

Model Solutions

HBCSE

INCHO 2002

Problem 1

15 marks

A. Wave functions and atomic orbitals

1.1 $2 \times 4 \times (-13.6) = -108.8 \text{ eV.}$

1.2 $|\psi_1(0.5)|^2 = 2 \times 1^2 = 2$

1.3 Yes

No

1.4 $|\psi(x_0)|^2 dx$ is the probability of finding the particle in a small interval dx around x_0 . Hence $|\psi(x_0)|^2$ can be greater than 1.

1.5

I → C
II → B
III → A

1.6

A 3p
B 3s
C 1s

B. Properties of oxygen molecule and MO theory

1.7 O_2 is paramagnetic or any other logical choice.

1.8 $O_2 : 2$

$O_2^- : 1.5$

1.9

$O_2 : 2$

$O_2^- : 1$

Problem 2

20 marks

A. Kinetics of the reaction between Nitric oxide and Oxygen

2.1

$$\frac{d[\text{NO}_2]}{dt} = K_2 [\text{N}_2\text{O}_2][\text{O}_2]$$

$$= \frac{k_2 k_1}{k_{-1}} [\text{NO}]^2 [\text{O}_2]$$

order $n = 3$

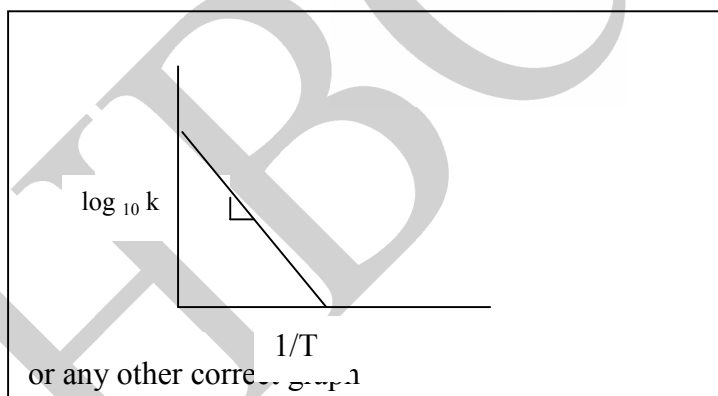
2.2

- i) Order $n = 3.004$
- ii) Units of k are $\text{dm}^6 \text{mol}^{-2} \text{s}^{-1}$

2.3

- i) Equilibrium constant $K^* = 12$
- $\Delta G^* = -6.20 \text{ kJ}$
- ii) Since ΔG^* is negative, the reaction is spontaneous.

2.4



B. Carbon monoxide

2.5 ii) $\Delta S_{\text{system}} + \Delta S_{\text{surrounding}} > 0$ X

2.6

- i) $\text{CO(g)} + \frac{1}{2} \text{O}_2 \text{(g)} \rightarrow \text{CO}_2 \text{(g)}$
- ii) $\Delta U = -169.05 \text{ kJ}$
 $\Delta H = -170.31 \text{ kJ}$
- iii) $\Delta S = -ve \rightarrow$
- iv) Entropy decreases as there is a decrease in volume.

2.7

$$\Delta S = 1.695 \times 10^{-3} \text{ kJ.}$$

$$\text{Work done} = \Delta S \times T = 0.5085 \text{ kJ.}$$

2.8

$$\text{i) Eff} = \frac{T_2 - T_1}{T_2} = \frac{373 - 77}{373} = 0.794 \text{ or } 79.4 \%$$

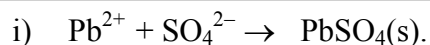
ii) Use superheated steam in the boiler so that T_2 increases.

Problem 3

10 marks

A. Electrochemical cell

3.1

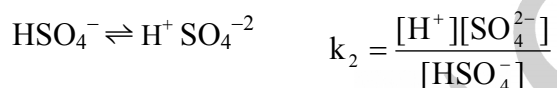


$$E_{\text{cell}} = E^0_{\text{cell}} - \frac{0.0592}{n} \log \frac{1}{[\text{Pb}^{2+}][\text{SO}_4^{2-}]}$$

$$0.061 = 0.230 - \frac{0.0592}{2} \log \frac{1}{(2.50 \times 10^{-5}) \times [\text{SO}_4^{2-}]}$$

Solving we get $[\text{SO}_4^{2-}] = 7.81 \times 10^{-2}$.

The dissociation reaction of HSO_4^- is as follows



Since there is only 1 H^+ produced for 1 SO_4^{2-} . $\therefore [\text{H}^+] = [\text{SO}_4^{2-}]$.

$$[\text{HSO}_4^-]_{\text{eq}} = 0.600 - (7.81 \times 10^{-2}) = 0.522$$

$$k_2 = \frac{(7.81 \times 10^{-2})^2}{(0.522)} = 1.17 \times 10^{-2}$$

B. Mohr's Method

3.2

i) $[\text{CrO}_4^{2-}] = 1.55 \times 10^{-2}$

ii) Percentage error (%) = 0.038

Problem 4

15 marks

A. Carbon dating

4.1

i) $t = 13763$ year

\therefore Date = 11764 B.C

ii) $a_0 = 0.3145$ dis/min

B. Power production in nuclear fusion

4.2

**C. Decomposition of Limestone**

4.3

i) Initial moles of $\text{CaCO}_3 = 0.2$

ii) $n = 0.1316$ mole

iii) % of CaCO_3 unreacted = 34.2

Problem 5

21 marks

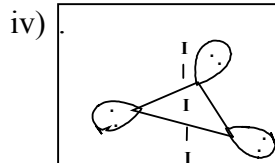
A. Co-ordination chemistry of copper

5.1

i) Γ^- is a base and I_2 is an acid.

ii) $2Na_2S_2O_3 + I_2 \longrightarrow Na_2S_4O_6 + 2NaI$

iii) Γ^- is oxidized to I_2 .



v) Octahedral with tetragonal elongation.
Octahedral

vi) It is a Cu(I) compound in which Cu has a d^{10} configuration. Therefore no d-d transitions are possible and hence colourless.

vii) $[Cu(H_2O)_6]^{++}$ $\mu_s = 1.73$ BM
CuI. $\mu_s = 0$

viii) 151 kJ mol^{-1}

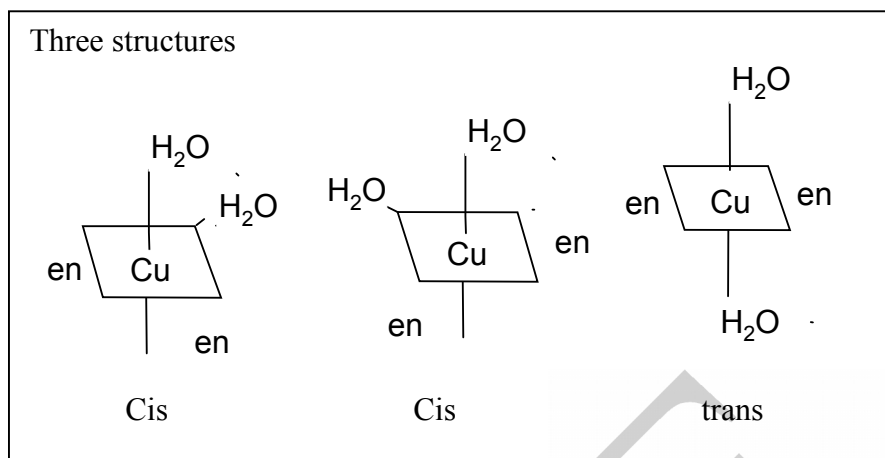
5.2

$[Cu(en)(H_2O)_4]^{++}$: Tetraaquo(ethylenediamine)Copper(II) ion.

i) $[Cu(en)_2(H_2O)_2]^{++}$: Diaquobis(ethylenediamine)Copper(II) ion.

$[Cu(en)_3]^{++}$: d or l tris(ethylenediamine)Copper(II) ion.

ii) .



