

CHEMISTRY PAPER - III

Time Allowed : 2 1/2 Hours

Maximum Marks : 200

- Note : 1) Attempt question one and fourteen other questions.
2) Log table is enclosed.

1. Attempt any three of the following 6

A) Deduce the structure from the given data

Mol. formula : C_9H_8O

IR : 1705, 1603, 1450, 750 cm^{-1}

PMR (δ) : 2.6 (2H, t, $J = 6.5$ Hz); 3.1 (2H, t, $J = 6.5$ Hz); 7.4 (3H, m); 7.8 (1H, d, $J = 8$ Hz).

B) Find out the structure of a compound which shows following spectral data : 6

Mass : M^+ at 198 and 200 (equal intensity), 91 (base peak)

IR : 1600, 1500, 750, 700 cm^{-1}

PMR (δ) : 2.1 (2H, quintet, $J = 7$ Hz); 2.7 (2H, t, $J = 7$ Hz); 3.4 (2H, t, $J = 7$ Hz); 7.25 (5H, m)

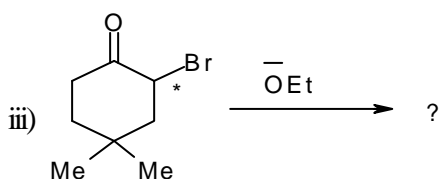
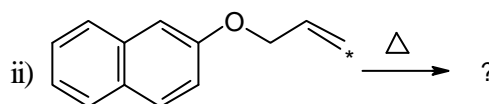
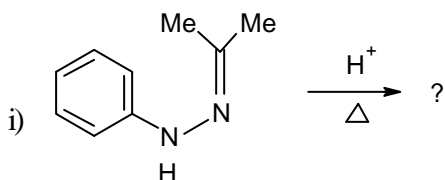
C) The vibrational spectrum of CO gives a strong band around 2143.26 cm^{-1} and a weak one at about 4260.04 cm^{-1} . Calculate the anharmonicity constant x_c . 6

D) Absorption spectrum of a substance shows two maxima at 200 and 400 nm. What is the energy difference, in cm^{-1} , in the two peaks? Which of the peaks corresponds to a higher transition? 6

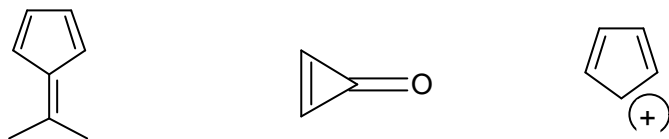
E) The compound $K_4 [Fe(CN)_6] \cdot 3H_2O$ gives single line Mossbauer spectrum with no quadrupole splitting. Explain. 6

F) Show how ESR derivative spectra having three lines can arise by (i) a hyperfine coupling with two nuclei with spin 1/2 and (ii) hyperfine coupling to a nucleus with spin 1. 6

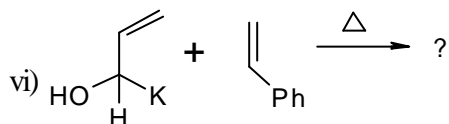
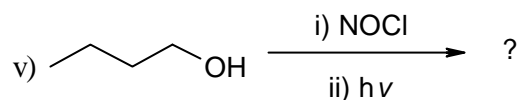
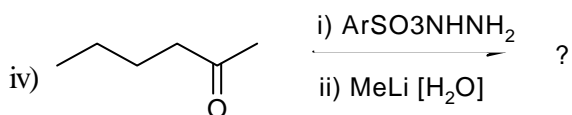
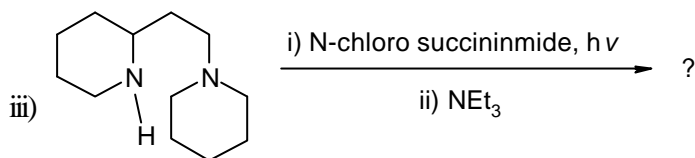
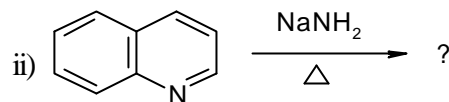
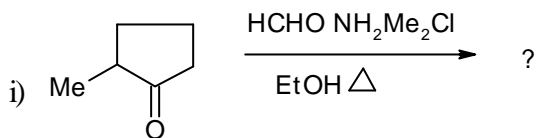
2. A) Predict the product and trace the position of the label in the product. Explain your answer. 7



