

CHEMISTRY SCIENCE PAPER - III**Time Allowed : 2 1/2 Hours****Maximum Marks : 200**

Note : (i) Attempt Question No. 1 and Fourteen other questions.
(ii) Log table is enclosed.

Q.1. Attempt any three of the following.

(A) Deduce the structure of a compound based on the following data : [6]

Molecular formula : $C_{12}H_{16}O_2$
I. R. : 1740, 1602, 1510, 1170, 760, 690 cm^{-1}
M. S. (m/z) : 192 (M^+), 119, 77, 43
P. M. R. (δ) : 1.45 (6H, S), 1.98 (3H, S), 4.1(2H, S) 7.25 (5H, S)

(B) Assign structure to a compound based on the following data : [6]

M.S. : 148 (M^+), 91 (100%), 65, 57, 51
U. V. : 260 (200), 210 (7500)
I. R.(cm^{-1}) : 1601, 1510, 740, 695
P. M. R.() : 0.90 (3H, t, $J = 7$ Hz), 1.30 (4H, m),
1.60 (2H, quintet, $J = 7$ Hz),
2.60 (2H, t, $J = 7$ Hz), 7.22 (5h,S)

(C) A solution of H_2O in isopropyl alcohol on photolysis results in formation of a free radical.

Its esr spectrum consists of seven lines. Which radical is responsible for the hyperfine spectrum ? what should be the intensity ratio of those lines ?

Given : ^{12}C ($I = 0$), 1H ($I = 1/2$) [6]

(D) Explain Zeeman effect on Mossbauer spectrum of ^{57}Fe compound with one example. [6]

(E) The rotational constant for ^{12}C ^{16}O is 1.9211 cm^{-1} , obtain the rotational constant for ^{13}C ^{16}O . [6]

(F) Consider the nucleus ^{19}F for which $g_n = 5.256$, what is the resonant frequency in flux density of exactly 1 T (nuclear magneton = 5.051×10^{-27} JT $^{-1}$) ? [6]

Q.2. (A) What is the significance of ρ^- σ_m^- ? Match the ρ^- σ_m^- values given below with the substituents. [5]

<u>Substituent</u>	ρ^- σ_m^-
(a) NO_2	(i) - 0.39
(b) OCH_3	(ii) - 0.28
(c) F	(iii) 0.11
(d) CF_3	(iv) 0.07

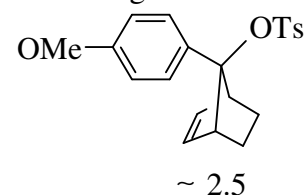
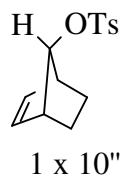
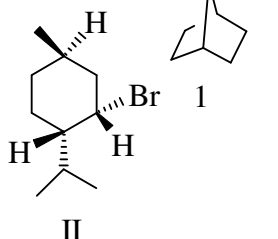
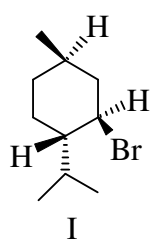
(B) Match the ρ^- σ_m^- values given below with the appropriate substituents. [4]

ρ^- σ_m^- : 0.70; 1.76; -0.07; 0.21

substituent : m - NHCOCH_3 ; m - IO_3 ; m - CH_3 ; m - [4]

(C) Account for the difference in the rates of acetolysis of following tosylates? [4]

Q.3. (A) a) What is the relation between I and II? Select your answer from the alternatives given below :



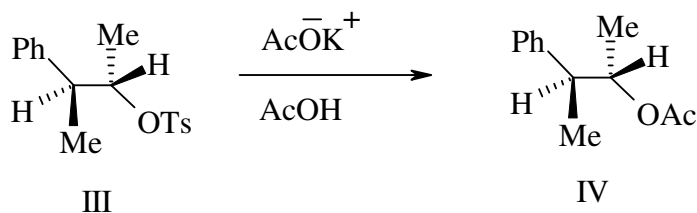
(i) identical (ii) enantiomers (iii) diastereomers (iv) conformational isomers
(v) constitutional isomers [1]

b) Draw their conformational structures in the most stable form. [2]

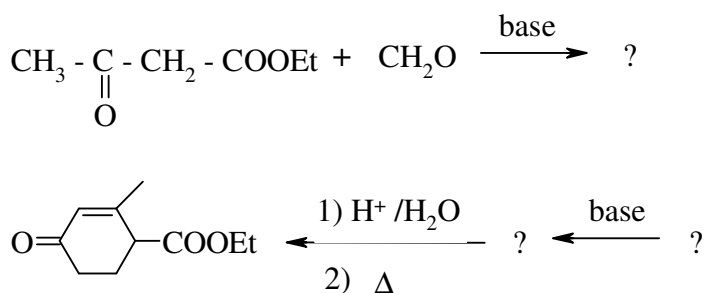
c) Both I and II undergo elimination of HBr on treatment with sodium ethoxide in ethanol. Write the stereostructures of the products formed in each case. [2]

d) Which will react faster and why? [2]

