.4771 = \frac{E_a}{2.303 \times 8.314}\left(\frac{20}{300 \times 320}\right)$$
$$E_a \approx 4.39 \times 10^4 \text{Jrnol}^{-1}$$
$$E_a \approx 44 \text{ kJrnol}^{-1}$$

64. Given:

$w_2 = 19.5$ g, $M = 78$, $w_1 = 500$ g $= 0.5$ kg

Moles of solute:

$$= \frac{19.5}{78} = 0.25$$

Molality:

$$m = \frac{0.25}{0.5} = 0.5$$

Observed:

$\Delta T_f = 1°C$

$\Delta T_f = iK_fm$

$1 = i(1.86)(0.5)$

$$i = \frac{1}{0.93} = 1.075$$

For acid dissociation:

$i = 1 + \alpha$

$\alpha = 1.075 - 1 = 0.075$

$\alpha = 0.075$ or 7.5%

65. **(A)** Geometrical isomers of $[Co(en)_2Cl_2]^+$:

• cis-isomer

• trans-isomer

Optically inactive isomer:

trans-isomer

because it has a plane of symmetry.

(B) For $[CoF_6]^{3-}$:

Oxidation state of Co:

$x + 6(-1) = -3 \Rightarrow x = +3$

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

$F^-$is weak field ligand - high spin complex.

Hybridisation:

sp^3d^2

Magnetic behaviour:

4 unpaired electrons present.

Paramagnetic

66. **(A)** When an aldehyde interacts with an excess of alcohol in the presence of dry HCl , alkoxyalcohol intermediates known as hemiacetals are created, which then react with one more molecule of alcohol to give acetal, a gem-dialkoxy chemical.

(B) The carboxylate ion, the conjugate base of carboxylic acid, is stabilised by two equivalent resonance structures in which the negative charge resides at the more electronegative oxygen atom. The phenoxide ion conjugate base of phenol possesses non-equivalent resonance structures with a negative charge at the less electronegative carbon atom. As a result, resonance in phenoxide ions is less essential than in carboxylate ions. As a result, carboxylic acids are more acidic than phenols.

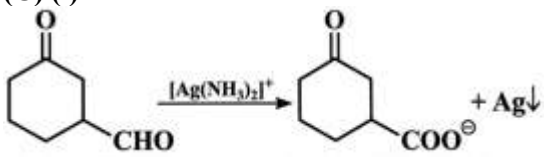
(C) (i)

$$(CH_3)_3C-\underset{\underset{O}{\|}}{C}-CH_3 < CH_3-\underset{\underset{O}{\|}}{C}-CH_3 < CH_3CHO$$

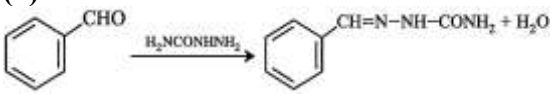
(ii) Even moderate oxidising agents like Tollen's reagent and Fehling's reagent oxidise aldehydes, generating carboxylic acid. Propanal, on the other hand, does not pass Tollen's test.

OR

(C) (i)



(ii)



67. (A) D-glucose pentaacetate does not react with hyroxylamine (NH_2OH). This is due to the lack of an aldehyde group and the open chain structure.

(B) Because vitamin C is water soluble, it dissolves in water and is eliminated from the body through the urine. As a result, the body cannot store vitamin C.

(C) (i) Peptide linkage $[-CO-NH-]$ is a peptide bond which is formed between two amino acids.

(ii) Protein found in a biological system with a unique three-dimensional structure and biological activity is called a native protein. When a protein in its native form, is subjected to physical change like change in temperature or chemical change like change in pH , the hydrogen bonds are disturbed. Due to this, globules unfold and helix get uncoiled and protein loses its biological activity. This is called denaturation of protein.

OR

(C) (i) Anomers are cyclic monosaccharides or glycoside epimers that differ in the configuration of C-1 if they are aldoses or C-2 if they are ketoses. The epimeric carbon in anomers is referred to as anomeric carbon or anomeric centre.

(ii) The two monosaccharides are joined together by an oxide linkage formed by the loss of a water molecule. Such a linkage between two monosaccharide units through an oxygen atom is called glycosidic linkage.

68. (A) (I) Account for the following

(i) $E^{\circ}(Mn^{3+}/Mn^{2+})$

is more positive than

$E^{\circ}(Cr^{3+}/Cr^{2+})$

because:

• Mn^{2+} has extra stable $3d^5$ half-filled configuration.

• Cr^{3+} already has stable $3d^3$ configuration.

Hence Mn^{3+} more readily gains electron to form stable Mn^{2+}.

(ii) • $Sc^{3+}: 3d^0 \rightarrow$ no unpaired electron, so colourless.

• $Ti^{3+}: 3d^1 \rightarrow$ d − d transition possible, hence coloured.

(iii) Actinoids show wide range of oxidation states because energies of 5f, 6d and 7s orbitals are very close.

(II) Preparation of $KMnO_4$ from MnO_2

Step 1: Formation of potassium manganate

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

Step 2: Conversion into potassium permanganate

$2\ K_2MnO_4 + Cl_2 \rightarrow 2KMnO_4 + 2KCl$

OR

(B) (I)

(i) Transition metals form alloys because

they have similar atomic sizes and can replace one another in crystal lattice.

(ii) Ce^{4+} is a strong oxidising agent because it easily changes to more stable Ce^{3+} state.

(II) Similarity:

Both lanthanoids and actinoids show variable oxidation states.

Difference:

• Lanthanoids involve filling of 4f orbitals.

• Actinoids involve filling of 5f orbitals.

(III) $Cr_2O_7^{2-} + 2OH^- \rightarrow 2CrO_4^{2-} + H_2O$

69. (A) (I) Give reasons:

(i) Aniline on nitration gives a significant amount of m-nitroaniline:

Nitration is carried out in a strongly acidic medium (H_2SO_4 and HNO_3). Under these conditions, the basic aniline group ($-NH_2$) gets protonated to form the anilinium ion ($-NH_3^+$). Unlike the amino group, the anilinium ion is a strongly deactivating and meta-directing group, leading to about 47%m-nitroaniline formation.

(ii) $(CH_3)_2NH$ is more basic than $(CH_3)_3$ N in aqueous solution:

In aqueous solution, basic strength is determined by the inductive effect, solvation effect (hydration), and steric hindrance. While $(CH_3)_3$ N has a stronger +I effect, it is less stabilized by hydration (hydrogen bonding with water) compared to ($CH_3)_2NH$ due to steric crowding. For the methyl-substituted amines, the order is: ($CH_3)_2NH > CH_3NH_2 > (CH_3)_3$ N.

(iii) Ammonolysis of alkyl halides is not good for preparing pure primary amines:

Ammonolysis leads to a mixture of primary, secondary, and tertiary amines, as well as quaternary ammonium salts. The primary amine formed acts as a nucleophile and reacts further with the remaining alkyl halide.

(II) Chemical Reactions:

(i) Carbylamine test:

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

(Produces a foul-smelling isocyanide; only for primary amines).

(ii) Gabriel phthalimide synthesis:

This involves reacting phthalimide with KOH to form potassium phthalimide, which reacts with an alkyl halide ($R-X$), followed by alkaline hydrolysis to yield a pure primary aliphatic amine.

OR

(B) (I) Identify structures A, B, and C:

• Reaction **(i):**

(1) A: Benzonitrile (C_6H_5CN) - formed via Sandmeyer-type reaction with CuCN .

(2) B: Benzoic acid (C_6H_5COOH) - formed by complete hydrolysis of the nitrile.

(3) C: Benzamide ($C_6H_5CONH_2$) - formed by reacting the acid with NH_3 and heating.

• Reaction **(ii):**

(1) A: Aniline ($C_6H_5NH_2$) - formed by the reduction of nitrobenzene with Fe/HCl.

(2) B: Benzene diazomium chloride ($C_6H_5\ N_2^+Cl^-$)-formed via diazotization.

(3) C: Benzene ($\mathbf{C_6H_6}$) - formed by the reduction of the diazonium salt using ethanol (C_2H_5OH).

(II) Why aniline does not undergo Friedel-Crafts reaction?

Aniline is a Lewis base, and the catalyst used in Friedel-Crafts ($AlCl_3$) is a strong Lewis acid. They react to form a salt. This places a positive charge on the Nitrogen ($C_6H_5NH_2^+ - AlCl_3^-$), which strongly deactivates the benzene ring toward electrophilic substitution.

(III) Increasing order of boiling point:

$(CH_3)_3$ N $< C_2H_5NH_2 < C_2H_5OH$

• Reason: Alcohols have stronger intermolecular hydrogen bonding than amines. Among amines, primary amines ($C_2H_5NH_2$) have higher boiling points than tertiary amines ($(CH_3)_3$ N) because tertiary amines lack hydrogen atoms bonded to Nitrogen for hydrogen bonding.

70. (A) Given: Conductivity (K) $= 8 \times 10^{-5}$ S cm^{-1}

Molarity (M) $= 2 \times 10^{-3}$M

Formula:

Molar conductivity, $\Lambda_m^c = \frac{K \times 1000}{C}$

Degree of dissociation, $\alpha = \frac{\Lambda_m^c}{\Lambda_m^0}$

$$\Lambda_m^0 = \frac{K \times 1000}{C}\ S\ cm^2\ mol^{-1}$$

$$= \frac{8 \times 10^{-5} \times 1000}{2 \times 10^{-3}}$$

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

$$\propto = \frac{\Lambda_m^c}{\Lambda_m^0}$$

$$= \frac{40}{404}$$

$$= 0.1$$

(B) $E_{cell}^0 = E_C^0 - E_A^0$

$= 0.80 - (-0.25)$
$= 1.05\ V$
$\Delta G^0 = -nFE^0_{cell}$
$= -2 \times 96500 \times 1.05$
$= -2 \times 10^5\ J$
$\Delta G^0 = 2.303RT\log K_c$
$\log K_c = \frac{2 \times 10^5}{2.303 \times 8.314 \times 298}$
$\log K_c = 35.52$

71. (c) • Enantiomers
• They have the same density, melting point, boiling point, and chemical reactivity in achiral environments.
• But they have opposite specific rotations, not the same.

72. (b) • Aspirin
• Aspirin (acetylsalicylic acid) is obtained by acetylation of salicylic acid.

73. (b)• Reactivity of Carbonyl Compounds
• Reactivity towards nucleophilic addition depends on:
• Electrophilicity of carbonyl carbon (less alkyl groups → more reactive).
• Order: Formaldehyde (I) > Acetaldehyde (II) > Acetone (III).

74. (d) • p-Toluidine (CH3 substituent): Methyl group is electron-donating (+1 effect), increases electron density on $-NH_2$, slightly stronger base than aniline.
• p-Nitroaniline (NO_2 substituent): Nitro group is strongly electron-withdrawing (-I and -M effects), decreases electron density on $-NH_2$, much weaker base.
• Aniline: Lone pair on nitrogen partially delocalized into ring, moderate base.
• Benzylamine ($-CH_2 - NH_2$): The $-NH_2$ group is attached to a saturated carbon (not directly conjugated with benzene). Lone pair is fully available for protonation, making it more basic than aniline derivatives.

75. (a) • Hydrolysis of Carbohydrates
• Starch → glucose + maltose (not only glucose).
• Fructose → monosaccharide, no hydrolysis.
• Lactose → glucose + galactose.
• Sucrose → glucose + fructose.
• Only starch hydrolyzes to give only glucose units.

76. (d) • Water-soluble Vitamin
• Fat-soluble: A, D, E, K.
• Water-soluble: Vitamin C (ascorbic acid).

77. (c) For a zero-order reaction, the rate is $k[A]^0 = k$. Therefore, the units for both are mol L^{-1} s^{-1}.

78. (b) According to the Kohlrausch equation, as the concentration (C) approaches zero (infinite dilution), the molar conductivity (Λ) becomes equal to the limiting molar conductivity (Λ_0).

79. (a) A maximum boiling azeotrope occurs when there is a large negative deviation from Raoult's law, meaning the vapor pressure is lower and the boiling point is higher than the individual components.

80. (a) Osmotic pressure is preferred for proteins because measurements are taken around room temperature (preventing denaturation) and it provides larger, more readable values for substances with high molar masses.

81. (c) Highest oxidation state is shown when maximum number of electrons can participate in bonding.
Configuration:
$3d^5 4s^2$
has total 7 valence electrons, so it can show highest oxidation state +7 .
Hence correct option is:
(Mn configuration)

82. (b) $[Ni(NH_3)_6]Cl_2$ dissociates as:
$[Ni(NH_3)_6]Cl_2 \rightarrow [Ni(NH_3)_6]^{2+} + 2Cl$
Total number of ions $= 3$

83. (b) Species not expected to be a ligand:
NH_4
It has no lone pair available for donation.

84. (b) The most stable complex species is:

$[Fe(CN)_6]^3$

because CN^- is a strong field ligand and forms highly stable complexes.

85. (d) Order vs Molecularity

• Assertion (A): Order and molecularity are always same → X False.

Order = experimentally determined; molecularity = number of species in elementary step. They can differ in complex reactions.

• Reason (R): Complex reactions involve multiple steps, slowest step is rate-determining → True.

• Conclusion: A is false, R is true.

86. (a) Electrolysis of NaCl (aq)

• Assertion (A): Electrolysis gives Cl_2 at anode instead of O_2 → True.

• Reason (R): Formation of O_2 requires overpotential → True, correct explanation.

87. (c) Nucleophilic substitution of haloalkanes

• Assertion (A): lodoethane substitution easier than chloroethane → True.

• Reason (R): Bond energy of $C-Cl < C-1$ → False (actually $C-1$ bond is weaker, so easier to break).

88. (a) Zinc as transition element

• Assertion (A): Zinc is not regarded as transition element → True.

• Reason (R): 3d orbitals completely filled in ground and oxidized state → True, correct explanation.

