SAMPLE PAPER 7

CHEMISTRY PAPER 1
(THEORY)

Maximum Marks: 70

Time Allowed: Three Hours

*(Candidates are allowed **additional 15 minutes** for **only** reading the paper.*

*They must **NOT** start writing during this time.)*

This paper is divided into four sections – A, B, C and D.
*Answer **all** questions.*
***Section – A** consists of **one** question **having sub-parts** of **one** mark each.*
***Section – B** consists of **ten** questions of **two** marks each.*
***Section – C** consists of **seven** questions of **three** marks each, and*
***Section – D** consists of **three** questions of **five** marks each.*
Internal choices have been provided in one question each in Section B,
Section C and Section D.
All working, including rough work, should be done on the same sheet as, and adjacent to the
rest of the answer.
The intended marks for questions or parts of questions are given in brackets [ ].
Balanced equations must be given wherever possible and diagrams where they are helpful.
When solving numerical problems, all essential working must be shown.
In working out problems, use the following data:
Gas constant $R = 1.987$ cal deg^{-1} mol^{-1} = 8.314 JK^{-1} mol^{-1} = 0.0821 dm^3 atm K^{-1}mol^{-1}
1 L atm = 1 dm^3 atm = 101.3 J, 1 Faraday = 96500 coulombs,   Avogadro's number = 6.023×10^{23}

SECTION A – 14 MARKS

Question 1

(A)

(i)
Ans.: increases, activation

(ii)
Ans.: octahedral, square planar

(iii)
Ans.: Oxidation, *p*-benzoquinone

(iv)
Ans.: alkyl cyanides, isocyanides

(B)

Ans.: (c) $101\ \Omega^{-1}\ cm^2\ mol^{-1}$

(ii)
Ans.: (c) 6 and +3
Explanation: As the number of atoms of the ligands that are directly bound to the central metal is known as coordination number. It is six here.

Let oxidation state of Cr be x.

$\Rightarrow 3\,(+1) + x + 3(-2) = 0 \Rightarrow 3 + x - 6 = 0$

$\Rightarrow x = +3$

(iii)
Ans.: (b) Variable oxidation states

(iv)
Ans.: (b) $CH_3CH_2NHCH_3$

(v)
 Ans.: (b) 800 g

(vi)
Ans.: (d) Assertion is false but Reason is true.

(vii)
Ans.: (c) Assertion is true but Reason is false.

Explanation: Due to delocalization of the lone pair of electrons of the nitrogen atom over the carbonyl group in the acyl derivative, the electron density on the N atom decreases to such an extent that it does not act as a nucleophile at all.

(C)

Ans.:
(i) $P_{C_2H_5OH} = x_{C_2H_5OH}$ x $P^o{}_{C_2H_5OH}$

$= 0.80$ x 40 mm
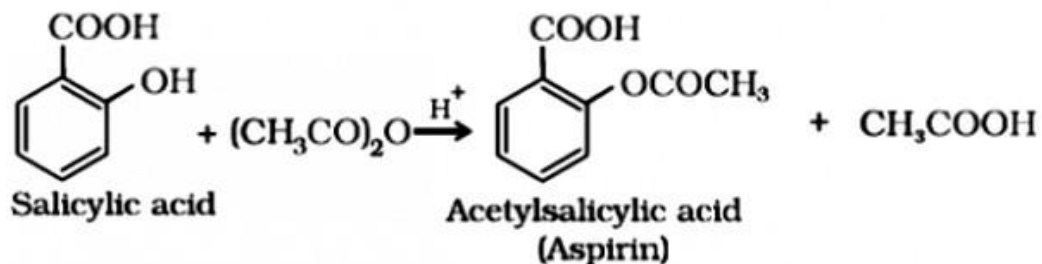
$= 32$ mm of Mercury

(ii) Because a mixture of 95.4% alcohol and 4.6% of water forms an azeotrope.

