LIBERTY PAPER SET

STD. 12 : Chemistry

Full Solution

Time : 3 Hours

ASSIGNMENT PAPER 7

Part A

1. (B) **2.** (A) **3.** (B) **4.** (A) **5.** (C) **6.** (D) **7.** (C) **8.** (A) **9.** (D) **10.** (D) **11.** (C) **12.** (B) **13.** (B) **14.** (B)
15. (A) **16.** (D) **17.** (C) **18.** (B) **19.** (C) **20.** (B) **21.** (D) **22.** (C) **23.** (A) **24.** (D) **25.** (B) **26.** (A)
27. (A) **28.** (A) **29.** (A) **30.** (C) **31.** (B) **32.** (A) **33.** (C) **34.** (A) **35.** (B) **36.** (A) **37.** (B) **38.** (C)
39. (A) **40.** (B) **41.** (B) **42.** (A) **43.** (D) **44.** (A) **45.** (D) **46.** (D) **47.** (A) **48.** (B) **49.** (C) **50.** (D)

Part B

Section A

➢ **Write the answer of the following questions : (Each carries 2 Mark)**

1.

➥ (i) 1 mol of H_2O to O_2

$2H_2O \rightarrow O_2 + 4H^+ + 4e^-$

4 mol of electron

$\therefore$ 4F = 4 × 96500 = 386000 C

➥ (ii) 1 mol of FeO to Fe_2O_3

$Fe^{+2} \rightarrow Fe^{+3} + e^-$

1 mol of electron

$\therefore$ 1F = 96,500 C

2.

➥ (i) At cathode : The following reduction reactions compete to take place at the cathode.

$Ag^+(aq) + e^- \rightarrow Ag(s) : E^0 = 0.80\ V$

$H^+(aq) + e^- \rightarrow \frac{1}{2} H_2(g) : E^0 = 0.00\ V$

The reaction with a higher value of E^0 takes place at the cathode. Therefore deposition of silver will take place at the cathode.

At Anode : The Ag anode is attacked by NO_3^- ions. Therefore, the silver electrode at the anode dissolves in the solution to form Ag^+

➥ (ii) At the cathode, the following reduction reaction occurs to produce H_2 gas.

$H^+(aq) + e^- \rightarrow \frac{1}{2} H_2(g)$

At the anode, the following processes are possible.

$2H_2O(l) \rightarrow O_2(g) + 4H^+(aq) + 4e^- ; E^0 = +1.23\ V$ ...... (i)

$2SO_4^{2-}(aq) \rightarrow S_2O_8^{2-}(aq) + 2e^- ; E^0 = +1.96\ V$ ...... (ii)

For dilute sulphuric acid, reaction (i) is preferred to produce O_2 gas. But for concentrated sulphuric acid, reaction (ii) occurs.

3.

➥ Solution : For reaction 2A → Product,

➥ $\Delta t = 10\ min$

$$\text{Rate} = -\frac{1}{2}\frac{\Delta[A]}{\Delta t}$$

$$= -\frac{1}{2}\left\{\frac{0.4 - 0.5}{10\ min}\right\}$$

$$= +\frac{0.1}{20}\ mol\ L^{-1}\ min^{-1}$$

$$= 5.0 \times 10^{-3}\ M\ min^{-1}$$

4.

➥ Ethanol to ethyl fluoride :

$$\underset{\text{Ethanol}}{CH_3CH_2OH} \xrightarrow[-HCl \\ -SO_2]{SOCl_2} \underset{\text{Ethyl chloride}}{CH_3CH_2Cl} \xrightarrow[-AgCl]{AgF} \underset{\text{Ethyl fluoride}}{CH_3CH_2F}$$

5.

- ${}_{26}M : [Ar]\ 3d^5\ 4S^2$

  $M^{3+} : [Ar]\ 3d^5$

  $\boxed{\uparrow}\boxed{\uparrow}\boxed{\uparrow}\boxed{\uparrow}\boxed{\uparrow}$

  unpaired electrons = 5

  $\therefore$ Magnetic Moment $(\propto) = \sqrt{n\,(n+2)}$

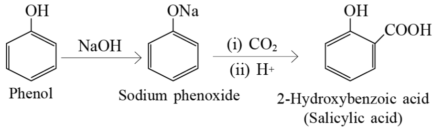
  $= \sqrt{5\,(5+2)}$

  $= \sqrt{35}$

  $= 5.92$ B.M

6.