89. (A) Reaction of methanal with $(CH_3)_2CHMgBr$ followed by hydrolysis

$$HCHO^3 + (CH_3)_2CHMgBr^2 \xrightarrow{\text{drg ether}} (CH_3)_2CHCH_2OMgBr \xrightarrow{H_3O^+} (CH_3)_2CHCH_2OH$$

Product structure:

$CH_3 - CH(CH_3) - CH_2OH$

IUPAC name: 2-Methylpropan-1-ol

(B) Reaction of phenol with conc. HNO_3

$C_6H_5OH + 3HNO_3 \rightarrow C_6H_2(NO_2)_3OH + 3H_2O$

Product 2,4,6-Trinitrophenol (Picric acid)

90. Given reaction:

$2\ N_2O_5(g) \rightarrow 4NO_2(g) + O_2(g)$

Increase in concentration of NO_2 :

$\Delta[NO_2] = 5 \times 10^{-8}$ mol L L^{-1}

Time $= 10$ s

(A) Rate of formation of NO_2

$$\text{Rate} = \frac{\Delta[NO_2]}{\Delta t}$$

$$= \frac{5 \times 10^{-8}}{10}$$

$$= 5 \times 10^{-9} \text{ mol } L^{-1} s^{-1}$$

(B) Rate of consumption of N_2O_5

From stoichiometry:

$$-\frac{1}{2}\frac{d[N_2O_3]}{dt} = \frac{1}{4}\frac{d[N_O]}{dt}$$

$$\frac{d[N_2O_5]}{dt} = \frac{1}{2}\frac{d[NO_2]}{dt}$$

$$= \frac{1}{2}(5 \times 10^{-9})$$

$$= 2.5 \times 10^{-9} \text{ mol } L^{-1} s^{-1}$$

91. (A) A fuel cell is an electrochemical cell that converts the chemical energy of fuel directly into electrical energy.

Two advantages:

(1) High efficiency.

(2) Eco-friendly and non-polluting.

OR

(B) Given:

$E^\circ_{X^{2+}/X} = -2.36$ V

$E^\circ_{Y^{2+}/Y} = -0.14$ V

$E^{\circ}_{F^{2+}/Fe} = -0.44\ V$
Metal X is better for coating iron.
Reason:
A metal having more negative reduction potential than iron acts as sacrificial anode and corrodes preferentially, protecting iron from corrosion.
Since:
$2.36\ V < -0.44\ V$
X is more reactive than Fe .

92. (A) (i) Storage of carbohydrates in animal body
Carbohydrates are stored as glycogen.
They are mainly present in:
• Liver
• Muscles
(ii) Structural difference between starch and cellulose
• Starch contains α-glucose units linked by $\alpha(1 \rightarrow 4)$ glycosidic bonds.
• Cellulose contains β-glucose units linked by $\beta(1 \rightarrow 4)$ glycosidic bonds.

OR

(B) (i) Peptide linkage vs Glycosidic linkage

Peptide linkage	Glycosidic linkage
Linkage between two amino acids	Linkage between two monosaccharides
Formed by $-CO-NH-$ group	Formed through oxygen atom

(ii) Nucleoside vs Nucleotide

Nucleoside	Nucleotide
Sugar + Nitrogen base	Sugar + Nitrogen base + Phosphate
No phosphate group	Contains phosphate group

93. (A) Carboxylic carbon is less electrophilic than carbonyl carbon of aldehydes and ketones. In carboxylic acids, the lone pair of electrons on the $-OH$ oxygen participates in resonance with the carbonyl group:
$R-C(=O)-OH \leftrightarrow R-C(-O^{-})=OH^{+}$
This decreases the positive charge on carbonyl carbon, making it less electrophilic.
(B) Propanal is more reactive than propanone towards addition of HCN .
• In propanone, two CH_3 groups show $+I$ effect and reduce the positive charge on carbonyl carbon.
• Propanone also has greater steric hindrance.
Therefore, nucleophilic addition of HCN occurs more easily in propanal.

94. (A) Carbylamine reaction
$C_2H_5NH_2 + CHCl_3 + 3KOH \rightarrow C_2H_5NC + 3KCl + 3H_2O$
(ethyl isocyanide formed)
(B) Gabriel phthalimide synthesis
$C_6H_4(CO)_2NH + KOH \rightarrow C_6H_4(CO)_2NK + H_2O$
$C_6H_4(CO)_2NK + RBr \rightarrow C_6H_4(CO)_2NR + KBr$
On hydrolysis:
$C_6H_4(CO)_2NR + H_2O \rightarrow RNH_2 +$ Phthalic acid

95. (A) Aquatic animals are more comfortable in cold water than warm water.

Solubility of gases increases with decrease in temperature. Therefore, cold water contains more dissolved oxygen needed for aquatic life.

(B) Sprinkling salt helps in clearing snow-covered roads.

Salt lowers the freezing point of water (freezing point depression), causing snow/ice to melt even below $0°C$

96. (A) Mechanism of dehydration of ethanol

Reaction:

$$CH_3CH_2OH \xrightarrow[443\ K]{H^+} CH_2 = CH_2 + H_2O$$

Step 1: Protonation of ethanol

$CH_3CH_2OH + H^+ \rightarrow CH_3CH_2OH_2^+$

Alcohol gets protonated.

Step 2 : Removal of water molecule

$CH_3CH_2OH_2^+ \rightarrow CH_3CH_2^+ + H_2O$

Ethyl carbocation is formed.

Step 3 : Elimination of proton

$CH_3CH_2^+ \rightarrow CH_2 = CH_2 + H^+$

Ethene is formed.

(B) Preparation of phenol from cumene

$C_6H_5CH(CH_3)_2 + O_2 \rightarrow C_6H_5C(CH_3)_2OOH$

(Cumene hydroperoxide)

On acidic hydrolysis:

$$C_6H_5C(CH_3)_2OOH \xrightarrow{H^+} C_6H_5OH + (CH_3)_2CO$$

Products formed are phenol and acetone.

97. (A) Organic Reaction Sequences

(i)• A: Benzamide $(C_6H_5CONH_2)$

• Benzoic acid reacts with ammonia (NH_3) under heating (Δ) to form benzamide via dehydration of the intermediate ammonium salt.

• B: Aniline $(C_6H_5NH_2)$

• Benzamide undergoes the Hofmann Bromamide Degradation reaction with $\mathbf{Br_2}/NaOH$ to form a primary amine with one less carbon atom.

• C: Benzene diazonium chloride $(C_6H_5\ N_2^+Cl^-)$

• Aniline reacts with nitrous acid (generated in situ from $NaNO + HCl$) at $0°C$ to undergo diazotization.

(ii)• A: Propanenitrile (CH_3CH_2CN)

• Ethyl bromide reacts with KCN via nucleophilic substitution (S_N2) to replace the bromide with a cyano group.

• B: Propan-1-amine $(CH_3CH_2CH_2NH_2)$

• Lithium aluminium hydride $(LiAlH_4)$ reduces the nitrile group to a primary amine.

• C: Propan-1-ol $(CH_3CH_2CH_2OH)$

• Aliphatic primary amines react with nitrous acid (HNO_2) at low temperatures to form unstable diazonium salts which immediately decompose into the corresponding alcohol and nitrogen gas.

OR

(B) Conversions

(i) Aniline to p-bromoaniline:

(1) Protect the $-NH_2$ group by acetylation: $C_6H_5NH_2 + (CH_3CO)_2O \rightarrow C_6H_5NHCOCH_3$ (Acetanilide).

(2) Bromination: $C_6H_5NHCOCH_3 + Br_2/CH_3COOH \rightarrow p-BrC_6H_4NHCOCH_3$.

(3) Deprotection (hydrolysis): $p-BrC_6H_4NHCOCH_3 + H_2O/H^+ \rightarrow p-BrC_6H_4NH_2$.

(ii) Ethanoic acid to methanamine:

(1) Convert to amide: $CH_3COOH + NH_3, \Delta \rightarrow CH_3CONH_2$.

(2) Hofmann Bromamide Degradation: $CH_3CONH_2 + Br_2/NaOH \rightarrow CH_3NH_2$.

(iii) Butanenitrile to 1-aminobutane:

• Reduction: $CH_3CH_2CH_2CN + H_2/Pd$ (or $LiAlH_4$)

$\rightarrow CH_3CH_2CH_2CH_2NH_2$.

98. Percentage Association of Acetic Acid

Given: $w_2 = 0.3\ g, M_2 = 60\ g\ mol^{-1}, w_1 = 30\ g, \Delta T_f = 0.45\ K, K_f = 5.12 Kkgmol^{-1}$.

(1) Calculate Observed Molar Mass (M_{obs}):

$$\Delta T_f = K_f \cdot \frac{w_2 \times 1000}{M_{obs} \times w_1}$$

$$0.45 = 5.12 \cdot \frac{0.3 \times 1000}{M_{obs} \times 30} \Longrightarrow M_{obs} = \frac{5.12 \times 10}{0.45} \approx 113.78 \text{ g mol}^{-1}$$

(2) Calculate van't Hoff Factor (i):

$$i = \frac{\text{Normal Molar Mass}}{\text{Observed Molar Mass}} = \frac{60}{113.78} \approx 0.527$$

(3) Calculate Degree of Association (α):

For dimerization, $i = 1 - \alpha/2$.

$0.527 = 1 - \alpha/2 \Longrightarrow \alpha/2 = 0.473 \Longrightarrow \alpha = 0.946$

Percentage Association = 94.6%

99. Activation Energy Calculation

Given: $T_1 = 300$ K, $T_2 = 310$ K, $k_2/k_1 = 2$, $R = 8.314$ J K^{-1} mol^{-1}.

Using the Arrhenius Equation:

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

$$\log(2) = \frac{E_a}{2.303 \times 8.314}\left[\frac{10}{300 \times 310}\right]$$

$$0.3010 = \frac{E_a}{19.147} \times \frac{10}{93000} \Longrightarrow E_a = \frac{0.3010 \times 19.147 \times 9300}{1} \approx 53598 \text{ J mol}^{-1}$$

$E_a \approx 53.6$ kJ mol^{-1}

100. Products of D-Glucose Reaction

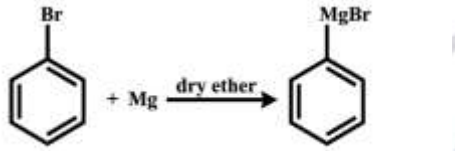
(A) HI: n-hexane ($CH_3(CH_2)_4CH_3$)

(B) Conc. HNO_3 : Saccharic acid (Glucaric acid) ($HOOC-(CHOH)_4-COOH$)

(C) Br_2 water: Gluconic acid ($HOOC-(CHOH)_4-CH_2OH$)

(D) HCN: Glucose cyanohydrin ($NC-CH(OH)-(CHOH)_4-CH_2OH$)

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



Bromobenzene **Phenylmagnesium bromide**

(ii) Compounds reacting faster in S_N1 reaction with OH^-

(1)

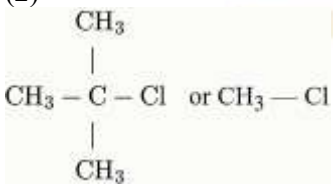
$CH_2 = CH - CH_2Cl$

reacts faster than

$CH_3CH_2CH_2Cl$

because allyl carbocation formed is resonance stabilised.

(2)



• The S_N2 mechanism involves the attack of the nucleophile at the atom bearing the leaving group. But, in case of $(CH_3)_3CCl$, the attack of the nucleophile at the carbon atom is hindered because of the presence of bulky substituents on that carbon atom bearing the leaving group. On the other hand, there are no bulky substituents on the carbon atom bearing the leaving group in CH_3Cl. Hence, CH_3Cl reacts faster than $(CH_3)_3CCl$ in S_N2 reaction with OH^-.

(iii) Preparation of 1-iodobutane

(1) From 1-chlorobutane

$CH_3CH_2CH_2CH_2Cl + NaI \rightarrow CH_3CH_2CH_2CH_2I + NaCl$

(Finkelstein reaction)

(2) From but-1-ene

$CH_2 = CHCH_2CH_3 \xrightarrow{HBr} CH_3CHBrCH_2CH_3$

$CH_3CHBrCH_2CH_3 \xrightarrow{NaI} CH_3CHICH_2CH_3$

(formation of butyl iodide)

OR

(iii)

(1) $CH_3 - CH(Br) - CH_3 + KOH$ (ethanol, heat)

• This is 2-bromopropane treated with alcoholic KOH .

• Reaction: Dehydrohalogenation (elimination, E2).

• Product: Propene ($CH_2CH - CH_3$).

$CH_3 - CH(Br) - CH_3 \rightarrow CH_2 = CH - CH_3 + HBr$

Major product: Propene

(2) Chlorobenzene $+CH_3COCl$ (anhyd. $AlCl_3$)

• This is Friedel-Crafts acylation.

• Reaction: Substitution of acetyl group onto benzene ring.

• Product: Acetophenone ($C_6H_5 - CO - CH_3$).

$C_6H_5Cl + \underset{Cl}{CH}COCl \rightarrow C_6H_5COCH_3 + HCl$

Major product: Acetophenone

102. **(i)** Formula and Secondary Valency for Nickel

• Structural Formula: $[Ni(H_2O)_6]Cl_2$

• Secondary Valency: 6 (The secondary valency equals the coordination number, which is the number of ligands directly attached to the central metal ion).

• Reasoning: The precipitation of 2 moles of AgCl per mole of compound indicates that both chlorine atoms are outside the coordination sphere as ionizable chloride ions, leaving the six water molecules inside as ligands.

(ii) IUPAC Name of the Ionisation Isomer

• IUPAC Name: Pentaamminesulphatocobalt(III) chloride

• Reasoning: The ionization isomer of $[Co(NH_3)_5(SO_4)]Cl$ is $[Co(NH_3)_5Cl]SO_4$, where the sulphate ion acts as the counter ion.

(iii) Using VBT (Valence Bond Theory)

(1) $[Ni(CO)_4]$:

• Geometry: Tetrahedral

• Magnetic Nature: Diamagnetic (all electrons are paired).

• Reasoning: Nickel is in the 0 oxidation state with a $3d^8 4s^2$ configuration. Strongfield CO ligands force electrons to pair up, causing 4s and 3d electrons to pair into the inner orbitals. This results in sp^3 hybridization.

