

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

A) Assign the structure to compound which exhibits the given data : 6

Mol. formula : C_8H_7OCl

IR : 3000, 1690, 1600, 1500, 830 cm^{-1}

MS : M^+ at 154/156 (3 : 1); 139/141 (3 : 1); 111/113 (3 : 1)

PMR : 2.5 (3H, *s*); 7.35 (2H, *d*, $J = 8Hz$); 7.9 (2H, *d*, $J = 8Hz$).

B) A compound having molecular formula $C_6H_{12}Cl_2O_2$ has the following spectral data. 6

Suggest the structure for it.

IR : 1150, 1240, 670 cm^{-1}

PMR (δ) : 1.2 (*t*, 6H); 3.7 (*q*, 4H); 4.6 (*d*, 1H); 5.6 (*d*, 1H)

C) Classify the following molecules as linear, spherical top and symmetric top.

CO_2 , SF_6 , NH_3 and C_6H_6

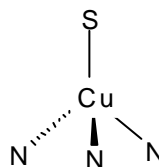
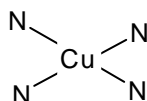
Which of the above will give a pure rotational spectrum ? Why ? 6

D) A compound give two NMR signals having chemical shifts 4.2 ppm and 4.6 ppm. What will be the separation between the signals if the instrument frequency is :

(i) 200 MHz (ii) 500 MHz ? 6

E) $K_3[Fe(CN)_6]$ gives quadrupole split Mossbauer spectrum. Explain. 6

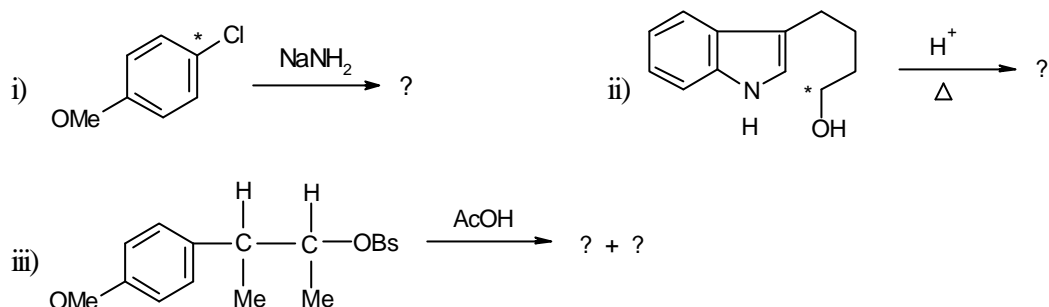
F) Schematic structures of two copper complexes (symbolically shown as) CuN_4 and CuN_3S and two sets of ESR parameters are provided below. Correlate the ESR parameters to the structures and justify your answer.



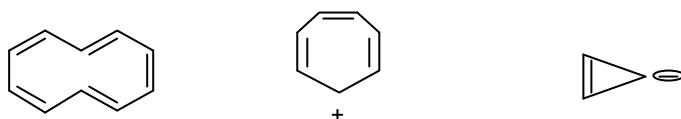
Set 1 : $g_{zz} = 2.2$; $g_{xx} = g_{yy} = 2.0$; $A_{zz} = 200$ G; $A_{xx} = A_{yy} = 40$ G.

Set 2 : $g_{zz} = 2.3$; $g_{xx} = g_{yy} = 2.18$; $A_{zz} = 80$ G; $A_{xx} = A_{yy} = 10$ G.

