

D.K.M. COLLEGE FOR WOMEN (AUTONOMOUS), VELLORE-1
INORGANIC CHEMISTRY-I

UNIT-I STRUCTURE AND BONDING

Section-A (6 Marks)

1. Explain the chemistry of carboranes.
2. Give the preparation and structure of S_2N_2 .
3. Discuss briefly the types and structure of silicates.
4. Explain the salient features of $Re_2Cl_8^{2-}$.
5. Give an account of phosphazene with their structural aspects.
6. What are carboranes? Describe the preparation, structure and relative stabilities of isomeric dicarboclosododeca boranes.
7. What are silicates? Mention the structural aspects and properties of silicates.
8. What are isopoly and heteropoly acids? How are isopoly molybdate prepared? Mention any two industrial application of poly acids.
9. What are metal clusters? Discuss the bonding in dinuclear and trinuclear taking examples for each.
10. Discuss about polyorganophosphazenes.

Section-B (15 Marks)

11. Write a short note on isopolyacids of chromium and vanadium
12. Give an account of the structure, properties and uses of orthosilicates
13. Discuss the equilibria involved in the formation of isopolyacids of molybdenum describe the structure of $Mo_7O_{24}^{6-}$
14. Write a note on molecular sieves
15. Write an account of organophosphazene polymers highlighting their formation structure and bonding
16. How are sulphur nitrogen ring compounds prepared? Discuss the characteristics properties. Explain the relative stability of sulphur nitrogen ring compounds

17. How is diborane prepared? Give two properties. Explain the structure of diborane
18. Discuss the structure of bi and trinuclear clusters of metal carbonyls
19. Predict the structure of pentaborane. Illustrate Wade's rule by choosing one example for each structural type observed in polyhedral boranes
20. Present the general features of a typical keppin structure for heteropoly anions.

UNIT-II COORDINATION CHEMISTRY - I

Section-A (6 Marks)

1. Determine the stability constant by spectrophotometric method.
2. Explain about Irving William's series.
3. What is meant by stability of complexes? Describe the factors affecting it
4. State 18 electron rule. Explain with suitable examples
5. Explain the thermodynamic stability of complexes
6. Explain spectrophotometric and potentiometric method
7. Explain the geometrical and optical isomerism in complexes
8. Explain with suitable examples the ligand isomerism
9. Describe the potentiometric method for the determination of stability constants of complexes
10. What is meant by thermodynamic stability of complexes? Among $[\text{Ni}(\text{NH}_3)_6]^{2+}$ and $[\text{Ni}(\text{en})_3]^{2+}$ which would have higher stability?
11. Explain HSAB theory with illustrations
12. Give the general picture of the various factors that contribute to variations in stability constants
13. Describe the procedure adopted for the determination of stability constant by the spectrophotometric method
14. Discuss the factors affecting the stability of inorganic complex
15. How will you determine the stability constant by potentiometric method

Section-B (15 Marks)

16. Discuss the stereo isomerism in inorganic complexes arising out of nature of the ligands

17. Define chirality. Describe the nomenclature of chiral complexes
18. Explain the stereoselectivity and conformation of chelate rings in complexes
19. With examples explain the use of optical rotator dispersion and circular dichroism in the assignment of absolute configuration of complexes
20. Which of the following will have higher stability constant and why?
 - a. $\text{Zn(5-methyl-8-hydroxy quinoline)}_2$ or $\text{Zn(7-methyl-8-hydroxy quinoline)}_2$
 - b. $[\text{Ni}(\text{NH}_3)_6]^{2+}$ or $[\text{Ni}(\text{en})_3]^{2+}$
 - c. $[\text{Co}(\text{NH}_3)_6]^{2+}$ and $[\text{Co}(\text{CH}_3\text{NH}_2)_6]^{2+}$
21. Which of the following would be optically active. Why?
 - a. $\text{cis-}[\text{CrCl}_2(\text{Ox})_2]^{2-}$
 - b. $\text{cis-}[\text{Rh H(CO) (PR}_3)_3]$
22. Write the isomeric structure possible for $\text{Ma}_2\text{b}_2\text{cd}$ type complexes. Identify the chiral and achiral isomer
23. Explain the term ORD and CD
24. What are stepwise and overall stability constant? How they are related to each other.
25. The log beta values for the ions $[\text{Ni}(\text{NH}_3)_6]^{2+}$ and $[\text{Ni}(\text{en})_3]^{2+}$ are 8.1 and 18.0 respectively. Explain, also discuss application of HSAB
26. Write the isomeric structures possible for the octahedral complex of the formula Ma_3b_3 (a and b are the monodentate ligands). What are the point groups and which of them will be optically active
27. Comment on the isomerism exhibited by the following types of complexes ML_4 , ML_3X_3 , ML_4X_2 , $\text{Ma}_2\text{b}_2\text{c}_2$. Suggest how the isomers can be differentiated
28. Discuss in detail about stereo isomerism of octahedral and tetrahedral complexes.

