Mahatma Gandhi Kashi Vidyapith,

Varanasi, UP-221002

M. Sc. (CHEMISTRY) SYLLABUS

(To be effective from session 2013-2014)

Each semester examination shall comprise four theory papers each of three hours duration and a practical examination of 12 hours duration (spread over two days).

Semester wise distribution of Courses and marks

Semester-I

Course /paper code	Papers No.	Course title		Marks
	I	Inorganic Chemistry-I		100
	II	Organic Chemistry-I		100
	III	Physical Chemistry-I		100
	IV	Sec-A: Computers for Chemists(Compulsory for all students)	60	100
		Sec-B: Mathematics For Chemists (For students without Mathematics in B.Sc.) OR Sec-C: Biology for Chemists (For students without Biology in B.Sc.)	40	
	Practical	Inorganic, Organic, Physical, Viva voce and Records		100
		Total		**500**

Semester-II

Course /paper code	Papers No.	Course title	Marks
	I	Inorganic Chemistry-II	100
	II	Organic Chemistry-II	100
	III	Physical Chemistry-II	100
	IV	Spectroscopy and Diffraction methods	100
	Practical	Inorganic, Organic, Physical, Viva voce and Records	100
		Total	**500**

Semester-III

Course /paper code	Papers No.	Course title		Marks
	I	Application of Spectroscopy		100
	II	Bioinorganic and Bioorganic Chemistry		100
	III	Environmental Chemistry	60	100
		Photochemistry	40	
	IV	Biophysical chemistry and Solid state chemistry		100
	Practical	Inorganic, Organic, Physical, Viva voce and Records		100
		Total		**500**

Semester-IV

Course /paper code	Papers No.	Course title	Marks
	I	Elective paper	100
	II	Elective paper	100
	III	Elective paper	100
	IV	Elective paper	100
	Practical	Inorganic, Organic, Physical, Viva voce and Records	100
		Total	**500**

Elective papers

1 Organotransition Metal chemistry
2 Bioinorganic and Supramolecular Chemistry,
3 Photo Inorganic chemistry
4 Analytical Chemistry
5 Inorganic Polymers
6 Organic Synthesis-I
7 Organic Synthesis II
8 Heterocyclic Chemistry
9 Chemistry of Natural products
10 Medicinal Chemistry
11 Physical Organic Chemistry
12 Chemistry of Materials
13 Computational Chemistry
14 Advanced Quantum Chemistry
15 Liquid State

Semester-I

Paper-I

Inorganic Chemistry -I

UNIT-I: Symmetry and Group Theory in Chemistry

Symmetry elements and symmetry operation, definitions of groups, subgroups, relation between orders of a finite group and its subgroup. Conjugacy relation and classes. Point symmetry group. Schonflies symbols, representation of groups by matrics (representation of the Cn, Cnv, Cnh, Dnh etc groups to be worked out explicitly). Character of a representation. Character tables and their use in spectroscopy.

UNIT-II: Stereochemistry and Bonding in Main Group Compounds

VSEEPR, Walsh diagrams (tri and penta-atomic Molecules), dπ-pπ bonds, bent rule and energetics of hybridization, some simple reactions of covalently bonded molecules.

UNIT-III: Metal-Ligand Equilibria in Solution

Stepwise and overall formation constants and their interaction, trends in stepwise constants, factors affecting the stability of metal complexes with reference to the nature of metal ion and ligand, chelate effect and its thermodynamic origin, determination of binary formation constants by pH metry and spectrophotometry.

UNIT – IV: Metal-Ligand Bonding

Limitation of crystal field theory, molecular orbital theory. Octahedral, tetrahedral and square planar complexes, π-bonding and molecular orbital theory.

Books Recommended

1. F.A. Cotton and G. Wilkinson *Advanced Inorganic Chemistry*, 6th Edn.(1999), John Wiley & Sons, New York.
2. James E. Huheey, *Inorganic Chemistry*, 4th Edn. (1993), Addison-Wesley Pub. Co., New York.
3. Chemistry of the elements, N. N. Greenwood and A. Earnshaw, Pergammon.
4. Inorganic Electronic Spectroscopy, A. B. P. Lever, Elsevier.
5. Comprehensive Coordination Chemistry eds., G Wilkinson, R. D. Gillars and J. A. Mc Cleverty. Pergammon.
6. Magneto Chemistry, R. L. Carlin, Springer Verlag.

Semester-I

Paper II - Organic Chemistry-I

UNIT-I:

Nature of bonding in Organic Molecules

Delocalized chemical bonding-conjugation, cross conjugation, resonance, hyperconjuation, bonding in fullerenes. Aromaticity in benzenoid and non-benzenoid Compounds, Huckel's rule, energy level of pi-molecular orbitals, annulenes, antiaromaticity.

UNIT-II

A- Stereochemistry Conformational analysis of cycloalkanes, decalines, effect of conformation of reactivity Elements of symmetry, chirality, molecule with more than one chiral center, threo and erythro isomers, stereospecific and stereoselective synthesis. Asymmetric synthesis. Optical activity in the absence of chiral carbon biphenyls, allenes and spiranes

B- Reaction mechanism, Structure and reactivity Methods of determining mechanism, isotope effect. Generation structure, stability and reactivity of benzynes, carbenes and nitrenes. Effect of structure on reactivity resonance and field effect, steric effect, quantitative treatment.

UNIT-III:

Aliphatic nucleophilic substitution

The SN_2, SN_1, mixed SN_I and SN_2, the neighboring group mechanism, neighboring group participation by Pi and Sigma bonds, anchimeric assistance Classical and non classical carbocations. The SN_i mechanism nucleophilic substitution at an allylic, aliphatic trigonal and a vinylic carbon. Reactivity effects of substrate structure, attacking nucleophile. leaving group and reaction medium, ambident nucleophile, regioselectivity.

UNIT-IV:

A- Aromatic electrophilic substitution

The arenium ion mechanism, orientation and reactivity, energy profile diagrams. The Ortho/Para ratio, ipso attack, orientation in other ring systems. Vilsmeir reaction, Gattemann-Koch reaction.

B- Aromatic nucleophilic substitution

The SNAr. SN_l, benzyne and SRN_I mechanism. Reactivity effect of substrate structure, leaving group and attacking nucleophile. The Von Richter, Sommelet Hauser, and Smiles rearrangements.

BOOKS SUGGESTED

1. Advanced Organic Chemistry-Reactions, Mechanism and Structure, Jerry March, John Wiley.
2. Advanced Organic Chemistry, F.A. Carey and RJ. Sundberg. Plenum.
3. A Guide Book to Mechanism in Organic Chemistry, Peter Sykes, Longman.
4. Structure and Mechanism in Organic Chemistry, C.K. Ingold, Cornell University press.
5. Organic Chemisty, RT. Morrison and RN. Boyd. Prentice Hall.
6. Modem Organic Reactions H.O. House, Benjamin
7. Principles of Organic Synthesis, R.O.C. Normon and J.M. Coxon, Blackie Academic and professional.
8. Pericyclic Reactions. S.M. Mukherji, Macmillan India.
9. Reaction Mechanism in Organic Chemistry : S.M. Mukherji and S.P. Singh, Macmillan.
10. Stereochemistry of Organic Compounds D. Nasipuri, New Age International.
11. Stereochemistry of Organic Compounds, P.S Kalsi, New Age, International.

Semester-I

Paper III: Physical Chemistry-I

UNIT-I

A-Unifying Principles

Electromagnetic radiation, interaction of electromagnetic radiation with matter-absorption, emission, transmission, reflection, refraction, dispersion, polarization and scattering. Uncertainty relation and natural line width and natural line broadening, selection rules, intensity of spectral lines, Born Oppenheimer approximation, rotational, vibrational and electronic energy levels.

B-Microwave Spectroscopy

Classification of molecules, rigid rotor model, Effect of isotopic substitution on the transition frequencies intensities, non rigid rotor. Stark effect. Applications.

UNIT-II: Vibrational Spectroscopy

A. Infrared Spectroscopy

Review of linear harmonic oscillator, vibrational energies of diatomic molecules, zero point energy, force constant and bond strength; anharmonicity, P.Q.R. branches, vibrations of ploy atomic molecules, Selection rules, normal modes of vibration, factors affecting. the band positions and intensities.

B. Raman Spectroscopy

Classical and quantum theories of Raman effect Pure rotational, vibrational and vibrational-rotational Raman spectra, selection rules, mutual exclusion principle. Applications of Raman spectroscopy.

UNIT- III : Quantum Chemistry

A.Fundamental Background

Operators, Postulates of Quantum Mechanics, Hamiltonian for different systems, Angular momentum.

B. Introduction to Exact quantum Mechanical Results:

The Schrodinger equation, discussion of solutions of the Schrodinger equation to some model system viz,particle in a box ,the harmonic oscillator, the rigid rotar, the hydrogen atom.

C.Approximate Methods:

The Variation theorem, linear variation principle. Perturbation theory(First order and nondegenerate)\ Application of variation method and perturbation theory to the Helium atom.

D. Electronic structures of Atoms:

Russel-Saunders terms and coupling schemes, term symbols for the p^n and d^n configurations Spin orbit coupling and Zeeman splitting, introduction to the methods of self-consistent field, Slaters type orbitals.

E. Molecular orbital theory:

Huckel theory of conjugated systems, bond order and charged density calculations.Application to ethylene, butadiene, cyclobutadiene and Benzene molecules.

UNIT- IV: Chemical Dynamics

Methods of determining rate law, collision theory of reaction rates steric factors Activated complex theory, Arrehenius equation and the activated complex theory, Ionic reactions kinetic salt effect, steady state kinetics. Dynamic chain(hydrogen-bromine reaction ,pyrolysis of acetaldehyde) photochemical (hydrogen-bromine reaction hydrogen-chloride reactions) and oscillatory reactions (Belousav Zhabotinsky reaction) homogeneous catalysis,kinetics of enzyme reaction General features of fast reaction study of fast reaction by relaxation method flash photolysis and the nuclear magnetic resonance method. Dynamics of unimolecular reactions (Lindemann Hinshelwood and Rice –Rampsperger-kassel –marcus (RRKM) theories of unimolecular reactions).

BOOKS SUGGESTED

1. Modem Spectroscopy, J.M. Hollas, John Wiley.
2. Physical methods in Chemistry, RS. Drago, Saunders College.
3. Introduction to Molecular Spectroscopy G.M. Barrow, Mc Graw Hill.
4. Physical Chemistry P.W. Atkins, ELBS.
5. Introduction to Quantum Chemistry, A.K. Chandra, Tata Mc Graw Hill.
6. Quantum Chemistry, Ira N. Levine. Prentice Hall.
7. Coulson's Valence, R.McWeeny, ELBS.
8. Chemical Kinetics, K.J. Laidler, Mcgraw-Hill.
9. Kinetics and Mechanism of Chemical Transformations J. Rajaraman and J .Kuriacose Mc Millan.

Semester-I

Paper IV

Sec-A: Computers for Chemists (Compulsory for all students)

This is a theory-cum-laboratory course with more emphasis on laboratory work.

UNIT- I: Introduction to Computer and Computing:

Basic structure and functioning of computers with a PC as an illustrative example Memory,I/O devices, Secondary storage. Computer languages. Operating systems with DOS as an example. Introduction to UNIX and WINDOWS Data Processing principles of programming. algorithms and flowcharts.

