

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_8H_7NO
I. R. : 2220, 1610 cm^{-1}
P. M. R.(d) : 3.8 (s, 15mm), 6.9 (d, J = 8 Hz, 10 mm),
7.5(d, J = 8 Hz, 10mm)

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

Molecular formula : $C_5H_{10}O$
I. R. : 280 nm, (ϵ 20)
Mass (m/z) : 86 (M^+), 71, 44, 43
P. M. R.(d) : 1.1 (d, J = 7 Hz, 30 mm), 2.0 (s, 15mm),
2.6 (septet, J = 7 Hz, 5 mm)

(C) Using ESR spectroscopy, differentiate between $[Cu(CH_3CN)_4]ClO_4$ and $Cu(ClO_4)_2$ compounds.

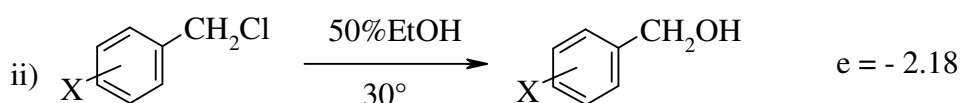
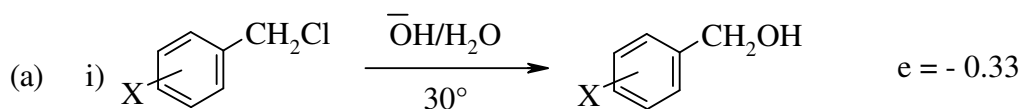
Given : $I(^{63}Cu) = 3/2$ [6]

(D) Potassium ferrocyanide and potassium ferricyanide compounds can be identified from their Mossbauer spectra. Explain. [6]

(E) $H^{35}Cl$ is irradiated with 435.8 nm mercury line. Calculate the Raman line in nm if the fundamental vibrational frequency of $H^{35}Cl$ is $8.667 \times 10^{13} s^{-1}$. [6]

(F) The pure rotation spectrum of HI consists of a series of lines separated by $13.10 cm^{-1}$. Calculate the bond length in molecule. [6]

Q.2. (A) Explain the following observations [7]



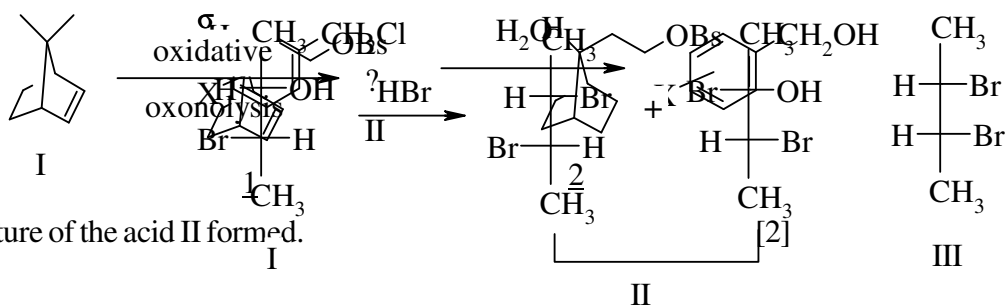
- (b) $\sigma_{p\text{-OCH}_3} = -0.27$ but $\sigma_{p\text{-SCH}_3} = 0.01$.
- (c) How much faster p-bromobenzyl chloride will solvolysise in H₂O than p-nitrobenzyl chloride in the reaction ?

Given $\rho = -1.31$; $\sigma_{p\text{-Br}} = 0.23$; $\rho_{p\text{-NO}_2} = 0.78$

- (B) Answer the following giving reasons. [6]
- (a) Acetolysis of brosylate 1 is 14000 times faster than 2.

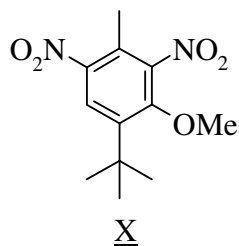
- (b) O-Carboxybenzamide is hydrolysed 10^5 times faster than benzamide.

