CHEMISTRY - 043

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Section A

91. $\Delta G^\circ = -2 \times 96500 \times 1.56$

$E^\circ_{cell} = 0.8 + 0.76$

$= 1.56$

$-\frac{2 \times 96500 \times 156}{100 \times 1000} = -\frac{156 \times 1930}{100} = -301.08 \text{ kJ/mol}$

-301.080 kJ/mol (A)

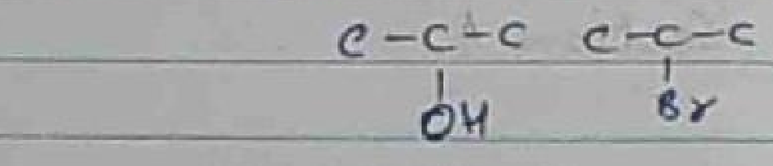
92. For complex reaction, molecularity has no meaning (B)

93. 1.5 (A)

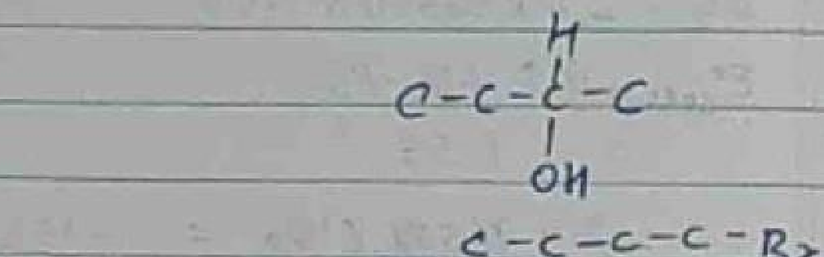
94. $[Ar]\, 3d^5 4s^1$ (C)

95. diammine dichlorido platinium (II) B)

Q6. $[Co(NH_3)_4Cl_2]^+$ (D)



Q7. Butan-2-ol (B)



Q8. ~~pentan-1-ol~~
propan-1-ol < butan-2-ol < butan-1-ol < pentan-1-ol (C)

Q9. $CH_3-CN \xrightarrow{LiAlH_4} CH_3-CH_2-NH_2$ ethylamine (A)

Q10. Thymine (C)

Q11. peptide bond (B)

Q12. Glucose exists in 2 different crystalline forms, alpha (α) and beta (β) (D)

Q13. Both A and R are true and R is correct explanation of A (A)

Q14. Both A and R are true and R is correct explanation of A (A)

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Q15. A is false but R is true (d)

Q16. A is true but R is false (c)

Section B-

Q17.

(B) In a first order reaction,

$\ln A = \ln A_0 - kt$ (let A_0 be a initial conc at $t=0$)

$\log_{10} A = \log_{10} A_0 - \frac{kt}{2.303}$

$A \longrightarrow$ Products

$kt = 2.303 \log \frac{A_0}{A}$

$\left[\ln \frac{A_0}{A} = kt\right]$

If $\frac{3}{4}$th of A_0 decomposes

[A] at time t = $\frac{A_0}{4}$ left

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$Kt = 2.303 \log \frac{4A_s}{A_0}$

(given, $K \rightarrow 2.54 \times 10^{-3} s^{-1}$) [$\log 4 = 0.6$]

K ↓ rate constant

$t = \frac{2.303 \times 0.6}{2.54 \times 10^{-3}}$ s

$= \frac{230.3 \times 6}{2.54}$ s

$= \frac{2303 \times 60}{254}$ s $= \frac{13818 \times 10}{254}$ s

$= 54.4 \times 10$ s

$= \underline{544 \text{ sec}}$

$$\begin{array}{r} 54.4 \\ 254\overline{)13818} \\ 127001 \\ \hline 1118 \\ 1016 \\ \hline 01020 \\ 1016 \\ \hline 4 \end{array}$$

24

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∴, time required for $\frac{3}{4}$th of reactant to decompose is <u>544 seconds</u>

Q18

a) The extra amount of energy required by reactant in order to cross the threshold barrier and reach the transition state to proceed the reaction is known as activation energy (E_a)

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$E_a = E_T - H_R$ ↳ Heat of reactant

↓ threshold energy

(b)

i) **zero order rxn reaction**

$A \longrightarrow$ Products (K → rate constant) (ROR → rate of reaction)

$ROR = K[A]^0$

$ROR = K$

unit of K = unit of ROR $= \frac{[C]}{T} = \frac{mol}{ls} = \underline{mol\ L^{-1}s^{-1}}$ [If gases $atm\ s^{-1}$]

ii) **Second order reaction**

$A \longrightarrow$ Products

$ROR = K[A]^2$

$\frac{mol}{ls} = K \frac{mol^x}{L^x}$

$\frac{L}{mol\ s} = K = \underline{L\ mol^{-1}\ s^{-1}}$ [For gases $\frac{atm}{s} = K\ atm^2$; $K = atm^{-1}s^{-1}$]

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Q19.

a) Ground state electronic configuration of Cr = [Ar] 3d⁵ 4s¹

$$Cr \xrightarrow{IE_1} Cr^+$$

[Ar] 3d⁵ 4s¹ → [Ar] 3d⁵

Since when ionisation enthalpy 1 is given, electron comes out of 4s subshell leading to stable half filled & symmetrical 3d⁵ configuration with large exchange energy, it is easy to remove the electron and thus IE 1 is low.