UNIT- II: Computer Programming in FORTRAN/C/BASIC:

The language features are listed here with reference to FORTRAN. The instructor my choose another language such as BASIC or C and the features may be replaced appropriately. Elements of the computer language. Constants and variables. operations and symbols, expressions. Arithmatic assignment statement. Input and Output. Format statement. Termination statements. Branching statements such as IF or GO TO statement. LOGICAL variables. Double precision variables. Subscripted variables and DIMENSION. DO statement FUNCTION and SUBROUTINE. COMMON and DATA statements. (Students learn the programming logic'and these language features by hands on experience on a personal computer from the very beginning of this topic)

UNIT- III : Programming in Chemistry:

Development of small computer codes involving simple formulae in chemistry such as van der Waals equation, pH titration. kinetics. radioactive decay. Evaluation of lattice energy and ionic radii from experimental data. Linear simultaneous equations to solve secular equations within the Huckel theory. Elementary stuctural features such as bond lengths. bond angles, dihedral angles etc. of molecules extracted from a database such as Cambridge data base.

UNIT- IV : Use of Computer Programmes:

The students will learn how to operate a PC and how to run standard programmes and packages. Execution of linear regression. X-Y plot. numerical intergration and differentiation as well as differential equation solution programmes. Monte Carlo and Molecular dynamics. Programmes with data preferably from physical chemistry laboratory Futher, the students will operate one or two of the packages such as MATLAB EASYPLOT LOTUS FOXPRO and Word processing software such as WORDSTAR/MS WORD.

Books Suggested

1. Computers and common Sense, R. Hunt and 1. Shelley. Prentice Hall.
2. Computational Chemistry, A.C. Norris.
3. Microcomputer Quantum mechanics, J.P. Killngbeck. Aoam Hilger.
4. Computer Programming in FORTRAN IV, V. Rajaraman, Prentice Hall.
5. An Introduction to Digital Computer Design. V. Rajaraman and T. Radhakrishana Prentice Hall.

Semester-I

Paper IV

Sec-B: Mathematics For Chemists

(For students without Mathematics in B.Sc.)

UNIT- I: Vectors and matrix Algebra

A- Vectors

Vectors, dot, Cross and triple products etc. The gradient, divergence and curl.

B- Matrix Algebra

Addition and multiplication: inverse, adjoint and transpose of matrices, special matrices (Symmetric, skew-symmetric Hermitian, skew-Hermitian, unit, diagonal, unitary etc) and their properties Matrix equations: homogeneous, non-homogeneous linear equations and conditions for the solution, matrix eigenvalues diagonalisation determinats (examples from Huckel theory)

UNIT- II: Calculus

A- Differential Calculus

Functions, continuity and differentiability, rules for differentiation, applications of differential calculus including maxima and minima (examples related to maximally populated rotational energy levels. Bohr's radius and most probable velocity from Maxwell's distribution etc) exact and inxact differentials with their applications to thermodynamic properties.

B- Integral calculus.

Basic rules for integration, integration by parts. partial fraction and substitution. Reduction formulae applications of integral calculus. Functions of several variables. partial differentiation. co-ordinate transformations (e.g. cartesian to spherical polar).

UNIT- III: Elementary Differential Equations

Variables-separable and exact first-order differential equations. homogeneous. exact and linear equations. Applications to chemical kinetics. secular equilibria, quantum chemistry etc . Solutions of differential equations by the power series method, Fourier series, solutions of harmonic oscillator and Legendre equation etc,. spherical harmonics second order differential equations and their solutions.

UNIT- IV: Permutation and Probability

Permutations and combinations, probability and probability theorems, probability curves, average, root mean square and most probable errors, examples from the Kinetic theory of gases etc.

Books Suggested

1. The chemistry Mathematics Book, E. Steiner, Oxford University Press.
2. Mathematics for Chemistry, Doggett and Sucliffe. Longman.
3. Mathematical preparation for Physical Chemistry. F.Daniels Mc Graw Hill.
4. Chemical Mathematics, D.M. Hurst, Longman.
5. Applied Mathematics for Physical Chemistry. J.R. Barrante. Prentice Hall.
6. Basic Mathematics for Chemists, Tebbutt. Wiley.

Semester-I

Paper IV Section - 'C'
Biology for Chemists
(For students without Biology in B.Sc.)

UNIT- I: A- Cell Structure and Functions

Structure of prokaryotic and eukaryotic cells, intracellular organelles and their functions, comparison of plant and animal cells. Overview biological energy currency. Introduction to biomolecules. building blocks of biomacromolecules.

B-Carbohydrates

Structure and functions of important derivatives of monosaccharides like glycosides, deoxy sugars, myoinositol, amino sugars. N-acetylmuramic acid, sialic acid, disaccharides and polysaccharides. Structural polysaccharides-cellulose and chitin. Structure and biological functions of glucosaminoglycans or mucopolysaccharides. Carbohydrates of glycoproteins and glycolipids. Role of sugars in biological recognition. Blood group substances. Carbohydrate metabolism, Kerb's cycle, glycolysis, glycogenesis, gluconeogenesis pentose-phosphate pathway.

UNIT- II: Lipids.

Fatty acids, essential fatty acids, structure and function of triacylglycerols, glycerophospholipids, sphingolipids, cholesterol, bile acids, prostaglandins. properties of lipid aggregates-micelles, bilayers, liposomes and their possible biological functions. Biological membranes. Fluid mosaic model of membrane stucture Lipid metabolism β oxidation of fatty acids.

UNIT- III : Amino-acids, Peptides and proteins

Chemical and enzymatic hydrolysis of proteins to peptides, amino acid sequencing. Secondary structure of proteins, forces responsible for holding of secondary structure α-helix, β sheets, super secondary structure, triple helix structure of collagen. Tertiary stucture of protein folding and domain structure. Quaternary structure. Amino acid metabolism-degradation and biosynthesis of amino acids. sequence determination chemical/enzymatic/mass spectral. racemization/detection. Chemistry of oxytocin and tryptophan releasing hormone (TRH).

UNIT- IV : **Nucleic Acids**

Purine and pyrimidine bases of nucleic., acids, base pairing via H-bonding structure of ribonucleic acid (RNA) and deoxyribonucleic acids (DNA), double helix model of DNA and forces responsible for helding it. Chemical and enzymatic hydrolysis of nucleic acids. The chemical basis for heredity and overview of replication of DNA, transcription, translation and genetic code. Chemical synthesis of mono and trinuoleoside.

Books Suggested

l. Principles of Biochemistry, A.L Lehniger Worth Publishers.
2. Biochemistry, L. Stryer, W.H. Freeman.
3. Biochemistry, J,David Rawn, Nell Patterson.
4. Biochemistry Voet and Voet, John Wiley.
5. Outlines of Biochemistry, E.E.Conn and P.K. Stumpt, John Wiley.

Semester-I

Practicals

Note:-

i) A complete records of practical exercises; in Inorganic, Organic and Physical Chemistry done during the session must be produced by the candidates in three separate Record Books at the time of practical examination.

Inorganic Chemistry

1. Qualitative analysis of mixtures 20

Qualitative analysis of mixture containing trace elements Tl, Mo, W, Zr, Ti, Th, V, U (Two metal ions in cationic/anionic forms) and insoluble oxides, sulphates and halides. The mixture should not contain more than five cations and should be analyzed by semi micro technique.

2. Paper chromatography 05

Paper chromatography separation of a mixture of the following and measurements of Rf values.

a) Pb^{+2}, Ag^{+}, Hg^{+2}(b) Co^{+2}, Ni^{2}, Cu^{+2} (c) Ba^{+2}, Ca^{+2}, Sr^{+2}

Organic Chemistry

1. Qualitative Analysis 15

   Separation, purification, and identification of binary mixture. Preparation of derivatives if possible

2. Organic Synthesis 10
   i. Adipic acid by chromic acid oxidation of cyclohexanol.
   ii. Triphenyl methanol from Benzoic acid.
   iii. Dibenzal acetone from Benzalehyde.
   iv. p-chlorotolune from p-toludine
   v. Synthesis of p-nitroaniline and p-bromoaniline.

Physical Chemistry (Any one) 25

1. Study the adsorption of acetic acid on charcoal and draw the Freundlich isotherm.
2. Show that the order of reaction between acetone and Iodine is zero with respect to Iodine
3. Determination of congruent composition and temperature of a binary mixture e.g. diphenylamine-benzophenone system.
4. Determination of glass transition temperature of a given salt (e.g., $CaCl_2$) conductometrically.
5. Determination of the velocity constant of hydrolysis of an ester / ionic reaction in micellar media.
6. Determination of the velocity Constant of decomposition of Benzene diazonium chloride.

Viva 15

Records 10

Semester-II

Inorganic-II (Paper I)

UNIT- I: Reaction mechanism of Transition Metal Complexes

Energy profile of a reaction, reaction reactivity of metal complexes, inert and labile complexes, kinetic application of valence bond and crystal field theories, kinetics of octahedral substitution, acid hydrolysis, factors affecting acid hydrolysis, base hydrolysis conjugate base mechanism, direct and indirect evidences in favour of conjugate mechanism, anation reaction, reactions without metal ligands bond cleavage. Substitution reaction in square planar complexes. Redox reactions, electron transfer reactions, mechanism of one electron transfer reactions, outer sphere type reactions,, cross- reactions and Marcus-Hush theory, inner sphere type reactions.

UNIT- II : Electronic spectra and Magnetic Properties of Transition Metal Complexes:

Spectroscopic ground states; Orgel energy level and Tanabe-Sugano diagrams for transition metal complexes (d^1-d^9 states); Charge transfer spectra; electronic spectra of octahedral and tetrahedral Co(II) and Ni(II) complexes and calculation of ligand-field parameters.

UNIT- III : Metal π-Complexes

Metal carbonyls, structure and bonding, vibrational spectra of Metal carbonyls for bonding and structural elucidation, important reactions of Metal carbonyls, preparation, bonding. Structure and important reactions of transition metal nitrosyl, dinitrogen and dioxygen complexes, tertiary phosphine as ligand.

UNIT- IV: A- Metal Clusters

Higher boranes, carboranes, metallocarboranes

B- Isopoly and heteropoly acids and salts

Books Recommended

1. F.A. Cotton and G. Wilkinson *Advanced Inorganic Chemistry*, 6th Edn.(1999), John Wiley & Sons, New York.
2. James E. Huheey, *Inorganic Chemistry*, 4th Edn. (1993), Addison-Wesley Pub. Co., New York.
3. Chemistry of the elements, N. N. Greenwood and A. Earnshaw, Pergammon.
4. Inorganic Electronic Spectroscopy, A. B. P. Lever, Elsevier.
5. Comprehensive Coordination Chemistry eds., G Wilkinson, R. D. Gillars and J. A. Mc Cleverty. Pergammon.

Semester-II

Organic-II (Paper II)

UNIT- I : Free radical reactions:

Free radical substitution mechanism, mechanism at an aromatic substrate, neighbouring group assistance. Reactivity for aliphatic and aromatic substrates at a bridgehead. The effect of solvent on reactivity. Arylation of aromatic compounds bydiazonium salt. Hunsdiecker reaction.

UNIT- II : A- Addition to carbon-carbon multiple bond:

Mechanistic and stereochemical aspects of addition reactions involving electrophile, nucleophile and free radicals, regio and chemo selectivity, orientation and reactivity. Hydrogenation of aromatic rings. Hydrobration. Michael reaction. Sharpless asymmetric epoxsidation.

B-Addition to carbon heteroatom multiple bonds:

Mechanism of metal hydride reduction of saturated and unsaturated carbonyl compounds, acids, esters and nitriles, Witting reaction mechanism of condensation reactions involving enolate, Knoevenagel, Mannich, Stobbe reactions. Hydrolysis of esters and amides, ammonolysis of esters.

