

## SYLLABUS FOR M.Sc FINAL ORGANIC CHEMISTRY

### III - SEMESTER

Paper I - Organic Reaction Mechanisms-I and pericyclic reactions

#### UNIT-I

Aliphatic Nucleophilic Substitution Mechanisms Nucleophilic substitution: Substitution reactions of ambident nucleophiles, neighbouring group participation of O, S, N, halogens, aryl groups, alkyl and cycloalkyl groups in nucleophilic substitution reactions. Sigma, Pi bond participation in acyclic and bicyclic systems (Non-classic carbocations) Substitution at allylic, trigonal and Vinylic carbons, hydrolysis of esters, Meyer's aldehydes, ketones and carboxylic acids, alkylation with trialkyl boranes.

Aliphatic Electrophilic substitutions:  $SE^1$   $SE^2$  and  $SE^i$  mechanisms hydrogen exchange, migration of double bonds, halogenation of aldehydes, ketones, acids, acylhalides sulphoxides and sulphones, aliphatic diazonium coupling, nitrosation at Carbon and nitrogen diazo transfer reaction carbene and nitrene insertion, formation of sulphur yield, metalation with organometallic compounds and with metals. Decarboxylation of aliphatic acids. Haloform reaction and Haller-Baner reaction.

#### UNIT-II

Aromatic nucleophilic substitution: A general introduction to different mechanisms of aromatic substitution  $SN_{Ar}$ ,  $AN$  and aryne Von Richter rearrangement, Sommelet, Hauser rearrangement Smiles rearrangement.

Radical substitution Mechanism: Reaction at  $Sp^3$  carbon: Reactivity in aliphatic substrates reactivity at bridged position, reactivity at  $Sp^2$  carbon. Reactivity in aromatic substrates, neighbouring group assistance in free radical reactions, effect of reactivity in the attacking radical effect of solvent on reactivity halogenation at an alkyl carbon and allylic carbon, hydroxylation at aromatic carbon by means of Fenton's reagent, oxidation of aldehydes to carboxylic acids, formation of cyclic ethers with  $Pb(OAc)_4$  Reed reaction, Sandmeyer reaction, Kolbe reaction and Hunsdiecker reaction.

#### UNIT-III

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 and secondary effects.

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 ketones secondary effects of substitutes on the rates of cycloadditions and chelotropic reactions.

#### UNIT-IV

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 rearrangements and Barton reaction.

- 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.

#### Reference Books:

- 1) Mechanisms and Theory in Organic Chemistry by T.H. Lowery and K.S. Richardson.
- 2) The modern structural theory in Organic Chemistry by L.N.Ferguson, Prentice Hall
- 3) Physical Organic Chemistry by Jack Hine, Mc. Graw Hill

## UNIT-I

Infrared spectroscopy: Units of frequency wave length and wave number, molecular vibrations, factors influencing vibrational frequencies, the IR spectrometer, sampling techniques, characteristic frequencies of organic molecules and interpretation of spectra.

## UNIT-II

Ultraviolet spectroscopy: Introduction. the absorptio $\lambda$  laws, measurement of the spectrum, chromophores, standard works of reference, definitions, applications of UV spectroscopy to Conjugated dienes, trienes, unsaturated carbonyl compounds and aromatic compounds.

## UNIT-III

Nuclear Magnetic Resonance Spectroscopy (Proton and Carbon -13 NMR)

The measurement of spectra: the chemical shift: the intensity of NMR signals and integration factors affecting the chemical shifts: spin-spin coupling to  $^{13}\text{C}$  IH-IH first order coupling: some simple IH-IH splitting patterns: the magnitude of IH-IH coupling constants:

Mass spectroscopy: Basic Principles: instrumentation: the mass spectrometer, isotope abundances; the molecular ion, metastable ions

## UNIT-IV

Separation techniques; solvent extraction Chromatography – Paper – thin layer partition – column chromatography. Electrophoresis.

