(M.Sc. IInd Semester)

Course No: CHM-201

Title: Inorganic Chemistry

Max. Marks- 100 **(50 hrs)**

Unit I: **(12 hrs)**

Magnetic Properties and Electronic Spectra of Transition Metal Complexes:

Types of magnetic behaviour, magnetic susceptibility and magnetic moment; methods of determining magnetic susceptibility; spin-only formula; L-S coupling, correlation of |^$_s$ and i^ff values; orbital contribution to magnetic moments; applications of magnetic moment data in investigation of nature of bonding and stereochemistry of first row transition metal complexes. High spin- low spin crossover.

Electronic spectra of Transition metal complexes:- General features; Types of electronic transitions, theoretical aspects of d-d spectra, selection rules; spectral terms of d^1 - d^{10} metal ions.

Selected examples of d-d spectra. Spectra of distorted octahedral and square planar complexes. Charge transfer spectra.

Unit II: **(12 hrs)**

Mechanisms of Ligand substitution reactions in Octahedral Metal Complexes:

Energy profile of a reaction; reactivity of metal complexes; inert and labile complexes.

Types of substitution reactions; mechanistic classification of substitution reactions:- Dissociative, Associative, Dissociative conjugate base and Interchange. Empirical criteria to differentiate the mechanism of substitution.

Substitution in octahedral complexes- Classification of metal ions based on water exchange rates. Metal-complex formation- the Eigen-Wilkins mechanism. Anation reactions.

Hydrolysis reactions; Simple Acid hydrolysis, Acid catalysed and Base hydrolysis. Stereochemical changes in octahedral substitution reactions.

Substitution reactions without metal-ligand bond breaking.

Unit III **(08hrs)**

(A) Ligand substitution reactions in square-planar complexes:-

Significance of the two-term rate^law, mechanism, and steric course of the substitution reaction. Factors affecting the rate of substitution - entering and leaving groups; nucleophilicity of entering group and the npt scale, central metal ion, solvent , and the non-leaving groups.

The Trans Effect- theories, applications in synthesis.

Cis-Trans isomerization in square planar complexes.

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(B) Electron Transfer Reactions in coordination Complexes: **(08hrs)**

Complementary and non-complementary reactions. Classification as outer sphere and inner sphere redox reactions.
Mechanism of outer sphere and inner sphere electron transfer reactions- the elementary steps involved; formation of precusor and successor complexes; rate laws. Characterization of redox processes as outer and inner sphere.

Factors affecting the rate of electron transfer- Chemical activation; sigma and pi nature of donor/ acceptor orbitals; electron configuration of oxidant/reductant. Bridging ligand effects in inner-sphere reactions.

Oxidative addition, reductive elimination and migration (insertion) reactions

Unit IV **(10hrs)**

Iso- and Heteropolymetallates and Metal Clusters:

Synthesis, reactions, and structures of polyanions of vanadium, molybdenum, and tungsten. Isopolyanions of Niobium and Tantalum, Applications of polyacids.

Metal Clusters:- Introduction to metal clusters; Dinuclear species; trinuclear clusters; metal-metal multiple bonds. Tetranuclear metal clusters.

Books Recommended:

1. Advanced Inorganic Chemistry, 6th ed. /5th ed. F.A. Cotton , G. Wilkinson (Wiley 1999/1988)
2. Inorganic Chemistry, 4th ed. J. E. Huheey, E. A. Keiter..... (Harper Collins, 1993)
3. Chemistry of the Elements 2nd ed. - N. N. Greenwood, A. Earnshaw (Butterworth, 1997)
4. Mechanisms of Inorganic Reactions - D. Katakis, G. Gordon (Wiley, 1987)
5. Reaction Mechanism of Inorganic and Organometallic systems, 2nd ed.- R. B. Jordan (Oxford, 1998)
6. Mechanisms of Inorganic Reactions, 2nd ed. - F. Basolo, R.G. Pearson (Wiley, 1967)
7. Inorganic Chemistry- K. F. Purcell, 1C. Kotz (Saunders, 1977).
8. Electronic Spectra of Transition Metal Complexes - D. Sutton (McGraw-Hill, 1968)
9. Elements of Magnetochemistry - R. L. Dutta, A. Syamal (Affiliated East -West, 1993).