B. Complexes of Nickel

5.3

- i) $[\text{Ni}(\text{H}_2\text{O})_6]^{++}$: octahedral (d^8)
 $\text{Ni}(\text{CN})_4^{--}$: Square planar (d^8)
 $[\text{Ph}_4\text{As}]_2[\text{NiCl}_4]$: tetrahedral (d^8)

ii)

crystal field splitting energy $[\text{NiCl}_4] = 3778 \text{ cm}^{-1}$

Problem 6

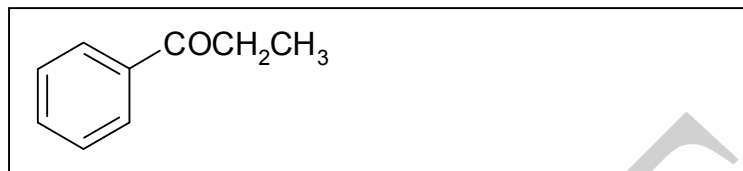
26 marks

A. Structure elucidation of organic compound

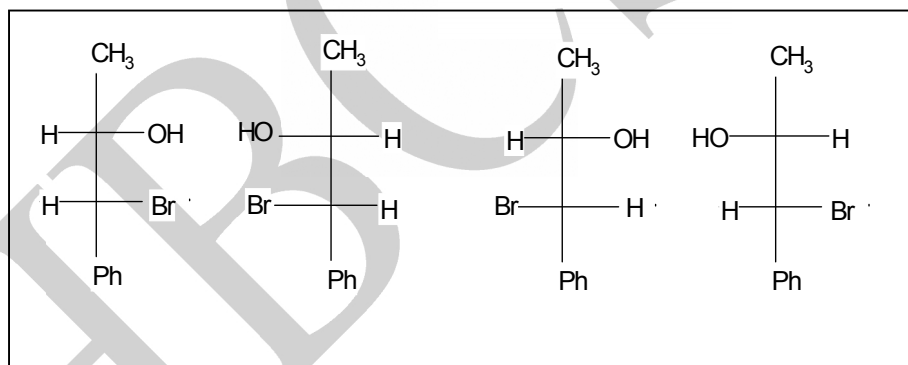
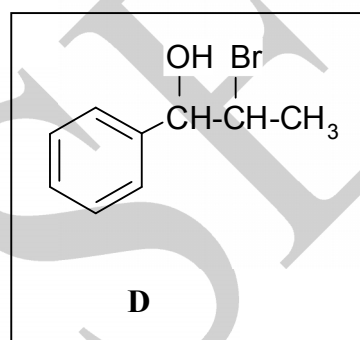
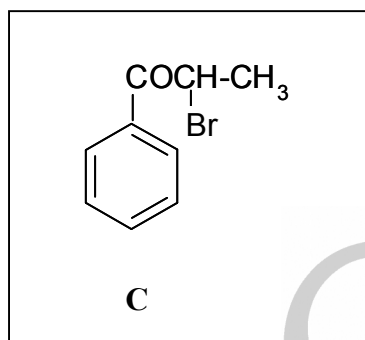
6.1 i)



ii)



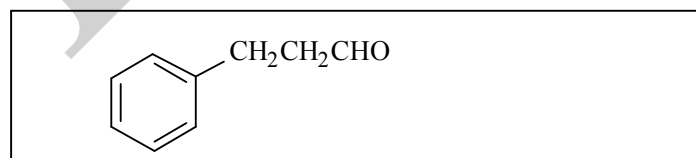
6.2 i)



6.3 i)

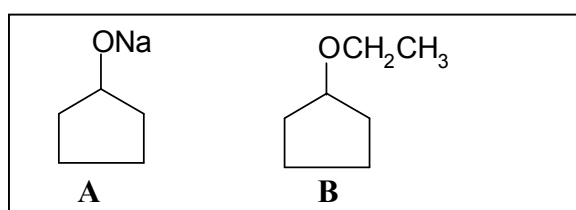


ii)

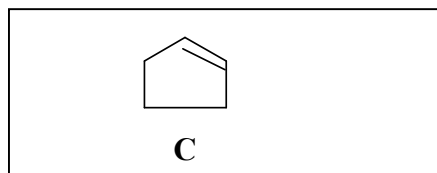


B. Organic reactions, mechanisms and stereochemistry

6.4 i)



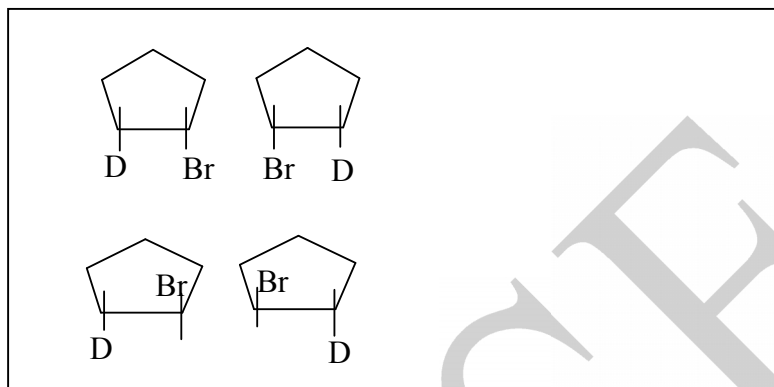
ii)



iii) c) Base



iv)



v)

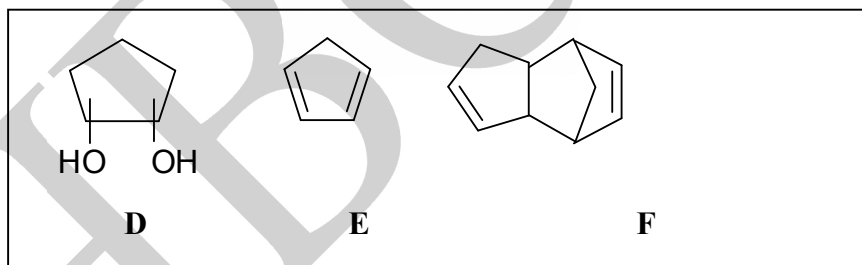


vi)

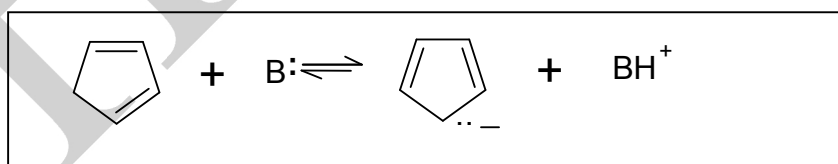
a) Sodium bromide is insoluble, and sodium iodide is soluble in acetone.



vii)



viii)



ix)

The conjugate base of **E** is an aromatic anion and the negative charge is delocalised over the entire ring. Hence all hydrogens are identical.

Problem 7

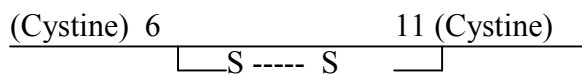
15 marks

A. Amino acids and proteins

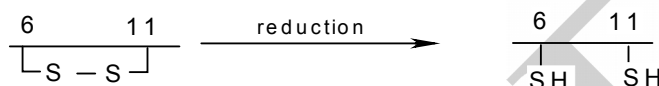
7.1 i)

Insulin

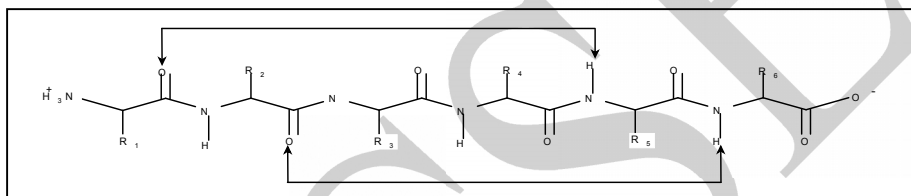
ii)



iii)



iv)



v)

Length before treatment: 45 Å

Length after treatment: 108 Å

vi)

Average mol wt of amino acid = 128 Da

Mol wt of chain A = 2328 Da

7.2

Sample

Direction of migration

A

No migration

B

Cathode

C

Anode

B. Structures and functions of nucleic acids

7.3 i)

total number of codons = 60.

ii)

the total number of bases = 360

iii)

G = 30 % and C = 30 %.

iv)

Nitrogen bases conjugate double bonds. These double bonds are responsible for absorption of U.V. radiation.

INCHO 2003

Problem 1

14 marks

Chemical Kinetics

1.1

$$[ES] = \frac{k_1[E][S]}{k_{-1} + k_2}$$

1.2

$$\therefore [ES] = \frac{k_1[E]_0[S]}{k_{-1} + k_2 + k_1[S]}$$

1.3

where $K_m = \frac{k_{-1} + k_2}{k_1}$

K_m has unit of concentration.

1.4

$v = k_2[E]_0 [S]$ when $[S] \ll K_m$

(first order in S)

$v = k_2[E]_0$ when $[S] \gg K_m$

(zero order in S)

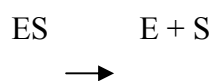
1.5

$$E \approx 52 \text{kJmol}^{-1}$$

1.6

ES

exothermic



E_2

Problem 2

17 marks

Ionic Equilibrium and Electrochemistry

A.

2.1

$$V = 30 \text{ mL}$$

2.2

$$pK_a = 6.1$$

2.3

$$pH = 9.4$$

B.

