# MARKING SCHEME

## **PRACTICE PAPER - 08**

 (i) (c) Carbylamine test is used to distinguish 1° amines (both aliphatic and aromatic) from 2° and 3° amines by using following reaction.

R—NH<sub>2</sub> + CHCl<sub>3</sub> + 3KOH(alc.)  $\xrightarrow{\Delta}$ 

R - N = C + 3KCI + 3HOH

- (ii) (d) Aniline does not show Friedel-Crafts reaction due to salt formation with anhydrous AICl<sub>3</sub> which is used as a catalyst. Here nitrogen of aniline will acquire positive charge and hence acts as a strong deactivating group.
- (iii) (c) Methyl isocyanide on reduction with lithium aluminium hydride will yield secondary amine.

$$CH_3 \longrightarrow N \cong C \xrightarrow{LiAIH_4} CH_3NHCH_3$$
  
Methyl isocyanide  $(2^{\circ} \text{ armine})$   
Or

(d) Ethyl methyl amine being secondary amine cannot be prepared by Gabriel phthalimide synthesis, while others are primary amines which can be prepared by this process.

- (iv) (c) Solubility in water decreases as the extent of H-bonding decreased. So, solubility in water follows the order I > II > III.
- (i) (b) Assertion and Reason both are correct but Reason is not correct explanation of Assertion. Corrected Reason is : In the mercury cell Zn + HgO → ZnO + Hg does not involve any ion whose concentration may change.
  - (ii) (a) Assertion and Reason both are correct and Reason is the correct explanation of Assertion. Sulphuric acid is consumed in the reaction due to the formation of lead sulphate and hence density decreases.
  - (iii) (c) Assertion is incorrect but Reason is correct. H<sub>2</sub>-O<sub>2</sub> fuel cell is preferred over ordinary cell as fuel cells do not cause any pollution and also these have high efficiencies.

Or

(c) Assertion is correct, but Reason is incorrect. Acidic NH<sub>4</sub>Cl corrodes the Zn container even when cell is not in use.

(iv) (a) Assertion and Reason both are correct and Reason is the correct explanation of Assertion. As by applying external voltage following reaction (which is reverse of normal reaction) takes place.

 $2PbSO_4 + 2H_2O \longrightarrow Pb(s) + PbO_2(s) + 4H^+ + 2SO_4^{2-}$ 

(d) On complete hydrolysis XeF<sub>6</sub> gives XeO<sub>3</sub>.

$$XeF_6 + 3H_2O \longrightarrow XeO_3 + 6HF$$
 (1)

4. (c) The mixture of carbon tetrachloride and chlorolorm show positive deviations from Raoult's law as CCl<sub>4</sub>—CHCl<sub>3</sub> interactions are lower than CCl<sub>4</sub>—CCl<sub>4</sub> interactions or CHCl<sub>3</sub>—CHCl<sub>3</sub> interactions. (1)

(a) Sodium phosphate Na<sub>3</sub>PO<sub>4</sub> will yield maximum ions on dissociation :

$$Na_3PO_4 \longrightarrow 3Na^* + PO_4^{3-}$$

Total 4 ions and that's why lowering of vapour pressure will be maximum here. (1)

- (a) Electronic configuration of metal in their respective complex are given below :
  - 1. Fe<sup>3+</sup> : 3d<sup>5</sup> 2. Pt<sup>2+</sup> : 5d<sup>8</sup> 3. Cu<sup>2+</sup> : 3d<sup>9</sup>

Therefore, in complex  $[Fe(CN_6)]^{3-}$ , the metal contains the maximum number of electorns. (1)

- (b) Carbohydrates made up of 2-10 monosaccharides are called oligosaccharides. Thus, upon hydrolysis, oligosaccharides form 2-10 monosaccharides.
   (1)
- (d) Mercury does not liberate hydrogen when reacted with hot water as its ionisation energy is very high due to its completely filled configuration of 6s<sup>2</sup>, 5d<sup>10</sup>. (1)

Or

(a) The solubility of silver bromide in hypo solution due to the formation of  $[Ag(S_2O_3)_2]^{3-}$ . (1)

- (a) Due to lanthanoid contraction order will be Yb<sup>3+</sup> < Pm<sup>3+</sup> < Ce<sup>3+</sup> < La<sup>3+</sup> (1)
- (b) Ice has the lowest melting point and as such it has weakest intermolecular forces. (1)