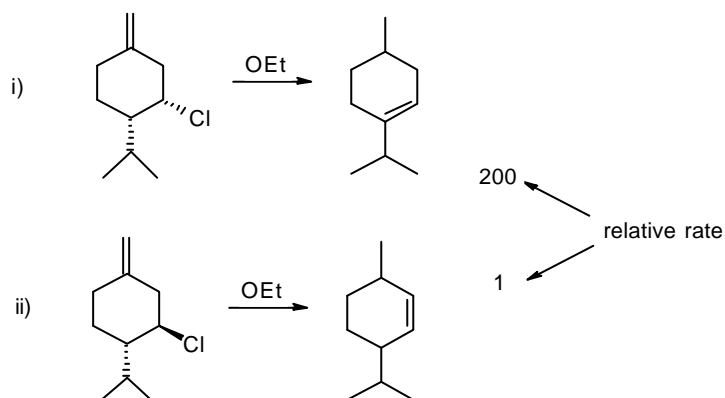
B) Classify the following systems into aromatic and antiaromatic compounds giving reasons : 6



3. Predict the product and name the reaction involved, wherever possible : 13



4. A) Explain the formation of the products and the observed relative rates : 4



B) Account for the difference in rho (ρ) values of the following reactions. 6

- i) Ionization of substituted benzoic acids 1
- ii) Ionization of substituted phenols 2.1
- iii) Ionization of substituted β -phenyl propionic acids. 0.2

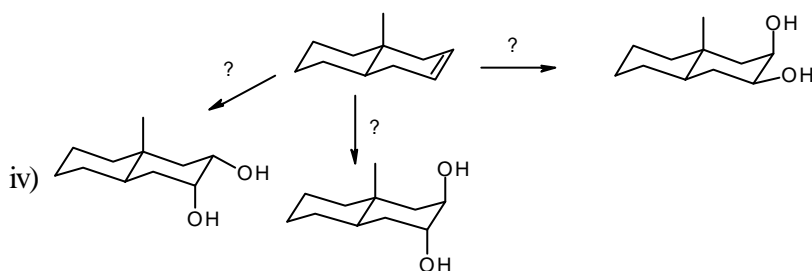
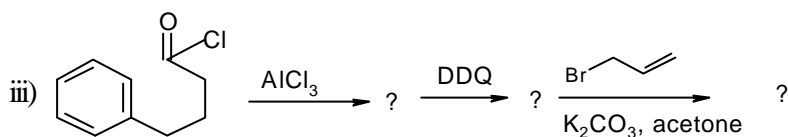
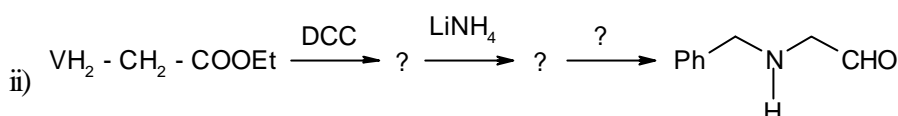
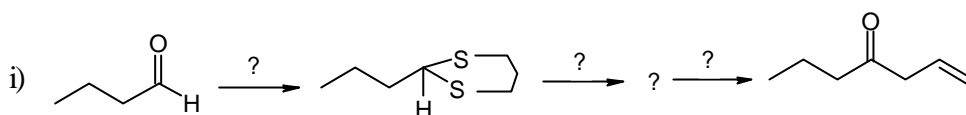
C) Estimate the sigma for p-OH, p-CF₃ and m-C₆H₅ groups, Given that

3

Acid	pK
benzoic acid	4.20
p-hydroxy benzoic acid	4.57
p-trifluoromethyl benzoic acid	3.77
m-phenyl benzoic acid	4.26

