# ANDHRA UNIVERSITY DEPARTMENT OF INORGANIC AND ANALYTICAL CHEMSITRY M.Sc. Previous Chemistry Syllabus, Semester I **Paper- II: Inorganic Chemistry-I**

# <u>UNIT-1</u>

Structure & Bonding: Applications of VSEPR, Valence Bond and Molecular orbital theories in explaining the structures of simple molecules- role of p and d orbitals in pi bonding.

Application of MO theory to square planar ( $PtCl_4^{2-}$ ) and Octahedral complexes ( $CoF_6^{3-}$ ,  $Co(NH_3)_6^{3+}$ ).

Walsh diagram for H<sub>2</sub>O molecule.

# UNIT-II

Inorganic cage and ring compounds – preparation, structure and reactions of boranes, carboranes, metallocarboranes, boron–nitrogen  $(H_3B_3N_3H_3)$ , phosphorus–nitrogen  $(N_3P_3Cl_6)$  and sulphurnitrogen  $(S_4N_4, (SN)_x)$  cyclic compounds.

Electron counting in boranes – Wades rules (Polyhedral skeletal electron pair theory). Isopoly and heteropoly acids.

# UNIT-III

Coordination compounds: Crystal field theory - crystal field splitting patterns in octahedral, tetrahedral, tetragonal, square planar, square pyramidal and trigonal bipyramidal geometries. Calculation of crystal field stabilization energies. Factors affecting crystal field splitting energies – Spectrochemical series – Jahn – Teller effect, nephelauxetic effect – ligand field theory.

Term symbols – Russell – Sanders coupling – derivation of term symbols for various configurations. Spectroscopic ground states.

# UNIT- IV

Electronic spectra of transition metal complexes: Selection rules, break down of selection rules – Orgel and Tanabe-Sugano diagrams for  $d^1 - d^9$  octahedral and tetrahedral transition metal complexes of 3d series – Calculation of Dq, B and  $\beta$  parameters. Charge transfer spectra.

Magnetic properties of transition and inner transition metal complexes – spin and orbital moments – quenching of orbital momentum by crystal fields in complexes.

#### Text books:

- 1. Advanced Inorganic Chemistry by F.A. Cotton and G. Wilkinson, IV Edition, John Wiley and Sons, New York, 1980.
- 2. Inorganic Chemistry by J.E. Huheey, III Edition, Harper International Edition, 1983.
- 3. Theoretical Inorganic Chemistry, II Edition by M.C. Day and J. Selbin, Affiliated East-West press Pvt. Ltd., New Delhi.
- 4. Inorganic Chemistry by Shriver and Atkins, Oxford University Press (1999

#### DEPARTMENT OF INORGANIC AND ANALYTICAL CHEMISTRY

MODEL QUESTION PAPER

M.Sc. Previous Chemistry Syllabus Semester I

Paper- II: Inorganic Chemistry-I

(Effective from 2011-2012 admitted batch)

Time: 3 hours

# SECTION-A

Max. Marks: 80

# ANSWER ALL QUESTIONS

4x5=20 Marks

1. a) Predict the geometries of ClF<sub>3</sub>, XeF<sub>4</sub> and SF<sub>4</sub> molecules using VSEPR theory.

Or

Or

- b) Draw the Walsh diagram for H<sub>2</sub>O molecule and predict its structure.
- 2. a) Discuss the structure and properties of borazole.
  - b) Write a short note on homopoly and heteropoly acids.
- 3. (a) Draw and explain the crystal field splitting of 'd' orbitals in square planar and trigonal bipyramidal geometries.
  - Or
  - (b) Write a note on nephelauxetic effect.

**ANSWER ALL QUESTIONS** 

- 4. (a) Draw the Orgel diagram for  $[TiCl_4]^-$  ion and explain the electronic transitions. Or
  - (b) Calculate the spin only magnetic moments of the following ions:
    (i) [MnCl<sub>6</sub>]<sup>3-</sup> (ii) [Fe(CN)<sub>6</sub>]<sup>3-</sup>

# SECTION-B

# 4x15=60 Marks

5. a) What is LCAO method? Predict bond order and bond lengths in O<sub>2</sub><sup>+</sup> and O<sub>2</sub><sup>-</sup> ions based on MO energy level diagram.