Or

 (a) Since, quartz glass is an amorphous solid having short range order of constituents. Hence, value of refractive index is same in all directions, can be measured and not be equal to zero always.
 (1)  (c) When excess of hot water is added to FeCl<sub>3</sub>, a positively charged sol of ferric hydroxide is formed due to adsorption of Fe3+ ions. Fe(OH)<sub>3</sub>/Fe3+ a positively charged sol. (1)0

(d) Physisorption is a process in which adsorbate get adsorbed on the adsorbent surface by weak van der Waals' force of attraction. On increasing temperature the interaction between adsorbate and adsorbent becomes weak and adsorbate particles get desorbed. (1)

(c) The correct IUPAC name of the given compound is

$$CH_{3} \xrightarrow{-CH} CH_{2} \xrightarrow{-CH} Br$$

$$|$$

$$CH_{2}$$

$$|$$

$$CH_{3}$$
1-bromo-2-methylbutane (1)

- 12. (a) According to Hardy-Schulze law, greater the charge/ valency on flocculating ion added greater will be its power to cause precipitation. Coagulating power ~ Valency of flocculating ion Hence, both Assertion and Reason are correct and Reason is correct explanation of Assertion. (1)
- 13. (a) Molar conductivity of weak electrolytic solution increases on dilution, because as we add excess water to increases the dilution degree of dissociation increases which led to increase in number of ions in the solution. Thus, Am show a very sharp increase. Hence, both Assertion and Reason are correct and Reason is the correct explanation of the Assertion. (1)
- 14. (d) Aromatic aldehydes and ketones undergo electrophilic substitution at the ring in which the carbonyl group acts as a deactivating and meta-directing group. Thus, Assertion is incorrect but Reason is correct. (1)
- 15. (b) Due to high electronegativity of oxygen it is more ionic than sulphur and so the di-negative anion of O2is quite common but the di-negative anion of sulphur. (S<sup>2-</sup>) is less common. The covalency of oxygen is two as it cannot expand its valency beyond the octet. Thus, both Assertion and Reason are correct and Reason is not the correct explanantion of Assertion. (1)
- 16. (b) Both Assertion and Reason are correct but Reason is not the correct explanation of Assertion.



During rearrangement only one 3d-orbital may be made available by pairing of electrons. Thus, inner d<sup>2</sup>sp<sup>3</sup>-hybridisation is not possible. So, only sp<sup>3</sup>d<sup>2</sup> hybridisation can occur. (1)

(b) Both Assertion and Reason are correct but greater stability is due to greater number of chelate rings formed by EDTA than by oxalate in the second case. (1) Given, as we know that,

At t = 30 sec, [R] = 0.31 M, [R]\_o = 0.55 M For pseudo first order kinetics,

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

$$\therefore \qquad k = \frac{2.303}{30} \log \frac{0.55}{0.31} = \frac{2.303}{30} \log 1.774$$

$$= \frac{2.303}{30} \times 0.2490 = 1.91 \times 10^{-2} \text{ s}^{-1}$$
At 
$$t = 60 \text{ s}, [R] = 0.17 \text{ M} [R]_0 = 0.55 \text{ M}$$

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

$$\therefore \qquad k = \frac{2.303}{60} \log \frac{0.55}{0.17} = \frac{2.303}{60} \times 0.5099$$

$$= 1.96 \times 10^{-2} \text{ s}^{-1}$$

$$k = \frac{2.303}{t} \log \frac{[R]_0}{R}$$
At 
$$t = 90 \text{ s}, [R] = 0.085 \text{ M}, [R]_0 = 0.55 \text{ M}$$

$$k = \frac{2.303}{90} \log \frac{0.55}{0.085} = \frac{2.303}{90} \times 0.8109$$

$$= 2.07 \times 10^{-2} \text{ s}^{-1}$$

Average rate constant,

•

$$k = \frac{1.91 \times 10^{-2} + 1.96 \times 10^{-2} + 2.07 \times 10^{-2}}{3}$$
  
= 1.98 × 10<sup>-2</sup> s<sup>-1</sup> (2)

