



ADIKAVI NANNAYA UNIVERSITY
FIRST SEMESTER CHEMISTRY SYLLABUS
(Common for M.Sc Analytical, Physical & Organic Chemistry)
(With effect from 2016-17 admitted batch)

General Chemistry - I

UNIT-1

Basic Quantum Chemistry-I- Wave equation-interpretation of wave function-properties of wave function-normalization and orthogonalisation, Operators- linear and non-linear- commutators of operators. Postulates of quantum mechanics; setting up of operators to observables; Hermitian operator- Eigen values and Eigen functions of Hermitian operator; Expansion theorems. Eigen functions of commuting operators-significance. Simultaneous measurement of properties and the uncertainty principle.

UNIT-II

Basic Quantum Chemistry-II- Wave mechanics of simple systems with constant potential energy, particle in one-dimensional box- factors influencing color transition- dipole integral, Symmetry arguments in deriving the selection rules, the concept of tunneling- particle in three -dimensional box. Calculations using wave functions of the particle in a box- Orthogonality, measurability of energy, position and momentum, average values and probabilities. Rigid rotor, Wave mechanics of systems with variable potential energy-simple harmonic oscillator- solution of wave equation- selection rules.

UNIT-III

Fundamentals of Molecular Spectroscopy-I: Microwave and IR- Spectroscopy- Rotational spectra of diatomic molecules- Rigid rotor-Selection rules- Calculations of bond length- Isotopic effect, Second order stark effect and its applications. Infrared spectra of diatomic molecules- harmonic and anharmonic oscillators- Selection rules- Overtones- Combination bands- Calculation of force constant, anharmonicity constant and zero point energy. Fermi resonance, simultaneous vibrational-rotational spectra of diatomic molecules.

UNIT- IV

Fundamentals of Molecular Spectroscopy-II: Raman and Electronic Spectra- Classical and quantum mechanical explanations- Rotational Raman and Vibrational Raman spectra. Electronic spectra of diatomic molecules- Vibrational Coarse structure- intensities of spectral lines- Franck-Condon principle- applications, Rotational Fine structure- band head and band shading. Charge transfer spectra

References/ Text books

1. Fundamentals of Molecular spectroscopy: by C.N. Banwell
2. Molecular spectroscopy: by B.K.Sharma
3. Molecular spectroscopy: by Aruldas
4. Introductory quantum mechanics: by A.K. Chandra
5. Quantum chemistry: by R.K. Prasad



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Paper- II: INORGANIC CHEMISTRY-I

UNIT-1

Structure & Bonding: Applications of VSEPR, Valence Bond and Molecular orbital theories in explaining the structures of simple molecules- role of p and d orbitals in pi bonding. Application of MO theory to square planar (PtCl_4^{2-}) and Octahedral complexes (CoF_6^{3-} , $\text{Co}(\text{NH}_3)_6^{3+}$). Walsh diagram for H_2O molecule.

UNIT-II

Inorganic cage and ring compounds – preparation, structure and reactions of boranes, carboranes, metallocarboranes, boron–nitrogen ($\text{H}_3\text{B}_3\text{N}_3\text{H}_3$), phosphorus–nitrogen ($\text{N}_3\text{P}_3\text{Cl}_6$) and sulphur-nitrogen (S_4N_4 , $(\text{SN})_x$) cyclic compounds. Electron counting in boranes – Wades rules (Polyhedral skeletal electron pair theory). Isopoly and heteropoly acids.

UNIT-III

Coordination compounds: Crystal field theory - crystal field splitting patterns in octahedral, tetrahedral, tetragonal, square planar, square pyramidal and trigonal bipyramidal geometries. Calculation of crystal field stabilization energies. Factors affecting crystal field splitting energies – Spectrochemical series – Jahn – Teller effect, nephelauxetic effect – ligand field theory. Term symbols – Russell – Sanders coupling – derivation of term symbols for various configurations. Spectroscopic ground states.

UNIT- IV

Electronic spectra of transition metal complexes: Selection rules, break down of selection rules – Orgel and Tanabe-Sugano diagrams for d^1 – d^9 octahedral and tetrahedral transition metal complexes of 3d series – Calculation of Dq , B and β parameters. Charge transfer spectra. Magnetic properties of transition and inner transition metal complexes – spin and orbital moments – quenching of orbital momentum by crystal fields in complexes.

Text books:

1. Advanced Inorganic Chemistry by F.A. Cotton and G. Wilkinson, IV Edition, John Wiley and Sons, New York, 1980.
2. Inorganic Chemistry by J.E. Huheey, III Edition, Harper International Edition, 1983.
3. Theoretical Inorganic Chemistry, II Edition by M.C. Day and J. Selbin, Affiliated East-West press pvt. Ltd., New Delhi.
4. Inorganic Chemistry by Shriver and Atkins, Oxford University Press (1999).



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Paper –III: ORGANIC CHEMISTRY -I

UNIT – I

Nature of bonding in organic molecules and Aromaticity

15 Hrs

(A) *Electronic Effects and Reactive intermediates*:-Inductive effect, Mesomeric effect (Resonance), Hyperconjugation, Steric effect, Tautomerism, acidity and basicity of organic molecules Generation, structure, stability and reactivity of carbocations, carbanions, free radicals, carbenes, nitrenes and arynes

(B) *Criteria of Aromaticity*:-The Energy, Structural and Electronic Criteria for Aromaticity, Relationship among the Energetic, Structural, and Electronic Criteria of Aromaticity. Huckle's rule and MO Theory, aromaticity in benzenoid non-benzenoid compounds, Aromaticity in Charged and Fused-Ring Systems, Hetero-aromatic Systems, Annulenes: Cyclobutadiene, Benzene, 1,3,5,7-Cyclooctatetraene, [10] Annulenes- [12], [14], [16] and [18] annulenes, azulenes, fulvenes, fullerenes, ferrocene, anti-aromaticity and homo-aromaticity.

UNIT – II

Stereo Chemistry & Molecular representation of organic molecules

20 Hrs

(A) *Molecular Symmetry and Chirality*:-Symmetry elements, Definition and classification of Stereoisomers, Enantiomer, Diastereomer, Invertomer, Homomer, Epimer, Anomer, Configuration and Conformation Configurational nomenclature: D,L and R, S nomenclature, Molecules with a single chiral center: Tetra and Tri coordinate chiral center, Molecules with two or more chiral centers; constitutionally unsymmetrical and symmetrical molecules.

(B) *Geometrical Isomerism and Conformations of Cyclic Systems*:- Cis-trans, E, Z- and Syn & anti nomenclature, Methods of determining configuration of Geometrical isomers using physical, spectral and chemical methods, Stability, Cis-trans inter conversion. Conformations of cyclobutane, cyclopentane, cyclohexane, mono and disubstituted cyclohexanes.

(C) *Prochirality and Prostereoisomerism*:- Homotopic ligands and faces; enantiotopic ligands and faces; diastereotopic ligands and faces; nomenclature of enantiotopic ligands and faces (Pro-R, Pro-S, Re, Si carbonyl compounds and Alkenes)

(D) *Stereoisomerism in molecules without chiral Center* -Axial chirality Allenes, Alkylidene cycloalkanes, spiranes, nomenclature. *Atropisomerism*: Biphenyl derivatives, nomenclature. *Planar chirality*: Ansa compounds, paracyclophanes, trans-cyclooctene and Helicity.

UNIT – III

Heterocyclic compounds

15 Hrs

Importance of heterocyclic compounds as drugs. Nomenclature of heterocyclic systems based on ring size, number and nature of hetero atoms. Chemistry of heterocyclic compounds, synthesis and reactivity of the following systems: Quinoline, Isoquinoline, Indole, Pyrazole, Imidazole, Oxazole, Isoxazole, Pyridazine, pyrimidine and Pyrazine.

UNIT - IV

Chemistry of some typical natural products (Alkaloids and Terpenoids)

10 Hrs

A study of the following compounds involving their isolation, structure elucidation, synthesis and biogenesis of *Alkaloids*; Atropine, Nicotine, and Quinine.

Terpenoids: α - Terpineol, α -Pinene and Camphor.



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Books Suggested:

1. Advanced Organic Chemistry-Reactions, Mechanism and structure, Jerry March, 6th Ed. (John Wiley & Sons).
2. Organic Chemistry, Paula Yurkanis Bruice, 4th Ed. (Printice Hall)
3. Organic chemistry-Clayden J. (Oxford)
4. Organic Chemsitry, Wade, L.G. Jr. 5th Ed. (Pearson)
5. Advanced Organic Chemistry: Reactions and mechanisms, Miller Bernard & Other, 2nd Ed. (Pearson)
6. Mechanism and Theory in Organic Chemistry, Thomas H. Lowry, Kathleen S. Richardson, Harper & Row, (Publishers, Inc.).
7. A Guide Book to Mechanism in Organic Chemistry, Peter Sykes, 6th Ed., (Longman).
8. Reaction Mechanism in Organic Chemistry, P.S. Kalsi, 2nd Ed. (New Age International).
9. Organic Chemistry, R. T. Morrison and R. N. Boyd (Prentice-Hall)
10. Stereochemistry to Organic Compounds, E.L. Eliel (John Wiley).
11. Stereochemistry, P.S. Kalsi, 5th Ed. (New Age International).
12. Organic Chemistry Structure and Reactivity, Ege Seyhan, 3rd Ed. (AITBS)
13. Heterocyclic Chemistry, J.A.Joule, K. Kills and G. F. Smith, Chapman and Hall
14. Heterocyclic Chemistry, T.L.Gilchrist, Longman Scientific Technical
15. Heterocyclic Chemistry, Raj.K. Bansal.
16. An Introduction to the Heterocyclic Compounds, R. M. Acheson, John Wiley.