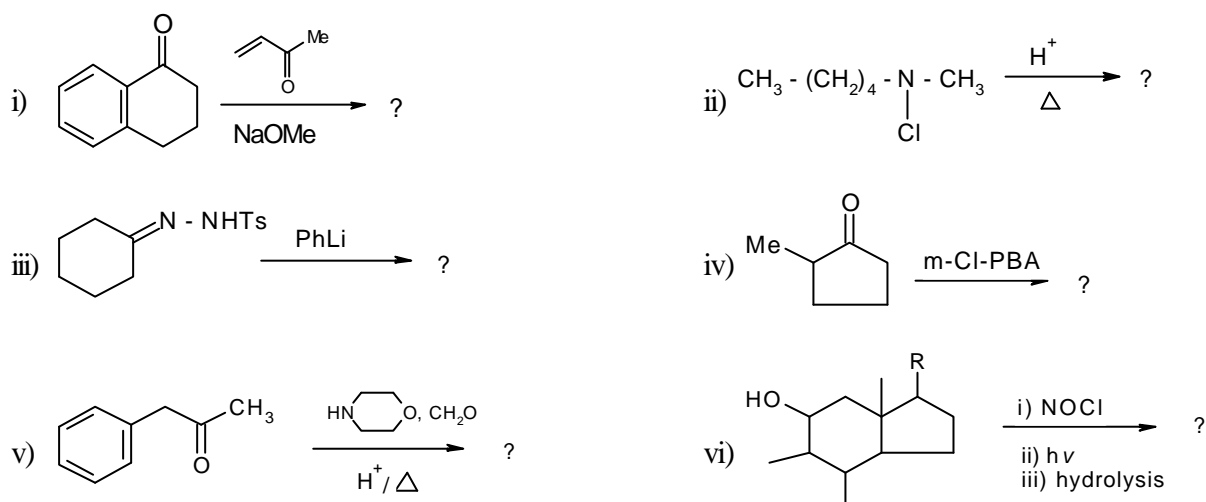
2. A) Predict the product and trace the position of label in the product. Explain your answer : 7



B) Classify the following compounds into aromatic, antiaromatic and non-aromatic compounds giving reasons : 6



3. Predict the product and name the reactions involved. 13



4. A) Meso-1, 2-Dibromo-1, 2-diphenylethane on treatment with a base gives (E)-1-bromo-1,2-diphenylethane, while the dl-pair of the same compound on similar treatment gives the Z isomer of the product. Explain. 4

B) Match the Hammett sigma values with the appropriate substituents. 3

Group	σ
m-N ⁺ Me ₃	0.12
m-SCH ₃	-0.10
p-NMe ₂	0.82
m-OH	0.15

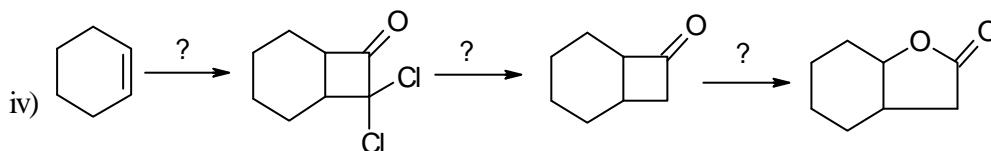
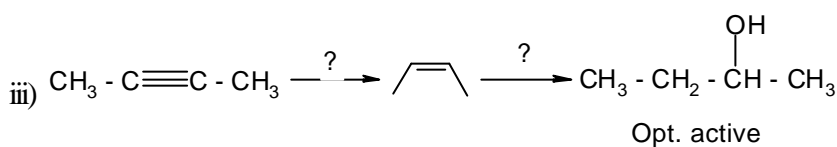
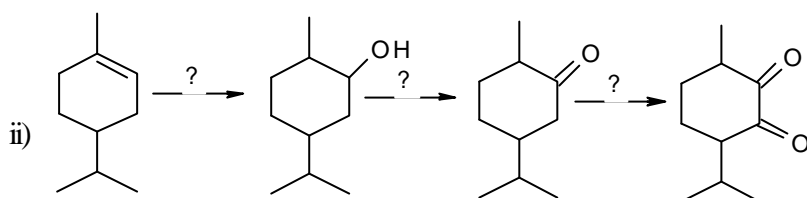
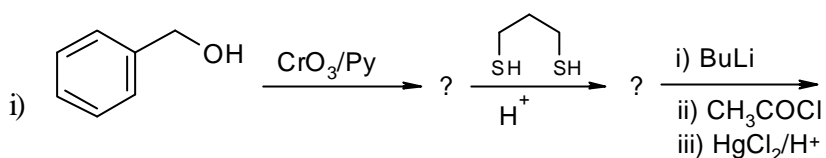
C) Explain the sign and magnitude of rho (ρ) values observed in the following reactions :

6

	ρ
i) Ionization of benzoic acids, H_2O , 25°C	1.0
ii) Ionization of benzoic acids, EtOH , 25°C	1.95
iii) Ionization of triarylmethyl chlorides, SO_2 , 0°C	-3.97
iv) Decomposition of substituted benzoyl peroxides	0.374

5. Complete the following reaction sequences

13



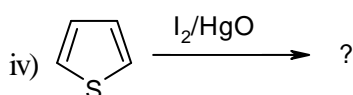
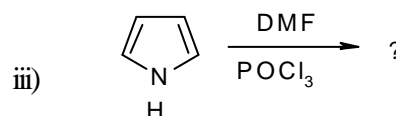
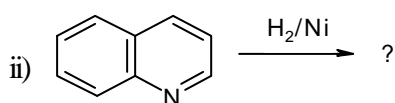
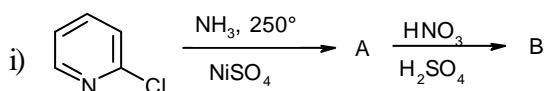
6. A) How will you bring about the following conversions ?