- (i) Reactions with higher molecularity (greater than three) are rare as probability of more than three molecules colloiding simultaneously to form product(s) is very low. (1)
- (ii) No, activation energy of a reaction cannot be zero because in that case, every collision among reactant molecules will be an effective collision. However, this is not possible. (1)
- (i) For tetrahedral complexes, the crystal field stabilisation energy is lower than pairing energy, so they are not formed in low spin state. (1)
  - (ii) In [Co(NH<sub>3</sub>)<sub>6</sub>]<sup>3+</sup>, pairing of 3d electrons takes place due to the presence of strong ligand (NH<sub>3</sub>), whereas in [Ni (H2O)6]2+ pairing of 3d electrons does not occur due to the presence of weak field ligand (H2O). Thus,  $[Co(NH_3)_6]^{3+}$  forms inner orbital complex, whereas  $[Ni (H_2O)_6]^{2+}$  forms outer orbital complex.

(1)

Outer orbital complex

 Given, with 0.1 mol L<sup>-1</sup>KCl, resistance is 100 Ω. with 0.02 mol L<sup>-1</sup> KCl resistance is 520 Ω. conductivity of 0.1 mol L-1 KCI solution is 1.29 S/m or Sm<sup>-1</sup>.

> Cell constant = Resistance (R)  $\times$  conductivity ( $\kappa$ ) 0.0400 -100

$$100 \times 0.0129 = 1.29 \text{ cm}^{-1}$$
 (1)

Calculating conductivity of 0.02 M KCl solution

Therefore, molar conductivity

$$\Lambda_{\rm m} = \frac{1000 \times \kappa}{M} = \frac{1000 \times 2.48 \times 10^{-3}}{0.02} = 124 \text{ S cm}^2 \text{ mol}^{-1}$$
(1)

Aqueous solution of CuSO<sub>4</sub> on electrolysis gives Cu at cathode, O2 at anode and H<sup>+</sup> ions in the solution.

Eq. of current = 
$$\frac{96.5A \times 10 \text{ s}}{96500C}$$
 = 0.01 eq =  $10^{-2}$  eq  
 $\therefore 10^{-2}$  eq of Cu =  $10^{-2}$  eq of O<sub>2</sub> =  $10^{-2}$  eq of H<sup>+</sup>  
[H<sup>+</sup>] =  $\frac{10^{-2}\text{ eq}}{\text{volume of solution (in L)}} = \frac{10^{-2} \text{ eq}}{1\text{ L}}$   
 $\therefore = 10^{-2} \text{ N or M}$   
 $\therefore \text{ pH} = -\log(10^{-2}) = 2$  (2)

20. (i) When ozone is passed through acidified SnCl<sub>2</sub> solution then SnCl4 is formed. Reaction is as follows :

$$3SnCl_2 + 6HCl + O_3 \longrightarrow 3SnCl_4 + 3H_2O \quad (1)$$

(b) 
$$HI > HBr > HCI > HF$$
 (1)

 $H_0O+N_0$ 

21.



22. (i) XeF<sub>4</sub> shows sp<sup>3</sup>d<sup>2</sup>-hybridisation. The orbital get mixed up to form six sp3d2 hybrid orbitals with two orbitals having lone pair of electrons. Thus, the structure of XeF<sub>4</sub> is square planar.

(ii) 
$$Cl_2$$
 being an oxidising agent oxidises Nal to  $l_2$ .  
 $2Nal + Cl_2 \longrightarrow 2NaCl + l_2$  (1)

23. [CoF<sub>6</sub>]<sup>3-</sup> oxidation state of Co is + 3 due to presence of 6 F<sup>-</sup> ligands.

2Nal

Since, F is a weak field ligand, it cannot pair 3d-electrons of Co3+.



#### Hybridisation = sp3d2-hybridised

Magnetic moment = 
$$\sqrt{n(n+2)}$$
  
=  $\sqrt{4(4+2)} = \sqrt{24}$  BM =  $2\sqrt{6}$  BM

Similarly, in  $[Co(H_2O)_6]^{2+}$  the hybridisation of  $Co^{2+}$  is sp<sup>3</sup>d<sup>2</sup> (due to the presence of unpaired electron).

sp<sup>3</sup>d<sup>2</sup>-hybridisation, six electron pairs from 6H<sub>2</sub>O

(2)

lagnetic moment = 
$$\sqrt{n(n+2)}$$
  
=  $\sqrt{3(3+2)} = \sqrt{15}$  BM

Hybridisation = sp3d2-hybridised

N

Aryl halides are less reactive towards nucleophilic substitution reaction. Presence of electron withdrawing group at o - and p-position increases the stability of intermediates and, hence increases the reactivity of aryl halides towards nucleophilic substitution reaction.