REFERENCE BOOKS:

1. Chemistry of Natural Products, K.W.Bentley
2. Stereochemistry of carbon compounds by E.Eliel, John Wiley & Sons, Inc.
3. Stereochemistry to Organic Compounds, D. Nasipuri, 2nd Ed. (New Age International).
4. Chemistry of Natural products by R.S. Kalsi Kalyani Publishers. 1983.



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Paper – IV: PHYSICAL CHEMISTRY-I

UNIT-I:

Thermodynamics-I: Concepts of partial molar properties – partial molar volume and its significance; Determination of partial molar volume: Graphical method, intercept method and apparent molar volume method. Partial molar free energy, chemical potential, Variation of chemical potential with T and P. Gibbs-Duhem equation-derivation and significance. Phase equilibrium- Derivation of phase rule from the concept of chemical potential. *Ideal solutions* - Thermodynamic properties of ideal solutions mixing quantities; Vapour pressure-Raoult's law; Thermodynamic properties of ideally dilute solutions. Vapour pressure- Henry's law.

Non-ideal systems -Concept of fugacity, fugacity coefficient. Determination of fugacity; Non ideal solutions. Activities and activity coefficients; Standard-state conventions for non ideal solutions; Determination of activity coefficients from vapour pressure measurements. Activity coefficients of non-volatile solutes using Gibbs-Duhem equation. Chemical equilibrium-effect of temperature on equilibrium constant- Van'tHoff equation

UNIT-II:

Micelles and Macro molecules: Surface active agents, classification of surface active agents, micellization, hydrophobic interaction, critical micellar concentration (CMC), factors affecting the CMC of surfactants, counter ion binding to micelles, thermodynamics of micellization- phase separation and mass action models, Solubilization, micro emulsion, reverse micelles.

Polymer- definition, types of polymers, electrically conducting, fire resistant, liquid crystal polymers, kinetics of free radical polymerization. Molecular mass- Number and mass average molecular weight, molecular weight determination-End group analysis, Osmometry, viscometry, ultracentrifugation and light scattering methods.

UNIT-III:

Chemical Kinetics: Theories of reaction rates- Collision theory- Limitations, Transition state theory. Effect of ionic strength - Debye Huckel theory-Primary and secondary salt effects; Effect of dielectric constant, effect of substituent, Hammett equation-limitations, Taft equation; Prediction of rate constants- Consecutive reactions, parallel reactions, opposing reactions (Uni molecular steps only, no derivation). Specific and general acid-base catalysis; Skrabal diagram; Fast reactions- different methods of studying fast reactions- flow methods, relaxation methods- temperature jump and pressure jump methods.

UNIT-IV:

Photochemistry: Electronic transitions in molecules, Franck-Condon principle. Electronically excited molecules- singlet and triplet states, spin-orbit interaction. Quantum yield and its determination; Actinometry - ferrioxalate and uranyl oxalate actinometers-problems. Derivation of fluorescence and phosphorescence quantum yields. Quenching effect- Stern Volmer equation. Photochemical equilibrium and delayed fluorescence - E type and P type. Photochemical primary processes, types of photochemical reactions-photodissociation, addition and isomerisation reactions with examples.



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Books:

1. Physical Chemistry by Peter Atkins and Julio de Paula, Oxford University Press.
2. Physical Chemistry by G.W. Castellon, Narosha Publishing House
3. Physical Chemistry by W.J.Moore, Prentice Hall
4. Thermodynamics for Chemists, Samuel Glasstone
5. Chemical Kinetics by K.J.Laidler, McGraw Hill Pub.
6. Photochemistry, R.P. Kundall and A. Gilbert, Thomson Nelson.
7. Polymer Chemistry by Billmayer
8. Introduction to Polymer Science, V.R. Gowriker, N.V.Viswanadhan and J. Sreedhar., Wiley Easter.
9. Micells, Theoretical and applied aspects, V.Morol, Plenum publishers.



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LABORATORY WORK (6 hrs/week)

INORGANIC CHEMISTRY - I

I. Inorganic Synthesis: Preparation of

- (i) Tetraamminecopper(II) sulphate
- (ii) Potassium tris-oxalato ferrate(III) trihydrate
- (iii) Tris-thiourea copper(I) sulphate

II. Semi micro qualitative analysis of six radical mixtures

(One interfering anion and one less familiar cation for each mixture)

Anions: CO_3^{2-} , S^{2-} , SO_3^{2-} , Cl^- , Br^- , I^- , NO_3^- , SO_4^{2-} , CH_3COO^-
 $\text{C}_2\text{O}_4^{2-}$, $\text{C}_4\text{H}_4\text{O}_6^{2-}$, PO_4^{3-} , CrO_4^{2-} , AsO_4^{3-} , F^- , BO_3^{3-}

Cations : Ammonium (NH_4^+)
1st group: Hg, Ag, Pb, Tl, W
2nd group: Hg, Pb, Bi, Cu, Cd, As, Sb, Sn, Mo
3rd group: Fe, Al, Cr, Ce, Th, Ti, Zr, V, U, Be
4th group: Zn, Mn, Co, Ni
5th group: Ca, Ba, Sr
6th group: Mg, K, Li

ORGANIC CHEMISTRY - I

Preparation, recrystallization, and determination of melting point & yield of the following compounds:

- (i) Aspirin, (ii) Nerolin, (iii) Chalcone,
- (iv) *p*-Nitro acetanilide, (v) 2,4,6- Tribromoaniline, (vi) *m*-Dinitrobenzene,
- (vii) Phthalimide, (viii) Diels-Alder adduct.

Books Suggested

1. Vogel's Text Book of Quantitative Chemical Analysis, J. Mendham, R. C. Denney, J. D. Barnes and M. J. Thomas, 4th & 6th Ed. (Pearson Education Asia).
2. Vogel's Text Book of Practical Organic Chemistry, B.S. Furniss, A.J. Hannaford, P.W.G. Smith, A.R. Tatchell, 5 Ed. (Longman Scientific & Technical)



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PHYSICAL CHEMISTRY-I

1. Determination of critical solution temperature of phenol-water system.
2. Effect of added electrolyte on the CST of phenol-water system.
3. Conductometric titration of Strong acid versus Strong base
4. Dissociation constant of weak acid (CH_3COOH) by conductometric method.
5. Conductometric titration of Weak acid vs Strong base.
6. Determination of cell constant
7. Adsorption of acetic acid on animal charcoal or silica gel.
8. Acid-catalyzed hydrolysis of methyl acetate
9. Determination of partial molar volume of solute - H_2O system by apparent molar volume method.



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Paper- I: GENERAL CHEMISTRY-II

UNIT-1

Basic Quantum Chemistry-III- Hydrogen atom- solution of $R(r)$, $\Phi(\phi)$ and $\Theta(\theta)$ equations. Probability density in orbitals- shapes of orbitals- Perturbation theory- Time independent perturbation theory(only first order perturbation is to be dealt with)- application to ground state energy of Helium atom- Variation principle- applications- calculation of zero-point energy of harmonic oscillator- many electron atom- Hartee-Fock self-consistent field method(qualitative treatment only)

UNIT-II

Molecular symmetry and Group Theory in chemistry: Basic concepts of symmetry and Group theory-Symmetry elements, symmetry operations and point groups- Schoenflies symbols- Classification of molecules into point groups- Axioms of Group theory- Group multiplication tables for C_{2v} and C_{3v} point groups- Similarity transformations- and classes- Representations- reducible and irreducible representations, Mullikan symbols, Orthogonality theorem and its implications, Character table and its anatomy.

UNIT-III

Treatment of analytical data: Accuracy and precision- Classification of errors- Determination of Indeterminate errors- Minimization of errors- Absolute and Relative errors, propagation of errors-Distribution of Indeterminate errors- Gaussian distribution- Measures of central tendency-Measures of precision- Standard deviation- Standard error of mean- student's t-test- Confidence interval of mean- Testing for significance- Comparison of two means- F-test- Criteria of rejection of an observation- Significant figures and computation rules.