UNIT-III COORDINATION CHEMISTRY – II

Section-A (6 marks)

1. Discuss in detail about the crystal field splitting in octahedral complexes
2. Explain in detail about the various factors which affect the CFSE values.
3. Describe in detail about the salient features of CFT.
4. How will you calculate the CFSE values for strong field and weak field octahedral complexes?
5. Predict the no. of unpaired electrons, the spin-only magnetic moments at 25 °C for each of the following. a) $[\text{Fe}(\text{CN})_6]^{4-}$ b) $[\text{Ru}(\text{NH}_3)_6]^{3+}$ c) $[\text{Cr}(\text{NH}_3)_6]^{2+}$ d) $[\text{EuCl}_6]^{4-}$ e) $[\text{Mo}(\text{CN})_6]^{3-}$ f) $[\text{Co}(\text{F}_6)]^{3-}$
6. Explain the Jahn-Teller distortion in $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$.
7. Determine the configuration, the number of unpaired electrons, and the ligand field stabilization energy as a multiple of Δ_o or Δ_t for each of the following complexes using the spectrochemical series to decide, where relevant, which are likely to be strong-field and which weak-field. (a) $[\text{Co}(\text{NH}_3)_6]^{3+}$; (b) $[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$; (c) $[\text{Fe}(\text{CN})_6]^{3-}$; (d) $[\text{Cr}(\text{NH}_3)_6]^{3+}$; (e) $[\text{W}(\text{CO})_6]$; (f) $[\text{FeCl}_4]^{2-}$ and (g) $[\text{Ni}(\text{CO})_4]$.
8. $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$ and $[\text{Cu}(\text{NH}_3)_4]^{2+}$ both appear blue in solution because of the presence of copper ions. However, the two solutions are not identical. How would the appearance of these solutions differ? If given an unlabeled sample of each, how could the two solutions be distinguished without collecting any spectra?
9. Describe in detail about the limitations of CFT
10. Enumerate the evidences for metal ligand covalency in metal complexes.
11. (a) Explain what is meant by CFSE and pairing energy (4)
(b) Give the reason for intense colour of $[\text{CrO}_4]^{2-}$ (2)
12. Give a brief account on spectro chemical series.
13. Describe in detail about the molecular orbital energy level diagram for sigma bonded strong field and weak field complexes
14. Ennumerate in detail about the Jahn Teller distortion

15. Discuss in detail about the various types of charge – transfer spectra with examples.
16. Derive the term symbols for d^1 - d^{10} systems by taking weak field complexes as an example.
17. Describe in detail about Orgel and Sugano – Tanabe diagrams.
18. Write short note on
 - (i) spin orbit coupling
 - (ii) Nephelauxetic effect
19. Explain in detail about the spectral and magnetic characteristics of octahedral weak field cobalt complexes.
20. What are spinels? How will you identify the spinels as normal and inverse spinels with the help of CFSE values?
21. Explain in detail about the selection rules for electronic spectrum.
22. Calculate the CFSE value for $[\text{CoF}_6]^{3-}$, $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$ and $[\text{Fe}(\text{CN})_6]^{4-}$.
23. Calculate the CFSE value of $[\text{Co}(\text{CN})_6]^{3-}$ and $[\text{NiCl}_4]^{2-}$. Which one is having the higher CFSE value?
24. Explain in detail about the term spectrochemical series.
25. Explain the following (3X2=6)
 - (i) The ${}^3\text{T}_1(\text{F}) \longrightarrow {}^3\text{T}_1(\text{P})$ transition in $[\text{NiCl}_4]^{2-}$ is stronger when compared to the corresponding ${}^3\text{A}_{2g} \longrightarrow {}^3\text{T}_{1g}$ transition in $[\text{Ni}(\text{H}_2\text{O})_6]^{2+}$
 - (ii) $[\text{FeF}_6]^{3-}$ is colourless while $[\text{CoF}_6]^{3-}$ is coloured
 - (iii) KMnO_4 is intensely coloured though Mn has d^0 configuration
26. (i) $[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$ is pale violet but CrO_4^{2-} is intensely yellow. What causes this color difference? (3)
 - (iii) Electronic absorption spectrum of $[\text{V}(\text{H}_2\text{O})_6]^{2+}$ displays three bands at $12,300\text{ cm}^{-1}$, $18,500\text{ cm}^{-1}$ and $27,900\text{ cm}^{-1}$ (3).