Ground state electronic configuration of Zn = [Ar] 3d¹⁰ 4s²

$$Zn \xrightarrow{IE_1} Zn^+$$

[Ar] 3d¹⁰ 4s² → [Ar] 3d¹⁰ 4s¹

Since when IE_1 is given, electron comes out of full filled 4s subshell ($4s^2 3d^{10}$), leading to unstable ($4s^1 3d^{10}$) configuration

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of valence shell, Zn doesn't want to lose its electron and thus IE, of Cr is lower than that of Zn.

b) Transition elements are **good catalysts** because →

1) They can adopt multiple oxidation ~~state~~ states
2) form complexes due to small size, large ionic charge and availability of vacant d-orbitals.

By doing so, they increase concentration of reactant on their surface and weakening the bond b/w reactant molecules and thus lowering activation energy.

Q20.

a) The no. of donor atoms of ligands surrounding the central metal atom directly linked to it by donating a lone pair of electron is known as coordination number.

eg → $[Co(NH_3)_6]^{2+}$ → coordination no. = 6

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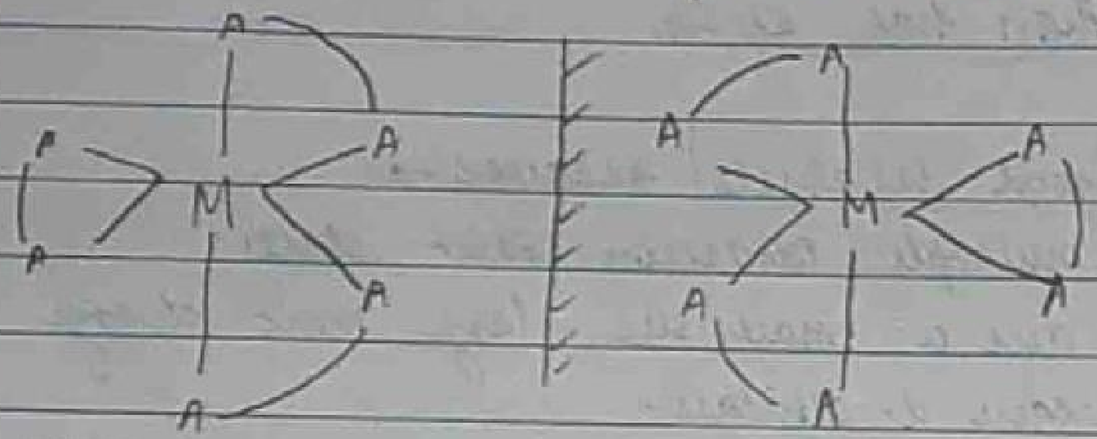
b) $[Co(en)_3]Cl_3$ exhibits optical isomerism $[M(AA)_3$ type$]$

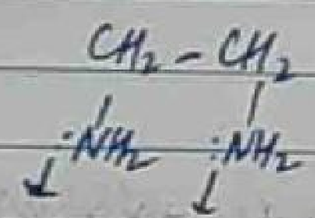


M → Co (central metal atom ion)

(AA → symmetric amb bidentate ligand)

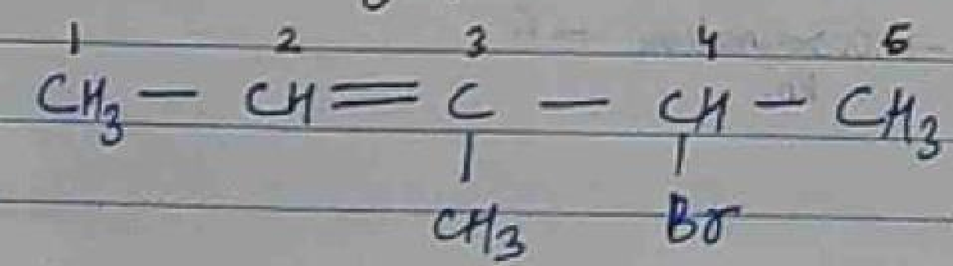
forms non-superimposable mirror images and exists in 2 enantiomeric forms (d and l form)

en → ethylene diamine



Q21.