Course No. CHM-202
Title: Organic Chemistry.

Max. Marks-100 **(50hrs)**

Unit-1 **(14hrs)**

Aromatic Electrophilic Substitution

The arenium ion mechanism, orientation and reactivity, energy profile diagrams. The ortho/para ratio, ipso attack. Orientation of substitution in benzene rings having more than one substituents. Orientation in other ring systems. Mechanisms of diazonium coupling, Vilsmeier-Haack and Gattermann-Koch reactions and Fries rearrangement.

^Aromatic Nucleophilic substitution

Discussion of different mechanism (S_N1, S_NAr, Benzyne and SRN!). Structure reactivity relationships. Effect of leaving group and attacking nucleophile. Mechanisms of Von-Richter, Sommelet-Hauser and Smiles rearrangements and Chichibabin reaction.

Free Radical Substitution

Free radical substitution mechanisms. Mechanism at an aromatic substrate, neighbouring group assistance, reactivity for aliphatic and aromatic substrates. Reactivity in the attacking radical. Effect of solvent on reactivity.

Allylic halogenation (NBS), oxidation of aldehydes to carboxylic acids, auto-oxidation, coupling of alkynes and arylation of aromatic compounds by diazonium salts, Sandmayer reaction, free radical rearrangement and Hunsdiecker reaction.

Unit-II **(14hrs)**

Addition to carbon Hetero multiple bonds,

Mechanism of metal hydride reduction of saturated and unsaturated carbonyl compounds, acids, esters and nitriles. Addition of Grignard reagent, organozinc and organolithiurn reagents to carbonyl and unsaturated carbonyl compounds. Wittig reaction. Mechanisms of condensations involving enolates: Aldol, Robinson annulation, Knoevenagel, Claisen, Dieckmann, Mannich, Benzion, Perkin and Stobbc reactions.

Hydrolysis of esters, amides and ammonolysis of esters.

Addition to carbon --Carbon multiple bonds

General mechanism, reactivity, orientation and stereochemical implications of additions reactions involving electrophiles, nucleophiles and free radicals. Addition to cyclopropane ring. Hydrogenation of double/triple bonds and aromatic rings. Hydroboration, Ene-reaction, Michael reaction and Sharpless assymetric epoxidation.

Unit-III **(10hrs)**

Molecular Rearrangements

General mechanistic treatment of mucleophilic, electrophilic and free radical rearrangments. Nature of migration and migratory aptitude and memory effect. Detailed study of following rearrangement: Wagner-Meerwein, Pinacol- Pinacolone, Demyanov, Benzil-Benzilic acid, Favorskii, Arndt-Eistert, Neber, Hofmann, Curtius, Lossen, Schmidt, Beckmann, and Baeyer-Villiger.

Unit-IV **(12hrs)**

Pericyclic reactions

Molecular orbital symmetry, Frontier orbitals of ethene, 1,3- butadiene, 1,3,5-hexatriene and allylic system. HOMO, LUMO concept, FMO approach. Classification of pericyclic reactions, Woodword Hofrnann rules for the following pericyclic reactions.

Cycloadditions'. Thermal and Photochemical 2+2 and 4+2 cycloadditions.

Suprafacial and antrafacial cyclo addition.

Electrocylic Reactions: Thermal and Photo-induced Electrocyclic reactions of 4n and 4n + 2 systems and their stereochemistry. Conrotatory and disrotatory motions.
Sigmatropic rearrangements: Classification, [1,3], [1,5] and [3,3] sigmatropic shifts. Cope and Claisen rearrangement. Suprafacial and antrafacial shifts of hydrogen atom.

