SEMESTER -II

INORGANIC CHEMISTRY-II

THEORY

Programme: M.Sc. **Max.Hours : 60**
Course Code: P20/CHE/DSC/201 **Hours per week: 4**
Type of course: DSC – 5 **Max.Marks: 100**
No. of credits: 4

Course Objectives:

1. Determinethe symmetry operations of any small and medium-sized molecule and apply point group theory to the study of optical and magnetic properties and selection rules for absorption.

2. Identifythe principles, structure and reactivity of selected coordination complexes, Interprettheir electronic spectra and magnetic properties.

3. To understand the stability of coordination complexes by the instrumental techniques.

4. To understand the nature of bonding between the metal and ligand. To study the structure and stereochemistry of metal carbonyl clusters.

Course Outcome:

CO1: Discuss the concept of symmetry element, symmetry operation and point groups
CO2: Classify & recognize the symmetry elements and their operations as required to specify Molecular symmetry & possible point groups from symmetry elements & be able to find Point group of molecule by systemic procedure.
CO3: Discuss the d-orbital splitting pattern in different geometries like octahedral, tetrahedral.
CO4: Calculate magnetic moment & crystal field stabilization energy of metal complexes.
CO5: Explain high spin and low spin complexes & formation of metal complexes in solution.
CO6: Discuss HSAB rule chelation, macro cyclic and cryptate effect.
CO7: Determine stability constant of particular complex through pH metry, polagraphic methods
CO8: Discuss bonding modes of CO, NO, 18-electron rule, different bond lengths &frequencies of CO, NO.
CO9: Explain different nitrogen complexes & how chemical fixation of dinitrogen takes place.

Module 1: Symmetry of Molecules (15 Hrs)

Concept of Symmetry in Chemistry – Symmetry Operations – Symmetry Elements: Rotational Axis of Symmetry and Types of Rotational Axes, Plane of Symmetry and types of Planes, Improper Rotational Axis of Symmetry , Inversion Center and Identity Element – More about Symmetry Elements – Molecular Point Groups: Definition and Notation of Point Groups, Classification Molecules in to C1, Cs, Ci, Cn,Cnv, Cnh, C∞v, Dn, Dnh, Dnd, D∞h, Sn (n=even), Td, Oh, Ih, Kh,C_{60}(Fullerenes) Groups. Descent in Symmetry with Substitution – Exercises in Molecular Point Groups – Symmetry and Dipole moment – Symmetry criteria for Optical activity.

Module 2: Bonding in metal complexes (15 Hrs)

Crystal Field Theory: Salient features of CFT. d-orbital splitting patterns in regular Octahedral, tetragonally distorted octahedral, Jahn-Tellartheorem , trigonal bipyramidal, trigonal planar, Pentagonal bipyramidal, and linear geometries. Concept of weak field and strong fields. - Calculation of crystal field stabilization energies (CFSE's) in six and four coordinate complexes. Types of magnetic behaviour – magnetic susceptibility – calculation of magnetic moment from magnetic susceptibility spin only formula ,- Quenching of orbital angular momentum – Determination of magnetic moment from Guoy's method.. Applications of magnetic moment data for the determination of oxidation states, bond type and stereochemistry. Spin crossover: High spin, low spin cross over phenomenon in $[Fe(Ophen)_2(NCS)_2]$ and $[Fe(R_2NCS_2)_3]$. Spinels. Limitations of Crystal field Theory, Adjusted CFT (Ligand field theory). Experimental Evidences for Metal covalency. Thermodynamic aspects of CFT

Module 3: Coordination Equilibria (15 Hrs)

Solvation of metal ions- Metal complex formation in Solution-Binary metal complexes.Stability constants (types and relationships between them). – Factors influencing the stability constants: (i) Metal ion effects (charge/size, IP, crystal field effect, John-Teller effect, Pearson theory of hard and soft acids and bases (HSAB), elecronegativity and hardness and softness, symbiosis. (ii) Ligand effects (Basicity, Substituent effect,Steric,chelate (size and number of chelate rings), Macrocyclic and Cryptate effects- crown ethers, crypton, size match selectivity or concept of hole size, limitations, Macrocycles with pendent groups– Methods used for the determination of Stability constants (Basic Principles only): pH metric, Spectrophotometric and Polarographic methods. Ternary Metal Complexes – definition – Formation of ternary metal complexes – Step-wise and simultaneous equilibria with simple examples.

Module 4: Ligational Aspects of Diatomic molecules (15 Hrs)

Metal Carbonyls: - Carbon monoxide as a ligand – Molecular orbitals of CO - Donor and Acceptor molecular orbitals of CO; Bonding modes of CO- Terminal and Bridging; Evidence for

multiple bonding from Bond lengths and Stretching frequencies; 18 Valence electron rule and its application.

Metal Nitrosyls: - NO as a ligand – Molecular orbitals of NO – Donor and Acceptor components; Bonding modes of NO – Terminal (Linear, Bent) and Bridging; Structural aspects of $[IrCl(PPh_3)_2(CO)(NO)]^+$ and $[RuCl(PPh_3)_2(NO)_2]^+$.

Stereo chemical control of valence in $[Co\ (diars)_2(NO)]^{2+}$ and $[Co(diars)_2(NO)(SCN)]^+$.