a) 4-Bromo-3-methyl pent-2-ene



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b) $CH_3CH_2-Cl \xrightarrow{aq\ KOH} CH_3-CH_2-OH + Cl^{\ominus}\ (KCl)$

Chloroethane — Ethanol

→ Nucleophilic substitution reaction (S_N2) takes place leading to alcohol formation
→ $Cl^{\ominus}$ → leaving group
→ $OH^{\ominus}$ → nucleophile

Section C

Q22. ΔT_b → increase in boiling point = 353.93 − 353.23
= 0.7 K

353.93
353.23
0 7 0

$K_b = 2.52\ K\ Kg/mol$

We know from colligative properties, $\boxed{\Delta T_b = i K_b m}$

$\Delta T_b = 2.52 \times m$

$\frac{0.7}{2.52} = m$

$\frac{70}{252} = m$

(molality → m
K_b → ebullioscopic constant
i → vanthoff factor)
(since non-volatile solute, i = 1)

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let x moles of solute be dissolved in 90g of benzene

$90 \rightarrow x$

$1 \rightarrow \frac{x}{90}$

$1000 \rightarrow \frac{1000}{90}x$

$\frac{100}{9}x$ moles are present in 1000g / 1Kg of solvent benzene

$m = \frac{100}{9}x$

$\frac{4\cancel{0}}{252} = \frac{10\cancel{0}x}{x}$

$\frac{1}{40} = x$

$\frac{1}{40} = \frac{1.5}{MM}$

$MM = 4\cancel{0} \times \frac{15}{1\cancel{0}} = 60 g/mol$

$\left[x = \text{no. of moles} = \frac{\text{mass (given)}}{\text{MM (molar mass}} \right]$

$\left[x = \frac{1.5}{MM} \right]$

∴, molar mass of non-volatile solute is 60g/mol

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Q23. Reduction (cathode) Reaction → $2H^+ + 2e^- \longrightarrow H_2(g)$
(0.01M) 1 bar

Oxidation (anode) reaction → $Sn \longrightarrow Sn^{2+} + 2e^-$
(0.001M)

Net cell Reaction → $2H^+ + Sn \longrightarrow Sn^{2+} + H_2(g)$
$10^{-2}M$ $10^{-3}M$ 1 bar

$E^\circ_{cell} = E^\circ_{cathode} - E^\circ_{anode}$
$= 0 - (-0.14)$
$= 0.14V$

From Nernst equation

$E_{cell} = E^\circ_{cell} - \frac{2.303RT}{nF} \log Q$

$= 0.14 - \frac{0.059}{2} \log \frac{[Sn^{2+}][H_2]}{[H^+]^2}$

$= 0.14 - \frac{0.059}{2} \log \frac{10^{-3} \times 1}{10^{-4} \times 10^{1}}$ $= 0.14 - \frac{0.059}{2} = 0.1105\,V = \underline{0.11V}$

[Q → Reaction quotient
n → no. of moles of e^- transferred [n = 2]
F → faraday constant → 96500C
T → absolute temp → 298K
R → universal gas constant]

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∴ emf of given cell is 0.11V

Rough Work

$\frac{0.14 - 0.06}{2}$

0.14 = 0.03

0.11

$\sqrt{59}$

0.01

0.0295

0.14 ap

0.0295

0.1105

Q24.

a)

i) $2KMnO_4 \xrightarrow{513\,K} K_2MnO_4 + MnO_2 + O_2$

Potassium permanganate — Potassium manganate — Manganese dioxide

ii) $Na_2Cr_2O_7 + 2KCl \longrightarrow K_2Cr_2O_7 + 2NaCl$

sodium dichromate — Potassium dichromate

b) In lanthanoids, progressive electron filling takes place in 4f subshell, having poor shielding effect. Due to which nuclear force of attraction on outermost shell increases, causing decrease in size i/a lanthanoid contraction. Due to similar sizes, lanthanoids exhibit similar physical

and chemical properties and is difficult to separate them in pure state by chemical methods. However, they can be separated by ion-exchange or chromatographic methods.

Atomic size order of lanthanoids →

Eu > La > Eu > Ce > Pr > Nd > Pm > Sm > Eu > Gd > Tb > Dy > Ho > Er > Tm > Yb > Lu

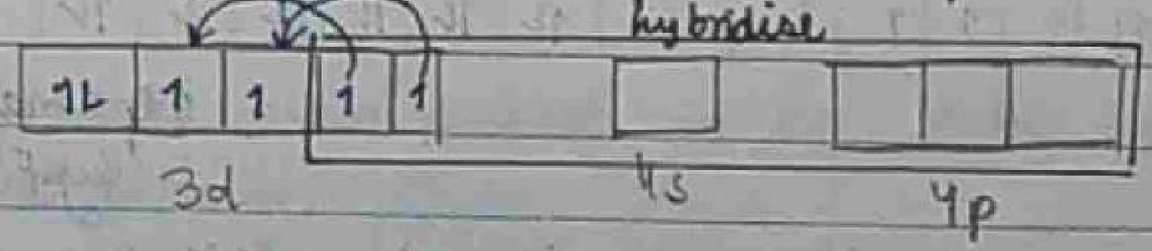
Q25.