7

- i) 2-Phenyl ethyl amine \rightarrow 1-Phenylisoquinoline
- ii) 2,5-Heptanedione \rightarrow 2-Ethyl-5-methyl furan
- ii) Ethylacetoacetate \rightarrow 2,4,6-Trimethyl pyridine + acetaldehyde

B) Predict the products of the following reactions :

6



7. A) Draw the atactic, syndiotactic and isotactic configurations of polystyrene 3

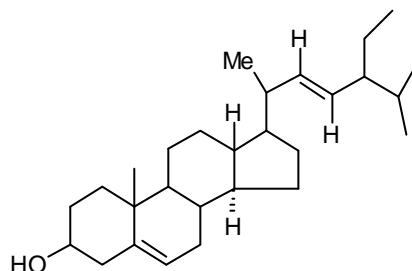
B) Comment on : 'Polyvinyl alcohol does not consume measurable amount of periodic acid or lead tetra-acetate'. 8

C) Match the following : 7

- | | |
|---------------------------------|-------------------------------------|
| i) DNA | a) Coenzyme |
| ii) RNA | b) Solid phase synthesis |
| iii) Enzymes | c) Analysis of amino acids |
| iv) Thiamine pyrophosphate | d) Colour reaction with amino acids |
| v) Chloromethylated polystyrene | e) Genetic information |
| vi) Electrophoresis | f) Proteins |
| vii) Ninhydrin | g) Protein Synthesis |

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

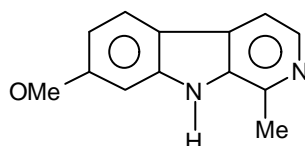
8. A) The following structure has been assigned to a natural product. 9



What data would you collect (Chemical / Spectroscopic) to prove the following ?

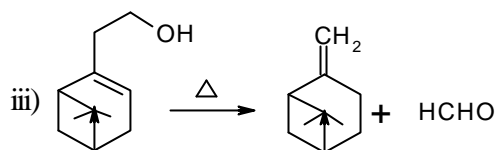
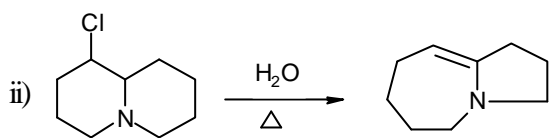
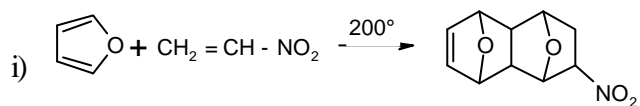
- It is tetracyclic
- Presence of *trans*-double bond in the side chain and a trisubstituted double bond in the ring.
- Presence of a secondary hydroxyl group.
- Presence of isopropyl group, ethyl group, secondary and tertiary methyl groups.

B) Explain the biogenesis of 4



9. A) Propose mechanisms for the following reactions :

9



B)

i) Using solid phase synthesis how will you prepare the following peptide ?

2

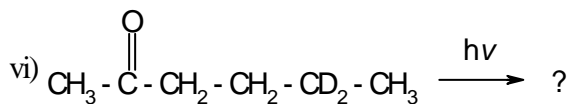
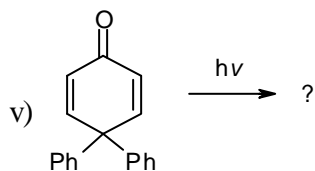
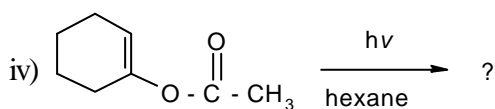
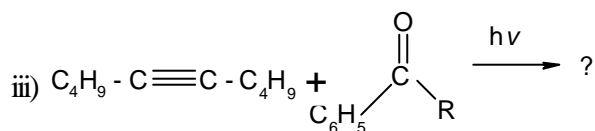
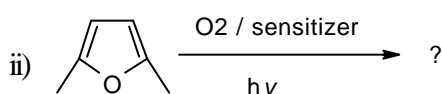
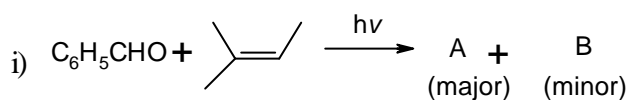


ii) 6-Chloropurine on heating with aq. NaOH gives hypoxanthine. Give the structure of hypoxanthine and write the reaction.