2.4

$$E^0 = 0.76 \text{ V}$$

C.

2.5

$$K_{eq} = 6.0 \times 10^{-7} \text{ M}$$

$$E^0_{cell} = -0.367 \text{ V}$$

2.6

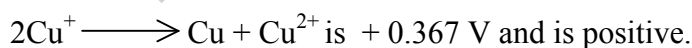
$$E^0_{cell} = 2 E^0_{Cu^{2+}/Cu} - 2E^0_{Cu^+/Cu}$$

$$\text{Or, } E^0_{Cu^+/Cu} = (E^0_{Cu^{2+}/Cu} - \frac{1}{2} E^0_{cell})$$

$$E^0_{Cu^+/Cu} = 0.521 \text{ V}$$

2.7

Since E^0_{cell} for the above cell is -0.367 V , E^0 for the cell corresponding to the reverse reaction



Hence this reaction is spontaneous and therefore Cu^+ does not exist in aqueous solution. This can also be predicted from the equilibrium constant of the above reaction (1).

Problem 3

17 marks

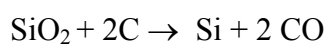
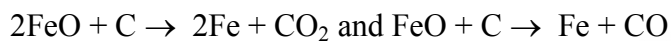
Metallurgy and Chemistry of Iron

3.1

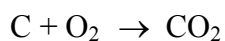
As temperature rises FeO will be reduced first.

Minimum Temperature for reduction of FeO = 750 °C

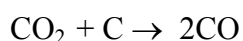
Minimum Temperature for reduction of SiO₂ = 1500 °C



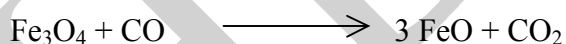
3.2



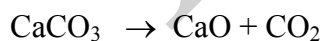
3.3



3.4



3.5

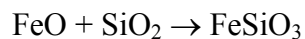


3.6



b) No, Iron oxide being much less acidic than SiO₂ will not react with calcium oxide, which is basic.

3.7



3.8

To feed the charge, and to prevent escape of the volatile matter.

3.9

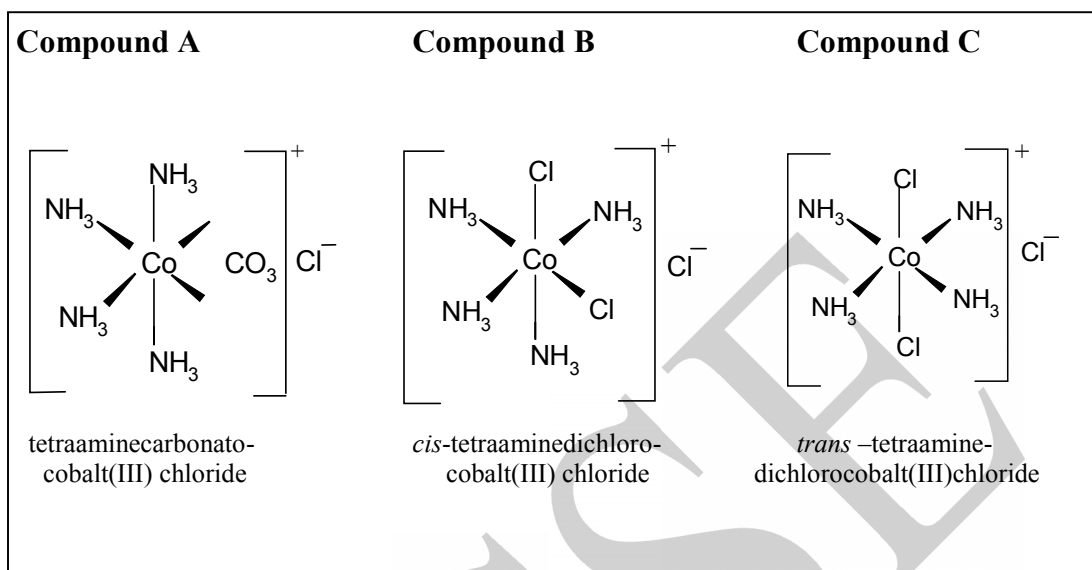
<i>Test tube</i>	Reagent added	Observations	Balanced chemical equation/s
1	NaOH	Reddish brown precipitate	$\text{Fe}^{3+}(\text{aq}) + 3 \text{OH}^{-}(\text{aq}) \rightarrow \text{Fe}(\text{OH})_3(\text{s}) \downarrow$
2	KSCN (under acidic condition)	Blood red colour	$\text{Fe}(\text{H}_2\text{O})_6^{3+}(\text{aq}) + \text{SCN}(\text{aq}) \rightarrow \text{Fe}(\text{H}_2\text{O})_5(\text{SCN})^{2+}(\text{aq}) + \text{H}_2\text{O}(\text{l})$
3	$\text{K}_4[\text{Fe}(\text{CN})_6]$	Blue colour precipitate	$3\text{Fe}(\text{CN})_6^{4-} + 4\text{Fe}^{3+} \rightleftharpoons \text{Fe}_4[\text{Fe}(\text{CN})_6]_3(\text{s})$

Problem 4

7 marks

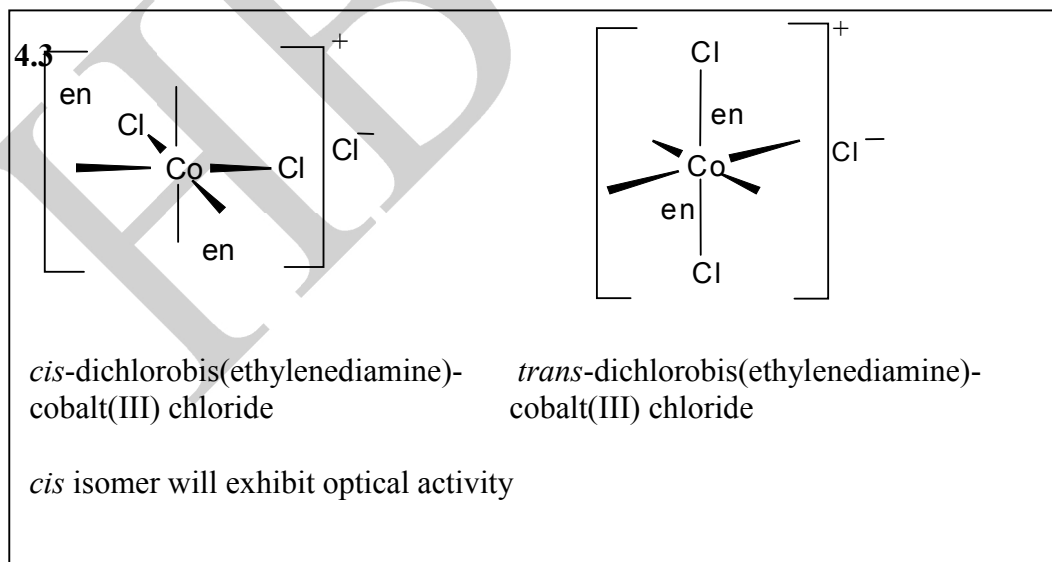
Coordination Chemistry

4.1



4.2

Geometrical Isomerism (*cis-trans*)



