

SAMPLE PAPER 4

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 \times 10²³

SECTION A – 14 MARKS

Question 1

(A)

(i)

Ans.: Two, zero

(ii)

Ans.: octahedral, sp^3d^2

(iii)

Ans.: greater, slower

(iv)

Ans.: sp^2 , shorter

(B)

(i)

Ans.: (d) 2

Explanation:

$$r=k[A]^n$$
 ...(i)

When concentration is doubled,

$$4r=k(2A)^n$$
 ...(ii)

Divide Eq. (ii) by (i)

 $4 = 2_{n}$

n=2

(ii)

Ans.: (b) $[Fe(H_2O)_6]^{3+}$

Explanation:

 H_2O is a weak field ligand, hence Δ_0 < pairing energy.

CFSE =
$$(-0.4x + 0.6y)\Delta_o$$

where, x and y are no. of electrons occupying t_{2g} and e_g orbitals respectively

For $[Fe(H_2O)_6]^{3+}$ complex ion,

$$Fe^{3+}(3d^5) = t_{2g}^3 e_g^2 = -0.4 \times 3 + 0.6 \times 2 = 0.0 \text{ or } 0Dq$$

(iii)

Ans.: (a) Complete d-subshell

Explanation:

The elements having incomplete d-orbital can show variable oxidation state (because the electrons move the two levels of d itself)

- ∴ Zn has completely filled d-orbital.
- : It does not show variable oxidation state. It always shows +2 oxidation state.

(iv)

Ans.: (c) Amide to amine

Explanation:

Hofmann's bromamide reaction is used to convert amide to amine.

$$RCONH_2 + Br + 4KOH \rightarrow RNH_2 + K_2CO_3 + 2KBr + 2H_2O$$

amide amine

 (\mathbf{v})

Ans.: (b) 0.31 mol/L

Explanation:

$$\pi = CRT : C = \frac{\pi}{RT} = \frac{7.8}{0.0821 \times 310} = 0.31 \text{ mol/L}$$

(vi)

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

(vii)

Ans.: (a) Both Assertion and Reason are true and Reason is the correct explanation of Assertion.

(C)

Ans.:

(i)
$$m = \frac{0.052}{180} \times \frac{1000}{80.2} = 0.0036$$

(ii)
$$\Delta T_f = K_f \times m = 1.86 \times 0.0036 = 0.067 \text{ K}$$

(iii) Moles of glucose =
$$\frac{0.052}{180}$$
 = 0.00028

Moles of water =
$$\frac{80.2}{18}$$
 = 4.455

Mole fraction of glucose =
$$\frac{0.00028}{4.45 + 0.00028} = 6.28 \times 10^{-5}$$

SECTION B – 20 MARKS

Question 2

Ans.: (i) $(CH_3)_3C-OH < (CH_3)_2CH-OH < CH_3CH_2OH$

More the number of methyl groups (electrons releasing) lesser will be the acidity. Hence the reactivity towards sodium metal will be tertiary alcohol < secondary alcohol < primary alcohol.

(ii) The ortho isomer of nitrophenol has the lowest boiling point and is least soluble in water due to stronger intramolecular hydrogen bonding, resulting in less effective intermolecular interactions and weaker attractions between molecules.

Question 3

Ans.: (i) Manganese (Mn) and technetium (Tc) have stable half-filled *d*-orbitals, causing electrons to be held tightly by the nucleus, resulting in lesser delocalization and weaker metallic bonds compared to the preceding elements.

(ii) Zr and Hf have almost identical atomic radii due to lanthanoid contraction, influenced by the occupation of 4f orbitals in the lanthanide series, leading to a decreased effective nuclear charge and a contraction in atomic size that extends to the following transition metals.

Ans.:

Question 5

Ans.: (i) Zn^{2+} ions are colorless due to the absence of unpaired electrons in its *d*-orbitals, while Ni^{2+} ions are green in color owing to the presence of unpaired electrons that undergo d-d transitions.