UNIT- III : Elimination reactions:

The E2, EJ and EI CB mechanism. Orientation of double bond. Reactivity effect of substrate structures. Attacking base, the *leaving* group' and the medium. Mechanism and orientation on Pyrolytic elimination.

UNIT- IV: Pericyclic reactions :

Molecular orbital symmetry, frontier orbitals of ethylene, 1, 3- butadiene, 1,3,5-hexatriene and allyl system. Classification of pericyc1ic reactions. Woodward-Hoffmann *correlation* diagranls. FMO and PMO approach. *Electrocyc1ic* reactions- *conrotatory* and disrotatory motions, 4n, 4n+2 and *alyl* systems. Cycloadditions-antarafacial and SuprafaciaI 'additions, 4n and- 4n+2 system, Sigmatropic rearrangements-superafacial an antarafacial shift of H,sigmatropic shifts *involving* carbon moieties, 3, 3 and 5, 5 sigmatropic rearrangements. *Claisen*- Cope and Azacope rearrangement. Fluxional tautomerism. Ene reaction.

BOOKS SUGGESTED

1. Advanced Organic Chemistry-Reactions, Mechanism and Structure, *Jerry* March, John Wiley.
2. Advanced Organic Chemistry, F.A. Carey and RJ. Sundberg. Plenum.
3. A Guide Book to Mechanism in Organic Chemistry, Peter Sykes, Longman.
4. Structure and I\.Jechanism in Organic Chemistry, c.K. Ingold, *Cornell* University press.
5. Organic Chemisty, RT. Morrison and RN. Boyd. Prentice Hall.
6. Modem Organic Reactions H.O. House, Benjamin
7. Principles of Organic Synthesis, RO.C. Normon and J.M. Coxon, Blackie Academic and professional.
8. Pericyclic Reactions. S.M. Mukherji, Macmillan India.
9. Reaction Mecnanism in Organic Chemistry S.M. Mukherji and S.P. Singh, Macmillan.
10. Stereochemistry of Organic Compounds D. Nasipuri, New Age International.

Semester-II

Physical -II (Paper III)

UNIT- I: Thermodynamics

A-Classical Thermodynamics: Brief resume of concepts of laws of thermodynamics, free energy and chemical potential. Partial, molar properties partial molar free energy,partial molar volume and its determination, Gibbs –Duhem equation, concept of fugacity(by graphical method), Activity and Activity coefficient.

B-Statistical Thermodynamics: Concept of distribution, thermodynamic probability and most probable distribution. Canonical, grand canonical and microcanonical ensembles ,The Boltzmann distribution law. Partition Functions-translational, rotational, vibrational and electronic partition function. Calculation of thermodynamic properties and equilibrium constant in terms of partition function. Fermi-Dirac and Bose-Einstein statistics.

C-Non-Equibrium Thermodynamics: Thermodynamic criteria for non-equilibrium states, entropy production and entropy flow, Entropy balance equation for different irreversible processes (e.g heat flow chemical reaction etc. Transformation of the generalized fluxes and forces non-equilibrium stationary ,phenomenological equations, Onsager's reciprocity relation, electro kinetic phenomena.

UNIT- II: Surface chemistry:

A-Adsorption: Gibbs adsorption isotherm estimation of surface area (BET equation), surface films on liquids(Electro kinetic phenomenon), catalytic activity at surfaces.

B-Micelles: Surface active agents ,classification of surface active agents, micellization hydrophobic interactions, Critical micellar concentration(CMC) Factors affecting CMC of surfactants counter ion binding to Micelles ,solubilization micro emulsion reverse micelles.

UNIT- III: Macromolecules:

Polymer-definition, types of polymer, electrically conducting fire resistant, liquid crystal polymer, Kinetics of polymerization, Molecular mass, number and mass average molecular mass , molecular mass determination (Osmometry, Viscometry diffusion and light scattering method) sedimentation chain configuration of macromolecules, Calculation of average dimension of various chain structures.

UNIT- IV: Electrochemistry:

Debye- Huckel theory of activity coefficient of electrolytic solutions, applicability and limitations of Debye-Huckel limiting law, ionic strength, stucture of electified interfaces, Helmholtz- perrin, Guoy-Chapman and stern models. Over potentials, exchange current density, derivation of Butler- volmer equation, Tafel plot. Electrocatalysis, Influence of various parameters, Hydrogen electrode. Polarography theory, interpretation of a polarographic curve, instrumentation, limiting current, residual and charging current, diffusion current. Supporting electrolytes, Llkovic equation, half wave potential and its significance. Introduction to corrosion, homogeneous theory, forms of corrosion, corrosion monitoring and prevention methods.

BOOKS SUGGESTED

1. Kinetics and Mechanism of Chemical Transformations J. Rajaraman and J .Kuriacose Me Millan.
2. Micelles, Theoretical and Applied Aspects, V. Moroi, Plenum .
3. Modem Electrochemistry Vol. **I** and Vol. II J.O.M. Bockris and AK.N. Reddy, Plenum.
4. Introduction to Polymer Science V.R. Gowarikar, N.V. Vishwanathan and J.Sridhar, Wiley Eastern.
5. Physical Chemistry P.W. Atkins, ELBS.

Semester-II

Spectroscopy and Diffraction method (Paper IV)

UNIT- I: Electronic Spectroscopy

A- Atomic Spectroscopy

Energies of atomic orbitals, spectra of hydrogen atom and alkali metal atoms.

B- Molecular Snectroscopy

Franck-Condon principle, electronic spectra of polyatomic molecules. Emission spectra; radiative and non-radiative decay, internal conversion, spectra of transition metal complexes, charge-transfer spectra.

C- Photoelectron Spectroscopy

Basic principles; photo-electric effect, ionization process, Koopman's theorem. Photoelectrion spectra of simple molecules, ESCA, chemical information from ESCA. Auger electron spectra of simple molecules.

UNIT- II : Nuclear Magnetic Resonance Spectroscopy

A- magnetic Resonance Spectroscopy

Nuclear spin, nuclear resonance, saturation, shielding of magnetic nuclei, chemical shift and its measurements, factors influencing chemical shift deshielding, spin-spin interactions, factors influencing coupling constant 'J' Effect of chemical exchange, spin decoupling, basic ideas about instrument, NMR studies of nuclei other than proton-l3C, 19F and 31P. FT NMR, advantages of FT NMR use of NMR in medical diagnostics.

B-Nuclear Quadrupole Resonance Spectroscopv

quadrupole nuclei quadrupole moments, electric field gradient, coupling constant, splittings, Applications.

UNIT- III :

A- Electron Spin Resonance-Spectroscopy

Basic principles, Zero field splitting and Kramer's degenerancy. Factors affecting the 'g' value. Isotropic' and anisotropic hyperfine coupling constants. measurement techniques and applications.

B-Photoacoustic Spectroscopy

Basic principles of photoacoustic spectroscopy (PAS), PAS- gases and condensed systems, chemical and surface applications.

UNIT- IV

A-X-ray Diffraction

Bragg method of X-ray stuctural analysis of crystals, index reflections. Structure of simple lattices and X-ray intensities.

B-Electron Diffaction

Scattering intensity vs. scattering angle, Wierl equation, measurement technique, elucidation of structure of simple gas phase molecules.

BOOK SUGGESTED

1. Modem Spectroscopy, J.M. Hollas, John Wiley.
2. Applied Electron Spectroscopy for Chemical Analysis ed. H. Windawi and F.L. Ho. Wiley interscience.
3. NMR, NQR, EPR and mossbauer Spectroscopy in inorganic Chemistry, R.V. Parish, Ellis Harwood.
4. Introduction to Molecular Spectroscopy G.M. Barrow, Mc Graw Hill.
5. Basic principles of Spectroscopy. R. Chang. Mc Graw Hill.
6. Theory and Applications of UV Spectroscopy, H.H. Jaffer and M. Orchin. IBH-oxford.
7. Introduction to Photoelectron Spectroscopy. P.K. Ghosh. John Wiley.
8. Introduction to Magnetic Resonance, A carrington and A.D. maclachalan, Harper & Row.

Practicals

Semester-II

Note:-

A complete record of practical exercises; in Inorganic, Organic and Physical Chemistry done during the session must be produced by the candidates in three separate Record Books at the time of practical examination.

Inorganic Chemistry

I. Quantitative estimation of two metal ions Cu-Ni, Ni-Zn, Cu-Fe etc involving volumetric and gravimetric methods. 20

II. Preparation of selective inorganic compounds (any one) 05

(a)$VO(acac)_2$,
(b)$Na[Cr(NH_3)_2(SCN)_4]$
(c)$K_3[Fe(C_2O_4)_3]$
(d)Prussian Blue
(e)$[Co(Py)_2Cl_2]$
(f) $[Cu(NH_3)_4]SO_4.H_2O$

Organic Chemistry **25**

Quantitative Synthesis (Any Two)

I. Determination of the percentage or number of hydroxyl groups in an organic compound by acetylation method. .
II. Estimation of amine/phenols using bromate bromide solution or acetylation method.
III. Determination of iodine and saponifiaction values of an oil sample.
IV. Determination of DO, *COD* and BOD of water sample.

Physical Chemistry (Any one) **25**

I. Determination of molecular weight of nonvolatile and nonelectrolyte/electrolyte by cryoscopic method and to determine the activity coefficient of an electrolyte.
II. Determination of the degree of dissociation of weak electrolyte and to study the deviation from ideal behaviour that occurs with a strong electrolyte.
III. Determination of the velocity constant, order of the reaction and energy of activation for saponification of ethyl acetate by sodium hydroxide conductometrically.
IV. Determination of solubility and solubility product of sparingly soluble salts (e.g $PbSO_4$, $BaSO_4$) conductometrically.
V. Determination of the strength of strong and weak acids in a given mixture conductometrically .
VI. Viva **15**
VII. Records **10**

Semester-III
Paper-I
(Applications of Spectroscopy)

UNIT- I: Applications of Spectroscopy in Inorganic Chemistry

A- Vibrational Spectroscopy

Symmetry and shapes of AB_2, AB_3 and AB_4, mode of bonding of ambidentate ligands such as thiocyanate, nitrate, sulphate and urea, application of Raman spectroscopy particularly for the study of ionic equilibrium in solution.

B- Electron Spin Resonance Spectroscopy

Hyperline coupling, spin polarization for atoms and transition metal ions, spin-orbit coupling and significance of g-tensors, application to transition metal complexes having one unpaired electron and inorganic free radicals such as PH_4, F_2^- and BH_3.

C- Mossbauer Spectroscopy

Basic principles, spectral parameters and spectrum display. Application of the techniques to the studies of (1) bonding and structures of Fe^{2+} and Fe^{3+} compounds including those of intermediate spin and (2) Sn^{2+} and Sn^{4+} compounds nature of M-L bond, coordination number, structure.

UNIT- II: Applications of Spectroscopy-I in organic Chemistry

A- Ultraviolet and Visible Spectroscopy

Various electronic transitions (185-800 nm).Beer Lambert law. Effect of solvent on electronic transitions, ultraviolet bands for carbonyl compounds, unsaturated carbonyl compounds, dienes, conjugated polyenes, ultraviolet spectra of aromatic and heterocyclic compounds.

B- Infrared Spectroscopy

Characteristic vibrational frequencies of aromatic compounds, alcohols, ethers, phenols and amines. Detailed study of vibrational frequencies of carbonyl compounds (ketones, aldehydes, esters, amides and acids), effect of hydrogen bonding and solvent effect on vibrational frequencies, overtones, combination bands and Fermi resonances.