Or

b) Draw the MO energy level diagram for  $[Co(NH_3)_6]^{3+}$  and discuss its magnetic properties.

6. a) Discuss the preparation of, structure of, and bonding in  $N_3P_3Cl_{6.}$ 

Or

b) Explain the method of counting skeletal electrons in cluster compounds.

7. (a) Discuss the factors affecting crystal field splitting energies.

- Or (b) (i) Write an account on Russell – Saunders coupling.
- (ii) Derive the term symbols for  $Ni^{2+}$  and identify the ground state term symbol.

# 8. (a) How do Tanabe – Sugano diagrams differ from Orgel diagrams? Draw Tanabe – Sugano diagram for $[V(H_2O)_6]^{3+}$ and explain the electronic transitions.

Or

(b) Discuss different types of paramagnetic behaviour of transiton metal complexes.

# AND HRA UNIVERSITY DEPARTMENT OF INORGANIC AND ANALYTICAL CHEMSITRY M.Sc. Previous Chemistry Syllabus, Semester - II **Paper- II: Inorganic Chemistry - II**

# <u>UNIT-I</u>

**Metal cluster compounds -** definition – evidences for existence of M-M bonds - conditions favorable for formation of M-M bonds – preparation, structure and bonding of the following metal cluster compounds.

 $Re_2Cl_8^{2-}$ ,  $Mo_2Cl_8^{4-}$ ,  $Re_2(RCOO)_4X_2$ ,  $Mo_2(RCOO)_4(H_2O)_2$ ,  $Cr_2(RCOO)_4(H_2O)_2$ ,  $Cu_2(RCOO)_4(H_2O)_2$ ,  $Cr_2Cl_9^{3-}$ ,  $Mo_2Cl_9^{3-}$ ,  $Re_3Cl_9$ ,  $Re_3Cl_{12}^{3-}$ ,  $Mo_6Cl_8^{4+}$ ,  $Nb_6X_{12}^{2+}$  and  $Ta_6X_{12}^{2+}$ . Polyatomic clusters – Zintle ions, Chevrel phases.

# <u>UNIT-II</u>

**Organometallic compounds** - 16 and 18 electron rules.

Isoelectronic relationship - Synthesis, structure, bonding and reactions of carbon monoxide, dinitrogen and nitric oxide complexes.

Isolobal relationship – H, Cl, CH<sub>3</sub>, Mn(CO)<sub>5</sub>; S, CH<sub>2</sub>, Fe(CO)<sub>4</sub>; P, CH, Co(CO)<sub>3</sub>

Synthesis, structure, bonding and reactions of metallocenes with special reference to ferrocene

# UNIT-III

# Metal Ligand equilibria in solution:

Step wise and overall formation constants and their interaction – trends in stepwise constants – factors affecting the stability of metal complexes – Pearson's theory of hard and soft acids and bases (HSAB), chelate effect and its thermodynamic origin, determination of stability constants of complexes – spectrophotometric method and pH –metric method.

Reactivity of metal complexes – inert and labile complexes. Explanation of lability on the basis of valence bond and crystal field theories.

# UNIT- IV

#### **Inorganic Reaction Mechanisms:**

Substitution reactions of metal complexes – D, Id, Ia and A mechanisms – Ligand replacement reactions of metal complexes – Acid hydrolysis – factors affecting acid hydrolysis – Anation and Base hydrolysis of Cobalt(III) complexes. Ligand displacement reactions of square planar complexes of platinum (II). Factors affecting square planar substitution – trans effect (theories).

Electron transfer reactions of complexes – concept of complementary and non-complementary reactions with examples. Inner and outer sphere mechanisms.

# Text books:

- 1. Advanced Inorganic Chemistry by F.A. Cotton and R.G. Wilkinson, IV Edition, John, John Wiley and Sons, New York, 1980.
- 2. Inorganic Chemistry by J.E. Huheey, III edition, Harper International Edition, 1983.
- 3. Organometallic Chemistry-A unified approach by A. Singh and R.C. Mehrotra, Wiley Eastern Ltd.
- 4. Inorganic Chemistry by Shriver and Atkins, Oxford University Press (1999)
- 5. Theoretical Inorganic Chemistry, II Edition by M.C. Day and J. Selbin, Affiliated East-West press Pvt. Ltd., New Delhi.
- 6. Mechanisims of Inorganic reactions in solution by D.Benson, MCgraw Hill, London, 1968.
- 7. Inorganic chemistry by K.F. Purcell and J.C.Kotz, W.B. Saunders company, New York, 1977.