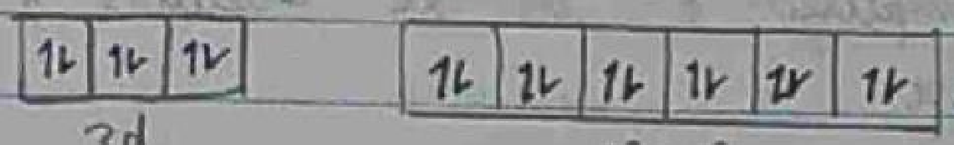
(a) In $[Co(NH_3)_6]^{3+}$, Oxidation state of Co = +3 $[Co = [Ar]\ 4s^2 3d^7]$

Coordination no = 6 (Octahedral) $[Co^{3+} = [Ar]\ 3d^6]$

Complex

In +3 Oxidation state of Co, NH_3 acts as strong ligand and causes pairing of e^- to form inner orbital complex of d^2sp^3 hybridisation



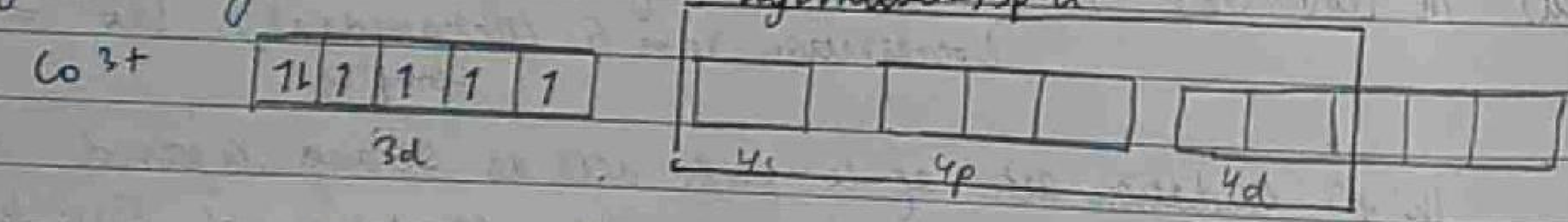


6 NH_3 donate 1 lp in each orbital

Since there is no unpaired electron, $[Co(NH_3)_6]^{3+}$ is diamagnetic.

In $[CoF_6]^{3-}$, O.N of Co = +3
C.N of Co = 6 (Octahedral)

Here $F^{\ominus}$ doesn't act as strong ligand and thus being weak is unable to pair e⁻ and forms outer orbital complex of sp^3d^2 hybridisation



since there are 4 unpaired e⁻ in 3d orbitals, $[CoF_6]^{3-}$ is paramagnetic complex.

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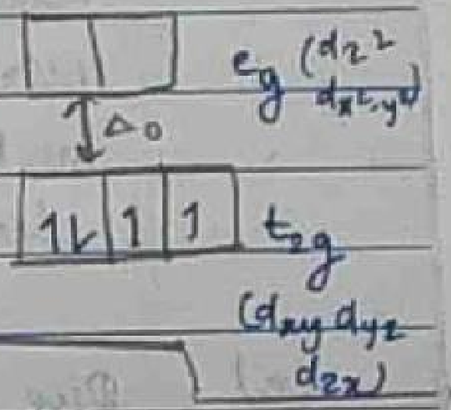
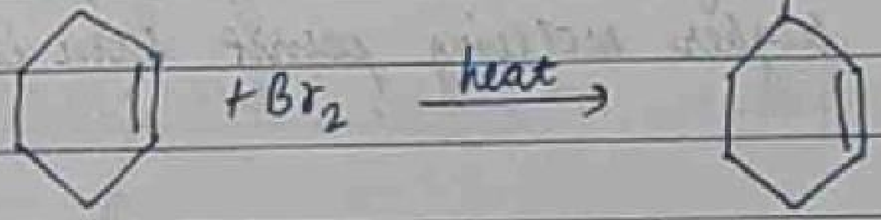
b) If $\Delta_o > P$ → ligand will act as strong ligand and will cause pairing of e^-

If d^4 ion → Electronic Configuration = $t_{2g}^4 e_g^0$

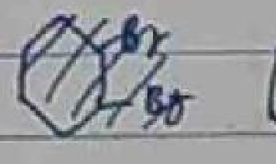


Q26.

a)



