

INORGANIC CHEMISTRY THEORY -III

Time: 3 Hrs

Max. Marks: 70

PART - A

I Answer any TEN of the following

(2×10=20)

- Give symmetry operation for H₂O molecule.
- Explain S_n symmetry operation with an example .
- List the symmetry elements and identify point group of CHCl₃.
- Using MOT, mention the atomic orbitals of the metal ion in octahedral complexes during the formation of σ bonding.
- Which important property of metal complexes does the valence bond theory fail to explain and why?
- Calculate CFSE of Co(II) complex in terms of Dq and P in an octahedral field.
- What is the ground term for d² ion.
- Name the calibrant used in Gouy's method and why is it preferred?
- What is nephelauxetic effect? Place the following ligands in order of increasing nephelauxetic effect: H₂O, I⁻, en, F⁻, CN⁻, NH₃.
- Differentiate a labile complex from an inert complex.
- Justify: The transfer of electron from [Cr(H₂O)₆]²⁺ to [Co(NH₃)₆]³⁺ in aqueous medium is slower than the transfer from [Cr(H₂O)₆]²⁺ to [Co(NH₃)₅OH]²⁺.
- What is trans effect? Give an example.

PART B

Answer any Five questions, selecting at least one question from each unit

(10×5=50)

UNIT -I

- Write a note on 5 symmetry elements and 5 symmetry operations.
 - Using the following Character table, calculate IR active and Raman active modes of vibrations for trans planar H₂O₂.

C _{2h}	E	C _{2z}	σ _{xy}	i	Linear function rotation	Quadratic functions
A _g	1	1	1	1	R _z	x ² , y ² , z ² , xy
B _g	1	-1	1	-1	R _x , R _y	xz, yz
A _u	1	1	-1	-1	z	-
B _u	1	-1	-1	1	x, y	-

(5+5)

- 3) a) Using following Character table, find out IR & Raman active vibrations in NH₃ molecule

C _{3v}	E	2 C ₃	3σ _v	Linear Function	Quadratic functions
A ₁	1	1	1	z	x ² , y ² , z ²
A ₂	1	1	-1	R _z	-
E	2	-1	0	(x,y) (R _x , R _y)	(x ² -y ² , xy) (xz,yz)

- a) Identify the symmetry elements for pyridine and propyne and find out their order. (5+5)

UNIT -II

- 4) a) Explain with the help of the MOT, why Cl⁻ act as a weak ligand where as CO act as a strong ligand in transition metal complexes?
 b) Explain crystal field theory and how does it differ from valence bond theory? [Co(NH₃)₆]³⁺ is diamagnetic but [CoF₆]³⁻ is paramagnetic though both are octahedral. Justify it with CFT. (5+5)
- 5) a) Distinguish between high-spin and low-spin complexes. Explain the thermodynamic effect of crystal field splitting on lattice energies of divalent metal ions of 3d-series.
 b) Construct the MO energy level diagram for the complex [Co(NH₃)₆]³⁺ and explain its salient features. (5+5)

UNIT -III

- 6) a) An octahedral Ni(II) complex shows spin-allowed bands at 10150, 16500 and 27000 cm⁻¹. Interpret the spectrum and calculate the nephelauxetic ratio. Given: B for Ni²⁺ free ion= 1040 cm⁻¹.
 b) How are charge transfer bands different from d-d bands? Discuss their origin, types and Characteristics. (5+5)
- 7) a) Set up an Orgel diagram for a complex in which the metal ion has a d⁷ configuration. What are the other electronic configurations which this diagram can represent? Explain the salient features of the diagram.
 b) How are Tanabe- Sugano diagrams different from Orgel diagrams? Draw the diagram for a d² system and explain. (5+5)

UNIT -IV

- 8) a) Discuss S_N1CB mechanism of coordination compounds with a suitable example.
 b) Explain non-complementary redox reactions with suitable examples. (5+5)
- 9) a) Explain in what way the acid hydrolysis of Cis[Co(en)₂Cl(OH)]⁺ complex differs from that of trans [Co(en)₂Cl(NO₂)]⁺
 b) Explain suitable examples of one electron transfer reaction. (5+5)

TECHNIQUES & APPLICATIONS OF SPECTROSCOPY

Time: 3 Hrs

Max. Marks: 70

PART A

I Answer any TEN of the following: (2×10=20)

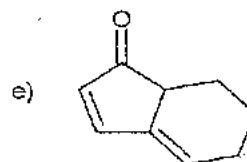
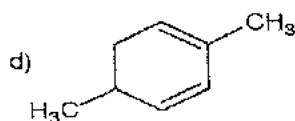
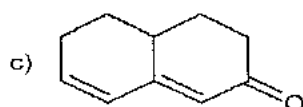
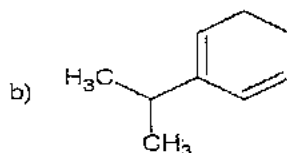
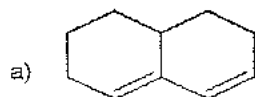
- Aniline absorbs at 280 nm (E_{\max} 8600) but in acidic solution it shifts to 203 nm (E_{\max} 7500). Give reason.
- Explain chromophore and auxochrome with suitable examples.
- In UV spectroscopy, methyl chloride shows λ_{\max} at 169 nm whereas methyl iodide shows λ_{\max} at 258 nm. Justify.
- Sketch and explain the ^{31}P NMR spectra of $\text{H}_5\text{P}_3\text{O}_{10}$.
- Write the Karplus relationship between Karplus curve and variation in coupling constant.
- Identify the number of ^{13}C -NMR resonance in 1,3-dichlorobenzene and 1-bromo-4-chlorobenzene.
- Vibrational frequency of C=O (Carbonyl group) in benzaldehyde is seen at 1700 cm^{-1} and salicylaldehyde at 1660 cm^{-1} why?
- In the mass spectrum of n-butane some prominent peaks at m/z values 43 & 15. What are the most probable species responsible for these peaks.
- The mass spectrum of ethyl bromide exhibits two peaks at m/z = 108 and 110. why?
- What are the factors that contribute to electric field gradient?
- Why Mossbauer spectrum for solid samples is recorded at low temperature? Explain.
- Which nuclei possess nuclear quadrupole and why?

PART B

Answer any Five questions selecting at least one question from each unit. (10×5=50)

UNIT -I

2) How are Woodward-Fischer rules useful in distinguishing the following compounds: (10)



3) a) What is the basic principle of UV spectroscopy and does the substitutions and the solvent plays major role in calculating λ_{\max} in UV spectroscopy?

b) Justify that in UV spectrometer quartz cuvettes are used and not glass cuvettes. (7+3)

UNIT -II

4) a) What is Chemical shift and discuss the various factors affecting the chemical shift.
b) Discuss the ^1H NMR splitting pattern in propyl chloride. (6+4)

5) a) The proton - decoupled and off-resonance C^{13} -NMR spectra provide the following data for 3 isomeric alcohols with formula $\text{C}_4\text{H}_{10}\text{O}$.

A: δ 31 (quartet), 69.5 (singlet)

B: δ 11 (quartet), 22 (quartet), 31 (triplet), 69.5 (doublet)

C: δ 19 (quartet), 31 (doublet), 69.8 (triplet)

Identify the alcohols responsible for each spectrum and assign each peak to an appropriate carbon atom or atoms.

b) An organic compound has the molecular formula $\text{C}_3\text{H}_6\text{O}_2$ shows the following spectral data:

^1H -NMR - δ 1.30 (t, 3H), 4.25 (q, 2H) & 8.05 (s, 1H)

IR - 2900 (m), 1727 (s), 1180(s), 1000 (m)

^{13}C NMR (proton decoupled) - δ -14, 60 & 161 ppm

Identify the structure of the compound

(6+4)

UNIT -III

6) a) Derive an expression to show that mass spectrometer would be unable to distinguish between a M^+ and 2M^{+2} from one another.

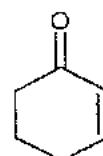
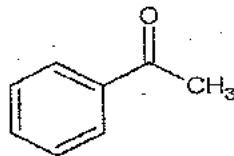
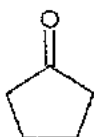
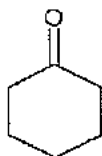
b) Write note on

i) McLafferty rearrangement

ii) Ring rule

(5+5)

7) a) With proper justification assign the C=O (carbonyl) stretching wave numbers given to the compounds shown below 1675, 1715, 1745 & 1690 cm^{-1}



b) Explain the factors affecting fragmentation pattern.

(6+4)

UNIT -IV

8) a) Discuss the principle of ESR spectroscopy. Explain zero field splitting & Kramer's degeneracy.

b) Write a note on application of NQR spectroscopy.

(6+4)

9) a) What are the factors on which isomer shift values depend in Mossbauer spectroscopy? Discuss.

b) Explain why the Mossbauer spectrum of $[\text{Fe}(\text{CN})_6]^{4-}$ shows a single absorption while that of $[\text{Fe}(\text{CN})_5(\text{NH}_3)]^{3-}$ shows a pair of resonance.

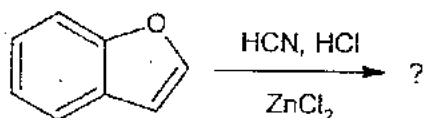
(6+4)

PART – A

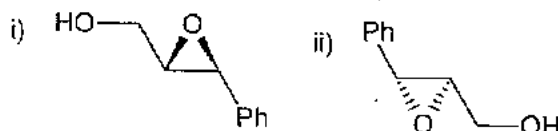
1. Answer any TEN of the following:

(2×10=20)

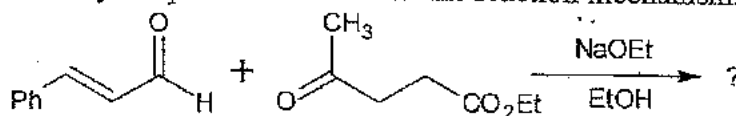
a) Predict the product and write the reaction mechanism.



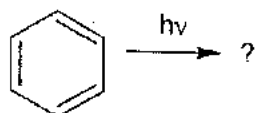
b) How would you make enantiomerically enriched samples of the following?



c) Identify the product and outline the reaction mechanism.

d) The intensity of $n \rightarrow \pi^*$ bond is less than that of $\pi \rightarrow \pi^*$ bond. Account for it.

e) Predict the product in the following:



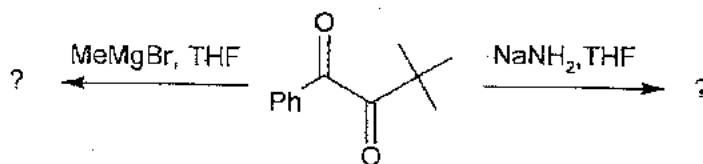
f) When butadiene is mixed with benzophenone it undergoes dimerization. Give reasons.

g) What is con-rotation? Explain with an example.

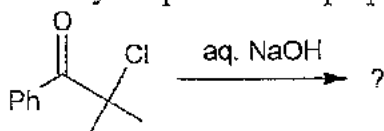
h) How cycloaddition reactions are classified?

i) What is aza-cope rearrangement? Outline its mechanism.

j) Predict the suitable products for following chemical conversions.



k) Identify the product and propose the reaction mechanism for the following reaction.



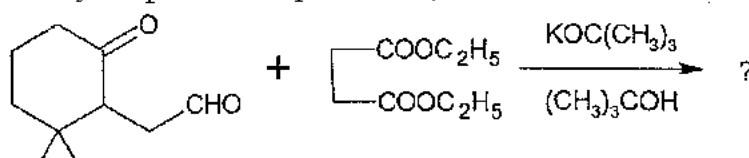
l) Write any two applications of pinacol-pinacolone rearrangement.

PART - B

Answer any FIVE questions selecting atleast one question from each unit. (10×5=50)

UNIT - I

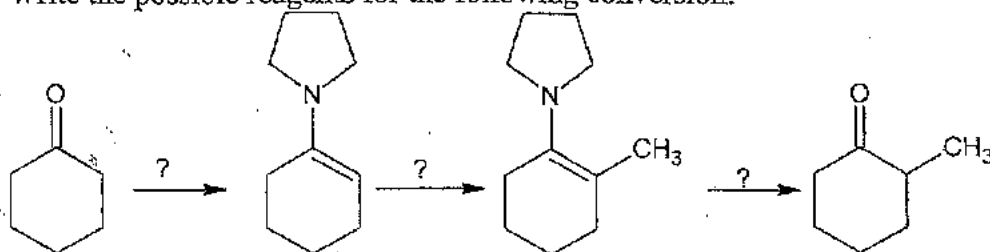
2. a) Identify the products explain the mechanism for the following.



b) What is Hoffmann-Loeffler-Freytag reaction? Discuss its reaction mechanism taking suitable example. (5 + 5)