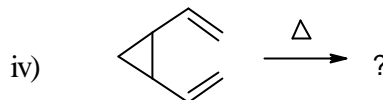
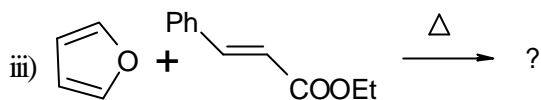
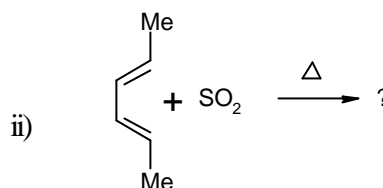
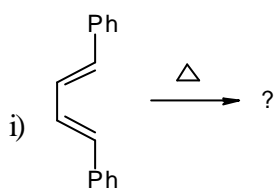
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10. Giving the mechanism predict the products of the following reactions :

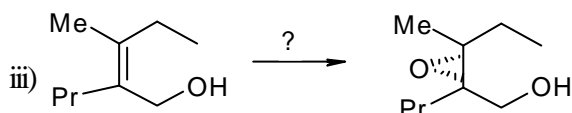
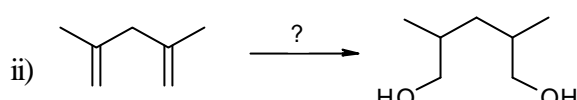
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11. In each of the following reactions (i) Predict the product and its stereochemistry, (ii) Name the reaction type and give selection rule. 13



12. A) Complete the following reactions : 6



- B) Draw the structure of 12-Crown-4. The reaction of 1-bromooctane with KF in benzene takes place only in the presence of 18-Crown 6. Explain. 3

- C) The reaction of n-butyl bromide with aq-sodium cyanide is greatly facilitated in the presence of benzyl trimethyl ammonium bromide. Explain. 2

- D) What is fullerene ? How many pentagons and hexagons does it contain ? 2

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

Molecular Formula : $C_{12}H_{16}O_3$

IR : 1742, 1600, 1250 cm^{-1} .

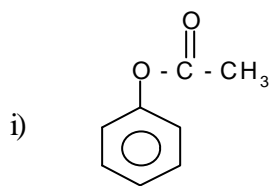
PMR (δ) : 1.83 (2H, quintet, $J = 7Hz$); 2.2 (2H, t , $J = 7Hz$); 2.53 (2H, t , $J = 7Hz$); 3.6 (3H, s); 6.7 (2H, d , $J = 8 Hz$); 7.0 (2H, d , $J = 8Hz$)

- B) A ketone $C_6H_{12}O$, shows the following Mass Spectral data. Deduce the structure and explain the formation of ions. 3

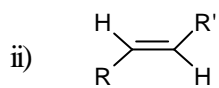
MS (m/z) : 100, 85, 72, 57, 43 :

C) Match the following :

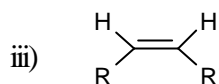
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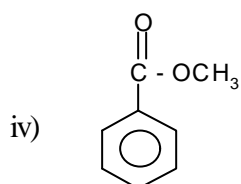
a) $J = 8 \text{ Hz}$



b) 1710 cm^{-1}



c) 1775 cm^{-1}



d) $J = 16 \text{ Hz}$

i)

ii)

iii)

iv)

14. A) State the results for the following commutators :

6

i) $[\hat{x}, \hat{p}_x]$

ii) $[\hat{L}_x, \hat{L}_y]$

iii) $[\hat{L}^2, \hat{L}_x]$

(Do not derive)

B) Show that $f(x) = 32e^{3x}$ is an eigenfunction of $\frac{d^2}{dx^2}$.

What is the corresponding eigenvalue ?

7

15. A) Make qualitative sketches of the hydrogenic functions R_{2p} and R_{3p} .

$$R_{2p} = re^{-r/2}$$

$$R_{3p} = (6 - r) re^{-r/3}$$

(r is measured in a.v.)