(2) $[Fe(CN)_6]^{3-}$:

• Geometry: Octahedral

• Magnetic Nature: Paramagnetic (has 1 unpaired electron).

• Reasoning: Iron is in the +3 oxidation state ($3d^5$). The strong-field CN^- ligands cause pairing of the 3d electrons, forcing them into lower energy orbitals. This makes available two empty 3d orbitals for d^2sp^3 hybridization.

OR

(iii) Give Reasons:

(1) Low spin tetrahedral complexes are not formed:

• In tetrahedral complexes, the crystal field splitting energy (Δ_t) is significantly lower than in octahedral complexes (roughly $\Delta_t = \frac{4}{9}\Delta_o$). Because this splitting energy is generally much smaller than the pairing energy (P), it is not energetically favorable for electrons to pair up. Thus, tetrahedral complexes remain high spin.

(2) $[Co(NH_3)_6]^{3+}$ is an inner orbital complex whereas $[Ni(NH_3)_6]^{2+}$ is an outer orbital complex:

• In $[Co(NH_3)_6]^{3+}$, Cobalt is in the +3 oxidation state ($3d^6$) and NH_3 acts as a strong ligand. It forces the unpaired electrons to pair up, vacating two 3d orbitals for d^2sp^3 inner orbital hybridization. In $[Ni(NH_3)_6]^{2+}$, Nickel is in the +2 oxidation state ($3d^8$). The presence of 8 electrons leaves only one empty 3d orbital, which is insufficient for d^2sp^3. Therefore, it uses the outer 4d orbitals, undergoing sp^3d^2 outer orbital hybridization.

103. **(i)** Account for the following :

(1) Transition metals form complex compounds.

Transition metal ions have:

• small size,
• high charge density, and
• vacant d-orbitals.
Therefore, they can accept lone pairs from ligands and form coordination complexes.
(2) $E^{\circ}_{Mn^{2+}/Mn}$ value for manganese is highly negative.
Mn: $3d^5 4s^2$
Mn^{2+}: $3d^5$
Mn^{2+} has extra stability due to half-filled $3d^5$ configuration. Hence, conversion of Mn to Mn^{2+} is favourable, making reduction potential highly negative.
(3) Cu^{+}ion is unstable in aqueous solution.
Cu^{+}undergoes disproportionation:
$2Cu^{+} \rightarrow Cu^{2+} + Cu$
Hence, $Cu^{+}$is unstable in aqueous solution.
(ii) Preparation of $KMnO_4$ from pyrolusite ore (MnO_2)
Step 1 : Formation of potassium manganate
$2MnO_2 + 4KOH + O_2 \xrightarrow{heat} 2\ K_2MnO_4 + 2H_2O$
Step 2 : Conversion of manganate into permanganate
$2\ K_2MnO_4 + Cl_2 \rightarrow 2KMnO_4 + 2KCl$

OR

(B) (i) Identify the following :
(1) Transition metal showing only one oxidation state
Scandium (Sc)
(usually shows only +3 oxidation state)
(2) Transition metal acting as strong reducing agent in +2 state
Chromium (Cr^{2+})
(ii) Complete and balance the equations
(1) $Cr_2O_7^{2-} + 14H^{+} + 6Fe^{2+} \rightarrow 2Cr^{3+} + 6Fe^{3+} + 7H_2O$
(2) $2KMnO_4 \xrightarrow{heat} K_2MnO_4 + MnO_2 + O_2$
(iii) Misch metal
Misch metal is an alloy of lanthanoids containing mainly cerium, lanthanum and neodymium with small amount of iron.
One use:
It is used in making cigarette lighter flints.

104. **(A) (i)** Molecular formula: $C_5H_{10}O$
(1) Gives positive iodoform test
Compound must contain CH_3CO - group.
Structure:
Pentan-2-one
$CH_3COCH_2CH_2CH_3$
(2) Shows Cannizzaro reaction
Cannizzaro reaction is shown by aldehydes without α-hydrogen.
Structure:
2,2-Dimethylpropanal
$(CH_3)_3CCHO$
(3) Reduces Tollens' reagent and has a chiral carbon
Must be an aldehyde with one chiral carbon.
Structure:
3-Methylbutanal
$CH_3CH(CH_3)CH_2CHO$
(Second carbon is chiral.)
(ii) Reactions
(1) Wolff-Kishner reduction
Aldehyde/ketone on heating with hydrazine in presence of strong base gives alkane.
$R - CO - R \xrightarrow[KOH,\ heat]{NH_2NH_2} R - CH_2 - R + N_2 + H_2O$

(2) Hell-Volhard-Zelinsky (HVZ) reaction

Carboxylic acids having α-hydrogen undergo α-halogenation.

$$RCH_2COOH \xrightarrow[\Delta]{Br_2/P} RCHBrCOOH$$

OR

(B) (i) Conversion to Benzoic acid

(1) Acetophenone → Benzoic acid

Oxidation:

$$C_6H_5COCH_3 \xrightarrow{KMnO_4/H^+} C_6H_5COOH$$

(2) Ethylbenzene → Benzoic acid

Strong oxidation:

$$C_6H_5CH_2CH_3 \xrightarrow{KMnO_4,\ heat} C_6H_5COOH$$

(3) Bromobenzene → Benzoic acid

$$C_6H_5Br \xrightarrow{Mg/\ dry\ ether} C_6H_5MgBr$$

$$C_6H_5MgBr \xrightarrow{CO_2/H^+} C_6H_5COOH$$

(ii) Arrange in increasing order

(1) Acidic character

Given:

$O_2NCH_2COOH, FCH_2COOH, NCCH_2COOH$

Electron withdrawing power:

$NO_2 > CN > F$

Hence acidity:

$FCH_2COOH < NCCH_2COOH < O_2NCH_2COOH$

(2) Reactivity in nucleophilic addition reactions

Given:

Ethanal, Propanal, Propanone, Butanone

Reactivity decreases with increase in +1 effect and steric hindrance.

Order:

Butanone < Propanone < Propanal < Ethanal

105. **(A)** EMF of cell

Cell :

$Zn(s)|Zn^{2+}(0.1M)||H^+(0.01M)|H_2(1bar), Pt$

Step 1 : Cell reaction

$Zn + 2H^+ \rightarrow Zn^{2+} + H_2$

Step 2 : Standard emf

$E^\circ_{cell} = E^\circ_{cathode} - E^\circ_{anode}$

$= 0.00 - (-0.76) = 0.76\ V$

Step 3 : Reaction quotient

$$Q = \frac{[Zn^{2+}]P_{H_2}}{[H^+]^2}$$

$$= \frac{0.1 \times 1}{(0.01)^2} = \frac{0.1}{10^{-4}} = 10^3$$

Step 4 : Nernst equation

$$E_{cell} = E^\circ_{cell} - \frac{0.0591}{n}\log Q$$

Here $n = 2$

$$E_{cell} = 0.76 - \frac{0.0591}{2}\log(10^3)$$

$$= 0.76 - \frac{0.0591}{2} \times 3$$

$$= 0.76 - 0.08865$$

$$= E_{cell} \approx 0.67\ V$$

(B) Kohlrausch law of independent migration of ions

Statement :

At infinite dilution, each ion contributes independently to the molar conductivity of the electrolyte irrespective of the nature of the other ion present.

$\Lambda_m^\circ = \lambda_+^\circ + \lambda^\circ$

Why conductivity decreases on dilution?

Conductivity decreases on dilution because the number of ions per unit volume decreases. Hence the solution carries less current.

106. **(b)** In complete tetramerization, 4 molecules combine to form 1 molecule.

So, if initially there are 4 particles, after association only 1 particle remains.

$$i = \frac{\text{final number of particles}}{\text{initial number of particles}} = \frac{1}{4} = 0.25$$

107. **(d)** For a zero order reaction,

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

where R is the initial concentration.

108. **(a)** In α-D-glucose, the CH_2OH group is above the plane and the OH group on the anomeric carbon $(C-1)$ is below the plane.

This corresponds to structure (a).

109. **(c)** Since Zn, Cd and Hg have completely filled d-orbitals (d^{10}), they do not show typical transition metal properties.

110. **(b)** In the two complexes, the anion inside and outside the coordination sphere gets exchanged.

$[Co(NH_3)_5NO_3]SO_4$ and $[Co(NH_3)_5SO_4]NO_3$

This is ionization isomerism.

111. **(a)** 1-Phenyl-2-chloropropane with alcoholic KOH undergoes β-elimination giving the more stable alkene.

Main product:

$C_6H_5CH = CHCH_3$

which is 1-phenylpropene.

112. **(d)** Diethyl ether reacts with excess HI as:

$C_2H_5OC_2H_5 + 2HI \rightarrow 2C_2H_5I + H_2O$

Hence product formed is ethyl iodide.

113. **(b)** Reduction of ethanenitrile (CH_3CN) with sodium and -lanhal sives a primary amine:

$CH_3CN \rightarrow Cr_3Cr_2IvII_2$

which is 1-aminoethane (ethylamine).

114. **(d)** Reduction reaction:

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

1 mole of MnO_4^- requires 5 moles of electrons = 5 Faradays.

115. **(a)** Let order $= n$.

Rate $\propto [R]^n$

Given:

$16 = 4^n$

$16 = (2^2)^n = 2^{2n}$

$2^{2n} = 2^4$

$2n = 4 \Rightarrow n = 2$

116. **(a)** On hydrolysis, the carbohydrate which gives only glucose is:

117. **(d)** Deficiency of which vitamin causes Pernicious anaemia?

118. **(b)** $C_6H_5CHO + CH_3COCH_3 \xrightarrow[\Delta]{OH^-} C_6H_5CH = CHCOCH_3$

This reaction is known as:

119. **(c)** The compound in which the central atom has oxidation state +3 is:

For $[Fe(C_2O_4)_3]^{3-}$:

Oxidation state of Fe $= x$

$x + 3(-2) = -3$

$x - 6 = -3$

$x = +3$

120. **(a)** Freezing Point Depression

• Assertion (A): When NaCl is added to water, a depression in freezing point is observed → True.
• Reason (R): Lowering of vapour pressure of a solution causes depression in freezing point → True.
• The reason correctly explains the assertion (colligative property).
So, Both A and R are true, and R is the correct explanation of A.

121. **(d)** Molar Conductivity of Weak Electrolytes
• Assertion (A): Λ_m for weak electrolytes shows a sharp decrease when diluted → False. Actually, molar conductivity increases with dilution.
• Reason (R): For weak electrolytes, degree of dissociation increases with dilution → True.
• Since A is false but R is true, the assertion is incorrect.

122. **(b)** Radii of Zr and Hf
• Assertion (A): Zr and Hf have almost identical radii → True.
• Reason (R): Both exhibit similar properties → True, but this is due to lanthanide contraction, not just similarity of properties.
• R is true but not the correct explanation of A.
So, Both A and R are true, but R is not the correct explanation of A.

123. **(a)** Monobromination of Aniline
• Assertion (A): Monobromination of aniline can be conveniently done by protecting the amino group via acetylation → True.
• Reason (R): Acetylation decreases the activating effect of the amino group → True.
• The reason correctly explains the assertion.
So, Both A and R are true, and R is the correct explanation of A.

124. Since both alkenes on hydrogenation give 2,3-dimethylbutane, the alkyl halide must be:
$(A) = CH_3 - CH(CH_3) - CH(CH_3) - CH_2Cl$
i.e. 1-chloro-2,3-dimethylbutane
On treatment with alcoholic KOH , elimination gives two alkenes:
$(B) = CH_2 = C(CH_3) - CH(CH_3) - CH_3$
(2,3-dimethylbut-1-ene)
and
$(C) = CH_3 - C(CH_3) = C(CH_3) - CH_3$
(2,3-dimethylbut-2-ene)

125. **(A)** Mixture of ethanol and acetone shows positive deviation from Raoult's law.
Reason:
The intermolecular hydrogen bonding present in pure ethanol becomes weaker when acetone is added.
Hence, intermolecular forces decrease and vapour pressure increases.

OR

(B) An azeotrope is a liquid mixture which boils at a constant temperture and has the same composition in liquid and vapour phases.
Negative deviation from Raoult's law forms a maximum boiling azeotrope.
Example: Mixture of nitric acid and water.

126. Types of Cells
(A) Fuel cell ($H_2 - O_2$ cell) → used in Apollo Space programme.
(B) Lead storage battery → used in automobiles and inverters.
(C) Mercury cell → suitable for hearing aids and watches.
(D) Dry cell → does not give steady potential, used in transistors.

