

Chemistry

(043)





SECTION A -

1. (A) Sodium bicarbonate test
2. (D) HCl solution
3. (D) Activation energy of reaction
4. (D) 2-chlorobutane
5. (C) Treatment with PCC
6. (B) N-Ethyl-N-methyl propan-1-amine
7. (D) Zero Order
8. (B) Nitroethane
9. (C) 1.0M Glucose



10. (B) $(\text{CH}_3)_3\text{C}-\text{CHO}$ ✓
11. (C) III and IV ✓
12. (B) i-d, ii-c, iii-a, iv-b ✓
13. (B) Both A and R are true but R not correct explanation of A. ✓
14. (A) Both A and R are true and R correct explanation of A. ✓
15. (A) Both A and R are true and R correct explanation of A. ✓
16. (D) A is false but R is true. ✓



SECTION B -

17. (b)

Dalton's Law of Partial Pressure for ideal solutions states:

$$P_{\text{total}} = P_1 + P_2$$

where $P_1 = P_1^\circ \times X_1$ and $P_2 = P_2^\circ \times X_2$ by Raoult's law.

Given solution contains equal moles of 'X' and 'Y'.

consider 'x' moles of X and 'y' moles of Y

$$X_x = \frac{\text{no. of moles of X}}{\text{total moles in soln.}} = \frac{x}{x+y} = \frac{x}{2x} = 0.5$$

similarly $X_y = 0.5$; as $x=y$

$$P_x = P_x^\circ \times X_x = 120 \times 0.5 = 60 \text{ mmHg}$$

$$(P_x^\circ = 120 \text{ mmHg})$$

$$P_y = P_y^\circ \times X_y = 160 \times 0.5 = 80 \text{ mmHg}$$

$$(P_y^\circ = 160 \text{ mmHg})$$

$$\longrightarrow P_{\text{total}} = P_x + P_y = 60 + 80$$



$$P_{\text{total}} = 140 \text{ mmHg}$$

- 18) • We observe that the conductivity of KCl decreases with increase in dilution [0.1113 Scm^{-1} at 1 M and 0.0129 Scm^{-1} at 0.1 M]. This is because the number of ions per unit volume of solution decreases on dilution.
- On the other hand, the molar conductivity of KCl increases with increase in dilution [$111.3 \text{ Scm}^2 \text{ mol}^{-1}$ at 1 M and $129 \text{ Scm}^2 \text{ mol}^{-1}$ at 0.1 M]. We know molar conductivity $\lambda_m = k \times V$, where 'k' is the conductivity and V is volume of solution. An increase in volume thus results in an increase in λ_m , as 'k' decreases by only a small amount.

19) (a) (next page)



Order	Molecularity
1. The order of a reaction can be positive, negative, fractional, or zero.	1. The molecularity of a reaction is always positive as molecularity is dependent on the number of reactant particles colliding simultaneously.
2. Order exists for elementary and complex reactions.	2. There is no meaning for molecularity in complex reactions.

(b) Given X and Y are both first order with respect to themselves.

Considering rate law as:

$$\text{rate} = k[X]^x[Y]^y \quad (\text{where } k = \text{rate const.})$$

as; $x=y=1$ (first order)

$$\therefore \text{rate} = k[X][Y]$$



$$\text{if } [X]' = 2[X]$$

$$[Y]' = 3[Y]$$

$$\text{new rate}' = k[X]'[Y]'$$

$$\text{rate}' = k(2[X])(3[Y])$$

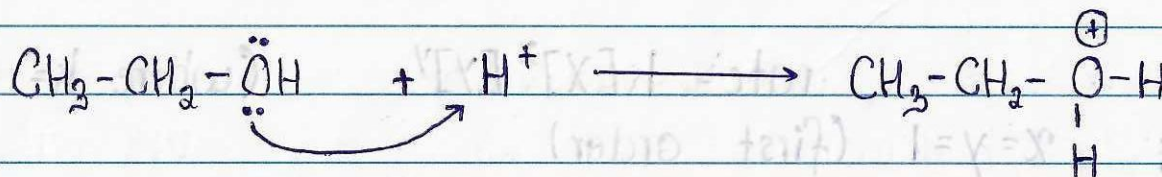
$$\text{rate}' = 6 \times (k[X][Y])$$

$$\text{rate}' = 6 \times \text{rate.}$$

→ The rate increases by six times.

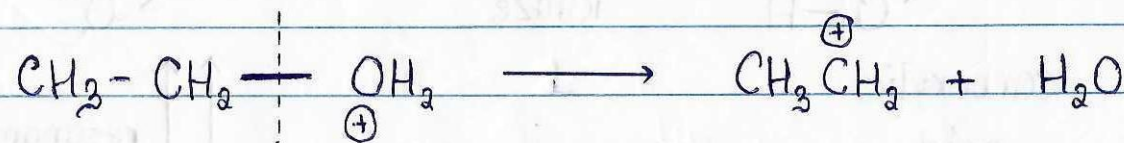
20) $\text{CH}_3\text{CH}_2\text{-OH}$ with H_2SO_4 at 443 K.