UNIT- IV

Introduction to computer programming- FORTRAN 77: Basic structures and functioning of computer with P.C. as an illustrative example- Main memory- Secondary storage memory- input/output devices- computer languages- operating systems- principles of algorithms-and flow charts-constants and variables- Arithmetic expressions- Arithmetic statements- Replacement statement- IF statement- logical IF and BLOCK IF statements- GOTO statements-subscripted variable and DIMENSION statement. DO statement- Rules for DO statement- Functions and subroutines- Development of FORTRAN statements for simple formulae in chemistry such as Vander Waals equation- pH of a solution- First order rate equation- Cell constant-Electrode potential.

Flowcharts and computer programs for

- Program for the calculation of Cell Constant, Specific Conductance and Equivalence.
- Rate Constant of First order reaction or Beer's law by linear least square method.
- Hydrogen ion concentration of a strong acid solution/Quadratic equation.
- Solution for Vander Waals equation or Hydrogen ion concentration of a monoprotic weak acid
- Standard deviation and Variance of univariant data

References/ Text books:

- Introductory Quantum chemistry: by A.K. Chandra
- Group theory for Chemistry: by A.K. Bhattacharya
- Introductory Group theory for chemists : by George Davidson
- Vogel's text book of quantitative analysis: byVogel
- Fundamentals of Analytical chemistry: by Skog and West
- Principles of computer programming(FORTRAN 77 IBM PC): by V.Rajaraman
- Basics of computers for chemists: by P.C. Jurs



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Paper- II: INORGANIC CHEMISTRY-II

UNIT-I

Metal cluster compounds - definition – evidences for existence of M-M bonds - conditions favorable for formation of M-M bonds – preparation, structure and bonding of the following metal cluster compounds.

$\text{Re}_2\text{Cl}_8^{2-}$, $\text{Mo}_2\text{Cl}_8^{4-}$, $\text{Re}_2(\text{RCOO})_4\text{X}_2$, $\text{Mo}_2(\text{RCOO})_4(\text{H}_2\text{O})_2$, $\text{Cr}_2(\text{RCOO})_4(\text{H}_2\text{O})_2$, $\text{Cu}_2(\text{RCOO})_4(\text{H}_2\text{O})_2$, $\text{Cr}_2\text{Cl}_9^{3-}$, $\text{Mo}_2\text{Cl}_9^{3-}$, $\text{W}_2\text{Cl}_9^{3-}$, Re_3Cl_9 , $\text{Re}_3\text{Cl}_{12}^{3-}$, $\text{Mo}_6\text{Cl}_8^{4+}$, $\text{Nb}_6\text{X}_{12}^{2+}$ and $\text{Ta}_6\text{X}_{12}^{2+}$.

Polyatomic clusters – Zintl ions, Chevrel phases.

UNIT-II

Organometallic compounds - 16 and 18 electron rules. Isoelectronic relationship - Synthesis, structure, bonding and reactions of carbon monoxide, dinitrogen and nitric oxide complexes. Isolobal relationship – H, Cl, CH_3 , $\text{Mn}(\text{CO})_5$; S, CH_2 , $\text{Fe}(\text{CO})_4$; P, CH, $\text{Co}(\text{CO})_3$; Synthesis, structure, bonding and reactions of metallocenes with special reference to ferrocene.

UNIT-III

Metal Ligand equilibria in solution: Step wise and overall formation constants and their interaction– trends in stepwise constants – factors affecting the stability of metal complexes–Pearson's theory of hard and soft acids and bases (HSAB), chelate effect and its thermodynamic origin, determination of stability constants of complexes–spectrophotometric method and pH–metric method. Reactivity of metal complexes–inert and labile complexes. Explanation of lability on the basis of VBT & CFT.

Bio-Inorganic Chemistry: Metalloporphyrins with special reference to Haemoglobin & Myoglobin. Biological role of alkali and alkaline earth metal ions with special reference to Ca^{2+} . Biological and abiological Nitrogen Fixation.

UNIT- IV

Inorganic Reaction Mechanisms: Substitution reactions of metal complexes – D, Id, Ia and A mechanisms – Ligand replacement reactions of metal complexes – Acid hydrolysis – factors affecting acid hydrolysis – Anation and Base hydrolysis of Cobalt(III) complexes. Ligand displacement reactions of square planar complexes of platinum (II). Factors affecting square planar substitution – trans effect (theories).

Electron transfer reactions of complexes – concept of complementary and non-complementary reactions with examples. Inner and outer sphere mechanisms.

Text books:

1. Advanced Inorganic Chemistry by F.A. Cotton and R.G. Wilkinson, IV Edition, John, John Wiley and Sons, New York, 1980.
2. Inorganic Chemistry by J.E. Huheey, III edition, Harper International Edition, 1983.
3. Organometallic Chemistry-A unified approach by A. Singh and R.C. Mehrotra, Wiley Eastern Ltd.
4. Inorganic Chemistry by Shriver and Atkins, Oxford University Press (1999)
5. Theoretical Inorganic Chemistry, II Edition by M.C. Day and J. Selbin, Affiliated East-West press Pvt. Ltd., New Delhi.
6. Mechanisms of Inorganic reactions in solution by D.Benson, McGraw Hill, London, 1968.
7. Inorganic chemistry by K.F. Purcell and J.C.Kotz, W.B. Saunders company, New York, 1977.
8. Elements of Bioinorganic Chemistry by G.N. Mukherjee and Arabinda Das, U.N. Dhur & sons Pvt. Ltd, Calcutta.



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Paper-III: ORGANIC CHEMISTRY-II

UNIT-I

Reaction Mechanism

15Hrs

(A) *Aliphatic Nucleophilic Substitution and Nucleophilic Aromatic substitution*: Stereochemistry of S_N^2 and S_N1 mechanisms, Neighboring Group Participation (Anchimeric assistance), NGP by O, S, N: Aromatic Nucleophilic substitution: S_N2 (Ar) (Addition – Elimination), S_N1 (Ar) and benzyne mechanisms (Elimination - Addition); evidence for the structure of benzyne. Von Richter Sommelet-Hauser and Smiles rearrangements.

(B) *Elimination Reactions*: Type of elimination reactions, mechanisms, Stereochemistry and Orientation, Hofmann and Saytzeff rules, Syn elimination versus anti-elimination, competition between elimination and substitution, dehydration, dehydrogenation, dehalogenation, decarboxylative eliminations and pyrolytic eliminations

UNIT-II

Addition Reactions

15 Hrs

(A) *Addition to Carbon – Carbon Multiple Bonds*: Mechanistic and stereo chemical aspects of addition reactions involving electrophiles, nucleophiles and free radicals, region and chemo selectivity, orientation and reactivity, Hydrogenation of double and triple bonds, hydrogenation of aromatic rings, Hydroboration.

(B) *Addition to Carbon-Hetero Multiple Bonds*: Steric course of addition reactions to C=O and C=N, Aldol, Cannizzaro, Perkin, Knoevenagel, Claisen-Schmidt, Claisen, Dieckman, Benzoin and Stobbe condensations, Reformatsky reaction, Tollen's reaction, Prins reaction: Wittig, Grignard, Mannich, and Michael reaction, Hydrolysis of Carbon-Nitrogen bond, Isocyanates and isothioyanates.

UNIT-III

Molecular Rearrangements

15 Hrs

Types of molecular rearrangements, migratory aptitude;

Rearrangements to electron deficient carbon: Pinacol-pinacolone, Wagner-Meerwein, Tiffeneau – Demjanov, Dienone – Phenol, Arndt-Eistert synthesis;

Rearrangements to electron deficient nitrogen: Beckmann, Hofmann, Curtius, Schmidt and Lossen rearrangements;

Rearrangements to electron deficient oxygen: Baeyer-villiger, Hydro peroxide rearrangement and Dakin rearrangements; Neber rearrangement, Benzil-Benzilic acid and Favorskii rearrangements

UNIT-IV

Spectroscopy and Protecting Groups

15 Hrs

- A. Basic principles and importance of UV, IR, NMR and Mass.
- B. Protection of carbonyl, Hydroxyl, carboxylic and Amine groups



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Books Suggested:

1. Advanced Organic Chemistry-Reactions, Mechanism and structure, Jerry March, 6th Ed. (John Wiley & Sons).
2. Modern Organic Reactions, H. O. House (Benjamin)
3. Structure and Mechanism in Organic Chemistry C. K. Ingold (Cornell University Press).
4. Organic Chemistry, Paula Yurkanis Bruice, 4th Ed. (Prentice Hall)
5. Organic chemistry-Clayden J. (Oxford)
6. Organic Chemistry, Wade, L.G. Jr. 5th Ed. (Pearson)
7. Organic Chemistry, Salmons, P.W. & Others, 8th Ed. (John Wiley & Sons)
8. Advanced Organic Chemistry: Reactions and mechanisms, Miller Bernard & Other, 2nd Ed. (Pearson)
9. Mechanism and Theory in Organic Chemistry, Thomas H. Lowry, Kathleen S. Richardson, Harper & Row, (Publishers, Inc.).
11. A Guide Book to Mechanism in Organic Chemistry, Peter Sykes, 6th Ed., (Longman).
12. Reaction Mechanism in Organic Chemistry, P.S. Kalsi, 2nd Ed. (New Age International).
13. Stereochemistry to Organic Compounds, E.L. Eliel (John Wiley). 13. Stereochemistry to Organic Compounds, Nasipuri, 2nd Ed. (New Age International).
14. Stereochemistry, P.S. Kalsi, 5th Ed. (New Age International). Organic Chemistry Structure and Reactivity, Ege Seyhan, 3rd Ed. (AITBS)
15. Spectroscopic Methods in Organic Chemistry- Forth Edition, D.H. Williams and I. Fleming Tata - McGraw Hill, New Delhi, 1990.
16. Organic Spectroscopy- Second Edition, W.Kemp, ELBS Macmillan, 1987.
17. Applications of absorption spectroscopy of Organic Compounds J.R.Dyer, Prentice Hall of India, New Delhi, 1984.
18. Spectrometric identification of Organic Compounds-Fourth Edition, R.M. Silverstein: G.C.Vassillr and T.C. Merrill, John Wiley, Singapore, 1981.
19. Introduction to spectroscopy-D.L.Pavia, G.M.Lampman, G.S.Kriz, 3rdEd (Harcourt college publishers).