Section-B (15 Marks)

1. (a) Why Fe_3O_4 has an inverse spinel structure whereas Co_3O_4 has a normal spinel structure. Explain based on CFT(5)

- (b) Compare the molecular orbital diagram of $[\text{CoF}_6]^{3-}$ and $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$. What are your conclusions (5)
- (c) Explain strong and weak field complexes with suitable examples (5)
2. (a) $[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$ shows a double humped peak. Explain it using Jahn teller distortion (5).
- (b) What is meant by nephelauxetic effect? (2)
- (c) Explain the Orgel diagram for d^2 and d^7 system in both octahedral and tetrahedral complexes (8).
3. (a) Predict the CFSE values for d^3 , d^4 and d^8 electronic configuration in both high spin and low spin octahedral complexes (6).
- (b) With the help of M.O theory explain how Cl^- acts as weak ligand while CN^- act as strong ligand (9).
4. (a) Give a brief account on spectrochemical series (5)
- (b) Explain the d orbital splitting in tetrahedral and trigonal bipyramidal complexes (8)
- (c) Account for the following
- (i) $[\text{Fe}(\text{CN})_6]^{3-}$ has only one unpaired electron but $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$ has five electrons (2)
5. (a) What are the postulates of crystal field theory? Explain the formation of octahedral complexes based on crystal field theory (10).
- (b) Account for the following
- (i) 10 Dq value is in the order of $[\text{Ru}(\text{H}_2\text{O})_6]^{3+} > [\text{Co}(\text{H}_2\text{O})_6]^{3+} > [\text{Co}(\text{H}_2\text{O})_6]^{2+}$ (5)
6. (a) Differentiate between Orgel and Tanabe Sugano diagrams with examples (10)
- (b) Explain MLCT and LMCT with examples (5)
7. Write short notes on
- (i) d-d transitions (7)
- (ii) magnetic properties of complexes (8)
8. (a) Explain the Orgel diagram for $[\text{V}(\text{H}_2\text{O})_6]^{2+}$ (5)
- (b) Outline the limitations of CFT (5)

- (c) What is meant by T-S diagram? Mention its importance (5)
9. Sketch the crystal field splitting pattern in Oh, Td, Sq planar complexes and label the orbitals (15).
- 10.(a) Explain the Orgel diagram of $[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$ (5)
- (b) Explain the possible electronic transition in $[\text{Ni}(\text{H}_2\text{O})_6]^{3+}$ complex (5)
- (c) Discuss the Tanabe and Sugano and Orgel diagram for the d^2 complex (5)
11. (a) For the $[\text{Cr}(\text{H}_2\text{O})_6]^{2+}$ ion the mean pairing energy P is found to be 23,500 cm^{-1} . The magnitude of Δ_o is 13,900 cm^{-1} . Calculate the CFSE for this complex ion corresponding to high spin and low spin state and predict which state is more stable? (5)
- (b) The electron pairing energy of Co^{3+} ion is 250 kJ/mole. Δ_o value for the complex ion $[\text{Co}(\text{NH}_3)_6]^{3+}$ is 275 kJ/mole. What would you expect whether the amine complex is paramagnetic or diamagnetic? Explain. Also calculate its CFSE value (5).
- (c) Explain the various term symbols of d^2 configuration (5)
12. Discuss how the following terms affect the magnitude of Δ_o
- (a) Nature of central metal ion (5)
- (b) Nature of the ligands (5)
- (c) Geometry of the complex (5)
13. Draw and explain the Orgel and Tanabe Sugano diagram of d^6 and d^7 electronic configurations in both octahedral and tetrahedral field (15).
14. (a) What is meant by CFSE? Discuss and calculate the CFSE for d^3 and d^5 configurations under Td and Oh geometry (5)
- (b) What do you understand by Nephelauxetic effect? Why does F^- occupy the top position in the ligand series with regard to this effect? (5)
- (c) Discuss briefly about metal ligand π bonding in octahedral complexes. Use energy level diagrams to explain this property in the case of halogen ligands (5).
15. (a) Explain the spinels and inverse spinels. Discuss the factors that influence the formation of spinels (7)

(b) Explain why the ${}^3T_1(F) \rightarrow {}^3T_1(P)$ transition in $[\text{NiCl}_4]^{2-}$ is stronger when compared to the corresponding ${}^3A_{2g} \rightarrow {}^3T_{1g}$ transition in $[\text{Ni}(\text{H}_2\text{O})_6]^{2+}$ (3).

(c) What are the selection rules for electronic absorption? Explain why the d-d transitions are normally found to be weak (5).