5. Complete the following reaction sequences :

13



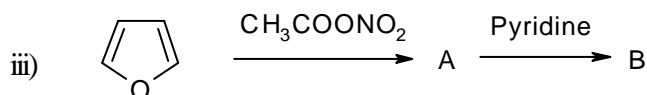
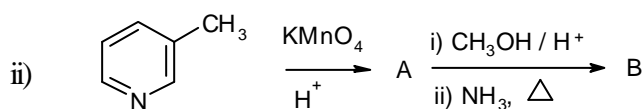
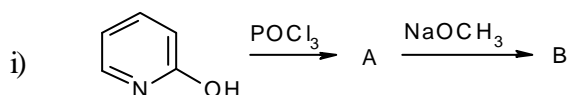
6. A) How will you bring about the following conversions ?

7

- 2,5-hexanedione \longrightarrow 2,5-dimethylpyrrole
- 3-methoxyaniline \longrightarrow 7-methoxyquinoline
- acetophenone oxime \longrightarrow 2-phenylindole

B) Predict the products of the following reactions :

6



7. A) Calculate the weight average molecular weight of a low molecular weight polyvinyl chloride sample having the following composition : 3

No. of monomer units in each molecular species (n)	Weight % of the molecular species
8	35
9	30
10	25
11	10

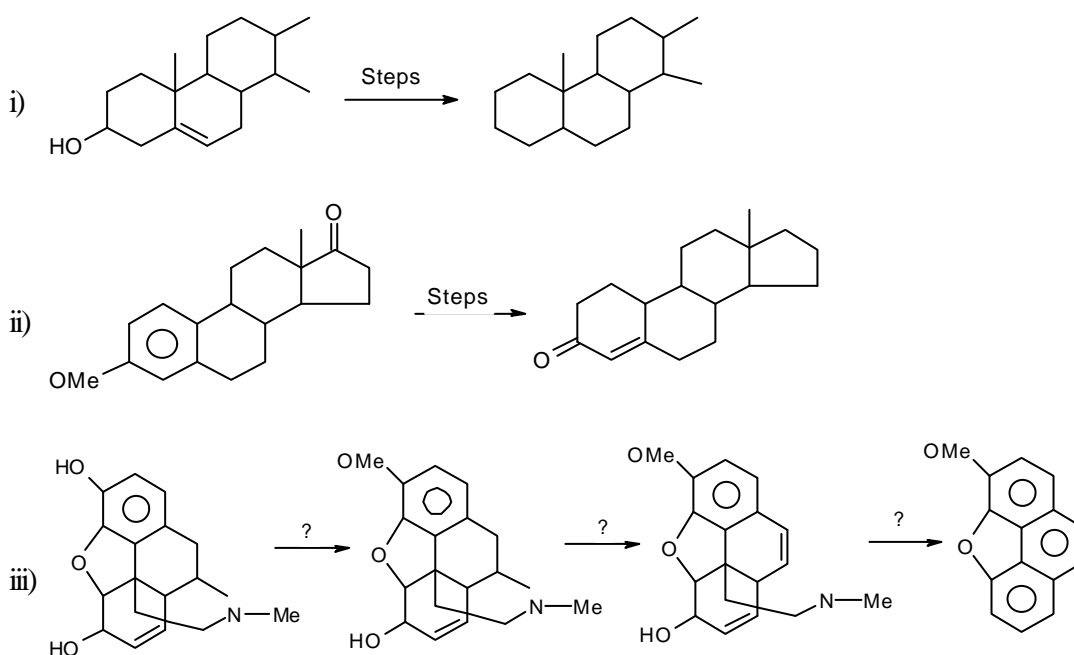
- B) How is polyvinyl alcohol prepared ? 3
 Depict the reactions involved.