- (B) Solvolysis of the tosylate III in the presence of potassium acetate and acetic acid gives the corresponding acetate IV with retention of configuration. Explain with mechanism and stereochemistry. [6]

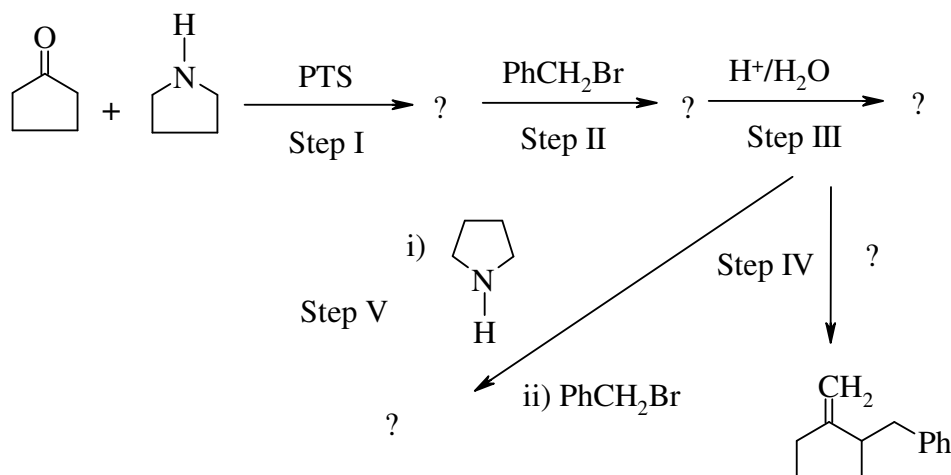


- Q.4. (A) Complete the following sequence of reactions by filling the gaps and answer the questions given below. [7]



- Name the reactions involved in all steps.
- Name the overall synthetic sequences.
- Explain the selectivity observed in the last reactions.

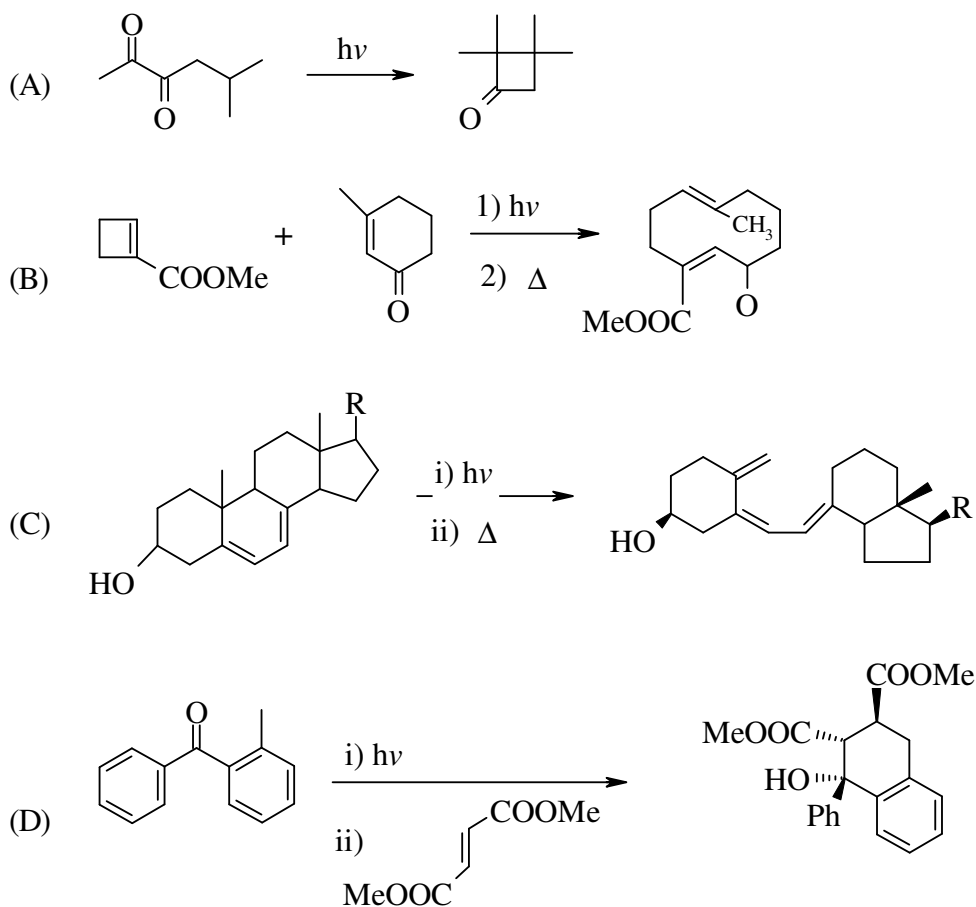
- (B) Complete the following sequence by giving missing structures or missing reagents. Answer the questions below : [6]