(iii) The hydrogen bond formed between phenolic proton and lone pairs of electrons of aniline is stronger than the interactions existing in pure phenol and in pure aniline.
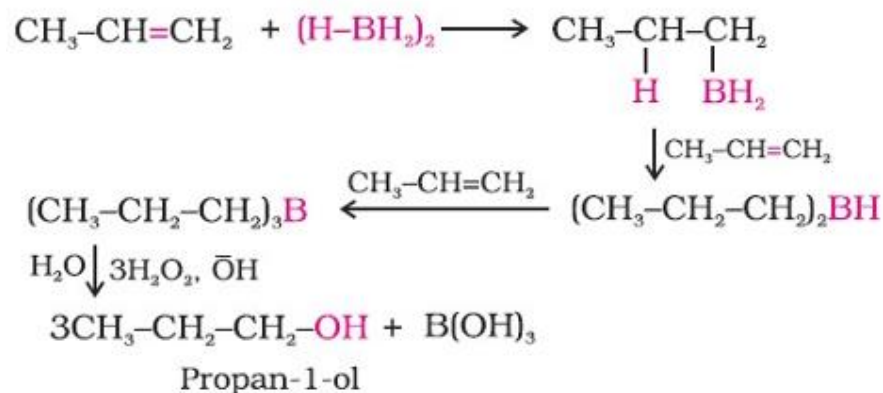
SECTION B – 20 MARKS

Question 2

Ans.: (i)

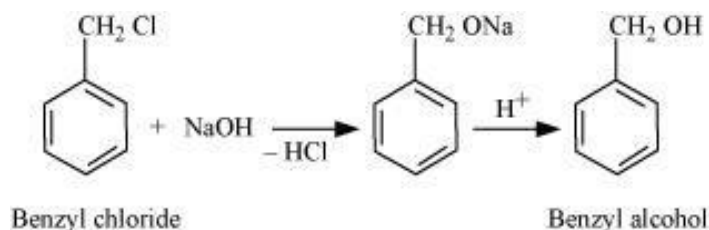**(ii)** Propan-1-ol is formed.

Question 3

Ans.:

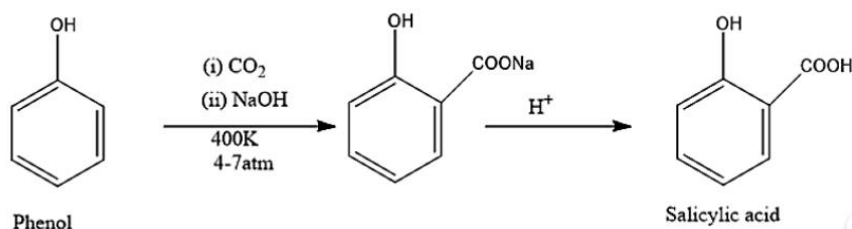**(i)** It is due to larger size, absence of unpaired electron and weak interatomic attraction and weaker metallic bond.

(ii) 'Ce' shows +4 oxidation state because it has stable noble gas electronic configuration.

Question 4
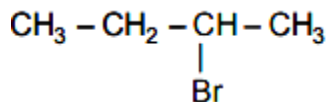
Ans.: (i)

(ii)

Question 5

Ans.:

(i) Due to lanthanoid contraction in second series after lanthanum, the atomic radii of elements of second and third series become almost same and hence show similarities in properties.

(ii) E∘ value for Mn^{3+}/Mn^{2+} couple is much more positive than that for Fe^{3+}/Fe^{2+} due to stable configuration of Mn^{2+} (d^5) ion.

Question 6

Ans.: (a) Optically active isomer of C_4H_9Br is 2-Bromobutane

$$CH_3 - CH_2 - CH - CH_3$$
$$|$$
$$Br$$

2-Bromo butane

(b) $CH_3CH_2CH_2CH_2Br$ (1-bromobutane) is highly reactive towards S_N2.

Question 7

Ans.:
(i) Cell reaction: $Ni + 2Ag^+ \rightarrow Ni^{2+} + 2Ag$,

(ii)

$$Ni_{(s)} \rightarrow Ni^{2+}_{(aq)} + 2e^-$$
$$2Ag^+_{(aq)} + 2e^- \rightarrow 2\,Ag_{(s)}$$
$$Ni_{(s)} + 2\,Ag^+_{(aq)} \rightarrow Ni^{2+}_{(aq)} + 2Ag_{(s)}$$
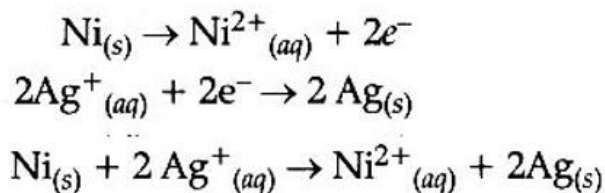
$$E^0_{cell} = E^0_{cathode} - E^0_{anode}$$

$$= 0.80 - (-0.25)$$

$$= 1.05\ V$$

$$E_{cell} = E^0_{cell} - \frac{0.0591}{2} \log \frac{\left[Ni^{2+}\right]}{\left[Ag^+\right]^2}$$

$$= E^0_{cell} - \frac{0.0591}{2} \log \frac{0.1}{(1)^2}$$

$$= 1.05 - \frac{0.0591}{2} \times (\log 10^{-1})$$

$$= 1.05 - 0.295 \times (-1)$$

$$= 1.05 + 0.0295 = 1.0795 \text{ V}$$

Question 8

Ans.: (i)

