SEMESTER –I

INORGANIC CHEMISTRY-I

THEORY

Programme: M.Sc. **Max.Hours : 60**
Course Code: P20/CHE/DSC/101 **Hours per week: 4**
Type of course: DSC – 1 **Max.Marks: 100**
No. of credits : 4

Course Objectives:

- Determine the 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.
- Identify the principles, structure and reactivity of selected coordination complexes, Interprettheir electronic spectra and magnetic properties.
- To understand the stability of coordination complexes by the instrumental techniques.
- 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.

MODULEI - 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 II - BONDING IN METAL COMPLEXES (15hrs)

Crystal Field Theory: Salient features of CFT. d-orbital splitting patterns in regular Octahedral, tetragonally distorted octahedral, Jahn-Tellartheorem , trigonalbipyramidal, 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 III - 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 IV - 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.

References Books:

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

Text Books:

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

SEMESTER -I

INORGANIC CHEMISTRY PAPER-1

MODEL THEORY QUESTION PAPER

Course Code : P20/CHE/DSC/101 **Max Marks:60**
Credits :- 4 **Max Hours:2½hrs**

SECTION-A

I Answer the following Questions **4 x 10 = 40 M**

1. (a) Define Plane of Symmetry. Explain the types of Symmetry planes with suitable Examples (CO1)
   (b) Explain the Improper Axis of Symmetry on BF_3 (CO1)

OR

2. (a) Explain the classification of Molecules into Point groups (CO2)
   (b) Explain the Descent in symmetry in ML_6 octahedral molecule with Substitution. (CO2)

3. (a) Discuss the consequences of Jahn-Teller distortion with any two examples. (CO3)
   (b) Calculate the crystal field splitting energy in i) $[Fe(CN)_6]^{4-}$ and ii) $[Ni(H_2O)_6]^{2+}$ (CO3)

OR

4. (a) Explain Guoy's methods for the determination of magnetic moment values. (CO4)
   (b) Quenching of orbital angular momentum and magnetic moment values. (CO4)

5. (a) Explain the Polarographic method for the determination of stability constants. (CO7)
   (b) Write a short note on Macrocyclic and Cryptate effects (CO7)

OR

6 .(a) Discuss the following i) HSAB principle ii) Irving-William's order. (CO6)
   (b) Explain the Spectrophotometric method of determination of Stability Constant of metal complexes..(CO7)

7. (a) Explain bonding in metal carbonyl Complexes. (CO8)
   (b) Discuss the linear and bent configurations in metal Nitrosyls with examples. (CO9)

OR

8. (a) Discuss the chemical fixation of Dinitrogen. (CO9)

(b) Explain how stretching frequency data is useful in bonding in metal carbonyls and metal Dinitrogen complexes. (CO9)

SECTION-B

II. Answer any FIVE **5 x 4 = 20 M**

9. Explain the difference between Principal axis and Secondary axes with an example.(CO1)
10 . Determine the Point group of Ferrocene (staggered) listing all symmetry elements.(CO2)
11. Draw the crystal field splitting diagram in Square Planar Complexes.(CO3)
12. Write a short note on Spin Cross Over.(CO4)
13. Explain thermodynamic and concentration stability constants (CO5)
14. Discuss the Applications of HSAB principle (CO6)
15. What is 18 electron rule? Explain the concept in trinuclear and tetranuclear metalCarbonyls (CO8)
16. Discuss the structural features of bridging metal Nitrosyls with Examples.(CO9)