- Phenoxide ion generated by treating phenol with sodium hydroxide is even more reactive than phenol towards electrophilic aromatic substitution. Hence, it undergoes electrophilic substitution with carbon dioxide, a weak electrophile. Ortho hydroxybenzoic acid is formed as the main reaction product.



7.

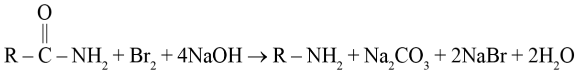
- A nucleoside is formed by the attachment of a base to 1' position of sugar.
- On the other hand all three basic component of nucleic acids (i.e. pentose sugar, phosphoric acid and base are present in nucleotide.)

8.

- In secondary structure of RNA, helices are present which are only single stranded.
- Sometimes they fold back on themselves.
- RNA molecules are of 3 types and they perform different functions.
- The are named as messenger RNA (m-RNA), ribosomal RNA (r-RNA) and transfer RNA (t-RNA).

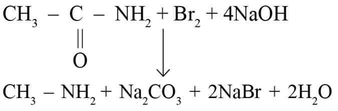
9.

- Hoffmann developed a method for preparation of primary amines by treating an amide with bromine in an aqueous or ethanolic solution of sodium hydroxide. In this degradation reaction, migration of an alkyl or aryl group takes place from carbonyl carbon of the amide to the nitrogen atom.
- The amine so formed contains one carbon less than that present in the amide.

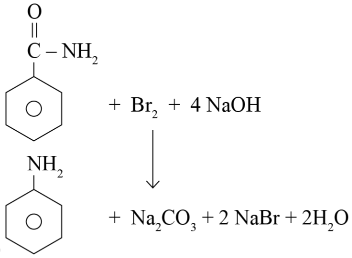


$$R-\overset{\overset{\displaystyle O}{\|}}{C}-NH_2+Br_2+4NaOH\rightarrow R-NH_2+Na_2CO_3+2NaBr+2H_2O$$

Example (1)



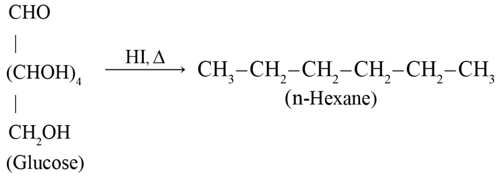
$$CH_3-\underset{\underset{\displaystyle O}{\|}}{C}-NH_2+Br_2+4NaOH \;\downarrow\; CH_3-NH_2+Na_2CO_3+2NaBr+2H_2O$$



(2)

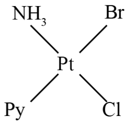
10.

- Reactions with HI :
  - When D-glucose is heated with HI for long time, n-Hexane is formed, it shows all 6–carbon atoms are linked in linear chain.

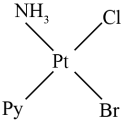


$$\underset{\text{(Glucose)}}{\begin{matrix}CHO\\ |\\ (CHOH)_4\\ |\\ CH_2OH\end{matrix}} \xrightarrow{HI,\ \Delta} \underset{\text{(n-Hexane)}}{CH_3-CH_2-CH_2-CH_2-CH_2-CH_3}$$

11.



cis



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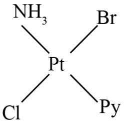


trans

- From the above isomers, none will exhibit optical isomers.
- Tetrahedral complexes rarely show optical isomerization.
- They do so only in the presence of unsymmetrical chelating agents.

12.

- (1) Linkage Isomerism :
  - Linkage isomerism arises in a coordination compound containing ambidentate ligand.
  - A simple example is provided by complexes containing the thiocyanate ligand, NCS^-, which may bind through the nitrogen to give M–NCS or through sulphur to give M–SCN.
  - Jorgenson discovered such behaviour in the complex $[Co(NH_3)_5(NO_2)]Cl_2$, which is obtained as the red form, in which the nitrite ligand is bound through oxygen (–ONO), and as the yellow form, in which the nitrite ligand is bound through nitrogen ($-NO_2$).

    e.g. : $\underset{\text{Red}}{[Co(ONO)(NH_3)_5]^{2+}}$ and $\underset{\text{Yellow}}{[Co(NO_2)(NH_3)_5]^{2+}}$

Section B

➢ **Write the answer of the following questions : (Each carries 3 Mark)**

13.