3. a) Discuss the mechanism and synthetic utility of Cannizaro reaction and Benzoin condensation.

b) Write the possible reagents for the following conversion: (6 + 4)



UNIT - II

4. a) Discuss the Norrish type I and type II reactions with suitable examples.

b) Write a note on photo oxidation and reduction reactions. (5 + 5)

5. a) What is Paterno-Buchi reaction? Explain its mechanism.

b) Discuss the following reactions.

i) Photo Fries rearrangement ii) Di- π methane rearrangement (4 + 6)

UNIT - III

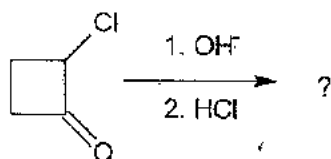
6. a) With the help of correlation diagram, predict whether the suprafacial cycloaddition of butadiene to ethylene is thermal or photochemical.

b) How do you analyse a sigmatropic rearrangement? Explain by taking 1,5 - sigmatropic shift. (5 + 5)

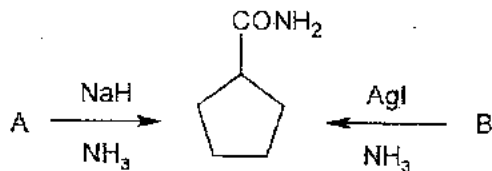
7. a) With the help of correlation diagram, show that the con-rotatory interconversion of hexatriene to cyclohexadiene is photochemical.
b) Discuss the mechanisms of Claisen and Cope rearrangements with suitable examples. (6 + 4)

UNIT - IV

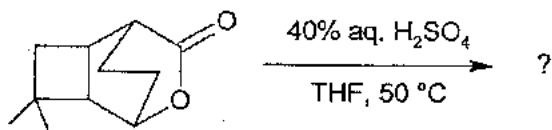
8. a) Predict the product and write suitable mechanism.



- b) Identify the starting materials and propose the reaction mechanism for the following conversions. (4 + 6)



9. a) Predict the rearranged product and explain the plausible reaction mechanism for the following reaction.



- b) What is Baker Venkatraman Rearrangement? Discuss its reaction mechanism with suitable example.
c) Discuss the synthetic applications of Beckmann rearrangement. (3 + 4 + 3)

PART – A

1. Answer any SEVEN of the following: (2×7=14)
- Name the trace constituent of the atmosphere with their approximate percentage by volume.
 - Name the important green house gases.
 - What is PAN? How is it formed?
 - Illustrate the term 'eutrophication'.
 - Explain the types of hardness of water.
 - Explain the role of oxidation pond in waste water treatment process.
 - Give the names of micronutrient elements present in soil.
 - Give the classification of soil pollutants.
 - Explain the harmful effects of fungicides as soil pollutants.

PART – B

Answer any FOUR questions selecting atleast one question from each unit. (14×4=56)

UNIT – I

2. a) Give the source and effects of the following air pollutants:
i) SO₂ and ii) CO
- b) What is Green house effect? Explain its effects on atmosphere.
- c) Discuss the characteristics of the major regions of the atmosphere. (5 + 5 + 4)
3. a) Describe the various mechanisms involved in the formation and depletion of ozone in the atmosphere. What are the consequences of ozone hole formation.
- b) Describe the effects of noise pollution and how it can be controlled?
- c) Write a note on environmental segments. (5 + 5 + 4)

UNIT – II

4. a) Discuss the harmful effects of chemical pollutants and organic wastes as major water pollutants. How they can be prevented?
- b) Write a note on criteria and standards of water quality.
- c) Write a brief account of sources and chemistry of sea water. (5 + 5 + 4)
5. a) Explain the importance of sedimentation and chlorination in domestic water treatment.
- b) Write a note on waste water treatment by secondary treatment.
- c) Explain the following terms:
i) Hard water ii) Soft water iii) Water alkalinity (5 + 5 + 4)

UNIT – III

6. a) Explain the sources and prevention of soil pollution.
- b) Give a short account of insecticides as major soil pollutants with respect to their harmful effects and prevention.
- c) Describe sampling and monitoring techniques of soil pollution. (5 + 5 + 4)
7. a) Write a brief account of composition of soil, inorganic and organic components in soil.
- b) Describe nitrogen and sulphur pathways.
- c) Discuss briefly the strategies adopted to control environmental pollution. (5 + 5 + 4)