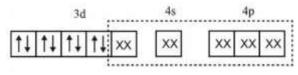
Question 6

Ans.:

Fe ([Ar]3 $d^64 s^2$)

Fe(CO)₅

CO is a strong field ligand, so pairing of electron takes place.



dsp³ hybridisation

xx = Electron pair from ligand CO

Hybridisation $\rightarrow dsp^3$

Magnetic character → Diamagnetic

Question 7

Ans.: At the anode the following oxidation reactions are possible:

$$Cl^{-}(aq) \rightarrow 1/2Cl_{2}(g) + e$$

$$E_{cell}^{0} = 1.36 \text{ V}$$

$$2H_{2}O(l) \rightarrow O_{2}(g) + 4H^{+}(aq) + 4e^{-}$$

$$E_{cell}^{0} = 1.23 \text{ V}$$

The reaction at anode with lower value of E° is preferred and therefore, water should get oxidised in preference to Cl⁻(aq). However, on account of over potential of oxygen, oxidation of Cl⁻is preferred.

Question 8

Ans.: (i)

(a) Anisole on reaction with HI produces only phenol and methyl iodide.

(b) When phenol is treated with bromine water, white precipitate of 2,4,6-tribromophenol is obtained.

2,4,6-tribromophenol

OR

(ii)

Ans.: Since C gives an addition reaction with Br₂ and H₂ and so it is an unsaturated hydrocarbon. It gives an alcohol with a phosphoric acid and water i.e., CH₃CH₂OH. So, C is ethene. Thus, A is ethanol which on oxidation with alkaline KMnO₄ gives ethanoic acid. So, we can conclude that A is ethanol, B is ethanoic acid and C is ethene.

Question 9

Ans.: Molality of sucrose solution (m)

$$= \frac{w_2 \times 1000}{M \times w_1} = \frac{4 \times 1000}{342 \times 96} = 0.121 \text{ m}$$

 ΔT_f for sucrose solution = 273.15 - 271.15 = 2

$$K_f = \frac{\Delta T_f}{m} = \frac{2}{0.121} = 16.52 \text{ K/m}$$

Molality of glucose solution = $\frac{5 \times 1000}{180 \times 95}$ = 0.292

$$\Delta T_f = K_f \times m = 16.52 \times 0.292 = 4.82K$$

Freezing point of glucose solution

$$= 273.15 - 4.82 = 268.33 \text{ K}$$

Ans.: (i) Because the positive charge on carbonyl carbon of CH₃CHO decreases to a lesser extent due to one electron releasing (+I effect) CH₃ group as compared to CH₃COCH₃ (two electron releasing CH₃ group) and hence more reactive.

(ii) Because carboxylate ion (conjugate base) is more resonance stabilized than phenoxide ion.

Question 11

Ans.:

- (i) This is due to lanthanide contraction. As the change in atomic radii is very small so they possess almost similar chemical properties.
- (ii) Cr^{2+} is a strong reducing agent with a d^4 configuration. Upon acting as a reducing agent, it is oxidized to Cr^{3+} (d^3), which forms a more stable configuration due to the presence of a half-filled set of d-orbitals. On the other hand, Mn^{3+} (d^4), acting as an oxidizing agent, gets reduced to Mn^{2+} (d^5), achieving a highly stable configuration with exactly half-filled d-orbitals.

SECTION C – 21 MARKS

Question 12

Ans.:

(i) Average rate of reaction

$$= \frac{\Delta[\text{ester}]}{\Delta \text{time}}$$

$$= \frac{0.17 - 0.31}{60 - 30} = -4.67 \times 10^{-3} \text{ mol L}^{-1} \text{ s}^{-1}$$

(ii)
$$K = \frac{2.303}{t} \log \frac{a}{(a-x)}$$

Where a is initial conc. of ester (t = 0) and x is the concentration of ester at time t.