- **Isotonic Solution :**
  - ***Two solutions having same osmotic pressure at a given temperature are called isotonic solutions.***
  - When such solutions are separated by semipermeable membrane no osmosis occurs between them.
  - For example, the osmotic pressure associated with the fluid inside the blood cell is equivalent to that of 0.9% (mass/volume) sodium chloride solution,
- **Hypertonic Solution :**
  - ***The solution which possess more osmotic pressure with respect to other solution is known as hypertonic solution.***
  - e.g. if we place the cells in a solution containing more than 0.9% (mass/volume) sodium chloride, water will flow out of the cells and they would shrink. Such a solution is called hypertonic.
- **Hypotonic Solution :**
  - ***The solution which possess less osmotic pressure with respect to other solution is known as hypotonic solution.***
  - e.g. : If the salt concentration is less than 0.9% (mass/volume), the solution is said to be hypotonic. In this case, water will flow into the cells placed in the solution and they would swell.

14.

- $Mg(s) \mid Mg^{2+}(0.001M) \parallel Cu^{2+}(0.0001M) \mid Cu(s)$

  cell reaction : $Mg(s) + Cu^{2+}(aq) \rightarrow Mg^{2+}(aq) + Cu(s)$ (n = 2)

  $$E^0_{cell} = E^0_{Cu2+ \mid Cu} - E^0_{Mg2+ \mid Mg}$$
  $$= 0.34 - (-2.36)$$
  $$= 2.70V$$
  $$E_{cell} = E^0_{cell} - \frac{0.059}{n} \log \frac{[Mg^{2+}]}{[Cu^{2+}]}$$
  $$= 2.70 \times \frac{0.059}{2} \log \frac{0.001}{0.0001}$$
  $$= 2.70 - 0.0295$$
  $$E_{cell} = 2.67\ V$$

15.

- Preparation :
- Potassium permanganate is prepared by fusion of MnO_2 with an alkali metal hydroxide and an oxidising agent like KNO_3. This produces the dark green K_2MnO_4 which disproportionates in a neutral or acidic solution to give permanganate.

  $$2MnO_2 + 4KOH + O_2 \rightarrow 2K_2MnO_4 + 2H_2O$$
  $$3MnO_4^{2-} + 4H^+ \rightarrow 2MnO_4^- + MnO_2 + 2H_2O$$

- Commercially it is prepared by the alkaline oxidative fusion of MnO_2 followed by the electrolytic oxidation of manganate (VI).

  $$\underset{}{MnO_2} \xrightarrow[\text{with air or } KNO_3]{\text{Fused with KOH, oxidised}} \underset{\text{manganate ion}}{MnO_4^{2-}}$$

  $$\underset{\text{manganate}}{MnO_4^{2-}} \xrightarrow[\text{alkaline solution}]{\text{Electrolytic oxidation in}} \underset{\text{permanganate ion}}{MnO_4^-}$$

- In the laboratory, a manganese (II) ion salt is oxidised by peroxodisulphate to permanganate.

  $$2Mn^{2+} + 5S_2O_8^{2-} + 8H_2O \rightarrow 2MnO_4^- + 10SO_4^{2-} + 16H^+$$

- In Acidic Medium oxidising action of $KMnO_4$

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

  (i) Acidified $KMnO_4$ solution oxidizes Fe (II) ions to Fe (III) ions i.e., ferrous ions to ferric ions.

  $$\begin{array}{r}
MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O \\
5Fe^{2+} \rightarrow 5Fe^{3+} + 5e^- \\
\hline
5Fe^{2+} + MnO_4^- + 8H^+ \rightarrow Mn^{2+} + 4H_2O + 5Fe^{3+}
\end{array}$$

  (ii) Acidified potassium permanganate oxidizes SO_2 to sulphuric acid.

  $$\begin{array}{r}
2\,MnO_4^- + 16H^+ + 10e^- \rightarrow 2Mn^{2+} + 8H_2O \\
5SO_2 + 10H_2O \rightarrow 5SO_4^{2-} + 20H^+ + 10e^- \\
\hline
2\,MnO_4^- + 5SO_2 + 2H_2O \rightarrow 2Mn^{2+} + 5SO_4^{2-} + 4H^+
\end{array}$$

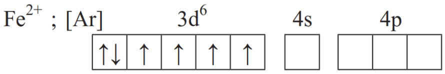
  (iii) Acidified potassium permanganate oxidizes oxalic acid to carbon dioxide.

  $$\begin{array}{r}
2MnO_4^- + 16H^+ + 10e^- \rightarrow 2Mn^{2+} + 8H_2O \\
5C_2O_4^{2-} \rightarrow 10CO_2 + 10e^- \\
\hline
5C_2O_4^{2-} + 2MnO_4^- + 16H^+ \rightarrow 2Mn^{2+} + 10CO_2 + 8H_2O
\end{array}$$

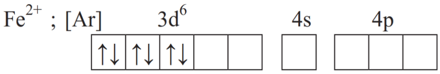
16.