- C) Match the following : 7

- | | |
|------------------------|----------------------------------|
| i) Glycolysis | a) Replication |
| ii) Acetyl co-enzyme-A | b) Coenzyme |
| iii) Guanine | c) Energy rich molecule |
| iv) Adenine | d) Fatty acid biosynthesis |
| v) DNA-Polymerase | e) Formation of lactate & ATP |
| vi) NAD | f) H-bonded with thymine in DNA |
| vii) ATP | g) H-bonded with cytosine in DNA |

- | | | | |
|----|-----|------|-----|
| i) | ii) | iii) | iv) |
| v) | vi) | vii) | |

8. A) How will you bring about the following conversions using appropriate reagents / reactions ? 9

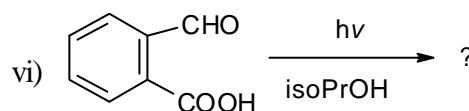
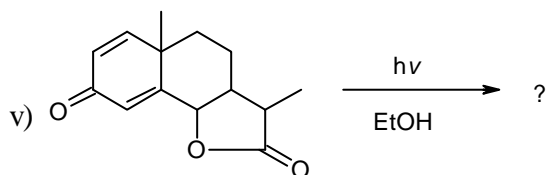
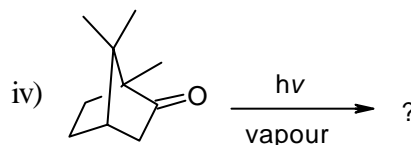
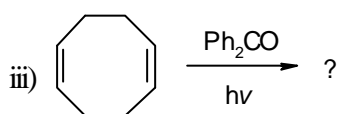
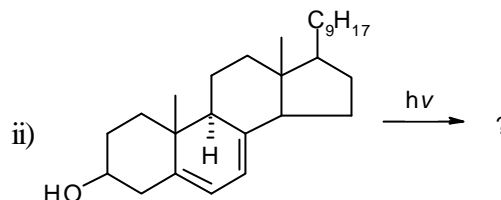
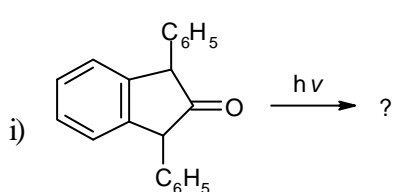


B) Suggest the biogenetic pathway for the following : 6
 Squalene → Cholesterol

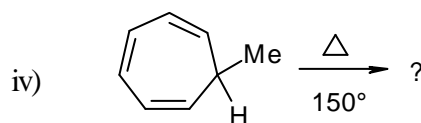
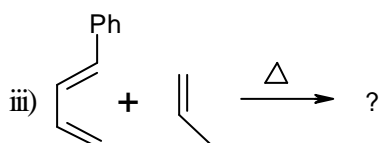
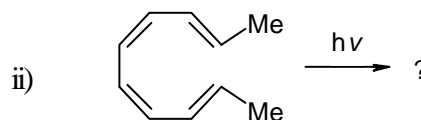
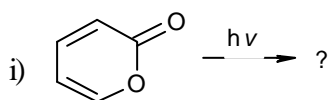
9. A) Propose mechanisms for the following reactions : 9
 i)
 ii)
 iii)

B) With respect to nuclei acids, answer the following : 4
 i) In what way does RNA differ from DNA ?
 ii) Give structures of the pyrimidine and purine bases in nuclei acids.

10. Giving the mechanisms predict the products of the following reactions : 13

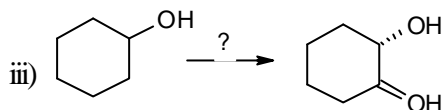
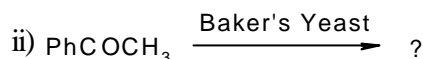
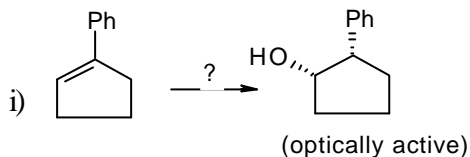


11. In each of the following pericyclic reactions (i) predict the product and its stereochemistry (ii) Name the reaction type and give selection rule : 13