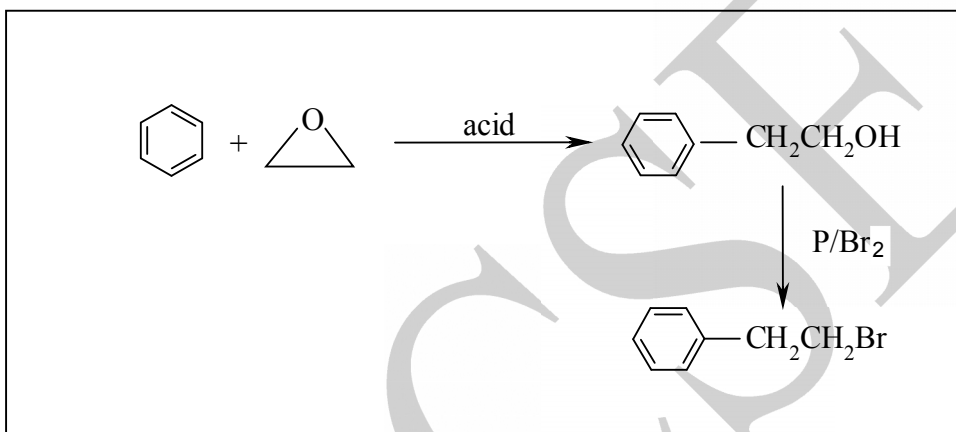
Problem 5

24 marks

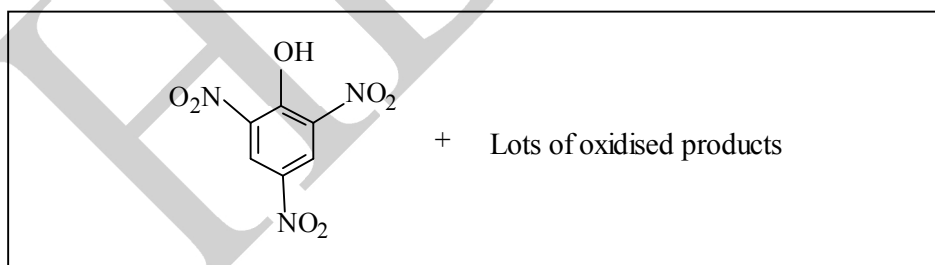
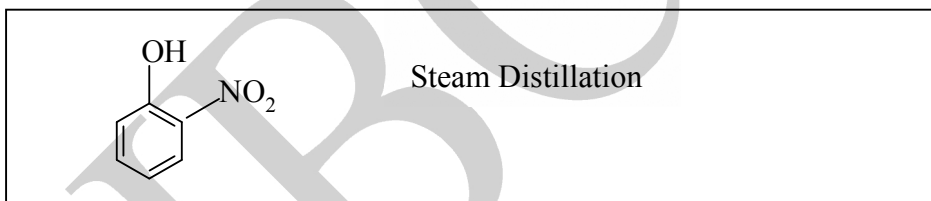
Synthesis of Drug

- 5.1 (i)
- (ii)
- (iii)

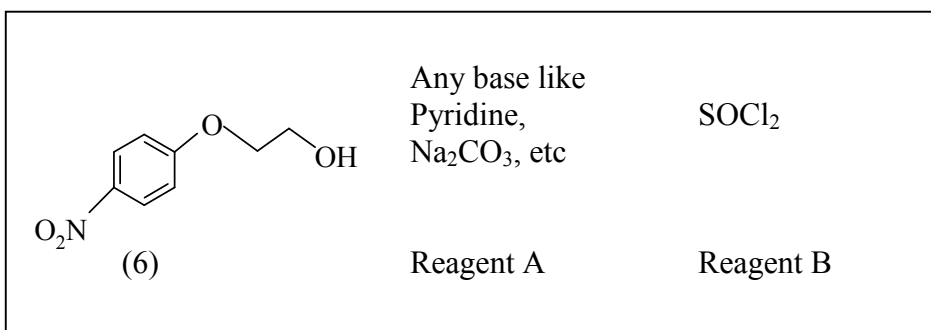
5.2 Suggest a method for the preparation of (2) starting from benzene.



5.3



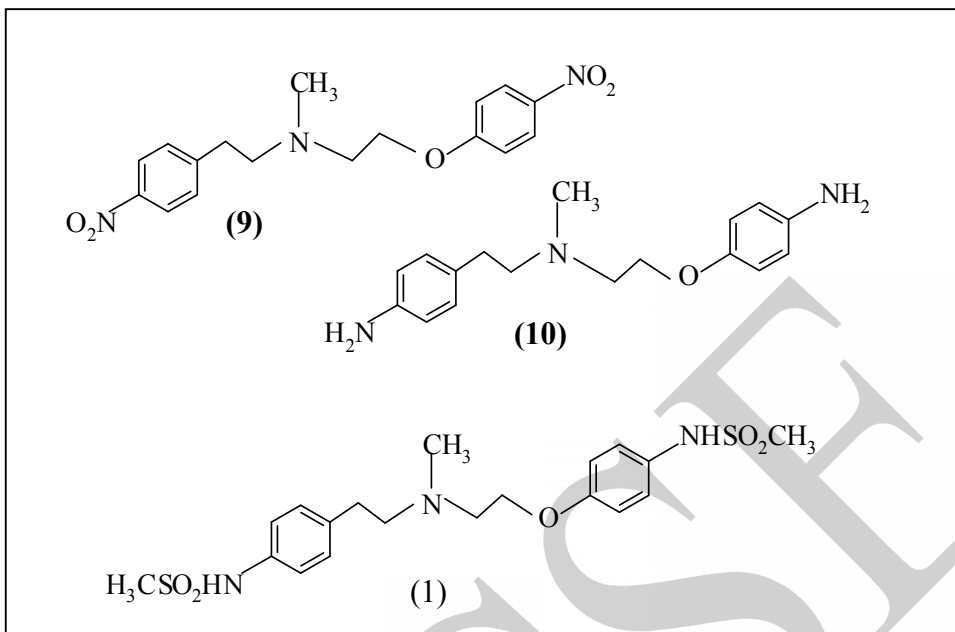
5.4



5.5

To avoid formation of the tertiary amine.

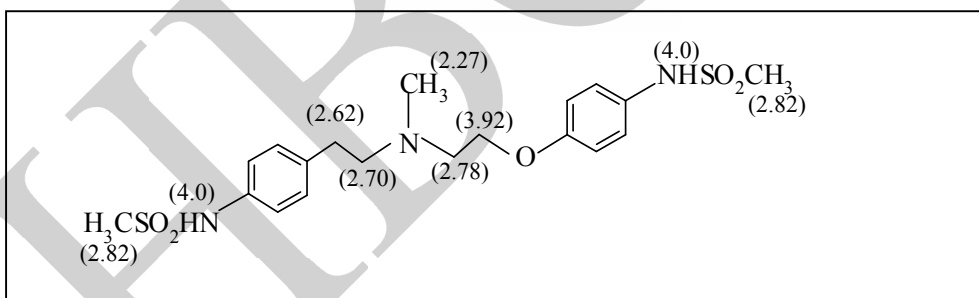
5.6



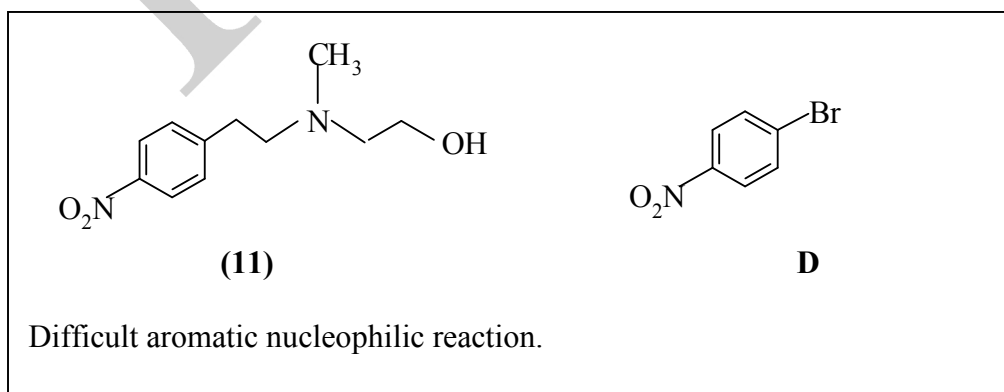
5.7

- 1) Oxidation of CHO by HNO_3 .
- 2) Reduction of NO_2 on the aromatic ring.
- 3) *o*-isomer may be formed.