## DEPARTMENT OF INORGANIC AND ANALYTICAL CHEMISTRY MODEL QUESTION PAPER M.Sc. Previous Chemistry Syllabus Semester II

Paper- II: Inorganic Chemistry-II

(Effective from 2011-2012 admitted batch)

Time: 3 hours

## SECTION-A

Max. Marks: 80

# ANSWER ALL QUESTIONS

4x5=20 Marks

1. a) Discuss the structure and magnetic property of Cu<sub>2</sub>(RCOO)<sub>4</sub> (H<sub>2</sub>O)<sub>2</sub>.

- Or b) Write a note on Chevrel phases.
- 2. a) Explain Isolobal relationship with suitable examples.

Or

- b) What is 18 electron rule? Illustrate with suitable examples.
- 3. (a) Describe the pH metric method for the determination of stability constants.
  - (b) What are inert and labile complexes? How are they explained by using crystal field stabilization energies?
- 4. (a) What is trans effect? Distinguish between the trans effect and trans influence. Or
  - (b) What are anation reactions? Discuss the mechanism of anation reactions.

# SECTION-B

# **ANSWER ALL QUESTIONS**

5. a) Discuss the preparation of, structures of and bonding in  $\text{Re}_2\text{Cl}_8^{2-}$ .

OR

- b) Describe the structures of hexanuclear metal clusters.
- 6. a) Explain the synthesis, structure and reactions of metal carbonyls.

#### OR

- b) Describe the preparation of, structure of and bonding in ferrocene.
- 7.(a) (i) Discuss a spectrophotometric method for the determination of binary formation constant of a complex.
  - (ii) Distinguish between stepwise and overall stability constants.

Or

(b) Explain the factors affecting the stability of coordination compounds.

8.(a) Explain the mechanisms of redox reactions of metal complexes.

- Or
- (b) (i) Give an account of base hydrolysis of Cobalt(III) complexes.
  - (ii) Discuss the various factors affecting the rates of substitution reactions of octahedral complexes.

## 4x15=60 Marks

#### DEPARTMENT OF INORGANIC AND ANALYTICAL CHEMISTRY

#### List of Experiments for M.Sc., previous Inorganic chemistry practicals

#### <u>Semester – I</u>

## I. Inorganic Synthesis: Preparation of

- Tetraamminecopper(II) sulphate
- Potassium tris-oxalato ferrate(III) trihydrate
- Tris-thiourea copper(I) sulphate

# II. Semimicro qualitative analysis of six radical mixtures

(One interfering anion and one less familiar cation for each mixture)

Anions:  $CO_3^{2-}$ ,  $S^{2-}$ ,  $SO_3^{2-}$ ,  $Cl^-$ ,  $Br^-$ ,  $l^-$ ,  $NO_3^-$ ,  $SO_4^{2-}$ ,  $CH_3COO^-$ 

Cations : Amn

Ammonium  $(NH_4^+)$   $1^{st}$  group: Hg, Ag, Pb, Tl, W  $2^{nd}$  group: Hg, Pb, Bi, Cu, Cd, As, Sb, Sn, Mo  $3^{rd}$  group: Fe, Al, Cr, Ce, Th, Ti, Zr, V, U, Be  $4^{th}$  group: Zn, Mn, Co, Ni  $5^{th}$  group: Ca, Ba, Sr  $6^{th}$  group: Mg, K, Li

# <u>Semester – II</u>

#### **III Quantitative analysis:**

- a) Volumetric : i) Determination of Ferric iron by photochemical reduction
  - ii) Determination of Nickel by EDTA
  - iii) Determination of Calcium and Magnesium in a mixture by EDTA
  - iv) Determination of Ferrocyanide by Ceric sulphate
  - v) Determination of Copper(II) in presence of iron(III)
- b) Gravimetric: i) Determination of Zinc as Zinc pyrophosphate
  - ii). Determination of Nickel from a mixture of Copper and Nickel.