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Paper – IV: PHYSICAL CHEMISTRY-II

UNIT-I:

Physical methods of molecular structural elucidation: NMR: Principle and theory, Nature of spinning particle and its interaction with magnetic field. Chemical shift and its origin. Spin-Spin interaction, Application of NMR to structural elucidation- Structure of ethanol, dimethylformamide, styrene and acetophenone.

Electron Spin Resonance: Principle and experimental technique- g-factor, line shapes and line widths- hyperfine interactions- applications of ESR studies.

UNIT -II:

Thermodynamics-II- Brief review on entropy; entropy changes accompanying specific process – expansion, phase transition, heating, measurement of entropy. Nernst heat theorem; Third law of thermodynamics- Determination of the absolute entropy- Apparent exceptions to Third law of thermodynamics.

Statistical Thermodynamics: Objectives of statistical thermodynamics, Concept of distributions, Types of ensembles. Thermodynamic probability, Most probable distribution Law – Partition Function, (Definition and significance): Molar and molecular partitions-translational, rotational, vibrational and electronic partition functions- Relation between thermodynamic functions (E, H, S, G and C_v) and the partition functions

UNIT-III:

Electrochemistry I: Electrochemical cell- Galvanic and electrolytic cell. Concentration cell with and without transference, Effect of complexation on redox potential- ferricyanide/ ferrocyanide couple, Iron (III) phenanthroline / Iron (II) phenanthroline couple. Determination of standard potential, solubility product equilibrium constant and activity coefficients from EMF data.

Bjerrum theory of ion association (elementary treatment) Concept of activity and activity coefficients in electrolytic solutions. The mean ionic activity coefficient. Debye-Huckel theory of electrolytic solutions. Debye-Huckel limiting law (derivation not required), Calculation of mean ionic activity coefficient; Limitations of Debye-Huckel theory. Effect of dilution on equivalent conductance of electrolytes - Anomalous behavior of strong electrolytes. Debye Huckel-Onsagar equation – verification and limitations, Fuel Cells.

UNIT-IV:

Electrochemistry II: The electrode-electrolyte interface. The electric double layer. The Helmholtz-Perrin parallel-plate model, the Gouy-Chapman diffuse-charge model and the Stern model.

Electrodics: Charge transfer reactions at the electrode-electrolyte interface. Exchange current density and over-potential. Derivation of Butler-Volmer equation. High field approximation, Tafel equation, Low field equilibrium, Nernst equation. Voltametry-Concentration polarization, experimental techniques.



ADIKAVI NANNAYA UNIVERSITY
SECOND SEMESTER CHEMISTRY SYLLABUS
(Common for M.Sc Analytical, Physical & Organic Chemistry)
(With effect from 2016-17 admitted batch)

Books:

1. Text book of Physical Chemistry by Samuel Glasstone, McMillan Pub.
2. Physical Chemistry by W.J.Moore, Prentice Hall
3. Physical Chemistry by G.W. Castellon, Narosha Publishing House
4. Physical Chemistry by Peter Atkins and Julio de Paula, Oxford University Press.
5. Modern Electrochemistry, 2A & 2B, JOM Bockris & A.K.N.Reddy, Plenum publishers
6. Introduction to Electrochemistry, S.Glasstone.
7. Fundamentals of Molecular Spectroscopy, Banwell
8. Spectroscopy by Straw & Walker.
9. Statistical thermodynamics , M.C.Gupta
10. Statistical Thermodynamics, M.Dole



ADIKAVI NANNAYA UNIVERSITY
SECOND SEMESTER CHEMISTRY SYLLABUS
(Common for M.Sc Analytical, Physical & Organic Chemistry)
(With effect from 2016-17 admitted batch)

LABORATORY WORK (6 hrs/ week)

INORGANIC CHEMISTRY PRACTICALS –II

Quantitative analysis:

Volumetric:

1. Determination of Ferric iron by photochemical reduction
2. Determination of Nickel by EDTA
3. Determination of Calcium and Magnesium in a mixture by EDTA
4. Determination of Ferrocyanide by Ceric sulphate
5. Determination of Copper(II) in presence of iron(III)

Gravimetric:

6. Determination of Zinc as Zinc pyrophosphate
7. Determination of Nickel from a mixture of Copper and Nickel.

ORGANIC CHEMISTRY PRACTICALS –II

Systematic qualitative analysis of an organic mixture containing two compounds

Identification of method of separation and the functional group(s) present in each of them and preparation of one solid derivative for the confirmation of each of the functional group(s).

PHYSICAL CHEMISTRY PRACTICALS –II

1. Distribution of iodine between CHCl_3 and water
2. Distribution of I_2 between CHCl_3 and aq. KI solution- calculation of equilibrium constant.
3. Determination of Coordination number of cuprammonium cation.
4. Titration of mixture Strong acid and weak acid versus Strong base by conductometry.
5. Titration of Strong acid Vs Strong Base – pH – metry.
6. Titration of mixture of ($\text{NaHCO}_3 + \text{Na}_2\text{CO}_3$) Vs HCl – pH- metry.
7. Titration of Strong acid Vs Strong Base using Quinhydrone electrode.
8. Titration of Fe^{+2} Vs $\text{K}_2\text{Cr}_2\text{O}_7$ – potentiometry
9. Verification of Beer-Lambert's law by Iron-thiocyanate system –colorimetry.
10. Determination of single electrode potential of Cu^{2+}/Cu and estimate the given unknown concentration.



ADIKAVI NANNAYA UNIVERSITY
DEPARTMENT OF CHEMISTRY

THIRD SEMESTER

**Paper – I- ORGANIC REACTION MECHANISMS-I and
PERICYCLIC REACTIONS**

(Effective from the 2016-17 Admitted Batch)

UNIT – I

15 Hrs

A) Aliphatic Nucleophilic Substitution:

Neighboring group participation by Bromine, Phenyl group, Non-Classical carbocations, NGP by Pi bond, Sigma bond and Cyclopropyl group, S_N at Allylic carbon (allylic rearrangements), S_N at Aliphatic trigonal carbon, S_N at Vinylic carbon, Ambident nucleophiles, Hydrolysis of esters (B_{AC}^2 , $A_{AC}2$, $A_{AC}1$, $A_{AL}1$, $B_{AL}1$), Mechanism of estrification of carboxylic acid with an alcohol using DCC, Mayers Synthesis of aldehydes, ketones and carboxylic acids Mitsunobu reaction, Von-Braun reaction

B) Aliphatic Electrophilic Substitution:

Mechanisms of S_E^2 , S_E^1 , S_{Ei} , *Hydrogen as electrophile*: Hydrogen exchange; Migration of double bonds, *Halogen electrophiles*. Mechanism of Halogenation of aldehydes and ketones; HVZ reaction; Halogenation of Sulphoxides & Sulphones, *Nitrogen Electrophiles*: Aliphatic diazo coupling, Diazo transfer reaction, Insertion of nitrenes, *Metal Electrophiles*: Metallation with Organometallic Compounds (Orthometallation), *Carbon as Leaving groups*: Decarboxylation of Aliphatic Acids; Dakin – West reaction; Haller–Bauer reaction.

UNIT – II

15 Hrs

Principles of asymmetric synthesis:

Introduction and terminology: Topicity in molecules Homotopic, stereoheterotopic (enantiotopic and diastereotopic) groups and faces, symmetry, substitution and addition criteria. Prochirality nomenclature: Pro-R, Pro-S, Re and Si. Stereoselective reactions: Substrate stereoselectivity, product stereoselectivity, enantioselectivity and diastereoselectivity. Conditions for stereoselectivity: Symmetry and transition state criteria, kinetic and thermodynamic control. Methods for inducing enantio and diastereoselectivity. Analytical methods: % Enantiomeric excess, enantiomeric ratio, optical purity, % diastereomeric excess and diastereomeric ratio. Techniques for determination of enantiomeric excess, specific rotation, Chiral NMR; Chiral derivatizing agents, Chiral solvent, Chiral shift reagents and Chiral HPLC.