5.8



5.9



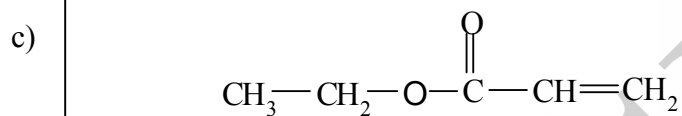
Problem 6

11 marks

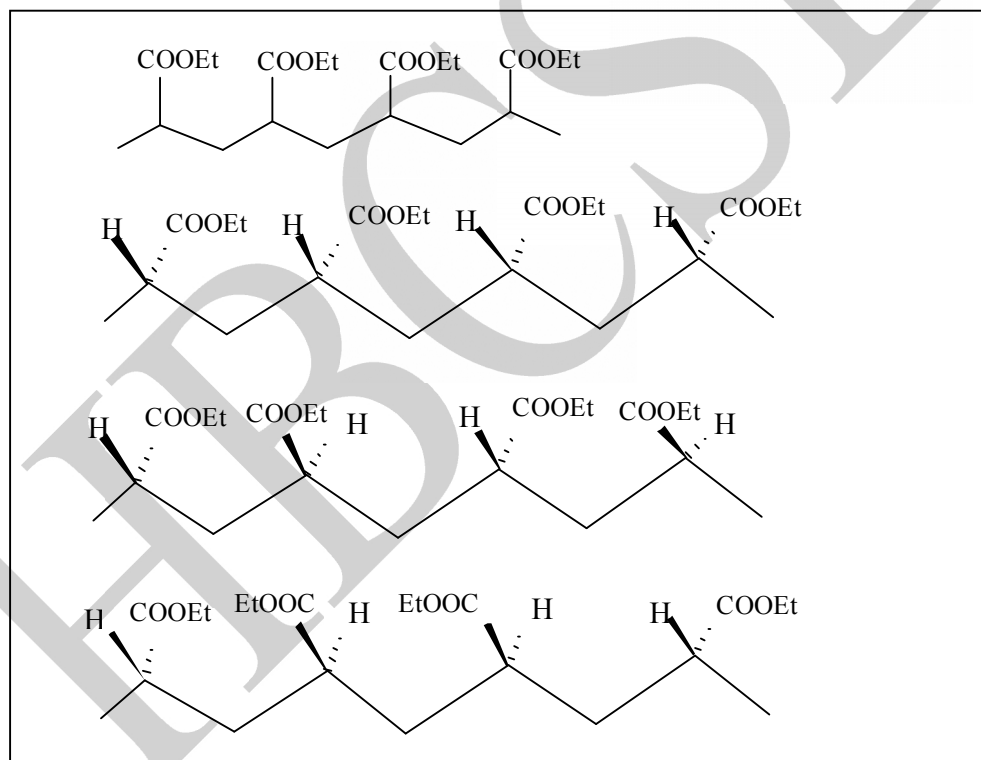
Structure Elucidation

6.1 a) Two double bond equivalents

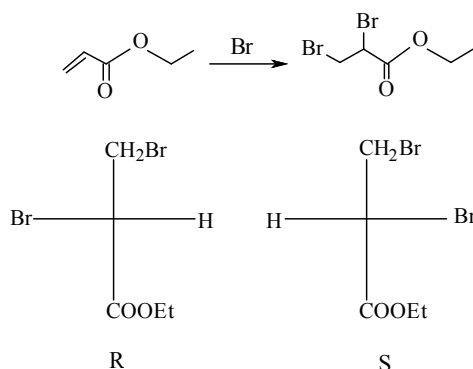
b) Ester carbonyl group



6.2



6.3



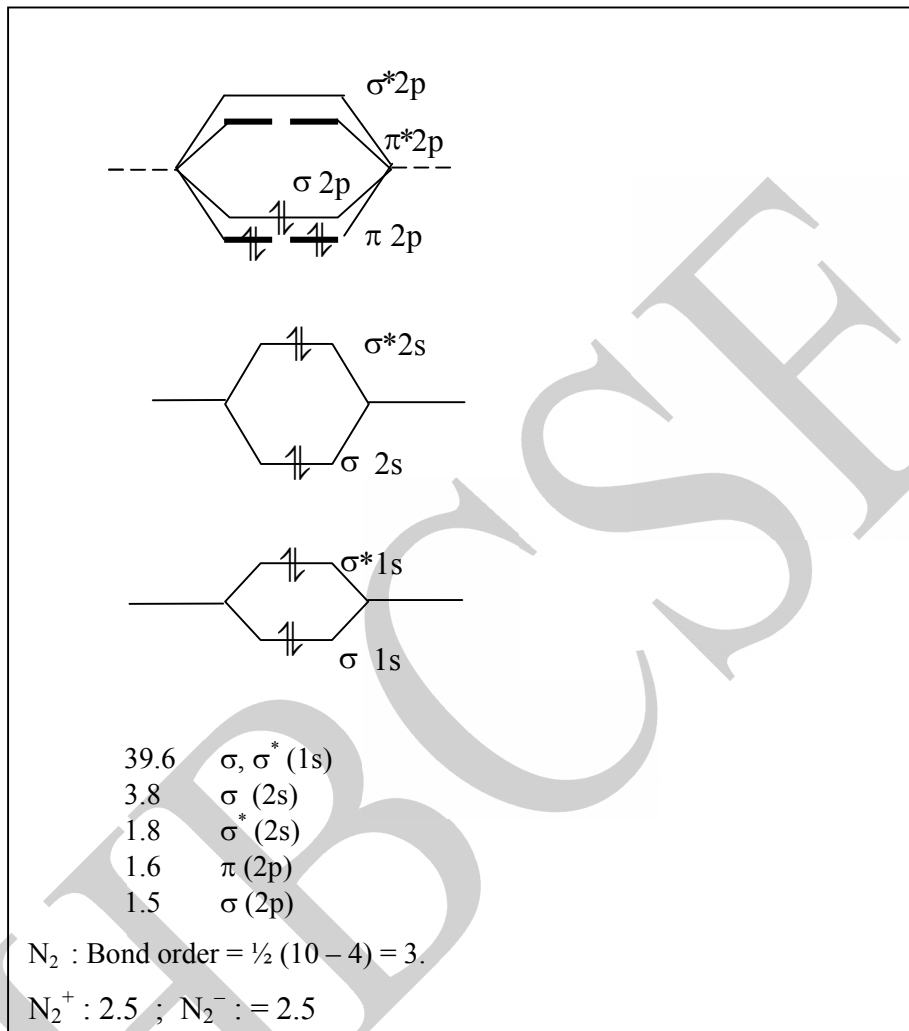
Problem 7

12 marks

Molecular Spectroscopy

A.

7.1



7.2

$$\therefore Z_{\text{eff}} = 0.78$$

B.

7.3

$$l = 3 \text{ m}$$

Problem 8

18 marks

Nucleic Acids

A.

8.1

The nucleic acids in **I**, **II** and **III** are DNA, since they all contain thymine, instead of uracil.

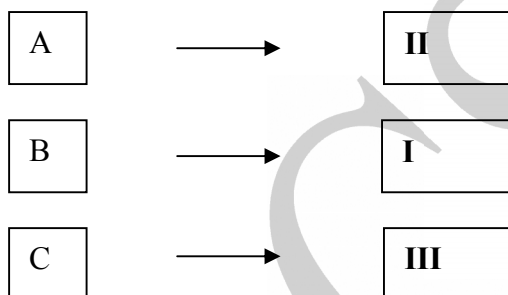
The direction of each strands is: $5' \rightarrow 3'$.

8.2

a) UV



b)



No. of hydrogen bonds in **III** > **I** > **II**. Higher the no of hydrogen bonds more is the stability.

For these reasons, the least stable nucleic acid **II** unstacks first, followed by **I**, and **III**.

c)

Complete unstacking of double helical structure.

All the above nucleic acids have same length (15 base pairs).

d)

Once the unfolding of double strand begins more number of bases are exposed to the radiation. This leads to sudden rise in relative absorbance for each nucleic acid.

Carbohydrates and Fats

B.

8.3

- a) Glucose is assimilated into the blood and is transported to each part of the body. Finally oxidation of glucose releases energy for the body to utilize and helps to recover.
- b) Lactose needs to be digested before conversion to glucose. Lactose (12%) present in the milk will yield less amount of glucose on hydrolysis compared to amount of glucose in the glucose solution. Therefore, the energy obtained will be less hence recovery will be slower.
- c) Calculate the energy content in (kJ) of a solution prepared by mixing 10 grams of a commercial health drink powder in 150 mL of water.

$$\text{Carbohydrate content} = 10 \times \frac{38.2}{100} = 3.82$$

$$\text{Fats content} = 10 \times \frac{21.5}{100} = 2.15$$

$$\begin{aligned} \text{Energy/150mL drink} &= \frac{\{(3.82 \times 16.8 + (2.15 \times 43.62))\} \text{ kJ}}{150 \text{ mL}} \\ &= \frac{157.959 \text{ kJ}}{150 \text{ mL}} \end{aligned}$$

