

Total number of printed pages-11

3 SEM PG (CBCS) CHM C 1

2024

(December)

CHEMISTRY

Paper : 301

(Core Course)

(Inorganic Chemistry-III)

Full Marks : 60

Time : Three hours

The figures in the margin indicate full marks for the questions.

UNIT-I

(Marks : 08)

1. Answer **any four** of the following questions :
2×4=8

(a) Why is there often a discrepancy between the theoretical (calculated) magnetic moment and the experimental magnetic moment of Eu^{3+} ions ?

Contd.

(b) With the help of a suitable example describe the mechanism by which lanthanide shift reagents (LSRs) induce shifts in the NMR spectra of organic molecules.

(c) Why do actinides exhibit a greater range of oxidation states than lanthanides, and how does this influence their chemical behavior ?

(d) What is elution time in chromatography ? Compare the elution times of La^{3+} and Lu^{3+} ions and discuss the factors contributing to any differences observed.
 $0.5+1.5=2$

(e) Why the lanthanide contraction occurs ? How does it affect the properties of 4d and 5d series transition metals ?
 $1+1=2$

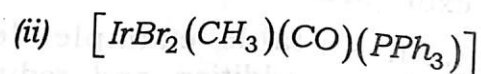
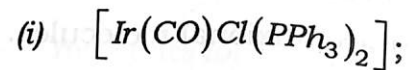
(f) Compare the spectral properties of lanthanides and actinides.

UNIT-II

(Marks : 16)

2. Answer the following questions :

(a) What is Effective Atomic Number (EAN) rule for coordination compound ? Mention if the following compounds obey 18-electron rule or not ? Give reason.
 $1+3=4$



Or

Write brief notes on : $2+2=4$

(i) Irving-William order of stability of metal complexes and its significance.

(ii) Relation between stepwise and overall stability constant.

(b) Answer any three questions of the following : $2 \times 3 = 6$

(i) What are the conditions for two fragments to be isolobal ? How do you account the isolobality of $Mn(CO)_5$ with CH_3 and Cl .

(ii) Discuss the reactivity of carbonyl ligand with reference to various chemical reactions.

(iii) Discuss how the following factors affect the magnitude of C-O stretching frequencies (ν_{CO} cm^{-1}) in various metal carbonyls. 1+1=2

(a) Charge on metal center

(b) Presence of other ligands.

(iv) What are fluxional molecules. Give examples.

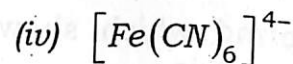
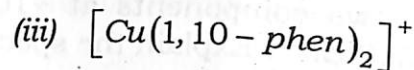
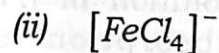
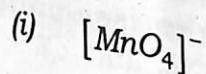
(v) With suitable example define oxidative addition and reductive elimination reaction. What are the factors that favour the oxidative addition reaction ?

3. Answer **any three** questions from the following : 2×3=6

(a) Define ground term. Identify the ground terms for the free ions V^{3+} and Cr^{3+} .

(b) What are the major differences between Orgel and Tanabe-Sugano diagram ?

(c) The complex that would show paramagnetic behavior is



(d) The expected spin-only magnetic moments for $[Fe(CN)_6]^{4-}$ and $[FeF_6]^{3-}$ respectively are

(i) 1.73 and 1.73 B.M.

(ii) 1.73 and 5.92 B.M.

(iii) 0.0 and 1.73 B.M.

(iv) 0.0 and 5.92 B.M.

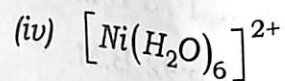
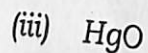
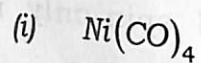
Or

Answer the following questions :

(a) The magnetic moments of Co(II) tetrahedral complexes lie in the range of 4.4–4.8 BM, whereas those of octahedral complexes are 4.8–5.2 B.M. at room temperature. Explain. 3

(b) An aqueous solution of $[Fe(H_2O)_6]^{2+}$ shows an absorption spectrum consisting of a single band that splits into two components at ~ 10400 and $\sim 8300\text{ cm}^{-1}$. Explain the spectrum with the necessary diagram. 2

(c) The compound which shows $M \rightarrow L$ charge transfer is - 1



UNIT-III

(Marks : 29)

(A)

(Marks : 07)

4. Answer **any two** questions from the following : 3.5×2=7

(a) Mention significance of spin-spin coupling in NMR spectroscopy. Draw 1H and ^{31}P NMR spectra of $(CH_3)_2PH$ molecule. 1+1.5+1=3.5

(b) Explain spin-spin and spin-lattice relaxation in NMR spectroscopy. Why solid-state NMR is usually broad in nature compared to liquid-state NMR ? 2+1.5=3.5

(c) (i) How can you distinguish *fac*- and *mer*- $[RhCl_3(PPh_3)_3]$ with the help of ^{31}P NMR spectroscopy ? 2

(ii) Write short note on NMR shift reagent. 1.5

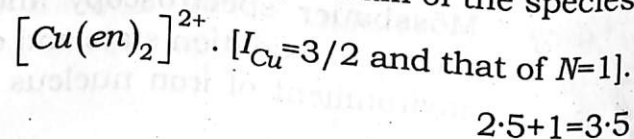
(B)