(i) $[Fe(CN)_6]^{4-}$

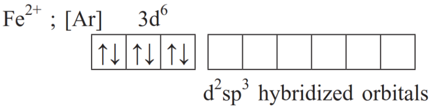
- In the above coordination complex, iron exists in the +2 oxidation state.



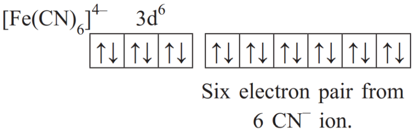
- As CN^- is a strong field ligand, it causes the pairing of the unpaired 3d electrons.



- Since, there are six ligands around the central metal ion, the most feasible hybridization is d^2sp^3.



- 6 electron pairs from CN^- ions occupy the six hybrid d^2sp^3 orbitals.



- Hence, the geometry of the complex is octahedral and the complex is diamagnetic (as there are no unpaired electrons).
- ∝ = 0 B.M.

17.

(i) 1-Iodobutane from 1-butanol

$$\underset{\text{1-butanol}}{CH_3-CH_2-CH_2-CH_2-OH} \xrightarrow[\text{Red P}]{I_2} \underset{\text{1-Iodobutane}}{CH_3-CH_2-CH_2-CH_2-I}$$

(ii) 1-Iodobutane from 1-chlorobutune

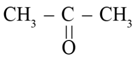
$$\underset{\text{1-chlorobutane}}{CH_3-CH_2-CH_2-CH_2-Cl} \xrightarrow[\text{Dry Acetone}]{\text{NaI}} \underset{\text{1-Iodobutane}}{CH_3-CH_2-CH_2-CH_2-I}$$
$$-\text{Nacl}$$

(iii) 1-Iodobutane from but-1-ene

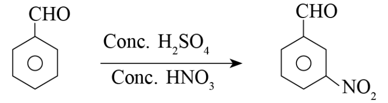
$$\underset{\text{But-1-ene}}{CH_3-CH_2-CH=CH_2} + HBr \xrightarrow{\text{Peroxide}} CH_3-CH_2-CH_2-CH_2-Br \xrightarrow[\text{NaI}]{\text{Dry Acetone}} \underset{\text{1-Iodobutane}}{CH_3-CH_2-CH_2-CH_2-I}$$
$$-\text{NaBr}$$

18.

$$\underset{\text{Butanal}}{CH_3CH_2CH_2CHO} \xrightarrow[\text{Tollen's reugent}]{\text{Amonical AgNo}_3} \underset{\text{Butanoic acid}}{CH_3CH_2CH_2COOH}$$



$$\underset{\text{Acetone}}{CH_3-\overset{\displaystyle O}{\overset{\|}{C}}-CH_3} \xrightarrow[\text{HCl}]{\text{Zn}-\text{Hg}} \underset{\text{Propane}}{CH_3-CH_2-CH_3} + H_2O$$



Benzaldehyde

m - nitrobenzaldehyde

19.

➥ (i) $C_6H_5NH_2 < C_6H_5N(CH_3)_2 < (C_2H_5)_2NH$

(ii) Aniline < p-nitro < p-toluidine

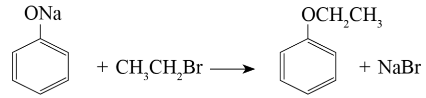
(iii) $C_6H_5NH_2 < C_6H_5NHCH_3 < C_6H_5CH_2NH_2$

20.

