

II SEMESTER

Ch-201: INORGANIC CHEMISTRY- II

UNIT-I

13h

Metal-Ligand equilibria in solution- Step-wise and overall formation constant and their relationship, trends in step-wise constant, kinetic and thermodynamic stability of metal complexes, factors affecting the stability of metal complexes with reference to the nature of the metal ion and ligand, chelate effect, macrocyclic effect and their thermodynamic origin. Determination of binary formation constant by pH metry, spectrophotometry, polarography and ion exchange methods.

Structure and bonding- hydride, dihydrogen, dioxygen, isocyanide, N₂ and tertiary phosphine complexes of transition metals, metal carbonyls-terminal and bridge carbonyls, detection, metal nitrosyls- terminal (linear and bent) and bridge.

UNIT-II

13h

Metal- ligand bonding- Coordination numbers 3 to 8. Crystal field theory, salient features, spectrochemical series, splitting of d-orbitals in tetrahedral, square planar, trigonal bipyramidal, square-pyramidal and octahedral geometry, applications of CFT- colors of transition metal complexes, magnetic properties of octahedral complex, Jahn Teller distortion, CFSE and their uses, factors affecting CFSE, limitations of CFT, experimental evidences for metal-ligand covalent bonding in complexes, nephelauxetic effect, Ligand Field Theory, MO theory: tetrahedral and octahedral complexes (including π -bonding), angular overlap model. Stereochemical non-rigidity and its detection.

UNIT-III

Electronic spectra of coordination compounds- Spectroscopic ground states, selection rules, term symbols for dⁿ ions, Racah parameters, Orgel, Correlation and Tanabe-Sugano diagrams, spectra of 3d metal-aqua complexes of trivalent V, Cr, divalent Mn, Co and Ni, CoCl₄²⁻, calculation of Dq, B and β parameters, CT spectra. Spectral properties of Lanthanide and Actinide metal complexes.

UNIT-IV

13h

Magnetic properties of coordination compounds- Types of magnetism, temperature effect, magnetic susceptibility and its determination- Gouy, Faraday, VSM method. Diamagnetic correction, orbital contribution, spin-orbital coupling, ferro- and antiferromagnetic coupling, spin-crossover. Magnetic properties of Lanthanide and Actinide metal complexes.

Photochemical reactions of transition metal complexes: Basic photochemical processes, Kasha's rule, quantum yield, Jablonskii diagrams, photo substitution reactions, photo-redox reactions, ligand photoreactions.

SUGGESTED BOOKS

1. Advanced Inorganic Chemistry- F. A. Cotton, G. Wilkinson and P. L. Gaus; John Wiley and sons. Inc, 6th edition (1999).
2. Chemistry of elements- N. N. Greenwood and A. E. Earnshaw, 2nd edition, Butterworth Heinemann (1997).
3. Inorganic Chemistry J. E. Huheey, E. A. Keiter and R. L. Keiter, 4th edition; Addison; Wesley (1993).
4. Inorganic Chemistry, D. F. Shriver, P. W. Atkins and C. H. Langford, 5th edition, ELBS; Oxford University Press, (2010)
5. Inorganic Electronic spectroscopy, A. B. P. Lever, 2nd edition, Elsevier. (1984).
6. Magnetochemistry, R.L. Carlin, Springer Verlag (1986).
7. Electronic Absorption Spectroscopy and related Techniques, D. N. Sathyanarayana, University Press (2001).
8. Inorganic Chemistry A Unified Approach by W. W. Porterfield, Elsevier 2005 2nd edition.
9. Inorganic chemistry G L Miessler, P J Fisher and D A Tarr 5th edition (2008).

Ch-202: ORGANIC CHEMISTRY – II

UNIT-I

Aromatic Substitution Reactions

13h

Electrophilic Substitution Reactions: The arenium ion mechanism. Orientation and reactivity. Energy profile diagrams. The *ortho/para* ratio, *ipso* attack, orientation in other ring systems. Quantitative treatment of reactivity in substrates and electrophiles. Effect of leaving group. Amination, sulfonylation reactions; Diazonium coupling, Vilsmeier-Haack reaction, Gatterman reaction, Gatterman-Koch reaction and Hoesch reaction.