### Text books:

- 1) Spectroscopic Methods in Organic Chemistry. Forth Edition D.M. Williams and I. Fleming Tata - McGraw Hill, New Delhi, 1990. For all spectral methods except ORD and CD and ESR.
- 2) Organic Spectroscopy, Second Edition, W.Kemp, ELBS Macmillan, 1987 for ORD and CD and ESR.

### Books in Reference:

- 1) Book 2 mentioned above.
- 2) Applications of absorption spectroscopy of Organic Compounds J.R.Dyer, Prentice Hall of India, New Delhi, 1984.
- 3) Spectrometric identification of Organic Compounds, Fourth Edition, R.M. Silverstein: G.C.Vassiellr and T.C. Merill, Johne Willey, Singapore, 1981.
- 4) For ORD and CD "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.Kirty John Wiley, 1972, Chapter VIII (only those aspects mentioned in the syllabus).

III - SEMESTER  
Paper III -- Organic Synthesis-I

UNIT-I

Formation of Carbon-Carbon single bonds: alkylations via enolate the enamine and related reactions umplong (dipole inversion) - The aldol reaction- applications of organ palladium, organo nickel and organo copper reagents , applications of thicarbonions- selenocarbonions and sulphur yields, synthetic applications of carbenes and carbenoids.

UNIT-II

Formation of carbon-carbon double bonds: Elimination reactions Pyrolytic, syneliminations, sulfoxide-sulphonate rearrangement the witting reaction-alkenes form arylsulphonyl-hydrazones-claisen rearrangement of allyl vinyl ethers.

UNIT-III

Methods of polymerization (a) Addition polymerization (b) Condensation polymerization and (c) Radical polymerizations (two examples of each method). Reactions of unactivated carbon-hydrogen bonds: The Hoffmann-Lieffier- Freytag reaction-the Barton reaction-Photolysis of organic hypohalites.

UNIT-IV

Synthetic applications of organoboranes

Organoboranes: Preparation of Organoboranes viz hydroboration with BH<sub>3</sub>-THF, dicyclohexyl borane, disiamyl borane, teryl borane, 9-BBN and disopinacamphyl borane, functional group transformations of Organo boranes-Oxidation, protonolysis and rearrangements. Formation, of carbon-carbon-bonds viz organo boranes carbonylation, the cyanoborate process and reaction of alkenyl boranes and trialkenyl borates.

Textbooks:

- 1) Some Modern Methods of Organic Synthesis W. Carothers, Third Edition, Cambridge University Press, Cambridge, 1988.
- 2) Organic Synthesis: The disconnection approach, S. Warratt John Wiley & sons, New York, 1984.

Books for Reference:

- 1) Modern Synthetic Reactions, Herbert O. House, Second Edition, W.A. Benzamine Inc. Menio Park, California, 1972.
- 2) Organic Synthesis viz Boranes, Herbert C. Brown Gray, W. Kramer Alan B. Levy and M. Mark Midland John Wiley & Sons, New York, 1975.

### III – SEMESTER

#### Paper IV- Natural Products and Biopolymers-I

Study of isolation, structure, stereochemistry, synthesis, biogenesis and biological properties of the following classes of natural products from plant, animal, and microbial sources and biopolymers.

#### UNIT-I

Acetogenins and shikimates:

Microbial metabolites: Pencillin G, Cephalosporin-Ö and streptomycin.

#### UNIT-II

Terpenes: Forskolin, taxol and azadirachtin.

#### UNIT-III

Alkaloids: Morphine, reserpine and vincristine

#### UNIT-IV

Biopolymers:

Peptides:  $\alpha$ -Aminoacids, their general properties and synthesis, Synthesis of peptides by Merrifield solid phase synthesis. Chemistry of oxytocin and dolastain-10.

Note: The scope of the topics of this unit, i.e., Unit IV is limited to the material contained in the books by Finar and Heathcock mentioned below.

