

III SEMESTER

CH H 511: COORDINATION CHEMISTRY

Course Outcome

- The students will learn the application of Crystal Field Theory, Molecular Orbital Theory and J-T effect in the study of complexes.
- Understand the application of spectrophotometric and polarographic methods in the determination of stability of metal complexes.
- Demonstrate the interpretation of spectra and magnetic properties of complexes.
- Understanding reaction mechanism in transition metal complexes.

UNIT-I

[12 Hours]

Coordination numbers 2-10 and their geometry, Crystal Field Theory- Salient features, d-orbital splitting in octahedral, tetrahedral, square planar and tetragonal complexes, Jahn-Teller distortions, measurement of $10 Dq$ and factors affecting it. Evidences for ligand field splitting. Molecular Orbital Theory-MOT of coordination compounds and MO diagrams for octahedral, tetrahedral and square planar complexes without and with pi-bonding. **Preparation of coordination compounds**-Simple addition reactions, substitution reactions, oxidation-reduction reactions, thermal dissociation reactions. **Stability of Metal Complexes**-Step-wise and overall formation constants, factors affecting stability of metal complexes, determination of stability constants of metal complexes by spectrophotometric and polarographic methods.

UNIT-II

[12 Hours]

Spectral properties of complexes: Term symbols for d^n ions, spectroscopic ground states, selection rules, nature of spectral bands- band shapes, band intensities, band widths, spin-orbit coupling, vibrational structures. Orgel diagrams, Tanabe-Sugano diagrams, interpretation of spectra of octahedral, distorted octahedral, tetrahedral and square planar complexes, Determination of Δ_o from spectra. Charge transfer bands-origin, types, and characteristics. Photochemistry of metal complexes-photosubstitution and photoredox reactions, ligand photoredox reactions, photoreactions and solar energy conversion.

UNIT-III

[12 Hours]

Type of magnetic behaviour, orbital contribution, spin orbit coupling, spin cross-over systems. **Measurement of magnetic susceptibility**-Gouy and Faraday methods, diamagnetic corrections, ferro- and antiferro-magnetic coupling, super paramagnetism. High and low spin equilibria. **Magnetic properties of lanthanides and actinides.** Infrared spectra of metal complexes, Group frequency concept. Changes in ligand vibrations on coordination- metal ligand vibrations. **Spectral applications of coordination compounds**-IR spectra of metal carbonyls-ESR spectra-Application to copper complexes, Mossbauer spectra-Application to iron complexes. NMR spectra-Application to diamagnetic complexes.

Reaction Mechanisms in Transition Metal Complexes: Energy profile of a reaction, inert and labile complexes, kinetics of octahedral substitution and mechanistic aspects. Acid hydrolysis, factors affecting acid hydrolysis, base hydrolysis, conjugate base mechanism and evidences in its favour. Anation reactions, reactions without M-L bond cleavage. Substitution reactions in square planar complexes, trans effect, mechanisms of substitution. Substitution reactions in tetrahedral complexes. Isomerization and racemization reactions of coordination compounds. Electron transfer reactions-inner sphere and outer sphere reactions, complimentary and non-complimentary reactions.

References

1. Concise Coordination Chemistry: R. Gopalan and V. Ramalingam, Vikas Publishing, 2014.
2. Inorganic Chemistry, 4th edn., C. E. Housecroft and A. G. Sharpe, Pearson Education (2012).
3. Inorganic Chemistry, 5th edn., G. L. Miessler, P. J. Fischer and D. A. Tarr, Pearson (2014).
4. Inorganic Chemistry, 6th edn., D. F. Shriver, M. Weller, T. Overton, J. Rourke and F. Armastrong, Oxford University Press (2014).
5. Physical Inorganic Chemistry: A Coordination Chemistry Approach, S. F. A. Kettle, Spektrum, Oxford (1996).
6. Inorganic Chemistry, 3rd edn., James E. Huheey, Harper and Row Publishers (1983).
7. Basic Inorganic Chemistry, 3rd edn., F. A. Cotton, G. Wilkinson and P. L. Gaus, John Wiley and Sons (2002).
8. Infrared and Raman Spectra of Coordination Compounds-Part-B, 6th edn., K. Nakamoto, John Wiley and Sons (2009).
9. Electronic absorption Spectroscopy and Related Techniques, D. N. Satyanarayana, OUP (2001).
10. Inorganic Reaction Mechanisms, F. Basolo and R. G. Pearson, Wiley Eastern (1979).
11. Inorganic chemistry-A Unified Approach, W. W. Porterfield, Elsevier (2005).
12. Elements of Magnetochemistry, R. L. Dutta and A. Syamal, Affiliated East-West (1993).
13. Inorganic Chemistry, 4th edn., J. E. Huheey, R. L. Keiter and A. L. Keiter, Addison Wesley (2000).
14. Inorganic Chemistry, 4th edn., J. E. Huheey, E. A. Keiter, R. L. Keiter & O. K. Medhi, Pearson Education (2013).