Nucleophilic substitution reactions: The S_NAr, S_N1, benzyne and S_{RN}1 mechanisms. Reactivity: effect of substrate structure, leaving group and attacking nucleophile. Goldberg reaction, Bucherer reaction, Schiemann reaction, von Richter reaction, Sommelet-Hauser and Smiles rearrangements.

UNIT-II

Addition Reactions

13h

Addition to carbon-carbon multiple bonds: mechanistic and stereochemical aspects of addition reactions involving electrophiles, nucleophiles and free radicals. Regio-, stereo- and chemo-selectivities. Orientation and reactivity. Addition to cyclopropane ring. Hydrogenation of double and triple bonds, hydrogenation of aromatic rings. Addition of alkenes and/or alkynes to alkenes and/or alkynes. Ene synthesis. Michael reaction.

Addition to carbon-heteroatom multiple bonds: Mechanism of metal hydride reduction (NaH, LiH, LiAlH₄, NaBH₄) of saturated and unsaturated carbonyl compounds, acids, esters and nitriles. Addition of Grignard reagents and organolithium reagents to carbonyl compounds and unsaturated carbonyl compounds. Conversion of aldehydes to nitriles. Hydrolysis of nitriles and addition of amines to isocyanates. Formation of xanthates, Wittig, Mannich and Stobbe reactions.

UNIT-III

13h

Elimination Reactions

The E2, E1 and E1cB mechanisms and their spectrum. E2C and E2H mechanisms. Orientation of the double bond. Reactivity-effects of substrate structure, attacking base, the leaving group and the medium. Mechanism and orientation in pyrolytic elimination reactions (including Chugaev reaction).

Rearrangement Reactions:

Carbon-carbon: Wagner-Meerwein, Pinacol-Pinacolone, Fries, Benzil-benzilic acid and Wolff rearrangement. Arndt-Eistert synthesis and Tiffeneau- Demjanov reaction. Fritsch-Buttenberg-Wiechell, Favorskii, Dienone-phenol and Baker-Venkataraman rearrangement.

Carbon-nitrogen: Beckmann, Hofmann, Curtius, Lossen, Schmidt, Stevens, Neber and Benzidine rearrangement.

Carbon-oxygen: Wittig rearrangement and Baeyer-Villiger oxidation.

UNIT-IV

Chemistry of biological molecules - II

Amino acids and Peptides

Amino acids essential and non essential. Classification and nomenclature of peptides. Sanger and Edman methods of sequencing. Cleavage of peptide bond by chemical and enzymatic methods. Peptide synthesis- Protection of amino group (Boc-, Z- and Fmoc-) and carboxyl group as alkyl and aryl esters. Use of DCC, EEDQ, HOBt and active esters, in peptide bond formation reactions. Deprotection and racemization in peptide synthesis. solid phase peptide synthesis carbohydrates techniques. Synthesis of oxytocin, and enkephalins.

SUGGESTED BOOKS

1. Advanced Organic Chemistry – Reactions, Mechanism and Structure, Jerry March, John Wiley (2008).
2. Advanced Organic Chemistry, F A Carey and R J Sundberg Plenum, (2000).
3. A Guide Book to Mechanism in Organic Chemistry, P Sykes, VI edition, Pearson, (2003).
4. Structure and Mechanism of Organic Chemistry, C. K. Ingold, II Edition, CBS, (2016).
5. Organic Chemistry, R T Morrison, R N Boyd and S K Bhattacharjee, VII edition, Pearson, (2018).
6. Principles of Organic Synthesis, III edition), R O C Norman and J M Coxon, Blackie Academic and Professional (Indian Reprint), (2012).
7. Natural Products: their chemistry and biological significance, J Mann, Longman, (2000)
8. Organic Chemistry, Volume I, I L Finar, VI edition, Pearson, (2018).
9. Organic Chemistry, Volume II, I L Finar, VI edition, Pearson, (2018).
10. Organic Chemistry, J Clayden, N Greeves and S Warren, II edition, Oxford University Press, (2014)
11. Name Reactions – A collection of detailed reaction mechanisms, J J Li Springer, (2012)
12. Modern Methods of Organic Synthesis W Carruthers and I Coldham, IV edition, Cambridge University Press, (2015).
13. Peptides Chemistry: A practical text book, M. Bodansky, Springer-Verlag NY, (1988).