➥ (i) $CH_3CH_2CH_2ONa + CH_3CH_2CH_2Br \longrightarrow C_2H_5CH_2{-}O{-}CH_2C_2H_5 + NaBr$

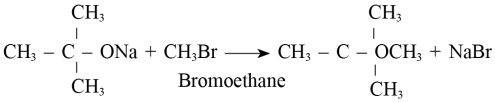
Sodium propoxide 1-Bromopropane 1-Propoxypropane

(ii)



Sodium phenoxide Bromoethane Ethoxybenzene

(iii)



$$CH_3-\underset{CH_3}{\overset{CH_3}{\underset{|}{\overset{|}{C}}}}-ONa + CH_3Br \longrightarrow CH_3-\underset{CH_3}{\overset{CH_3}{\underset{|}{\overset{|}{C}}}}-OCH_3 + NaBr$$

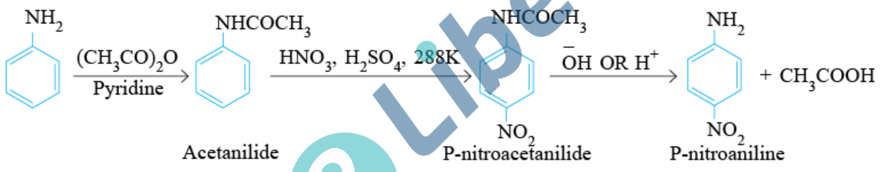
Bromoethane

Sodium 2 - methyl 2-propoxide

2-Methoxy-2-methylpropane

21.

➥ By protecting the $-NH_2$ group by acetylation reaction with acetic anhydride, the nitration reaction can be controlled and the P-nitro derivative can be obtained as the major product.



Section C

➢ **Write the answer of the following questions : (Each carries 4 Mark)**

22.

➥ (i) $W_2 = 18$ g $M_2 = 180$ g.mol^{-1}

$W_1 = 1$ kg $K_b = 0.52$ k.kg.Mol^{-1}

$= 1000$ g $T_b^0 = 373.15$ k

$T_b = (?)$

$$\Delta T_b = K_b \cdot \frac{W_2 \times 1000}{M_2 \times W_1}$$

$$= 0.52 \times \frac{18 \times 1000}{180 \times 1000}$$

$\Delta T_b = 0.052$ K

$\Delta T_b = T_b - T_b^0$

$\therefore\ 0.052 = T_b - 373.15$

$\therefore\ T_b = 373.15 + 0.052$

$= 373.202$ K

- (ii) $V = 200\ cm^3 = 200\ ml = 0.2\ L$

  $W_2 = 1.26\ g,\ \pi = 2.57 \times 10^{-3}$ bar

  $T = 300\ K\ M_2 = (?)$

  $R = 0.083\ L.bar.Mol^{-1}.K^{-1}$

  $$\pi = \frac{W_2 RT}{M_2 V}$$

  $$\therefore M_2 = \frac{1.26 \times 0.083 \times 300}{2.57 \times 10^{-3} \times 0.2}$$

  $= 61.0389 \times 10^3$

  $= 61{,}038.9\ g.mol^{-1}$

23.

- Nuclear explosion is first order reaction.
- $t_{\frac{1}{2}} = 28.1$ years and $[R]_0 = 1\ \mu g$.
- For first order reaction,

  $$k = \frac{0.693}{t_{\frac{1}{2}}} = \frac{0.693}{28.1} = 2.466 \times 10^{-2}\ year^{-1}$$

- Calculation for amount of ^{90}Sr remain after 10 years :

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

  $$\therefore \log \frac{[R]_0}{[R]_t} = \frac{k \times t}{2.303}$$

  $$\therefore \log \frac{[R]_0}{[R]_t} = \frac{2.466 \times 10^{-2} \times 10}{2.303}$$

  $$\therefore \log \frac{1}{[R]_t} = 0.1070$$

  $$\therefore \frac{1}{[R]_t} = \text{anti log } 0.1070 = 1.2794$$

  $\therefore [R]_t = \frac{1}{1.2794} = 0.7816\ \mu g\ ^{90}Sr$ is left after 10 years.

- Calculation for amount of ^{90}Sr remain after 60 years :

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

  $$\therefore \log \frac{[R]_0}{[R]_t} = \frac{k \times t}{2.303}$$

  $$\therefore \log \frac{[R]_0}{[R]_t} = \frac{2.466 \times 10^{-2} \times 60}{2.303}$$

  $$\therefore \log \frac{1}{[R]_t} = 0.6425$$

  $$\therefore \frac{1}{[R]_t} = \text{anti log } 0.6425 = 4.39$$

  $\therefore [R]_t = \frac{1}{4.39} = 0.228\ \mu g\ ^{90}Sr$ is left after 60 years.

24.