16. (a) The complex $[\text{Cr}(\text{malonate})_3]^{3+}$ in its electronic spectrum shows bands at 17,000 and 24,000 cm^{-1} . Weak bands were observed at 15,000 and 22,000 cm^{-1} which are forbidden. Assign the transitions and interpret the spectrum. (5)

(b) In the electronic spectrum of $[\text{V}(\text{H}_2\text{O})_6]^{3+}$, three bands were obtained at 17,200 cm^{-1} , 25,600 cm^{-1} and 20,000 cm^{-1} have been observed. Assign the bands and calculate the 10 Dq (5).

(c) Account for the colour of permanganate ion (5)

17. Write short note on

- (i) orbit orbit coupling (3)
- (ii) Spin spin coupling (3)
- (iii) Russel saunder coupling (3)
- (iv) jj coupling (3)
- (v) Term symbols (3)

18. Construct the molecular orbital diagram for an octahedral sigma and pi bonding complexes using examples (15).

19. Account for the following

- (i) H_2O is a stronger ligand than OH^- (3)
- (ii) Nephelauxetic effect (4)
- (iii) The electronic absorption spectrum of $[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$ shows three bands at 16,200 cm^{-1} , 22,000 cm^{-1} and 33,580 cm^{-1} (3)
- (iv) Metal ligand bond shows covalence (5)

20. (a) List out the differences between Orgel and Tanabe Sugano diagrams (7)

(b) Why is the ${}^3T_1 \rightarrow {}^3A_{2g}$ transition generally not observed in the spectrum of Oh complex of d^2 metal ions (3)

(c) Electronic spectra of $[\text{Cr}(\text{NCS})_6]^{3-}$ shows absorption bands at 16,000 cm^{-1} , 17,700 cm^{-1} , 23,800 cm^{-1} and 32,400 cm^{-1} . Interpret these data. (5)

21. (a) Electronic spectrum of $[\text{CrF}_6]^{3-}$ shows three bands at 34,400 cm^{-1} , 22,700 cm^{-1} and 14,900 cm^{-1} . Identify the electronic transition with suitable energy level diagram (5)

(b) Identify the electronic transition responsible for the characteristic colours of the following (10).

(i) $[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$

(ii) KMnO_4

UNIT-IV ORGANOMETALLIC CHEMISTRY- I

Section-A (6 Marks)

1. Explain the Carbonylation. Decarbonylation,
2. Write a note on oxidative addition
3. Give an account on fluxionality
4. Write a short note on bonding in carbonyls and nitrosyls.
5. Describe the synthesis, structure and bonding and Metallocenes.
6. Deduce the association and substitution reactions.
7. Explain the addition and elimination reaction.
8. Briefly explain the ligand promotion reaction.

Section-B (15 marks)

9. i. Describe in detail about the bonding in metallocenes. (10)
ii. Explain the metalation reaction.
10. Explain in detail about the oxidative addition and fluxionality.
11. i. Discuss in detail about the Carbonylation and decarbonylation reaction. (10)
ii. Write a short note on synthesis of metallocenes.

UNIT-V ORGANOMETALLIC CHEMISTRY- II

Section-A (6 marks)

1. How does palladium chloride help in the commercial conversion of ethylene to acetaldehyde?
2. Applying 16 and 18 electron rule explain the oxo process promoted by $\text{Co}_2(\text{CO})_8$.
3. Explain the stereochemistry of Ziegler Natta polymerization
4. Discuss the mechanism of hydrogenation reaction promoted by $[\text{Rh}(\text{PPh}_3)_3\text{Cl}]$.
5. Explain in detail about the cyclooligomerization of olefins using Reppes catalyst
6. Give a brief account on cyclooligomerization.
7. Discuss the mechanism of conversion of ethylene to propionaldehyde using the rhodium catalyst.
8. Discuss the mechanism of hydrogenation of ethylene by triphenylphosphine phosphine rhodium complex.

Section-B (15 marks)

1. Discuss the mechanism of the following
 - (i) Hydrogenation of olefins (5)
 - (ii) Wackers process (5)
 - (iii) Polymerization of alkenes by Ziegler Natta catalyst (5)
2. Describe the hydroformylation reaction promoted by cobalt, rhodium and ruthenium catalyst (15).
3. Describe the catalytic cycle involved in the oxidation of olefins using palladium chloride catalyst (15)
4. How is Zeigler Natta catalyst prepared? Discuss in detail the mechanism involved possible products and their isolation in Zeigler Natta catalysis of propylene.(15)
5. (a) Describe in detail about the polymer bound catalyst (7)
 (b) Discuss the mechanism of hydrogenation reaction promoted by $[\text{Rh}(\text{PPh}_3)_3\text{Cl}]$ (8)