UNIT – III

15 Hrs

Pericyclic Reactions-I

Molecular orbital symmetry, frontier orbitals of ethylene, 1,3 Butadiene, 1,3,5- Hexatriene, allyl system, classification of pericyclic reactions FMO approach, Woodward- Hoffman correlation diagram method and perturbation of molecular (PMO) approach for the explanation of pericyclic reactions under thermal and photochemical conditions.

Electrocyclic Reactions: Conrotatory and disrotatory motions ($4n$) and ($4n+2$), allyl systems Cycloadditions: Antarafacial and suprafacial additions, notation. of cycloadditions, ($4n$) and ($4n+2$) systems with a greater emphasis on ($2+2$) and ($4+4$) - cycloadditions, ($2+2$) - additions of ketenes and chelotropic reactions.



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UNIT-IV

15 Hrs

Pericyclic Reactions-II

FMO approach and perturbation of molecular (PMO) approach for the explanation of sigma tropic rearrangements under thermal and photochemical conditions. suprafacial and antarafacial shifts of H Sigmatropic shift involving carbon moieties, retention and inversion of configurations, (3, 3) and (5, 5) sigmatropic rearrangements detailed treatment of Claisen and Cope rearrangements, fluxional tautomerism, aza-Cope rearrangement and Barton reaction.

Text Books and Reference Books:

- 1) Advanced Organic Chemistry: Reactions Mechanisms and Structure by Jerry March, Mc.Graw Hill and Kogakush.
- 2) Molecular reactions and Photochemistry by Charles Dupey and O. Chapman, Prentice Hall.
- 3) Pericyclic reactions by S.N. Mukharji, Mcmilan.
- 4) Mechanisms and Theory in Organic Chemistry by T.H. Lowery and K.S. Rich gardson.
- 5) The modern structural theory in Organic Chemistry by L.N.Ferguson, Pretice Hall
- 6) Physical Organic Chemistry by jack Hine, Mc. Graw Hill
- 7) Advanced Organic Synthesis, Part B-Reactions and Synthesis, Francis A. Carey and Richard J. Sudenburg, Fourth edition, Kluwer academic publishers, New York
- 8) Organic Synthesis, Christine Willis and Martin Willis, Oxford Chemistry primers.
- 9) Principles of Organic Synthesis, ROC Norman and JM Coxon, third edition, CBS, Publisher, Delhi.
- 10) Organic Synthesis, M. B. Smith, Mc Graw Hill, International Edition.
- 11) Organic Chemistry, Clayden, Greeves and Stuwart Warren.
- 12) Modern Organic Synthesis-an introduction by George S.Zweifel and Michael H. Nantz, W. H. Freeman & company, New York.
- 13) Pericyclic Reactions — a problem solving approach, Lehr and Merchand.
- 14) Conservation of Orbital Symmetry by Woodward and Hoffmann.



ADIKAVI NANNAYA UNIVERSITY
DEPARTMENT OF CHEMISTRY

THIRD SEMESTER

Paper – II- ORGANIC SPECTROSCOPY-I

(Effective from the 2016-17 Admitted Batch)

UNIT-I 15 Hrs

UV-Visible spectroscopy:

A) Beer-Lambert's law-Deviations from Beers law-Instrumentation-Mechanics of measurement- Energy transitions–Simple chromophores- Auxochrome, Absorption shifts (Bathochromic, Hypsochromic, Hyper chromic and Hypo chromic shifts) UV absorption of Alkenes-Polyenes unsaturated cyclic systems.

B) UV absorption of carbonyl compounds: α,β -unsaturated carbonyl systems-UV absorption of aromatic systems-solvent effects-geometrical isomerism-acid and base effects-typical examples-calculation of λ max values using Woodward Fieser rules, applications.

UNIT-II 15 Hrs

Infrared spectroscopy:

A) Mechanics of measurement-Fundamental modes of vibrations-stretching and bending vibrations-Factors effecting Vibrational frequency-hydrogen bonding.

B) Finger print region and its importance, typical group frequencies for –CH,-OH, N-H, CC,-CO and aromatic systems-Application in structural determination–Examples-simple problems.

UNIT-III 15 Hrs

Nuclear Magnetic Resonance Spectroscopy (^1H NMR):

A) Introduction: Basic principle of- NMR Nuclear spin- nuclear resonance-saturation-Relaxation-Instrumentation (CW&FT).

B) Shielding and deshielding of magnetic nuclei-chemical shift and its measurements, factors influencing chemical shift – spin-spin interactions- factors influencing –coupling constant J and factors effecting J value.

C) ^{13}C NMR Spectroscopy: Similarities and Differences between PMR and CMR, general considerations, chemical shift (aliphatic, olefinic, alkyne, aromatic, hetero aromatic and carbonyl carbon), coupling constants, typical examples of CMR spectroscopy-simple systems.

UNIT-IV 15 Hrs

Mass spectrometry

A) Introduction: Ion production-E1, C1, ES, MALDI and FAB- determination of Molecular weight and formulae-Behavior of organic compounds in mass spectrometer- factors affecting fragmentation, ion analysis, and ion abundance.

B) Mass spectral fragmentation of organic compounds, Common functional groups, molecular ion peak, meta stable peak, Mc Lafferty rearrangement, Nitrogen rule, High resolution mass spectrometry, Examples of mass spectral fragmentation of organic compounds with respect of their structure determination.



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Suggested Books:

- 1) Spectroscopic Methods in Organic Chemistry- Forth Edition, D.H. Williams and I.Fleming
Tata McGraw Hill, New Delhi, 1990.
- 2) Organic Spectroscopy- Second Edition, W.Kemp, ELBS Macmillan, 1987.
- 3) Applications of absorption spectroscopy of Organic Compounds J.R.Dyer,
Prentice Hall of India, New Delhi, 1984.
- 4) Spectrometric identification of Organic Compounds-Fourth Edition, R.M.
Silverstein: G.C.Vassiellr and T.C. Merill, Johne Willey, Singapore, 1981.
- 5) Introduction to spectroscopy-D.L.Pavia, G.M.Lampman, G.S.Kriz, 3rdEd
(Harcourt college publishers).
- 6) Absorption spectroscopy of organic molecules-V.M.Parkih.
- 7) Nuclear Magnetic Resonance-Basic principles-Atta-Ur-Rehman, Springer-Verlag, 1986.



ADIKAVI NANNAYA UNIVERSITY
DEPARTMENT OF CHEMISTRY

THIRD SEMESTER

Paper – III- MODERN ORGANIC SYNTHESIS-I
(Effective from the 2016-17 Admitted Batch)

UNIT-I

Formation of C-C single bonds 15 Hrs

Alkylations via enolate, Thermodynamic and kinetic enolate, Asymmetric Aldol reaction: a) Chiral enolate and achiral aldehyde b) Achiral enolate and chiral aldehyde – explanation by Zimmerman Traxler model; Stork enamine reaction and its synthetic applications; Organo sulphur chemistry: Umpolung and its synthetic applications (Corey Seebach Reaction), sulphur ylides: dimethyl sulphonium methylide, dimethyloxosulphonium methylide preparations and their synthetic applications; Organo Palladium Chemistry: Heck Reaction, Stille coupling, Suzuki coupling, Sonogashira coupling, Negishi coupling, Wacker Oxidation; Organo copper chemistry: Gilman's reagent and synthetic applications; Synthetic applications of carbenes and carbenoids; Baylis Hilman reaction.

UNIT-II

Formation of Carbon-Carbon double bonds 15 Hrs

Stereochemistry of E1 and E2 reactions (Different examples of acyclic and cyclic molecules, Saytzeff rule, Hofmann rules and Bredt's rule); Pyrolytic Syn eliminations (focus should be given on stereochemistry of syn eliminations of amine oxides, xanthates and esters of acyclic and cyclic molecules); Sulphoxide-Sulphenate rearrangement (Mislow-Evans rearrangement); Wittig reaction, Wadsworth Emmons reaction, Corey-Fuchs reaction, Aza Wittig reaction, Wittig-Horner reaction and stereo chemistry of Wittig reaction; Shapiro reaction, Eschen-Moser Tanabe fragmentation, Claisen rearrangement of allyl vinyl ethers, Julia Lythgoe olefination, Mc Murray coupling, Peterson Olefination, Tebbs reagent and its application, Metathesis: Grubbs 1st and 2nd generation catalyst, Olefin cross coupling (OCM), ring closing (RCM) and ring opening (ROM) metathesis, applications, olefination by Nysted reagent.

