BACHELORS WITH CHEMISTRY AS MAJOR
7th SEMESTER
CHM722J3: CHEMISTRY _ COORDINATION CHEMISTRY AND INORGANIC REACTION MECHANISM
CREDITS: THEORY-4, PRACTICALS-2

THEORY (4 CREDITS: 60 HOURS)

Course Objectives:
To provide an understanding of metal ligand equilibria, basic understanding of bonding in coordination compounds and insight into reaction mechanism in complexes.

Learning outcomes:
- *Understanding of metal ligand equilibria in solution, stability of uncommon oxidation states, stereochemistry and stability of lanthanide complexes*
- *Understanding of structure and bonding in transition metal nitrosyls, dinitrogen and dioxygen complexes*
- *Understanding of basic reaction mechanism in coordination complexes*

Unit-I Metal-Ligand Equilibria in Solution (15 hours)
Types of Ligands. Stepwise and overall formation constants (normal and abnormal trends). Mechanisms of selected complexation processes. d^n configuration and lability, Chelate effect and the factors affecting stability of metal chelates. Ligand preorganization, complexes of Macrocyclic ligands (crown ethers and cryptands), Determination of formation constants by spectrophotometric methods. Stability of uncommon oxidation states. Structural (ionic radii) and thermodynamic (hydration and lattice energies) effects of crystal field splitting. Jahn -Teller distortion. Selected examples of lanthanide complexes with nitrate, β-Diketonate, and porphyrin type ligands.

Unit-II Bonding in Coordination Compounds: (15 hours)
Experimental evidences in favor of Metal Ligand Orbital Overlap, The nephelauxetic effect. Adjusted crystal field theory. Molecular orbital theory of bonding in octahedral complexes (composition of ligand group orbitals; and energy level diagram for sigma bonded ML_6) ; Effects of pi bonding (pi donors and acceptors). Molecular orbital treatment and energy level diagram for bonding in square-planar and tetrahedral complexes. Binding modes in dioxygen complexes.

Unit-III Inorganic Reaction Mechanism – Basics (15 hours)
Energy profile of reactions, reaction intermediates and transition states. Kinetic and thermodynamic stability. Identification of inert and labile complexes. Types of substitution reactions; mechanistic classification of substitution reactions: Dissociative, Associative, and Interchange mechanism. Empirical criteria to differentiate the mechanism of substitution reaction. Rate laws. Factors effecting reaction rates: Nature of entering group-Nucleophilicity and basicity, nucleophilic constants n_{pt} and n_{pt}^{o} scales. Leaving group. Central metal ion.

Unit-IV Ligand Substitution Reactions in Square Planar and Octahedral Metal Complexes (15 hours)
General reaction mechanism of square planar complexes, K S and K Y pathways. Trans-effect: Theories and application in synthesis. Trans influence. Cis-effect. Substitution in octahedral complexes-Replacement of coordinated water- Eigen-Wilkins mechanism. Classification of metal ions based on water exchange rates. Anation reactions. Solvolysis/Hydrolysis: Hydrolysis under acidic conditions, Hydrolysis under basic conditions-Conjugate base (CB) mechanism. Substitution reactions without breaking of metal-ligand bond.

Books Recommended

1. Huheey, J. E.; Keiter, E.A. &Keiter, R.L. Inorganic Chemistry, Principles of Structure and Reactivity 4th Ed., Harper Collins 1993, Pearson, 2006.
2. Sharpe, A.G. Inorganic Chemistry, 4th Indian Reprint (Pearson Education) 2005.
3. Lee, J.D. Concise Inorganic Chemistry 5th Ed., John Wiley and sons 2008.
4. Housecraft
5. Miessler, G. L. &Tarr, D.A. Inorganic Chemistry 4th Ed., Pearson, 2010.
6. Crabtree, R. H., The Organometallic Chemistry of the Transition Metals, New York, NY: John Wiley, 2000.
7. Mechanisms of Inorganic Reactions - D. Katakis, G. Gordon (Wiley, 1987)
8. Reaction Mechanism of Inorganic and Organometallic systems, 2nd ed.- R. B. Jordan (Oxford,1998)
9. Mechanisms of Inorganic Reactions, 2nd ed. - F. Basolo, R.G. Pearson (Wiley, 1967)
10. Inorganic Chemistry- K. F. Purcell, 1C. Kotz (Saunders, 1977).
11. Chemistry of the Elements 2nd ed. - N. N. Greenwood, A. Earnshaw (Butterworth, 1997)

PRACTICALS (2 CREDITS: 60 HOURS)

I. Multi-stage Inorganic Preparations: (Any 03 Experiments)

- ✓ Preparation of tetraamminecarbonatocobalt (III) nitrate and its conversion to pentaamminecholorocobalt (III) chloride.
- ✓ Preparation of trans dicholorobis (ethylenediamine) cobalt (III) chloride and its conversionto cis-isomer.
- ✓ Preparation of tris (ethylenediamine) nickel (II) chloride dihydrate and its conversion to bis(ethylenediamine) nickel (II) chloride.
- ✓ Preparation of pentaamminecholorocobalt (III) chloride and study of Linkage isomers by its conversion to pentaamminenitritocobalt (III) chloride and to nitro isomer followed by IR characterization.

II. Separation by Column Chromatography and Estimations: (Any 02 Experiments)

- ✓ Separation of Permanganate and Dichromate ions on Alumina column and their Estimationfrom Beer Law plots.
- ✓ Determination of lonisable chloride in a Complex by cation exchange column (separation followed by Mohr's titration of elute for estimation).
- ✓ Ion exchange separation of Hydration / ionization isomers of Chromium (III) Chloride.

III. Spectrophotometry: (**Any 02 Experiments**)

- ✓ Estimation of Iron (II) in a water sample with 1,10-Phenanthroline.
- ✓ Determination of formula of Iron (III) thiocyanate complex by Job's Continuous variation method.
- ✓ Determination of composition of Iron (II)—2,2-bipyridyl complex by Mole ratio method.

IV. Potentiometry/ pH metry

- ✓ Complexation effect on redox potential of iron redox couple: Simultaneous potentiometric estimation of iron binary mixtures (iron aqua and iron phenanthroline).
- ✓ iv) Simultaneous determinations of chloride and iodide ions with Standard $AgNO_3$ over Ag and Calomel electrode assembly.
- ✓ pH Titration for estimation of chromate-dichromate mixtures

BOOKS RECOMMENDED

1. Svehla, G. *Vogel's Qualitative Inorganic Analysis*, Pearson Education, 2012.
2. Mendham, J. *Vogel's Quantitative Chemical Analysis*, Pearson, 2009.
3. J. B. Yadav**,** *Advanced Practical Physical Chemistry*; Edition, 16; Goel Pub., 2006.
4. L. H. Kalbus, R. H. Petrucci, J. E. Forman, and G. E. Kalbus, *J. Chem. Educ.* 1991, 68, 8, 677.
5. M. A. Rizvi, R. M. Syed, and B. U. Khan; *J. Chem. Educ. 2011, 88, 2, 220–222*.