INCHO 2004

Problem 1

19 marks

A. Crystal Structure

1.1

$$a = \sqrt{3} \cdot d = 687 \text{ pm}$$

1.2

$$\text{Number} = 8 \times \frac{1}{8} = 1$$

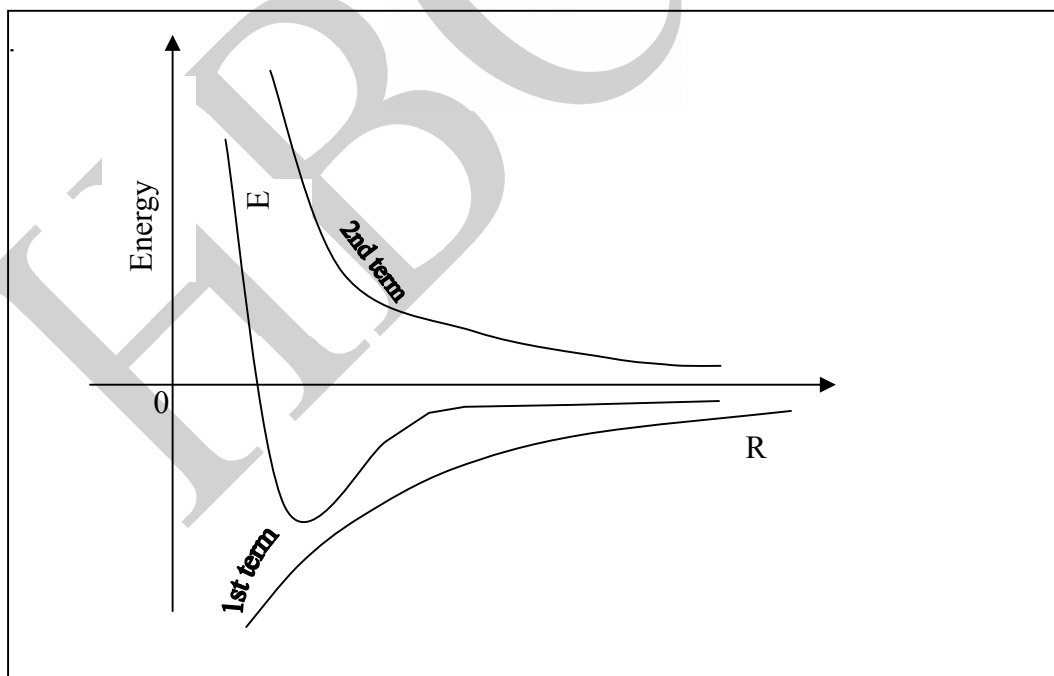
1.3

% of the occupied volume is 52

1.4

$$A = \frac{1}{n} \frac{q^2}{4\pi\epsilon_0} \cdot R_e^{n-1}$$

1.5



1.6

$$E_{\text{ion-ion}} = -432.4 \text{ kJ mol}^{-1}$$

1.7 $\Delta E = 165.89 \text{ kJ mol}^{-1}$

B. Spectroscopy

1.8 Reduction of intensity will be by a factor of f^2 .

1.9 Since $\Delta(n) = \pm 1$ corresponds to $\Delta E = h\nu$, only one line will be observed

1.10 No. Since the energy required to separate the atoms is infinite as is clear from the harmonic oscillator potential energy expression
 $V(R) = \frac{1}{2} k (R - R_e)^2$.

1.11 x_e is dimensionless

1.12 $\Delta E_{(n)} = E_{(n+1)} - E_{(n)} = h\nu [1 - 2x_e(n+1)]$.

1.13 The total number of vibrational energy levels possible is $n_{\max} + 1 = 1/2x_e$. Since $n = 0$ is also one energy levels.

1.14 $\bar{\nu} = 2897 \text{ cm}^{-1}$

1.15 $\bar{\nu}_2 = 1488.9 \text{ cm}^{-1}$

Problem 2

12 marks

Thermodynamics of Solutions

2.1

- a) Freezing point of the solution = $-5\text{ }^{\circ}\text{C}$.
- b) molecular mass of **R** = $12/0.188 = 63.83\text{g}$
- c) $\Delta T_f = 1.612\text{ mol kg}^{-1}$
 $K_f = 5.73\text{ K kg mol}^{-1}$

2.2

The molecular mass of 300.15 g will be ruled out.

2.3

% of acetic acid dissociated = 4.83

2.4

The molecular mass of acetic acid in benzene = 118 g

Since the molecular mass of acetic acid in benzene is twice its molecular mass
 \Rightarrow acetic acid dimerizes in benzene

Problem 3

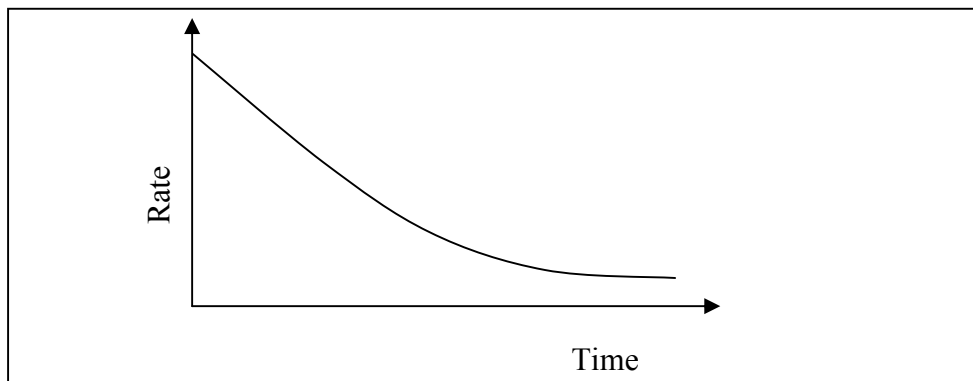
10 marks

Chemical Kinetics

3.1 iv) The reacting substances are present in less concentrated form.



3.2



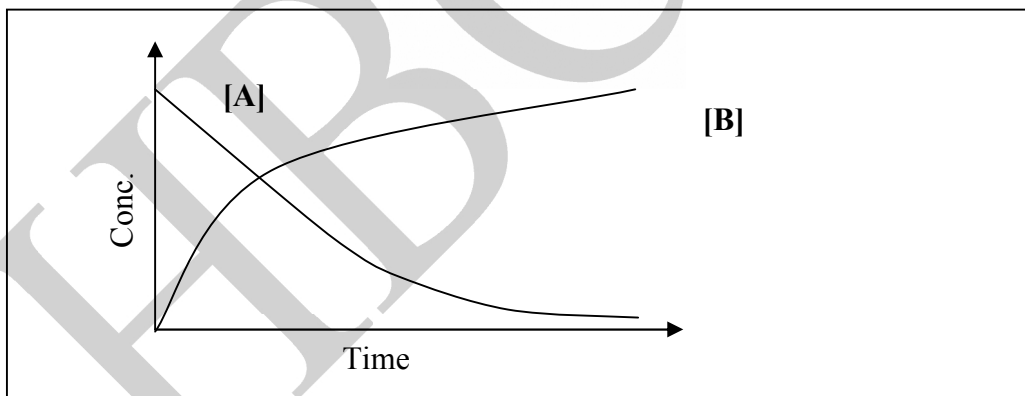
3.3

$$R_0 = k.a_0$$

3.4

$$t = \frac{1}{k}$$

3.5



3.6

[A] + [B] is constant

3.7

$$\alpha = 0, \quad \beta = R_0, \quad \gamma = \frac{R_0 k}{2}$$

3.8

Plot of $\ln(V_\infty - V_t)$ vs t is linear. First order reaction.

$$k = 1.32 \times 10^{-4} \text{ s}^{-1}$$

Problem 4

15 marks

Chemistry of Iron

4.1

a) ii) oxygen/sulphur



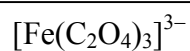
b) i) iron gets oxidized by aerial oxygen from iron(II) to iron(III)
which is hydrolyzed



c) ii) as a catalyst for Friedel-Craft reaction

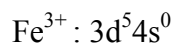
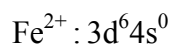
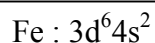


4.2

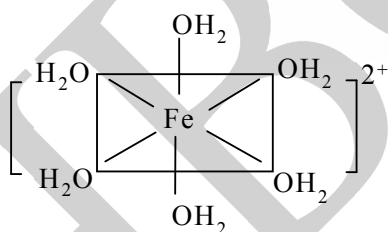


Name : tris oxalato ferrate(III)

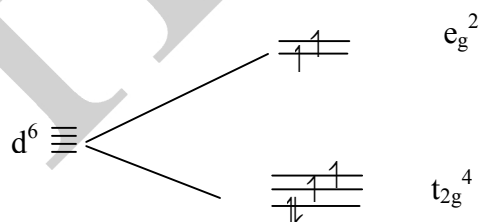
4.3



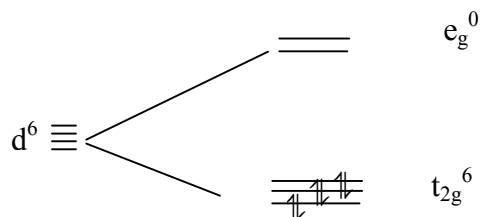
4.4



4.5



4.6

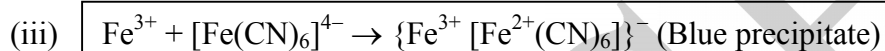
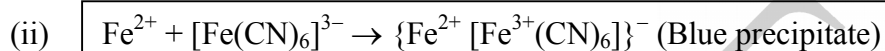
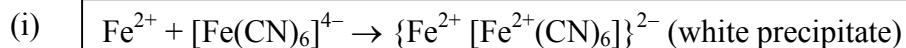