Now, more the number of EWG at o- and p-position, higher will be the reactivity of aryl halide. Compound (III) has three EWG, So it is most reactive and compound (I) has only one EWG, so it is least reactive.

So, the order of reactivity is 
$$(I) < (II) < (III)$$
. (2)

25. For hydrogen electrode,

Е

$$H^+ + e^- \longrightarrow 1/2H_2$$

Applying Nernst equation,

$$\left(H^{+}/\frac{1}{2}H_{2}\right) = E_{\left(H^{+}/\frac{1}{2}H_{2}\right)}^{+} - \frac{0.0591}{n}\log\left(\frac{1}{H^{+}}\right)$$

$$= 0 - \frac{0.0591}{1} \log \left(\frac{1}{10^{-10}}\right)$$

$$= 0 - \frac{0.0591}{1} \times (10 \log 10)$$

$$E_{\left(H^{+}/\frac{1}{2}H_{2}\right)} = -0.591 V \qquad (2)$$

$$\Delta T_{f(observed)} = 0.062^{\circ}C$$

$$\Delta T_{f(calculated)} = K_{f} \times m = 1.86 \times 0.01 = 0.0186^{\circ}C$$

$$i = \frac{\Delta T_{f(observed)}}{\Delta T_{f(calculated)}} = \frac{0.062}{0.0186} = 3.33$$

$$K_{3}[Fe(CN)_{6}] \longrightarrow 3K^{+} + K_{3}[Fe(CN)_{6}]^{3-}$$
At time,  $t = 0 - 1 = 0 = 0$ 
At time,  $t = 0 - 1 = 0 = 0$ 
At time,  $t = 1 + 3\alpha$ 

$$\therefore \quad i = \frac{1 + 3\alpha}{1} \implies \alpha = \frac{i - 1}{3} = \frac{3.33 - 1}{3} = 0.777 = 77.7 \quad (2)$$

 (i) The change in specific rotation of an optically active compound in solution is called mutarotation, e.g. in aqueous solution, glucose exists as,

$$\begin{array}{c} \alpha\text{-D-(+)-glucose} & \longleftarrow & \text{Equilibrium mixture} \\ [\alpha]_{D} = +112^{\circ} & [\alpha]_{D} = +52.7^{\circ} \\ & \longleftarrow & \beta\text{-D(+)-glucose} \\ [\alpha]_{D} = +19^{\circ} & (1\frac{1}{2}) \end{array}$$

(ii) DNA is a double stranded molecule. The two strands are complementary to each other. H-bonds are formed in between specific pairs of bases, i.e. adenine (A) is attached with thymine (T) by two H-bonds and guanine (G) is attached to cytosine (C) by three H-bonds. The other combination of bases are energetically less favoured and hence, do not occur in normal DNA. Thus, the two strands of DNA are not identical but are complementary. (1<sup>1</sup>/<sub>2</sub>)

 (i) It is saccharic acid which is formed as per the reaction given below:

$$\begin{array}{ccc} \mathsf{CHO} & \mathsf{COOH} \\ | & & | \\ (\mathsf{CHOH})_4 & \xrightarrow{\mathsf{Oxdation}} & (\mathsf{CHOH})_4 \\ | & & | \\ (\mathsf{CH}_2\mathsf{OH}) & & (\mathsf{CH}_2\mathsf{OH}) \\ \mathsf{D}\operatorname{-Glucose} & \operatorname{Saccharic} \operatorname{acid} \end{array}$$

(ii) Difference between α-helix and β-pleated structures

a-helix structure	β-pleated structure
If the size of R-group is	If size of R-group is
large, intramolecular	small intermolecular
H-bonds are formed	H-bonds forms between
between C=O of molecule	C = O of polypeptide
and NH of amino acid in	chain with N - H of
polypeptide chain that gives	other giving β-pleated
right handed a-helix	sheet structure.
structure.	i.e. It is formed by the
i.e. It is formed by the	folding in more than
folding of a single	one polypeptide chain
polypeptide chain due to	due to hydrogen
hydrogen bonding.	banding.