(a) Acetyl group is introduced at *ortho* and *para* positions of anisole.
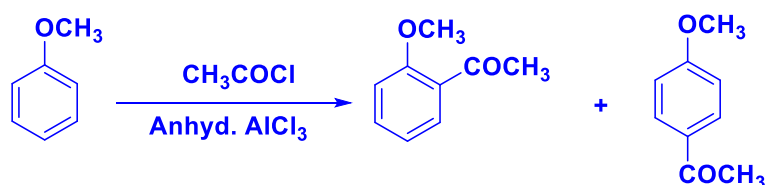
(b) *p*-Hydroxy azobenzene is formed.
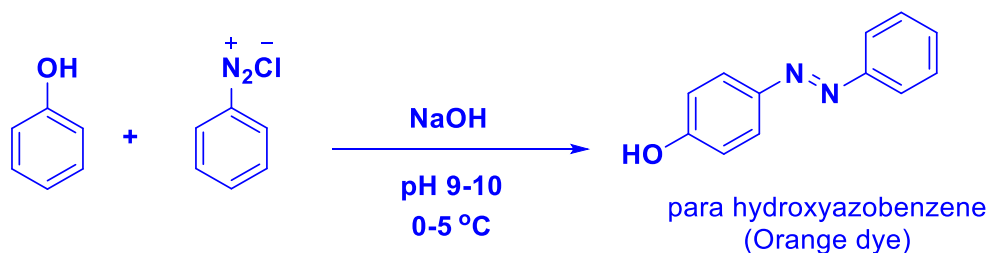
OR

(ii)

Ans.:

Since it forms a 2,4-DNP derivative, it contains a carbonyl group and must be an aldehyde or a ketone.

Since it does not reduce Tollens' reagent, it cannot be an aldehyde and is therefore a ketone.

Since it gives the iodoform reaction, it must have a methyl group linked to the carbonyl carbon atom and is, therefore, a methyl ketone.

Since it gives 1,2-benzenedicarboxylic acid on oxidation, it is a 1,2-substituted benzene derivative.

Using the molecular formula together with the points above, we arrive at the structure of the compound.
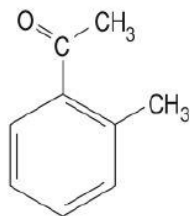
Question 9

Ans.: Isotonic solutions have same osmotic pressure. If osmotic pressure of KCl solution is $i_1\pi_1$. and osmotic pressure of urea solution is $i_2\pi_2$.

Then $i_1\pi_1 = i_2\pi_2$ $\pi_1 = C_1RT$ at same temperature

$\pi_2 = C_2RT$

$i_1 = ?$

$i_2 = 1$ because urea neither associate nor dissociate.

According the question

$i_1C_1RT = i_2C_2RT$

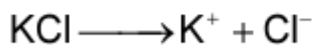$i_1C_1 = C_2$ $C_1 = \dfrac{n_1}{V}, C_2 = \dfrac{n_2}{V}$

$i_1 = \dfrac{C_2}{C_1}$ or $\dfrac{n_2}{V} \times \dfrac{V}{n_1}$ $n_1 = \dfrac{1.9}{74.5}, n_2 = \dfrac{3}{60}$

$i_1 = \dfrac{n_2}{n_1}$

$i_1 = \dfrac{3}{60} \times \dfrac{74.5}{1.9} = 1.96$

KCl dissociates as

$KCl \longrightarrow K^+ + Cl^-$

Degree of Dissociation of KCl $\alpha = \dfrac{i-1}{n-1}$, $n = 2$

$\alpha = \dfrac{1.96-1}{2-1} = 0.96$

$\alpha = 0.96$ **Ans.**

Question 10

Ans.: (i) In benzaldehyde the carbocation is less electrophilic than in formaldehyde due to resonance with the ring electrons. The initial nucleophilic addition of hydroxide anion is therefore faster on formaldehyde than on benzaldehyde. The aldehyde that undergoes nucleophilic attack by OH^- is converted to the sodium salt of the acid and the other aldehyde to the alcohol.