UNIT-III

Reactions of unactivated C-H bonds and organoboranes 15 Hrs

The Hoffmann Loeffler- Freytag reaction, the Barton reaction and Photolysis of organic hypothalites;

Organoboranes: Preparation of Organoboranes



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viz hydroboration with $\text{BH}_3\text{-THF}$, dicyclohexyl borane, disiamyl borane, theryl borane, 9-BBN mono isopinacamplyl borane (IPC_2BH_2) and diisopinacamplyl borane (IPC_2BH) functional group transformations of Organo boranes-Oxidation, protonolysis and isomerisation. Formation of carbon-carbon-bonds viz organo boranes carbonylation and cyanidation, reactions of alkenyl boranes and trialkyl alkynyl borates.

UNIT-IV

Protecting groups and simple applications of microwave and ultrasound assisted reactions 15 Hrs

(A) Protecting Groups

- 1) Protection of **alcohols** as **ethers** [methyl ether (RO-Me), Tertiary butyl ether (ROCM_3), Benzyl ethers (RO-Bn), *p*-methoxybenzylethers (RO-PMB)], as **Silyl ethers** [Trimethyl silylether (R-OTMS), tri ethyl silyl ethers (RO-TEs), *t*-butyldimethylsilyl ether (R-OTBDMS in the presence of imidazole), tri isopropylsilyl ether (RO-TIPS), *t*-butyl diphenylsilyl ether (RO-TBDPS)], as **acetals** [tetrahydropyranyl ethers (RO-THP), methoxymethyl ethers ($\text{RO-CH}_2\text{-OCH}_3 = \text{RO-MOM}$) and **ester formation** (carboxylic acid ester and *p*-toluene sulphonate esters).
- 2) Protection of 1,2-diols by acetal, ketal and carbonate formation.
- 3) Protection of amines by acetylation, benzylation, benzoyloxy carbonyl, Fmoc and triphenyl methyl groups.
- 4) Protection of carbonyl by acetal, ketal and thio acetal (Umpolung) groups.
- 5) Protection of carboxylic acids by esters and ortho ester formation.

(B)

Synthetic applications of PTC and crown ethers

1. Microwave Technology: Microwave equipment, activation-benefits, limitations, microwave effects. Microwave assisted reactions in organic solvents-Esterification reactions, Fries rearrangement, Orthoester Claisen rearrangement, Diels- Alder reaction, decarboxylation.
2. Ultrasound assisted reactions: introduction, substitution reactions, addition, oxidation, reduction reactions.
3. Click chemistry: criterion for click reaction, Sharpless azides cycloadditions



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Textbooks and Books for Reference:

- 1) Some Modern Methods of Organic Synthesis W. Carruthers, Third & Fourth Edition, Cambridge University Press, Cambridge, 1988.
- 2) Modern Organic Synthesis-an introduction by George S.Zweifel and Michael H. Nantz, W. H. Freeman & company, New York.
- 3) Advanced Organic Synthesis, Part B-Reactions and Synthesis, Francis A. Carey and Richard J. Sudenburg, Fourth edition, Kluwer academic publishers, New York
- 4) Organic Synthesis, Christine Willis and Martin Willis, Oxford Chemistry primers.
- 5) Principles of Organic Synthesis, ROC Norman and JM Coxon, third edition, CBS, Publisher, Delhi.
- 6) Organic Synthesis, M. B. Smith, McGraw Hill, International Edition.
- 7) Organic Chemistry, Clayden, Greeves and Stuart Warren.
- 8) Guide Book to Organic Synthesis (3rd edition), R. Mackie, D. M. Smith and Aitken.
- 9) Organo Boranes and Silanes, Thomson, Oxford Chemistry primers.
- 10) Strategic applications of named reactions in organic synthesis, Laszlo Kurti and Barbara Czako.
- 11) Modern Synthetic Reactions, Herbet O. House, Second Edition, W.A. Benzamine Inc. Menio Park, California, 1972.
- 12) Organic Synthesis viz Boranes, Herbet C. Brown Gray, W. Kramer Alan B. Levy and M. Mark Midland John Wiely &. Sons, New York, 1975.
- 13) Organic Synthesis: Special Techniques, V. K. Ahluwalia and Renu Agarwal.
- 14) Organic Synthesis, Jagadamba Singh and Dr. A. Yadav, Pragati Edition.



ADIKAVI NANNAYA UNIVERSITY
DEPARTMENT OF CHEMISTRY

THIRD SEMESTER

Paper – IV- : CHEMISTRY OF NATURAL PRODUCTS

(Effective from the 2016-17 Admitted Batch)

UNIT–I: Alkaloids 15 Hrs

Introduction, isolation, general methods of structure elucidation and physiological action, degradation, classification based on nitrogen heterocyclic ring, structure, stereochemistry, synthesis and biosynthesis of morphine, strychnine, vincristine, colchicine, camptothecin and reserpine.

UNIT–II: Terpenoids 15 Hrs

Occurrence, isolation, general methods of structure determination, isoprene rule. Structure determination, stereochemistry, biosynthesis and synthesis of Farnesol, Zingiberene, Forskolin, Taxol, Azadirachtin and β -amyrin.

UNIT–III: Steroids 15 Hrs

Occurrence, nomenclature, basic skeleton, Diel's hydrocarbon and its stereochemistry. Isolation, structure determination and synthesis of cholesterol (total synthesis not expected), androsterone, testosterone, estrone and progesterone, Biosynthesis of steroids.

UNIT–IV: Flavonoids and Isoflavonoids 15 Hrs

Occurrence, nomenclature and general methods of structure determination, Isolation, structure elucidation and synthesis of Kaempferol, Quercetin, Cyanidin, Genestein, Butein and Daidzein. Biosynthesis of flavonoids and Isoflavonoids: Acetate Pathway and Shikimic acid Pathway.

Books Suggested:

1. Natural Products: Chemistry and Biological Significance, J. Mann, R.S.Davidson, J. B. Hobbs, D. V. Banthrope and J. B. Hatrbnome, Longman, Essex.
2. Organic Chemistry, Vol. 2, I. L. Finar, ELBS.
3. Chemistry of Organic Natural Products, O. P. Agrawal, Vols. 1 &2, Goel Pubs.
4. Natural Products Chemistry K. B. G. torsell, John Wiley, 1983
5. New Trends in Natural Products Chemistry, Atta-ur-Rahman and M.I.Choudhary, Harwood Academic Publisher.
6. Chemistry of Natural products P. S. Kalsi, Kalyani Publishers
7. Biosynthesis of steroids, terpenes and acetogenins, J. H. Richards & J. R. Hendrieson
8. The biosynthesis of secondary metabolites, R. D. Herbert, Chapman & Hall
9. The Biosynthesis of Secondary Metabolite, R. D. Herbert, Second edn, Chapman and Hall 1984
10. Chemical aspects of Biosynthesis, John Mann, Oxford University Press, Oxford, 1996.



ADIKAVI NANNAYA UNIVERSITY
DEPARTMENT OF CHEMISTRY

FOURTH SEMESTER

Paper – I- ORGANIC REACTION MECHANISMS-II and
ORGANIC PHOTO CHEMISTRY

(Effective from the 2016-17 Admitted Batch)

UNIT – I 15 Hrs

A) **Free Radical Reactions:**

Free radical substitution mechanisms; Mechanism at an aromatic substrate; Neighboring group assistance in free radical reactions; Reactivity for aliphatic substrates; Reactivity in aromatic substrates; Reactivity at bridge head; Reactivity in the attacking radical; Effect of solvent on reactivity, Allylic halogenations using NBS (Wohl – Ziegler bromination); Hydroxylation at aromatic carbon by Fentons reagent; Oxidation of aldehydes to carboxylic acids; Formation of cyclic ethers using Leadtetraacetate; Formation of hydroperoxides (autooxidation); Coupling of alkynes (Eglinton reaction and Glacer reaction); Arylation of Aromatic compounds by diazonium salts(Gomberg – Bachman reaction); Mechanisms of Sandmeyer reaction, Kolbes reaction, Hunsdiecker reaction, Reed reaction; free radical rearrangements.

B) **Quantitative relationships between Molecular structure and Chemical reactivity:**

Hammett and Taft Equations

C) **Rearrangements:** Wagner – Meerwein Rearrangement, Demjanov Rearrangement, Wittig Rearrangement and Stevens Rearrangement

Unit – II: 15 Hrs

Methodologies in asymmetric synthesis

Strategies in Asymmetric Synthesis: 1. Chiral substrate controlled, 2. Chiral auxiliary controlled, 3. Chiral reagent controlled and 4. Chiral catalyst controlled.

1. **Chiral Substrate controlled asymmetric synthesis:** Nucleophilic additions to chiral carbonyl compounds. 1, 2- asymmetric induction, Cram's rule and Felkin-Anh model.

2. **Chiral auxiliary controlled asymmetric synthesis:** α -Alkylation of chiral enolates, azaenolates, imines and hydrazones. 1, 4-Asymmetric induction and Prelog's rule. Use of chiral auxiliaries in Diels-Alder reaction.

3. **Chiral reagent controlled asymmetric synthesis:** Asymmetric reductions using BINAL-H. Asymmetric hydroboration using IPC2 BH and IPCBH2.

4. **Chiral catalyst controlled asymmetric synthesis:** Sharpless and Jacobsen asymmetric epoxidations. Sharpless asymmetric dihydroxylation. Asymmetric hydrogenations using chiral Wilkinson biphosphine and Noyori catalysis. Enzyme mediated enantioselective synthesis

5. **Asymmetric aldol reaction:** Diastereoselectivity aldol reaction (chiral enolate & achiral aldehydes and achiral enolate & chiral aldehydes) its explanation by Zimmerman-Traxel model.

UNIT – III 15 Hrs

Photo Chemistry-I

Photochemical energy, Frank Condon Principle, Types of Electronic Excitation and Molecular orbital view of excitation, Jablonski Diagram, singlet and triplet states, dissipation of photochemical energy, photosensitization, quenching, quantum efficiency and quantum yield, Determination of Quantum yield

Photo Chemistry of Carbonyl Compounds: Norrish Type I reaction (alpha cleavage reaction), Norrish Type – II reaction, Paterno- Buchi reaction, Photo reduction & photo enolisation; photochemical Oxidations [Backstrom mechanism], Photo oxidation of alkenes with singlet oxygen.



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Unit – IV

Photochemistry-II

Di – Pi methane Rearrangement, Aza di – Pi methane rearrangement; Photochemistry of Benzene and substituted benzene, 1, 2 , 1,3 ,& 1, 4-additions; Photo Fries rearrangement of Phenolic acetates and Anilides; Photochemistry of unsaturated systems, Cis- Trans Isomerisation of alkenes (Direct and sensitized) (Photoisomerisation of Stilbene), Photochemistry of Butadiene; Dimerisations of alkenes, Intramolecular dimerisation.

Photochemical rearrangement of Cyclohexadienenones; Photochemistry of alpha, beta Unsaturated ketones (dimerisations and addition across the double bond); Photochemical rearrangement reactions of Cyclohexenone, Photorearrangements of Beta, gamma unsaturated systems (Mechanism of 1,2 & 1,3 – acyl shifts); Photochemistry of Nitrite esters (Barton reaction); Photochemistry of alpha diazoketones; Photo Aromatic Substitutions; Photochemistry of Pyridinium ylides.

Text Books and Reference Books:

- 1) Advanced Organic Chemistry: Reactions Mechanisms and Structure by Jerry March, Mc.Graw Hill and Kogakush.
- 2) Molecular reactions and Photochemistry by Charles Dupey and O. Chapman, Prentice Hall.
- 3) Mechanisms and Theory in Organic Chemistry by T.H. Lowery and K.S. Richardson.
- 4) The modern structural theory in Organic Chemistry by L.N.Ferguson, Prentice Hall
- 5) Physical Organic Chemistry by Jack Hine, Mc. Graw Hill
- 6) Advanced Organic Synthesis, Part B-Reactions and Synthesis, Francis A. Carey and Richard J. Sudenburg, Fourth edition, Kluwer academic publishers, New York
- 7) Organic Synthesis, Christine Willis and Martin Willis, Oxford Chemistry primers.
- 8) Principles of Organic Synthesis, R.C. Norman and J.M. Coxon, third edition, CBS, Publisher, Delhi.
- 9) Organic Synthesis, M. B. Smith, Mc Graw Hill, International Edition.
- 10) Organic Chemistry, Clayden, Greeves and Stuart Warren.
- 11) Modern Organic Synthesis-an introduction by George S.Zweifel and Michael H. Nantz, W. H. Freeman & company, New York.
- 12) Organic Photochemistry by D Coyle
- 13) Molecular Photochemistry by Gilbert & Baggo
- 14) Organic Photochemistry by Turro
- 15) Photochemistry by C W J Wells



ADIKAVI NANNAYA UNIVERSITY
DEPARTMENT OF CHEMISTRY

FOURTH SEMESTER

Paper – II- ORGANIC SPECTROSCOPY-II

(Effective from the 2016-17 Admitted Batch)

UNIT-I:

A) Optical Rotatory Dispersion: Theory of Optical Rotatory Dispersion-Cotton effect –CD curves-types of ORD and CD curves–similarities and difference between ORD and CD curves

B) The octant rule-application in structural studies- α - halo keto rule.

UNIT-II

A) Improving the PMR spectrum: Chemical and Magnetic Equivalence. Chemical exchange, First and Non-First Order Spectra and analysis of AB, AMX and ABX systems.

B) Simplification of complex spectra-: Nuclear Magnetic double resonance, Lanthanide shift reagents, solvent effects, Fourier transforms technique, Nuclear Overhauser Effect (NOE), Deuterium Exchange, spectra at higherfields. Hindered Rotations and Rate processes. Resonance of other nuclei- ^{19}F and ^{31}P

C) 2D NMR spectroscopy: Definitions and importance of COSY, DEPT, HOMCOR, HETCOR, INADEQUATE, INDOR INEPT, NOESY, HOM2DJ, HET2DJ and DQFCOSY.

UNIT-III

Solution of structural problems by joint application of UV, IR, NMR (^1H & ^{13}C) and mass spectrometry.

UNIT-IV

A) Separation Techniques: Solvent extraction chromatography-paper-thin layer partition-column chromatography, Electrophoresis.

B) Instrumentation – Gas Chromatography, High performance Liquid Chromatography, X – Ray diffraction (XRD)

Suggested Books:

- 1) Spectroscopic Methods in Organic Chemistry- Forth Edition, D.H. Williams and I. Fleming
Tata - McGraw Hill, New Delhi, 1990.
- 2) Organic Spectroscopy- Second Edition, W.Kemp, ELBS Macmillan, 1987.
- 3) Spectrometric identification of Organic Compounds-Fourth Edition, R.M. Silverstein: G.C.Vassillr and T.C. Merill, John Willey, Singapore, 1981.
- 4) Introduction to spectroscopy-D.L.Pavia, G.M.Lampman, G.S.Kriz, 3rdEd
(Harcourt college publishers).
- 5) "Applications of Optical rotation and Circular Dichroism", G.C. Barret, in
"Elucidation of Organic structures by Physical and Chemical Methods"
Part I (Eds) K.W. Bentley and G.W.Rirty John Wiley, 1972, Chapter VIII
(only those aspects mentioned in the syllabus).
- 6) Instrumental methods of chemical analysis by H.Kaur, Pragati Prakasan,meerut.
- 7) Separation Techniques by M.N.Sastri, Himalaya publishing House (HPH), Mumbai.



ADIKAVI NANNAYA UNIVERSITY
DEPARTMENT OF CHEMISTRY

FOURTH SEMESTER

Paper – III- MODERN ORGANIC SYNTHESIS-II

(Effective from the 2016-17 Admitted Batch)

UNIT-I

Organo Silanes

15 Hrs

Synthetic applications of trimethylsilyl chloride dimethyl-*t*-butylsilyl chloride, trimethylsilyl cyanide, trimethylsilyl iodide and trimethylsilyl triflate, synthetic applications of α -silyl carbanion and β -silyl carbonium ions. Synthetic applications of silyl enol ethers, Preparation and synthetic applications of alkynyl silanes, aryl silanes, allyl silanes and vinyl silanes, Nazarov cyclization, Synthetic conversion of α , β -epoxy silanes, Peterson Olefination, Brook rearrangement and Rubottom oxidation.

UNIT-II

15 Hrs

Oxidation

Synthetic applications of the following reagents in the oxidation of functional groups like alkenes, alkynes, alcohols, aldehydes and ketones: 1) $\text{Pb}(\text{OAc})_4$ 2) HIO_4 3) SeO_2 4) CrO_3 (Sodium or potassium dichromate in H_2SO_4 , Collins reagent, Jones reagent, Etard reagent, CrO_3 in acetic anhydride, PCC (Coreys reagent), PDC, Babler oxidation), 4) MnO_2 5) KMnO_4 6) OsO_4 7) Oxidations by using DMSO involving alkoxy sulphonium salts (Kornblum oxidation), DCC- DMSO (Pfitzner-Muffat reagent), Swern oxidation, Corey-Kim oxidation, Albright-Goldman oxidation 8) Oxidations by using IBX, DMP, TPAP, TEMPO, CAN 9) Bayer villager oxidation and Prilezhev epoxidation 10) Oxidation of alkenes using Woodward and Prevost reagents 11) Oxidation by using DDQ 12) Sharpless asymmetric epoxidation and Sharpless asymmetric dihydroxylation 13) Thallium nitrate 14) Oxidative coupling of phenols and alkynes.

UNIT-III

Reduction

15 Hrs

- (1) Catalytic reductions: Homogeneous (Wilkinson's Catalytic reduction) and heterogeneous catalytic reductions and their synthetic applications.
- (2) Reductions by using electrophilic nucleophilic metal hydrides: LiAlH_4 (Various examples of reductions and Cram's rule), related reagents of LAH, NaBH_4 , NaBH_3CN , Trialkyl Borohydrides (Super Hydride and Selectride).
- (3) Reductions by using electrophilic metal hydrides: BH_3 , DIBAL



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- (4) Reductions by dissolving metals: Clemenson reduction, Acyloin condensation, Bouveault-Blanc reduction, Birch reduction (Various examples should be discussed).
- (5) Reductions by using Diimide and Wolf-Kishner Reduction (6) Hydrogenolysis
- (7) Reductions by using tri n-butyl tin hydride.

UNIT-IV

Retro Synthetic Analysis

15 Hrs

1. Basic definitions of the following:
 - a) Retro synthetic analysis
 - b) Disconnection
 - c) Target molecule
 - d) Synthone
 - e) Synthetic equivalent
 - f) Functional Group Inter Conversion (FGI)
 - g) Functional Group Addition (FGA)
2. Guidelines for the order of events: One group C-X disconnections One Group C-X disconnections (Carbonyl derivatives, ethers, sulphides and alcohols); Two group C-X disconnections (1,1-difunctionalised, 1,2-difunctionalised and 1,3-difunctionalised compounds), One group C-C disconnections (Alcohols and carbonyl compounds, 1,1-C-C, 1,2-C-C and 1,3-C-C); Synthesis of alkenes (Wittig disconnections and diene synthesis), Two group disconnections (Diels Alder reaction and 1,3-difunctionalised compounds); Linear and convergent synthesis.

Textbooks and Books for Reference:

- 1) Some Modern Methods of Organic Synthesis W. Carothers, Third Edition, Cambridge University Press, Cambridge, 1988.
- 2) Modern Organic Synthesis-an introduction by George S.Zweifel and Michael H. Nantz, W. H. Freeman & company, New York.
- 3) Advanced Organic Synthesis, Part B-Reactions and Synthesis, Francis A. Carey and Richard J. Sudenburg, Fourt edition, Kluwer academic publishers, New York.
- 4) Organic Synthesis, Christine Willis and Martin Willis, Oxford Chemistry primers.
- 5) Principles of Organic Synthesis, ROC Norman and JM Coxon, third edition, CBS, Publisher, Delhi.
- 6) Organic Synthesis, M. B. Smith, McGraw Hill, International Edition.
- 7) Organic Chemistry, Clayden, Greeves and Stewart Warren.
- 8) Guide Book to Organic Synthesis (3rd edition), R. Mackie, D. M. Smith and Aitken.
- 9) Organo Boranes and Silanes, Thomson, Oxford Chemistry primers.
- 10) Strategic applications of named reactions in organic synthesis, Laszlo Kurti and Barbara Czako.
- 11) Organic Synthesis: The disconnection approach, S. Warrant John Wiley & sons, New York, 1984.
- 12) Modern Synthetic Reactions, Herbet O. Horase, Second Edition, W.A. Benzamine Inc. Menio Park, California, 1972.



ADIKAVI NANNAYA UNIVERSITY
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FOURTH SEMESTER

Paper – IV- BIO-ORGANIC CHEMISTRY
(Effective from the 2016-17 Admitted Batch)

UNIT-I 15 Hours

Biopolymers and Enzymes

Peptides: α -Amino acids, their general properties and synthesis, Synthesis of peptides by Merrified solid phase synthesis. Chemistry of oxytocin and dolastain-10
Enzymes-Oxidoreductases, hydrolases, transferases, synthesis of ATP, Baker's Yeast.
Enzyme models-NADH models, Bio transformations, Remotefunctionalization

UNIT-II 15 Hours

Antimalarials & Antibiotics

i. Antimalarials

Chemotherapy, synthesis and activity of antimalarial drugs- quinoline group-quinine, acridine group-quinacrine and guanidine group-paludrine.

ii. Antibiotics

General characteristics, structure- activity relationships, synthesis and activity of antibiotics: Pencillin G, Cephalosporin-C and streptomycin.

UNIT-III 15 Hours

Vitamins and Prostaglandins

Definition, occurrence, structural formulae, physiological functions and synthesis of Vitamins.

Vitamins: Structure determination and synthesis of Retinol (A), Thiamine (B₁), Riboflavin (B₂), Pyridoxine (B₆) and Biotins (H), Nicotininc acid.

Prostaglandins

Occurrence, nomenclature, classification, biogenesis and physiological effects. Synthesis of PGE₂ and PGF₂

UNIT-IV 15 Hours

Nucleic Acids:

Nucleic acids: Basic concepts of the structures of RNA and DNA and their hydrolysis products, nucleotides, nucleosides and heterocyclic bases, Genetic Code, Finger Print test.

Application of recombinant DNA technology in production of pharmaceuticals, diagnosis of diseases, insect control, improved biological detergents, gene therapy-examples.



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Reference Books and Material:

1. Chemical Aspects of Biosynthesis, John Man, Oxford University Press, Oxford, 1996.
2. Chemistry of Natural Products: A Unified Approach, N. R. Krishnaswamy, University Press (India) Ltd., Orient Longman Limited, Hyderabad, 1999.
3. Introduction to Organic Chemistry, A Streitwieser, CH Heathcock and E.M./Kosover IV Edition, McMillan, 1992. (For Merrifield synthesis of peptides and also for other aspects of Unit IV)
4. Bio-organic Chemistry, H.Dugas and C. Penney, springer, New York, 1981.
5. Details of Primary literature: Nomenclature: Structure: Dolastatin-10: JACS, 1987, 109, 6883 (structure), ibdi, 1989, 111, 5463, JCS, Parkin I, 1996, 859 (synthesis).



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III SEMESTER
Laboratory Course-1

100 M

Multistep Synthesis of Organic Compounds:

The experiments should illustrate the use of organic reagents and may involve purification of the products by chromatographic techniques.

1. Beckmann rearrangement: Benzanilide from Benzophenone
Benzophenone → Benzophenone oxime → Benzanilide
2. Benzilic acid rearrangement: Benzilic acid from benzoin
Benzoin → Benzil → Benzilic acid
3. P-Bromo Aniline from Aniline :
Aniline → Acetanilide → P-Bromo Acetanilide → P-Bromo Aniline
4. Symmetrical Tribromo Benzene from aniline:
Aniline → Tribromoaniline → Tribromobenzene
5. 2,4,6-trimethylquinoline from p-toluidine
p-toluidine → 4-(p-tolylamino) pent-3-ene-2-one → 2,4,6-trimethylquinoline
6. Flavone from o-hydroxy acetophenone
o-hydroxy acetophenone → o-benzoyl acetophenone → o-hydroxy- dibenzoylmethane → Flavone
7. 2-phenylindole from phenylhydrazine
phenylhydrazine → acetophenone phenylhydrazone → 2-phenylindole

Laboratory Course-2

100 M

Spectral Identification of Organic Compounds (UV, IR, 1^{H} - and ^{13}C - NMR, MASS).

A minimum of 40 representative examples should be studied

Books Suggested

1. Modern Organic Synthesis in the Laboratory *A Collection of Standard Experimental Procedures*, Jie Jack Li, Chris Limberakis, Derek A. Pflum
2. Practical organic chemistry by Mann & Saunders
3. Text book of practical organic chemistry by Vogel
4. Spectrometric Identification of organic compounds, R.M. Silverstein, F.X. Webster and D.J. Kiemle, 7th Ed., (Wiley)



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IV – SEMESTER
Laboratory Course-1

100 M

Chromatographic Separation and Isolation & identification of Natural Products

1. Thin layer chromatography: Determination of purity of a given sample, monitoring the progress of chemical reactions, identification of unknown organic compounds by comparing the R_f values of known standards.
2. Isolation and identification of Natural Products
 - (a) Isolation of caffeine from tea leaves
 - (b) Isolation of eugenol from cloves
 - (c) Isolation of casein and lactose from milk
 - (d) Isolation of limonene from lemon peel
 - (e) Isolation of piperines from black pepper
 - (f) Isolation of lycopene from tomatoes
 - (g) Isolation of β-carotene from carrots

Laboratory Course-2
Estimations and Chromatography

100 M

1. Estimation of (a) Glucose (b) Phenol (c) Aniline (d) Acetone (e) Aspirin (f) Ibuprofen (g) Paracetamol
2. Separation by column chromatography: Separation of a mixture of *ortho* and *para* nitroanilines using silicagel as adsorbent and chloroform as the eluent. The column chromatography should be monitored by TLC.

Books Suggested:

1. Ikan, R. *Natural Products, A Laboratory Guide*, 2nd ed.; Academic Press: New York, 1991.
2. Adapted from *Introduction to Organic Laboratory Techniques: A Microscale Approach*. Pavia, Lampman, Kriz and Engel. (1999) Saunders College Publishing.
3. Pharmaceutical drug analysis by Ashutoshkar
4. Quantitative analysis of drugs in pharmaceutical formulations by P D Sethi
5. Practical pharmaceutical chemistry part-1 and part-2 by A H Beckett and J B Stenlake
6. Practical organic chemistry by Mann & Saunders
7. Text book of practical organic chemistry including qualitative organic analysis by A.I. Vogel (Longman)