#### 27. (i) Ethanal and propanal As ethanal has

responds positively towards iodoform test, whereas propanal (CH<sub>3</sub>CH<sub>2</sub>CHO) does not.

$$\begin{array}{c} \text{CH}_{3}\text{CHO} + 3\text{NaOI} \xrightarrow{I_{2}/\text{NaOH}} & \text{CHI}_{3} \downarrow \\ \text{Ethanal} & \text{Heat} & \text{(Iodoform)} \\ & \text{yollow ppt} \\ & + \text{HCOONa} + 2\text{NaOH} \\ \text{CH}_{3}\text{CH}_{2}\text{CHO} + 3\text{NaOH} & \xrightarrow{I_{2}/\text{NaOH}} & \text{No test} \\ & \text{Heat} & (1\frac{12}{2}) \end{array}$$

 Phenol and benzoic acid Benzoic acid reacts with sodium bicarbonate to produce effervescence of carbon dioxide, whereas phenol (C<sub>6</sub> H<sub>5</sub>OH) does not.



**28.** (i) Molar mass of chloroform,  $(CHCI_3) = 119.5 \text{ g/mol}$ Molar mass of dichloromethane,  $(CH_2CI_2) = 85 \text{ g/mol}$ Moles of  $CHCI_3 = \frac{25.5}{119.5} = 0.213 \text{ mol}$ 

Moles of 
$$CH_2CI_2 = \frac{40}{85} = 0.47 \text{ mol}$$

Total number of moles = 0.213 + 0.47 = 0.683 mol

Mole fraction of  $CH_2CI_2 = \frac{0.47}{0.683} = 0.688$ 

Mole fraction of  $CHCl_3 = 1 - 0.688 = 0.312$ Vapour pressure of the solution can be found out using the following equation,

$$p_{\text{total}} = p_1 + (p_2 - p_1)\chi_2$$

$$p_{\text{total}} = 200 + (415 - 200) \times 0.688$$

$$= 347.9 \,\text{mm Hg}$$
(2)

(1)

(ii) Using the relation,  $y_1 = \frac{p_i}{p_{\text{total}}}$ , mole fraction of the

components in vapour phase (y<sub>1</sub>) is  

$$\rho_{CH_2Cl_2} = 0.688 \times 415 \text{ mmHg}$$
  
 $= 285.5 \text{ mm Hg}$   
 $\rho_{CHCl_3} = 0.312 \times 200 \text{ mm Hg}$   
 $= 62.4 \text{ mm Hg}$   
 $y_{CH_2Cl_2} = \frac{285.5 \text{ mm Hg}}{347.9 \text{ mm Hg}} = 0.82$   
 $y_{CHCl_3} = \frac{62.4 \text{ mm Hg}}{347.9 \text{ mm Hg}} = 0.18$ 

(1)

### Or

Given, No. of moles of liquid A,  $(n_A) = 1$  mole

No. of moles of liquid B,  $(n_B) = 3$  mole ....

....

We know that, 
$$p = \rho_A \chi_A + \rho_B \chi_B$$
 ...(1)  
where,  $\chi_A = \frac{n_A}{n_A + n_B} = \frac{1}{1+3}$   
 $\chi_B = \frac{n_B}{n_A + n_B} = \frac{3}{1+3}$ 

The value of  $\chi_A$  and  $\chi_B$  put in Eq. (i)

$$\left(\frac{1}{1+3}\right)\rho_{A}^{*} + \left(\frac{3}{1+3}\right)\rho_{B}^{*} = 500 \text{ mm of Hg}$$
$$\frac{1}{4}\rho_{A}^{*} + \frac{3}{4}\rho_{B}^{*} = 500 \text{ mm of Hg}$$

$$1 p_A + 3 p_B = 2000 \,\mathrm{mm} \,\mathrm{of} \,\mathrm{Hg}$$
 ...(ii)

When 1 mole of B was added, the equation we get will be.

$$\left(\frac{1}{1+4}\right)\rho_{A}^{*} + \left(\frac{4}{1+4}\right)\rho_{B}^{*} = 510 \text{ mm of Hg}$$
$$\frac{1}{5}\rho_{A}^{*} + \frac{4}{5}\rho_{B}^{*} = 510 \text{ mm of Hg}$$
$$\rho_{A}^{*} + 4\rho_{B}^{*} = 2550 \text{ mm of Hg} \qquad \dots (iii)$$

On substracting Eq. (ii) from (iii), we get

$$p_B = 550 \text{ mm of Hg}$$

On putting the value of  $p_B^*$  in Eq. (ii), we get

$$p_A^* = 350 \text{ mm of Hg}$$
 (3)

29. (i) The initial material used in the industrial preparation of phenol is cumene (isopropyl benzene).