127. Activation Energy Calculation
Equation:
$$\log k = 23.6 - \frac{2 \times 10^4}{T}$$
This is in the form of Arrhenius equation:
$$\log k = \log A - \frac{E_a}{2.303R} \cdot \frac{1}{T}$$
Comparing:
$$\frac{E_a}{2.303R} = 2 \times 10^4$$
$$E_a = 2 \times 10^4 \times 2.303 \times R$$

Substitute $R = 8.314\ \text{J/(mol} \cdot \text{K)}$:
$E_\alpha = 20000 \times 2.303 \times 8.314$
$E_\alpha \approx 3.83 \times 10^5\ \text{J/mol} = 383\ \text{kJ/mol}$
Activation energy = 383 kJ/mol
Quick Recap
• Alkyl halide structures
• Positive deviation ethanol-acetone
• Azeotrope definition
• Types of cells
• Activation energy calculation

128. Mechanism of Hydration of Ethene
Reaction:
$CH_2 = CH_2 + H_2O \xrightarrow{H^+} CH_3CH_2OH$
Mechanism (Electrophilic Addition):
(1) Protonation of double bond:
$CH_2 = CH_2 + H' \rightarrow CH_3 - CH_2'$
(formation of carbocation)
(2) Nucleophilic attack by water:
$CH_3 - CH_2' + H_2O \rightarrow CH_3 - CH_2OH_2'$
(3) Deprotonation:
$CH_3 - CH_2OH_2' \rightarrow CH_3 - CH_2OH + H'$
Product: Ethanol

129. Reactions / Conversions
(A)(i) Benzaldehyde + Conc. $NaOH, \Delta \rightarrow$ Cannizzaro Reaction
• One molecule oxidized to benzoic acid.
• Other reduced to benzyl alcohol.
Products: $C_6H_3COOH + C_6H_3CH_2OH$
(ii) Cyclopentanone $+H_2NNH - CO - NH_2$ (semicarbazide) → Semicarbazone derivative
Product: Cyclopentanone semicarbazone

OR

(B) Conversions:
(i) Toluene → Benzoic acid
Step 1: Side-chain oxidation with $KMnO_4$.
$C_6H_5CH_3 \xrightarrow{KMnO_4} C_6H_5COOH$
(ii) Benzaldehyde → 1-Phenylethanol
Step 1: Benzaldehyde $+CH_3MgBr$ (Grignard reagent) → 2-phenylpropan-2-ol intermediate.
Step 2: Hydrolysis → 1-Phenylethanol

130. IUPAC Names of Coordination Compounds
(A) $[Co(NH_3)_4Cl(NO_2)]Cl$
• Ligands: 4 ammines, 1 chloro, 1 nitro.
• Complex cation: Tetraamminechloronitrocobalt(III) chloride
(B) $[PtCl_2(en)_2]^{2'}$
• Ligands: 2 chloro, 2 ethylenediamine.
• Complex cation: Dichlorobis(ethane-1,2-diamine)platinum(IV)
Quick Links for Revision
• Hydration of ethene mechanism
• Cannizzaro reaction products
• Cyclopentanone semicarbazone
• Toluene to benzoic acid conversion
• Benzaldehyde to 1-phenylethanol
• IUPAC names of coordination compounds

131. **(A) (i)** Hydroboration-oxidation reaction
Addition of diborane followed by oxidation gives alcohol.
Example:

$CH_2 = CH_2 \xrightarrow[BH_3]{THF} CH_3CH_2BH_2 \xrightarrow{H_2O_2/OH} CH_3CH_2OH$

Ethene gives ethanol.

(ii) Product of the reaction

Anisole reacts with HBr to give phenol and methyl bromide:

$C_6H_5OCH_3 + HBr \rightarrow C_6H_5OH + CH_3Br$

(iii) Why is p -nitrophenol more acidic than phenol?

The $-NO_2$ group is an electron-withdrawing group. It stabilizes the phenoxide ion by resonance and inductive effect, hence proton removal becomes easier. Therefore, p-nitrophenol is more acidic than phenol.

OR

(B) (i)

(1) Reaction with conc. HNO_3

$C_6H_5OH + 3HNO_3 \xrightarrow{conc.} 2,4,6\text{-trinitrophenol} + 3H_2O$

(picric acid formed)

(2) Reaction with $CHCl_3$ and aqueous NaOH followed by acidification

$C_6H_5OH \xrightarrow[NaOH]{CHCl_3} o\text{-hydroxybenzaldehyde}$

(Reimer-Tiemann reaction)

(ii) Why does CH_3ONa with $(CH_3)_3CBr$ give 2-methylpropene?

$(CH_3)_3CBr$ is a tertiary alkyl halide. Due to steric hindrance, nucleophilic substitution is difficult, so elimination occurs preferentially, producing 2-methylpropene.

132. **(A)** Benzyl chloride is highly reactive towards S_N1 reaction.

Benzyl chloride forms a benzyl carbocation:

$C_6H_5CH_2^+$

This carbocation is resonance stabilized by the benzene ring, making S_N1 reaction fast.

(B) (±)-Butan-2-ol is optically inactive though it contains a chiral carbon atom.

$(\pm)$-Butan-2-ol is a racemic mixture containing equal amounts of dextrorotatory and levorotatory forms. Their optical rotations cancel each other, so the mixture is optically inactive.

(C) Chloroform is stored in closed dark coloured bottles.

Chloroform slowly reacts with oxygen in presence of light to form poisonous phosgene gas ($COCl_2$).

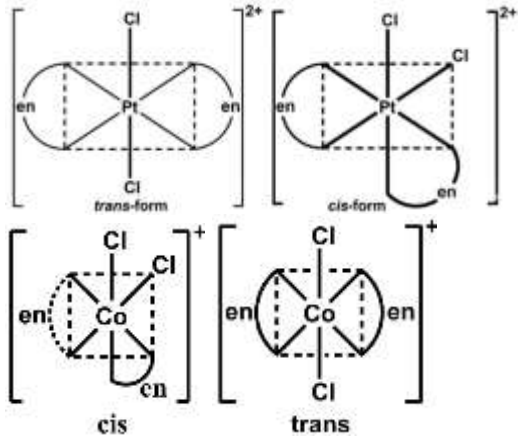
$2CHCl_3 + O_2 \xrightarrow{light} 2COCl_2 + 2HCl$

Therefore, it is stored in dark coloured closed bottles to prevent this reaction.

133. **(A)** Hybridization in $[Fe(CN)_6]^{3-}$ (Valence Bond Theory)

- Fe atomic number $= 26 \rightarrow$ electronic configuration: $[Ar]3\ d^6 4\ s^2$.
- In $Fe^{3+} \rightarrow [Ar]3\ d^5$.
- CN^- is a strong field ligand (spectrochemical series).
- It causes pairing of $3d$ electrons $\rightarrow$ configuration: $3d^6$ (paired), $4s^0, 4p^0$.
- Hybridization: d^2sp^3 (inner orbital complex).
- Geometry: Octahedral.
- Diamagnetic.

(B)



(C) $[NiCl_4]^{2-}$ vs $[Ni(CO)_4]$

• $[NiCl_4]^{2-}$: $Cl^-$is weak field ligand → no pairing → configuration 3 $d^8 4\ s^2$ → sp^3 hybridization, tetrahedral, paramagnetic (2 unpaired e^-).
• $[Ni(CO)_4]$: CO is strong field ligand → pairing occurs → 3 d^{10} → dsp^2 hybridization, square planar, diamagnetic.
Difference due to ligand field strength.
(D) Isomerism with ambidentate ligands
• Type: Linkage isomerism.
• Example: NO_2^-ligand → can bind via N (nitro) or O (nitrito).
Ambidentate ligand: NO_2^-, SCN^-.

134. Percentage Association of Benzoic Acid
Given:
• Mass $= 6.1$ g, M $= 122$ g/mol → moles $= 6.1/122 = 0.05$ mol.
• Volume $= 0.1$ L → concentration $= 0.5$M.
• Osmotic pressure $(\pi) = 6.5$ atm, T $= 300$ K.
• Expected (no association):
$\pi = cRT = 0.5 \times 0.0821 \times 300 \approx 12.3$ atm
• Observed $= 6.5$ atm.
• Van't Hoff factor $i = \frac{6.5}{12.3} \approx 0.53$.
• For dimerization: $i = 1 - \alpha/2$.
$0.53 = 1 - \alpha/2 \Rightarrow \alpha \approx 0.94$
Percentage association ≈ 94%

135. Rate Constant for First Order Decomposition of C_2H_5Cl
Reaction:
$C_2H_5Cl \rightarrow C_2H_4 + HCl$
• Initial pressure $= 0.4$ atm (only C_2H_3Cl).
• At time $t = 100$ s, total pressure $= 0.6$ atm.
• Let $x =$ pressure of products formed.
• Total pressure $= 0.4 + x$.
• At 100 s → $0.6 = 0.4 + x \rightarrow x = 0.2$ atm.
• Remaining $C_2H_2Cl = 0.4 - 0.2 = 0.2$ atm.
First-order rate law:

$$k = \frac{2.303}{t}\log\frac{[A]_0}{[A]_1}$$

$$k = \frac{2.303}{100}\log\frac{0.4}{0.2}$$

$$k = \frac{2.303}{100}\log 2$$

$$k = \frac{2.303}{100} \times 0.3010 \approx 0.00694\ s^{-1}$$

Rate constant k ≈ $6.9 \times 10^{-3}\ s^{-1}$
Quick Links for Revision
• Hybridization in $Fe(CN)_c^{3-}$
• Geometrical isomers of $PtCl_2(en)_2$
• $NiCl_4^{2-}$ vs $Ni(CO)_4$ magnetism
• Linkage isomerism with ambidentate ligands
• Percentage association of benzoic acid
• Rate constant for C_2H_5Cl decomposition

Peptide linkage	Glycosidic linkage
It is $-CONH-$ a linkage that exists in proteins formed by condensation of amino acids.	It is-O-linkage. In disaccharide two monosaccharide units are joined through oxygen atom i.e. glycosidic linkage.

136. **(i)** Difference Between Glycosidic Linkage and Peptide Linkage

Glycosidic Linkage	Peptide Linkage
A bond that joins two monosaccharide units (sugars).	A bond that joins two amino acids.
Formed by the condensation of hydroxyl (OH) groups of sugars.	Formed by the condensation of the carboxyl $(-COOH)$ group of one amino acid and the amino ($-NH_2$) group of another.
Found in carbohydrates such as maltose, sucrose, starch, and cellulose.	Found in proteins and peptides.
Has the general structure C-O-C.	Has the general structure- $CO-NH$ - (amide bond).
Example: The bond between two glucose molecules in maltose.	Example: The bond between glycine and alanine in a dipeptide.

(ii) Essential amino acids

Essential amino acids are α-amino acids that cannot be synthesized by the human body and therefore must be obtained directly through the daily diet.

(iii) Secondary structures of proteins and stabilizing forces

• Common types: The two most common types of secondary structures are the α helix structure and the β-pleated sheet structure.

• Stabilizing forces: The secondary and tertiary structures of proteins are stabilized by forces such as hydrogen bonds, disulphide linkages, van der Waals forces, and electrostatic forces of attraction.

OR

(iii) Denaturation of proteins

• Definition & Example: Denaturation is the process that alters the physical and biological properties of a protein-without breaking the primary structure-typically caused by changes in temperature (e.g., heating) or pH (e.g., adding acid). A common example is the coagulation or hardening of egg white (albumin) upon boiling.

• Structures affected: During denaturation, the higher-level structures of the protein (such as the secondary, tertiary, and quaternary structures) unfold and are disrupted, causing the protein to lose its biological activity.

137. **(i)** Increasing order of pK_b values in aqueous solution

The basic strength of ethylamines in an aqueous solution follows the order:

Diethylamine > Ethylamine > Triethylamine $[(C_2H_5)_2NH > C_2H_5NH_2 > (C_2H_5)_3N]$.

Because basic strength is inversely proportional to pK_b values, the increasing order of their pK_b values is:

$(C_2H_5)_2NH < C_2H_5NH_2 < (C_2H_5)_3\ N$

(ii) Nitration of Aniline

In aromatic electrophilic substitution reactions, the amino group ($-NH_2$) is typically ortho/para-directing. However, during direct nitration, a substantial amount of m nitroaniline is formed.

Reason: Nitration is carried out in a strongly acidic medium (using concentrated HNO_3 and H_2SO_4). In this acidic medium, the basic amino group gets protonated to form the anilinium ion $(-NH_3^+)$. The anilinium ion is electron-

withdrawing and strongly meta-directing, leading to the formation of the meta product.

(iii) Identification of A, B, and C

• A: Benzoic acid ($C_7H_6O_2$)

Structure: C_6H_5COOH

• B: Benzamide (C_7H_7NO)

Structure: $C_6H_5CONH_2$

• C: Aniline ($C_6H_7\ N$)

Structure: $C_6H_5NH_2$

Chemical Equations:

(1) $C_6H_5COOH + NH_3 \xrightarrow{\Delta} C_6H_5CONH_2 + H_2O$

(2) $C_6H_5CONH_2 + Br_2 + 4KOH \rightarrow C_6H_5NH_2 + K_2CO_3 + 2KBr + 2H_2O$

OR

(iii) (1) Reaction of Aniline with Br_2 (aq)

• In aqueous medium, the $-NH_2$ group strongly activates the benzene ring.

• Bromine reacts rapidly, giving 2,4,6-tribromoaniline as the major product.

$C_6H_5NH_2 + 3Br_2 \xrightarrow{aq} C_6H_2Br_3NH_2 + 3HBr$

Product: 2,4,6-tribromoaniline

(2) Reaction of Benzene Diazonium Chloride

Step (i): With HBF_4 → diazonium fluoroborate salt (stable crystalline).

$C_6H_5\ N_2^+Cl^- + HBF_4 \rightarrow C_6H_5\ N_2^+BF_4^-$

Step (ii): On heating with $NaNO_2/Cu$ (Sandmeyer-type reaction) → decomposition to fluorobenzene.

$C_6H_5\ N_2^+BF_4^- \xrightarrow{NaNO_2Cu,\Delta} C_6H_5F + N_2 + BF_3$

Product: Fluorobenzene

138. **(A)(i)** EMF of the Cell

Cell:

$Al(s)|Al^{3+}(0.001M)||Ni^{2+}(0.1M)|Ni(s)$

Standard reduction potentials:

• $E^*_{Al^{3+}/A1} = -1.66$ V

• $E^{2-}_{Na^{2+}/Ni} = -0.25$ V

Which is cathode?

• More positive potential = Ni^{2-}/Ni → cathode.

• Al^{3+}/Al → anode.

Standard cell potential:

$E^*_{coll} = E^*_{cathode} - E^*_{kinde} = (-0.25) - (-1.66) = +1.41$ V

Nernst equation:

$$E_{cell} = E_{cell} - \frac{0.0591}{n}\log Q$$

Reaction:

$2Al + 3Ni^{2+} \rightarrow 2Al^{3+} + 3Ni$

So $n = 6$.

Reaction quotient:

$$Q = \frac{[Al^{3+}]^2}{[Ni^{2+}]^3} = \frac{(0.001)^2}{(0.1)^3} = \frac{10^{-6}}{10^{-3}} = 10^{-3}$$

$\log Q = \log(10^{-3}) = -3$

$$E_{coll} = 1.41 - \frac{0.0591}{6}(-3)$$

$E_{cell} = 1.41 + 0.02955 \approx 1.44$ V

EMF ≈ 1.44 V

(ii) Why Λm° cannot be obtained by extrapolation for weak electrolytes

• For strong electrolytes, Λ m vs $\sqrt{\ }$ C gives a straight line (Debye-Hückel-Onsager equation). Extrapolation to C → 0 gives Λm°.