(b) Yes. It does not have an alpha hydrogen atom.

Question 11

Ans.: (i) The ions in d^1 configuration tend to lose one more electron to get into stable d0 configuration

(ii) E^0 value for the Mn^{2+}/Mn is much more than expected due to greater stability of half-filled d-subshell (d^5) in Mn^{2+}.

SECTION C – 21 MARKS
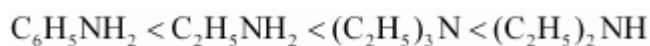
Question 12

Ans.:
$P_0 = 0.30$ atm $P_t = 0.50$ atm $t = 300$ s

Rate constant, k =

$$= \frac{2.303}{t} \log \frac{P_0}{2P_0 - P_t}$$

$$= \frac{2.303}{300} \log \frac{0.30}{2 \times 0.30 - 0.50}$$

$$= \frac{2.303}{300} \log \frac{0.30}{0.60 - 0.50}$$

$$= \frac{2.303}{300} \log \frac{0.30}{0.10}$$

$$= \frac{2.303}{300} \log 3$$

$$= \frac{2.303}{300} \times 0.4771$$

$$= \frac{1.099}{300}$$

$$= 0.0036 \text{ s}^{-1} = 3.66 \times 10^{-3} \text{ s}^{-1}$$
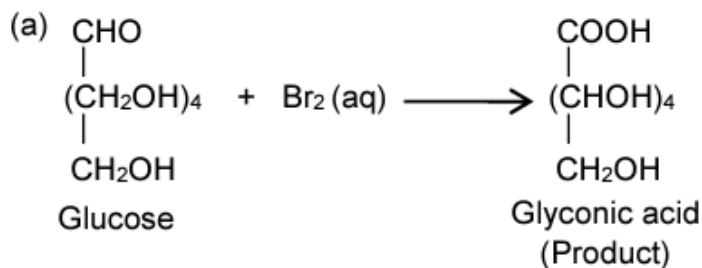
Question 13

Ans.:

(ii)

$$C_6H_5NH_2 < C_2H_5NH_2 < (C_2H_5)_3N < (C_2H_5)_2NH$$

(i)

$$C_6H_5NH_2 < C_6H_5CH_2NH_2 < (CH_3)_3N < CH_3NH_2 < (CH_3)_2NH$$

Question 14

Ans.:

(a)

$$\underset{\text{Glucose}}{\begin{array}{c} CHO \\ | \\ (CH_2OH)_4 \\ | \\ CH_2OH \end{array}} + Br_2\,(aq) \longrightarrow \underset{\substack{\text{Glyconic acid} \\ \text{(Product)}}}{\begin{array}{c} COOH \\ | \\ (CHOH)_4 \\ | \\ CH_2OH \end{array}}$$
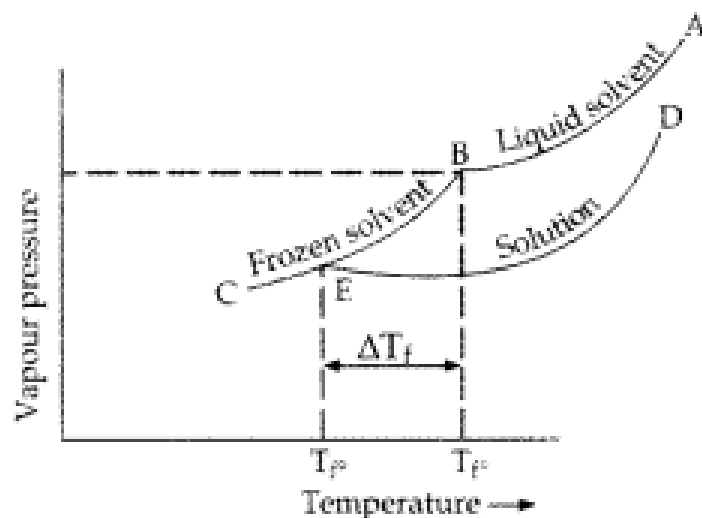
(b) Hydrogen-bonding provides stability to α-helix structure of protein.
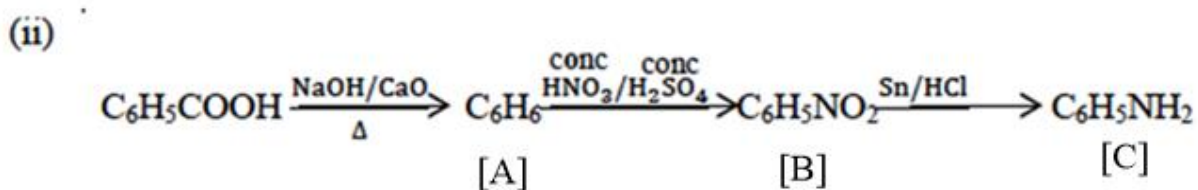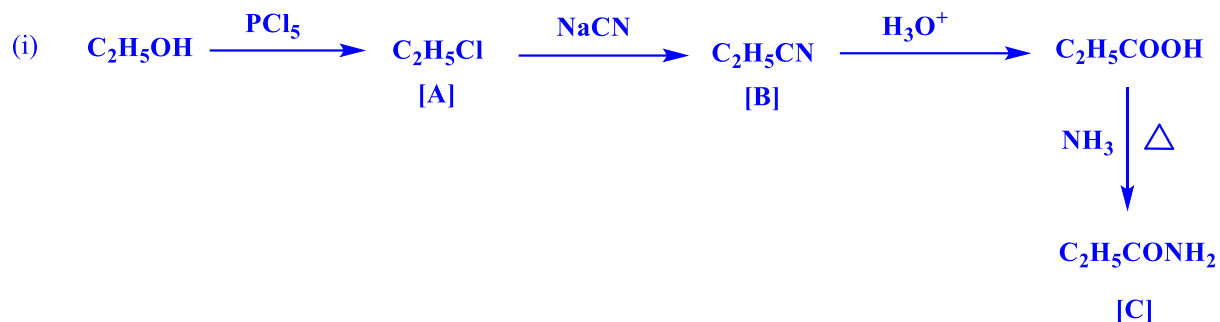(c) Vitamin B_{12}