> CH(CH<sub>3</sub>)<sub>2</sub> Structure of cumene

(ii) Bromination of phenol in non-aqueous medium



Bromination of phenol in aqueous medium



2,4,6-tribromophenol (1/2)

(1)

- (iii) In bromination of phenol, the polarisation of Br<sub>2</sub> molecule takes place even in the absence of Lewis acid. It is due to the highly activating effect of -OH group attached to the benzene ring. Thus, Lewis acid is not required in bromination of phenol. (1)
- Number of atoms in 0.5 mole

$$= 0.5 \times 6.023 \times 10^{23} = 3.01 \times 10^{23}$$

Number of octahedral voids = Number of atoms in close packing

$$V = 3.01 \times 10^{23}$$

Number of tetrahedral voids = 2 × number of atoms

$$2N = 2 \times 301 \times 10^{23} = 6.02 \times 10^{23}$$

Total number of voids = N + 2N

$$= 3.01 \times 10^{23} + 6.02 \times 10^{23}$$

$$= 9.03 \times 10^{23}$$
 (3)

31. (i) The lower the reduction potential, the higher is the reducing power. The given standard electrode potential are in the order.

$$K^+/K < Mg^{2+}/Mg < Cr^{3+}/Cr < Hg^{2+}/Hg < Ag^+/Ag$$

Hence, order is

$$Ag < Hg < Cr < Mg < K$$
 (2)

$$E_{\text{cell}}^{-}$$
 = + 0.46 V and log 10<sup>*n*</sup> = *n*, *T* = 25° C

$$E_{\text{cell}} = E_{\text{cell}}^{*} - \frac{0.059}{n} \log \frac{[\text{Cu}^{2+}]}{[\text{Ag}^{+}]^{2}}$$
  
= 0.46 -  $\frac{0.059}{n} \log \frac{(10^{-1})}{(10^{-3})^{2}}$   
= 0.46 - 0.1475 = 0.3125 V (3)  
Or

(i) 
$$E^* = \frac{0.0591}{n} \log K$$
  
If  $K < 1$   
then,  $E^* = \frac{0.0591}{n} \log 0.01 = \frac{-2 \times 0.0591}{n}$ 

E<sup>\*</sup> is thus negative.

If 
$$E^{*} = 0$$
 V, then  $K = 1$ .

(3)

(ii) 
$$E_{\text{cell}} = E_{\text{cell}}^{\circ} - \frac{0.059}{n} \log \frac{[\text{Mg}^{2^{-1}}]}{[\text{Cu}^{2^{+}}]}$$
  
= 2.71 V -  $\frac{0.059}{2} \log \frac{0.1}{0.001}$   
= 2.71 V -  $\frac{0.059}{2} \log 10^{2}$  = 2.651 V (2)

 Compound B is formed by the reaction of benzene and acid chloride in the presence of anhyd. AICla. So, B is an aromatic ketone. When compound B reacts with iodine and aqueous NaOH, it produces iodoform; thus B is acetophenone. Compound A should be a derivative of acetylene. Also, it has

degree of unsaturation = 6 (i.e. has one ring,  $5\pi$ -bonds) and undergoes hydration under acidic conditions to form *B* which is a ketone, i.e. acetophenone. (2)



$$(b) \underbrace{\downarrow}_{Acetophenone} \underbrace{\downarrow}_{I_2/NaOH} \underbrace{\downarrow}_{Iodoform} \underbrace{\downarrow}_{Sodium} \underbrace{\downarrow}_{Sodium} \underbrace{\downarrow}_{H_3O^+} \underbrace{\downarrow}_{Benzoic} \underbrace{\downarrow}_{acid} (1)$$

$$(c) \underbrace{\downarrow}_{Styrene} \underbrace{KMnO_{\epsilon}/OH^-}_{Heat} \underbrace{\downarrow}_{Potassium} \underbrace{\downarrow}_{Benzoic} \underbrace{\downarrow}_{acid} (1)$$

$$(ii) (a) \underbrace{\bigcirc}_{CHO} \underbrace{\leftarrow}_{CHO} \underbrace{\triangleleft}_{Aq,KOH} \underbrace{\bigcirc}_{V_{A'}, benzyl alcohol} \underbrace{\leftarrow}_{A', benzyl alcohol} \underbrace{\downarrow}_{A', benzyl alcohol} \underbrace{\downarrow}_{Benzoic} (1)$$

(b)  $CH_3COOH + CH_3OH \xrightarrow{Conc. H_2SO_3} O$  ||  $CH_3 \longrightarrow O - CH_3$  $C^{-}$ , Methyl acetate (1)

- 33. (i) (a) Cr<sup>3+</sup> / Cr<sup>2+</sup> has a negative reduction potential. Hence, Cr<sup>3+</sup> cannot be reduced to Cr<sup>2+</sup>, i.e. Cr<sup>3+</sup> is most stable. Mn<sup>3+</sup> / Mn<sup>2+</sup> has large positive E° value. Hence, Mn<sup>3+</sup> can be easily reduced to Mn<sup>2+</sup>, i.e. Mn<sup>3+</sup> is least stable. E° value for Fe<sup>3+</sup> / Fe<sup>2+</sup> is positive but small. Hence, Fe<sup>3+</sup> is more stable than Mn<sup>3+</sup> but less stable than Cr<sup>3+</sup>.
  - (b) Oxidation potentials for the given pairs will be + 0.9 V, + 12 V, + 0.4 V. Thus, the order is Mn > Cr > Fe.
     (2)
  - (ii) (a) **Electronic configuration** The general electronic configurations of actinoids is  $5f^{1-14}6d^{0-1}7s^2$ . The irregularities in the electronic configuration of actinoids is due to the stabilities of  $f^0$ ,  $f^7$  and  $f^{14}$  occupancies of 5f-orbitals. (1)
    - (b) **Ionic size** The radii of trivalent and quadrivalent ions of actinoids contract slightly with increasing atomic number due to **actinoid contraction**. This contraction results from poor shielding experienced by 5f-electrons. (1)
    - (c) Oxidation states Actinoids show a variety of oxidation states due to comparable energies of 5/, 6d and 7s energy levels. The dominant oxidation state of actinoids is + 3 which show increasing stability for the heavier elements.

(i) In Cu, all the *d*-electrons are paired (3*d*<sup>10</sup> 4s<sup>1</sup>). In Cr, all the *d*-electrons are unpaired (3*d*<sup>5</sup>4s<sup>1</sup>). Hence, *d* - *d* electron repulsions in Cu are much greater than those in Cr. Hence, Cu atom is larger in size than Cr. In Cu<sup>2+</sup> (3 *d*<sup>9</sup>), *d* -*d* electron repulsions decrease due

to presence of one unpaired *d*-electron. Moreover, the electrons are attracted by 29 protons of the nucleus whereas in  $Cr^{2+}$ , three unpaired electrons are still present but they are attracted by only 24 protons of the nucleus. Thus,  $Cu^{2+}$  is smaller in size than  $Cr^{2+}$ . (2)

- (ii) (a) Electronic configuration of Mn<sup>2+</sup> = [Ar]<sup>18</sup>3d<sup>5</sup> Electronic configuration of Fe<sup>2+</sup> = [Ar]<sup>18</sup>3d<sup>6</sup> Mn<sup>2+</sup> having half-filled*d*-orbitals will be more stable than Fe<sup>2+</sup>, as it has partially filled *d*-orbitals. (1)
  - (b) Zinc has completely filled *d*-orbitals, which limits its tendency to form metallic bonds. Thus, it requires least enthalpy to get atomised. (1)
  - (c) Ti<sup>3+</sup> has one electron in the *d*-orbital (3*d*<sup>1</sup>) which can absorb energy corresponding to yellow wavelength and jump from t<sub>2g</sub> to e<sub>g</sub> set of *d*-orbitals. But, Sc<sup>3+</sup> has no electron in the *d*-orbital.