• For weak electrolytes, Λ m increases sharply with dilution due to increasing ionization. The curve is not linear, so extrapolation is impossible.

• Instead, Am^0 is obtained using Kohlrausch's law of independent migration of ions.

OR

(B)(i) Molar Conductivity and Degree of Dissociation

Given:

• $\Lambda m^\circ = \Lambda(NH_4^+) + \Lambda(Cl^-) = 73.8 + 76.2 = 150\ S\ cm^2\ mol^{-1}$

• Conductivity $K = 1.29 \times 10^{-2}\ S\ cm^{-1}$

• Concentration $c = 0.1M = 0.1\ mol/L = 0.1/1000 = 1 \times 10^{-4}\ mol/cm^3$

Molar conductivity:

$$\Lambda_m = \frac{\kappa}{c} = \frac{1.29 \times 10^{-2}}{1 \times 10^{-4}} = 129 Scm^2\ mol^{-1}$$

Degree of dissociation:

$$\alpha = \frac{\Lambda_m}{\Lambda_m^2} = \frac{129}{150} \approx 0.86$$

$\Lambda m = 129\ S\ cm^2\ mol^{-1}, \alpha \approx 86\%$

(ii) Half-cell potential for Zn^{2^+}/Zn

Nernst equation:

$$E = E^- - \frac{0.0591}{n} \log \frac{1}{[Zn^{2\prime}]}$$

Here, $n = 2, E'' = -0.76\ V, [Zn^{2+}] = 0.1M.$

$$E = -0.76 - \frac{0.0591}{2} \log \frac{1}{0.1}$$

$$E = -0.76 - 0.02955 \cdot \log 10$$

$$E = -0.76 - 0.02955 \cdot 1$$

$$E \approx -0.79V$$

Half-cell potential $\approx -0.79\ V$

139. (A) (i) Account for the following :

(1) Zn^{2+} salts are colourless while Ni^{2+} salts are coloured.

$Zn^{2+}: 3d^{10}$

All d-orbitals are completely filled, so no $d - d$ transition is possible; hence salts are colourless.

$Ni^{2+}: 3d^8$

It has partially filled d-orbitals, so $d - d$ transitions occur, causing colour.

(2) Cr^{2+} is a strong reducing agent.

$Cr^{2+}: 3d^4$

It easily loses one electron to form the more stable $Cr^{3+}(3d^4)$ configuration. Hence, it acts as a strong reducing agent.

(3) Transition metals and their compounds show catalytic activities.

They show variable oxidation states and form intermediate complexes with reactants, thereby providing an alternative reaction path of lower activation energy.

(ii) Ionic equations for oxidising action of MnO_4^- in acidic medium

(1) With I^- ion

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

(2) With Fe^{2+} ion

$$MnO_4^- + 5Fe^{2+} + 8H^+ \rightarrow Mn^{2+} + 5Fe^{3+} + 4H_2O$$

OR

(i) Two oxometal anions of the 3d series where the metal exhibits an oxidation state equal to its group number are permanganate $(MnO_4^-)$and chromate (CrO_4^{2-}). Manganese is in the +7 state (Group 7), and Chromium is in the +6 state (Group
6).

(ii) Increasing the pH shifts the orange dichromate ion $(Cr_2O_7^{2-})$ into the yellow chromate ion (CrO_4^{2-}). The exact reversible equilibrium reaction is:

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

(iii) $Cu^+$is not stable in an aqueous solution because it undergoes a disproportionation reaction to form Cu^{2+} and Cu :

$$2Cu^+ \rightarrow Cu^{2+} + Cu$$

The Cu^{2+} ion is highly stable in water due to its significantly higher hydration enthalpy compared to Cu^+, which easily compensates for the energy required to remove the second electron.

(iv) Cerium (Ce) (Atomic number 58) is a well-known lanthanoid that prominently exhibits the +4 oxidation state.
(v) Two elements of the 3d series that show anomalous electronic configurations are Chromium (Cr) and Copper (Cu). Chromium has $[Ar]3d^5 4s^1$ instead of $3d^4 4s^2$, and Copper has $[Ar]3d^{10} 4s^1$ instead of $3d^9 4s^2$ to achieve the extra stability of half-filled and completely filled subshells, respectively.

140. **(A)** Structure of 2,4-dinitrophenylhydrazone of benzaldehyde
• Reaction: Benzaldehyde + 2,4-dinitrophenylhydrazine → hydrazone derivative.
• Structure:
$C_6H_5 - CH = N - NH - C_6H_3(NO_2)_2$
(where nitro groups are at positions 2 and 4 of the phenyl ring).
2,4-DNP hydrazone is a crystalline derivative used for aldehyde/ketone identification.
(B) Stronger acid comparison
• Between $F_3C - C_6H_4 - COOH$ and $CH_3 - C_6H_4 - COOH$:
• The -CF; group is strongly electron-withdrawing (-I effect), stabilizing the carboxylate anion.
• The $-CH_3$ group is electron-donating (+I effect), destabilizing the carboxylate.
Stronger acid $= F_3C - C_6H_4 - COOH$
(C) Rosenmund's reduction
• Reaction:
$R - COCl \rightarrow R - CHO$
• Example: Benzoyl chloride → Benzaldehyde.
Rosenmund reduction converts acid chlorides to aldehydes.
(D) Acidity of α-hydrogens in aldehydes/ketones
• α-hydrogens are attached to carbon adjacent to carbonyl group.
• The carbonyl group $(C = O)$ is strongly electron-withdrawing.
• Removal of $\alpha - H$ forms a carbanion stabilized by resonance with the carbonyl group (enolate ion).
Hence α-hydrogens are acidic.
(E) Test to distinguish Benzaldehyde and Benzoic acid
• Tollen's test: Benzaldehyde (aldehyde) gives silver mirror; Benzoic acid does not.
• Sodium bicarbonate test: Benzoic acid effervesces (CO_2 release); Benzaldehyde does not.
Either test can distinguish them.

141. **(b)** Reason: A chiral center (or asymmetric carbon) must be bonded to four different groups. In molecule (b), the carbon marked with an asterisk is attached to a hydrogen atom, a chlorine atom, a methyl group ($-CH_3$), and a bromomethyl group ($-CHCH_2Br$). All four groups are different. In (a) and (d), the carbons are attached to two identical groups, and in (c), the molecule is achiral.

142. **(c)** Reason: This is a tertiary (3°) alcohol. Tertiary alcohols do not have hydrogen atoms on the carbon attached to the $-OH$ group, making them resistant to oxidation under normal conditions without breaking the carbon-carbon bonds. Primary and secondary alcohols can be oxidized. e

143. **(b)** • Sn is oxidised and the voltage of the cell is 0.91 V
• Reason: Oxidation occurs at the anode (the half-cell with the lower standard reduction potential). Here, Sn has a lower potential $(-0.14\ V)$ than $Fe^{3+}(+0.77\ V)$, so Tin (Sn) will be oxidized.
Cell potential $E^\circ_{cell} = E^\circ_{cathode} - E^\circ_{anode} = 0.77\ V - (-0.14\ V) = 0.91\ V$.

144. **(b)** Reason: During the electrolysis of concentrated brine (aqueous NaCl), there is a competition at the electrodes. At the anode, chloride ions are preferentially oxidized to chlorine gas over water/hydroxide ions due to high concentration. At the cathode, hydrogen ions (from water) are preferentially reduced to hydrogen gas over sodium ions because hydrogen has a higher reduction potential than sodium.

145. **(d)** Reason: Transition metals can exhibit variable oxidation states by losing varying numbers of electrons from their d-orbitals. This property allows them to form intermediate compounds and provide reaction surfaces with varying oxidation states, making them highly effective as catalysts.

146. **(b)** Dichromate ion structure
• Dichromate ion ($Cr_2O_7^{2-}$) has two tetrahedral CrO_4 units sharing one oxygen.
• In this structure: 6 terminal $Cr - O$ bonds are equivalent, while the bridging $Cr - O$ bonds are longer.

147. **(b)** Vapour pressure of solution
• Raoult's law (ideal solution):
$P = x_A P_A^0 + x_B P_B^0$

• Mole fraction: $x_A = \frac{1}{3}, x_B = \frac{2}{3}$.
• Expected pressure:
$P = \frac{1}{3}(45) + \frac{2}{3}(30) = 15 + 20 = 35\text{torr}$
• Actual pressure $= 40$ torr > 35 torr → positive deviation .

148. **(a)** Reduction of nitrobenzene
• Nitrobenzene → aniline reduction requires mild reducing agents.
• Common: $Sn/HCl, Fe/HCl, H_2/Ni$.
• $LiAlH_4$ is too strong and not suitable for aromatic nitro reduction.

149. **(d)** Molal elevation constant K_b
• K_b is a property of the solvent:
$K_b = \frac{RT^2M}{1000\Delta H_{vap}}$
• Independent of solute concentration.
• Unchanged

150. **(a)** Hydrolysis of sucrose
• Hydrolysis of sucrose → glucose + fructose.
• Optical rotation changes from positive to negative.
• This process is called inversion of sugar.

151. **(b)** The lower the pK_a value, the stronger the acid. Electron-withdrawing groups (EWGs) like the nitro $(-NO_2)$ group stabilize the conjugate base through the inductive effect. This stabilization makes it significantly easier to release a proton, meaning it has the highest acidic strength and therefore the lowest pK_a value among the choices.

152. **(c)** Hydrogen-oxygen fuel cells were used during the Apollo space missions to provide a reliable source of electrical energy. This type of fuel cell generates electricity by combining hydrogen and oxygen, and its byproduct is pure, potable water that was used for the astronauts.

153. **(c)**

Order with respect to $\mathbf{A}_{(g)}$	Order with respect to $\mathbf{B}_{(g)}$
Second	Zero

Explanation:
Rate of reaction $R = k[A]^n[B]^m$
where n and m are the order of reaction w.r.t
A and B from the given table change $A_{(g)}$, keeping $B_{(g)}$ constant,
$R_1 = k[3 \times 10^{-2}]^n[4 \times 10^{-2}]^m = 1.89 \times 10^{-4}$
$R_2 = k[6 \times 10^{-2}]^n[4 \times 10^{-2}]^m = 7.56 \times 10^{-4}$
$\left(\frac{1}{2}\right)^n = \frac{1}{4} \Rightarrow n = 2$
Change $B_{(g)}$, keeping $A_{(g)}$ constant,
$R_1 = k[3 \times 10^{-2}]^n[2 \times 10^{-2}]^m = 1.89 \times 10^{-4}$
$R_2 = k[3 \times 10^{-2}]^n[4 \times 10^{-2}]^m = 1.89 \times 10^{-4}$
$\left(\frac{1}{2}\right)^m = 1 \Rightarrow m = 0$
Therefore the order of reaction with respect to $A_{(g)}$ and $B_{(g)}$ will be second order and zero order, respectively.

154. **(b)** Magnetic moment of $[NiCl_4]^{2-}$
• Ni atomic number $= 28$ → electronic configuration: $[Ar]3\,d^8 4\,s^2$.
• $\ln[NiCl_4]^{2-}: Ni^{2+} = 3\,d^8$.
• Chloride is a weak field ligand → tetrahedral geometry → no pairing of electrons.
• So Ni^{2+} has two unpaired electrons.
• Magnetic moment:
$\mu = \sqrt{n(n+2)} = \sqrt{2(2+2)} = \sqrt{8} \approx 2.82\text{BM}$

155. **(c)** • Assertion (A): True

Proteins are polymers of α-amino acids joined by peptide bonds.

• Reason (R): False

A tetrapeptide contains 4 amino acids but only 3 peptide bonds.

156. **(a)** • Assertion (A): True

For zero order reaction:

Rate $= k$

Hence unit of rate constant equals unit of rate.

• Reason (R): True

Rate is independent of concentration.

• Reason correctly explains the assertion.

157. **(b)** • Assertion (A): True

Acetic acid undergoes Hell-Volhard-Zelinsky reaction, but formic acid does not because it lacks α hydrogen.

• Reason (R): True

Formic acid is stronger than acetic acid.

• But this is not the reason for halogenation behavior.

So, Both A and R are true, but R is not the correct explanation of A.

158. **(d)** Optical Isomerism in Complexes

• Assertion (A) is false: The trans isomer of $[CrCl_2(ox)_2]^{3-}$ has a plane of symmetry and is superimposable on its mirror image, making it optically inactive. Only the cis isomer of this complex is chiral and shows optical isomerism.

• Reason (R) is true: Optical isomerism is common in octahedral complexes, especially those involving didentate (bidentate) ligands like oxalate (ox), which create chiral arrangements.

159. **(A) (i)** Signs for a Spontaneous Redox Reaction

• E°_{Cell} : Positive (> 0)

• ΔG° : Negative (< 0)

(ii) Faraday's First Law of Electrolysis

Faraday's first law states that the mass of a substance deposited or liberated at an electrode is directly proportional to the total quantity of electricity (charge) passed through the electrolyte.

Expressed as: $m \propto Q$ or $m = Z \cdot I \cdot t$, where m is the mass, Z is the electrochemical equivalent, I is the current, and t is the time.

OR

(B) Calculating the EMF of the Cell

Given cell: $Fee_{(s)}|Fe^{2+}(0.01M)\|H^+(1M)|H_{2(g)}(1\text{ bar}), Pt_{(s)}$

Given $E^\circ_{cell} = 0.44$ V

(1) Cell Half-Reactions:

• Oxidation (Anode): $Fe_{(s)} \rightarrow Fe^{2+} + 2e^-$

• Reduction (Cathode): $2H^+ + 2e^- \rightarrow H_{2(g)}$

• Overall Reaction: $Fe_{(s)} + 2H^+_{(1M)} \rightarrow Fe^{2+}_{(0.01M)} + H_{2(g)}$

Number of electrons transferred, $n = 2$.