- Q.3 (A) Oxidative Ozonolysis of I gives a dicarboxylic acid II having the same number (nine) of carbon atoms.

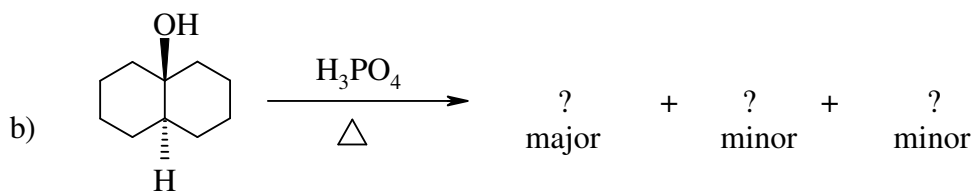
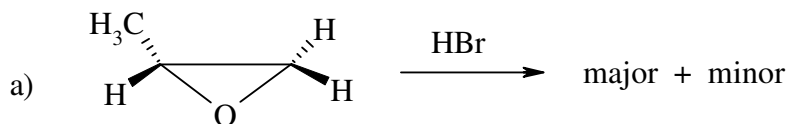


- (a) Draw the stereostructure of the acid II formed. [2]
- (b) Assign R/S configuration to the chiral centres if any in both the reactant I and the product II. [4]
- (c) Are these molecules I and II chiral/optically active ? [2]
- (B) Treatment of (\pm)-threo-3-bromo-2-butanol I with HBr gave only the racemic 2,3-dibromobutane II and no trace of the meso compound III was obtained. Explain with mechanism and stereochemistry. [5]

- Q.4. (A) Musk ambrette X is essential in perfumes to enhance and retain the odour. plan the synthesis of ambrette X from meta cresol. [7]

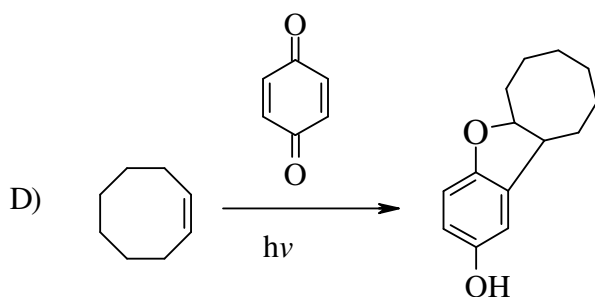
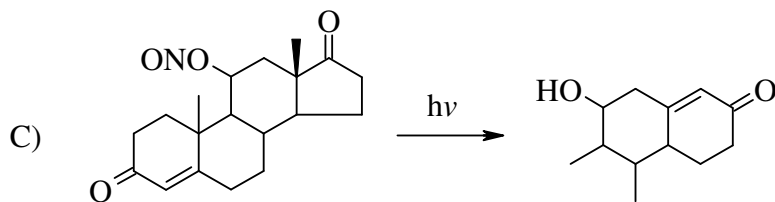
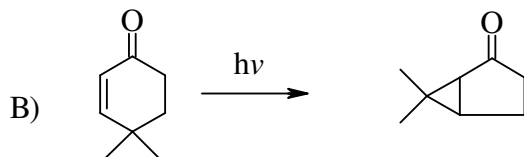
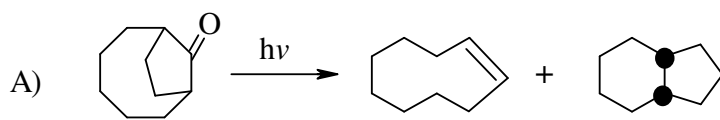


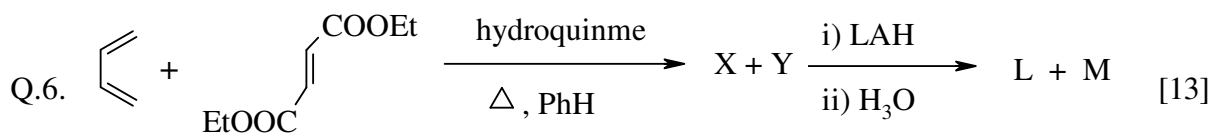
- (B) Predict the products of the following reactions with stereochemistry. [6]



(assign configuration to the chiral centre present in minor products)

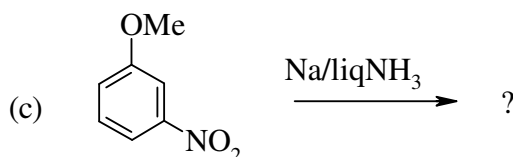
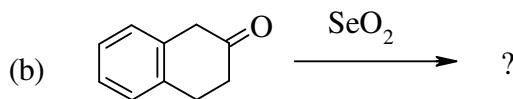
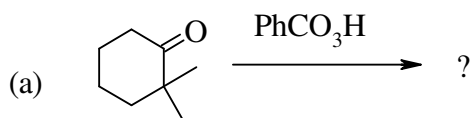
- Q.5. Indicate the type of reaction and mechanism involved in each step of the following transformations [13]

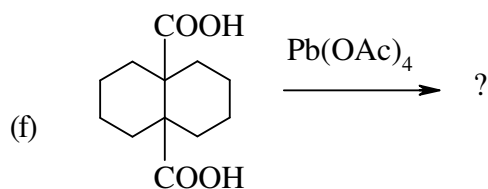
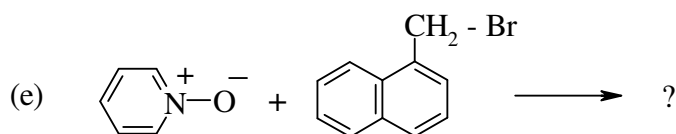
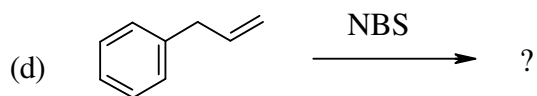




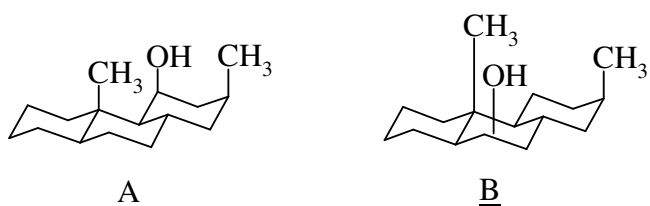
- (A) Write the products X, Y, L and M.
- (B) What are the names of the reactions involved in both the steps ?
- (C) What is the stereochemistry of the functional groups in X, Y, L & M ? Why ?
- (D) What will be the change in the products, if in the first step (-) dimethylester is used instead of diethylester ?
- (E) If (-) dimethylester is used, what is this strategy called as.
- (F) What is the role of (-) dimethyl part of the ester. Explain drawing the structure of the ester.

Q.7. (A) Predict the product of the following reactions. [6]

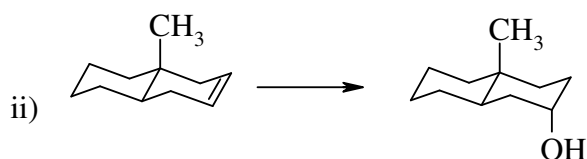
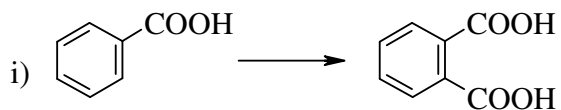




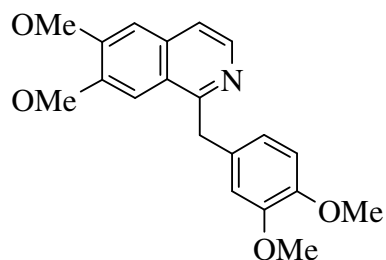
(B) a) Amongst A and B which will be oxidized faster by chromic acid and why? [3]



b) Write the reagents for the following transformations. [4]

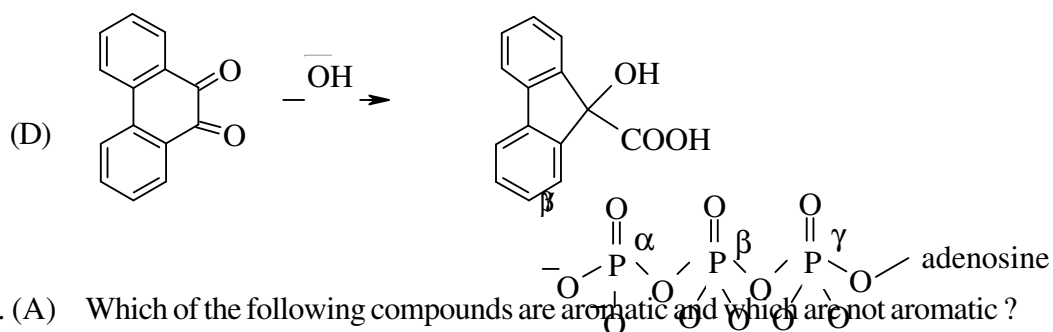
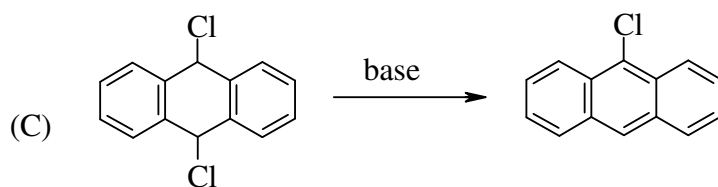
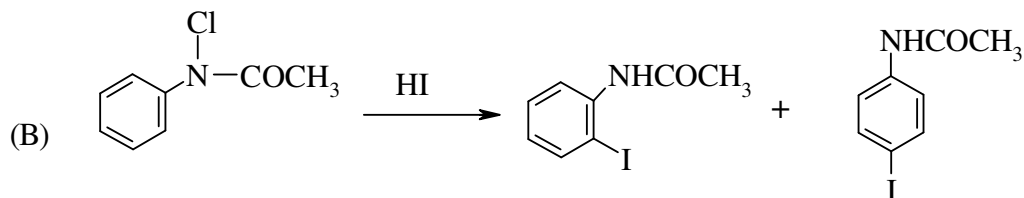
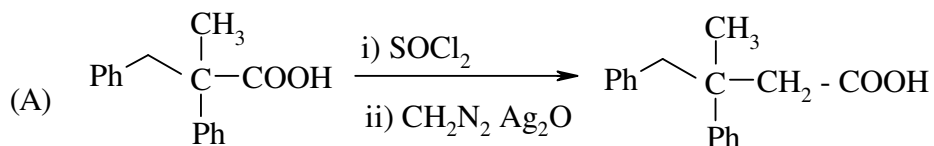


Q.8. (A) Using Bischler-Napierlaski synthesis how will you prepare following molecule: [7]

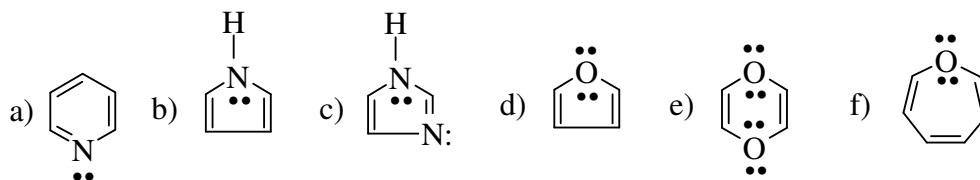


(B) When 3-ethyl-3-methyl-3H-indole is reacted with acid two products having molecular formula $C_{11}H_{13}N$ are obtained. Give their structures and explain their formation. [6]

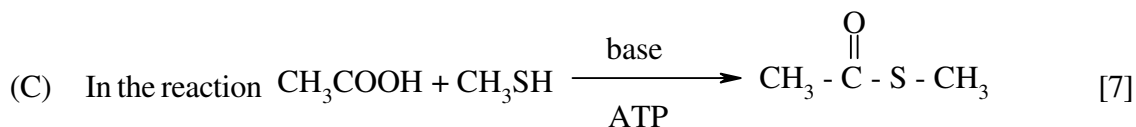
Q.9. Propose the mechanism for the following conversion and name the reaction involved. [13]



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

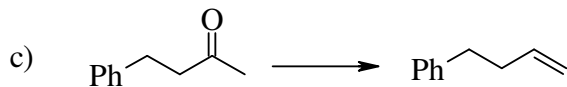
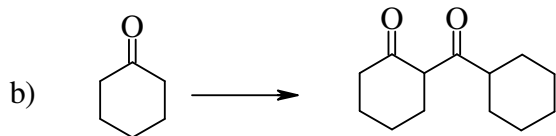
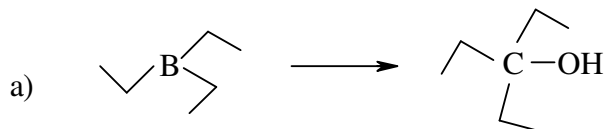


(B) The acidity of cyclopentadiene ($pK_a = 16$) is comparable to that of water ($pK_a = 15.7$). Explain. [3]

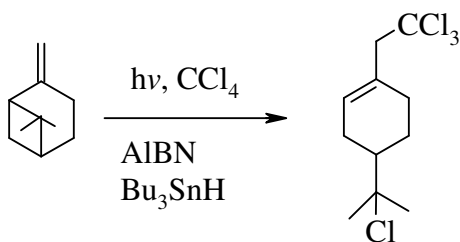


What products are formed, if acetate ion attacks α , and phosphorus atoms of ATP? Explain the formation of thioester.

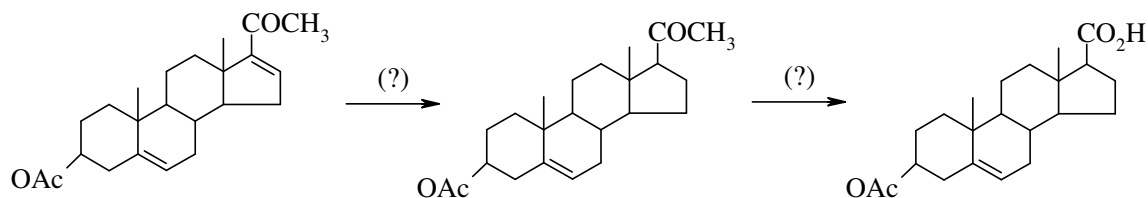
Q.11. (A) How the following transformation can be effected ? Identify the steps involved. [10]



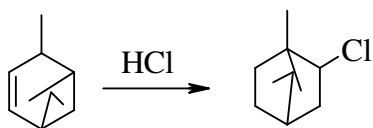
(B) Explain the following reaction. [3]



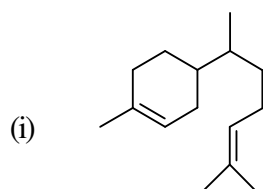
Q.12. (A) Give reagents for the following conversion. [4]

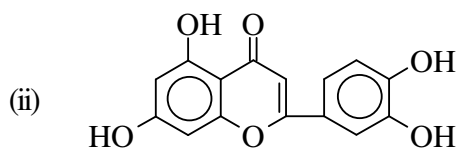


(B) Explain the following conversion with mechanism. [4]



(C) Explain the biogenesis of [5]





Q.13. (A) Derive the structure of a compound based on the following data : [6]

Molecular formula	:	$C_7H_5NO_3$
U. V.	:	225, (ϵ 3000), 256 (7800), 335 (160)
I. R.	:	2720, 1700, 1605, 1530, 1350 cm^{-1}
Mass (m/z)	:	151 (M), 150, 105, 77, 51
P. M. R.(d)	:	7.8 (t, J = 8.5 Hz, 6mm), 8.3 (dt, J = 8.5 and 2Hz, 6 mm), 8.43(dt, J = 8.5 and 2Hz, 6mm), 8.6 (t, J = 2Hz, 6mm), 10.0 (s, 6mm)

(B) Deduce the structure based on the following carbon-13 N. M. R. data : [5]

Molecular formula : $C_6H_{12}O$

Carbon-13 : 24(q), 26 (q, strong), 44(s), 214(s)

Q.14. (A) Match the entries in column A from those given below : [7]

<u>Column A</u>	\in	<u>Column B</u>
(i) Logarithms of large numbers	
(ii) Free electron gas	
(iii) Ultracentrifugation	
(iv) - electron theory	
(v) Law of corresponding states	
(vi) Unimolecular reactions	
(vi) Potential energy curve	

Column B

Critical state

Stirlings approximation

morse

Svedberg

Born-Openheimer approximation

Lindemann

Hermann-Mauguin

Huckel

Fermi-Dirac

- (B) A part of the character table of a group containing six symmetry elements is [6]

E	2A	3B
1	1	1
1	X	Y
2	W	Z

Identify X, Y, Z and W. Explain your answer

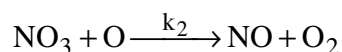
- Q.15. (A) Evaluate the commutator : [6]

- (B) What is the degeneracy of the level having energy level $\frac{15\pi^2\hbar^2 a^2}{8ma^2}$ for a cubic box of length a ? Write down the corresponding eigen functions. [7]

- Q.16. (A) What type of hybridization is present in the MX_4 square-planar complexes. State which d orbitals are involved in this case. Justify your answer. [7]

- (B) Sketch the wavefunctions and probability densities for $n=2, 3$ in case of particle on a line and the quantum mechanical harmonic oscillator. [6]

- Q.17. (A) Ozone is decomposed by the catalytic chain. [6]



What is the steady -state rate law for the formation of O_2 ?

- (B) Sketch qualitatively the normal vibrations in BF_3 and ClO_3 systems. Which of these are Infra active and Raman active ? How you can distinguish the shapes of these molecules from ClF_3 . [7]

- Q.18. (A) What is Born-Oppenheimer approximation ? Comment on the validity of this approximation [5]

- (B) Estimate the grounds state energy for a particle in a box with $0 \leq x \leq 1$ using a trial function as $\psi = x(1-x)$. [8]

- Q.19. (A) Define the canonical ensemble. State the principle of equal a priori probabilities. Write the expression for canonical partition function and show that :

$$U - U(0) = - \left(\ln Q \right)_V$$
 [7]
- (B) Write the expression relating entropy and the partition function. Derive $S = K \sum P_i \ln P_i$ where P_i is the proportion of members of the ensemble having the energy E_i [6]
- Q.20. (A) An element exists in two solid forms, M and M' with standard enthalpies of combustions to MO_2 and $M'O_2$ of -400 and -405 kJ mol^{-1} respectively at 298^0K . Calculate the enthalpy change for the transfer of M to M' under standard conditions at 298^0K . [6]
- (B) 5 moles of benzene and 3 moles of toluene are mixed together at 1 atm and 25^0c . Calculate G_{mix} , S_{mix} , H_{mix} assuming toluene and benzene form ideal solution. [7]
- Q.21. (A) What is an equilibrium ? How can one prove the phase rule ($F=C-P+2$) with the help of this concept ? Explain the congruent and incongruent melting points in solid-liquid equilibria. [7]
- (B) Discuss the concepts of electric dipole moment of a molecule and the polarization of a dielectric. Write down the Debye equation and explain its utility for the determination of dipole moment. [6]
- Q.22. (A) Define mean ionic activity coefficients. State the Debye - Huckel limiting equation. Estimate the activity coefficients of Ba^{2+} and Cl^- ions and mean ionic activity coefficients of these ions in a solution of $BaCl_2$ (0.002 molal). [8]
- (B) How the activity coefficients can be measured using the emf method ? [5]
- Q.23. (A) The decomposition of phosphine on tungsten surface is first order at low pressures and zeroth order at high pressures. Account for this observation. [6]
- (B) Distinguish between homogenous and heterogenous catalysis. Explain with example of each. [7]
- Q.24. (A) What are electro kinetic potentials ? Discuss their relations with each other and utility. [6]

- (B) Show that dQ term (heat flow) occurring in first law of thermodynamics is not a perfect differential. [7]
- Q.25. (A) Explain the terms binding energy and mass defect. Calculate the binding energy of an α -particle. Express the results in MeV. [6]
- (B) The molar mass of egg albumin is 40,000 g. Calculate the osmotic pressure at 25^o C of an aqueous solution containing 10 g L⁻¹ of this protein. [7]
- Q.26. (A) Discuss defects and its consequences in non-stoichiometric compounds, where metal is deficient. [6]
- (B) Describe the crystal structure and properties of CdI₂. [4]
- (C) Calculate the number of molecules in a unit cell of CaF₂. [3]
- Q.27. (A) Explain why Lithium has a great tendency to form covalent compounds? [4]
- (B) Give reason - "BF₃ and BCl₃ are gases, BBr₃ is a liquid, while BI₃ is a solid". [4]
- (C) Give reactions to show the formation of two and three dimensional silicones [5]
- Q.28. (A) How are P₄, P₄O₆ and P₄O₁₀ structurally related? [8]
- (B) Describe the structures and uses of SF₄ and SF₆. [5]
- Q.29. (A) Discuss structure and bonding in [6]
- (i) ClO₃⁻ (ii) ClF₃
- (B) Write a brief note on Fluorocarbons. [4]
- (C) Draw structure of XeF₂ and mention the hybridisation that Xenon undergoes. [3]
- Q.30. (A) Using the 18-electron rule as a guide predict the probable number of carbonyl ligands (value of n) in the following: [6]
- i) [W(η^6 -C₆H₆)(CO)_n]
- ii) [Rh(η^5 -C₅H₅)(CO)_n]
- iii) [Ru₃(CO)_n]

- (B) The complex $[\text{Mo}(\text{Py})_2(\text{CO})_4]$ (Py = pyridine) exists in two isomeric forms with one showing a single CO stretching frequency and the other isomer showing four singals in the infrared spectrum. Draw the structures of the two isomers and explain the spectrum. [7]
- Q.31. (A) Explain with the help of suitable MO diagrams, how ν_{CO} values are affected by π -bonding for π -acids and π -bases as ligands. [5]
- (B) Arrange the following complex species in the order of increasing value of crystal field splitting, giving brief explanation :
 $[\text{Rh}(\text{H}_2\text{O})_6]^{2+}$, $[\text{Rh}(\text{en})_3]^{3+}$, $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$ [5]
- (C) "Diamagnetism is an universal property". Elaborate on this statement. [3]
- Q.32. (A) Explain the various crystal field transitions possible for octahedral and tetrahedral Ni^{2+} complexes on the basis of Orgel diagram. What would be their intensities ? [5]
- (B) Which of the following statements is/are correct ? Give reasons for your answer. [5]
- (i) The electronic spectral bands due to d-d transitions in transition metal complexes are broad.
- (ii) The intensities of d-d bands for $[\text{NiCl}_4]^{2-}$ and $[\text{Ni}(\text{H}_2\text{O})_6]^{2+}$ are the same.
- (iii) The d-d transitions in octahedral transition metal complexes are Laporte forbidden; nevertheless, they are observed.
- (C) What is spin selection rule ? what are its consequences ? [3]
- Q.33. (A) Work out the ground state term symbols for Mn^{2+} , Cu^{2+} and Gd^{3+} . [6]
 (At. No. Mn : 25, Cu : 29, Gd : 64)
- (B) Explain the mechanism of base hydrolysis of $[\text{Co}(\text{NH}_3)_5\text{Cl}]^{2+}$. [7]
- Q.34. (A) Discuss the spectral properties of lanthanides. Why are electronic absorption bands of lanthanides relatively sharp and not affected by ligands ? [6]
- (B) What is the expression used to calculate the magnetic moments for lanthanides ions ? Calculate the expected magnetic moments for Nd^{3+} and Tb^{3+} , if the values for g are 8/11 and 3/2 respectively. [7]