UNIT- III: Applications of Spectroscopy-II in organic Chemistry

A- Nuclear Magnetic Resonance Spectroscopy

General introduction and definition, chemical shift, spin-spin interaction, shielding mechanism, mechanism of measurement, chemical shift values and correlation for protons bonded to carbon (aliphatic, olefinic, aldehydic and aromatic) and other nuclei (alcohols, phenols, enols and carboxylic acids) chemical exchange, effect of deuteration, complex spin-spin interaction between two, three, four and five nuclei (first order spectra).

B- Carbon-13 NMR Spectroscopy

General considerations, chemical shift (aliphatic, olefinic, alkyne, aromatic, heteroaromatic and carbonyl carbon), coupling constants.

UNIT- IV: Applications of Spectroscopy-III in organic Chemistry

Mass Spectrometry

Introduction, ion production- E1, C1, FD and FAB, factors affecting the fragmentation, ion analysis, ion abundance, mass spectral fragmentation of organic compounds, common functional groups, molecular ion peak, metastable peak, Mclafferty rearrangement, Nitrogen rule.

Books suggested

1. Physical Methods for Chemistry, R.S.Dargo, Saunders Company
2. Structural Methods in Inorganic Chmesistry, E.A.V. Ebsworth, Rankin and Cradock- ELBS.
3. Infrared and Raman Spectra Inorganic and Coordination Compounds, K. Nakamoto, Wiley.
4. Progress in Inorganic Chemistry, 8th edition, F. A. Cotton
5. Transition Metal Chemistry, edR.L.Carlin, vol. 3, Dekker.
6. Inorganic Electronic Spectroscopy, A.P.B. Lever, Elsevier.
7. NMR, NQR, EPR and Mossbauer Spectrosocpy in Inorganic Chenmsitry, R.V. Parish, Ellis Horwood.
8. Practical NMR Spectroscopy, M. L.Martin, J. J. Delpeuch and G. J. Martin, Heyden.
9. Spectrometric Identification of Organic Compounds, R.M. Silverstein. G.C. Bassler and T.C. Morill, John Wiley.
10. Introduction to NMR Spectroscopy, R.J. Abraham, J. Fischer and P. Loftus, Wiley.
11. Application of Spectroscopy of Organic Compounds, J. R. Dyer, Prentice Hall,
12. Spectroscopic Methods in Organic Chemistry, D.H. Williams, I. Fleming, Tata Mc-Graw Hill.

Semester-III
Paper-II
Section-'A':(Bioinorganic Chemistry)
UNIT- I

A- Metal Ions in Biological Systems
Essential and trace metals
B- Na^+/K^+ Pump
Role of metal ions in biological processes

UNIT- II

A-Bioenergetics and ATP cycle
DNA polymerization, glucose storage, metal complexes in transmission of energy: chlorophylls
B- Transport and Storage of Dioxygen
Heme proteins and oxygen uptake, structure and function of haemoglobin, myoglobin, haemocyanins and hemerythin model synthetic complexes in iron, cobalt and copper

UNIT- III

Electron Transfer in Biology
Structure and function of metalloproteins in electron transport processes-cytochromes and ion-sulphur proteins.

UNIT- IV

Nitrogenase
Biological nitrogen fixation, molybdenum nitrogenase

Books suggested

1. Principle of Bioinorganic Chmeistry, S. J. Lippard and J.M. Berg, University Science Books
2. Bioinorganic Chemistry, Bertini H.B. Gray, S.J. Lippard and J.S. Valentine, University Science Books
3. Inorganic Biochemistry, vols. I and II ed. G.L. Eichhorn, Elsevier.
4. Progress in Inorganic Chemistry, Vols 18 & 38 ed. J.J. Lippard, Wiley.

Section-'B'
Bioorganic Chemistry
UNIT- I

A-Introduction
Basic consideration Proximity effects and molecular adaptation
B-Enzymes
Introduction and historical perspective chemical and biological catalysis, remarkable properties of enzymes like catalytic power, specificity and regulation. Nomenclature and classification, Fischer's lock and key and koshland's induced fit hypothesis, concept and identification of active site by the use of inhibitors. Enzyme kinetics, Michaelis Menten and Lineweaver Burk plots, reversible and irreversible inhibition.

UNIT- II

A-Mechanism of Enzyme Action
Transition-state theory, orientation and steric effect, acid-base catalysis, covalent catalysis, strain or distortion. Examples of some typical enzyme mechanisms for chymotrypsin, ribonuclease, lysozyme and carboxypeptidase-A.
B-Kinds of Reactions Catalysed by Enzymes
Nucleophilic displacement on a phosphorus atom, multiple displacement reations and the coupling of A TP cleavege to endergonic processes Transfer of sulphate, addition and elimination reactions, enolic intermediates in isomerization reactions, 13-c1eavage and condensation, some isomerization and rearrangement reactions. Enzyme catalyzed carboxylation and decarboxylation.

UNIT- III

A- Co-Enzyme Chemistry
Cofactor as derived from vitamins coenzyme S, Prosthetic groups, apoenzmes structure and biological functions of coenzyme A thiamine pyrophosphate, pyridoxal phosphate. NAD^+I, $NADP^+$, FMN, FAD, lipoic acid, vitamin B_{12}.
B-Enzyme Models.
Host-guest chemistry, chiral recognition and catalysis, molecular recognition, molecular asymmetry and prochirality. Biomimetic chemistry crown ethers, cryptates Cyc1odextrins. cyclodextrin- based enzme models calixarenes ionophores. micelles. synthetic enzymes or synzymes.

UNIT- IV

Biotechnological Applications of Enzymes
Large-scale production and purification of enzymes, techniques and methods of immobilization of enzymes, effect of immobilization on enzyme activity, application of immobilized enzymes, use of enzymes as targets for drug design. Clinical uses of enzymes, enzyme therapy.

Books Suggested

1. Bioorganic Chemistry: A chemical Approach to Enzyme Action, Hermann Dugas and C. Penny. Springer Verlag.
2. Understanding Enzymes, Trevor Palmer, Prentice Hall.
3. Enzyme Chemistry: Impact and Applications, Ed. Collin J.Suck Chapman and Hall.
4. Enzyme Mechanisms De. M.1. Page and A. Williams. Royal Society of Chemistry
5. Fundamentals of Enzymology. N.C. Price and L. Stevens. Oxford University Press.
6. Immobilized Enzymes: An introduction and application in Biotechnology- Michael D. Trevan- John Wiley.
7. Enzyme Structure and Mechanism, A Fersht, W.H. Freeman.
8. Biochemistry: The Chemical Reactions of Living Cells. D.E. Metzler. Academic Press.

Semester- III
Paper- III
Section-'A'
(Environmental Chemistry)
UNIT- I

A-Environment

Introduction, Composition of atmosphere, vertical temperature, heat budget of the earth atmospheric system, veritical stability atmosphere. Biogeochemical cycles of C, N, P, S and O. Biodiatribution of elements.

B- Hydrosphere

Chemical composition of water bodies-lakes, streams, rivers and wet lands etc. Hydrological cycle. Aquatic Pollution- inorganic, organic, pesticide, agricultural industrual and sewage, detergents, oil spills and oil pollutants, Water quality parameters-dissolved oxygen biochemical oxygen demand, solids, metals, contemt of chloride, sulphate, phosphate, nitrate and mcro-organisms. Water quality standards. Analytical methods for measuring BOD, DO, COD, F, Oils, metals (As, Cd, Cr, Hg, Pb, Se, etc.), residual chloride and chlorine demand. Purification and treatment of water.

UNIT- II

A- Soils

Composition micro and macro nutrients. Pollution-fertilizers, pesticides plastics and metals. Waste treatment.

B- Atmosphere

Chemical compostion of atmosphere-particles, ions and radicals and their formation Chemical and photochemical reactions in atmosphere, smog formation, oxides of N.C.S.O. and their effect, pollution by chemicals, petroleum, minerals, chlorofluorohydrocarbons Green house effect, acid rain, air pollution controls and their chemistry. Analytical methods for measuring air poilution, Continuous monitoring instruments

UNIT- III

Industrial Pollution

Cement, sugar, distillery, drug, paper and pulp, thermal power plants, nuclear power plants, metallurgy, polymers, drugs etc. Radionuclide analysis. Disposal of wastes and their management.

UNIT- IV

Environmental toxicology

Chemical solutions to environmental problems, biodegrade ability, principles of decompostion better industrial processes. Bhopal gas tragedy, Chernobyl, three *mile* istand. Sewozo and Minamata disasters.

Books Suggested

1. Environmental Chemistry, S.E. Manahan, Lewis Publishers.
2. Environmental Chemistry, Sharma & Kaur, Krishna Publishers
3. Environmental Chemistry, A.K. De, Wiley Eastern. .
4. Environmental Pollution Analysis, S.M. Khopkar, Wiley Eastern
5. Standard method of Chemical Analysis, *F.I.* Welcher Vol. III Van Nostrand Reinhold Co
6. Environmental Toxicology. *Ed.I.* Rose, Gordon and Breach Science Publication.
7. Elemental Analysis of Airborne Particles. Ed. S.Landsberger and M. Creatchman, Gordon and Breach Science Publication.
8. Environmental Chemistry. C. Baird. W.H. Freeman.

Semester- III

Paper- III

Section-'B'

(Photo Chemistry)

UNIT- I:Photochemical Reactions

Interaction of electromagnetic radiation with matter, types of excitations, fate of excited molecule, quantum yield, transfer of excitation energy actinoimetry.

UNIT- II:Determination of Radical Mechanism

Classification rate constants and life times of reactive energy, states-determination of rate constants of reactions.Effect of light intensity on the rate of photochemical reactions.

UNIT- III :

A-Photochemistry of Alkenes: Intramolecular reactions of the olefinic bond-geometrical isomerism, cyclization reactions, rearrangement of 1,4- and 1,5- dienes.

B- Photochemistry of Carbonyl Compounds

Intramolecular reactions of carbonyl compounds- saturated cyclic, acyclic β, γ unsaturated and α,β unsaturated compounds, cyclohexadienones.

Intermolecular cycloaddition reactions-dimerization and oxetane formation.

UNIT- IV Photochemistry of Aromatic Compounds

Isomerizations, additions and substitutions.

Books suggested

13. Fundamentals of Photochemistry, K.K. RohtagiMukherji, Wiley Eastern.
14. Essentials of Molecular Photochemistry, A. Gilbert, BaggotBalckwell Scientific Publications.
15. Introductory Photochemistry, A. Cox and T. Camp, McGraw Hill.
16. Photochemistry, R. P. Kundall and A. Gilbert, Thomson Nelson.
17. Organic Photochemistry, J. Coxon and B. Halton, Cambridge University Press.

Semester- III
Paper- IV
(Biophysical chemistry and Solid state chemistry)

UNIT- I:

A- Biological cell and its Constituents

Biological cell, structure and functions of proteins, enzymes. DNA and RNA in living systems. Helix coil transition.

B- Bioenergetics

Standard free energy change in biochemical reactions, exergonic, endergonic. Hydrolysis of ATP, synthesis of ATP from ADP.

UNIT- II

A-Biopolymer Interactions

Forces involved in biopolymer interactions. Electrostatic charges and molecular expansion, hydrophobic force, dispersion force interactions. Multiple equilibria and various types of binding processes in biological systems. Hydrogen ion titration curves.

B-Themodynamics of Biopolymer Solutions

Thermodynamics of biopolymer solutions, osmotic pressure membrane equilibrium, muscular contraction and energy generation in mechanochemical system.