#### Reference Material:

- 1) Organic Chemistry, Volume 2. Stereochemistry and chemistry of natural products, I.L. Finar, 5\* Edition, ELBS, 1975 (overall and for Unit IA., morphine and Unit IV).
- 2) Chemical Aspects of Biosynthesis, John Mann, Oxford University Press, Oxford, 1996
- 3) Chemistry of Natural Products: A Unified Approach, N.R. Krishnaswamy, University Press (India) Ltd., Orient Longman Limited, Hyderabad, 1999. (Overall and for certain aspects of, azadirachtin, morphine, reserpine,).
- 4) Introduction to Organic Chemistry, A Streitweiser, CH Heathcock and E.M/ Kosover IV Eeition, Me.Milan, 1992. (For Merrifield synthesis of peptides and also for other aspects of Unit IV),
- 5) Primary literature, For Unit 1B, forskolin, taxol, azadirachtin, Unit III (minus morphine) and dolastatin-10, Details and copy of the relevant material are

available with the Department of Organic Chemistry, FD & W, Andhra University, Visakhapatnam.

Details of Primary literature:

Nomenclature:

Structure: TL, 1969, 5185.

Forskolin: TL, 1977, 19, 1669; IJC, 1977. 15B, 880(structure) Tetrahedron, 48, 963, 1992 (synthesis).

Taxol: JACS, 1971, 93, 2325 (structure), Tetrahedron, 1996, 45, 14081-102, 14103-146, 14147-176 (synthesis).

Azadirachtin: JCS Perkin I, 1972, 2445; JACS, 1975, 97, 1975; JCS Chem Comm. 1985, 968, *ibid*, 1986, 46; Compendium of Indian Medicinal plants, Vol. 4, 1985-88, R.P.

Rastogi and B.N. Malhora, CDRI & Publications & Information Directorate, New Delhi, pp. 87-95.

Reserpine: Alkaloids, Manske, Vol.VIII, 1065,pp. 287-335.

Vincristine: JACS. 1964,86,1441, Alkaloids, Manske, Vol.VIII, 1965, pp, 269-285.

Dolastatin-10: JACS, 1987,109,6883(Structure), *ibid*, 1989, 111, 5463, JCS, Parkin 1, 1996,859(synthesis).

**Department of Chemistry**  
**M.Sc. Chemistry (Final Year)**  
**Specialization: ORGANIC CHEMISTRY**  
Practical syllabus for III Semester CH-305

**Practical-I: Multi stage organic synthesis**

Multistage Organic synthesis involving three or four stages

Paracetamol, 6-Methyluracil, Methyl orange, p-Aminobenzoic acid, Acridone and 2-Iodobenzoic Acid

Practical syllabus for III Semester CH-306

**Practical-II: Chromatography and Viva-Voce**

1. Thin layer chromatography: Determination of purity of a given sample and identification of unknown organic compounds by comparing the  $R_f$  values of known standards.

2. Separation by column chromatography

3. Viva-voce

## SYLLABUS FOR M.Sc FINAL ORGANIC CHEMISTRY

### IV - SEMESTER

#### Paper I - Organic Reaction Mechanisms-II and organic photochemistry

#### UNIT-I

Addition Elimination Mechanisms: (a) Addition to carbon multiple bonds- Addition reactions involving electrophiles, nucleophiles and free radicals, cyclic mechanisms, orientation and stereochemistry, hydrogenation of double and triple bonds, hydroboration, birch reduction. Michael reaction, addition of oxygen and N<sub>2</sub>O<sub>4</sub>; (b) Addition to carbon-hetero atom multiple bonds: Mannich reaction Aldol reductions of Carbonyl compounds acids, esters, nitrites, addition of Grignard reagents, Reformatsky reaction, Tollen's reaction, Wittig reaction, Prins reaction: (c) Elimination reactions: Stereochemistry of eliminations in acyclic and cyclic systems, orientation in eliminations - Saytzeff and Hoffman elimination propargylic elimination.

#### UNIT-II

Rearrangements: Classification and general mechanistic treatment of nucleophilic, free radical and electrophilic rearrangements, Wagner-Meerwein and related reactions Tiffman Demjanov rearrangement,  $\alpha$ -ketone rearrangement, Neber, Hofmann, Bayer-Villiger, Stevens Wittig rearrangements.