(2) Nernst Equation:

$$E_{Cell} = E^\circ_{Cell} - \frac{0.0591}{n}\log\frac{[Fe^{2+}]}{[H^+]^2}$$

(3) Calculation:

$$E_{Cell} = 0.44 - \frac{0.0591}{2}\log\frac{0.01}{(1)^2}$$

$$E_{Cell} = 0.44 - 0.02955\log(10^{-2})$$

$$E_{Cell} = 0.44 - 0.02955 \cdot (-2)$$

$$E_{Cell} = 0.44 + 0.0591$$

$E_{Cell} = 0.4991$ V (approx. 0.5 V)

160. Temperature Effects on Rate Constant and Activation Energy

• Rate Constant (k): As temperature increases, the rate constant k increases.

• Activation Energy (E_a): Activation energy E_a remains constant (independent of temperature).

Justification:

According to the Arrhenius Equation:

$k = A \cdot e^{-\frac{E_a}{RT}}$

When the temperature (T) is increased, the average kinetic energy of the molecules increases. This causes a significantly larger fraction of molecules to possess energy greater than or equal to the activation energy. As a result, the number of effective collisions increases, causing the rate constant k to increase exponentially. However, E_a is the inherent energy barrier of the reaction itself, which does not change with temperature.

161. **(A)** Ligand Capability

NH_4^+ cannot act as a ligand. A ligand must be a Lewis base that can donate at least one pair of electrons to a central metal ion. The ammonium ion (NH_4^+) has no lone pair of electrons on its nitrogen atom to donate, as all of its valence electrons are used in forming four covalent bonds.

(B) Linkage Isomer

The linkage isomer of $[Co(NH_3)_5(NO_2)]Cl_2$ is formed when the ambidentate nitrite ligand binds through the oxygen atom instead of the nitrogen.

• Linkage isomer formula: $[Co(NH_3)_5(ONO)]Cl_2$

• IUPAC Name: Pentaammine(nitrito-O)cobalt(III) chloride - Filo

162. Boiling and Melting Point of Dichlorobenzene

• Boiling Point: Ortho-dichlorobenzene has a higher boiling point than paradichlorobenzene because it is a polar molecule with a net dipole moment. This results in stronger dipole-dipole interactions, requiring more energy to vaporize. The para-isomer is non-polar and symmetrical, leading only to weaker London dispersion forces.

• Melting Point: The melting point of the para-isomer is higher than the ortho-isomer because the para-isomer has a highly symmetrical structure. As a result, it packs tightly and more closely into a crystal lattice. The stronger intermolecular forces require greater energy to break, giving it a much higher melting point.

163. Phenol vs. Cyclohexanol

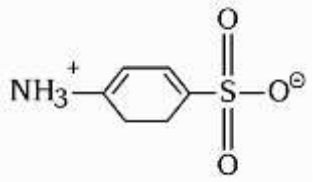
(A) Acidity Difference

Phenol is more acidic than cyclohexanol because the loss of a proton from phenol yields a phenoxide ion. This phenoxide ion is highly stabilized by resonance, delocalizing the negative charge across the aromatic ring. Cyclohexanol yields a cyclohexoxide ion, which lacks this resonance stabilization and is thus much less stable. &

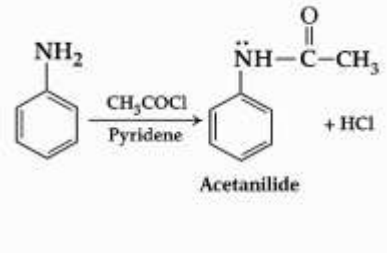
(B) Chemical Test to Distinguish

You can use the Neutral $FeCl_3$ Test. When a few drops of neutral ferric chloride solution are added to an aqueous solution of phenol, a distinct purple or violet colored complex forms. Cyclohexanol does not give this test and shows no observable color change.

164. **(A) (i)**

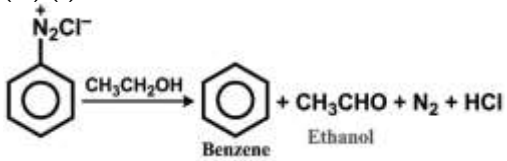


(ii) Acetylation of the $-NH_2$ group can influence the activating impact of the $-NH_2$ group.



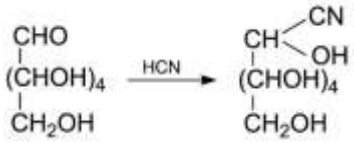
OR

(B) (i)



(ii) $\underset{\text{Bromoethane}}{CH_3-CH_2-Br} \xrightarrow{\text{alc·KCN}} \underset{\text{Propanenitrile}}{CH_3CH_2CN} \xrightarrow{LiAlH_4} \underset{\text{Propanamine}}{CH_3CH_2CH_2NH_2}$

165. The reaction of glucose with hydrogen cyanide:



This reaction confirms the presence of the carbonyl group ($>C=O$) in glucose.

166. **(A)** $2\,N_2O_5(g) \longrightarrow 4NO_{2(g)} + O_{2(g)}$

$\frac{-d[N_2O_5]}{dt} = 1.4 \times 10^{-3}\ ms^{-1}$ ... (Given)

Rate of reaction

$\frac{-1}{2}\frac{d[N_2O_5]}{dt} = \frac{1}{2} \times 1.4 \times 10^{-3}$

$= 0.7 \times 10^{-3}\ ms^{-1}$

$= 7 \times 10^{-4}\ ms^{-1}$

(B) First-Order Reaction Derivation

For a first-order reaction, the rate constant k is given by:

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

(1) For 99% completion ($t_{99\%}$) :

$[A] = [A]_0 - 0.99[A]_0 = 0.01[A]_0$

$t_{99\%} = \frac{2.303}{k}\log\frac{[A]_0}{0.01[A]_0} = \frac{2.303}{k}\log(100) = \frac{2.303}{k} \times 2$

(2) For 90% completion ($t_{90\%}$) :

$[A] = [A]_0 - 0.90[A]_0 = 0.10[A]_0$

$t_{90\%} = \frac{2.303}{k}\log\frac{[A]_0}{0.1[A]_0} = \frac{2.303}{k}\log(10) = \frac{2.303}{k} \times 1$

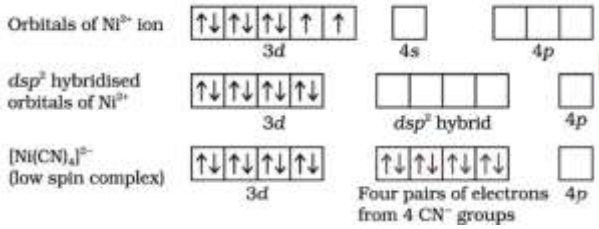
Comparison:

Dividing the equations: $\frac{t_{99\%}}{t_{90\%}} = \frac{2}{1}$

Therefore, $t_{99\%} = 2t_{90\%}$.

167. **(A)** If $\Delta_0 > P$, it becomes more energetically favourable for the fourth electron to occupy a t_{2g} orbital with configuration $t_{2g}^5 e_g^0$. Ligands which produce this effect are known as strong field ligands and form low-spin complexes.

(B) In $[Ni(CN)_4]^{2-}$, nickel is in a +2 oxidation state and the ion has the electronic configuration 3 d^8. The hybridisation scheme is shown in the diagram.



Whereas in $[Ni(CO)_4]$, Ni is in a +2 oxidation state and shows sp^2 hybridisation due to which its geometry is tetrahedral.

168. **(A)** Sandmeyer reaction

In Sandmeyer reaction, diazonium salts are converted into haloarenes or cyanides using cuprous salts.

Example:

$C_6H_5\,N_2^+Cl^- + CuCl \rightarrow C_6H_5Cl + N_2$

(B) $(CH_3)_2NH$

is more basic than $(CH_3)_3\,N$

in aqueous solution because protonated dimethylamine is better stabilized by solvation (hydrogen bonding with water).

In trimethylamine, bulky three methyl groups hinder solvation of the protonated ion, decreasing its basic strength.

169. Reasons

(A) Penta-acetate of glucose does not react with hydroxylamine

In glucose penta-acetate, the free aldehyde group is absent because glucose exists in cyclic acetal form.
Hence it does not react with hydroxylamine.

(B) Amino acids behave like salts

Amino acids contain both acidic (-COOH) and basic ($-NH_2$) groups and exist as zwitter ions:
$H_2NCHRCOOH \rightleftharpoons H_3\ N^+CHRCOO$
Therefore they behave like salts.

(C) Water soluble vitamins must be taken regularly

Water soluble vitamins are not stored in the body and are readily excreted through urine, so they must be supplied regularly in diet.

(D) Two strands of DNA are complementary

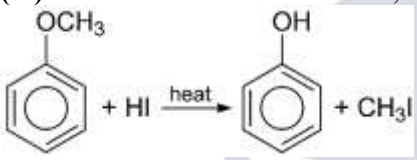
In DNA:

- Adenine pairs only with Thymine
- Guanine pairs only with Cytosine

170. **(A) (i)** The carbon-oxygen bond length in phenol (136 pm) is somewhat shorter than that in methanol. This is owing to the partial double bond character of the unshared electron pair of oxygen conjugated with the aromatic ring and the sp^2 hybridised state of carbon to which oxygen is connected

(ii) n-butane < ethoxyethane < butanal <butanol

(iii) When anisole reacts with HI , the primary products are phenol and CH_3I.



OR

(B) (i) Mechanism of formation of ether from ethanol

Step 1: Protonation of ethanol
$CH_3CH_2OH + H^+ \rightarrow CH_3CH_2OH_2^+$
Step 2: Nucleophilic attack by another ethanol molecule
$CH_3CH_2OH + CH_3CH_2OH_2^+ \rightarrow CH_3CH_2OCH_2CH_3 + H_2O + H^+$
Thus diethyl ether is formed.

(ii) Hydroboration-oxidation reaction

Alkenes react with diborane followed by oxidation with alkaline H_2O_2 to form alcohols.
Example:

$$CH_3CH = CH_2 \xrightarrow[BH_3]{\frac{H_2O_2}{OH^-}} CH_3CH_2CH_2OH$$

Propene gives propan-1-ol.

171. **(A)** Because the carbocation intermediate generated in S_N1 reactions is a planar molecule, it will lead to the formation of d - and l -form products. As a result, racemisation occurs.

(B) Because water has two hydrogen atoms bonded to oxygen $\overset{\overset{O}{\wedge}}{[HH]}$ while alcohol, like ethanol, has a hydrogen atom and alkyl [ethyl] group bonded to an oxygen.

$\overset{\overset{O}{/\ \backslash}}{H\quad C_2H_5}$ [Ethanol]

(C) (i) $CH_3 - CH_2 - I$ undergoes S_N2 reaction faster than $CH_3CH_2 - Cl$.

(ii) The first compound  Cl is cyclohexyl chloride [2° halide] and the second compound is cyclohexyl methyl chloride is the primary halide; therefore, in  CH_2Cl undergoes S_N2 reaction faster.

OR

(C) (i) 2-Bromo-2-methylbutane < 2-Bromo-pentane < 1-Bromo-pentane
(ii) 1-Bromo-3-methylbutane < 2-Bromo3-methylbutane < 2-Bromo-2-methylbutane

172. **(A)** The conductivity of a solution is defined as the conductance of ions in a unit volume of the solution. When a solution is diluted, the number of ions (responsible for carrying current) drops. As a result, solution conductivity diminishes with dilution.

(B) Λ_m^0 (KCl) $= 150.0$ S cm^2 mol^{-1}
$\Lambda_m(0.01\text{MKCl}) = 141$ S cm^2/mol
As we know
$$\alpha = \frac{\Lambda_m}{\Lambda_m^0}$$
$$= \frac{141}{150}$$
$$= 0.94$$

(C) If Rahul had used HCI instead of KCl , the Λ_m value for a given concentration would have been greater. The explanation for the increase in molar conductivity of $H\oplus$ over $K\oplus$ is that $H\oplus$ has the maximum molar conductance in an aqueous state because the proton is transported from one water molecule to another in the hydrogen-linked chain of water molecules.

OR

(C) Amit discovered that while molar conductivity improves with dilution, specific conductivity decreases.

173. **(A) (i)** Because the van't Hoff factor of 1 M NaCl (2) solution is bigger than that of 1 M glucose (1) solution, boiling point is directly proportional to molality and van't Hoff factor. As a result, the boiling point of 1 M NaCl is higher than that of 1 M glucose solution.

(ii) Relative lowering of vapour pressure:
$$\frac{P^0 - P_s}{P_s} = \frac{n_B}{n_A}$$
$$\frac{P^0 - 0.9P^0}{0.9P^0} = \frac{W_B}{50} \times \frac{78}{78}$$
$$\Rightarrow W_B = \frac{0.1}{0.9} \times 50$$
$$= \frac{50}{9}$$
$$= 5.5 \text{ g}$$

(iii) Given:
• Mass of $MgCl_2 = 10$ g
• Mass of water $= 200$ g $= 0.2$ kg
• $K_b = 0.512$ K kg mol^{-1}
• Molar mass of $MgCl_2 = 95$ g mol^{-1}
For complete dissociation:
$MgCl_2 \rightarrow Mg^{2+} + 2Cl^-$
Van't Hoff factor:
$i = 3$
Moles of solute:
$$n = \frac{10}{95} = 0.105 \text{ mol}$$
Molality:
$$m = \frac{0.105}{0.2} = 0.525 \text{ mol kg}^{-1}$$
Boiling point elevation:
$\Delta T_b = iK_b m$
$\Delta T_b = 3 \times 0.512 \times 0.525$
$\Delta T_b \approx 0.81$ K
Boiling point elevation $= 0.81$ K

OR

(B) (i) In benzene, two molecules of ethanoic acid associate to form a dimer.
$2CH_3COOH \rightleftharpoons (CH_3COOH_2)$

Thus, the van't Hoff factor,

$$i = \frac{\text{Number of solutes after dissociation or associations}}{\text{Number of solutes before dissociation or associations}}$$

$$= \frac{1}{2}$$

$$= 0.5$$

(ii) Amount of K_2SO_4 dissolved $= 2.32 \times 10^{-2}$ g

Volume of solution $= 2$ L

Temperature $= 25 + 273 = 298$ K

Molar mass of $K_2SO_4 = (2 \times 39) + 32 + 4 \times 16 = 174$ g/mol

Since K_2SO_4 dissociates completely as

$K_2SO_4 \longrightarrow 2\ K^+ + SO_4^{2-}$

Total ions produced after dissociation $= 3$

So, $i = 3, \pi = iCRT$

$$C = \frac{4}{V}$$

$$\pi = \frac{3 \times 2.32 \times 10^{-2}}{174 \times 2} \times 0.082 \times 298$$

$$= \frac{85.14}{174 \times 100}$$

$$= 0.0048$$

$$= 4.8 \times 10^{-3}\ \text{atm}$$

(iii) K_f for benzene $= 5.12$ K kg mol^{-1}

$W_B =$ mass of solute $= 25.6$ g

$W_A = 1000$ g

$\Delta T_f = 5.12$ K kg mol^{-1}

Atomic mass of sulphur $= 32$ g mol^{-1}

$$M_B = \frac{K_f \times W_B \times 1000}{\Delta T_f \times W_A}$$

$$= \frac{5.12 \times 25.6 \times 1000}{0.512 \times 1000}$$

$$= \frac{131.072}{0.152}$$

$$= 256$$

Now the molecular mass of

$S_x = x \times 32 = 256$

$$x = \frac{256}{32} = 8$$

Therefore, the formula of sulphur $= S_8$.