UNIT- III

A-Cell membrane and Transport of ions

Structure and functions of cell membrane, ion transport through cell membrane, irreversible thermodynamic treatment of membrane transport. Nerve conduction.

B- Biopolymers and their Molecular Weights

Evaluation of size shape molecular weight and extent of hydration of biopolymers by various experimental techniques. Sedimentation equilibirium, hydrodynamic methods, diffusion, sedimentation velocity viscosity electrophoresis and rotational motions.

UNIT- IV: Solid state chemistry

A- Solid State Reactions

General Principles for reaction between two solids: Reaction conditions, structural considerations, surface area, reactivity, kinetics of solid state reactions.

B- Crystal Defects and Non-Stoichiometry

Perfect and imperfect crystals, intrinsic and extrinsic defects- point defects, vacancies- Schottky defects and Frenkel defects. Thermodynamics of Schottky and Frenkel defect formation, non-stoichiometry and defects.

C- Electronic Properties and Band Theory

Metals, insulators and semiconductors, electronic structure of solids-band theory, band structure of metals, insulators and semiconductors, intrinsic and extrinsic semiconductors, doping semiconductors, p-n junctions, super conductors. Optical properties- optical reflectance, photoconduction- photoelectric effects.

Book Suggested

1. Principles of Biochemistry, A.L. Lehninger, Worth Publishers.
2. Biochemistry, L. Stryer, W.H. Freeman.
3. Biochemistry, J.David Rawn, Neil Patterson.
4. Biochemistry, Voet and Voet, John Wiley.
5. Outlines of Biochemistrc, E.E. Conn and f.K. Stumpf, John Wiley.
6. Bioorganic Chemistry: A Chemical Approach to Enzyme Action, H.Dugas and C. Penny, Springer-Verlag.
7. Marcomolecules: Structure and Functions, F. Wold, Prentice Hall.
8. Solid sate Chemistry and its Applications, A.R. West, Plenum.
9. Principles of the Solid State, H. V. Keer, Wiley Eastern.
10. Solid State Chemsitry, N. B. Hannay.
11. Solid State Chemistry, D.K. Chakrabarty, New Age Interrnational.

Semester III
Practicals

Inorganic **25**

I. Preparation of selected inorganic compounds and structural elucidation on the basis of given spectra (IR, ESR and MS) Selection can be made from the following

1- Sodium amide
2- Dichlorophenyl borane $PhBCl_2$
3- Sn(IV) Iodide, Tin (IV) chloride and Tin (II) iodide
4- Ammonium hexachorostannate CNH4h $Sncl_6$,
5- Trichlorodiphenyl antimony (v) hydrate
6- Sodium Tetrathionate, $Na_2S_4O_6$
7- Metal Complexes of dimethyl Sulfoxide, $CuCl_2$, 2DMSO.
8- Metal acetylacetonate.
9- Ion exchange separation of oxidation state of V.
10- Preparation of Fe(II) Chloride.
11- Phosphine Ph_3P and its transition metal complexes.
12- Ferrocene
13- Copper glycine Complex

II. Chromatographic Separations:

a- Thin layer chromatographic separation of Nickel, Manganese Cobalt and Zinc. Determination of Rf values.
b- Cadmium and Zinc
c- Zinc and Magnesium

ORGANIC CHEMISTRY **25**

I. Qualitative Analysis

Separation and identification of components of a mixture of three organic compounds (three solids or two liquids and one solid, two solids and one liquid). Suitable derivatives to be prepared where possible. Purity of the separated components should also be checked on TLC plates, Chemical analysis.

II. Isolation of the following
i) Caffeine from tea leaves.
ii) Casein from milk
iii) Lactose from milk
iv) Nicotine dipicrate from tobacco
v) Lycopene from tamtoes.

PHYSICAL CHEMISTRY **25**

Thermodynamics:

I- Determination of partial molar volume of solute (e.g, KCI) **I** and solvent in a binary mixture.'

II- Determination of the temperature dependence of the solubility of a compound in two solvents having similar inter molecular interactions (benzoic acid in water and in DMSO water mixture) and to calculate the partial molar heat solution

Spectroscopy

i Determination of pK_a of an indicator (e.g. methyl red) 10 (a) aqueous and (b) micellar media.
ii. Determination of stoichiometry and stability constant of inorganic (e.g. ferric-salicyclic acid) and organic (e. g. amine iodine) complexes. Characterization of the complexes by electronic and IR spectral data.

Viva voce 15
Records 10

Semester- IV

Student has option to select any four papers out of all elective papers.

Elective Paper I

Organotransition metal chemistry

UNIT- I

A- Alkys and Aryls of Transition metals

Types, routes of synthesis, stability and decomposition pathways, organicopper in organic synthesis

B- Compounds of Transition metal-Carbon Multiple Bonds

Alkyledenes, alkylidynes, low valent carbenes and carbines-synthesis, nature of bond, structural characteristics, nucleophilic and electrophilic reactions on the ligands, role in organic synthesis.

UNIT- II

A- Transition Metal π-Complexes

Transition metal π-complexes with unsaturated organic molecules, alkenes, alkynes, allyldiene, dienyl, arene and trienyl complexes preparations, properties, nature of bonding and structural features, Important reaction relationing to nucleophilic and electrophillic attack on ligands and to organic synthesis.

B- Transition metal compounds with Bonds to Hydrogen

UNIT- III

Homogeneous Catalysis

Stoichiometric reaction for catalysis, homogenous catalytic hydrogenation, Zeigler-Nattapolymerization of olefins, catalytic reaction involving carbon monoxide such as hydrocarbonylation olefin (oxo reaction), oxopalladation reaction, activation of C-H bond.

UNIT- IV

Fluxional Organometallic Compounds

Fluxionality and dynamic equilibria in compounds such as η^2 olefine, η^3-allyl and dienyl complexes.

Books Suggested

1. Principles and application of organotransition Metal Chemistry, J.P. Collman, L.S. Hegsdus, JR Norton and R.G. Finke, University Science books
2. The organomettalic chemistry of transition metals, R. H. Crabtree, John Wiley
3. Metallo-organic Chemistry, A. J. Pearson Wiley
4. Organometallic Chemistry, R. C. Mehrotra and A. Singh, New age International.

Semester- IV

Elective Paper II

Bioinorganic and Supramolecular Chemistry,

UNIT- I

A-Metal Storage Transport and Biomineralization Ferritin, transferrin, and siderophores

B-calcium in Biology

Calcium in living cells, transport and regulation, molecular aspects of' intramolecular processes, extracellular binding proteins.

UNIT- II

Metalloenzymes

Zinc enzymes-caroxypeptidase and carbonic anhydrase, lron enzymes-catalase, peroxidase and cytochrmoe P-450, Copper- enzyrnes-superoxide dismutase, Molybdenum oxatransferaseenzymes-xanthine oxidase, Coenzyme vitamin B12:

UNIT- III

A-Metal-Nucleic Acid Interactions

Metal ion and metal complex interactions, Metal complexes-nucleic acids

B- Metals in Medicine

Metal deficiency and disease, toxic effects of metals, metals for diagnosis and chemotherapy with particular reference to anticancer drugs.

UNIT- IV

supramolccular Chemistry

(A) molecular recognition: Molecular receptors for different types of molecules including arisonic substrates. Design and synthesis of coreceptor molecules and multiple recognition,

(B) Supramolecular reactivity

(C) Transport processes and carrier design

(D) Supramolecular devices: supramolecular photochemistry, supramolecular electronic. ionic and switching devices, Some example of self-assembly in supramolecular chemistry.

Books Suggested

1. Principles' of Bioinorganic Chemistry S J. Lippard and J. M.Borg University Science Books.
2. Bioinorganic Chemistry.T. Bertini. RB. Gray. SJ. Lipbard J.S. Valentine, University Science Books.
3. Inorganic Biochmistry vols lland II. ed. G.T. Eichborn, Eisevier.
4. Progress in Inorganic Chemistry. Vols 18 and 38 ed. J.J. Lipard. Wiley.
5. Supramolecular Chemistry. J. M. Lehn, VCH

Semester- IV
Elective Paper III

Photoinorganic chemistry
UNIT- I

Basics of Photochemistry

Absorption excitation, photochemical laws, quantum yield electronic excited states, life times-measurements of the times flash phoyolysis, stopped flow techniques. Energy dissipation by radiative and non-radiative processes,absorption spectra, Franck -Condon principle, photochemical stages-primary and secondary processes.

UNIT- II

A- Properties of excited states

Structure, dipole moment, acid-base strengths,reactivity.photochemical kkinetics calculation of rates of radiative processes. Biomolecular deactivation-quenching.

B-Excited states of metalcomplexes

Excited states oof metal complexes: comparision with organic compounds, electronically excited states of metal complexes, charge transfer spectra, charge transfer excitations methods for obtaining charge-transfer spectra.

UNIT- III

A- Ligand field photochemistry

Photosubstitution photooxidation and photoreduction,lability and selectivity, zero vibrational levels of ground state and excited state, energy content of excited state, zero, zero spectroscopic energy, Development of the equations for redox potentials of the excited states.

B- Redox reactions by excited metal complexes

Energy transfer under conditions of weak interaction and strong interaction-exciplex formation; conditions of the excited states to be useful as redox reactants, excited electron transfer, metal complexes as attractive candidates (2,2-bipyridine and 1,10-phenanthroline complexes), illustration of reducing and oxidising character of ruthenium $^{+2}$ (bipyridil complex, comparision with Fe $(bipy)_3$ role of spin coupling life time of these complexes. Application of redox processes of low energy reactants into high energy products, chemicalenergy into light.

UNIT- IV

Metal complex sensitizers

Metal complex sensitizer, electron relay, metal colloid systems, semiconductor supported metal or oxide systems, water photolysis nitrogen fixation and carbon dioxide rreduction.

Books suggested

1. Concepts of inorganic photochemistry,A.W.Adamson and P.D.Fleischauer,Wiley.

2. Inorganic photochemistry, J.Chem.Educ. Vol. 60, no, 10,1983

3. Progress in inorganic chemistry, vol, 30. Ed. S.J.Lippard,Wley.

4. Coordination chem. revs. 1981, vol.39, 121, 131:1975,15.321:1990,97313.

5. photochemistry of coordination compounds.V. Balzan and V.Carassiti, academic press.

6. Elements of inorganic photochemistry. G.J.Ferraudi,Wiley.

Semester- IV
Elective Paper IV
Analytical chemistry
UNIT- I

Introduction

Role of analytical chemistry.Classification of analytical methods-classical and instrumental.Types of instrumental analysis,selecting an analytical method.Neatness and cleanliness, laboratory operations and practices,analytical balance. Techniques of weighing,errors.Volumetric glassware-cleaning and calibration of glassware. Sample preperations, dissolution and decompositions.gravimetric techniques. Selecting and handling of reagents.Laboratory notebooks. Safety in the analytical laboratory.

UNIT- II

Errors and evaluation

Definition of terms in meamn and median.Precision-standarddeviation,relativestandard deviation.Accuracy-absolute error,relative error.Types of error in experimental data determinate (systematic), indeterminate(of random) and gross. Sources of errors and the effects upon the analytical results.Methods for reporting analytical data .Statistical evaluation of data-indeterminte errors.the uses of statistics.

UNIT- III

A- Food analysis

Moisture, ash, crude protein,fat,crude fibre,carbohydrates,calcium,potassium,sodium and phosphate.Food adulteration-common adulterants in food,contamination in foodstuffs.Microscopic examination of food for adulterants.Pesticide analysis infood products.Extraction and purification of sample.HPLC,gas chromatography for organophosphates.Thin layer chromatography for identification of chlorinated pesticides in food products.