$$K_1 = \frac{2.303}{30} \log \frac{0.55}{0.31} = 1.91 \times 10^{-2}$$

$$K_2 = \frac{2.303}{60} \log \frac{0.55}{0.17} = 1.96 \times 10^{-2}$$

$$K_3 = \frac{2.303}{90} \log \frac{0.55}{0.085} - 2.01 \times 10^{-2}$$

$$K = \frac{K_1 + K_2 + K_3}{3}$$

$$= \frac{1.91 \times 10^{-2} + 1.96 \times 10^{-2} + 2.01 \times 10^{-2}}{3}$$

Ans.: (i) Formula of the compound 'C' indicates it to be an amine. Since it is obtained by the reaction of Br₂ and KOH with the compound 'B' so compound 'B' can be an amide. It is also indicated because 'B' is obtained from compound 'A' by reaction with ammonia followed by heating. So compound 'A' could be an aromatic acid. Formula of compound 'C' shows it to aniline, then 'B' is benzamide and compound 'A' is benzoic acid. The sequence of reactions can be written as follows:

COOH

(i) NH₃

(ii)
$$\Delta$$

Benzoic acid

Benzamide

(A)

(B)

(C)

(ii) *N*-Ethyl-*N*-methylethanamine.

Question 14

Ans.:

- (i) Sugars with a free aldehyde and a ketone group are known as reducing sugars. All monosaccharides (both aldoses and ketoses) and disaccharides except sucrose are reducing sugars.
- (ii) Essential amino acids are amino acids that the human body cannot produce on its own, and thus must be obtained through the diet. Non-essential amino acids, on the other hand, can be synthesized by the body and are not strictly required in the diet.

Examples of essential amino acids:

- 1. Leucine
- 2. Valine

Examples of non-essential amino acids:

- 1. Glycine
- 2. Alanine

Ans.: (i)

Ideal solution	Non-ideal solution
1. The interactions between the components are similar to those in the pure components.	The interaction between the components are different from those of the pure components.
2. There is no enthalpy change on mixing. $(\Delta_{\text{mixing}} H = 0)$	There is enthalpy change on mixing. $(\Delta_{\text{mixing}} H \neq 0)$
3. There is no volume change on mixing. $(\Delta_{\text{mixing}}V=0)$	There is volume change on mixing. $(\Delta_{\text{mixing}}V \neq 0)$
4. Each compound obeys Raoult's law at all temperatures and concentrations.	Their components do not obey Raoult's law. They show positive and negative deviations from Raoult's law.
i.e., $p_A = p_A \times x_A$ and $p_B = p_B^o \times x_B$	i.e., $p_A \neq p_A^o \times x_A$ and $p_B \neq p_B^o \times x_B$

(ii) The solution shows positive deviation from ideal behaviour.

(iii) According to Raoult's law, $p_A = p_A^o x_A$

Vapour pressure of pure ethyl alcohol $(p_A^o) = 40 \text{ mm}$ of Hg

Mole fraction of ethyl alcohol $(x_A) = 0.80$

Vapour pressure of ethyl alcohol in solution $(p_A) = 40 \times 0.80 = 32$ mm of Hg,

Ans.:

(i)
$$CH_3CH_2CI \xrightarrow{NaCN} CH_3CH_2CN \xrightarrow{H_2O/H^+} CH_3CH_2COOH$$

[A]

[B]

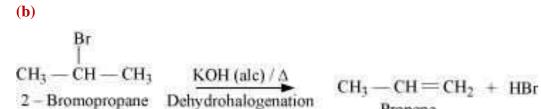
 $LiAlH_4$
 $CH_3CH_2CH_2OH$

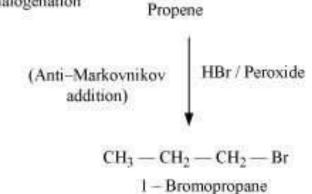
[C]

Question 17

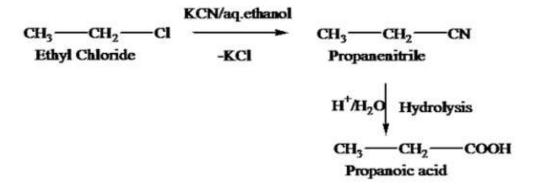
Ans.: (i) (a)