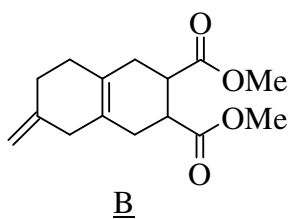
- What strategy is used in the first step.
- Name the reactions involved in step II and step IV.

Q.5. Indicate the type of the reaction and mechanism involved in each step of the following transformations.

[13]

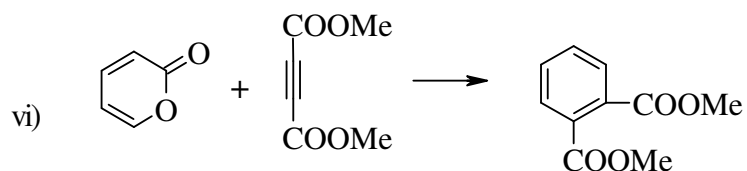
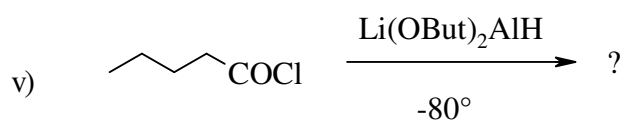
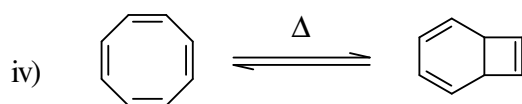
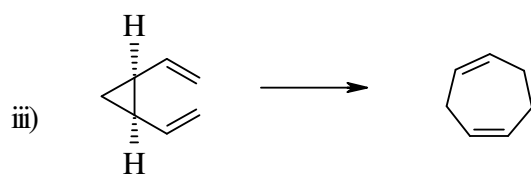
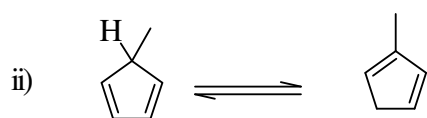
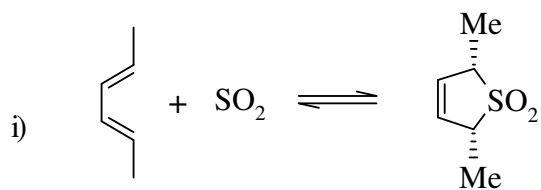


Q.6. (A) Allene ($\text{CH}_2 = \text{C} = \text{CH}_2$) can be converted to a trimer A of molecular formula C_9H_{12} . A reacts with dimethyl acetylene dicarboxylate to give B.

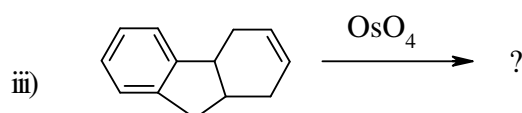
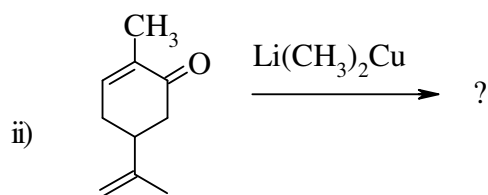
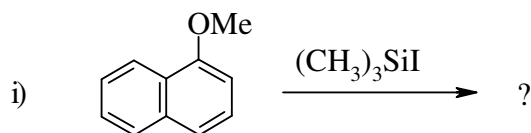


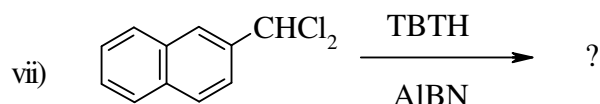
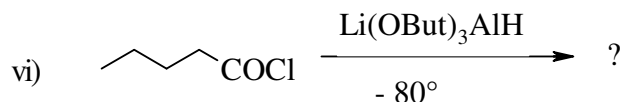
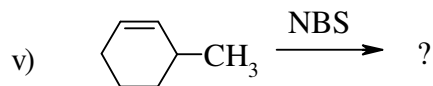
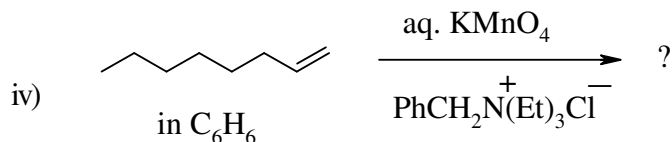
- Write the sequence of reactions along with the structure of compound A.
- Indicate the mechanism of trimer formation.
- Give the name and type of the second reaction.