4.7

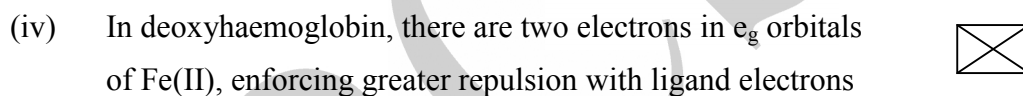
High Spin: $t_2g^4 e_g^2 = 4$ unpaired electrons: $\sqrt{24}$ BM (spin only)

Low Spin: $t_2g^6 e_g^0 = 0$ unpaired electrons: 0 BM (spin only)

4.8



4.9

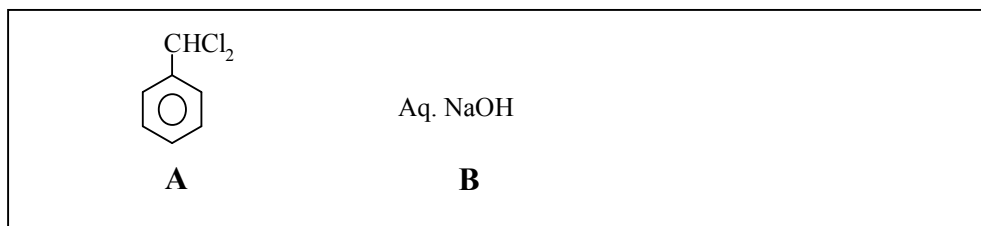


Problem 5

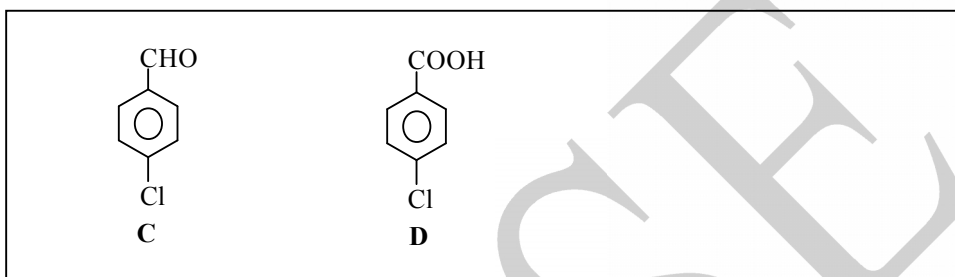
28 marks

Organic Chemistry of Perfumery Compounds

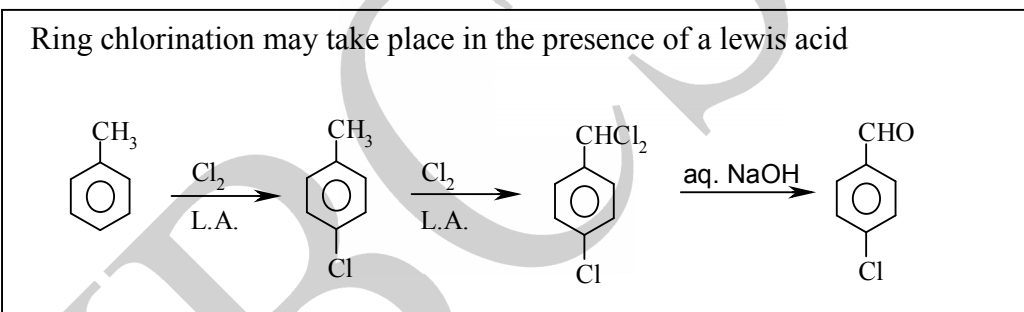
5.1



5.2

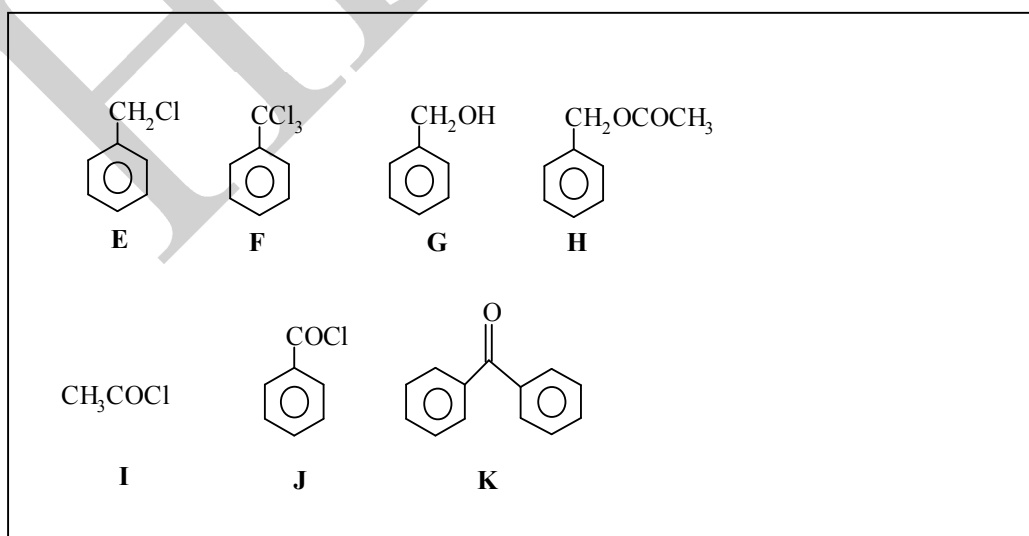


5.3



5.4

Identify E to K.



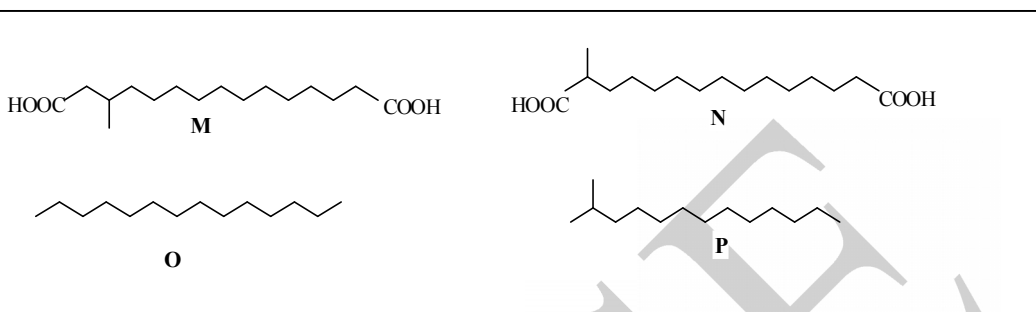
5.5

Saturated cyclic ketone.

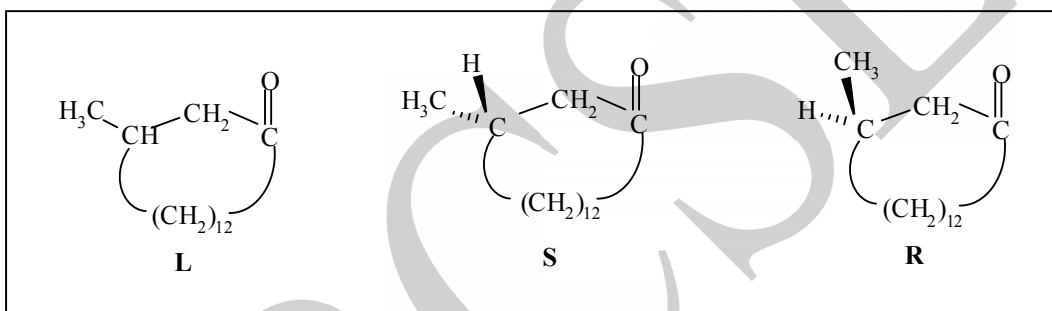
5.6

The acids are dicarboxylic acids.