12. A) Complete the following reactions :

6



B) The oxidation of toluene using KMnO_4 in benzene is possibly only if the reaction is carried out in the presence of appropriate crown ether. Give the structure of the crown ether needed and explain its role in the reaction. 3

C) The reaction of aqueous sodium cyanide with 1-chlorooctane is considerably accelerated in the presence of benzyl trimethyl ammonium bromide. Explain. 2

D) How many signals will be exhibited by fullerene (C_{60}) in its CMR spectrum ? 2

13. A) Deduce the structure of a compound based on the following data : 6

Molecular formula : $\text{C}_{10}\text{H}_{15}\text{N}$

IR (cm^{-1}) : 3350 (broad), 1600

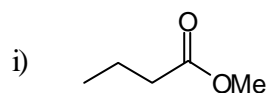
MS (m/z) : 149, 134, 91 (base peak)

PMR (δ) : 1.1 (6H, d, $J = 7$ Hz), 1.5 (1H, bs, exchangeable with D_2O), 2.75 (1H, septet, $J = 7$ Hz), 3.7 (2H, s), 7.25 (5H, s)

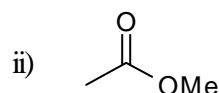
B) A compound shows the following mass spectral fragmentation pattern. Deduce the structure, explaining the formation of ions. 3

MS (m/z) : 121 ($M+1$, 9.9% of M), 120, 105, 77, 51.

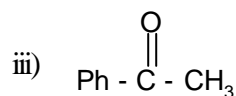
C) Match the following 4



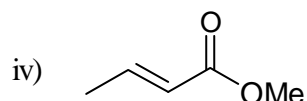
a) Singlet for 3H at (δ) 2.1



b) 1720 cm^{-1}



c) 1750 cm^{-1}



d) m/z 74

14. A) Evaluate the commutators (a, b are constants) 9

i) $\left[\frac{d^2}{dx^2}, ax + b \right]$ ii) $[\hat{x}, \hat{p}_y]$ iii) $[\hat{x}, \hat{x}^2]$

B) Identify “valid” trial function/s for the particle-in-a-box problem with 4

$0 \leq x \leq 1$

i) $C_1 x + C_2 (1 - x)$ ii) $C_1 x (1 - x) + C_2 x^2 (1 - x)^2$
 [C_1, C_2 are constants]

15. Consider the problem of particle of unit mass in cubic box of unit length. 13

List the energy eigenvalues of this system satisfying

$$E \leq \frac{12h^2}{8} = \frac{3h^2}{2}$$

What are the corresponding quantum numbers and degeneracies ?

16. Show that the terms arising from $3d^2$ configuration are : 13

${}^3F, {}^3P, {}^1G, {}^1D$ and 1S

Identify the ground state.

17. A) Identify the diamagnetic species from the following list. 6

Li_2, B_2 and C_2 .

Explain briefly your reasoning.

B) Given the benzene occupied HMO's as 7

$$\psi_1 = \frac{1}{\sqrt{6}} (\phi_1 + \phi_2 + \phi_3 + \phi_4 + \phi_5 + \phi_6)$$

$$\psi_2 = \frac{1}{2\sqrt{3}} (\phi_1 + 2\phi_2 + \phi_3 - \phi_4 - 2\phi_5 - \phi_6)$$

$$\psi_3 = \frac{1}{2} (\phi_2 + \phi_3 - \phi_5 + \phi_6)$$

Calculate bond order P_{12} .

18. A) The rotational spectrum of DCI exhibits lines at 107, 14, 117.81 and 128.26 cm^{-1} . Assign the bands to appropriate J'' to J' transitions. Estimate the vibrational frequency of DCI. 8

B) Consider the uniform expansion and contraction of the benzene ring. Rationalize the IR and Raman activity of this vibration. How many normal modes of vibration does benzene have ? 5

19. A) Write the Clapeyron–Clausius relationship for a solution for which the vapour pressure for the solvent and solution are p_0 and p_1 and the boiling points are T_0 and T respectively. 4
- B) Substitute p_0 and p in the above relation by mole fraction using the Raoult law and show that the elevation in boiling point is given by $\Delta T = \text{const.} \times x_2$ where x_2 is the mole fraction of solute. 4
- C) The equilibrium constant for the reaction $2\text{H}_2\text{O} \rightleftharpoons 2\text{H}_2 + \text{O}_2$ and $2\text{CO}_2 \rightleftharpoons 2\text{CO} + \text{O}_2$ and K_1 and K_2 respectively. Obtain the equilibrium constant K_p for the reaction. 5
- $$\text{CO}_2 + \text{H}_2 \rightleftharpoons \text{CO} + \text{H}_2\text{O}$$
- in term of K_1 and K_2 .
20. A) Draw the phase-diagrams for the following two component systems 9
- The components are completely soluble in solid and liquid phase.
 - The components are completely immiscible in solid phase but soluble in liquid phase.
 - The components form a stable compound and the solid phase are insoluble.
- B) What are the number of phases in the following systems ? 4
- $2\text{Pb}_3\text{O}_4(\text{s}) \rightleftharpoons 6\text{PbO}(\text{s}) + \text{O}_2(\text{g})$
 - $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}(\text{s}) \rightleftharpoons \text{CuSO}_4 \cdot 3\text{H}_2\text{O}(\text{s}) + 2\text{H}_2\text{O}(\text{g})$
21. A) By using the formula for the entropy of mixing, show that entropy always increase on mixing. Find out the concentration at which the entropy of mixing becomes maximum for a two component system. 5
- B) Calculate the change in entropy if 2 mol of N_2 , 3mol of H_2 and 2mol of NH_3 are mixed at constant temperature assuming no chemical reaction is occurring. 8
22. A) What are the assumptions made in deriving the Langmuir adsorption isotherm ? Obtain an expression for the Langmuir isotherm. 8
- B) Identify the symmetry elements of allene. 5
23. A) Among N molecules of an ideal gas n_1 have energy E_1 , n_2 have energy E_2 , and n_L have energy E_L . In how many ways can this distribution be achieved ? Let us represent this number of ways by W . How is W related to equilibrium ? 6
- B) The canonical partition function is defined as $Q = \sum_i e^{-\beta E_i/kT}$. Deduce the formula for the average energy in terms of Q . 7

24. A) The entropy is defined as $S = -k \sum_i e^{-\beta E_i}$ 7

where $P_i = e^{-\beta E_i/Q}$ and $Q = \sum_i e^{-\beta E_i/Q}$

Express S in terms of Q.

B) A collision theory bimolecular rate constant is given by 6

$$K_2 = \sigma N_A \left(\frac{8k_B T}{\pi \mu} \right)^{1/2} e^{-E_a/RT}$$

How does this differ from the Arrhenius reaction rate theory? For k_2 , what is the Arrhenius activation energy?

25. A) For a collinear collision between D_2 and D giving D and D_2 draw a potential energy contour diagram showing a reactive collision in which excess translational energy is converted to product vibrational energy. Indicate the location of the transition state and define the reaction coordinate. 10

B) For the reaction $A \xrightleftharpoons[K^{-1}]{K_1} B$, $K_1 = 10 \text{ s}^{-1}$ and the equilibrium constant is 20. Calculate the relaxation time for the reaction. 3

26. A) Draw all possible isomers of (i) $[\text{Os}(\text{bpy})_2\text{Cl}_2]$ (bpy = 2, 2'-bipyridyl) (ii) $[\text{Cr}(\text{H}_2\text{O})_5\text{Cl}]^{2+}$ and (iii) $[\text{Pt}(\text{NH}_3)_2\text{Cl}_2]$ 8

B) Is $[\text{Co}(\text{en})_3]\text{Cl}_3$ optically active? What is the point group for the cationic part of this complex? Provide the structure of the complex. 5

27. A) Both Ni and Pt belong to the same family of the periodic table. But the complexes $[\text{NiCl}_4]^{2-}$ and $[\text{PtCl}_4]^{2-}$ differ considerably in geometry, colour and magnetism. Using the valence bond theory, rationalize this observation. 8