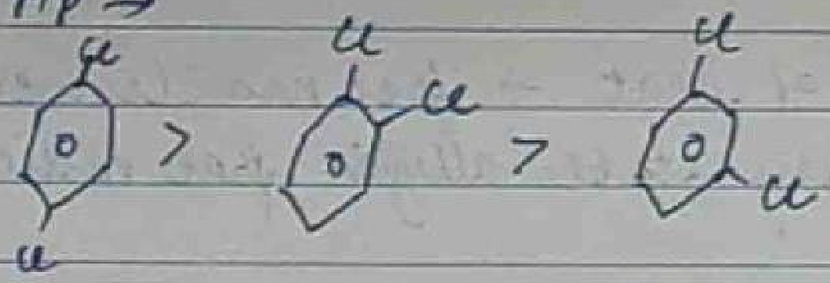
since, Br_2 is added in presence of heat → free radicle mechanism will be followed making very stable allylic free radicle 

(If Br_2 would have been added in CCl_4 then, halogenation would have occured forming )

b) Mixture containing 2 enantiomeric forms of an optically active compound (non-superimposable mirror images of each other) mixed in equal proportion to form overall optically inactive mixture is known as racemic mixture (±)
↳ due to external compensation

c) Due to symmetry, p-dichlorobenzene forms a more tightly packed crystal lattice and thus has higher melting point than its ortho & meta isomers.

MP →



para ortho meta

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Q27.

a) **Rosenmund Reduction**

$$R-\overset{O}{\overset{\|}{C}}-Cl + H_2 \xrightarrow[\text{Lindlar's catalyst}]{Pd/BaSO_4} R-\overset{O}{\overset{\|}{C}}-H + HCl$$

acid chloride → aldehyde

b) **Cannizzaro's Reaction** → disproportionation reaction involving aldehydes or ketones with no αH

$$2H-\overset{O}{\overset{\|}{C}}-H \xrightarrow[NaOH]{conc.} CH_3-OH + HCOONa$$

formaldehyde → methanol + sodium formate → self cannizzaro



$$+ HCHO \xrightarrow[NaOH]{conc.}$$



$$+ HCOONa$$

benzaldehyde → benzyl alcohol → cross cannizzaro

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c) **Hell - Volhard - Zelinsky Reaction**

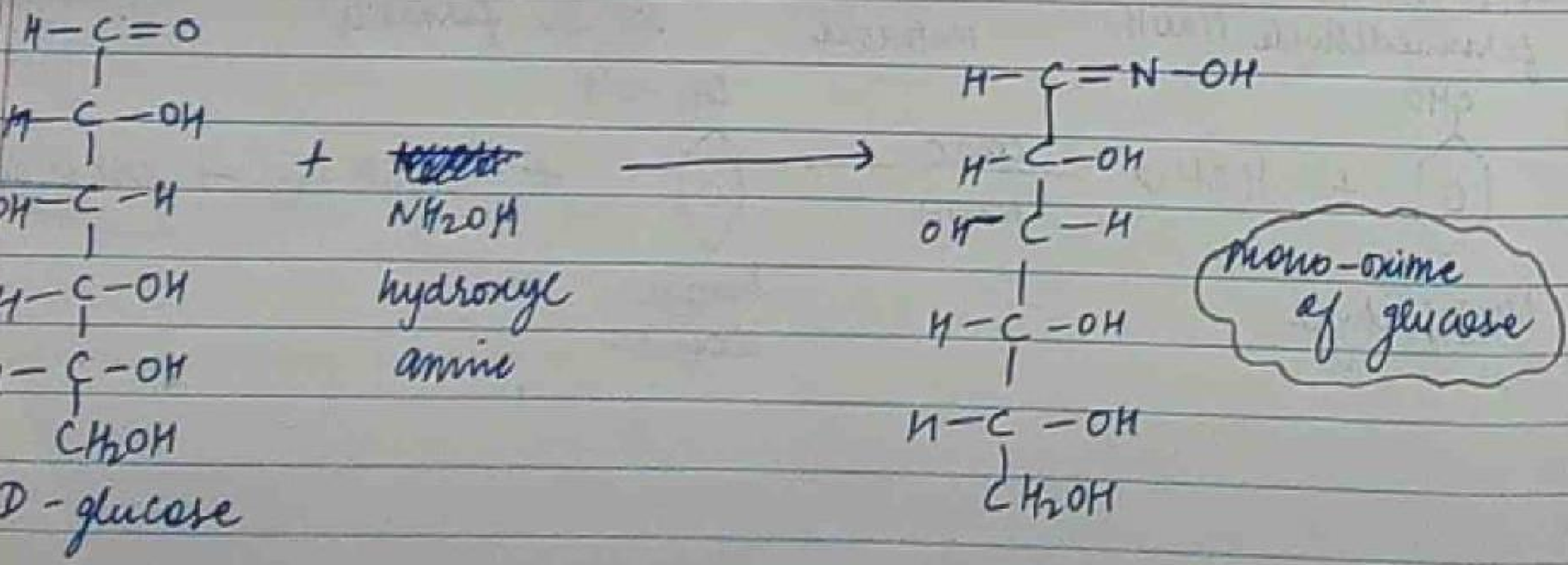
$R-CH_2-COOH \xrightarrow[2)\ H_2O,\ H^+]{1)\ Red\ P,\ X_2} R-\underset{\displaystyle X}{\underset{|}{CH}}-COOH \qquad (X \rightarrow Cl, Br)$

