RANI RASHMONI GREEN UNIVERSITY

DEPARTMENT OF CHEMISTRY

Semester – IV, Final Examination – 2025

M.Sc. Course in Chemistry

Course ID: CHEM-CB43I

Full Marks: 40 **Time: 2 h**

Answer any one question from each unit in your own words with proper scientific justification.

Unit-1: Magnetochemistry

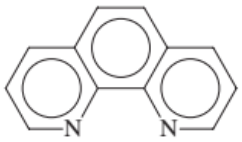
1. (a) Determine the number of unpaired electrons present in a ground-state Al atom (Z =13).

(b) The stabilization of a half-filled d shell is more pronounced than that of the p subshell. Why?

(c) Draw the *d*-orbital splitting diagram for an eight-coordinate cubic complex.

(d) How does the 10Dq value of an octahedral complex depend on the radial distance of a *d* orbital from the nucleus? **[2+2+2+2]**

3. (a) What type of isomerism is found in $[Ru(phen)_3]^{2+}$? Draw the crystal field diagram for the d orbitals in this complex ion and comment on its magnetic property.

Phen = 1,10-phenanthroline = 

(b) What is the ground state term of octahedral $[Co(NH_3)_6]^{2+}$?

(c) Predict the number of unpaired electrons for a coordination compound with a magnetic moment of 5.1 Bohr magnetons.

(d) What would you predict for the number of unpaired electrons and spin-only magnetic moment of an octahedral Fe(IV) complex in (i) a weak field and (ii) a strong field environment? **[2+2+2+2]**

Unit-2: Separation Techniques

3. **(a)** What are the two main components of any chromatographic system? Name at least two different solid-liquid chromatographic systems.

(b) In liquid liquid chromatography "Reversed phase extraction chromatography (RPEC)" is popular. How it is designed?

(c) Draw an arbitrary chromatogram of two components A and B. Show what is (i) FWHM and (ii) No of theoretical plates in the chromatogram? (iii) What is theoretical plate height?

(d) What is "hyphenated techniques"? **[2+2+3+1]**

4. **(a)** From a mixture of cobalt and copper in an aqueous solution, one has to separate these two elements. For this an aqueous biphasic system (ABS) was designed with 2 M Na_2So_4 and 50% PEG. After vigorous shaking and settlement concentration of Co and Cu was measured in the aqueous solution and found as given below.

	Conc of Co in aq solution	Conc of Cu in aq solutin
Initial concentration	100 μg/L	10 μg/L
After shaking with PEG	100 ng/L	9.95 μg/L

Find the D values for Co and Cu and the Separation Factor (S)

(b) One could also perform the above experiment by conventional liquid liquid extraction (LLX) system. Design a LLX system (mention reagents names both in aqueous and organic phases). Also compare LLX and ABS system.

(c) Design a system to separate trace amount of Cd from bulk amount of silver using ionic liquid. What are the advantages/disadvantages of using ionic liquid in separation science? **[2+3+3]**

Unit-3: Chemistry of f-Block elements

5. **(a)** Write down the name of two ore of lanthanide. Discuss the method of separation of lanthanide elements in ion exchange chromatography.

(b) Although Ce^{3+} and Yb^{3+} have unpaired electrons in their f-orbitals, yet they are colorless. Rationalized the fact?

(c) Why actinide complex shows variable oxidation state?

(d) Explain the stability of oxo-cation of actinide elements. Why lanthanide cannot form oxo-cation like actinides? **[3+2+1+2]**

6. **(a)** Write with example the synthetic route of an arene complex of lanthanide elements.

(b) What is antenna effect of lanthanide elements?

(c) $[Cp_2LnCl]$ dimerize in benzene but remain as monomer in THF. Justify.

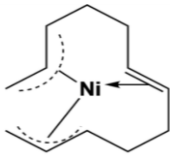
(d) The experimental magnetic moment (3.4 BM) of a hydrated salt of Eu^{3+} at 27^0C is significantly different from the calculated value. Explain. **[2+2+1+1+2]**

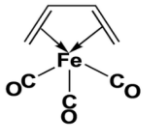
Unit-4: Spectral Study and Thermal Analysis

7. **(a)** What is a ligational motif and chelate loop size?