- At a standard temperature of 298K, the EMF of a cell can be measured by pairing the standard hydrogen electrode with the second half cell, constructed by taking the SHE as the anode (reference half cell) and the other half cell as the cathode.
- standard hydrogen electrode | | other half-cell

➥ If the concentrations of the oxidised and the reduced forms of the species in the right hand half-cell are unity, then the cell potential is equal to standard electrode potential. E^0_R

$E^6 = E^6_R - E^6_L$

As E^6_L for standard hydrogen electrode is zero.

$E^6 = E^6_R - 0 = E^6_R$

➥ Electrode potential of copper

$Pt(s) \mid H_2(g, 1\ bar) \mid H^+(aq, 1\ M) \parallel Cu^{2+}(aq, 1\ M) \mid Cu$

➥ EMF of above cell is 0.34 V

So,

$E^0 = E^0_R - E^0_L$

$0.34 = E^0_{Cu+2 \mid Cu} - 0.0$

$\therefore E^0_{Cu+2 \mid Cu} = 0.34V$

Electrode potential of Cu is 0.34 V

➥ Electrode potential of Zinc

$Pt(s) \mid H_2(g, 1bar) \mid H^+(aq, 1M) \mid \mid Zn^{2+}(aq, 1\ M) \mid Zn$

➥ EMF of above cell is – 0.76 V

So,

$E^0 = E^0_R - E^0_L$

$-0.76 = E^0_{Zn+2 \mid Zn} - 0.0$

$\therefore E^0_{Zn+2 \mid Zn} = -0.76\ V$

Electrode potential of Zinc is – 0.76 V

25.

➥

(i) $K_3 [Co (CO_2O_4)_3]$
IUPAC Name : Potassium Trioxalate Cobaltate (III)
No of unpaired electrons in $K_3 [Co (CO_2O_4)_3]$
Then, $\mu = \sqrt{n(n+2)}BM$
$= \sqrt{3(3+2)}BM$
$= \sqrt{3(5)}BM = \sqrt{15}$
$= 3.87$ BM

(ii) $Cs[FeCl_4]$
IUPAC Name: Cesium tetrachloride ferrate(III)
No of Unpaired Electrons in $Cs[FeCl_4]$
$\mu = \sqrt{n(n+2)}$
$= \sqrt{5(5+2)}$
$= \sqrt{5(7)}$
$= \sqrt{35}$
$= 5.87$ BM

26.

➥ (i) $CH_3CH_2Br \xrightarrow{KCN} \underset{\text{Ethyl cyanide}}{CH_3CH_2CN} + KBr \xrightarrow[\text{(ii) } H_2O]{\text{(i) Di-BAIH}} \underset{\text{Propenal}}{CH_3CH_2CHO}$

(ii) $C_6H_5NO_2 + 3H_2 \xrightarrow{Fe/HCl} C_6H_5NH_2 + 2H_2O \xrightarrow[\text{pyridine}]{(CH_3CO)_2O} \underset{\text{N - phenyl Acetamide}}{C_6H_5NHCOCH_3} + CH_3COOH$

27.

➥

(i) Alcohols react with hydrogen halides to form alkyl halides.

$$\text{R-OH} + \text{HCl} \xrightarrow{ZnCl_2} \text{R-Cl} + H_2O$$

➥ The difference in reactivity of three classes of alcohols with HCl distinguishes them from one another.

➥ Alcohols are soluble in Lucas reagent (conc. HCl and $ZnCl_2$) while their halides are immiscible and produce turbidity in solution.

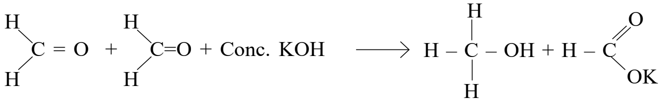
➥ In case of tertiary alcohols, turbidity is produced immediately as they form the halides easily.

➥ Primary alcohols do not produce turbidity at room temperature.

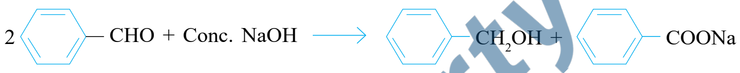
➥ This is how alcohols can be distinguished by Lucas test.

(ii)

➥ **Cannizzaro reaction :** ***"Aldehydes which do not have an α-hydrogen atom, undergo self oxidation and reduction (disproportionation) reaction on treatment with concentrated alkali. In this reaction, one molecule of the aldehyde is reduced to alcohol while another is oxidised to carboxylic acid salt."***



Formaldehyde Methanol Potassium formate



Benzaldehyde Benzyl alcohol Sodium benzoate