(Marks : 07)

5. Answer **any two** questions from the following : 3.5×2=7

(a) Water is not a suitable solvent for the ESR experiment, why ? What are the factors which affect the value of g ? 2.5+1=3.5

(b) Explain super hyperfine splitting with one suitable example. Predict the number of lines exhibited by a high-resolution EPR spectrum of the species



(c) What is Kramer's doublet? For a tetragonally distorted Cr(III) complex, zero-field splitting results in the following numbers of Kramer's doublets:
 $2 \cdot 5 + 1 = 3 \cdot 5$

(i) One

(ii) Two

(iii) Three

(iv) Four

(d) Spectrum of a single crystal of Mn^{2+} doped into MgV_2O_6 , showing five allowed transitions, each again splits to six lines ($Mn = I = 5/2$). Explain the spectral pattern. Draw the ESR spectrum of an aqueous solution of $CuSO_4 \cdot 5H_2O$ at room temperature.
 $2 \cdot 5 + 1 = 3 \cdot 5$

(C)

(Marks : 06)

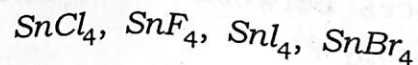
6. Answer **any two** of the following questions:
 $3 \times 2 = 6$

(a) Explain the concept of isomer shift in Mössbauer spectroscopy and how it relates to oxidation state and electronic environment of iron nucleus ?

(b) What is recoil energy ? A Mössbauer source emits gamma rays with an energy of 14.4 keV . The mass of the emitting nucleus is $2.3 \times 10^{-25} \text{ kg}$. Calculate the recoil energy of the nucleus when it emits the gamma photon.
 $1 + 2 = 3$

(c) What is the electric quadrupole moment? How does the quadrupole moment affect the hyperfine splitting observed in Mössbauer spectra ?
 $1 + 2 = 3$

(d) How do spin state and ligand symmetry affect the isomer shift/Mössbauer spectra ? In which of the following complexes quadruple splitting is possible and why ?
 $2 + 1 = 3$



(D)

(Marks : 05)

7. Write the basic principle of nuclear quadruple resonance (NQR) spectroscopy. Provide examples of molecules/nuclei with different nuclear quadruple moment.
 $2 + 1 = 3$

Or

Why is NQR spectroscopy referred to as zero-field NMR spectroscopy? Explain the correct increasing order of ^{35}Cl QCC (quadrupole coupling constant) values for Cl-C, Cl-F, Cl-Cl and Cl-Si bonds. 1+2=3

8. The NQR frequency for a nucleus with $I = 3/2$ in an axially symmetric EFG is 100 MHz. Calculate e^2Qq/h . 2

(E)

(Marks : 04)

9. Give the principle of photoelectron spectroscopy (PES) briefly. What are the differences between XPES and UVPES spectroscopy? 2+2=4

UNIT-IV

(Marks : 07)

10. Answer the following questions :
- (a) Define the term intensity of magnetization, magnetic permeability and magnetic susceptibility. 3

Or

Show how magnetic susceptibility varies with temperature for paramagnetic, ferromagnetic and diamagnetic compound. Define the Neel temperature (T_N) and Curie temperature (T_C). 1+2=3

- (b) Comment on the contributions of the orbital magnetic moment for the following species : 1+1=2
- (i) d^4 (high spin)
- (ii) d^7 (high spin)
- (c) $\mu_{obs}(\mu_{eff})$ of a Co^{2+} octahedral complex may be as high as 5.2 B.M. Explain. 2

Or

Explain the spin-crossover diagrammatically taking a suitable example.

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(Organic Chemistry-III)

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The figures in the margin indicate full marks for the questions.

Write the answers of Unit-(I and II) and Unit-(III and IV) in separate books.

UNIT-I

(Marks : 15)

1. Answer **any five** of the following : $3 \times 5 = 15$

(a) Explain different types of casing used in drilling. Explain, why casing is important in the drilling process?

2+1=3

Contd.

(b) What are the primary petrochemicals? Give an overview of the products derived from the primary petrochemicals. 1+2=3

(c) Give a schematic overview of the purification process of raw natural gas in a Gas Processing Plant.

(d) Why is mud used in the drilling process? Write the general composition of mud. 2+1=3

(e) What is Octane number and why it is important? What are the references used in determining the octane rating of a fuel? 1+2=3

(f) Write about *any two* process variables in catalytic reforming. For an aromatic conversion which feedstock shall you consider amongst naphthenes and paraffin and why? 2+1=3

(g) Write a note on : (*any one*) 3

(i) Pollutant emission sources in the petroleum and petrochemical industry.

(ii) Waste management and environmental pollution control strategies.

UNIT-II

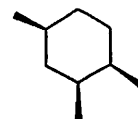
(Marks : 15)

2. Answer *any five* from the following : 3×5=15

(a) Why the equilibrium mixture of 4-*t*-butyl-1, 2-dibromocyclohexane contains almost equal amounts of the two diastereomers A and B ?



(b) Draw all the chair conformations of the following compound and comment on their stability. 2+1=3



(c) In the chair conformation, (*Z*)-2-methylcyclohexylideneacetic acid exist mostly with the *Me* group on axial position while (*E*)-2 methylcyclohexylideneacetic acid exist with the *Me* group on equatorial position. Explain.

(d) What is a CD spectrum ? Describe with a suitable example how the conformational change of a molecule can be studied with the help of a CD spectrum.

(e) Explain with proper structure : Dehydrochlorination of menthyl chloride takes place with a much slower rate than neomenthyl chloride.

(f) Draw the conformations of the following perhydrophenanthrene diastereomers :

(i) *cis-syn-cis*

(ii) *trans-syn-trans*

(iii) *cis-syn-trans*

(g) (S)-2-Bromocyclohexanone can have two conformations. Which one of these will display a strong Cotton effect and which a weak Cotton effect ?

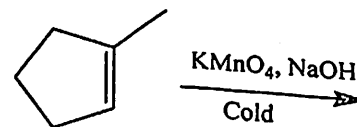
(h) (R)-(+)-3-Methylcyclohexanone on chlorination gives 2-chloro-5-methyl derivative which shows a negative Cotton effect in octane. What is the conformation of the product ?

UNIT-III

(Marks : 15)

3. Answer **any five** of the following : $3 \times 5 = 15$

(a) Write the mechanism and the product of the following reaction. What will be the product if the reaction is carried out in warm condition ? $2+1=3$



(b) Write the mechanism of oxidation of a primary alcohol with chromic acid and write the advantage of oxidation of that alcohol with Pyridinium Chloro Chromate ? $2+1=3$

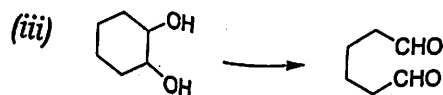
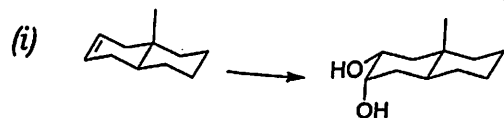
(c) Explain with mechanism why chromic acid oxidation of *cis*-4-*t*-butylcyclohexanol is faster than that of *trans*-4-*t*-butylcyclohexanol.

(d) Taking cyclohexene as the substrate, illustrate the mechanism of Woodward and Prevost dihydroxylation.

(e) Describe the reagents used in Sharpless asymmetric dihydroxylation of an alkene. Write the mechanism and the products mentioning the role of the chiral auxiliaries. $1\frac{1}{2}+1\frac{1}{2}=3$

(f) Write the mechanism of Swern oxidation. Mention the advantages and disadvantages. 2+1=3

(g) Suggest reagents for the following conversions. 1×3=3



UNIT-IV

(Marks : 15)

4. Answer **any five** questions : 3×5=15

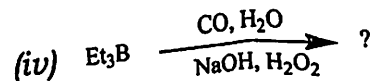
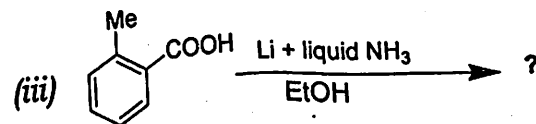
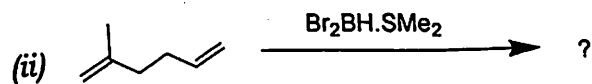
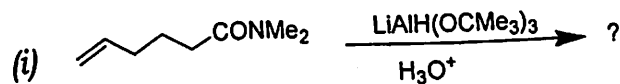
(a) Write the mechanism of hydrogenation of an alkene by using Wilkinson's catalyst.

(b) Write one synthesis and selectivity of DIBAL and 9-BBN. 1½×2=3

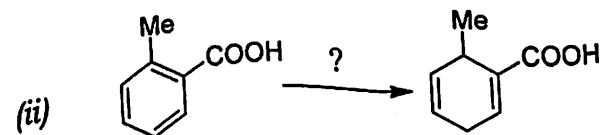
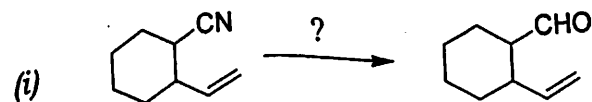
(c) Write about advantages and disadvantages of heterogeneous hydrogenation. 1½×2=3

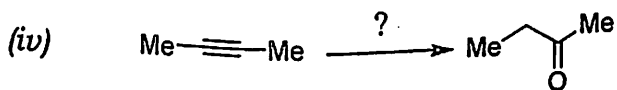
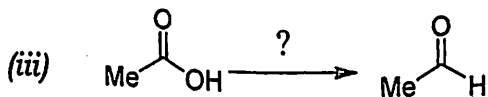
(d) Write a short note on superhydride or selectrides.

(e) Write the products for the following conversions : **(any three)** 1×3=3



(f) Suggest suitable reagents for the following conversions : **(any three)** 1×3=3





(g) Write the products and possible mechanism for the following conversions : $1\frac{1}{2} \times 2 = 3$