carboxylic acid

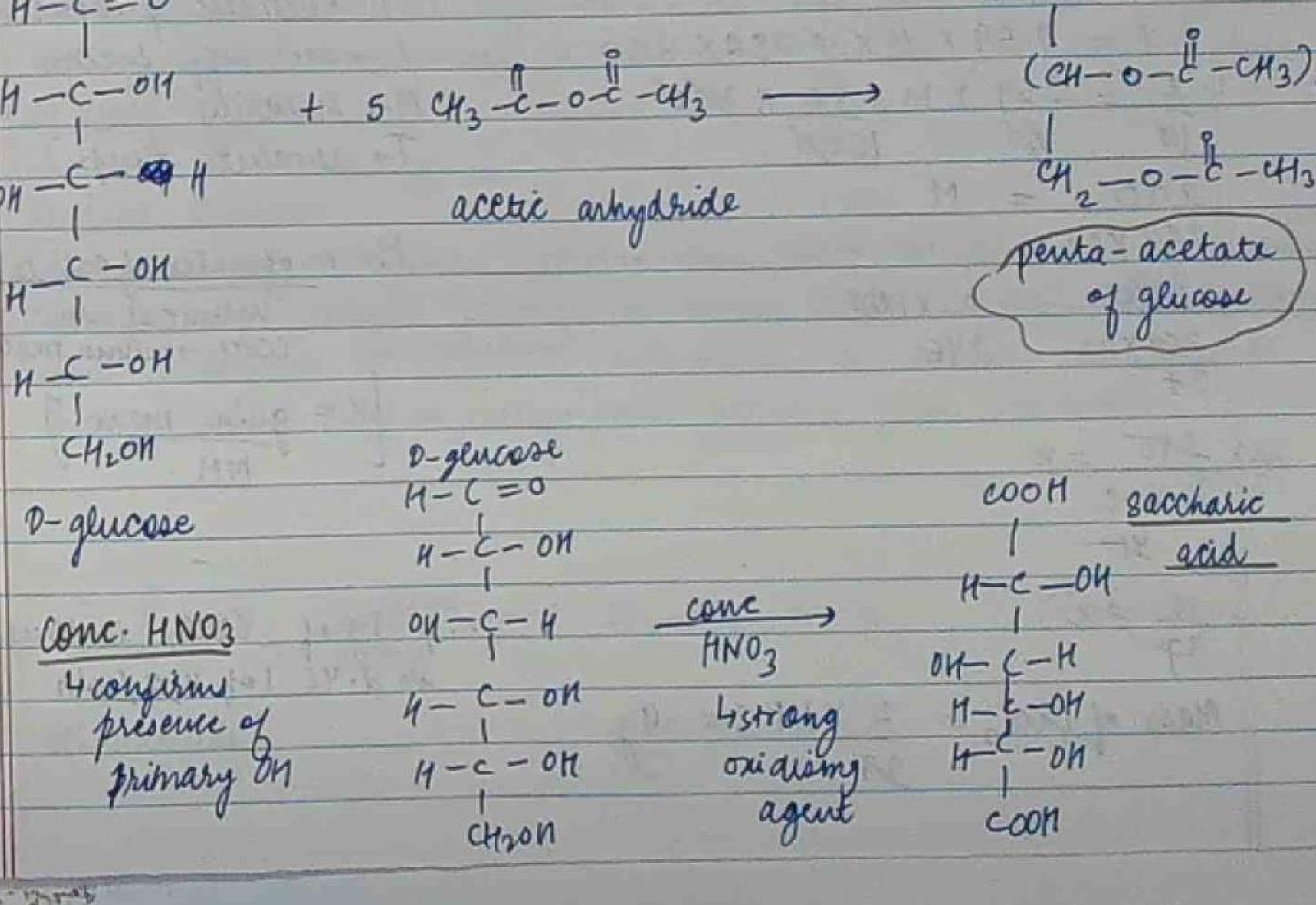
α-halo carboxylic acid

928.

a) NH_2-OH → confirms presence of carbonyl group



b) $(CH_3CO)_2O$ → confirms presence of 5 OH grps on different C. atoms.



c) Conc. HNO_3 → confirms presence of primary OH

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Section D

Q29.