14. Solid-phase peptide synthesis: A practical Approach-E. Artherton & R.C. Sheppard, I R L, Oxford Univ. Press, (1989).
15. Peptides: Chemistry and Biology, N Selwad and H.-D. Jakubke, Wiley-VCH, (2002).

C-203: PHYSICAL CHEMISTRY- II

UNIT-I

Thermodynamics-I

13h

Thermodynamics: Concepts of partial molar properties – partial molar free energy, chemical potential, partial molar volume and its significance. Gibbs-Duhem equation, Gibbs-DuhemMargulus equation. Determination of partial molar volume : Graphical method, intercept method and Apparent molar volume method. Concept of fugacity; Determination of fugacity by graphical method and compressibility factor method. Activity and activity coefficient : Determination of activity coefficient by EMF and solubility method. Thermodynamics of nonideal system-Excess thermodynamic function, G^E , S^E , H^E etc. Phase Rule : Derivation of phase rule from the concept of chemical potential. Application of Phase Rule to three components system :Principle of triangular diagram : Plots for a mixture of three liquids consisting of one ,two and three pairs of partially miscible liquids. Statistical Thermodynamics: Objectives of statistical thermodynamics, Concept of distributions, Types of ensembles. Thermodynamic probability, Most probable distribution Law – Partition Function, (Definition and significance): Molar and molecular partitions- translational, rotational, vibrational and electronic partition functions- Relation between thermodynamic functions (E , H , S , G and C_v) and the partition functions.

UNIT-II

Thermodynamics-II

13h

Sackur-Tetrode equation for entropy of translation function. Relation between equilibrium constant and partition function. Different Distribution Laws:Types of Statistics : Maxwell – Boltzmann, Bose-Einstein and Fermi-Dirac statistics. Derivation of the equations for above three distribution Laws. Comparison of Bose-Einstein and Fermi-Dirac statistics with Maxwell – Boltzmann statistics. Problems and their Solutions.

Non-equilibrium Thermodynamics : Thermodynamic criteria for non-equilibrium states- Phenomenological Laws and Onsager's reciprocity relations, Coupled and Non-coupled reactions, Entropy production and entropy flow. Electro kinetic Phenomenon. Postulates and methodologies: Uncompensated heat and thermodynamics fuction production. deDonder's inequality. Rate of entropy production. Transformations of the generalized fluxes and forces :eg., Chemical reaction, heat flow, Diffusion or material flow, flow of electric current.

UNIT-III

Electrochemistry-I

13h

Elctrochemistry of solutions: Ionic atmosphere, Debye-Huckel theory for the problem of activity coefficient, Debye-Huckel limiting Law, Debye-Huckel equation for appreciable concentration, Debye-HuckelOnsagar conductance equation and its extension to ion solvent

interactions, Debye-Huckel Bjerrum mode, Ion association, triple ions, triple ions and conductance minima. Thermodynamics of electrified interface, derivation of electro capillary Lipmann's equation, surface excess, thermodynamic aspects of surface excess. The method of determination and measurement of interfacial tension as a function of applied potential difference across the interface.

UNIT-IV

Electrochemistry-II

13h

Structure of electrified interface: Helmholtz theory, Guoy- Chapman theory, Stern model. Overpotential: Concentration, activation and ohmic overpotential; Derivation of Butler- Volmer equation.

Semiconductor- solution interface: Theory of double layers at semiconductor- electrolyte interface.

Electrocatalysis: Definition and Influence of various parameters. Quantum aspects of charge transfer at electrode solution interface, quantization of charge transfer, tunneling of electrons for hydrogen evolution with reference to electrocatalysis.

Polarography technique-Principle, DME- Merits and limitations, experimental, polarogram, half wave potential, diffusion controlled current, Ilkovic equation (no derivation), qualitative and quantitative estimation of metal ions.

Advanced Electrodes: Rotating disc electrodes, Membrane electrodes (Definition, examples with diagrams and applications to each), carbon electrodes.