Metal Dinitrogen complexes: - N_2 as aligand – Molecular orbitals of N_2; Bonding modes – Terminal and Bridging; Stretching frequencies; Structures of Ru (II) and Os (II) dinitrogen complexes; Chemical fixation of dinitrogen.

Suggested References:

1. Symmetry and Group theory in Chemistry, Mark Ladd, Marwood Publishers, London (2000).
2. Molecular Symmetry and Group Theory, Robert L.Carter, John Wiley & Son (1998).
3. Symmetry and Spectroscopy of Molecules. K.Veera Reddy, New Age International (P) Limited (1999).
4. Advanced Inorganic Chemistry. F.A.Cotton, G.Wilkinson, C.A.Murillo and M.Bochmann, 6th Edition, Wiley Interscience, N.Y (1999
5. Inorganic Chemistry, J.E. Huheey, K.A.Keiter and R.L.Keiter 4 th Edition Harper Cottens College Publications (1993).
6. *Ligand Field Theory* and *Its Applications* (*Special Topics* in *Inorganic Chemistry*) by *Brian N. Figgis* and *Michael*
7. Homogeneous Catalysis by Metal complexes Vol I, M MTaqui Khan and A E Martell, Academic Press NY (1974).
8. Inorganic Chemistry, Keith F.Purcell and John C.Kotz, Holt-Saunders International Editions, London (1977).
9. N.N.Greenwood and A.E. Earn Shaw, Chemistry of the elementals, 2nd ed., Butterworth Heinemann, 1997.
10. M.L.Tobe and John Burgess, Addison Wesley Longman Inorganic Mechanisms (1999)
11. K.Veera Reddy Metal ions in Reaction Mechanisms. Golgotia Publications (P) Ltd
12. Richard A Henderson Mechanisms of Reactions in Transition Metal Sites, Oxford Science Publications, London (1993).

Text Books:

1. K.Veera Reddy, Symmetry and Spectroscopy of Molecules. New Age International (P) Limited (1999).
2. F.A.Cotton, Wilkinson, Advanced Inorganic chemistry, 6th ed., John Wiley & sons, 2009.
3. Puri, Sharma and KhaliaSelected topics in Inorganic Chemistry.
4. J.E.Huheey,E.A.Keiter, Inorganic Chemistry-Principles of Structure and Reactivity .4th ed., Pearson Education Asia Pvt .Ltd. 2000.
5. D.F.Shriver. P.W. Atkins and C.H.Langford. Inorganic Chemistry, 3rd edition, ELBS: Oxford University Press, Oxford. UK. 1999.
6. J.D.Lee, Concise Inorganic Chemistry, 5th Edition, Chapman & hall: Hong reprint 2009.
7. K.Hussain Reddy, Bioinorganic Chemistry, New Age International Publishers, reprint 2007.

SEMESTER -II

INORGANIC CHEMISTRY-II

MODEL THEORY QUESTION PAPER

Course Code: P20/CHE/DSC/201 **Max Time: 2½ Hrs**
Credits: 4 **Max. Marks:60**

SECTION A

I Answer the following Questions:- **4 x10 = 40 M**

1.(a) Explain different types of Substitution reaction in Metal Complexes. Explain acid Hydrolysis Mechanism and the factors effecting Acid Hydrolysis .(CO1)
.
(b) Explain Trans effect by the Grienberg's theory (CO2)

OR

2. (a) Draw the Energy Profile diagram of SN^1&$SN^2$and Explain .(CO1)
(b) Explain SN^1 CB Mechanism in base hydrolysis with Evidences.(CO1)

3. (a) Derive the Terms for p^2 Configuration (CO4)
(b) Draw the Orgel diagram for ^3F Energy Term. (CO4)

OR

4. (a) Write a short note on Inter electronic repulsions with Racah parameters . (CO5)
(b)Write an Account on Hund's Rules to explain the Energy Ordering of Terms. (CO5)

5. (a) Write a brief account on Polyhedral Skeletal Electron pair theory (CO6)
(b) Explain the Classification of Metal halide Clusters (CO7)

OR

6.(a)Explain the structure and bonding in $[Re_2Cl_8]^{-2}$metal halide cluster **(CO7)**
(b) Explain the Stereochemical non-rigidity in [Rh4(CO)12] and [Fe2(Cp)2(CO)4]. (CO6)

7.(a)Write in detail the structural, electronic and magnetic properties of Heamerythrin with Haemoglobin. **[CO9]**
(b) Write short note on Globin chain **[CO9]**

OR

8.(a) Explain Photosystem I and Photosystem II **[CO10]**
(b) Explain the reaction mechanism of Decarboxylation of Vitamin B_6 **[CO10]**

SECTION-B

II Answer any <u>FIVE</u> : 5 x 4 = 20 M

9. Write a short note on Applications of Trans Effect. (CO2)
10. Write a note on Electron Transfer reactions. (CO3)
11. Calculate the number of Microstates for d^2 configuration. (CO4).
12. Explain in brief the L-S coupling and j-j Coupling **.(CO5)**
13. Explain the factors which effect the M--M bonding in Metal carbonyl Clusters **(CO6)**
14. Write Short note on capping Rule .Give the structure of $[Os_8(CO)_{22}]^{-2}$ **(CO7)**
15. Write a short note on relation between concentration of metal ion and their physiological effects (CO8)
16. Write the functions of Haemoglobin (CO9)