174. (A) (i) Reaction involved in Cannizzaro's reaction

The Cannizzaro reaction is a disproportionation reaction where aldehydes that lack an α-hydrogen (e.g., formaldehyde or benzaldehyde) undergo self-oxidation and reduction when treated with a concentrated alkali. One molecule of the aldehyde is reduced to an alcohol, while another is oxidized to a carboxylic acid salt.

Chemical Equation (using Benzaldehyde):

$2C_6H_5CHO +$ conc. $NaOH \rightarrow C_6H_5CH_2OH + C_6H_5COONa$

(Benzaldehyde → Benzyl alcohol + Sodium benzoate)

(ii) Association occurs in carboxylic acids due to the development of intermolecular H -bonding. As a result, the boiling point rises faster than that of comparable molecular mass aldehydes, ketones, and alcohols.

(iii) Since A forms a dioxime with hydroxylamine, it must contain two carbonyl groups.

Given:

Molecular formula $= C_5H_8O_2$

Gives Tollens' test → contains an aldehyde group (-CHO)

Gives lodoform test → contains a methyl ketone group (- $COCH_3$)

On Wolff-Kishner reduction (NH_2NH_2/KOH, glycol), it gives n-pentane

Therefore, A $= CH_3COCH_2CH_2CHO$ (4-oxopentanal).

Wolff-Kishner Reduction

$CH_3COCH_2CH_2CHO \xrightarrow[\text{glycol}]{NH_2NH_2/KOH} CH_3CH_2CH_2CH_2CH_3$

lodoform Test

$CH_3COCHCH_2CHO + 3I_2 + 4NaOH \rightarrow CHI_3 \downarrow + NaOOCCH_2CH_2CHO + 3NaI + 3H_2O$

(Yellow precipitate of iodoform, CHI_3 is formed.)

Tollens' Test

$CH_3COCH_2CH_2CHO + 2[Ag(NH_3)_2]^+ + 3OH^- \rightarrow CH_3COCH_2CH_2COO^- + 2Ag \downarrow + 4NH_3 + 2H_2O$

(Silver mirror is formed.)

Hence, A = 4-oxopentanal, $CH_3COCH_2CH_2CHO$.

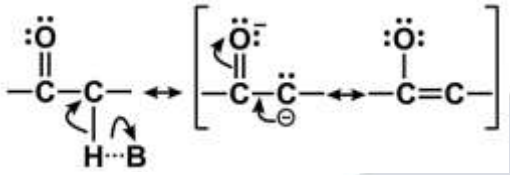
OR

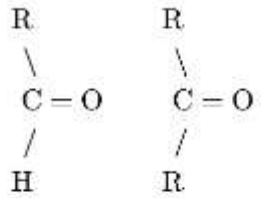
(B) (i) Sodium carbonate test: Ethanal does not react with metal carbonates like sodium carbonates, whereas ethanoic acid does, forming salt, water, and CO_2. Effervescence will be detected in this reaction.

For example:

$2CH_3COOH + Na_2CO_3 \longrightarrow 2CH_3COONa + CO_2 \uparrow + H_2O$

(ii) Because of the strong electron-withdrawing nature of the carbonyl groups and the resonance stabilisation of the conjugate base, aldehydes and ketones are acidic in nature.





Aldehyde **Ketone**

(iii) (1) Identification of A, B, and C

• Compound B is Ethanoic acid (CH_3COOH) : The sodium salt of ' B ' (sodium acetate) reacts with soda lime ($NaOH + CaO$) to undergo decarboxylation, producing methane (CH_4).

• Compound C is Ethanol (C_2H_5OH) : Since ' C ' oxidizes to ' B ' (Ethanoic acid) using acidified potassium permanganate, it must be the corresponding primary alcohol with two carbon atoms.

• Compound A is Ethyl ethanoate ($CH_3COOC_2H_5$) : Acid hydrolysis of this ester yields ethanoic acid (B) and ethanol (C). Its molecular formula, $C_4H_8O_2$, matches the requirement.

Summary:

• A: Ethyl ethanoate

• B: Ethanoic acid

• C: Ethanol

(2) Boiling Point Comparison

Compound B (Ethanoic acid) will have a higher boiling point than Compound C (Ethanol).

Reason:

While both compounds can form intermolecular hydrogen bonds, Ethanoic acid forms stronger and more extensive hydrogen bonds than Ethanol. Specifically, carboxylic acid molecules can form stable cyclic dimers through two hydrogen bonds per pair of molecules. This increases the effective molecular size and the energy required to break these bonds, resulting in a higher boiling point compared to the single hydrogen bonds formed by Ethanol.

175. **(A)** The energy difference between the 6d, 7s and 5f orbitals is very small in actinoids. In addition, the 5f orbitals of the actinoids are less shielded than the 4 f orbitals of the lanthanoids. Thus, in the lanthanoids, only 4 f electrons of Ce participate in chemical bonding, whereas in the lighter actinoids, up to americium, the 5f electrons also take part. This makes the chemistry of actinoids more complicated than that of lanthanoids

(B) $3MnO_4^{2-} + 4H^+ \longrightarrow 2MnO_4^- + MnO_2 + 2H_2O$

This is a disproportionation reaction since the same element [Mn] is oxidised and reduced in this process.

(C) Chromium has the greatest number of unpaired electrons in its valence shell $[Ar.\,3d^5 4s^1]$. These unpaired electrons contribute to the creation of strong metallic bonds. As a result, the elements of the chromium group have extremely high melting points. Manganese has a half-filled d-orbital configuration, which means that all of its electrons spin in the same direction. Mn has a lower melting point because it has fewer interatomic forces of attraction, which are easier to break.

176. **(b)** When an electrolyte dissociates, it forms more particles than were originally present, increasing the Van't Hoff factor ($i > 1$).

177. **(c)** Mercury cells provide a constant voltage (1.35 V) because the overall cell reaction does not involve any ions in solution whose concentration might change.

178. **(a)** The reduction $Sn^{4+} + 2e^- \rightarrow Sn^{2+}$ involves 2 moles of electrons, which equals 2 Faradays.

179. **(d)** According to the stoichiometry of the reaction, the rate is expressed as: $-\frac{d[A]}{dt} = -\frac{1}{2}\frac{d[B]}{dt} = \frac{1}{3}\frac{d[C]}{dt} = \frac{d[D]}{dt}$. Solving for $\frac{d[C]}{dt}$ gives $\frac{3}{2}\left(-\frac{d[B]}{dt}\right)$.

180. **(a)** In a zero-order reaction, Rate $= k[A\rho^0 = k$. Therefore, the units of both are mol $L^{-1}s^{-1}$.

181. **(d)** Scandium (Sc) typically shows only a +3 oxidation state because it loses all three of its valence electrons $(3d^1 4s^2)$ to achieve a stable noble gas configuration.

182. **(c)** In the complex $[Ag(NH_3)_2]Cl$, silver is bonded to two ammonia (NH_3) ligands, making its coordination number 2.

183. **(a)** Reason: Oxalate $(C_2O_4^{2-})$ is a bidentate chelating ligand. It forms stable chelate rings with the central Fe^{3+} ion. Complexes with chelating ligands are significantly more stable than those with monodentate ligands due to the "chelate effect".

184. **(b)** Reason: The reduction of an acyl chloride (acid chloride) to an aldehyde using hydrogen gas in the presence of palladium supported on barium sulphate (Pd - $BaSO_4$) is known as the Rosenmund reduction. The $BaSO_4$ acts as a poison, preventing the aldehyde from being further reduced to an alcohol.

185. **(b)** Reason: Gabriel phthalimide synthesis is a highly effective method utilized exclusively for the preparation of pure primary aliphatic amines. It prevents the formation of secondary or tertiary amines and is not suitable for aromatic amines because aryl halides do not undergo nucleophilic substitution with potassium phthalimide.

186. **(d)** Reason: When ethylamine $(CH_3CH_2NH_2)$ reacts with nitrous acid (HNO_2, typically generated in situ from $NaNO_2$ and HCl), it produces a highly unstable diazonium salt, which subsequently decomposes to yield nitrogen gas, water, and ethyl alcohol (CH_3CH_2OH).

187. **(c)** Reason: The secondary structures of proteins, such as the α-helix and β-pleated sheets, are primarily stabilized by regular hydrogen bonds formed between the amide hydrogens and carbonyl oxygens of the peptide backbone.

188. **(d)** Reason: A deficiency in Vitamin D interferes with the body's ability to absorb and metabolize calcium and phosphorus, which leads to the softening and weakening of bones in children, a condition clinically known as rickets.

189. **(d)** Reason: By definition, oligosaccharides are carbohydrates that, upon complete hydrolysis, yield a relatively small number (typically ranging from 3 to 10) of monosaccharide units.

190. **(a)** Molarity and Temperature

- Assertion (A): Molarity of solution in liquid state changes with temperature → True.
- Reason (R): Volume of a solution changes with change in temperature → True.
- Since molarity = moles of solute / volume of solution, and volume varies with temperature, the reason correctly explains the assertion.

So, Both A and R are true, and R is the correct explanation of A.

191. **(a)** Fe^{2+} as Reducing Agent

- Assertion (A): Fe^{2+} acts as a reducing agent → True.
- Reason (R): Fe^{3+} state is stable due to 3 d^5 configuration → True.
- Because $Fe^{3+}(3\ d^3)$ is more stable, Fe^{2+} tends to get oxidized to Fe^{3+}, hence acts as a reducing agent.

So, Both A and R are true, and R is the correct explanation of A .

192. **(d)** Nucleophilic Substitution of Optically Active Halide

• Assertion (A): Nucleophilic substitution reaction of an optically active halide gives a mixture of enantiomers → False.
• Reason (R): S_N2 reactions of optically active halides are accompanied by inversion of configuration → True.
• In S_N2, only inversion occurs (Walden inversion), not a mixture. A mixture arises in S_N1 due to racemization.

193. **(d)** Boiling Point of Ethanol vs Diethyl Ether
• Assertion (A): The boiling point of ethanol is lower than that of diethyl ether → False.
• Reason (R): In ethanol, molecules are associated by hydrogen bonding, whereas in ether this is not possible → True.
• Actually, ethanol has a higher boiling point than ether due to hydrogen bonding .

194. Chloroform and acetone solution show negative deviation from Raoult's law.
Reason: Strong intermolecular hydrogen bonding occurs between chloroform ($CHCl_3$) and acetone (CH_3COCH_3) molecules, which decreases vapour pressure.

195. **(A)** Lead Storage Battery
Anode reaction:
$Pb + SO_4^{2-} \rightarrow PbSO_4 + 2e^-$
Cathode reaction:
$PbO_2 + 4H^+ + SO_4^{2-} + 2e^- \rightarrow PbSO_4 + 2H_2O$
Overall reaction:
$Pb + PbO_2 + 2H_2SO_4 \rightarrow 2PbSO_4 + 2H_2O$

OR

(B) Fuel Cell
A fuel cell is a cell that converts chemical energy of fuel directly into electrical energy.
Example:
Hydrogen-oxygen fuel cell.
Advantages:
(1) High efficiency.
(2) Non-polluting (water is formed as product).

196. Differences between Order and Molecularity

Order of Reaction	Molecularity
Sum of powers of concentration terms in rate equation	Number of molecules participating in elementary step
Can be zero, fractional or whole number	Always a whole number
Determined experimentally	Obtained from mechanism

197. **(A)** IUPAC Names
(i) $K_3[Fe(CN)_6]$
Potassium hexacyanoferrate(III)
(ii) $[Co(en)_2Cl_2]^+$
Dichloridobis(ethane-1,2-diamine)cobalt(III) ion

OR

(B) Role of Coordination Compounds
(i) Biological system:
Haemoglobin contains Fe-coordination complex and carries oxygen in blood.
(ii) Extraction of metals:
In extraction of silver and gold, cyanide forms complexes:
$[Ag(CN)_2]^-, [Au(CN)_2]^-$
which help in extraction process.

198. What happens when:

(A) 1-chlorobutane is treated with alcoholic KOH ?

Dehydrohalogenation occurs and but-1-ene is formed.

$$CH_3CH_2CH_2CH_2Cl \xrightarrow[ale.]{KOH} CH_3CH_2CH = CH_2 + KCl + H_2O$$

(B) Chlorobenzene is treated with sodium in dry ether?

Fittig reaction occurs to form biphenyl.

$$2C_6H_5Cl + 2Na \xrightarrow[\text{dry ether}]{} C_6H_5 - C_6H_5 + 2NaCl$$

199. Chemical equations:

(A) Reimer-Tiemann reaction

Phenol on treatment with chloroform and NaOH gives salicylaldehyde.

$$C_6H_5OH + CHCl_3 + 3NaOH \rightarrow o - HOC_6H_4CHO + 3NaCl + 2H_2O$$

(B) Williamson ether synthesis

Alkyl halide reacts with sodium alkoxide to form ether.

$$C_2H_5ONa + C_2H_5Br \rightarrow C_2H_5OC_2H_5 + NaBr$$

200. Give reasons:

(A) Oxidation of aldehydes is easier than that of ketones.