SUGGESTED BOOKS

1. Molecular thermodynamics, Donald A. Mc Quarrie, John D. Simon University Science Books California, (1999).
2. Thermodynamics for Chemists by S. Glasstone, East-West Press, New Delhi, (1960).
3. Thermodynamics, by Rajaraman and Kuriacose, East-West Press, (1986).
4. Statistical Thermodynamics, M. C. Gupta (Wiley Eastern Ltd.) 1993.
5. Elements of Classical and Statistical Thermodynamics, L. K. Nash, Addison-Wiley (1979).
6. Thermodynamics, Statistical Thermodynamics and Kinetics by Thomas Engel & Philip Reid, Pearson Education inc. (2007).
7. Modern Electrochemistry Vol-1 and 2, J. O. M. Bockris and A. K. N. Raddy, Plenum, New York (1978).
8. An introduction to electrochemistry: Samuel Glasstone East-West, edition New Delhi (1942)
9. Text book of physical chemistry Samuel Glasstone, 2nd edition, Mac Millan India Ltd (1991)
10. Principles and applications of Electrochemistry- D. R. Crow 3rd edition, Chapman hall London (1988).
11. Physical chemistry thorough problems by S K Dogra and S Dogra, Wiley Eastern Ltd., 4th Edn. 1993.
12. Electrochemical methods by A J Bard and I R Faulkner, 2nd Edn., Wiley New York, 2000.

Ch-204: MOLECULAR SPECTROSCOPY

UNIT-I

Symmetry and Group Theory in Chemistry

Definition of groups, subgroups, cyclic groups, conjugate relationships, classes, simple theorems in group theory. Symmetry elements and symmetry operations, point groups, Schönflies notations, representations of groups by matrices, reducible and irreducible representations, characters of representations, Great Orthogonality Theorem (without proof) and its applications, character tables and their uses (representations for the C_n , C_{nv} , C_{nh} , D_{nh} etc groups to be worked out explicitly) Mulliken symbols for irreducible representations. Direct products, Applications of group theory to quantum mechanics identifying non-zero matrix elements, derivation of the orthonormalization conditions.

UNIT-II

Unifying principles

Interaction of electromagnetic radiation with matter- time-dependent perturbation theory, transition moment integral, selection rules- symmetry and spin forbidden transitions.

Infrared Spectroscopy-I

Vibrations of molecules, harmonic and anharmonic oscillators- vibrational energy expression, energy level diagram, vibrational wave functions and their symmetry, selection rules, expression for the energies of spectral lines, computation of intensities, hot bands, effect of isotopic substitution

Diatomic vibrating rotor, Born-Oppenheimer approximation, vibrational-rotational spectra of diatomic molecules, P, Q and R branches, breakdown of the Born-Oppenheimer approximation.

Infrared Spectroscopy-II

Vibrations of polyatomic molecules: Normal coordinates, translations, vibrations and rotations, vibrational energy levels and wave functions, fundamentals, overtones and combinations
Vibration-rotation spectra of polyatomic molecules- parallel and perpendicular vibrations of linear and symmetric top molecules
Techniques and instrumentation, FTIR

UNIT-III

Microwave Spectroscopy

Rotations of molecules, rigid diatomic molecule- rotational energy expression, energy level diagram, rotational wave functions and their symmetry, selection rules, expression for the energies of spectral lines, computation of intensities, effect of isotopic substitution, centrifugal distortion and the spectrum of a non-rigid rotor.

Rotational spectra of polyatomic molecules- linear, symmetric top and asymmetric top molecules, Stark effect, techniques and instrumentation.

Raman Spectroscopy

Classical theory of the Raman effect, polarizability as a tensor, polarizability ellipsoids, quantum theory of the Raman effect, Pure rotational Raman spectra of linear and asymmetric top

molecules, vibrational Raman spectra, Raman activity of vibrations, rule of mutual exclusion, rotational fine structure- O and S branches, Polarization of Raman scattered photons Structure determination from Raman and IR spectroscopy-AB₂ and AB₃ molecules Techniques and instrumentation

UNIT-IV

Electronic Spectroscopy

Born-Oppenheimer approximation, vibrational coarse structure, intensities by Franck-Condon principle, Dissociation energy, rotational fine structure, Fortrat diagram, pre-dissociation

Electronic structure of diatomic molecules- basic results of MO theory, classification of states by electronic angular momentum- Σ, Π, Δ , and Φ molecular orbitals, selection rules, spectrum of singlet and triplet molecular hydrogen

Electronic spectra of polyatomic molecules- localized MOs, spectrum of HCHO, change of shape on excitation

Decay of excited states- radiative (fluorescence and phosphorescence) and non-radiative decay, internal conversion

SUGGESTED BOOKS

1. Chemical Applications of Group Theory, F. A. Cotton, Wiley Eastern (1976).
2. Molecular Symmetry, D. S. Schonland, Van Nostrand (1965).
3. Introduction to Molecular Spectroscopy, C. N. Banwell, TMH Edition (1994).
4. Introduction to Molecular Spectroscopy, G. M. Barrow, McGraw Hill (Int. Students Edition) (1988).
5. Molecular Spectroscopy, J. D. Graybeal, McGraw Hill (Int. Students Edition) (1990).
6. Spectroscopy, Vols. 1-3, B. P. Straughan and W. Walker, Chapman Hall (1976).

Ch-205: GREEN SYNTHESIS (SOFT CORE)

36 h

UNIT-I

Use of ultrasound and Microwaves in organic Synthesis

12 h

Use of ultrasound: Introduction, instrumentation, the phenomenon of cavitation. Sonochemical esterification, substitution, addition, alkylation, oxidation, reduction and coupling reactions.

Use of microwaves: Introduction, concept, reaction vessel/medium, specific effects, atom efficiency (% atom utilization), advantages and limitations. N-alkylation and alkylation of active methylene compounds, condensation of active methylene compounds with aldehydes and amines. Diels-Alder reaction. Deprotection of esters and silyl ethers. Oxidation of alcohols and sulfides.

Ionic-liquids: Introduction, structure, synthesis and applications of some important ionic liquids in organic synthesis.

UNIT-II

Polymer supported reagents in organic synthesis

12 h

Introduction- properties of polymer support, advantages of polymer supported reagents and choice of polymers. Applications.

Substrate covalently bound to the support: Synthesis of oligosaccharides, Dieckmann cyclisation. Preparation of polymer bound aldehyde and application in aldol and Wittig reactions. Synthesis of polystyrylboronic acid and use in diol protection reaction.

Reagent linked to a polymeric material: Preparation of sulfonazide polymer and application in diazotransfer reaction. Synthesis of polymer bound per acid and its applications.

Polymer supported catalytic reactions: Preparation of polymer supported $AlCl_3$ and application in etherification and acetal formation reactions.

Phase transfer catalysis and Crown ethers

Phase transfer catalysis: Introduction, definition, mechanism of phase transfer catalysis. Types of phase transfer catalysts and reactions and their Advantages.

Preparation of catalysts and their application in substitution, elimination, addition, alkylation, oxidation and reduction reactions.

Crown ethers: Introduction, nomenclature, features, nature of donor site. General synthesis of Crown ethers.

Synthetic applications: Alkylation, generation of carbenes, aromatic substitution and displacement reactions. Generation and application of superoxide anions. Cation deactivation reactions.

UNIT-III

Multi-component Reactions

12 h

Studies on the mechanistic aspects and use of the following reactions in organic synthesis: Passerini-Ugi; Hantzsch; Biginelli; Doebner-Miller; Ritter; Jacobson; Betti; Robinson-Schopf; Barbier; Baylis-Hillmann; Petasis; Ivanov and Suzuki coupling reaction.