B-Analysis of water pollution

Origin of waste types water pollutants and effects. Sources of water pollution domestic,industrial,agricultural,soil and radioactive waste as sources of pollution, objectives of analysis-parameter for analysis-colour turbidity total solid conductivity, acidity, alkalinity, hardness, chloride, sulphate, fluoride ,silica, phosphates and different forms of mifrogen.Heavymetal pollution, public health significance of Cadmium, Chromium, copper, lead, zinc, manganese, mercury and arsenic. General survey of instrumental technique for the analysis of heavy metals in aqueous systems. Measurement at Do,BOD,COD.Pesticides as water pollutants and analysis.Water pollution law and standards.

UNIT- IV

Analysis of soil,fuel,body fluids and drugs

(a) Analysis of soil:moisture, pH, total nitrogen, phosphorus, silicon, lime, magnesia, manganese, sulphur and alkali salts.

(b) Fuel analysis: solid,liquid and gas,ultimate and proximate analysis-heating and value grading of coal.Liquid fuels-flash point,aniline point,octane number and carbon residue. Gaseous fuels-producer gas and water gas-calorific value.

(c) Chemical chemistry: Composition of blood collection and preservation of samples. Clinical analysis, serum electrolytes, blood glucose, blood urea, nitrogen, uric acid, albumin, globulins, barbiturates, acid and alkaline phosphatises. Immunoassay: principles of radioimmunoassay (RIA) and applications. The blood gas analysis trace elements in the body.

(d) Drug analysis: Narcotic and dangerous drugs. Screening by gas and thin layer chromatography and (spectrophotometric) measurements.

Books suggested

1. Analytical chemistry, G.D.Christian,J.Wiley.
2. Fundamentals of analytical chemistry,D.A.Skoog,D.M.Westand F.J.Holler,W.B.Saunders.
3. Analytical chemistry principles,J.S.Kennedy,W.B.Saunders.
4. Analytical chemistry principles and techniques, L.G.Hargis,Prentice Hall.
5. Principles of instrumental analysis,D.A.Skoog,J.L.Loary,W.B.Saunders.
6. Principles of instrumental analysis,D.A.Skoog,W.B.Saunders.
7. Quantitative analysis,R.A.DayJrand A.L.Underwood,Prentice Hall.
8. Environmental solution analysis,S.M.Khopkar,Wiley Eastern.
9. Basic concepts of analytical chemistry, S.M.Khopkar,Wiley Eastern.
10. Handbook of instrumental techniques for analytical chemistry,F.Settle,Prentice Hall.

Semester- IV
Paper V
Inorganic Polymers
UNIT- I

Basics

Importance of polymers. Basic concepts: Monomers, repeat units, degree of polymerization. Linear, branched and network polymers, Classification of polymers Polymerization: condensation, addition, radical chain-ionic and co-ordination and copolymerization. Polymerization conditions and polymer reactions. Polymerization in bomogeneous and heterogeneous systems.

UNIT- II

Polymer Characterization

Polydispersion-average molecular weight concept. Number, weight and viscosity average molecular wights. Polydispersity and molecular weight distribution. The practical significance of molecular weight. Measurement of molecular weights. End group, viscocity. light scattering, osmotic and ultracentrifugation methods. Analysis and testing of polymers. Chemical analysis of polymers, spectroscopic methods, X-ray diffraction study. Microscopy. Thermal analysis and physical testing-tensile strength. Fatigue, impact, tear resistance. Hardness and abrasion resistance.

UNIT- III

Structure and Properties

Morphology and order in crystal fine polymers-configurations of polymer chains. Crystal structures of polymers. Morphology of crystalling polymers polymers, strain-induced morphology, crystallization and melting. Polymer structure and physical properties-crystailing melting point Tm-melting points of homogeneous series, effect of chain flexibility and other steric factros, entropy and heat. of fusion. The glas transition temperature, Tg-Relationship between Tm and Tg, Effects of molecular weight, diluents, chemical structure, chain topology, branching and cross linking. Property requirements and polymer utilization.

UNIT- IV

A-Polymer Processing

Plastics, elastomers and fibers Compounding Processing techniques Caledering diecasting, rotational casting film casting injection moulding. blow moulding. extrusion moulding thermolorming, foamian, reinforcing and fibre spinning.

B- Properties of Commerical Polymers

Polyethylene, Polyvinyl chloride polyamides polyesters, phenolic resins. epoxy resins and silicone polymers. Functional polymers, tire retarding polymers and electrically conducting polymers. Biomedical polymers-contact lens, dental polymers, .artificial heart. kindney, skin and blood cells.

Books Suggested

1. Textbook of Polymer Science, F.W. Billmeyer lr. Wiley.
2. Polymer Science, V.R. Gowarker, N.V. Viswanathan and 1 Sreedhar, Wiley-Eastern.
3. Functional Monomers and Polymers. K. Takemoto, Y. Inaki and RM. Rttanbrite.
4. Contemporary Polymer Chamistry, HR. Alcock and F.W. Lambe, Prentice Hall.
5. Physics and Chemistry of Polymer, 1.M.G. Cowie, Blackie Academic and Professional.

Semester- IV
Elective Paper VI

Organic Synthesis-I

UNIT- I

Organometallic reagents

Principles,preperations,properties and applications of the following in organic synthesis with mechanistic details.

A. Group I and II metal organic compounds

Li,Mg,Hg,Cd,Zn compounds.

B. Transition metals

Cu,Pd,Ni,Fe,Co,Ti compounds.

UNIT- II

A-Oxidation

Introduction different oxidative processes.

Hydrocarbons-alkenes,aromatic rings,saturated C-Hgroups (activated and unactivated). Alcohols, diols, aldehydes, ketones, ketals and carboxylic acid.

Amines,hydrazines and sulphides.

Oxidation with ruthenium tetraoxide, iodobenzene diacetate and thallium(III) nitrate.

B- Reduction

Introduction,different reductive processes.

Hydocarbons-alkanes,alkynes and aromatic rings.

Carbonyl compound-aldehydes ,ketones, acids and their derivates.Epoxides.

Nitro, nitroso,azo and oxime groups. Hydrogenolysis.

UNIT- III

Rearrangements

General mechanistic consideration: nature of migration, migratory aptitude,memory effects.

A detailed study of the following rearrangements

Pinacol-pinacolone, wagner-meerwein, Demjanov, Benzil-Benzilic acid, Favorskii, Aarndt-Eistert synthesis, Neber, Beckmann, Curtius, Schmidt,Baeyer-Villiger, Shapiro reaction.

UNIT- IV

Metallocenes, Nonbenzenoid Aromatic and polycyclic aromatic compound

General consideration, synthesis and reactions of some representative compounds.

Books suggested

1. Modern synthetic reactions,H.O.House, W.A.Benjamin.
2.Some modern methods of organic synthesis, W.Carruthers, Cambridge Univ. Press.
3.Advanced organic chemistry, reactions mechanisms and structure,J.March, John Wiley.
4. Principles of organic synthesis, R.O.C. Norman and J.M.Coxon, Blackie academic and professional.
5. Advanced organic chemistry part B, F.A.Carey and R.J.Sundherg.Plenum Press.
6. Rodd's chemistry of carbon compounds, Ed.S.Coffey Elevier.

Semester- IV

Elective Paper VII

Organic Synthesis II

UNIT- I

Disconnection approach

An introduction to synthons and synthetic equivalents,disconnection approach, functional group interconversions, the importance of the order of events in organic synthesis, one group C-X and two group C-X disconnections,chemoselectivity,reversal of polarity, cyclisation reactions, amine synthesis.

UNIT- II

A-Protecting groups

Principle of progenction of alcohols, amine, carbonyl andcarboxyl groups.

B-one group C-C disconnections

Alcohols and carbonyl compounds, regioselectivity. Alkene synthesis, use of acetylenes and aliphatic nitro compounds in organic synthesis.

UNIT- III

Two group C-C disconnections

Diels-Alder reaction, 1,3-disfunctionalised compounds, αβ unsaturated carbonyl compounds, control in carbonyl condensations, 1,5-disfunctionalised compound. Michael addition and robinson annelation.

UNIT- IV

Ring synthesis

Saturated heterocycles, synthesis of 3,4,5 and 6 memebered rings, aromatic heterocycles in organic synthesis.

Synthesis of some complex molecules

Application of the above in the synthesis of following compounds:camphor, longifoline, cortisone, reserpine, vitamin D juvabione, aphidicolin and ffredericamycin A.

Books suggested

1. Designing organic synthesis, S.Warren,Wiley.
2. Organic synthesis-concept, methods and starting mmaterials , J.Fuhrhop and G.Penzillin, verlage VCH.
3. Some modern methods of organic synthesis , W.Carruthers, Cambridge Univ. Press.
4. Modern synthetic reactions, H.O.House, W.A.Benjamin.
5. Advanced organic chemistry: reactions mechanism and structure, J.March, Wiley.
6. Principles of organic synthesis,R.Norman, J.M.Coxon, Blackie academic and professional.
7. Advanced organic chemistry part B. F.A.Carey and R.J.Sundherg, Plenum press.

Semester- IV
Elective Paper VIII
Heterocyclic chemistry
UNIT- I

A- Nomenclature of Heterocycles

Replacement and systematic nomenclature (Hantzsch Widman system) for monocyclic, fused and bridged heterocycles.

B- Aromatic heterocycles

General chemical behavior of aromatic heterocycles, classification (Structural type), criteria of aromaticity (bond lengths ring current and chemical shifts in 1H-NMR- spectra. Empirical resonance energy) resonance energy, delocalization energy and deqar resonance energy, diamagnetic susceptibility exaltations). Heteroaromatic reactivity and tautomerism in aromatic heterocycles.

C-Non-aromatic Heterocycles

Strain bond angle and torsional strains and their consequence in small ring heterocycles.

Conformation of six- membered heterocycles with reference to molecular geometry, barrier to ring inversion, pyramidal inversion and 1,3- diaxial interaction. Stereo-electronic effects-anomeric and related effects. Attractive interactions-hydrogen bonding and intermolecular nucleophillic interactions.

UNIT- II

A- Heterocyclic Synthesis

Principles of heterocyclic synthesis, cyclization reactions and cycloaddition reactions.

B- Small Ring Heterocycles

Three membered and four membered heterocycles-synthesis and reaction of aziridine, oxiranes. Thiranes, azetidines, oxetanes and thietanes.

UNIT- III

A- Benzo-Fused Five-membered Heterocycles

Synthesis and reactions including medicinal application of benzopyrroles, benzofurans and benzothiophenes.

B- Meso-ionic Heterocycles

General classification, chemistry of some important mesoionic heterocycles of type A and B and their applications.

C- Six-membered Heterocycles with one Heteroatoms

Synthesis and reaction of pyrylium salts and pyrones and their comparison with pyridinium and thiopyrylium salts and pyridines.

Synthesis and reactions of quinolizinium and benzpyrinium salts, coumarins and chromones.

UNIT- IV

A- Six-membered Heterocycles with two or more Heteroatoms

Synthesis and reaction of diazines, triazines and thiazines.

B- Seven-and large –Membered Heterocycles

Synthesis and reaction of azepines, oxepines, thiepines, diazepines, thiazepines, azocine, diazocines, dioxocines and dithiocines.