Books Recommended

1. Advanced Organic Chemistry Reactions, Mechanism and Structure, 4th Ed.-Jerry March. (Wiley, 1999).
2. Advanced Organic Chemistry 4th Ed. - F. A. Carey and R. J. Sundberg. (Plenum, 2001).
3. A Guide Book to Mechanism in Organic Chemistry 6th Ed.- Peter Sykes. (Longman, 1996).
4. Structure and Mechanism in Organic Chemistry 2nd Ed. - C. K. Ingold. (CBS, 1994).
5. Modern Organic Reactions 2nd Ed. - H.O. House (Benjamin, 1972)
6. Principles of Organic Synthesis 2nd Ed. - R.O.C. Norman (Chapmann Hall, 1978)
7. Reaction Mechanism in Organic Chemistry 3rd Ed. - S.M. Mykherjee and S.P. Singh. (Macmillan, 1998).
8. Organic Chemistry - J. Hornba,pk. (Brooks/Cole, 1998)
9. Fundamentals of Organic Cbemjstry , 5th ed.- Solomons. (Wiley, 1992)
10. Organic Chemistry, 5th Ed.- John McMurry. (Brooks/Cole, 2000)

Course NO: CHM- 203
Title: Physical Chemistry

Max. Marks:100 **Time: 50 hrs**

Unit-I: Quantum Chemistry (15 hrs)

Approximation methods

The Variation theorem, linear variation principle, application to hydrogen atom and helium atom. Perturbation theory -first order(non-degenerate & degenerate). Application of perturbation method to helium atom. (4 hrs)

Chemical Bonding

LCAO-MO approximation, H_2^+molecular ion, brief introduction to H_2. Molecular term symbols. Valence bond treatment of H_2, comparison of M O and V B methods in the light of H_2 molecule. Hybridization of orbitals (sp, sp^2 & sp^3).

(6 hrs)

Huckel's Pi-MO theory of conjugated systems; Application to linear and cyclic polyenes . Pi-electron charge and bond-order. Alternant hydrocarbons, heteroatomic conjugated systems. Limitations of Huckel theory and improvement. (5 hrs)

Unit- II: Statistical Thermodynamics (12 hrs)

Concept of distribution, thermodynamic probability and most probable distribution. Sterling approximation. Derivation of Boltzmann distribution law. Bose-Einestein and Fermi-Dirac distribution equations (without derivation) and comparison of the three statistics.

(5 hrs)

Partition function & its significance. Translational, rotational, vibrational and electronic partition functions. Calculation of thermodynamic properties in terms of partition functions , application to ideal monoatomic & diatomic gases. Equilibrium constant in terms of partition functions. (7hrs)

Unit-III: Electrochemistry-I (12 hrs)

Electrified interface, concept of surface excess. Thermodynamics of electrified interface, lipman equation, electrocpillary curves. Methods for determination of surface excess

Structural models of metal-electrolyte interface: Helmholtz-Perrin, Gouy-Chapman and Stern models.

Ionic Adsorption at electrodes – isotherms for adsorption (Langmuir, Frumkin and Temkin isotherms)

Adsorption of organic molecules – an introduction

Unit- IV: Electrochemistry-II (11 hrs)

Electron transfer at electrified interface at and away from equilibrium. Derivation of Butller-Volmer equation, low and high field approximations, meaning of β.

Introduction to corrosion - mechanism and types of corrosion, corrosion current and corrosion potential. Electrodics of corrosion in absence of oxide layer, monitoring of corrosion, and inhibiting corrosion.

Books Recommended:

1. Physical Chemistry - P. W. Atkins, ELBS Oxford, 1997.
2. Physical Chemistry- A Molecular Approach - D. A. McQuarie & J. D. Simon, University Science Books, 1997.
3. Introduction to Quantum chemistry - A. K. Chandra, TataMcGraw Hill, 1997.
4. Quantum Chemistry - Ira. N. Levine, Prentice Hall, 2000.
5. Molecular Quantum Mechanics - P. W. Atkins and R. S. Friedmann, Oxford, 1997.
6. Coulson's Valence, R. Mcweeny, ELBS.
7. Electrochemical methods, Fundamentals and Methods, A.J. Bard, L.R. Faulkner, Wiley, 1980.
8. Modern Electrochemistry Vol-I,Vol-II A and Vol-II B, J.O.M. Bockris and A.K.N. Reddy, Plenum,1998.
9. Statistical Thermodynamics, M.C.Gupta, New Age International, 1993.
10. Statistical Mechanics, Agarwal, Eisner, Wiley, 1991.
11. Introduction to Statistical Thermodynamics, Chandler, OUP, 1987.
12. An introduction to Statistical Thermodynamics, Hill, Addison-wesley, 1987.