Question 15

Ans.:

An aqueous solution of sodium chloride freezes below 273 K because vapour pressure of the solution is less than that of the pure solvent.
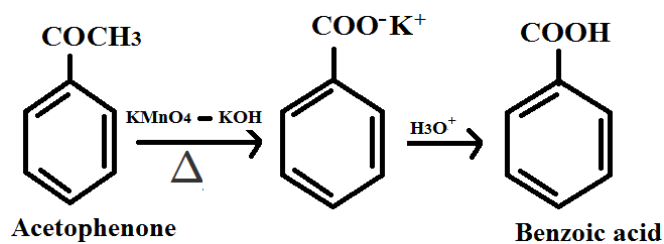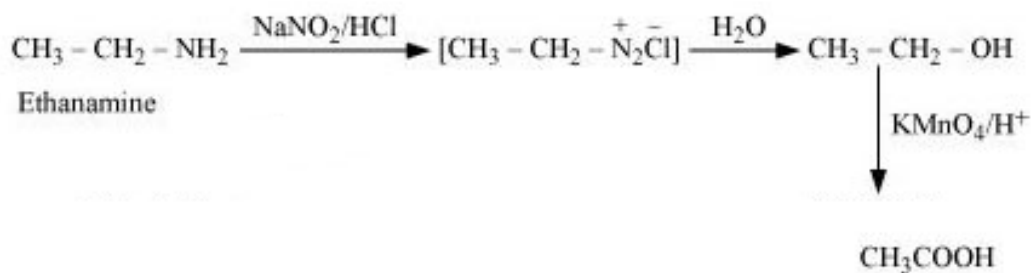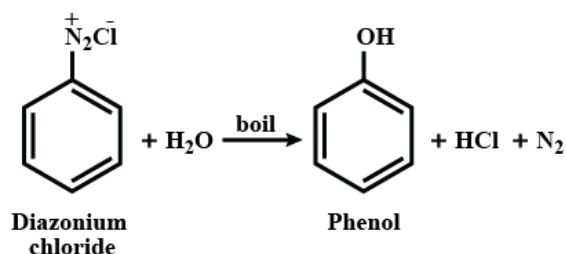
Question 16

Ans.:

(i) $C_2H_5OH \xrightarrow{PCl_5} C_2H_5Cl \xrightarrow{NaCN} C_2H_5CN \xrightarrow{H_3O^+} C_2H_5COOH$

$\qquad\qquad\qquad$ [A] $\qquad\qquad\qquad$ [B]

$C_2H_5COOH \xrightarrow{NH_3 \mid \triangle} C_2H_5CONH_2$

$\qquad\qquad\qquad\qquad\qquad$ [C]

(ii)

