## PAPER-IV: COORDINATION CHEMISTRY

| Semester | Subject Code | Category | Instruction Hours | | | | | | Credits |
|---|---|---|---|---|---|---|---|---|---|
| | | | Lecture | | Theory | | Practical | | |
| | | | Per Week | Per Semester | Per Week | Per Semester | Per Week | Per Semester | |
| II | 21CPCH2A | Core | 3 | 45 | 3 | 45 | 0 | 0 | 3 |

**COURSE OBJECTIVES:**

- To learn about thermodynamic and stereochemical aspects of complex formation, various theories of complexes, magnetic properties, term symbols and energy level diagram of weak and strong field ligands, charge transfer spectra and spectral properties of lanthanides and actinides.
- To learn about various mechanisms of substitution and electron transfer reactions and to study the recent development in the catalysis

**COURSE OUTCOMES:**

- On the successful completion of course, students will be able to

| CO Number | CO statement | Knowledge level |
|---|---|---|
| **CO1** | Get better understanding of stability constant, types of macrocyclic ligands and nomenclature of chiral complexes | **K2 & K4** |
| **CO2** | Identify the principles, structure and reactivity of selected coordination complexes with the help of crystal field theory and molecular orbital theory | **K2 & K3** |
| **CO3** | Interpret their electronic spectra, magnetic properties and can gain knowledge about the distortion in co-ordination complexes concept of sigma and pi bonding in complexes | **K2 & K4** |
| **CO4** | Get clear knowledge about the ISM, OSM, reaction mechanism of coordination compounds and the application of substitution reactions in the synthesis of Platinum and Cobalt complexes | **K3 & K4** |
| **CO5** | Identify the bonding aspects of simple organometallic compounds, different types of organometallic reactions and to explain different catalytic reactions | **K2 & K3** |

* CO-Course Outcomes

Knowledge level K1-Remember; K2-Understand; K3-Apply; K4-Analyze

**MAPPING WITH PROGRAM OUTCOMES**

| COS | PO1 | PO2 | PO3 | PO4 | PO5 | PO6 |
|---|---|---|---|---|---|---|
| **CO1** | M | M | M | M | S | S |
| **CO2** | M | M | S | S | S | M |
| **CO3** | S | S | S | S | S | S |
| **CO4** | M | S | S | M | M | M |
| **CO5** | M | S | S | S | M | M |

**UNIT-I: STABILITY OF COMPLEXES** **9 hours**

Stability of complexes – Factors affecting stability of complexes with respect to the nature of metal ion and ligands – Thermodynamic aspects of complex formation – Stepwise and overall formation constants – Stability correlations – statistical factors and chelate effect – Determination of stability constant and composition of the complexes – Formation curves and Bjerrum's half method – Potentiometric method – Spectrophotometric method – Ion exchange method – Polorographic method and Continuous variation method (Job's method)

Stereochemical aspects – Stereoisomerism in inorganic complexes – Isomerism arising out of ligand distribution and ligand conformation – Chirality and nomenclature of chiral complexes; Application of ORD and CD in the identification of complexes.

Macrocyclic ligands – Porphyrins, Corrins, Schiff's bases and crown ethers.

**UNIT-II: METAL – LIGAND BONDING** **9 hours**

Crystal field theory – Splitting of d – orbitals under various geometries – factors affecting splitting, CFSE, evidences for CFSE (Structural and thermodynamic effects), spectrochemical series – Jorgensen relation – site preferences – Jahn Teller distortion – Dynamic and Static Jahn Teller effect – Application of CFT – Magnetic properties – spectral properties and Kinetic properties – Limitations of CFT – Evidences for Metal – Ligand overlap.

Molecular Orbital Theory – MO theory and energy level diagrams concept of Weak and strong fields – Sigma and pi bonding in octahedral, square planar and tetrahedral complexes – Nephlauxetic effect – Magnetic properties of complexes – Comparison of CFT and MOT of bonding in octahedral complexes.

**UNIT-III: ELECTRONIC SPECTRA OF COMPLEXES** **9 hours**

Spectroscopic term symbols for $d^n$ ions – derivation of term symbols and ground state term symbol – Hund's rule – Selection rules – breakdown of selection rules – spin orbit coupling, band intensities, weak and strong field limits – correlation diagram – Energy level diagrams – Orgel diagram for weak field Oh and Td complexes – Splitting of energy level due to Jahn-Teller distortion – Modified orgel diagram – Limitiations of orgel diagram Tanabe–Sugano(T-S)

diagrams – Evaluation of Dq and B values for $d^2$ –$d^8$ complexes – charge transfer – spectra – Complications in band classification between ligand field(d-d) and Charge Transfer bands – Comparison between d-d bands and CT bands – Numerical problems – Lanthanides and Actinides – Spectral properties-Lanthanide contraction.