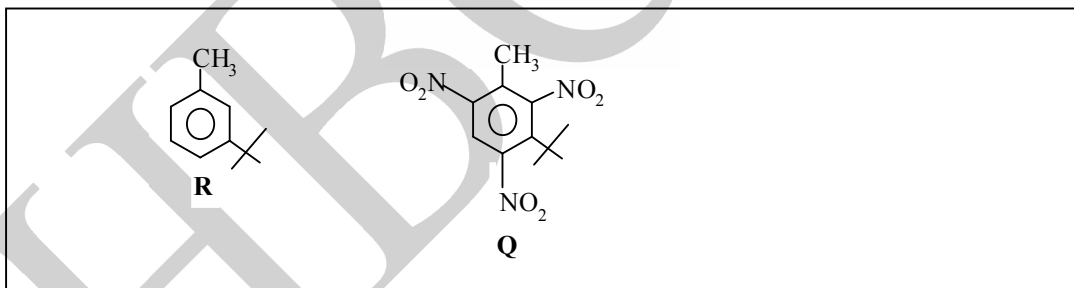
5.7



5.8



5.9



5.10

(iii) the warmth of the skin produces vapour of the compound in high concentration



5.11

(iv) the detectable concentration of ethanol is much higher than that of the perfume ingredient



Problem 6

12 marks

6.1

$$[\text{H}^+] = 1.32 \times 10^{-3} \text{ mol L}^{-1}.$$

$$[\text{A}^-] = 1.32 \times 10^{-3} \text{ mol L}^{-1}.$$

$$[\text{HA}] = 0.1 - 1.32 \times 10^{-3} = 0.0987 \text{ mol L}^{-1}$$

6.2

(i) Change in pH = 3.94

(ii) Change in pH = 1.943

6.3

$$\Delta\text{pH} / \Delta V = 3.94/0.2 = 19.7$$

$$\Delta\text{pH} / \Delta V = 1.943/0.02 = 97.15$$

6.4

Both Phenol red and Phenolphthalein can be used as indicators. The pH range for change in colour for these indicators coincides with the pH change at the equivalence point

6.5

From Curve **B** buffer range for acid **HX** $\approx 8 - 10$, $\Rightarrow \text{pKa} \approx 9$

From Curve **A** buffer range for acetic acid $\approx 4.5 - 5.3$, $\Rightarrow \text{pKa} \approx 4.8$

So acid **HX** is a weak acid as compared to acetic acid.

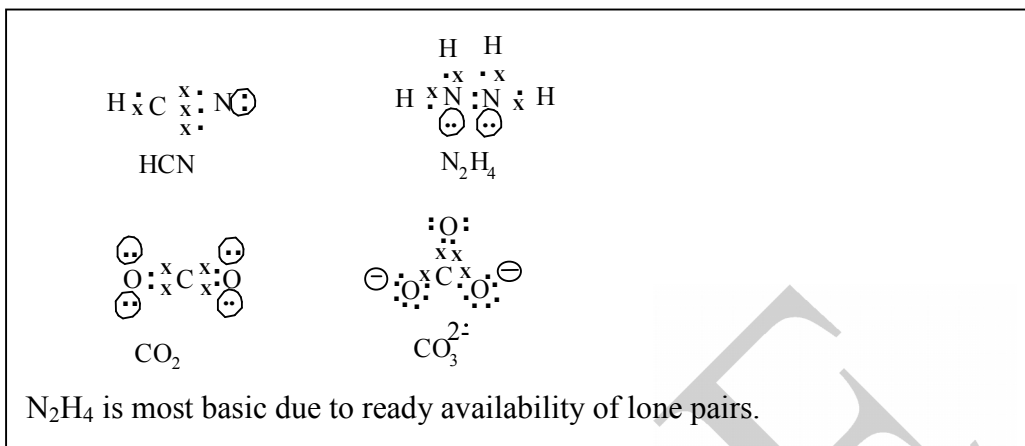
6.6

So, we need to mix 42.8 mL of 0.426 M NaOH and 57.2 mL of 0.5 M acetic acid to prepare 100 mL the desired buffer

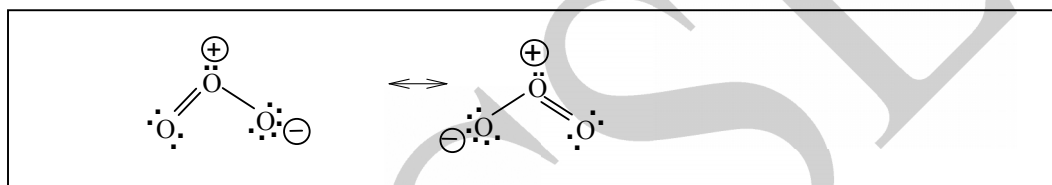
Problem 7

9 marks

7.1



7.2



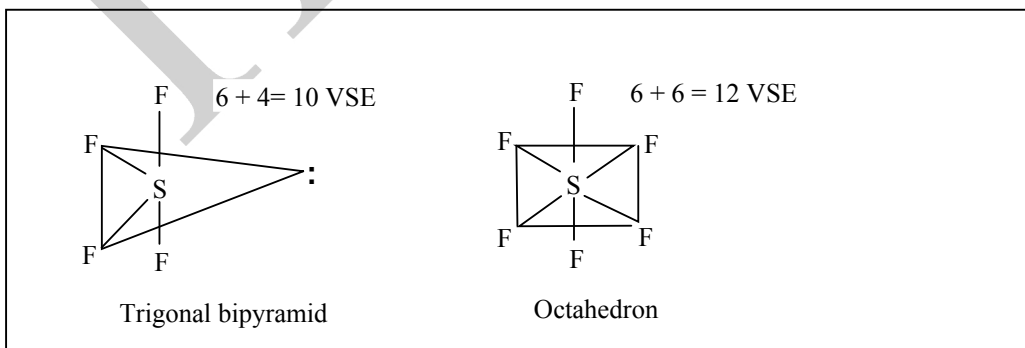
7.3

HCN and O_3 are expected to have a non-zero dipole moment.

7.4

A is energetically most favorable. Oxygen is more electronegative than nitrogen. The structure with negative charge on 'O' is more favorable than the one with negative charge on 'N'.

7.5

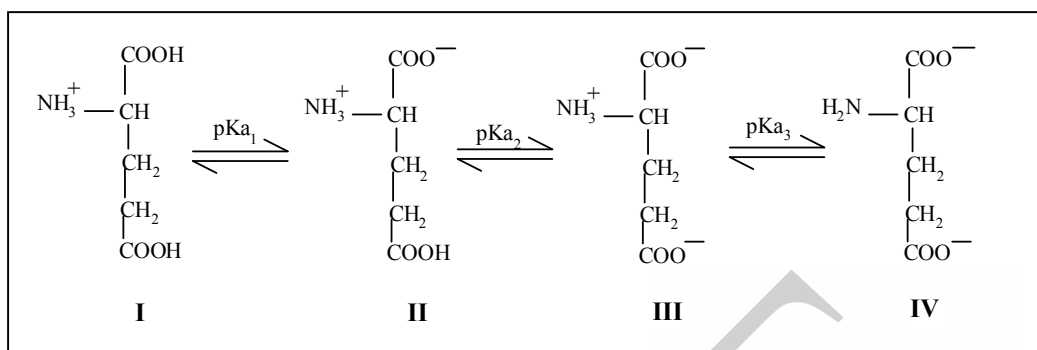


Problem 8

15 marks

Amino Acids and Proteins

8.1



8.2

Isoelectric point (pI) of glycine = $(2.34 + 9.60)/2 = 5.97$

pI of glutamic acid = $(2.19 + 4.25)/2 = 3.22$

pI of glutamic acid is less than glycine since glutamic acid contains an ionizable $-\text{COOH}$ group in the side chain.

8.3

(i) Negatively charged group

Justify your answer.

At pH 3.0, both the amino acids have positive charge. So, negatively charged resins should be used for their separation.

(ii)

The amino acid with lower pI elutes first, that is, glutamic acid in this case.

8.4

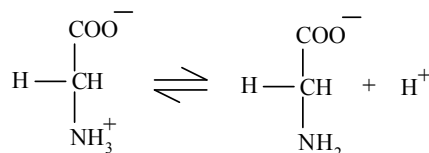
(i) Glycine : 2.34 and 9.60

(ii) Glutamic acid : 2.19, 4.25 and 9.67

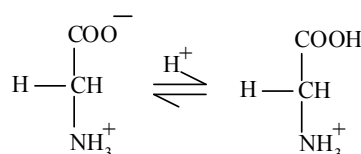
(iii) Neither of the amino acids can act as buffer at pH of 7.4. The buffering region varies by ≈ 1.2 units about the pK_a . For glycine, this region will be 9.6 ± 1.2 and similarly for glutamic acid = 9.67 ± 1.2 .

8.5

As proton donor (acid)



As proton acceptor (base)



- 8.6 (i) At alkaline pH, the side chain -COOH group will be negatively charged.
- Hence repetitive sequence of glutamic acid will have repulsive force destabilizing the α -helical structure.
- Glycine has small side chain with only hydrogen that allows the peptides to have flexibility of assuming multiple conformations hence destabilizes the α -helical structure.
- (ii) Glutamic acid can contribute in formation of the H-bond due to the presence of -COOH group in the side chain.