$C_6H_5COOH \xrightarrow[\Delta]{NaOH/CaO} C_6H_6 \xrightarrow[\text{conc}\ \text{conc}]{HNO_3/H_2SO_4} C_6H_5NO_2 \xrightarrow{Sn/HCl} C_6H_5NH_2$

$\qquad\qquad\qquad\qquad$ [A] $\qquad\qquad\qquad$ [B] $\qquad\qquad\qquad$ [C]

Question 17

Ans.: (a)

Acetophenone $\xrightarrow[\triangle]{KMnO_4 - KOH}$ COO⁻K⁺ $\xrightarrow{H_3O^+}$ Benzoic acid

(b)

$CH_3 - CH_2 - NH_2 \xrightarrow{NaNO_2/HCl} [CH_3 - CH_2 - \overset{+}{N_2}\overset{-}{Cl}] \xrightarrow{H_2O} CH_3 - CH_2 - OH$

Ethanamine

$CH_3 - CH_2 - OH \xrightarrow{KMnO_4/H^+} CH_3COOH$

(c)

Diazonium chloride + H_2O $\xrightarrow{\text{boil}}$ Phenol + HCl + N_2

OR

(ii)
Ans.:

Carbocation intermediate
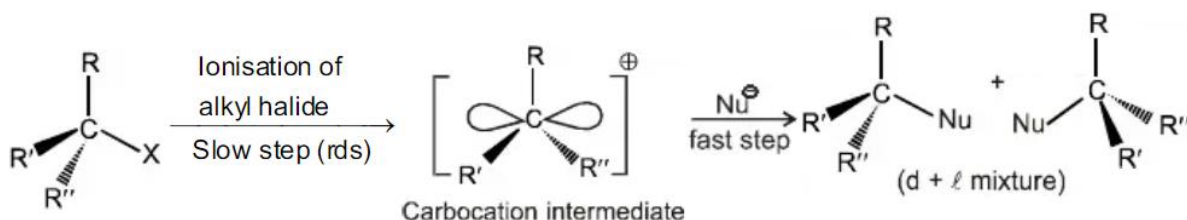
Question 18

Ans.: (a)

Here, $T_1 = 298$ K, $T_2 = 308$ K, $k_1 = k$, $k_2 = 2k$
We know,

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

$$\log \frac{2k}{k} = \frac{E_a}{2.303 \times 8.314}\left(\frac{308 - 298}{308 \times 298}\right)$$

$$\log 2 = \frac{E_a}{2.303 \times 8.314} \times \frac{10}{308 \times 298}$$

$$\Rightarrow \quad E_a = \frac{(\log 2)(2.303 \times 8.314)(308 \times 298)}{10}$$

$$= 52897.7 \, \text{J mol}^{-1} = 52.8 \, \text{kJ mol}^{-1}$$

(b) If temperature is infinite k = A so that Ea = 0, this will not feasible.

(c) Catalyst increases the rate of forward and backward reaction to the same extent. therefore, equilibrium attain quickly but the position equilibrium does not change.

SECTION D – 15 MARKS

Question 19

Ans.: (i)

(a) Carboxylic acid forms a dimer due to double H-bonding. So it has higher boiling point than alcohols.

(b) This is because PCC is a mild oxidizing agent and can oxidize methanol to methanal only. while $KMnO_4$ is strong oxidizing agent which oxidizes it to methanoic acid.

(c) The electron-withdrawing Cl group stabilizes the $ClCH_2COO^-$ anion and increases the acidic strength. Hence, chloroacetic acid has a lower pKa value than acetic acid.

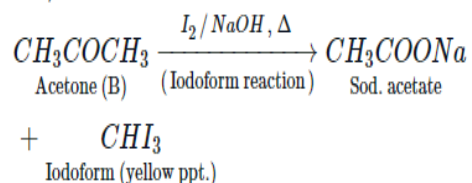$Cl \leftarrow CH_2 \leftarrow C\!-\!O^-$ is more stable than
$$\underset{\displaystyle O}{\overset{\displaystyle \|}{}}$$
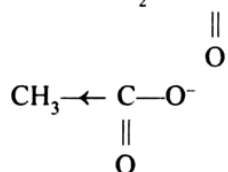
$CH_3 \leftarrow C\!-\!O^-$
$$\underset{\displaystyle O}{\overset{\displaystyle \|}{}}$$

(ii)

Ans.:

Two possible functional isomes having the M.F. C_3H_6O are: CH_3CH_2CHO CH_3COCH_3
                                                Propanal (A)   Acetone (B)

Since isomer B on heating with NaOH and I_2 forms yellow ppt. of CHI_3, therefore, it must be a methyl ketone,
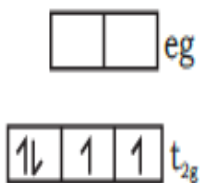
i.e., isomer B is acetone

$$\underset{\text{Acetone (B)}}{CH_3COCH_3} \xrightarrow[\text{(Iodoform reaction)}]{I_2/NaOH,\,\Delta} \underset{\text{Sod. acetate}}{CH_3COONa}$$

$+$ $\underset{\text{Iodoform (yellow ppt.)}}{CHI_3}$

In other words, isomer A which does not give any ppt. with $NaOH/I_2$ must be propanal

$$\underset{\text{Propanal (A)}}{CH_3CH_2CHO} \xrightarrow[\Delta]{I_2/NaOH} \text{No ppt. of } CHI_3.$$
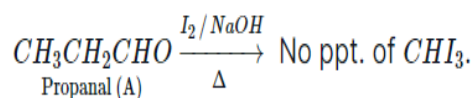
Question 20

Ans.: (i)

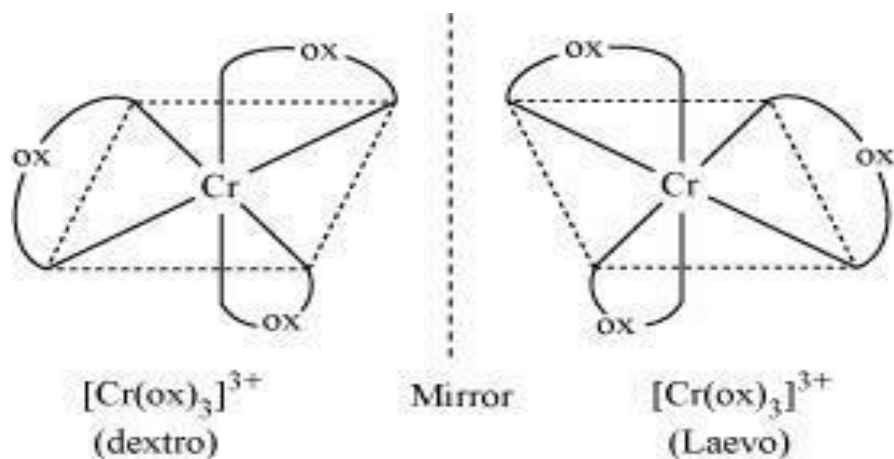(a) If $g \Delta_0 > P$, pairing will occur in the t_{2g} orbitals and eg orbitals will remain vacant.

Electronic configuration $t_{2g}^4 eg^0$

(b) d^2sp^3 (as there as three bidentate ligands to combine.

(c) $[M(AA)_3]$ type complexes show geometrical isomerism.

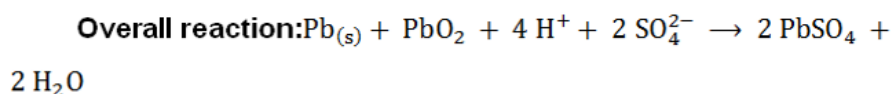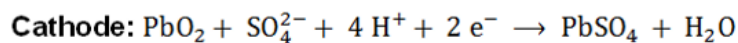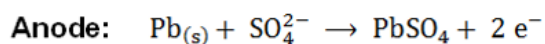**Ans.: (ii) (a)** Tris(ethylenediamine)cobalt(III) ion

(b)

$[Cr(ox)_3]^{3+}$ Mirror $[Cr(ox)_3]^{3+}$
(dextro)   (Laevo)

Question 21

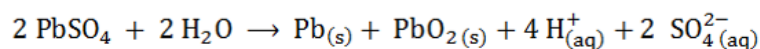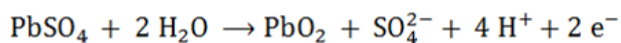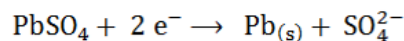**Ans.: (i)**

Anode: Lead

Cathode: PbO_2

Electrolyte: dilute H_2SO_4.

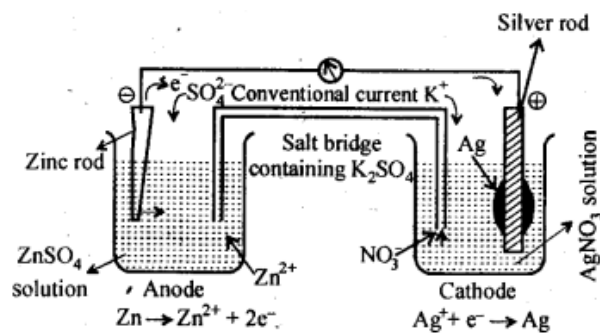The electrodes are arranged alternately, separated by thin wooden or fiber glass sheet.
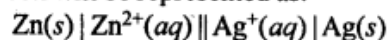
Electrode reaction (during discharging)

Anode: $Pb_{(s)} + SO_4^{2-} \longrightarrow PbSO_4 + 2\ e^-$

Cathode: $PbO_2 + SO_4^{2-} + 4\ H^+ + 2\ e^- \longrightarrow PbSO_4 + H_2O$

Overall reaction: $Pb_{(s)} + PbO_2 + 4\ H^+ + 2\ SO_4^{2-} \longrightarrow 2\ PbSO_4 + 2\ H_2O$

During charging, reverse reactions take place

$$PbSO_4 + 2\ e^- \longrightarrow Pb_{(s)} + SO_4^{2-}$$

$$PbSO_4 + 2\ H_2O \longrightarrow PbO_2 + SO_4^{2-} + 4\ H^+ + 2\ e^-$$

$$2\ PbSO_4 + 2\ H_2O \longrightarrow Pb_{(s)} + PbO_{2\,(s)} + 4\ H^+_{(aq)} + 2\ SO_4^{2-}{}_{(aq)}$$

(ii) The set-up will be similar to as shown below,

The cell will be represented as:

$$Zn(s) \mid Zn^{2+}(aq) \parallel Ag^+(aq) \mid Ag(s)$$

(i) Anode, i. e, zinc electrode will be negatively charged.

(ii) The current will flow from silver to copper in the external circuit.

(iii) At anode: $Zn(s) \rightarrow Zn^{2+}(aq) + 2e^-$

At cathode: $2Ag^+(aq) + 2e^- \rightarrow 2Ag(s)$

OR

(ii) (a)

Ans.: (ii)

(a) Calculation of $E°_{cell}$,

$$E°_{cell} = E°_{cathode} - E°_{anode} = -0.40 - (-0.74) = +0.34 \text{ V}$$

Calculation of $\Delta G°$,

$$\Delta G° = -nF E°_{cell} = -(6 \text{ mol}) \times (96500 \text{ C mol}^{-1}) \times (0.34 \text{ V})$$

$$= -196860 \text{ CV} = -196860 \text{ J} = -196.86 \text{ kJ}$$

Calculation of Equilibrium Constant (K_c)

$$\Delta G° = -2.303 \text{ RT} \log K_c$$

$$\log K_c = \frac{(-)\Delta G°}{2.303 \text{ RT}} = (-)\frac{(-)196860}{2.303 \times 8.314 \times 298} = 34.501$$
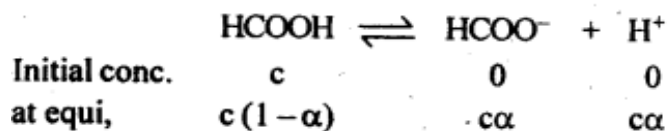
$$K_c = \text{Antilog}(34.501) = 3.17 \times 10^{34}$$

(b)

$$\Lambda°_m(HCOOH) = \lambda°(H^+) + \lambda°(HCOO^-)$$

$$= 349.6 + 54.6$$

$$= 404.2 \text{ S cm}^2 \text{ mol}^{-1}$$

$$\Lambda^C_m = 46.1 \text{ S cm}^2 \text{ mol}^{-1}$$

$$\therefore \quad \alpha = \frac{\Lambda^C_m}{\Lambda°_m} = \frac{46.1}{404.2} = 0.114$$

$$\begin{array}{cccccc}
& HCOOH & \rightleftharpoons & HCOO^- & + & H^+ \\
\text{Initial conc.} & c & & 0 & & 0 \\
\text{at equi,} & c(1-\alpha) & & c\alpha & & c\alpha
\end{array}$$

$$\therefore \quad K_a = \frac{c\alpha.c\alpha}{c(1-\alpha)} = \frac{c\alpha^2}{1-\alpha}$$

$$= \frac{0.025 \times (0.114)^2}{1 - 0.114} = 3.67 \times 10^{-4}$$

**************************** The End ****************************