a) $\pi = iMRT$

$0.7 = 2.59 \times M \times 0.082 \times 300$

$\frac{7}{10} = \frac{259}{100} \times M \times \frac{82}{100} \times \frac{300}{100}$

$\frac{700}{259 \times 82} = M$

$\frac{700}{259 \times 82} = \frac{x \times 1000}{246}$

$\frac{246}{37} = x$

$\frac{3}{37} = x$

Mass of $CaCl_2 = \frac{3}{37} \times 111 = 9g$

($\pi \rightarrow$ osmotic pressure
$i \rightarrow$ vant hoff factor
$M \rightarrow$ Molarity
$T \rightarrow$ absolute temp)

$M = \frac{\text{no. of moles of solute}(x)}{\text{Volume of soln.}}$

($CaCl_2 \rightarrow$ volume negligible)

$\left[x = \frac{\text{given mass}}{mM}\right]$

$\therefore$, 1g of $CaCl_2$ is dissolved in 2.46 l of H_2O/soln

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b) Osmosis.

As water conc inside raisins is low due to high salt concentration, water moves from its high conc. to its low conc. through a semi-permeable membrane → causing raisins to get swollen due to endo-osmosis.

c) Reverse Osmosis

When we apply pressure greater than Osmotic pressure on solution side causing solvent particles to move solution to solvent through semi-permeable (in solution) membrane is known as reverse Osmosis which helps in getting pure solvent (H_2O) from sea water.

Q30.

a)

i) $CH_3-\overset{O}{\overset{\|}{C}}-NH_2 \xrightarrow[2)H_2O]{1)\ LiAlH_4} CH_3-CH_2-NH_2$ (Reduction)

ethanamide) (ethylamine)

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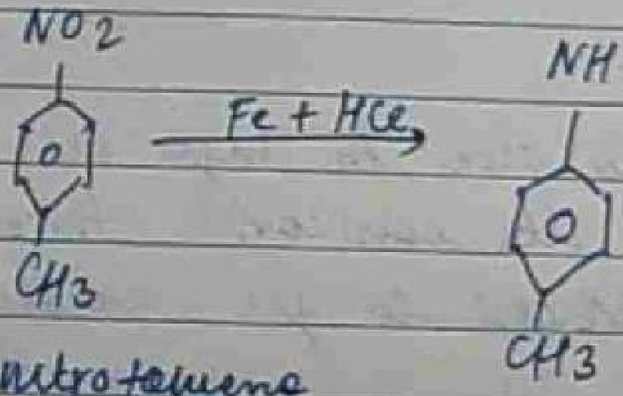
ii) 

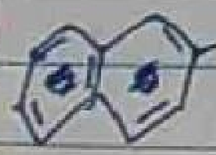
(Reduction)

p-nitrotoluene → p-methyl aniline

b) Primary amines have 2 H atoms connected to electronegative atom N, which involve in intermolecular H-bonding with N whereas tertiary amines dont have any H atom connected to N and thus cant form intermolecular H-bonding.
∴, primary amines have higher boiling point than tertiary amines.

c)
i) 

Tertiary amine
(3 R grps connected to N)

ii) 

Primary amine
(only 1 R grp connected to N)

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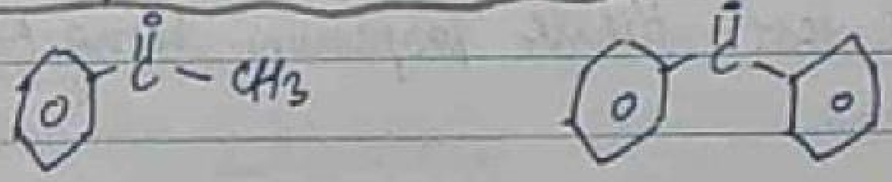
Section E

Q31.

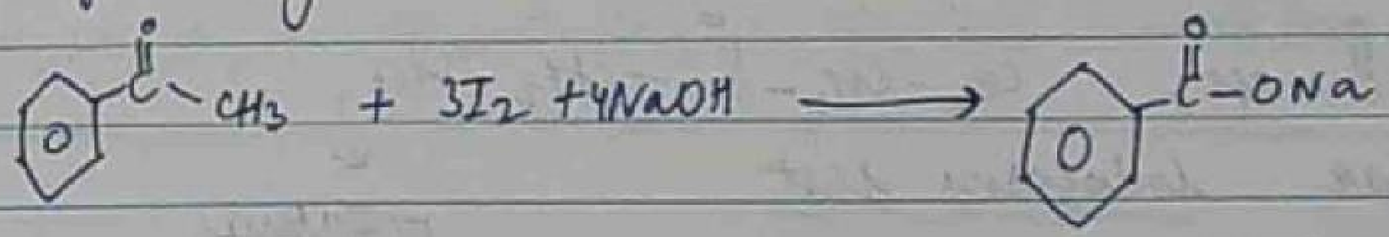
(B)

a)

i) Acetophenone & Benzophenone



These can be distinguished by Iodoform test because acetophenone contains a-methyl group and will give positive test while benzophenone will give negative test