SUGGESTED BOOKS

1. Some modern methods of Organic Synthesis, W. Caruthers, Cambridge Univ. Press London, 2nd Edition, 1998.
2. Organic synthesis: Special techniques, V. K. Ahluwalia and R. Aggarwal, Narosa, New Delhi, 2003.
3. Green Chemistry, environment friendly alternatives, R. Sanghi and M. M. Srivastava, Narosa, New Delhi, 2003
4. Green Chemistry-an introductory text, M. Lancaster, Royal Society of Chemistry, UK, 2003.
5. Organic chemistry Vol. 2, 6th Edition, I. L. Finar, Longman, 1992.
6. Crown ethers & cryptands, G. W. Gokel, Royal Society of Chemistry, UK, 1991.
7. Macrocyclic Polyether Chemistry, G. W. Gokel, S. M. Korzeniowski, Vol 1 to3, Wiley, NY, 1978, 1981, 1987.
8. Phase Transfer Catalysis in Organic Synthesis, W. B. Weber, G. W. Gokel, Springer, Berlin, 1977.
9. Phase Transfer Catalysis, E. V. Dehmlov, S. S. Dehmlov, 2nd Edn., Verlag chemie, Wienheim, 1983.
10. Polymers as aids in Organic synthesis, N. K. Mathur, C. K. Narang and R.E. Williams, Academic Press, NY, 1980.

Ch -205: PHOTO CHEMISTRY (SOFT CORE)

UNIT-I

12h

Importance of Photochemistry, Laws of Photochemistry: Grothus –Draper Law, Stark-Einsteins Law, Laws of light absorption, Quantum yield and numerical problems. Photochemistry and spectroscopy, units and dimensions. Electronic energy states of atoms, term symbols for atoms, energy levels for the electronic configuration of carbon and oxygen illustrating spin orbit coupling and Hund's rules, inverted multiplets as applied to simple atoms and also for inner transition metals, Laporte's selection rules. Physicochemical Properties of electronically excited molecules: Nature of changes on electronic excitation: acidity, dipole moment, redox potentials etc. Fates of excited species, Electronic, vibrational, rotational energies-potential energies diagram. Shapes of absorption band and Franck Condon principle.

UNIT-II

12h

Quantum mechanical formulation of Franck Condon, crossing of potential energy surfaces, Non crossing rule of Teller for potential energy surface. Emission spectra, fluorescence and phosphorescence Environmental effect on absorption and emission spectra, solvent red shift and blue shift in absorption spectra. Experimental techniques to determine the intermediates in photochemical reactions Classification of photochemical reactions, Rate constants and life times of reactive energy state Effect of light intensity on the rate of photochemical reaction.

UNIT-III

12h

Photosensitized reactions: photodissociation-Gas phase photolysis, photofragmentation in liquid phase, photodegradation of polymers, Isomerization and other rearrangement reactions, Atmospheric photochemistry.

Photoelectrochemistry: Introduction, efficiency of conversion of light to chemical and electrical

energy, frequently measured quantities. Photosplitting of water using colloidal suspensions.
Semi conductors: Bonding, conductivity, mechanism of conductivity, energy bands in semiconductors; impurity semiconductors.
Photo voltaic effect: p-n junction, solar cells, silicon cells, GaAs solar cells, schottky barrier solar cells.
Photocatalysis: Photocleavage of environmentally hazardous waste matter by using TiO₂, ZnO and MgO. Photooxidation and photoreduction reactions.

SUGGESTED BOOKS

1. Fundamentals of photochemistry, K.K. Rohatgi Mukherjee, Wiley Eastern Limited (1986)
2. Photochemistry, Carol E Wayne and Richard P Wayne, Oxford University Press (1996)
3. Introduction to Semiconductor Materials and devices M S Tyagi, John Wiley and sons (1991)
4. Organic Photochemistry, J. M. Cozen and B. Halton, Cambridge University Press (1st Edition) 1974.
5. Molecular Reactions and Photochemistry, C H Deputy and D S Chapman, Prentice Hall India, New Delhi (1st Edition), 1972.
6. Concepts of Inorganic photochemistry, A. W. Adamson and P D Fleischaves, John Wiley & Sons Inc. (1975).
7. Physical Chemistry, P. W. Atkins, Julio de Paulo ELBS 7th Edition (2002)

Ch- 206, 207, 208, 209 Practicals

(4 hrs per day, 4 days per week)

**Inorganic Chemistry Practicals - I, II, III & IV
Organic Chemistry Practicals - I, II, III & IV
Physical Chemistry Practicals - I, II, III & IV**

Experiments are as in first semester. Every student will carry out experiments in each of the three branches of chemistry on a rotation basis from 1st to 3rd Semester.