Course NO: CHM-204.

Title: Spectroscopy and Diffraction Methods

Max. Marks:100 **Time: 50 hrs**

Unit I: Magnetic Resonance Spectroscopy (12 hrs)

Basic principles-Nuclear spin; spin angular momentum, spin quantum number, magnetic nuclei, directional quantization, magnetic quantum number of nucleus; nuclear magnetic moment, precessional (Larmor) frequency; energy levels in a magnetic field; resonance absorption of radio frequency radiation. Population of energy levels; Relaxation processes (T_1 , T_2).

Shielding and deshielding of magnetic nuclei; anisotropic shielding in unsaturated/ aromatic compounds. (6hrs).

Chemical shift, its measurement and factors influencing chemical shifts.

Signal splitting – spin- spin coupling, coupling constants. Low and high resolution ^{1}H NMR spectrum of protons undergoing chemical exchange (ethanol). Spin decoupling.

Instrumentation; FT-NMR and its advantages. NMR studies of nuclei other than proton – ^{13}C , ^{19}F and ^{31}P. (6hrs)

Unit II: Electron Spin and Nuclear Quadrupole Spectroscopy (12 hrs)

Electron Spin Resonance spectroscopy

Basic principles- electron spin, magnetic moment of an electron and its interaction with applied magnetic field. The g value. Fine structure and hyperfine structure (electron-electron and electron-nucleus coupling) Zero field splitting and Kramer's degeneracy Isotropic and anisotropic hyperfine coupling constants; spin densities and McConnel relationship; Applications

(6hrs)

Nuclear Quadrupole Resonance spectroscopy

Consequences of nuclear spin greater than ½ ; NQR isotopes, Nuclear quadrupole moment; Electric field gradient; nuclear quadrupole coupling constant; Effect of applied magnetic field, Applications. (6hrs)

Unit III: Diffraction Techniques (12 hrs)

Lattices and Unit cells; Miller indices; Laue, Bragg, and Debye-Scherrer method of X-ray structural analysis of crystals.

Indexing the reflections; identification of cubic unit cells from systematic absences in diffraction pattern.

Structure of simple lattices and X-ray intensities; structure factor and its relation to intensity and electron density; phase problem.

Introduction to neutron and electron diffraction techniques. Their comparison with X-ray diffraction technique.

Unit IV: Chromatography and Electroanalytical methods (14 hrs)

Classification; principles – differential migration, nature of partition forces, partition coefficient, retention time, retention volume..

Plate theory, HETP, band broadening, efficiency and resolution. (2 hrs)

Basic principles and applications of – Liquid-Solid and Liquid-Liquid column chromatography. Paper and thin layer chromatography, ion exchange (size exclusion), HPLC and Gas-Liquid chromatography. Electrophoresis. (6 hrs)

Polarography – diffusion current, half-wave potential, Ilkovic equation, DME. (applications in organic/inorganic analysis); Amperometric titrations.

Principles of – cyclic voltametry, Anodic stripping voltametry, Coulometric titrations (Controlled current). (6 hrs)

Books Recommended:

1. Physical Methods for Chemists , 2nd edn. R.S.Drago (Saunders, 1992)
2. Fundamentals of Molecular Spectrsocopy, 4th edn- C.N.Banwell, E.M.Mc Cash (Tata McGrawHill, 1994)
3. Modern Spectroscopy- J.M.Hollas (Wiley, 1987)
4. Basic Principles of Spectroscopy- R.Chang (McGraw Hill, 1971)
5. Introduction to Magnetic Resonance-A Carrington, A.D.McLachlan (Harper & Row, 1967)
6. NMR and Chemistry, 2nd edn-J.W.Akitt (Chapman and Hall, 1983)
7. Theory and Applications of Ultraviolet Spectroscopy. H.H.Jaffe, M.Orchin (Wiley, 1962)
8. NMR, NQR, EPR, and Mossbauer Spectroscopy in Inorganic Chemistry- R. V. Parish, (Ellis Horwood,1990).
9. Solid State Chemistry and its Applications - West, Wiley, 1989.
10. Nuclear Magnetic Resonance - P. J. Hore (Oxford, 1995)

Course No: CHM- 205
Title: Bio-Organic and Bio-Physical Chemistry

Max. Marks- 50 **(25 hrs)**

Unit-1: Enzymes and Kinds of reactions catalysed by Enzymes (10 hrs)

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Introduction, nomenclature & classification. Activation & inhibhion. saturation of enzymes. Fischer lock and key, koshlands induced fit hypothesis, orientation & steric effect. Acid base catalysis, control of enzyme activity.