**UNIT IV: ELECTRON TRANSTER REACTIONS** **9 hours**

Electron transfer reactions – Potential energy well diagram – Inner sphere electron transfer (ISET) and Outer sphere electron transfer (OSET) electron transfer processes – Differences between ISM and OSM – Role of bridging ligand with ISET reaction – formation and rearrangement of precursor complexes – Nature of bridging ligand – fission of successor complexes – Complementary and non complementary ET reactions – Cross reactions and Marcus Hush theory.

Reaction mechanism of coordination compounds – Types of ligand substitution reactions – mechanism; Dissociative mechanism (D), Associative mechanism (A) and interchange mechanism (I).

**UNIT-V: SUBSTITUTION REACTIONS** **9 hours**

Labile and Inert complexes – Substitution Reaction in octahedral complexes – replacement of coordinated water, mechanism of acid hydrolysis, base hydrolysis – DCB mechanism – direct and indirect evidences in favour of the mechanism – Ligand substitution reactions without cleavage of M-L Bond – Anation Reactions – Substitution in square planar complexes – General mechanism, Trans effect – influences of entering, leaving and other groups. Application of trans effect – synthesis of isomers of Pt(II) complexes – theories of trans effect and cis-trans isomerization reaction – Application of substitution reactions in the synthesis of Platinum and Cobalt complexes.

**Distribution of hours:** Theory-70%; Problems-30%

**TEXT BOOKS**

| S.No | Authors | Title | Publishers | Year of publication |
|---|---|---|---|---|
| 1. | H. J. Emelius and Sharpe | Modern aspects of Inorganic chemistry | Universal book stall, New Delhi | 1989 |
| 2. | F. Basolo and R.G. Pearson | Mechanism of Inorganic reactions | Wiley Eastern | 1967 |
| 3. | J. E. Huheey, E. A. Keiter and R. L. Keiter | Inorganic chemistry- Principles on structure and reactivity | $4^{th}$ Ed, Pearson-education | 2002 |
| 4. | F. A. Cotton and G.Wilkinson | Advanced Inorganic Chemistry | Wiley Eastern | 1988 |
| 5. | S. F. A. Kettle | Co-ordination compounds | ELBS | 1973 |
| 6. | K. F. Purcell and J. C. Kotz | Inorganic Chemistry | WB Sanders Co, USA, | 1977 |
| 7. | D. F. Shriver, P. W. Atkins and C. H. Longford | Inorganic Chemistry | ELBS, $2^{nd}$ Ed | 1994 |
| 8. | R. B. Heslop and K. Jones | Inorganic Chemistry | Elsevier | 1976 |
| 9. | D. Bannerjea | Co-ordination Chemistry | TATA Mcgraw Hill | 1993 |
| 10. | M. L. Tobe | Inorganic Reaction Mechanism | Nelson | 1972 |
| 11 | K.Burjer | Co-ordination Chemistry Experimental Methods, | Butterworths | 1973 |
| 12 | B.N.Figgis, | Introduction to Ligand Fields | Wiley Eastern Ltd, | 1976 |
| 13 | W.E.Addision | Structural Principles of Inorganic Chemistry | Longman | 1961 |

**REFERENCE BOOKS**

| S.No | Authors | Title | Publishers | Year of publication |
|---|---|---|---|---|
| **1.** | S.F.A. Kettle | Coordination Chemistry | EIBS | 1973 |
| **2.** | K. Burger | Coordination Chemistry | Burter Worthy | 1973 |
| **3.** | K.F. Purcell and J.C. Kotz | Inorganic Chemistry | WB Saunders Co., USA | 1977 |

**TEACHING METHODOLOGY:**

- PowerPoint presentation
- Models
- Group discussion
- Seminar and Assignments
- Animated videos
- Board and chalk

**SYLLABUS DESIGNERS:**

1. 1. Dr. T. Gomathi, Assistant Professor, Department of Chemistry
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3. Dr. D. Shakila, Assistant Professor, Department of Chemistry