- (B) Name the pericyclic reactions involved in the following transformations indicating the number of electrons involved and if applicable the rotation type for the reaction. [8]



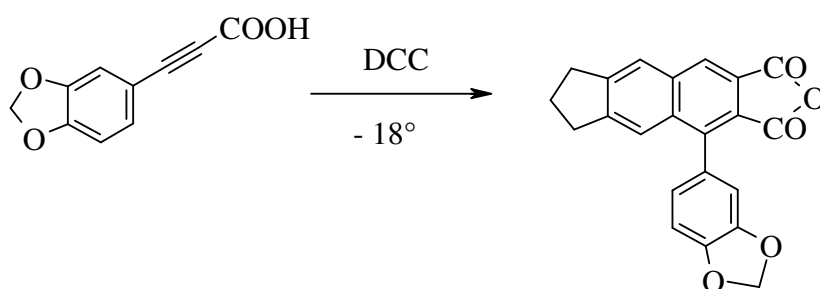
- Q.7. (A) Give products of the following reactions. [7]



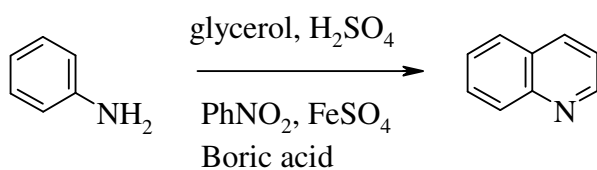


(B) Give reagent to convert maleic acid to (2R, 3S) - tartaric acid. [3]

(C) Explain the following transformation. [3]



Q.8. (A) Following is synthesis of quinine by Skraup method. [9]

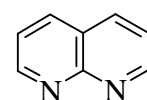


i) Give mechanism of formation of acrolein from glycerol. Why acrolein is not used instead of glycerol?

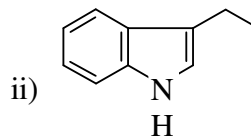
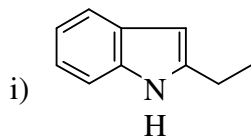
ii) Give function of nitrobenzene, FeSO_4 & boric acid.

iii) What products will be obtained if

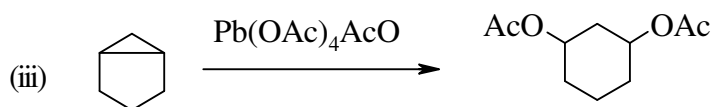
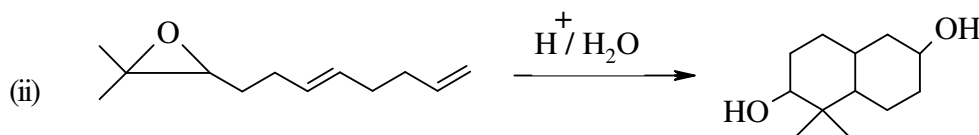
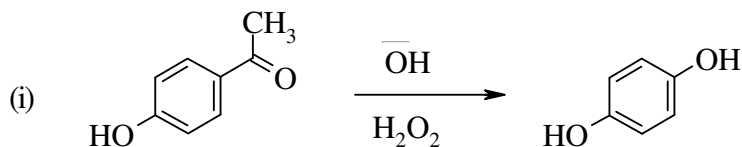
a) $\text{CH}_3\text{CH}=\text{CH}-\text{CHO}$ b) $\text{CH}_3-\text{CO}-\text{CH}=\text{CH}_2$ are used instead of glycerol?

iv) Write starting material for the formation of 

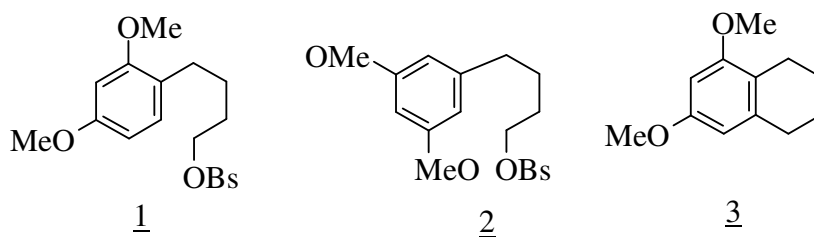
- (B) Write the structures of the starting materials required for the synthesis of following using Fischer indole method. [4]



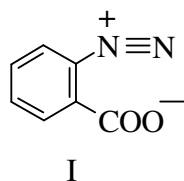
- Q.9. (A) Propose the mechanism for the following conversions and name the reaction involved. [6]