Nucleophilic displacement on a phosphorous action, displacement reactions & the coupling of ATP transfer of sulphate, addition & elimination reactions. Enzyme mechanism of chymotrypsin lysozyme & carboxypeptidase.

Unit-ll: Coenzyme chemistry (05 hrs)

Cofactor as derived from vitamins, coenzymes, prosthetic groups. apoenTyme structure and biological function of coenzyme A, thiamine pyrophosphate. pyridoxal phosphate, NAD+, NADP+, FMN, FAD. Lipoic acid, vitamin B12. Mechanism of reaction catalyzed by above cofactors.

Unit-lll: Bioenergetics (05 hrs)

Relevence of thermodynamics to Biological systems, Biochemists standard state, standard energy changes in biochemical reactions, ATP as energy currency of cell (synthesis & hydrolysis). Principles of coupled reactions and their importance for living systems.

Unit- IV: Bio-electrochemistry (05 hrs)

Transport of ions across biological membranes, theory of membrane potential- Nernst Plank, Goldman equation, Electrochemistry of Nerve conduction.

Enzymes as electrodes- problems and future application, medical applications of electrochemistry.

Books Recommended:

1. Organic Chemistry, Vol. II 5th Ed., I.L. Finar (Addison- Wesley-2000).
2. Organic chemistry, 7th ed., G. Solomons and Graig Fryhle (Wiley 2000).
3. Organic chemistry, 2nd Ed., Paula, Y. Bruice, (Prentice-Hall-1998).
4. Fundamentals of general Biochemistry, 4th Ed., Jhon. R. Holum (Wilcy-1990).
5. Principles of biochemistry, 3rd Ed., David. L. Nelson, Michael. M.Cox (Worth

Piib. 2002). Physical Chemistry for the Chemical and Biological Sciences, R. Chang,

University Science Books, 2000.

6. Concepts in Biochemistry, R. Boyer, Brroks/Cole Publishing Company, 1999.
7. Fundamentals of Biochemistry, D. Voet, J. G. Voet, C.W. Pralt, Wiley, 1999.
8. Lehninger Principles of Biochemistry, D.L. Nelson, N. M. Cox, Worth publishers, 2000.

Course No, CHM-206L

Title: Laboratory Course in Organic Chemistry

Max. Marks-100 **(50 hrs)**

Qualitative analyses:

Separation, Purification and identification of compounds from three component mixture (All solids). Identification on the basis of chemical tests, preparation of derivatives, Melting point comparison and IR spectroscopy . (5 weeks).

Quantitative analyses:

Quantitative estimation of glucose

Quantitative estimation of Glycerin

QuaEtltatiw estimation of amms/PnenoL IMng r3F8fflidg§ toffliug . Solution OF acetylation methods.

%cmc of-OHgroups.

Determination of iodine and saponification values of an oil sample (2 weeks).

Organic Synthesis:

i. Acetyation Acetylation of Cholesterol or salicylic acid

ii. Oxidation of Cyclohexanol by chromic acid to get adipic acid.

iii. Aldol condensation: Dibenzal acetone for benzaldehyde ;

iv. Cannizarro's reaction of 4-Chlorabenzaldelyde.

v. Aromatic electrophillic substitution in benzene, benzoic acid or aniline.

vi. Beckman rearrangement starting from acetophenone.

Books Recommended:

1. Experiments and Techniques in Organic Chemistry - D. Pasto, C. Johnson and M. Miller (Prentice-Hall, 1992)
2. Microscale and Macroscale Organic Experiments- K.L. Williamson (D.C. Heath and Co., 1989).
3. Advanced Practical Organic Chemistry, 2nd ed. - N.K. Vishnoi (Vikas, 1999).
4. Vogel's Textbook of Practical Organic Chemistry, 5th ed.- A.R. Tatchell (ELBS, • 1996)