Books Suggested

1. "Heterocyclic Chemistry" Vol, 1-3 R.R. Gupta, M.Kumar and V. Gupta, Springer, Verlag
2. The Chemistry of Heterocycles, T. Eicher and S. Hauptmann, Thieme.
3. Heterocyclic chemistry, J.A. Joule, K. Mills and G.F.Smith, Chapman and Hall.
4. Heterocyclic chemistry, T.L. Gilchrist, Longmane Scientific Technical.
5. Contermporary Heterocyclic chemistry. G.R. Newkome and W.W. Poaudler, Wiley-Inter Science.
6. An Introduction to the Heterocyclic Compounds, R.M. Acheson, John Wiley.
7. Comprehensive Heterocyclic Chemistry, A. R. Katritzky and C.W. rees. Eds. Pergamon Press.

Semester- IV
Elective Paper IX
Chemistry of Natural products
UNIT- I

Trapezoids and Carotenoids

Classification, nomenclature, occurrence, isolation, general methods of structure determination, isoprene rule. Structure determination stereochemistry, biosynthesis and synthesis of the following representative molecules: Citral Geranoil, α-terpeneol, Menthol, farnesol, Ziniberene, Santonin, Phytol, Abietic acid and β-Carotene.

UNIT- II

A- Alkaloids

Definition, nomenclature and physiological action, occurrence, isolation, general methods of structure elucidation, degradation,classification based on nitrogen heterocyclic ring role of alkaloids in plants.Structure, stereochemistry, synthesis and biosynthesis of the following : ephedrine, (+)-Conline, Nicotine, Atropine, Quinine and morphine.

B- Steroids

Ocurrence, nomenclature, basic skeleton, Diel's hydrocarbon and stereochemistry.

Isolation, structure determination and synthesis of Cholestrol, Bile acids, Androsterone, Testosterone, Estrone, Progestorne, Aldosterone, Biosynthesis of steroids.

UNIT- III

A- Plant Pigments

Ocurrence, nomenclature and general methods of structure determination, Isolation and synthesis of Apigenin, Luteolin, quercetin, myrcetin, Quercetine 3-glucoside, Vitexi Diadzein, Butein, Aureusin, Cyanidin-7-arabinoside, acid pathway.

B- Porphyrins

Structure and synthesis of Haemohlobin and Chlorophyll.

UNIT- IV

A- Prostaglandins

Ocurrence, nomenclature, classification, biogenesis and physiological effects, Synthesis of PGE_2 and $PGF_{2\alpha}$

B- Pyrethroids and Rotenones

Synthesis and reaction of Pyrethroids and Rotenones (For structure elucidation, emphasis is to be placed on the use of spectral parameters wherever possible).

Books Suggested

1. Natural Products: Chemistry and Biological Significance,
2. Mannm R.S. Davidson, J.B. Hobbs, D.V. Banthrope and 1.B. Harbome, Longman, Essex.
3. Organic Chemistry, Vol-2, I.L. Finar, ELBS
4. Stereos elective Synthesis: A Practical Approach, M. Nogradi, VCH.
5. Rodd's' Chemistry of Carbon Compounds, Ed. S. Coffey, Elsevier.
6. Chemistry, Biological and Pharmacological Properties of Medicinal Plants from the Americas, Ed Kurt hostettmann, M.P. Gupta and A. Marston, Harwood Academic Publishers.
7. Introduction of Flavonoids, B.A. Bohm, Harwood Academic Publishers.
8. New Trends in Natural Product Chemistry, .Atta-ur-Rahaman and M.I. Choudhary, Harwood Academic Pubhshers.
9. Insectcides of Natural Origin, Sukh Dev, Harwood Academic Publishers.

Semester- IV
Elective Paper IX
Medicinal Chemistry

UNIT- I

A- Drug design :
Relationship between Chemical structure and biological activity (SAR). Receptor site theory approach to drug design. Introduction to combinatorial synthesis in drug discovery.

B- Phormacokinetics:
Introduction of drug absorption, desorption, eliminationusing pharmacokinetics, important pharmacokinetics parameters in detining drug disposition and in therapeutics. Mention of uses of pharmacokinetics in drug development process.

UNIT- II

A- Antineoplastic Agents:
Introduction, cancer chemotherapy, role of alkylating agents and antimetabolites in treatment of cancer. Synthesis of mechlorethamine, cyclophosphamide, melphan, mechalorethamine, cyclophosphamide melphalan, uracil, mustards, and 6- mercaptopurine.di

B- Cardiovascular Drug:
Introduction, cardiovascular diseases, drug inhibitors of peripheral sympathetic function central intervenation of cardiovascular output. Directacting arteriolar dialators. Synthesis of amyl nitrate sorbitrate, deltizem, quitridine, veramil and atenolal.

UNIT- III

A- Local Antiinfective Drugs:
Introduction and general mode of action. Synthesis of sulphonamides, turatolidone, ciprofloxacin, norfloxacin, dopone, aminosasalicylic acid, isoniazid, ethionamid, thambutal, fluconatole, ariseofulvin, chlorogenin, primaqion.

B- Psychoactive Drugs- The Chemotherapy of mind
Introduction, neurotransmitters, CNS depresseant, general anaesthetics, mode of action of hypnotics, sedatives, antianxiety drugs, Antipsychotic drugs- the neuroleptics, antidepressant, butyrophenones, serendipity and drug development. Synthesis of diatepam, oxatepam, chloratepam, alpratalam, phenyloin 2 barbiturates.

UNIT- IV

Antibiotics:
Cellwall biosynthesis inhibitors, β-lactam rings antibiotics inhibiting protein synthesis, synthesis of penicillin, chloramphenicol, cephalosponin and streptomycin.

Books Suggested

1. Introduction to Medical Chemistry, A. Gringuage, Wiley-VCH.
2. Wilson and Gisvold's Text Book of Organic Medicinal and Pharmaceutical Chemistry. Ed. Robert F. dorge
3. An Introduction to Drug Design, S.S. Pandeya and J.R. Dimmock, New Age International.
4. Burger's Medicinal Chemistry and Drug Discovery, Vol-I (Chapter-9 and Ch-14) Ed.M.E. Wolff, John wiley.
5. Goodman and Gilman's Pharmacological Basis of Therapeutics, Mc Graw-Hill.
6. The Organic Chemistry of Drug Design and Drug Action, R.B. Silverrnanm, Academic Press.
7. Strategies for Organic Drug Synthesis and Design. D. Lednicer, John Wiley.

Semester- IV
Elective Paper XI
Physical Organic Chemistry
UNIT- I

Concepts in Molecular Orbital (MO) and Valence bond (VB) Theory

Introduction. to Huckel molecular orbital (MO) method as means to explain modem theoretical methods. Advanced techniques in PMO and FMO theory. Molecular mechanics. semiempirial methods and *ab into* and density fictional methods. Scope and limitation of several computational programmes. Quantitative MO theory-Huckel molecular orbital (HMO) method as applied to ethene, allyl and butadiene. Qualitative MO theory-ionisation potential. Electron affinities MO energy levels. Orbital symmetry. Orbital interaction diagrams. MO of simple organic systems such as ethene, allyl, butadiene, methane and methyl group. Conjugation and hyperconjugation. Aromaticity. Valance bond (VB) configuration mxing diagrams. Relationship between VB confiuration mixing and resonance theory. Reaction profiles. potential energy diagrams. Curve crossing model- nature of activation barrier in chemical reactions.

UNIT- II

A- Principles of Reactivity

mechanistic significane of. entropy, enthaply and Gibb's free energy. Arthenius equation Transition state theroy. Uses of activation parameters, Hammonod's postulate. Bell-Evans Polanyi principle. Potential energy surface model. Marcus theory of electron transfer. Reactivity and selectivity principles.

B- Kinetic Isotope Effect

Theory of isotope effects Primary and secondary kinetic isotope effects. Heavy atom isotope effects. Tunneling effect. Solvent effects.

C- Structural Effects on Reactivity

Linear free energy relationships (LFER). The Hammelt equation, substituent constants, theories of substituent effects. Interpretation of p-values. Reaction ponstant p-Deviations from Harnmelt equation. Dual-parameter correlations, inductive subsituent constant. The Taft model σ_1 and σ_R scales

UNIT- III

A- Solvation and Solvent Effects

Qualitative understanding of solvent-solute effects on reactivity. Theromodynamic measure of solvation. Effects of solvation on reaction rates and equilibria. Various emprirical indexes of solvation based on physical properties, solventsensitve reaction rate, spectroscopic properties and scales for specific solvation. Use of solvation scales in mechanistic studies Solvent effects from the curve-crossing model.

B- Acids, Bases, Electrophiles, Nuclephiles and Catalysis

Acid-base dissociation. Electronic and structural effects, acidity and basicity. Acidity functions and their applications. Hard and soft acids and bases. Nucleophi1city scales Nucleofugacity. The α-effect. Ambivalent nucleophiles. Acid base catalysis-specific and general catalysis. Bronsted catalysis. Nucleophilic and electrophilic catalysis by non-covalent binding-micellar catalysis.

C- Steric and Conformational Properties

Various type of steric strain and their influence on reactrvrty. Steric acceleration. Molecular measurements of steric effects upon rate. Steric LFER. Conformational barrier to bond rotation-spectroscopic detection of individual confonners. Acylic and monocyclic systems. Rotation around partial double bonds. Winstein-Holness and Curtin-Hammett principle.

D- Nucleophilic and Electrophilic Reactivity

Structural and electronics effects on SNI and S_N2 reactivrty. Solvent effects. Kinetic isotope effects Intramolecular assistance. Electron transfer nature of SN reaction. Nucleophilicity and S_N2 reactivity based on curve crossing model. Relationship between polar and electron transfer reactions. SRN I mechanism. Electrophilic reactivity, general mechanism. Kinetic of S_E2-Ar reaction. Structural effects on rate and selectivity. Curvecrossing approach to electrophilic reactivity.

UNIT- IV

A- Radical and Pericvclic Reactivitv

Redical stability, polar influence, solvent and steric effects. A curve crossing apprach to radical; addition, factors effecting barrier heights in additions, regioselectivity in radical reactions. Reactivity, specificity and periselectivity in pericyclic reactions.

B- Supramolecular Chemistry

Properties of covalent bonds-bond length, inter-bond angles, force constant, bond and molecular dipole moments. Molecular and bond polarizability, bond dissociation enthalpy, entropy. Intermolecular forces hydrophonic effects. Electrostatic, induction, dispersion and resonance energy, magnetic interactions, magnitude of interaction energy, forces between macroscopic bodies, medium effects, Hydrogen bond. Principles of molecular association and organisation as exemplified in biological macromolecules like enzymes, nucleic acids, membranes and model systems like micelles and vesicies. Molecular respector and design principles. Supramolecular reactivity and catalysis. Molecular channels and transport processes. Molecular devices and nanotechnology.

Books Suggested

1. Molecular Mechanics, U.B. Burkert and N.L. Allinger, ACS Monograph 177, 1982.
2. Organic Chemists Book of Orbitals, L. Salem and W.L. Jorgensen, Academic Press.
3. Mechanism and theory in Organic Chemistry, T.H. Lowry and KC. Richardson, Harper and Row.
4. Introduction to Theoretical Organic Chemistry and Molecular Modeling, W.B. Smith, VCH, Weinheim
5. Physical Organic Chemistry, N.S. Isaacs, ELBS.Longman.
6. Supermolecular Chemistry: Concept and perspectives, J.M. lehn, VCH
7. The Physical Basis of Organic Chemistry, H. Maskill, Oxford University press.

Semester- IV
Elective Paper XII
Chemistry of Materials
UNIT- I

A- Multiphase Materials

Ferrous alloys: Fe-C phase transformation in ferrous alloys: stainless steels, non-ferrous alloys, properties of ferrous and non-ferrous alloys and their applications.

B- Glasses, Ceramics, Composites and nanomaterials

Glassy state, glass formers and glass modifiers, applications. Ceramic structures, mechanical properties, clay products. Refractories, characterizations, properties and application. Microscoipc composites; dispersion-strengthened and particle- reinforces, fibre-reinforced composites, macroscoipc composite. Nanocrystalling phase, preparation procedures, special properties. aplications.

C- Thin films and Langmuir-Blodgett Films

Preparation techniques; evaporation/sputtering. chemical processes, MOCVD, sol-get etc.Langmuir-Blodgett (LB) film, growth techniques, photolithography, properties and applications of thin and LB lilms.

UNIT- II

A- Liguid Crystals

mesmorphic behaviour, thermotropic liquid crystals, positional order, bond orientational order, nematic and smectic mesophases; smectic-nematic transtion and clearing ternperature-horneotropic, planar and schlieren textures, twisted nematics, chiral nemations, molecular arrangement in smectic A and smectic C phases, optical properties of liquid crystals.Dielectric susceptidility and dielectric comstants. Lyotropic phases and their description of ordering in liquid crystais.

B- Polymeric Materials

Molecular shape, structure and configuration, crystallinity, and their applications. conducting and ferro-electric polymers.

UNIT- III

A- Ionic Conductors

Types of ionic conductors. mechanism of ionic conduction, interstitial jumps (Frenkel).vacancy mechanism. diffusion superiohic conductors. phase teransitions andmechanism of conduction in superionic conductors examples and applications of ionic conductors

B- High Tc Materials

Defect perovskites, high Tc superconductivity in cuprates, preparation and characterization of 1-2-3 and 2-1-4 materials, normal state properties; anisotropy; anisotropy; temperature dependence of electrical resistance; optical phonon modes, supenerconducting state; heat capacity; coherence length, elastic constants, position lifetimes, microwave absorption-pairing and multigap structure· in high Tc materials applications of hich tc materials.

UNIT- IV

A- Materials for solid State Devices

Rectifiers, transistors, capacitors-IV - V compounds, low- dimensional quantum structures; optical properties.

B- Organic Solids. Fullerenes. Molecular Devices:

Conducting organics, organic superconductors, magnetism in organic materials. Fullerenes-doped, fullerenes as superconductors. Molecular rectifiers and transistros, articicial photosynthetic devices. optical storage memory and switces-sensors. Nonlinear optical materials: nonlinear optical effects. second and third order-molecular hyperpolarisability and second order electric susceptibility-materials for second and third harmonic generation.

Books Suggested

1. Solid State Physics, N.W. Ashcroft and N.D. Mermin Saunders College.
2. Material Science and Engineering. An Introduction. ·W.D. Callister. Wiley.
3. Principles of the Solid State, H.v. Keer. Wiley Eastern.
4. Materials Science, J.e. Anderson, K.D. Leaver, J.M. Alexander and R.D. Rawlings, ELBS
5. Thermotropic Liquid Crystalsm Ed. G.W. Gray. John Wiley.
6. Handbook of Liquid Crystals. Kelker and Hafz. Chemie Verlag.

Semester- IV

Elective Paper XIII

Computational Chemistry

UNIT- I: Fortran/C prograrnming and Numerical methods

Advanced programming features of FORTRAN/e. Basic theory. discusion of algorithms and errors for the following mumerical methods. Examples from chemistry shoud select ANY THREE of the following subtopics considering the background of students, available time etc.

a.Solution of Equations

Bisection, regular falsi, Newton-Raphson and related methods for solving polynomial and transcendental equations. Convergence. Errors and ill conditioning.

b.Linear simultaneous Equations

Gaussian elimination, Gauss- Seidel method. Gauss- jordan method. Pivoting strategy. Errors and ill conditioning.

c.Eigenvalues and Matrix Diagonalization , Jacobi and Householder methods, analysis or errors.

d. Interpolation

Newton forward and backward difference, central differenced formulae. Lagrange and Harmite interpolation. Polyomial wiggle problem.

e. Numerical Differentiation

Solution of simple differential equations by Tayior series and Runge-Kutta methods.

f. Numerical Integration

Newton-Cotes formulae, Romberg integration errors in integration formulae.

The students should develop computer programs for some of the above numerical methods.

UNIT- II: Running of Advanced Scientific packages

The students are expected to get hands or expenence of running a few selected advanced level scientific software packages after a brief introduction to the basic theory and methodology. ad intio quantum chemical packages such as GAUSSIAN/GAMES with carefull designed exercises for illustrating various features of the packages Semlempircal/Dynamica/Simulation packages such as MOPAC, CHARM. AMBER. QUANTA etc. Basic ideas on structure activity relation. drug and catalysis design etc. '

UNIT- III: Introduction to Networking and Search using Internet

UNIT- IV: Project

The students will develop utilities such as analysis of spectra, simulation programmes which will supplement laboratory or theory exercises in physical, organic, inorganic chemistry or biochemistry. The list is only indicative and a variety of small projects designed by the teacher based on the interest of the student and capabilities should be worked out.

Books Suggested

1. Computational Chemistry, A.c. Norris, John Wiley.

1.Computer Programming in FORTRAN 77. R. Rajaraman. Prentice Hall. .

2.NumericalAnalysis-APractical Approach. M.J. Maron. John Wiley.

3.Numerical Methods for Scientists and Engineers. H.M. Antra. Tata Mc Graw Hill.

Semester- IV

Elective Paper XIV

Advanced Quantum Chemistry

(Pre-requisite; Mathematics at least up to 'First Year B.Sc. level is necessary. At least one PC among 4 students should be available)

UNIT- I

A-Theoretical and Computational Treatment of Atoms and Molecules. Hartree-Fock Theorv

Review of the principles of quantum mechanica, Born Oppenheimer approximation. Slater-Condon Rules, Hartee-Fock equation, Koopmans and Brillouin theories, Roothan equation, Gaussian basis sets.

B- Configuration Interaction and MC-SCF

Introduction to CI, full and truncated Cl theories, size consistency. Introductiory treatment of coupled cluster and MC- SCF methods.

UNIT- II

Semi-Emprical Theories

A review of the Huckel, EHT and PPP treatments, ZDO approximation, detailed treatment of CNDO and INDO theories. A discussion of elecftronic energies and properties. An introduction toMOPAC and AMI with hands on experience on personal computer.

UNIT- III

Density Functional Theory

Derivation of Hohenberg-Kohn theorem, Kohn-Shamformulation, N-and V-representabilites; review of the performance of the existing local (e.g. Slater Xa and other methods) and non-local functionals, treatment of chemical concepts with the density functional theory.

UNIT- IV

Computer Experiment

Computer experiments using quantum chemistry-software packages such as *GAUSSIAN/GAMESS/MOPAC* and modelling software e.g. *MM21* AMBER/CHARM etc.

Books Suggested

1. Modern quantum Chemistry, N.s. Ostlund and A. Szabo, McGraw Hill.
2. Methods of Molecular Quantum Mechanics R. McWeeny and B.T. Sutclifffe. Academic Press.
3. Density Functional Theory **O'** Atoms and Molecules R.G. Parr and W. Yang. Oxford
4. Explorng Chemistry with Electron Structure Methods. 18. Foresman and E. Frish. Goussian Inc.
5. Semi-empirical MO theory. J. Pople and D.L. Beveridge.

Semester- IV

Elective Paper XV

Liquid State

UNIT- I

General Properties of Liquids

a. Liquids as dense gases, liquids as disordered solids, some thermodynamic relations, internal pressure and its significance in liquids, Equations of state, critical constants. Different types of intermolecular forces in liquids, different potential functions for liquids, additively of pair potential approximation.

b. A classical, partition function for liquids, correspondence principle, configuration integral, configuration properties.

UNIT- II

Theory of Liquids

Theory of liquids, partition function method of model approach; single cell moders, communal energy and entropy L TD moder, significant structure modern.

UNIT- III

A- pistribution Function and related Equations

Redial distribution function method, equation of state in terms of RDF. Molecular distribution functions, pair distribution function. Relationship between pair distribution function and pair potential function. The IBG equation, the HNC equation, the PY equation, cluster expansion.

B- Methods for Structure Determination and Computational techniques

Spectroscopic techniques for liquid dynamic structure studies, Neutron and X-ray scattering spectroscopy, Computation Techniques-Monte Carlo and molecular dynamics methods.

UNIT- IV

Supercooled and Ionic Liquids

Supercooled and ionic liquids, theories of transport properties; non Arrhenius behaviour of transport properties, Cohen Turnbull free volume moder configurational entroopy moder, Macedo- Litovitz hybrid moder, glass transition in supercooled liquids.

Books Suggested

I. An Introduction to Liquid State, P.A. Egelstaff. Academic press.

2. The Dynamic Liquid State, A.F.M. Barton, Longman.

3. Introduction to Statistical ThemlOdynamics, T.L. Hill, Addision Wiley.

4. The Liquid State, J.A. Pryde. SigniIicant Liquid Stmctures. H. Eyring and M.S. John.

Semester-IV

Practicals (100)

Inorganic Chemistry (25)

Any two of

(A) Spectrophotometric Determination

a- Manganess/chromiumlvanadium in steel sample.

b- Nickel/molybdenum/tungsten/vanadium/uranium by extractive spectrophotometric method.

c-Fluoride/nitrate/phosphate

d- lron-phenanthroline complex: job Method.

(B) **Flame Photometric Determinations**:

a- Sodium and Patassium when Present together

b- Lithiuin/caicium/Barium/Strontium

c- Cadmium and Magnesium in tap water.

Organic Chemistry (25)

(A) Multi Step Synthesis of organic Compounds

Preparation of organic compounds involving not more than three stages.

i) Benzanilide from Benzene

ii) Benzilic acid from Benzoin

iii) Quinoline from Aniline

iv) 2-phenylindole from phenyl hydrazine.

V) Alkylation of diethyl malonate with an alkyl halide.

(B) Paper Chromatogaphy

Separation and identification of the sugars present in the given mixture of glucose, fructose and sucrose by paper chromatography and determination of R, values. Identification of organic compounds on the basis of given spectral data (UV, IR, PMR, CMR and MS)

Physical Chemistry (25)

(A) Polorography

i- Estimation of Pb^{2+} and Cd^{2+}/Zn^{2+} and Ni^{2+} ions in a mixture of Pb^{2+} and $Cd^{2}+/Zn^{2}+$ and Ni^{2+} by polarography. Determination of dissolved oxygen in aqueous solution of organic solvents.

(B) E.M.F. Measurement

i- Determination of the equlibrium constant of the reaction

$H_2Q + 2\ Ag^{+} \quad \leftrightarrow \quad Q+2W+2Ag$

(Hydro quinone) (Quinhydrone)

ii-Determination of activity coefficient of electrolytes.

iii-Potentiometric titration of a solution of $Fe^{2}+$ against Cr_2O_7 and the determination of the redox potential of $Fe^{2+} \leftrightarrow Fe^{3+}$ system.

iv) Determination of ionic product of water (K_c)

Viva vice	15
Records	10

Book Suggested

1. Inorganic Experiments. 1. Derek Woolline VCH
2. Microscale Inorganic Chemistry, Z Szafrsn R.M. Pike, M.M. Singh. Wiley.
3. Practical Inorganic Chemistry, G. Mar and B.W. Bookett. Van Nostrand.