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(ii) Propanal and propanone

$CH_3-CH_2-\overset{O}{\overset{\|}{C}}-H$ $CH_3-\overset{O}{\overset{\|}{C}}-CH_3$

We can use tollen's test to distinguish as propanal being aldehyde will give positive test while propanone being ketone will give negative test.

$$CH_3CH_2-\overset{O}{\overset{\|}{C}}-H + 2[Ag(NH_3)_2]^+ + 3OH^- \longrightarrow CH_3-CH_2COO^- + 2Ag + 3H_2O + 4NH_3$$

silver mirror

iii) Pentan-2-one and pentan-3-one

$CH_3-CH_2-CH_2-\overset{O}{\overset{\|}{C}}-CH_3$ $CH_3-CH_2-\overset{O}{\overset{\|}{C}}-CH_2-CH_3$

We can use Iodoform test

Positive test due to α-methyl group → gives yellow precipitate of CHI_3

negative test due to no α-methyl group

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b)

i) $CH_2F-COOH > CH_3COOH$

CH_2FCOOH is stronger acid because F due to its -I effect would stabilise carboanion formed on losing H^+ and thus it would lose H^+ more readily than CH_3COOH where CH_3 by showing +I would reduce stability of carboanion formed.

EWG (e⁻ withdrawing group) increases acidic character (F)
EDG (e⁻ donating group) decreases acidic character (CH_3)

ii) $CH_3CH_2CH_3 < CH_3-O-CH_3 < CH_3CHO < CH_3CH_2OH$

Q32
(B)

a) $K = G \times$ cell constant (G^*)

$K_1 = \frac{1}{100} \times G^*$

$100K_1 = G^*$

$100 \times 1.29 \times 10^{-2} = G^*$

[$G^* = 1.29\ cm^{-1}$] [$G^* = \frac{l}{A}$]

[K_1 → conductivity of 0.1 M KCl]

[G → conductance = $\frac{1}{\text{Resistance}}$]

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$K_2 = \frac{1}{R_2} \times G^*$ (K_2 → conductivity of 0.01 M KCl)

$= 1.29 \times \frac{1}{300} = \underline{0.43 \times 10^{-2}\ S\ cm^{-1}}$

Λ_m = Molar conductivity $= \frac{K \times 1000}{M(\text{Molarity})} = \frac{0.43 \times 10^{-2} \times 10^3}{10^{-2}} = 430\ S\ cm^2\ mol^{-1}$

K in $S\ cm^{-1}$

∴, conductivity of 0.01 mol/L KCl solution is $\underline{0.43 \times 10^{-2}\ S\ cm^{-1}}$ and molar conductivity is $\underline{430\ S\ cm^2 mol^{-1}}$.

b) i) * H_2-O_2 fuel cell converts energy of combustion of hydrogen directly into electrical energy and is about 70% efficient while efficiency of thermal plants is about 40%.

* Moreover H_2O_2 fuel cell is more environment friendly as it doesn't involve combustion of fossil fuels, thereby reducing pollution & global warming.

∈ H_2O vapour produced was used as drinking water when H_2-O_2 fuel cell was used in Apollo space programme

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iii) In mercury cell, net cell reaction is

$$Zn(Hg) + HgO(s) \rightarrow Hg(l) + ZnO$$

Since net cell reaction doesn't involve any substance whose concentration changes over time, cell potential of mercury cell is constant throughout its life. (1.35 V)

Q33

(A) A → C_2H_6O → C_2H_5OH (ethanol)

$CH_3CH_2-OH + Na \longrightarrow CH_3CH_2O^{\ominus}Na^{\oplus} + \frac{1}{2}H_2(\uparrow)$

(Sodium ethoxide)

B → $CH_3CH_2O^{\ominus}Na^{\oplus}$ → Sodium ethoxide

$CH_3CH_2-OH + 3I_2 + 4NaOH \longrightarrow CHI_3 + HCOONa + 3NaI + 3H_2O$

(iodoform)

C → iodoform (CHI_3) (sodium formate is also formed)

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$CH_3CH_2OH \xrightarrow[413\,K]{H_2SO_4} CH_3-CH_2-O-CH_2-CH_3$

diethyl ether.

D → diethyl ether ($C_4H_{10}O$)

$CH_3CH_2-O-CH_2-CH_3 \xrightarrow[excess]{HI} 2\ CH_3-CH_2-I$

E → CH_3CH_2I → ethyl iodide (C_2H_5I)

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