#### UNIT-III.

Organic Photochemistry:

Photochemical energy plank Condon Principle, Jablonski diagram singlet and triplet states, dissipation of photochemical energy, photosensitization, quenching, quantum efficiency and quantum yield, experimental methods of photochemistry.

Photochemistry of carbonyl compounds  $n \rightarrow \pi$ ,  $\pi \rightarrow \pi^*$  transitions Norrish type I and Norrish type II cleavages, Paterno-Buchi reaction.

#### UNIT-IV

Photoreduction photochemistry of enone - Hydrogen abstraction, rearrangement of  $\alpha$ ;  $\beta$  - unsaturated ketones and cyclohexadienes, Photochemistry of p- Benzoquinones, photochemistry of unsaturated systems - Olefins, cis trans Isomerisation and dimerization hydrogen abstractions and, addition acetylenes dimerisation, dienes - Photochemistry of 1,3 butadienes (2+2) additions leading to cage structures photochemistry of cyclohexadienes.

Photochemistry of aromatic compounds - Excited state of benzene its 1,2-1,3 1-4 additions, photo Fries rearrangements, photofries reactions of anilides, photosubstitution reactions of benzene derivatives.

Photochemistry of pyridinium yields, pyrolysis of nitrites esters and barton reaction. -

Text books:

- 1) Advanced Organic Chemistry: Reactions Mechanisms and Structure by Jerry March, Me.Graw Hill and Kogakush.
- 2) Molecular reactions and Photochemistry by Charles Dupey and O. Chapman, Prentice Hall.

Reference Books:

- 1) Mechanisms and Theory in Organic Chemistry by T.H. Lowery and K.S. Richardson.
- 2) The modern structural theory in Organic Chemistry by L.N.Ferguson, Prentice Hall
- 3) Physical Organic Chemistry by Jack Hine, Mc. Graw Hill

#### IV - SEMESTER Paper II- Organic Spectroscopy -- II

##### UNIT-I

Optical rotatory dispersion and circular dichroism: Phenomena of ORD and CD. Classification of ORD and CD Curves; Cotton effect curves and their application to stereochemical problems; the Octant rule and its application to alicyclic ketones.

##### UNIT-II

Improving the NMR spectrum: the mean, pulse experiment, new techniques in FT NMR spectroscopy: the separation of chemical shift and coupling on to different axes (2D-NMR, cosy), spin decoupling, the nuclear Overhauser effect associating the signals from directly bonded  $^{13}\text{C}$  and  $^1\text{H}$ . ESR Derivative curves: values and hyperfine splitting.

##### UNIT-III

Fragmentation processes; fragmentation associated with functional groups; rearrangement and mass spectra of some chemical classes.



Structural elucidation of Organic compounds by a combined application of the special methods of Units 1-III.

#### UNIT-IV

Separation Techniques; Instrumentation – Gas Chromatography, High performance Liquid Chromatography, X – Ray diffraction (XRD)

Text books:

- 1) Spectroscopic Methods in Organic Chemistry. Forth Edition D.M. Williams and I. Fleming Tata - McGraw Hill, New Delhi, 1990. For all spectral methods except ORD and CD and ESR.
- 2) Organic Spectroscopy, Second Edition, W.Kemp, ELBS Macmillan, 1987 for ORD and CD and ESR.

Books in Reference:

- 1) Book 2 mentioned above.
- 2) Applications of absorption spectroscopy of Organic Compounds J.R.Dyer, Prentice Hall of India, New Delhi, 1984.
- 3) Spectrometric identification of Organic Compounds, Fourth Edition, R.M. Silverstein; G.C.Vasslellr and T.C. Merill, John Willey, Singapore, 1981. For ORD and CD "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).

### IV-SEMESTER

#### Paper III - Organic Synthesis-II

##### UNIT-I

Organo silanes. Synthetic applications of trimethylsilyl chloride dimethyl-t-butylsilyl chloride, trimethylsilyl cyanide, trimethylsilyl iodide and trimethylsilyl triflate, synthetic applications of: silyl carbanion and B-silyl carbonium ions.