6

B) What is the degeneracy of the level of hydrogen atom with energy $-R_H/9$

What is the corresponding ionization potential in eV ?

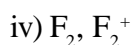
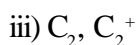
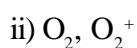
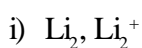
7

16. Work out the table of microstates and derive the term symbols for the $3d^1 s^1$ configuration. Identify the ground state.

13

17. A) Which species in each pair given below is expected to have higher dissociation energy ? Why ?

8



- B) CF_4 is planar, but XeF_4 is tetrahedral. Explain on the basis of VSEPR theory. 5
18. A) Distinguish between photoelectron spectroscopy, X-ray fluorescence and Auger spectroscopy. 6
- B) List the assumptions made in obtaining the Langmuir isotherm. State the final result and sketch it as a function of pressure. 7
19. State the third law of thermodynamics. What do you understand by the terms third law entropies and residual entropy? Two compounds N_2 and CO are heated from 0 K to 300 K. Write down the formula for calculating the third law entropies for these two. N_2 exhibits two phase transition in the solid state at T_1 and T_2 K. 13
20. A) Give the Debye–Huckel limiting law for activity coefficients for electrolytes in the form of final expression (without derivation) and explain the terms appearing therein. 6
- B) Calculate the ionic strength of a solution containing 50 ml of 0.2 M KNO_3 , 20 ml of 0.10 M K_2SO_4 and 30 ml of 0.05 M $\text{Cu}(\text{NO}_3)_2$. 7
21. A) How is the free energy of a chemical reaction between ion in aqueous solutions is connected to the standard e.m.f. of the electrochemical cell? 4
- B) The free energy of formation of liquid water at 298 K is $-237.2 \text{ kJ mol}^{-1}$ and the free energy of ionization of liquid water to hydrogen and hydroxyl ions is 97.7 kJ mol^{-1} . Calculate the reversible e.m.f. the cell $\text{H}_2(1 \text{ atm}) | \text{H}^+ || \text{OH}^- | \text{O}_2(1 \text{ atm})$.
Given value of Faraday $F = 96500 \text{ C}$. 9
22. A) Explain the terms physisorption and chemisorption. What is the difference in types of atomic / molecular forces involved in these two phenomena? How would you distinguish between these two types by simple thermal measurements? 8
- B) The following molecules get adsorbed on activated charcoal. CH_4 , H_2 , C_2H_4 , CO and NH_3 .
Arrange the molecules in the order of increasing enthalpies of adsorption. 5
23. A) For N molecules of an ideal gas, the weight W of a distribution is defined as the number of ways in which n_1 molecules can take on energy E_1 , n_2 can take on energy E_2 and finally n_L can take up energy E_L . How is W related to N and n_i ? How is W maximized? What are the constraints to which this maximization is subject to? 6

- B) The molecular partition function for translation is $q = \left[\frac{2\pi m}{h^2 \beta} \right]^{3/2} V$ and the entropy for N molecules is given by $S = U_{av}/T + Nk \ln q - k(N \ln N - N)$, Where E_{av} is the average energy of N molecules and k is the Boltzmann constant, $\beta = 1/kT$ and so on. Express S in terms of T , V and N . 7
24. A) Water has three normal modes of vibration with wave numbers about 3600, 3700 and 1600 cm^{-1} . What is the total vibrational partition function when $kT = 200 \text{ cm}^{-1}$? What is the temperature corresponding to this value of kT ? 7
- B) For a reaction $X \xrightleftharpoons[k_{-1}]{k_1} Y$, $k_1 = 1 \text{ s}^{-1}$ and $k_{eq} = 3$. What is the relaxation time for this process? How does temperature affect this relaxation time? 6
25. A) The transition state theory rate constant is given by $k = k \frac{RT}{p^0} \frac{k_B T}{h} e^{-\Delta G^\ddagger / RT}$. How is the activation entropy for the reaction expressed in terms of the rate constant? What does $k(\kappa)$ represent? 7
- B) The vapour phase reaction for a given collision of NaCl and KBr giving NaBr and KCl is completed in 5 ps. Illustrate graphically how the distances r_{NaCl} , r_{NaBr} , r_{KCl} and r_{KBr} change with time. Here, r_{AB} is the distance between A and B. 6
26. A) $(\text{CH}_3)_2\text{N}-\text{PF}_2$ has two basic atoms, P and N. One is bound to B in a complex with BH_3 and the other to B in a complex with BF_3 . Decide which is which and state your reason. 5
- B) Arrange the oxides CO_2 , B_2O_3 , Al_2O_3 and SO_3 in order from the most acid to most basic. 4
- C) Pauling electronegativities of H, B, Al, Ga are 2.20, 2.04, 1.61 and 1.81 respectively. What is the trend in hydridic character of $[\text{BH}_4]^-$, $[\text{AlH}_4]^-$ and $[\text{GaH}_4]^-$? Which is the strongest reducing agent. Why? 4
27. A) Answer the following in brief: 8
- Will π -back bonding increase or decrease the $t_{2g} - e_g$ energy difference?
 - What is the effect of tetragonal compression on the e_g orbitals of an O_h complex.
 - How does Racah parameter of a complex ion differ from that of the corresponding free ion?
 - What are the Crystal field stabilization energies (CFSE) of Co^{2+} ion in strong field and weak field O_h environments?