Step 1: Protonation of alcohol

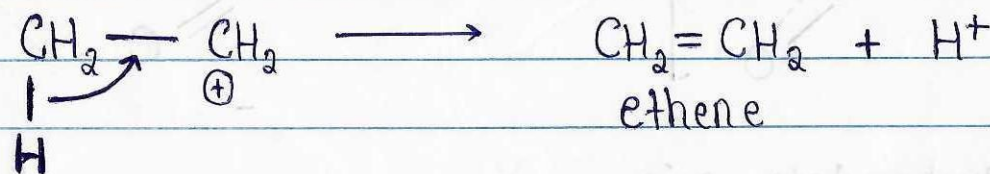




Step 2: Formation of primary carbocation



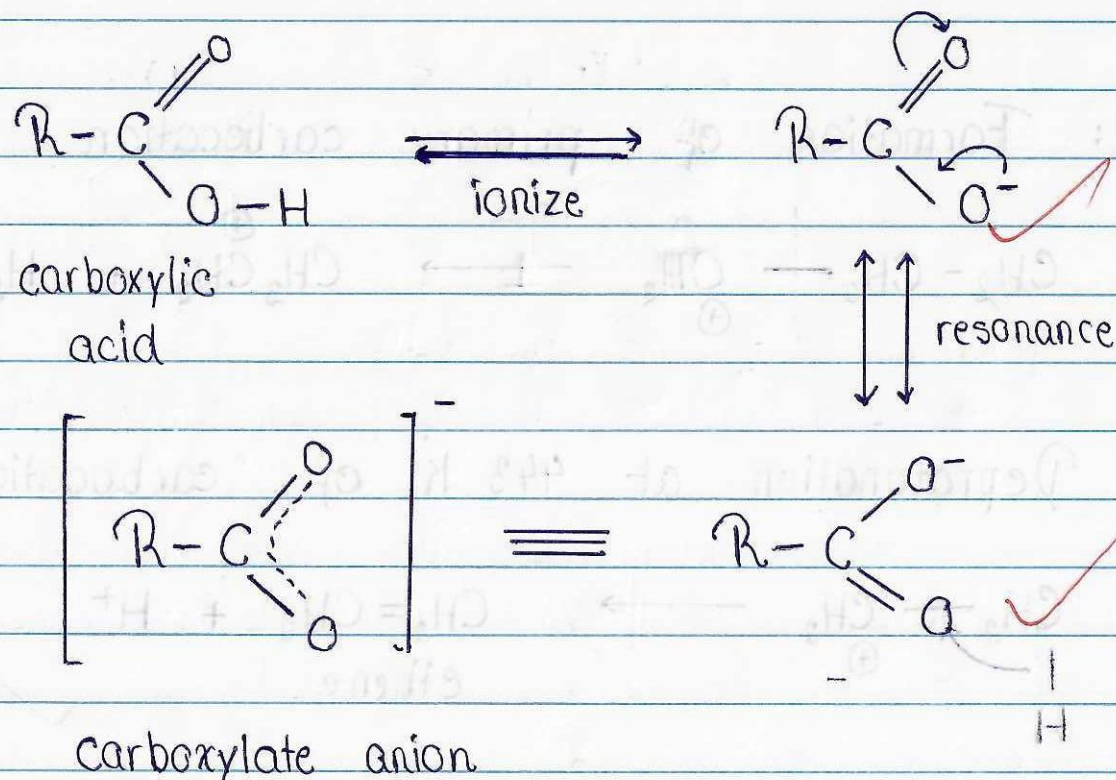
Step 3: Deprotonation at 443 K of carbocation.



(a)

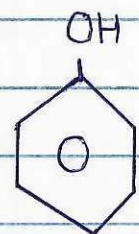
21) Both carboxylic acids and phenol are ionized in an aqueous solution to form carboxylate anion and phenoxide ion.

The carboxylate anion is stabilized by two equivalent resonance structures in which the negative charge is delocalized over two more electronegative oxygen atoms as shown.

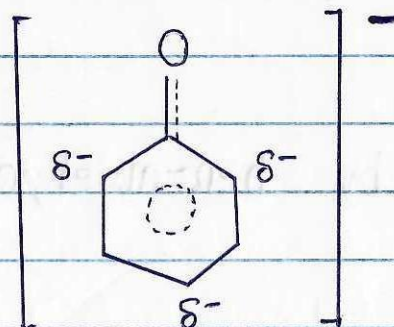
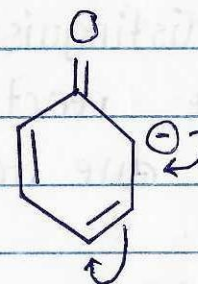
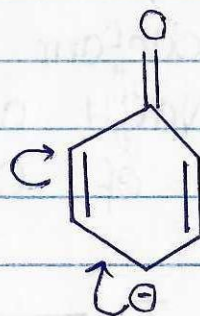
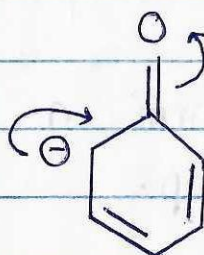
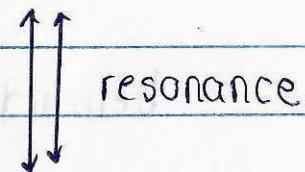
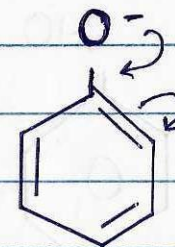
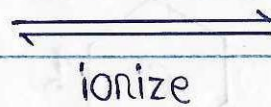


The phenoxide ion is less stabilized by multiple resonating structures where the negative charge is delocalized over one oxygen atom and over less electronegative carbon atoms.

Thus, carboxylic acids are more acidic than phenol.



phenol



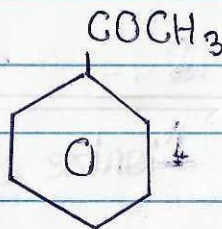
phenoxide ion



(b)



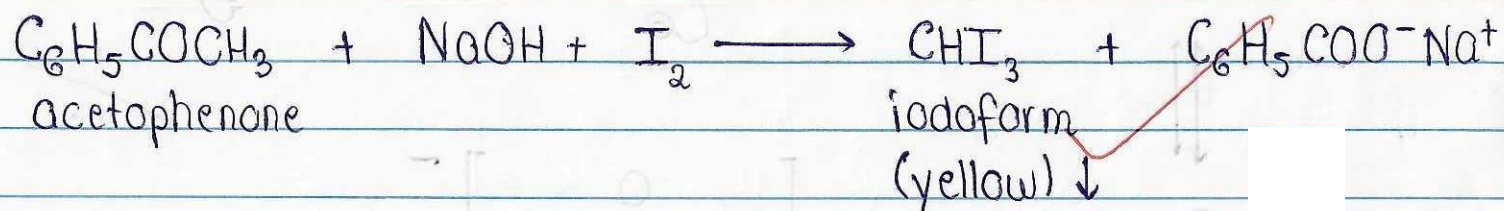
benzaldehyde



acetophenone

Can be distinguished by Iodoform test.

Acetophenone reacts with NaOH and I_2 to form a yellow precipitate due to presence of CH_3-CO- group.



This is not shown by benzaldehyde, due to absence of CH_3-CO- group.

SECTION C -

22. a) Volume expected = $10 + 10 = 20 \text{ mL}$. Actual Volume = 20.2 mL

i) The volume increase occurs as the mixture of the two liquids show positive deviation from Raoult's law. In such a case, newly formed A-B interactions are weaker than A-A and B-B interactions leading to increased vapour pressure, repulsion, and increased volume.

ii) Positive deviations show a positive enthalpy of reaction. As $\Delta H > 0$, the temperature would decrease (endothermic).

iii) Ethanol and Acetone mixture.

23. Consider the rate law for reaction $A + B \rightarrow P$ as

$$\text{rate} = k[A]^x[B]^y \quad \text{where } k \text{ is the rate constant.}$$

from Sl No. ① and ②, we can write

$$\text{rate}_1 = k[0.1]^x[0.1]^y \quad || \quad \text{rate}_2 = k[0.2]^x[0.1]^y$$



$$\frac{\text{rate}_2}{\text{rate}_1} = \frac{0.10}{0.05} = \frac{[0.2]^x}{[0.1]^x}$$

$$\Rightarrow 2 = 2^x \quad \text{or} \quad x=1 \quad \checkmark$$

from Sl. No. ① and ③,

$$\text{rate}_1 = k[0.1]^x [0.1]^y \quad \parallel \quad \text{rate}_3 = k[0.1]^x [0.2]^y$$

$$\frac{\text{rate}_3}{\text{rate}_1} = \frac{0.05}{0.05} = \frac{[0.2]^y}{[0.1]^y}$$

$$1 = 2^y \quad \text{or} \quad y=0 \quad \checkmark$$

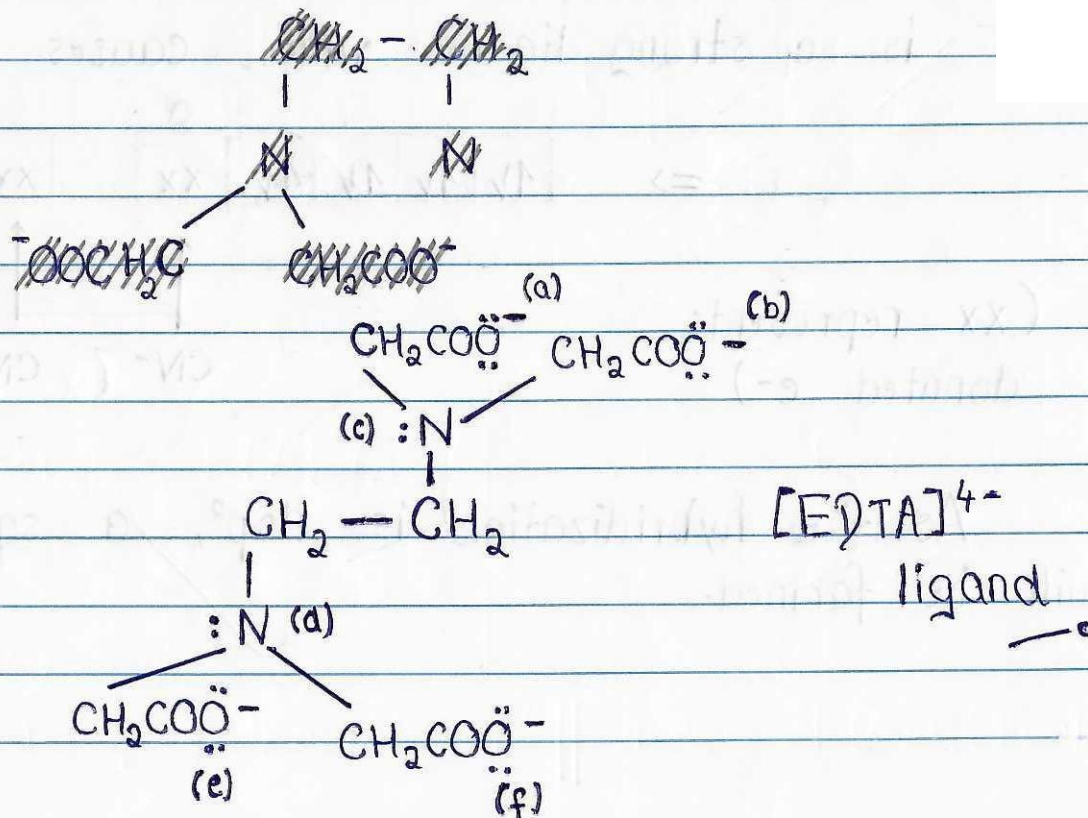
$$\text{Overall eqn} \Rightarrow \text{rate} = k[A]^1[B]^0$$

$$\Rightarrow \text{rate} = k[A]^1[B]^0$$



Order of rxn with respect to $A = x = \underline{1}$.
 order of rxn with respect to $B = y = \underline{0}$.
 overall order = $x + y = \underline{1}$.

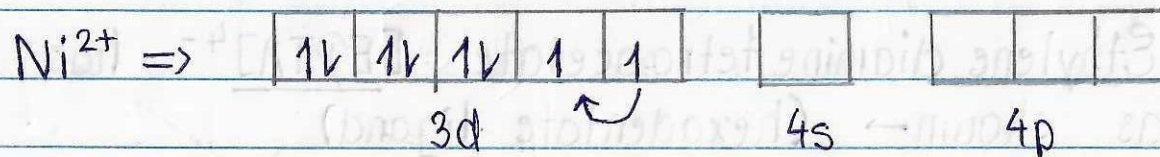
- 24) Ethylene diamine tetraacetate $[EDTA]^{4-}$ has 6 donor sites as shown \rightarrow (hexadentate ligand)



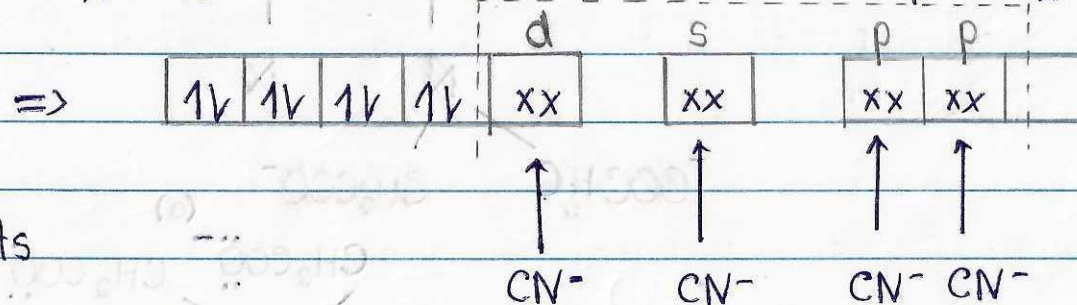


(b) This can be explained by VBT.

$[\text{Ni}(\text{CN})_4]^{2-}$ has $\text{Ni}^{2+} = [\text{Ar}] 3d^8$ ✓



CN^- is a strong ligand which causes inner pairing.

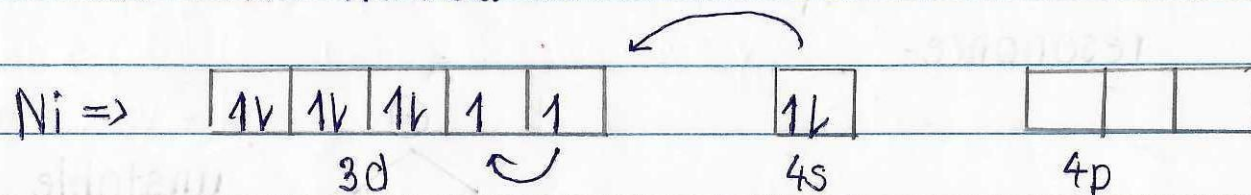


(xx represents
donated e^-)

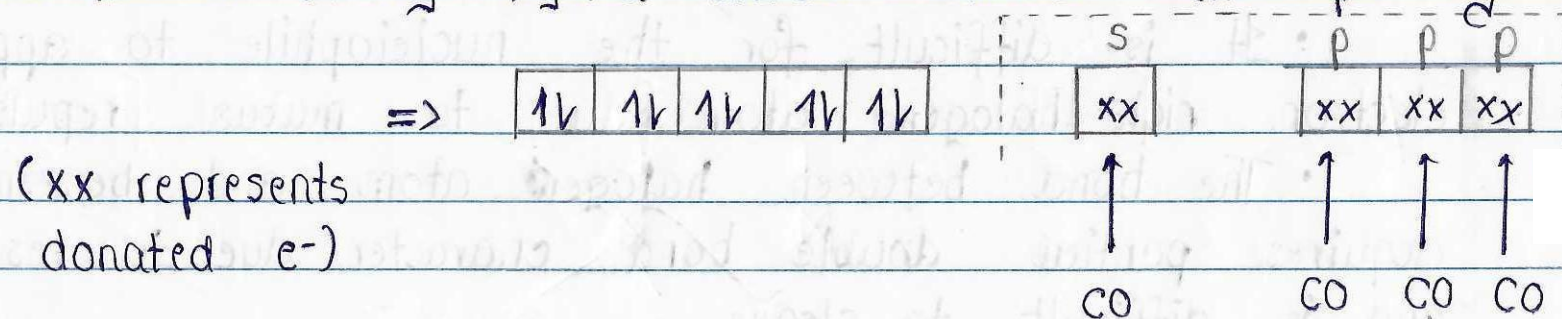
As the hybridization is dsp^2 , a square planar complex will be formed. ✓



$[\text{Ni}(\text{CO})_4]^{2-}$ has $\text{Ni} = [\text{Ar}]3d^8 4s^2$



CO is a strong ligand which causes inner pairing.



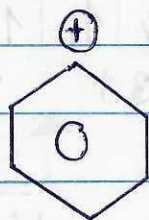
As the hybridization is sp^3 , a tetrahedral complex is formed.

Thus, $[\text{Ni}(\text{CN})_4]^{2-}$ is square planar; $[\text{Ni}(\text{CO})_4]$ is tetrahedral.

25. (a) Haloarenes are less reactive towards nucleophilic substitution due to the following:



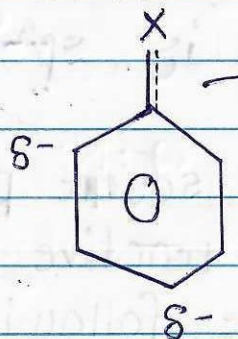
- The phenyl carbocation formed is not stabilized by resonance.



unstable phenyl
carbocation

- It is difficult for the nucleophile to approach the electron rich halogen atom due to mutual repulsion.

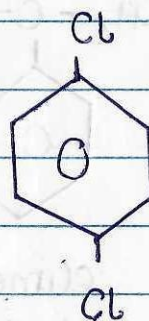
- The bond between halogen atom and benzene group acquires partial double bond character due to resonance, and is difficult to cleave.



(X = halogen)
partial double bond

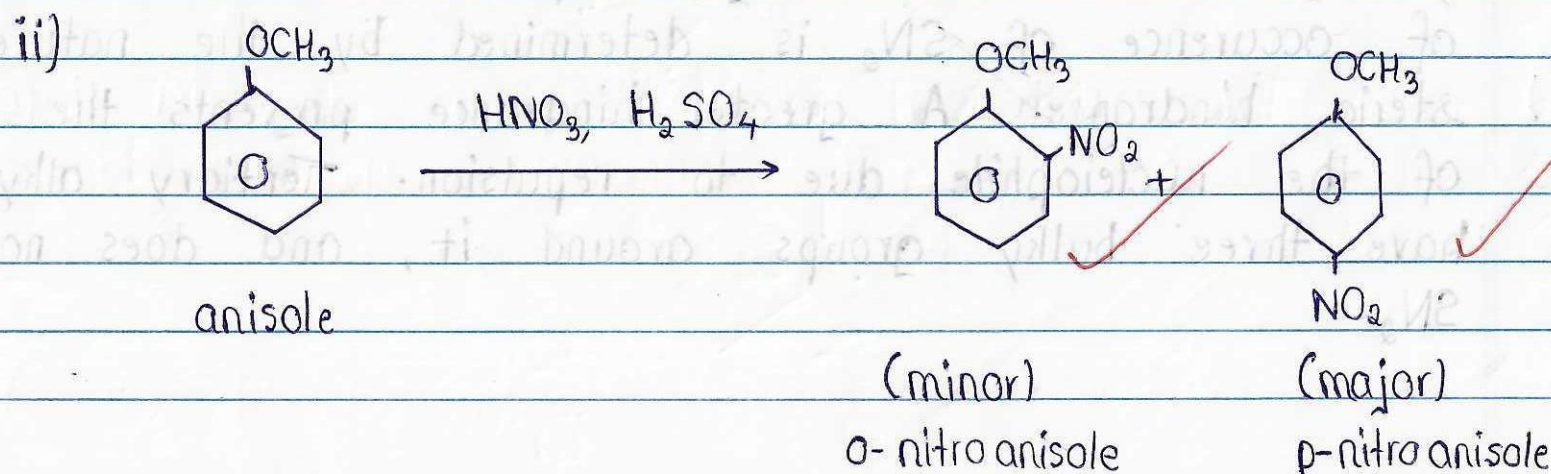
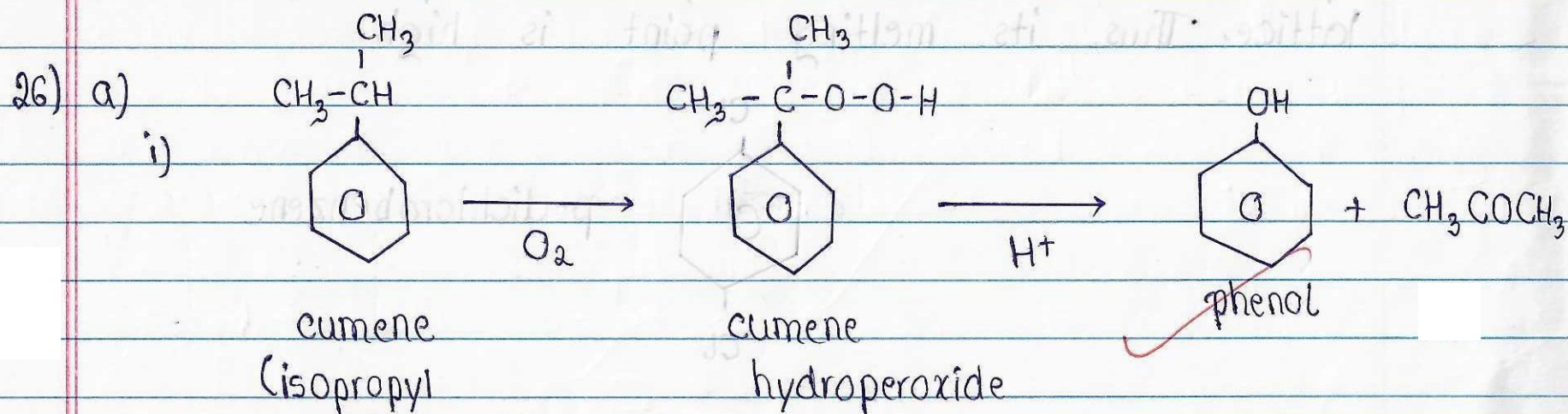
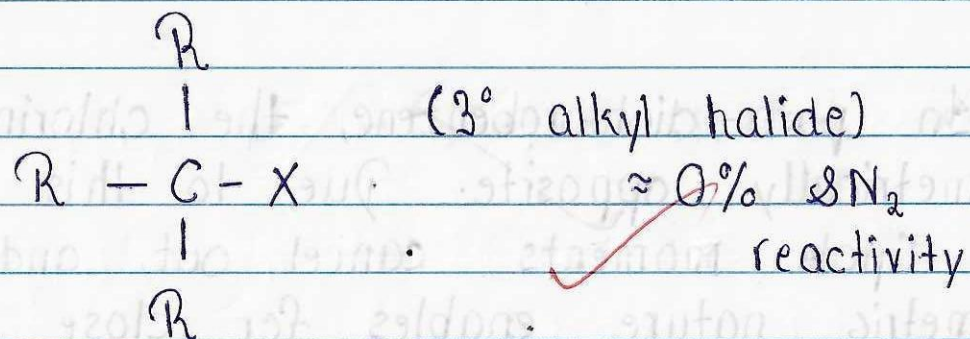


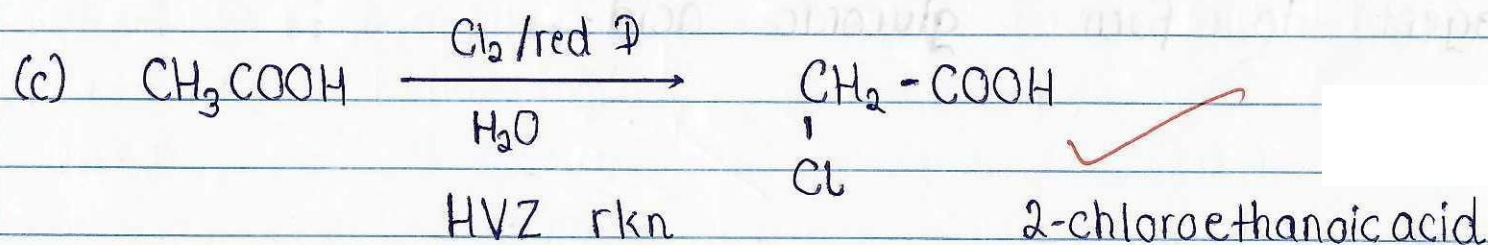
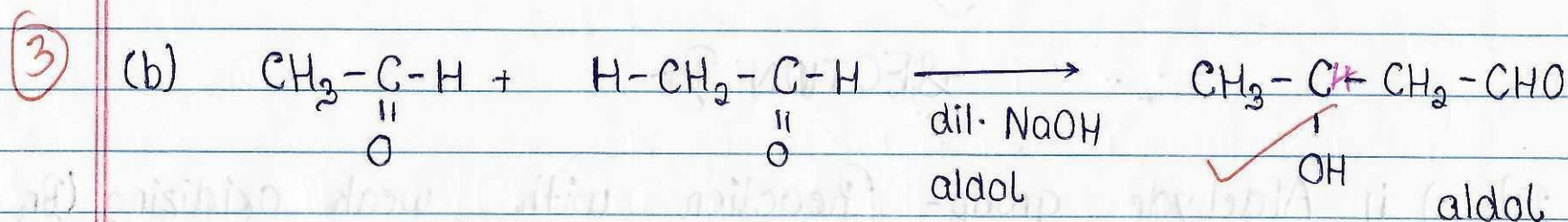
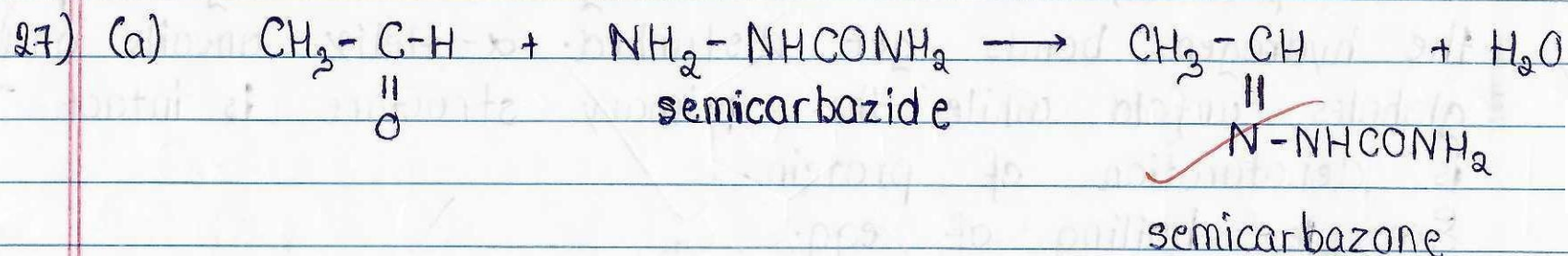
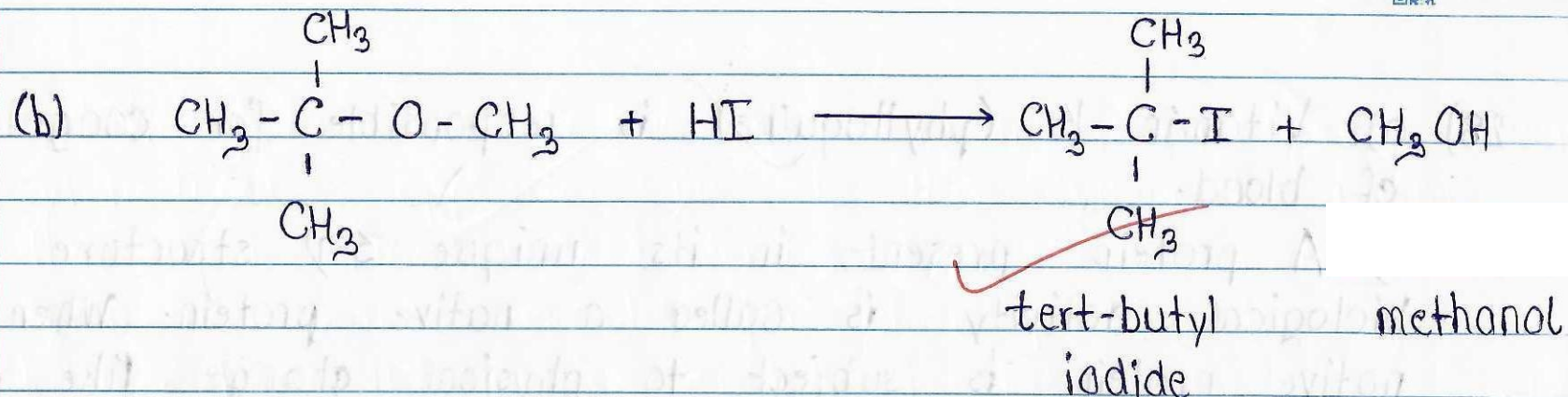
b) In para-dichlorobenzene, the chlorine atoms are attached symmetrically opposite. Due to this symmetric nature, the dipole moments cancel out, and in addition, the symmetric nature enables for close packing in crystal lattice. Thus, its melting point is high.



p-dichlorobenzene

c) S_N2 reactions are single step in nature and the ease of occurrence of S_N2 is determined by the nature of steric hindrance. A greater hindrance prevents the approach of the nucleophile due to repulsion. Tertiary alkyl halides have three bulky groups around it, and does not give S_N2 .



Space for writing
Question Number



28) a) Vitamin - K (phylloquinone) is responsible for coagulation of blood.

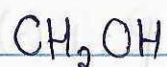
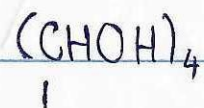
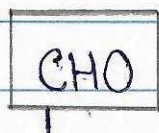
b) A protein present in its unique 3-D structure and biological activity is called a native protein. When a native protein is subject to physical change like change in temperature, or chemical change like change in pH, the hydrogen bonds get disturbed. α -Helix uncoils and globules unfold while the primary structure is intact. This is denaturation of protein.

Example - boiling of egg.

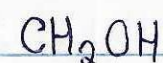
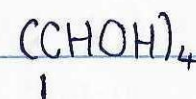
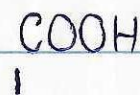
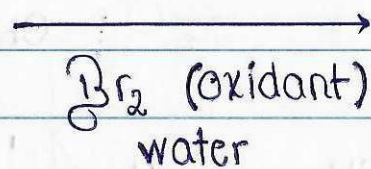
SECTION D -

29) a) i) Aldehyde group - Reaction with weak oxidizing (Br_2 water) agent to form gluconic acid.

Space for writing
Question Number

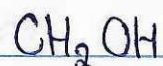
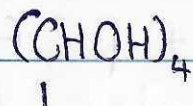
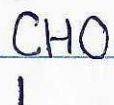


glucose

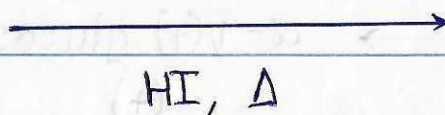


gluconic acid

Straight chain- Reaction with HI and heat to give n-hexane.



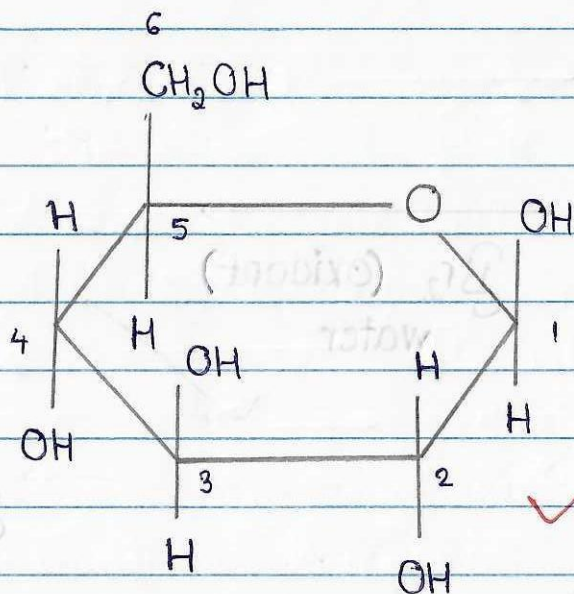
glucose



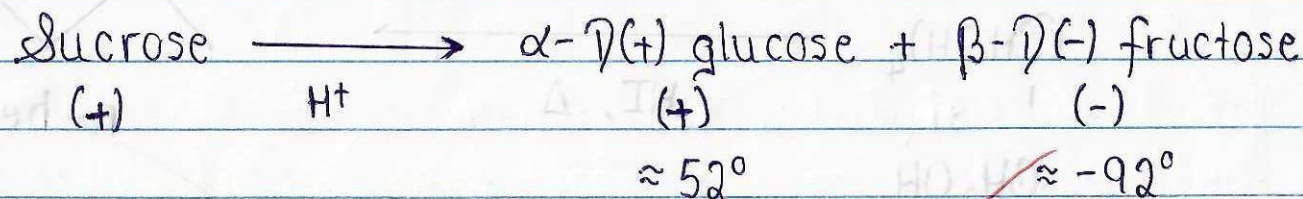
n-hexane



b) ii)

 β -D(+) glucopyranose

c) Sucrose is dextrorotatory. On hydrolysis under acidic medium (H^+) or invertase it forms α -D(+) glucose and β -D(-) fructose.



As the levorotation of fructose ($\approx -92^\circ$) is more than the



dextrorotation of glucose ($\approx 52^\circ$), the mixture obtained after hydrolysis is predominantly levorotatory.

As the optical activity of sucrose changes from (+) to (-) after hydrolysis, it is called invert sugar.

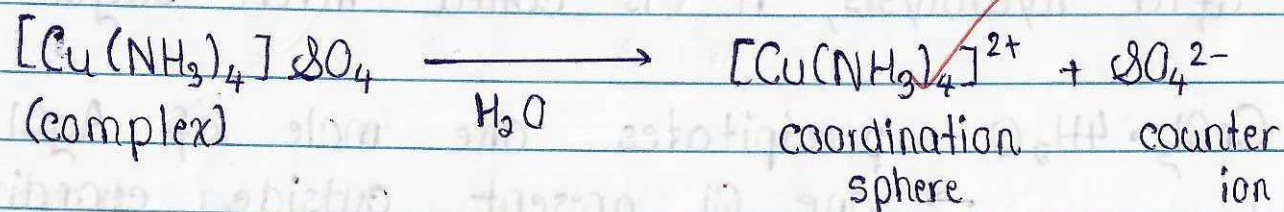
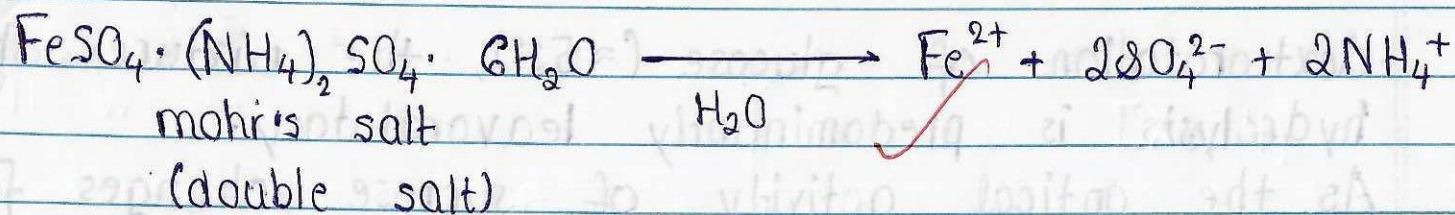
30. a) $\text{CrCl}_3 \cdot 4\text{H}_2\text{O}$ precipitates one mole of AgCl .
→ one Cl present outside coordination sphere.

i) Structure of complex = $[\text{Cr}(\text{H}_2\text{O})_4\text{Cl}_2]\text{Cl}$

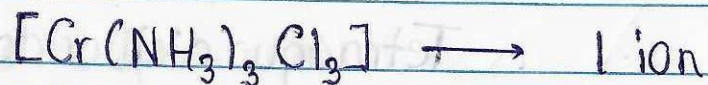
Tetraaqua dichloridochromium(III)
chloride

ii) Secondary valency of Cr = 6

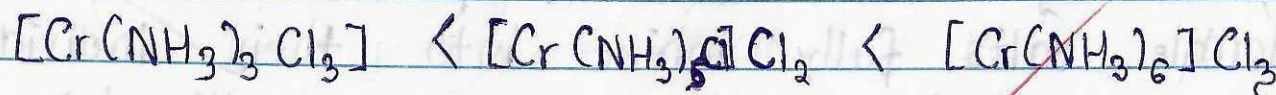
b) Even though both complexes and double salts are formed by mixing two stable compounds in a stoichiometric ratio, double salts fully ionize into their individual ions in aqueous solution while complexes split into counter ions and coordination sphere only.

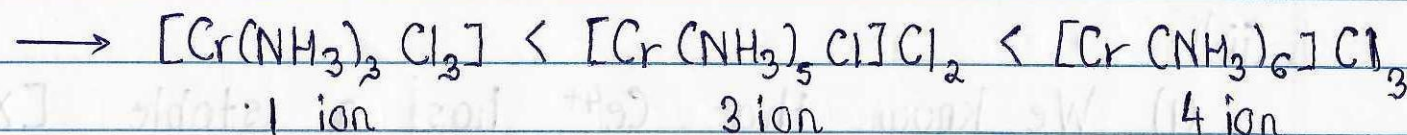


c) i) Any coordination compound splits into its counter ion and coordination sphere.



more the no. of ions, more conductivity.





* order of conductivity ✓

SECTION E-

31. a) i) I) A is K_2MnO_4 (green) manganate ion.
B is KMnO_4 (purple) permanganate ion.

II) In acidic medium:

Reduction:



Oxidation:

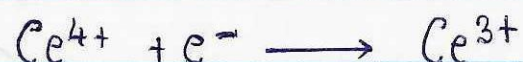


'ionic equation'



(ii)

(i) We know that Ce^{4+} has a stable $[\text{Xe}]4f^0$ configuration. However it can readily reduce to the common +3 state of lanthanoids by gain of an electron.



Thus, it behaves as a good oxidizing agent.

(ii) Actinoid contraction is the steady decrease in the atomic radii of the actinoids due to filling of electrons in the 5f orbitals. Since the shielding effect offered by the 5f orbital is much less than that of 4f, actinoid contraction is more drastic.

(iii) Zn readily loses electrons to achieve a stable $\text{Zn}^{2+} \Rightarrow [\text{Ar}]3d^{10}$ fully filled d-orbital configuration. Due to this fact it has a more negative value of Zn^{2+}/Zn couple than expected.



The Cu^{2+}/Cu couple turns out to be positive as the high enthalpy of atomization of Cu along with the high energy required to convert Cu to Cu^{2+} is not balanced by its low negative hydration enthalpy.

32) (b) i) Kohlrausch's law of independent migration of ions states that the limiting molar conductivity of any electrolyte is defined as the sum of the individual contributions of its anion and cation.

$$\Lambda_m^\circ A_x B_y = x \Lambda_m^\circ A^{y-} + y \Lambda_m^\circ B^{x-}$$

- it is used to find the limiting molar conductivity of weak electrolytes which cannot be found by extrapolation -
- it is used to calculate the degree of dissociation (α) of weak electrolytes - given by $\alpha = \frac{\Lambda_m}{\Lambda_m^\circ}$



(ii) given,

$$\Lambda_m^\circ \text{NH}_4\text{Cl} = 129.8 \text{ S cm}^2 \text{ mol}^{-1} \quad \checkmark$$

$$\Lambda_m^\circ \text{NaOH} = 217.4 \text{ S cm}^2 \text{ mol}^{-1} \quad \checkmark$$

$$\Lambda_m^\circ \text{NaCl} = 108.9 \text{ S cm}^2 \text{ mol}^{-1}$$

by Kohlrausch's law, we know

$$\Lambda_m^\circ \text{NH}_4\text{Cl} = \Lambda_m^\circ \text{NH}_4^+ + \Lambda_m^\circ \text{Cl}^- \quad (1)$$

$$\Lambda_m^\circ \text{NaOH} = \Lambda_m^\circ \text{Na}^+ + \Lambda_m^\circ \text{OH}^- \quad (2)$$

$$\Lambda_m^\circ \text{NaCl} = \Lambda_m^\circ \text{Na}^+ + \Lambda_m^\circ \text{Cl}^- \quad (3) \quad \checkmark$$

(1) - (3) + (2) gives us

$$\begin{aligned} \Lambda_m^\circ \text{NH}_4\text{Cl} - \Lambda_m^\circ \text{NaCl} + \Lambda_m^\circ \text{NaOH} \\ = \Lambda_m^\circ \text{NH}_4^+ + \cancel{\Lambda_m^\circ \text{Cl}^-} - \cancel{\Lambda_m^\circ \text{Na}^+} - \cancel{\Lambda_m^\circ \text{Cl}^-} + \cancel{\Lambda_m^\circ \text{Na}^+} \\ + \Lambda_m^\circ \text{OH}^- \end{aligned}$$

$$= \Lambda_m^\circ \text{NH}_4^+ + \Lambda_m^\circ \text{OH}^- \quad \checkmark$$

$$= \Lambda_m^\circ \text{NH}_4\text{OH}$$



$$(129.8 - 108.9 + 217.4) \text{ Scm}^2\text{mol}^{-1} = \Lambda_m^\circ \text{NH}_4\text{OH}$$

$$\Lambda_m^\circ \text{NH}_4\text{OH} = 238.3 \text{ Scm}^2\text{mol}^{-1}$$

we know $\alpha = \frac{\Lambda_m}{\Lambda_m^\circ}$

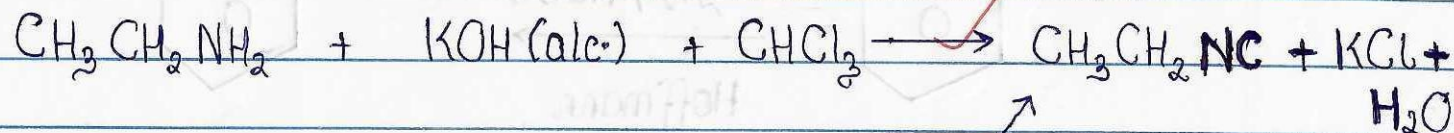
$$\Lambda_m = 9.33 \text{ Scm}^2\text{mol}^{-1}$$

$$\Lambda_m^\circ = 238.3 \text{ Scm}^2\text{mol}^{-1}$$

$$\alpha = \frac{9.33}{238.3} = 3.91 \times 10^{-2}$$

\therefore degree of dissociation
 $\alpha = 3.91 \times 10^{-2}$

33. i) The reaction is Carbylamine reaction.

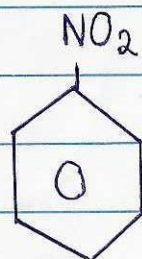


ethyl amine

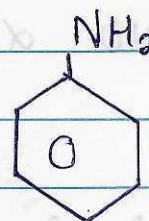
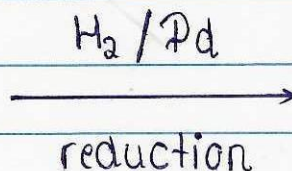
ethyl isocyanide
(foul smell)



ii) A is Nitrobenzene.

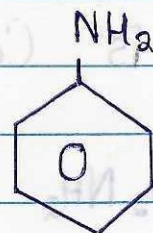
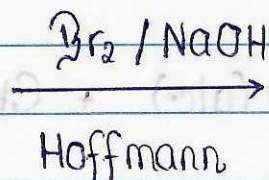
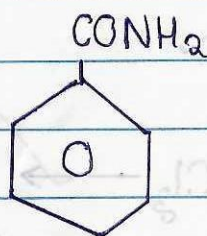
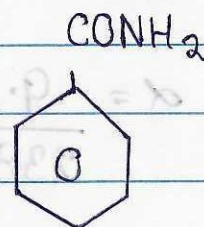


(A)



aniline

B is Benzamide.



+ NaBr + Na₂CO₃

aniline

Space for writing
Question Number

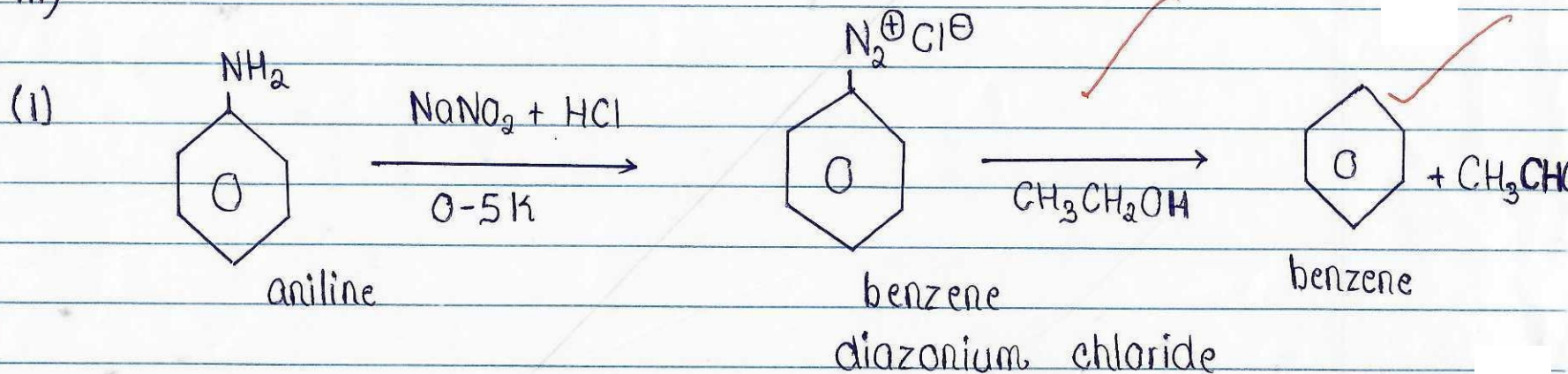
Fictitious Roll No.
(To be entered by Board)

अपना अनुक्रमांक इस उत्तर-पुस्तिका
पर न लिखें

Please do not write your
Roll Number on this Answer-Book

अतिरिक्त उत्तर-पुस्तिका (ओं) की संख्या
Supplementary Answer-Book(s) No.

iii)



(II)