Phase transfer catalysis-Principle and applications.

##### UNIT-II

Oxidation: Oxidations of hydrocarbons, alkenes, alcohols aldehydes and ketones oxidative coupling reactions. Use of  $Pb(OAc)_4$ ,  $Nb_2O_5$ ,  $CrO_3$ ,  $SeO_2$ ,  $NiO_2$  Dc- alkoxyphonium yields,  $KMnO_4$ ,  $OsO_4$ , peracids and Ti (III) nitrate.

##### UNIT-III

REDUCTION: Catalytic hydrogenation (homogeneous and heterogeneous), reduction by dissolving metals. reduction by hydride transfer -reagents, reduction with hydrazine and diamide, selectivity in reduction of nitroso and nitro compounds, reductive cleavage.

#### UNIT-IV

Design of Organic Synthesis: Retrosynthesis the disconnection approach-basic principles convergent and linear synthesis.

##### Textbooks:

- 1) Some Modern Methods of Organic Synthesis W. Carothers, Third Edition, Cambridge University Press, Cambridge, 1988.
- 2) Organic Synthesis: The disconnection approach, S. Warren John Wiley & sons, New York, 1984.

##### Books for Reference:

- 1) Modern Synthetic Reactions, Herbert O. House, Second Edition, W.A. Benjamin Inc. Menlo Park, California, 1972.
- 2) Organic Synthesis via Boranes, Herbert C. Brown Gray, W. Kramer Alan B. Levy and M. Mark Midland John Wiley & Sons, New York, 1975.

IV - SEMESTER  
Paper IV- Natural Products and Biopolymers-II

Study of isolation, structure, stereochemistry, synthesis, biogenesis and biological properties of the following classes of natural products from plant, animal, and microbial sources and biopolymers.

UNIT-1

Acetogenins and shikimates:

Prostaglandin 15 R F GAy podophyllotoxin, etoposide and rotenone.

UNIT-II

Terpenes and Steroids:

cholesterol, progesterone And  $\beta$ - amyryn •

UNIT-III

Alkaloids:

strychnine, colchicines and camptothecin.

UNIT-IV

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

Reference Material:

- 1) Organic Chemistry, Volume 2, Stereochemistry and chemistry of natural products, I.L. Finar, 5<sup>th</sup> Edition. ELBS, 1975 (overall and for Unit IA., cholesterol, progesterone, and Unit TV).
- 2) Chemical Aspects of Biosynthesis, John Mann, Oxford University Press, Oxford, 1996
- 3) Chemistry of Natural Products: A Unified Approach, N.R. Krishnaswamy, Universe Press (India) Ltd., Orient Longman Limited, Hyderabad, 1999. (Overall and for certain aspects of rotenone,  $\beta$ -amyryn, strychnine, and colchicines).

Primary literature, For Unit 1, Unit III (minus morphine) and Details and copy of the relevant material are available with the Department of Organic Chemistry, FD & W, Andhra University, Visakhapatnam.

**Department of Chemistry**  
**M.Sc. Chemistry (Final Year)**  
**Specialization: ORGANIC CHEMISTRY**  
Practical syllabus for IV Semester CH405

**Practical-I: Organic mixture analysis**

Separation of two component mixtures by chemical methods and their identification by chemical reactions — separation by using solvent ether, 5 % aqueous sodium bicarbonate, 5% sodium hydroxide and dil hydrochloric acid, checking the purity of the two components by TLC, identification of the compounds by a systematic study of the physical characteristics (mp/bp), extra elements (nitrogen, halogens and sulfur), solubility, functional groups, preparation of crystalline derivatives and identification by referring to literature. A minimum of 5 mixtures should be separated and analyzed by these procedures.

**Department of Chemistry**  
**M.Sc. Chemistry (Final Year)**  
**Specialization: ORGANIC CHEMISTRY**  
Practical syllabus for IV Semester CH406

**Practical-II: Estimations and Isolation**

A) Estimation of the following compounds

i) Glucose ii) