3 SEM PG (CBCS) CHM C 1

2025

(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) What is the cause of lanthanide contraction ? How does it affect the electrochemical potential for the conversion of $Ln \rightarrow Ln^{3+} + 3e^-$? 1+1=2

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

(c) What is the role oion-exchange resins in lanthanide separation ? How does the elution time vary across the lanthanide series ? 1+1=2

(d) What is a lanthanide shift reagent ? Why are lanthanide shift reagents used in NMR spectroscopy ? 1+1=2

(e) Why do actinides form oxocations but lanthanides do not ? Out of lanthanides and actinides which one show maximum ability to form complex and why ? 1+1=2

(f) Discuss the absorption spectra of trivalent actinide ions.

UNIT–II

(Marks : 16)

2. Answer ***any three*** of the following questions : 3×3=9

(a) (i) What is 18-electron rule ?

(ii) On the basis of the 18-electron rule, predict the stability of $[V(CO)_6]$ and $[Mn(CO)_5]$.

(iii) Which of the above two carbonyls dimerize quickly ? 1+1+1=3

(b) Mention the factors associated with metals that influence metal complex stability. Why macrocyclic complexes are usually more stable than conventional chelated complexes ? 2+1=3

(c) What are the principles of isolobal analogy ? Propose examples of organometallic fragments isolobal with CH_2^+. 2+1=3

(d) How does the presence of other ligands affect the magnitude of *C–O* stretching frequencies $(\nu_{CO}\ cm^{-1})$ in various metal carbonyls ? Explain with examples. Arrange the following metal carbonyls in the increasing order of *C–O* stretching frequencies $(\gamma_{co}\ cm^{-1})$

$[Cr(CO)_6]$, $[Mn(CO)_6]^+$, $[V(CO)_6]^-$ and $[Ti(CO)_6]^{2-}$ 2+1=3

3. Define oxidative addition and reductive elimination reaction with a suitable example. 1

Or

Discuss with examples the bonding patterns of *M–NO* unit in metal nitrosyl compounds.

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

(a) Write the Hund's rule to determine a ground term. Identify the ground term for the free ion Fe^{3+}.

(b) What are the major drawbacks of the Orgel diagram ? Why does it arise ?

(c) Usually, the transition metal complex electronic spectra are characterized by broad and weak lines. Give a brief explanation with adequate reason.

(d) What are the 'Laporte' and 'Spin' selection rules ? Why are charge transfer bands allowed ?

(e) An aqueous solution of Fe^{3+} ions appears faintly colored. Would you expect one broad, very weak absorption peak or many weak peaks ? Explain in the light of the Tanabe-Sugano diagram.

UNIT–III

(Marks : 29)

(A) *Marks : 07*

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

(a) Explain NMR chemical shift. Draw tentatively the ^{19}F NMR spectra of SF_6 and BrF_6 molecule. 1+1+1.5=3.5

(b) Draw ^{1}H, ^{19}F and ^{31}P NMR spectra of HPF_2 molecule. 1+1+1.5=3.5

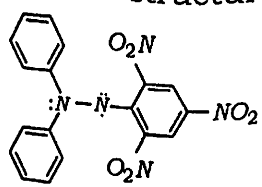
(c) Explain on the basis of ^{31}P NMR, how can you distinguish between *mer* – and $fac-\left[RhCl_3\,(PPh_3)_3\right]$. Draw tentative spectra of both the isomers.

(B) *Marks : 07*

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

(a) High dielectric constant solvents are not suitable for ESR measurements, why ? Why are ESR spectra usually recorded in a derivative mode ? Draw the ESR spectrum of a frozen aqueous solution of $CuSO_4.5H_2O$ at 77K. 1.5+2=3.5

(b) DPPH is a common reference in EPR spectroscopy. Its structure is-



Predict the number of lines exhibited by it in concentrated xylene solution and in a 10^{-3} M xylene solution. Also predict the number of ESR lines exhibited by NH_2 and C_6H_5 radicals.

(c) What is Kramer's doublet ? Spectrum of a single crystal of Mn^{2+} doped into MgV_2O_6, showing five allowed transitions, each again splits to six line $(Mn=I=5/2)$. Explain the spectral pattern. 2+1.5=3.5

(d) (i) How does '*g*' value vary with crystal symmetry, physical state of the paramagnetic system and temperature ?

(ii) Define superhyperfine splitting. 2+1.5=3.5

(C) *Marks : 6*

7. Answer ***any two*** of the following questions : 3×2=6

(a) A Fe^{57} source emits γ – rays of energy $E_\gamma = 14.4$ keV. The source is moving toward the stationary absorber with $V_e = 5mm/s$. Calculate the energy ΔE received by the absorber.

(b) What is isomer shift in Mössbauer spectroscopy ? Arrange the following *Fe* compounds in increasing order of isomer shift and explain. 1+2=3

(i) $\left[Fe(CN)_6\right]^{3-}$

(ii) $Fe(CN)_6]^{3-}$

(iii) $FeSO_4 \cdot 7H_2O$

(iv) Fe_2O_3

(c) Predict and justify the Mössbauer spectral pattern of $Fe(CO)_5$ at (a) 298 K and (b) 77 K. Would you expect any magnetic hyperfine splitting in $Fe(CO)_5$? Give reason for your answer. 2+1=3

(d) How would you distinguish $Sn(II)$ and $Sn(IV)$ compounds using ^{119}Sn Mössbauer spectroscopy ? Compare the extent of quadrupole splitting in these two compounds. 2+1=3

(D) Marks : 5

8. For $I = \frac{7}{2}$, find the number of NQR lines and also determine the energy required (ΔE) for $m_I = \pm\frac{3}{2} \rightarrow m_I \pm \frac{5}{2}$ transition. 3

Or

Explain the correct increasing order of ^{35}Cl QCC (quadrupole coupling constant) values for $Cl-C$, $Cl-F$, $Cl-Cl$ and $Cl-Si$ bonds. A molecule $C_6F_5PCl_4$, may have two possible isomers. It gives four NQR signals for ^{35}Cl at 33.480, 34.380, 34.290 and 25.300 MHz (at $77K$). Draw the correct geometry of this molecule and also justify your answer. 1+2=3

9. Why NQR spectroscopy is known as zero-field NMR spectroscopy ? What is the difference between NMR and NQR spectroscopy ? 2

(E) Marks : 4

10. What is the role of binding energy in photoelectron spectroscopy (PES) ? Mention the information one can obtain from PES. 2+2=4

Or

Explain the principle behind Auger electron spectroscopy (AES). Summarize the key differences between the AES and XPS techniques. 2+2=4

UNIT–IV

(Marks : 7)

11. Answer the following questions :

(a) What is the origin of temperature-independent paramagnetism ? Explain with an example. 2

(b) Define molar magnetic susceptibility. What is Weiss-constant (θ) ? What does its sign indicate ? 1+1+1=3

(c) What is meant by high-spin low-spin crossovers ? Give an example of a system known to exhibit spin crossover behaviour. 1+1=2

Or

Comment on the contribution of the orbital magnetic moment for the following : 1+1=2

(i) Cr^{3+} (high spin)

(ii) Fe^{2+} (low spin)