CH₃CHO dil NaOH
$$\rightarrow$$
 CH₃ \rightarrow CH₂ \rightarrow CH₂ \rightarrow CH₃ \rightarrow CH₃ \rightarrow CH \rightarrow CH \rightarrow CHO Ethanal \rightarrow CH₂O \rightarrow CH₃ \rightarrow CH \rightarrow CH \rightarrow CHO But \rightarrow 2 - enal





(c)



OR

Ans.: (ii)

Step III If however, excess of HI is used, methyl alcohol formed in step II is also converted into methyl iodide. It can be explained by the following mechanism:

$$CH_{3} \longrightarrow CH_{3} \longrightarrow CH_{3} \longrightarrow CH_{3} \longrightarrow CH_{4} \longrightarrow CH_{3} \longrightarrow CH_{4} \longrightarrow CH_{5} \longrightarrow CH_{3} \longrightarrow CH_{5} \longrightarrow C$$

Question 18

Ans.:

(i) For a first order reaction

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

where $[R]_0$ = initial concentration,

[R] = conc. after time t

When half of the reaction is completed, $[R] = [R]_0/2$.

Representing, the time taken for half of the reaction to be completed, by $t_{1/2}$, equation becomes:

$$k = \frac{2.303}{t_{1/2}} log \frac{[R]_0}{[R]_2/2}$$

$$\Rightarrow t_{1/2} = \frac{2.303}{k} log \ 2$$

$$\Rightarrow t_{1/2} = \frac{2.303}{k} \times 0.3010$$

$$\Rightarrow t_{1/2} = \frac{0.693}{k}$$

The above equation shows that half-life first order reaction is independent of the initial concentration of the reactant.

(ii) For a first order reaction

$$t = \frac{2.303}{k} \log \frac{a}{a - x}$$

$$t_{99\%} = \frac{2.303}{k} \log \frac{100}{1}$$

$$= \frac{2.303}{k} \log 100$$

$$= \frac{2.303 \times 2}{k}$$

$$= \frac{4.606}{k}$$

and
$$t_{90\%} = \frac{2.303}{k} log \, \frac{100}{10}$$

$$=\frac{2.303}{k}\log 10 = \frac{2.303}{k}$$

$$\begin{aligned} \frac{t_{99\%}}{t_{90\%}} &= 2\\ t_{99\%} &= 2 \times t_{90\%} \end{aligned}$$

SECTION D - 15 MARKS

Question 19

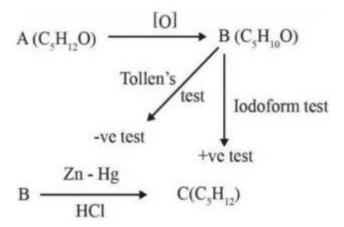
Ans.: (i)

- (a) Benzoic acid is somewhat stronger acid than acetic acid. The carboxyl group of benzoic acid is attached to an sp²-hybridized carbon which is more electronegative and electron-withdrawing than the sp³-hybridized carbon attached to acetic acid.
- **(b)** Boiling points of aldehydes are lower than those of alcohols of similar molecular masses due to absence of intermolecular hydrogen bonding. This bonding makes the alcohol more stable at certain level of temperatures.
- (c) Carboxylic acids do not give reactions of carbonyl group because the lone pairs on oxygen attach to hydrogen in the –COOH group are involved in resonance which makes the carbon less electrophilic.



Resonance structures of carboxylic acids

Ans.: (ii)



Since B gives a negative Tollen's test but positive Iodoform test, it is methyl ketone, i.e, $CH_3COCH_2CH_2CH_3$. Also, it is formed by oxidation of A.

Therefore, A is secondary alcohol i.e.,

CH₃CHCH₂CH₂CH₃

on reduction B gives pentane with Zn - Hg/HCl.