(b) What do you mean by "Redox site of non-innocent ligands"? Explain with examples.

(c) Identify the η-fashion of the following complexes.





(d) What would be the expected metal in complex (X), assuming the ligand in maximum haptacity and the complex (X) follows 18 electron rule.

$[(C_6H_6)M(C_4H_4)]$ (X)

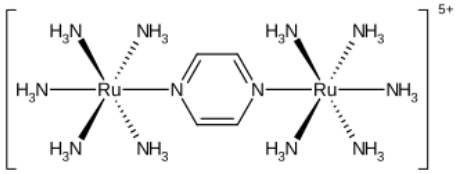
(e) What is "Intensity stealing"? **[2+2+2+1+1]**

8. **(a)** Write down the Basic conditions of MMCT transitions.

(b) Which type of transition is observed in the following colored complexes? Explain

i) $Fe_4[Fe(CN)_6]_3$

ii)



(c) What are the basic differences between DTA and DSC techniques in respect to their principle and instrumentation?

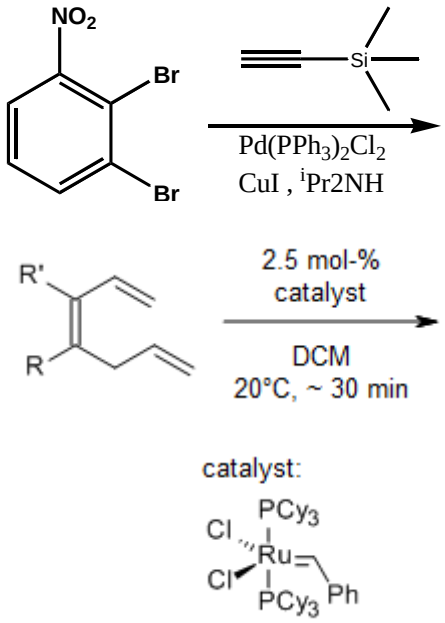
(d) How can you explain the stability of the given polymer by the interpretation of TGA graph: PVC (polyvinyl chloride}; LDPE(low density poly ethylene) and PTFF(ploytetra fluoroethylene) **[2+1+3+2]**

Unit-5: Organometallics-2

9. **(a)** Explain the change in ^{1}H NMR spectrum of $[Fe(\eta^1\text{-}C_5H_5)(\eta^5\text{-}C_5H_5)(CO)_2]$ on cooling to -77^0C.

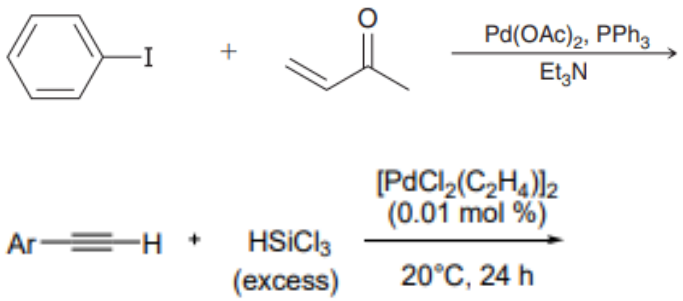
(b) Show the steps for product formation in the Oxo process catalytic cycle, taking propene as starting material and cobalt-carbonyl system as the catalyst.

(c) Predict the product of following reactions stating the name and type of reaction:



(d) Between Ziegler-Natta catalyst and kaminsky catalyst why later acts as a better catalytic system for olefin polymerization? **[2+3+2+1]**

10. (a) [Sc(η^5-Cp)$_2$(η^1-Cp)] exhibits only one signal above 30°C. What change in the ^{1}H-NMR spectrum do you expect on lowering the temperature? Explain the phenomenon.
(b) Explain the method employed for the regeneration of active catalyst in Wacker process of aldehyde synthesis.
(c) Draw the catalytic cycle for the commercial synthesis of acetic acid by Cativa process of British Petroleum.
(d) Predict the product of following reactions stating the name and type of reaction:



[1+2+3+2]