- B) Rationalize the fact that Δ_0 (or Dq) increases in the order : 5
- $$[\text{Cr}(\text{H}_2\text{O})_6]^{2+} < [\text{Co}(\text{H}_2\text{O})_6]^{3+} < [\text{Rh}(\text{H}_2\text{O})_6]^{3+}$$
28. A) Is the bridging ligand transfer a prerequisite for the inner sphere electron transfer reactions involving the transition metal complexer ? Comment. Illustrate your answer with a suitable example. 8
- B) Write down the structure of $[(\text{NH}_3)_5\text{Ru}-\text{pyz}-\text{Ru}(\text{NH}_3)_5]$ (pyz = pyrazine). What is the oxidation state of the metal center in this complex and what is the origin of its absorption band at approx. 1570 nm in aqueous solution ? 5
29. A) What do you understand by the term "Lanthanide contraction" ? What are its consequences ? 8
- B) What are the essential differences between the electronic spectral properties of transition and lanthanide metal complexes. 5
30. A) Write short notes on : 8
- Ferritin and
 - Transferrin
- B) Why is Superoxide considered cytotoxic ? What enzyme is involved in the destruction of this reaction oxygen species in the body ? Write a skeletal diagram of the prosthetic group of the enzyme. 5
31. A) What are the main assumptions of Crystal field theory ? What are Δ_0 and B ? How does Δ_0 vary with oxidation state of the metal ion ? How does B in a free ion compare with that in a complex? ($\Delta_0 = 10 \text{ Dq}$ is the Crystal field splitting energy and B = Nephelauxetic ratio). 8
- B) Calculate (in units of Dq or Δ_0) octahedral site preference energy for a d^4 ion in its high spin configuration. 5
32. A) Name, draw the structure and provide a method of preparation each of (a) ferrocene and (b) $\text{Cr}(\eta^6-\text{C}_6\text{H}_6)_2$. 8
- B) Although oxygen is more electronegative than carbon, why does carbon get attached to metals in metal carbonyls ? 5
33. A) What are fluxional molecules ? Give two examples of fluxional molecules. Illustrate the usefulness of NMR spectroscopy in the study of fluxionality of organometallic compounds. 8
- B) The complex $[\text{Cr}(\text{CO})_4(\text{P}(\text{O} \phi)_3)_2]$ has one IR absorption band in the CO stretching region. What is its structure ? 5

34. A) Discuss the ionic conductivity of KCl doped with SrCl_2 . 7
- B) Discuss the mechanism involved in sulphidisation of silver. 6
35. A) Explain the segregation mechanism in the purification of solid state materials. 7
- B) Calculate half life period of a nucleus if at the end of 16.2 days 20% of it has disintegrated. 6
36. A) Define the following terms : 8
- i) Coulometric titration;
 - ii) Controlled-cathode-potential electrolysis;
 - iii) Cathode depolarizer;
 - iv) Hydrodynamic voltammetry.
- B) Mention the differences between the following and list any particular advantage possessed by one over the other :
- i) H_2 -discharge lamp and D_2 -discharge lamp as sources for ultraviolet radiation;
 - ii) Phototubes and photomultiplier tubes. 5
37. i) List the factors that lead to zone broadening in chromatography.
- ii) List the desirable characteristics of HPLC-detectors.
- iii) How can the limit of detection of atomic absorption spectrometry be increased by hydride generation technique ? 13