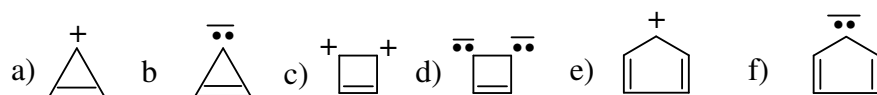
- (B) The solvolysis of 1 and 2 gives tetralin 3. Formulate the mechanism. [4]



- (C) When (I) was subjected to flash discharge in the mass spectrum peaks were observed at 28.44 and 76. The peak at 76 disappeared and a peak at mass 152 appeared. Account for all peaks and explain why peak at 76 vanishes with time. [3]



- Q.10. (A) Which of the following are aromatic and which are not aromatic? [3]

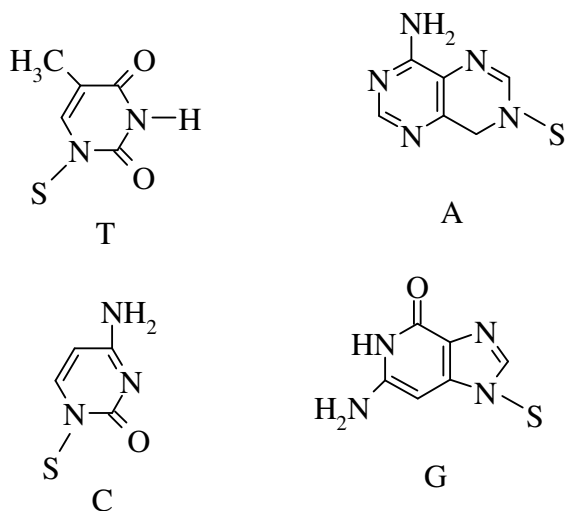


(B) a) What is the state of hybridization of the carbon atoms in C₆₀ fullerene? [1]

b) How many signals will be observed in the ¹³C NMR spectrum of C₆₀ fullerene? [1]

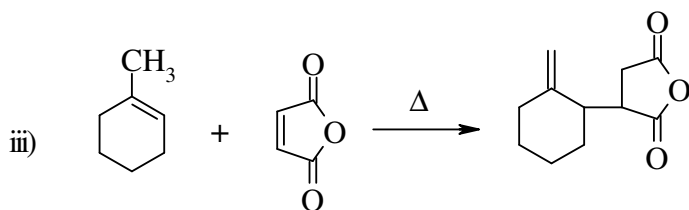
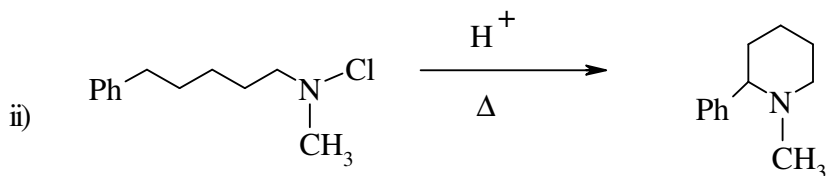
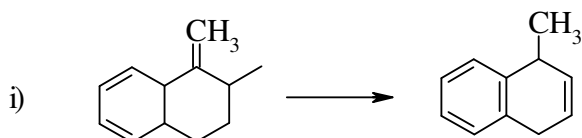
(C) Draw the structure of [10]annulene and explain why this compound is not aromatic. [2]

(D) Show hydrogen bonds in adenine - thymine and cytosine - guanine bases. [3]

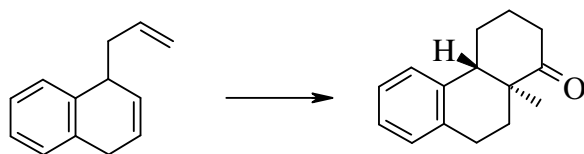


(E) Indicate 3 main differences between DNA and RNA. [3]

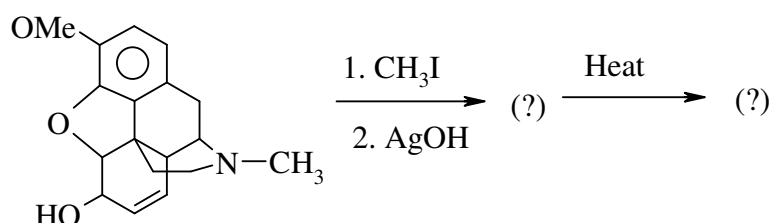
Q.11. (A) How can the following transformation be effected? Identify the steps. [9]



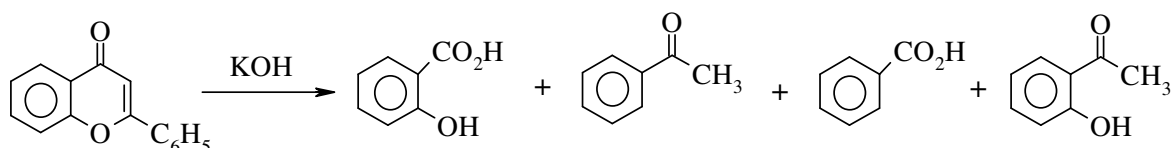
(B) How will you achieve following conversion ? Name the reactions involved. [4]



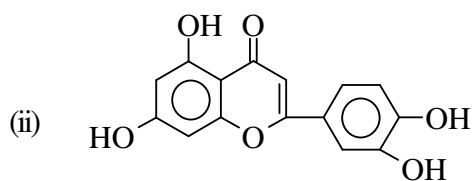
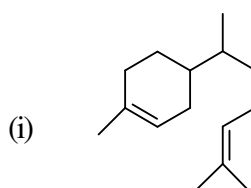
Q.12. (A) Write the structures of the products in the following transformations. [4]



(B) Explain with mechanism the formation of following products from flavone. [4]



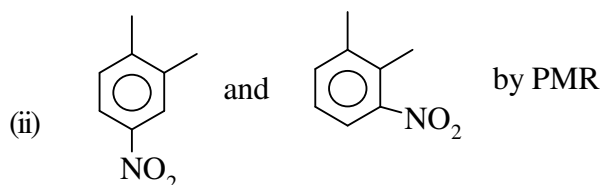
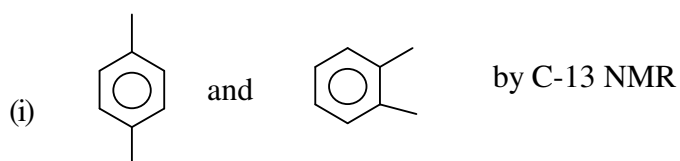
(C) Explain the biogenesis of following. [5]



Q.13. (A) Deduce the structure of a compound based on the following data : [7]

Molecular formula	: $C_{12}H_{18}ON_2$
I. R. (cm^{-1})	: 3430, 1660, 1602, 1540, 762, 672
M. S. (m/z)	: 206 (m^+), 135, 120, 92, 77
P. M. R. (d)	: 1.22 (6H, t, $J = 6.5$ Hz), 3.25 (4H, q, $J = 6.5$ Hz), 4.22 (2H, s), 7.30 (5H, m), 8.2 (1H, s, exchange with D_2O).

(B) How will you distinguish the following compounds by the indicated spectral method? [6]



Q.14. (A) What are the hermitian operators? Prove that the product of two hermitian operators is hermitian if they commute. [8]

(B) Obtain the expression for the sp hybrid orbitals. Sketch these orbitals qualitatively. [5]

Q.15. (A) For butadiene the Huckel MOs are given as.

$$\begin{aligned} \psi_a &= 0.3755 (\psi_1 + \psi_4) + 0.6070 (\psi_2 + \psi_3) \\ \psi_b &= 0.3755 (\psi_1 - \psi_4) - 0.6070 (\psi_2 + \psi_3) \\ \psi_c &= 0.6070 (\psi_2 + \psi_4) - 0.3755 (\psi_1 - \psi_3) \\ \psi_d &= 0.6070 (\psi_1 - \psi_4) - 0.3755 (\psi_2 - \psi_3) \end{aligned}$$

Sketch qualitatively these MOs. State the energy rank-order for the same. [8]

(B) What is the degeneracy of energy levels? Determine the degeneracy of the level ma^2 where a denotes the box length. [5]

Q.16. (A) Explain in brief the first order non degenerate perturbation theory. [5]

(B) For the anharmonic oscillator with [8]

Estimate the first order correction to the ground state energy.

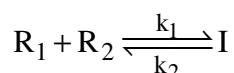
[Given the normalized wavefunction for the ground state of harmonic oscillator is :

$$\psi_0(x) = \left(\frac{\alpha}{\pi}\right)^{1/4} e^{-\alpha x^2/2}$$

Q.17. (A) Heisenberg uncertainty principle is by far the most important in governing the line-widths of nmr and esr spectra and are of relatively less important in the electronic spectra .
Why ? [7]

(B) What are fast reactions ? Explain in brief the underlying principle of field-jump method for determining the rates of fast reactions. [6]

Q.18. (A) What is steady hypothesis ? In the following reaction mechanism. [8]



Where I denotes the reaction intermediate. Derive the rate law.

(B) What are the potential energy surfaces ? Sketch qualitatively the curves for the $H + H_2$ reaction assuming the atoms are collinear. Depict the MEP in this. What can you infer from the saddle point [5]

Q.19. (A) Match the entries in column A from those given below in B. [7]

Column A

- 1) Birge sponer extrapolation
- 2) Heisenbergs uncertainty principle
- 3) Bohr's Magnetons
- 4) Molar polarization
- 5) Saxens Relations
- 6) Composition of liquid phase and partial vapour pressure data
- 7) Molecular beam method

Column B

- I $\xrightarrow{k_2}$ P
-
-
-
-
-
-

Column B

- 1) Verification of distribution law
- 2) Electrokinetic potentials
- 3) Debye
- 4) Life-time of the species during spectral transitions
- 5) Detection of free radicals by ESR method
- 6) Dissociation energy
- 7) Crompton effect
- 8) Gibbs-Duhem effect
- 9) Distillation

- (B) XeF_4 molecule belongs to D_{4h} point group. Show that the reflection σ_{xy} is equivalent to a two fold rotation about z - axis followed by inversion. [6]
- Q20. (A) What are the partial molar quantities ? State Gibbs-Duhem equation. Explain its utility. [8]
- (B) Calculate the activity of water and its activity coefficient from the following data for the vapour pressure of water at different sucrose molality (at 298 K) [5]
- | | | | | |
|----------------------------------|-------|-------|-------|-------|
| m (sucrose)mol. kg ⁻¹ | 0 | 0.2 | 0.5 | 1.00 |
| P/Torr | 23.75 | 23.66 | 23.52 | 23.28 |
- Q.21. (A) Obtain the transformation matrices for clockwise and anticlockwise rotation about z-axis by 120° . [5]
- (B) Find the symmetry elements for the following molecules / ions and identify their point groups .
 B_2H_6 , SO_4^{2-} , trans oxamide and HCN. [8]
- Q.22. (A) What is calomel electrode ? It is reversible with respect to chloride ion, justify. [5]
- (B) What is micelle ? Enlist different of determining CMC (critical micelle concentration) of surfactants. Give details of any two methods. [8]
- Q.23. (A) What will be electrostatic force between two fission fragments of equal masses and sizes and of equal atomic numbers produced in the fission of ^{235}U (by a thermal neutron) in which four neutrons are emitted. Assume that $R_0 = 1.5 \text{ f}$ ($f = 1.11265 \times 10^{-10} \text{ C}^2 \text{ N}^{-1} \text{ m}^{-2}$, $e = 1.602 \times 10^{-19} \text{ C}$) ? [8]
- (B) Identify 'X' in the following nuclear reactions and justify your answer. [5]
- i)
- ii)
- Q.25. (A) i) What are ensembles ? What are different types of ensembles ? [4]
- ii) Distinguish between Bose - Einstein and Fermi - Dirac statistics. [4]

- (B) Calculate the rotational partition function for F_2 at 298 K. Given the moment of inertia of F_2 is $32.5 \times 10^{-47} \text{ kg. m}^2$ and $\sigma = 2$. [5]
- Q.25. (A) What are atactic, syndioactic and isotactic polymers of propylene ? [7]
- (B) Explain the role of Ziegler - Natta catalyst in synthesis of isotactic polymers ? [6]
- Q.26. (A) What is a point defect ? State the types of point defects. [5]
- (B) Describe the crystal structure of CsCl. How many Cs^+ and Cl^- ions are present in unit cell. [5]
- (C) What is the information obtained from the ratio of ionic radii (r^+/r^-) ? [3]
- Q.27. (A) "Anhydrous $AlCl_3$ is covalent, while $AlCl_3 \cdot 6H_2O$ is ionic in character" - Explain. [5]
- (B) Explain, why $SnCl_2$ is 'V' shaped molecule ? [5]
- (C) Polymeric (C_2F_4) is abbreviated as PTFE. What is the full form of PTFE ? Give one use of PTFE. σ [3]
- Q.28. (A) Match the entries in column A with those given in column B. [5]
- | [A] | [B] |
|--------------------|------------------|
| i) Pyrosilicate | a) $Mg(OH)$ |
| ii) Kaolinite | b) $Sc_2Si_2O_7$ |
| iii) Pseudohalogen | c) Clay mineral |
| iv) Brucite | d) Colored gases |
| v) Halogens | e) (CN_2) |
- Answer (i) b (ii) c (iii) e (iv) a (v) d
- (B) Draw the structures of sulphuric acid (H_2SO_4) and thiosulphuric acid ($H_2S_2O_3$). Mention the hybridisation involved and oxidation state of sulphur in each case [6]
- (C) What is Calgon ? [2]

- Q.29. (A) Draw structures and mention the geometry and hybridisation involved for the following compounds. [6]
 i) XeF_2 ii) XeOF_2
- (B) Draw structure, give nomenclature and mention the hybridisation involved for the following compounds - [6]
 i) Cl_2O_7 ii) ClF_3
- (C) Name the radioactive element amongst the halogens. [1]
- Q.30. (A) Draw the structures of the following [Hint. Use the concept of hapticity] [4]
 i) $[\text{Ti}(\eta^5\text{-C}_5\text{H}_5)_2(\eta^1\text{-C}_5\text{H}_5)_2]$
 ii) $[\text{Mo}(\eta^6\text{-C}_6\text{H}_6)(\text{CO})_3]$
- (B) Using the 18-electron rule as a guide indicate the probable number of carbonyl ligands in [6]
 i) $[\text{Cr}(\text{CO})_n]_6$
 ii) $[\text{Rh}(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_n]$
 iii) $\text{Ru}_3(\text{CO})_n$
- (C) Which metal carbonyl $[\text{Fe}(\text{CO})_4]^{2-}$ or $[\text{Co}(\text{CO})_4]^-$ should be more basic towards a proton [3]
- Q.31. (A) What d-orbital splitting pattern will you expect from an ML_8 complex with the ligands at the corners of a cube? How would the magnitude of the splitting, compare with that in an analogous tetrahedral ML_4 complex? [7]
- (B) The Re-Re bond in the dinuclear complex $[\text{Re}_2\text{Cl}_8]^{12-}$ is a quadruple bond. Explain. [6]
- Q.32 (A) Draw the plots of magnetic susceptibility versus temperature for paramagnetic, ferromagnetic and antiferromagnetic compounds. [6]
- (B) Calculate the crystal field and bonding parameters for $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$ using following data :
 Given
 i) visible spectrum : 8100, 16000 and 19400 cm^{-1} [7]
 ii) $10 Dq = 2 - 1$
 iii) $15 B = 2 + 3 - 3 - 1$
 iv) $B_0 = 971 \text{ cm}^{-1}$

Q.33. (A) What is trans effect ? How would you prepare Cis - and trans isomers of $[\text{Pt}(\text{NH}_3)(\text{NO}_2)\text{Cl}_2]$ starting from $[\text{PtCl}_4]^{2-}$? [7]

(B) Work out the ground state spectral term symbols for Cr^{2+} , Fe^{2+} and Ni^{2+}
Given At. No. : Cr = 24. Fe = 26 & Ni = 28. [6]

Q.34. (A) Match the entries in column A from those given in column B. [8]

Column A

Column B

[Magnetic moments /w J in B. M.]

i) Ce (III)

a) 7.94 B.M.

ii) Pr (III)

b) zero B.M.

iii) Eu (III)

c) 2.54 B.M.

iv) Gd (III)

d) 3.58 B.M.

Answer i) = _____ , ii) = _____

iii) = _____ , iv) = _____

Hint : At. No. = Ce = 58, Pr = 59, Eu = 63 & Gd = 64.

(B) Compare briefly the chemistry of elements of d-block with those of f-block. [5]

Q.35. (A) What is the basic difference in Atomic Emission and Atomic Absorption spectroscopy ? [3]

(B) Calculate percentages of following compounds separated by GLC using area normalization method. [5]

Given :

Compound	Relative peak area	Detector response correction Divisor
Methyl acetate	16.4	0.60
Methyl propionate	45.2	0.78
Methyl butyrate	30.2	0.88

(C) Give reasons : [5]

i) Nitrous oxide - acetylene flame is used for Ca^{+2} estimation by AAS.

ii) Potassium salts are used in estimation of analyte by AAS.

Q.36. (A) Explain amperometric titration curve for pb^{+2} estimation by sulfate ions. [4]

(B) Na^+ ion in a 200 ml solution containing 10g/L of NaCl is to be removed by passing through a cation exchange resin in the H^+ form. If the exchange capacity of resin is 5.1 meq/g of a dry resin, what is the minimum weight of dry resin required ?
Given : At. wt. of Na = 22.99, Cl = 35.45 [5]

(C) Define following terms (any two) : [4]
i) FSOT column
ii) normal phase HPLC
iii) Thermogram

Q.37. (A) Match the entries in column A with those given in column B. [7]

[A]	[B]
i) Na^+ / K^+ - ATP ase	a) Organometallic reactivity
ii) Catalytic redox sites	b) membrane potentials
iii) Oxidation of water	c) monomeric iron site
iv) ferritin	d) Mn_4 cluster
v) Hb and Mb	e) $\text{Fe}_4 \text{S}_4$ cluster
vi) Cobalamin coenzyme	f) iron storage
vii) Carboxy peptidase	g) zinc

Answer i) _____ , ii) _____ , iii) _____ , iv) _____ , v) _____ ,
vi) _____ , vii) _____ .

(B) Explain with one example Hard and Soft coordination centers in metalloenzyme. [4]

(C) Fill in the blanks :
_____ means 'blue blood' found in snails (mollusks) and crabs (arthropods). It functions as _____ carrier. [2]