Therefore, C is CH₃CH₂CH₂CH₂CH₃

Therefore,

$$A = CH_3CHOHCHCH_2CH_3$$

$$B = CH_{3}COCH_{2}CH_{2}CH_{3}$$

$$C = CH_{3}CH_{2}CH_{2}CH_{2}CH_{3}$$

$$CH_{3}CHCH_{2}CH_{2}CH_{3}$$

$$OH (A)$$

$$CH_{3}CHCH_{2}CH_{2}CH_{3}$$

$$OH (B)$$

$$CH_{3}CCH_{2}CH_{2}CH_{2}CH_{3}$$

$$O (B)$$

$$CH_{3}CH_{2}CH_{2}CH_{2}CH_{3}$$

$$O (B)$$

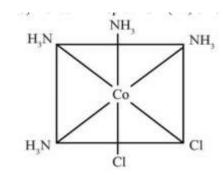
Question 20

Ans.: (i)

Double salt	Complex
They dissociate into simple ions when dissolved in water	They do not dissociate into simple ions completely when dissolved in water.
e.g., KCl·MgCl ₂ ·6H ₂ O.	e.g., [Co(NH ₃) ₆]Cl ₃

(ii) (a) Potassium trioxalatoferrate (III)

(b) Hexaammineplatinum (IV) chloride.



cis - isomer of
$$[Co(NH_3)_4Cl_2]^+$$

Ans.: (i) (a)

Al (s) |
$$Al^{3+}(aq)(0.01M) \parallel Cu^{2+}(aq)(0.01M) \mid Cu(s)$$

$$[Al(s) \rightarrow Al^{3+}(aq) + 3e^{-}] \times 2$$
 (Oxidation at anode)

$$[Cu^{2+}(aq) + 2e^{-} \rightarrow Cu(s)] \times 3$$
 (Reduction at cathode)

$$\therefore$$
 n = 6

$$E_{cell} = E_{cell}^{o} - \frac{0.0591}{6} log \frac{[Al^{3+}]^2}{[Cu^{2+}]^3}$$

$$E_{\text{cell}}^{\text{o}} = E_{\text{cell}} + \frac{0.0591}{6} \log \frac{[\text{Al}^{3+}]^2}{[\text{Cu}^{2+}]^3}$$

$$= 1.98 + \frac{0.0591}{6} \log \frac{(0.01)^2}{(0.01)^3}$$

$$= 1.98 + \frac{0.0591}{6} \log 10^2$$

$$= 1.98 + \frac{0.0591}{6} 2\log 10$$

$$= 1.98 + \frac{0.0591}{6} \times 2[\because \log 10 = 1]$$

$$= 1.98 + 0.0197 = 1.9997 \text{ V}$$

(b) As corrosion is a phenomenon of oxidation of iron considering the oxidation potentials of all the elements is essential. Element with more negative reduction potential than Fe can undergo reduction faster than iron preventing corrosion in iron.

Reduction potential of Fe = -0.44 V

Reduction potential of A = -2.37 V

Reduction potential of B = -0.14 V

As A has more negative reduction potential, A is more prone to undergo reduction and can act as a sacrificial coating on the surface of iron. This sacrificial protection helps prevent the corrosion of iron, as element A will oxidize preferentially, protecting the iron from undergoing oxidation (corrosion).

OR

(a)

$$E_{cell}^{o} = E_{cathode}^{o} - E_{anode}^{o}$$

$$= (-0.44) - (-0.74)V = 0.30 V$$

$$E = E^{\circ} - \frac{0.0591}{n} \log \frac{[Products]}{[Reactants]}$$

$$= 0.30 - \frac{0.0591}{6} \log \frac{[Cr^{3+}]}{[Fe^{2+}]}$$

$$= 0.30 - \frac{0.0591}{6} \log \frac{[0.01]^{2}}{[0.1]^{3}}$$

$$= 0.30 - \left(\frac{-0.059}{6}\right) = 0.3098 V$$

(b)
$$Ag_{(aq)}^+ + e^- \rightarrow Ag(s); E^\circ = +0.80 \text{ V}$$

$$H_{(aq)}^+ + e^- \rightarrow \frac{1}{2} H_2(g); E^\circ = 0.00 \text{ V}$$

On the basis of their standard reduction potential (E°) values, cathode reaction is given by the one with higher E° values.

Thus $Ag_{(aq)}^+ + e^- \rightarrow Ag(s)$ reaction will be more feasible at cathode.