Aldehydes contain a hydrogen atom attached to the carbonyl carbon, so they are easily oxidized to acids. Ketones lack this hydrogen and resist oxidation.

(B) Carboxylic acid is a stronger acid than phenol.

Carboxylate ion formed from carboxylic acid is highly stabilized by resonance over two oxygen atoms. whereas phenoxide ion is less stable. Hence carboxylic acids are stronger acids.

201. Percentage association of benzoic acid

Given:

- Mass of benzoic acid $w_2 = 5\ g$
- Molar mass $M = 122\ g\ mol^{-1}$
- Mass of benzene $w_1 = 35\ g = 0.035\ kg$
- $\Delta T_f = 2.94\ K$
- $K_f = 4.9\ K\ kg\ mol^{-1}$

Using:

$\Delta T_f = iK_f m$

Molality:

$$m = \frac{5/122}{0.035} = 1.171$$

$$2.94 = i \times 4.9 \times 1.171$$

$$i = \frac{2.94}{5.738} \approx 0.512$$

For dimerisation:

$$i = 1 - \frac{\alpha}{2}$$

$$0.512 = 1 - \frac{\alpha}{2}$$

$$\frac{\alpha}{2} = 0.488$$

$$\alpha = 0.976$$

Percentage association:

$0.976 \times 100 = 97.6\%$

202. Energy of activation

Given:

$k_1 = 2 \times 10^{-2}\ s^{-1}$

$k_2 = 8 \times 10^{-2}\ s^{-1}$

$T_1 = 300\ K, T_2 = 340\ K$

Arrhenius equation:

$$\log\frac{k_2}{k_1} = \frac{E_a}{2.303R}\left(\frac{T_2 - T_1}{T_1T_2}\right)$$

$$\log\frac{8\times10^{-2}}{2\times10^{-2}} = \log 4 = 0.6021$$

$$0.6021 = \frac{E_a}{2.303\times8.314}\times\frac{40}{300\times340}$$

$$0.6021 = \frac{E_a}{19.147}\times0.000392$$

$$E_a = \frac{0.6021\times19.147}{0.000392}$$

$$E_a \approx 2.94\times10^4\ J\ mol^{-1}$$

203. **(A)** Chelate complex

A chelate complex is a coordination compound in which a multidentate ligand forms ring structure by bonding through two or more donor atoms to the central metal atom.

Example:

$[Cu(en)_2]^{2+}$

(where en = ethane-1,2-diamine)

(B) Hybridisation and magnetic character of $[FeF_6]^{3-}$

For Fe^{3+} :

Fe: $[Ar]3d^64s^2$

$Fe^{3+}: 3d^5$

Since F' is a weak field ligand, pairing does not occur.

Hybridisation:

sp^3d^2

Magnetic character:

5 unpaired electrons are present, so it is paramagnetic.

Answer:

• Hybridisation: sp^3d^2

• Magnetic character: Paramagnetic

(C) The coordination compound $[Cr(H_2O)_5Br]SO_4$ shows ionisation isomerism.

Explanation:

It can exchange the ligand inside the coordination sphere with the counter ion outside the sphere.

Example:

$[Cr(H_2O)_5Br]SO_4$ and $[Cr(H_2O)_5SO_4]Br$

Both have same composition but give different ions in solution.

204. **(A)** p-Nitrochlorobenzene undergoes nucleophilic substitution faster than chlorobenzene because the $-NO_2$ group is electron withdrawing and stabilizes the intermediate formed during reaction.

(B) (±)-Butan-2-ol is optically inactive because it is a racemic mixture containing equal amounts of dextrorotatory and laevorotatory forms, whose optical rotations cancel each other.

(C) Chloroform is kept in airtight dark coloured bottles because in presence of air and sunlight it gets oxidized to poisonous phosgene gas ($COCl_2$).

$$2CHCl_3 + O_2 \rightarrow 2COCl_2 + 2HCl$$

(D) When 2-bromobutane is heated with alcoholic KOH , dehydrohalogenation occurs to give major product but-2-ene.

$$CH_3CHBrCH_2CH_3 \xrightarrow[\text{alc. KOH}]{} CH_3CH=CHCH_3$$

205. **(A)** Conversions

(i) Phenol to Benzene

$$C_6H_5OH \xrightarrow[\Delta]{Zn_n} C_6H_6$$

(Phenol heated with zinc dust gives benzene)

(ii) Ethanol to propan-2-ol

$$CH_3CH_2OH \xrightarrow{PCO} CH_3CHO$$

$$CH_3CHO + CH_3MgBr \xrightarrow{H_3O^+} CH_3CHOHCH_3$$

(Propan-2-ol formed)

(iii) Anisole to 2-methoxyacetophenone

Anisole undergoes Friedel-Crafts acylation:

$C_6H_5OCH_3 \xrightarrow[AlCl_3]{CH_3COCl}$

Gives 2-methoxyacetophenone (ortho product).

OR

(B) (i) Distinguish alcohols by Lucas reagent

Lucas reagent = Conc. HCl + anhydrous $ZnCl_2$

• Tertiary alcohol → turbidity immediately

• Secondary alcohol - turbidity in few minutes

• Primary alcohol → no turbidity at room temperature

(ii) o-Nitrophenol is steam volatile because it shows intramolecular hydrogen bonding.

p-Nitrophenol forms intermolecular hydrogen bonding, so its boiling point is higher and it is not steam volatile.

206. **(i)** Out of aniline and methylamine, which is a stronger base and why?

Methylamine is a stronger base than aniline.

Reason: In methylamine, the CH_3 group shows + I effect and increases electron density on nitrogen. In aniline, the lone pair on nitrogen is delocalized into the benzene ring by resonance, making it less available for donation.

(ii) Why does tertiary amine have lower boiling point than primary amine of comparable molecular masses?

Tertiary amines do not contain $N-H$ bonds, so they cannot form intermolecular hydrogen bonding effectively.

Primary amines form strong hydrogen bonding, hence have higher boiling points.

(iii) What happens when:

(1) Ethanamide is heated with Br_2 and aqueous KOH ?

Hofmann bromamide reaction occurs and methylamine is formed.

$CH_3CONH_2 + Br_2 + 4KOH \rightarrow CH_3NH_2 + 2KBr + K_2CO_3 + 2H_2O$

(2) Benzene diazonium chloride is treated with ethanol?

Benzene is formed.

$C_6H_5\ N_2Cl + C_2H_5OH \rightarrow C_6H_6 + N_2 + HCl + CH_3CHO$

OR

(iii) Short notes

(1) Carbylamine reaction

Primary amines on heating with chloroform and alcoholic KOH give foul-smelling isocyanides.

$RNH_2 + CHCl_3 + 3KOH \rightarrow RNC + 3KCl + 3H_2O$

This test is used for identification of primary amines.

(2) Acetylation of aniline

Aniline reacts with acetyl chloride or acetic anhydride to form acetanilide.

$C_6H_5NH_2 + CH_3COCl \rightarrow C_6H_5NHCOCH_3 + HCl$

This reaction is called acetylation.

207. **(i)** Difference between glycosidic linkage and peptide linkage

• Glycosidic linkage: Linkage formed between two monosaccharide units through an oxygen atom in carbohydrates.

• Peptide linkage: Linkage formed between amino acids by combination of -COOH group of one amino acid and $-NH_2$ group of another.

(ii) Denaturation destroys the secondary and tertiary structures of proteins without breaking peptide bonds. As a result, proteins lose their biological activity.

(iii)

(1) Essential amino acids

Amino acids which cannot be synthesized by the human body and must be obtained through diet are called essential amino acids.

(2) Anomers

Carbohydrates which differ in configuration at the anomeric carbon atom are called anomers.

Example: α-glucose and β-glucose.

OR

(iii) Hydrolysis products

(1) Sucrose

$\text{Sucrose} + H_2O \rightarrow \text{Glucose} + \text{Fructose}$

(2) Lactose

$\text{Lactose} + H_2O \rightarrow \text{Glucose} + \text{Galactose}$

208. **(A)** Identify ' A ' and ' B '

Molecular formula: C_3H_6O
Functional isomers are:
• Propanal (CH_3CH_2CHO)
• Propanone (CH_3COCH_3)
Since compound B gives iodoform test, it must contain CH_3CO - group.
Therefore:
• A = Propanal (CH_3CH_2CHO)
• B = Propanone (CH_3COCH_3)
(B) Give reasons
(i) Carboxylic acids do not give reactions of carbonyl group.
In carboxylic acids, the carbonyl carbon is less electrophilic due to resonance involving the OH group. hence nucleophilic addition reactions are not favored.
(ii) Propanone is less reactive towards nucleophilic addition than propanal.
Propanone has two electron-releasing alkyl groups which decrease the positive charge on carbonyl carbon and also create steric hindrance. Therefore, nucleophilic attack becomes difficult compared to propanal.
(C) Chemical test to distinguish between benzoic acid and phenol
Sodium bicarbonate test:
• Benzoic acid reacts with $NaHCO_3$ giving brisk effervescence of CO_2.
$C_6H_5COOH + NaHCO_3 \rightarrow C_6H_5COONa + CO_2 + H_2O$
• Phenol does not react with $NaHCO_3$ -

209. **(A) (i)** Account for the following:
(1) Mn shows highest oxidation state of +7 with oxygen but with fluorine it shows highest oxidation state of +4 .
Oxygen stabilizes higher oxidation states of Mn due to formation of multiple bonds in oxides like Mn_2O_7.
Fluorine cannot stabilize such very high oxidation states effectively, hence Mn shows only +4 in fluorides.
(2) Cr^{2+} is a strong reducing agent.
Cr^{2+} easily loses one electron to form more stable Cr^{3+} having $3d^3$ configuration. Hence it acts as a strong reducing agent.
(3) Cu^{2+} salts are coloured while Zn^{2+} salts are white.
Cu^{2+} has incomplete $3d^p$ configuration, so $d-d$ transitions occur causing colour.
Zn^{2+} has completely filled $3d^{10}$ configuration, so no $d-d$ transition occurs and salts are white.
(ii) Complete and balance equations:
(1)

$$2MnO_2 + 4KOH + O_2 \xrightarrow{\Delta} 2\,K_2MnO_4 + 2H_2O$$

(2)

$$Cr_2O_7^{2-} + 14H^+ + 6I \rightarrow 2Cr^{3+} + 3I_2 + 7H_2O$$

OR

(B)(i)
(1) Element with highest melting point and why?
Chromium (Cr) has the highest melting point due to maximum number of unpaired electrons leading to strong metallic bonding.
(2) Element most stable in +2 oxidation state and why?
Zn is most stable in +2 oxidation state because Zn^{21} has completely filled $3d^{10}$ configuration.
(3) Element with lowest enthalpy of atomisation and why?
Zn has the lowest enthalpy of atomisation because of weak metallic bonding due to fully filled $3d^{10}$ configuration.
(ii) Preparation of $Na_2Cr_2O_7$ from chromite ore
Chromite ore:
$FeCr_2O_4$
It is heated with sodium carbonate in presence of air:
$4FeCr_2O_4 + 8Na_2CO_3 + 7O_2 \rightarrow 8Na_2CrO_4 + 2Fe_2O_3 + 8CO_2$
Sodium chromate is acidified to form sodium dichromate:
$2Na_2CrO_4 + H_2SO_4 \rightarrow Na_2Cr_2O_7 + Na_2SO_4 + H_2O$

210. **(A) (i)** Calculate E°_{cell}
Given reaction:
$2Al(s) + 3Cu^{2+}(0.01M) \rightarrow 2Al^{3+}(0.01M) + 3Cu(s)$
Given:

$E_{coll} = 1.98\ V$
Using Nernst equation:
$E_{cell} = E^{\circ}_{cell} - \frac{0.0591}{n} \log Q$
For reaction:
$n = 6$
$Q = \frac{[Al^{3+}]^2}{[Cu^{2+}]^3} = \frac{(0.01)^2}{(0.01)^3} = 10^2$
$\log Q = 2$
$1.98 = E^{\circ}_{cell} - \frac{0.0591}{6} \times 2$
$1.98 = E^{\circ}_{cell} - 0.0197$
$E^{\circ}_{cell} = 1.9997 \approx 2.00\ V$
Answer:
$E^{\circ}_{coll} = 2.00\ V$
(ii) Better metal for coating iron
Given:
$E^{\circ}_{Fe^{2+}/Fc} = -0.44V$
$E^{\circ}_{A^{2+}/A} = -2.37V$
$E^{\circ}_{B^{2+}/B} = -0.14V$
Metal A is better because it has more negative reduction potential than iron, so it oxidizes more easily and protects iron sacrificially from corrosion.
Answer:
A is better for coating iron

OR

(B) (i) Degree of dissociation (α)
Given:
$\kappa = 3.905 \times 10^{-5}\ S\ cm^{-1}$
$C = 0.001M$
Molar conductivity:
$\Lambda_m = \frac{\kappa \times 1000}{C}$
$\Lambda_m = \frac{3.905 \times 10^{-5} \times 1000}{0.001} = 39.05 Scm^2\ mol^{-1}$
Limiting molar conductivity:
$\Lambda^{\circ}_m = \lambda^{\circ}_{H^+} + \lambda^{\circ}_{CH_3COOO^-}$
$= 349.6 + 40.9 = 390.5\ S\ cm^2\ mol^{-1}$
Degree of dissociation:
$\alpha = \frac{\Lambda_m}{\Lambda^{\circ}_m} = \frac{39.05}{390.5} = 0.10$
Answer:
$\alpha = 0.10$
(ii) Faraday's second law of electrolysis
When the same quantity of electricity is passed through different electrolytes, the masses of substances liberated are proportional to their equivalent masses.
(iii) What happens if external potential becomes greater than E°_{cell} ?
The electrochemical cell stops working as galvanic cell and reaction proceeds in reverse direction; the cell behaves as an electrolytic cell.