B) $[\text{Co}(\text{NH}_3)_6]^{2+}$ and $[\text{Co}(\text{NO}_2)_6]^{4-}$ are easily oxidizable. Explain this observation. 5

28. A) Answer the following in brief. 8

i) How would you distinguish between the tetrahedral and octahedral Ni(II) complexes using electronic absorption spectroscopy?

ii) Why $[\text{Mn}(\text{H}_2\text{O})_6]^{2+}$ is pale pink, whereas KMnO_4 is intensely coloured purple?

iii) Among Cu^{2+} , Tl^{3+} , Mn^{2+} (low spin), which ions do not show Jahn-Teller distortion?

iv) Why is it that the intensity of d-d transitions in cis CoL_2X_2 is higher than trans isomer?

(L = Ligand).

- B) Why does that t_{2g} set of orbitals in metal ions remain non-bonding in octahedral complexes of σ -donors ? 5
29. A) Enlist the changes that occur around the Fe(II) ion in hemoglobin and myoglobin during their oxygenation and deoxygenation reactions. Rationalize why these changes have a profound biochemical influence in the case of hemoglobin but not so far myoglobin. 8
- B) Identify two significant biological roles for Fe and Cu, each providing examples. 5
30. A) What is Wilkinson's Catalyst ? Provide the cyclic catalytic mechanism of hydrogenation of olefins using this catalyst. 8
- B) What do you understand by the term "Cluster valence electron count" ? Provide the cluster valence electron count for $Rh_4(CO)_{12}$ and $[Re_4(CO)_{16}]^{2-}$. 5
31. A) Nonezymatic hydration of CO_2 by water proceeds at a rate of $3.5 \times 10^{-3} s^{-1}$ at 293 K whereas the corresponding enzymatic rate is close to $6 \times 10^5 s^{-1}$. Name the enzyme involved in the biological hydration. Give the skeletal diagram of the prosthetic group of the enzyme and also the possible catalytic mechanism involved. 8
- B) Why is it that zinc is not present in the prosthetic groups of those enzymes which are involved in the transport and / or activation of O_2 ?
32. A) Provide the mechanism involved in the base catalysed hydrolysis of $[Co(NH_3)_5 Cl]^{2+}$. 8
- B) What do you understand by the terms 'stoichiometric' and 'intimate' reaction mechanisms ? 5
33. A) Provide the molecular orbital diagram for $Fe(CO)_5$. 8
- B) How is $Fe(CO)_5$ synthesized ? 5
34. A) $BaTiO_3$ (Barium titanate) is heated to $120^\circ C$ when it adopts a perfect cubic structure. What series of phase changes it undergoes on cooling ? 7
- B) How does a plot of $1/x$ versus T look like for 6
- i) paramagnetic ii) ferrimagnetic
- iii) ferromagnetic and iv) antiferromagnetic substances ?
35. A) What is the essential difference between Type I and Type II superconductors ? 7

B) An old wood chair shows 80% of its $^{14}_6\text{C}$ activity today. Calculate the age of the sample. $t_{1/2}$ for $^{14}_6\text{C} = 5770$ yrs). 6

36. A) Define the following terms as applied to chromatography : 8

- | | |
|--|-------------------------------------|
| i) Selectivity factor | ii) Longitudinal and eddy diffusion |
| iii) Retention time and retention factor | iv) Column resolution |

B) Draw an energy level diagram clearly illustrating 5

- | | |
|------------------------|--------------------------|
| i) Internal conversion | ii) intersystem crossing |
| iii) fluorescence | iv) phosphorescence |

37. A) Define the following terms as applied to atomic absorption spectrometry 8

- | | |
|-----------------------|------------------------------|
| i) Releasing agent | ii) Ionization suppressor |
| iii) Radiation buffer | iv) Laminar - flow nebulizer |

B) Differentiate between (i) amperostatic coulometry and potentiostatic coulometry , (ii) kinetic polarization and concentration polarization. 5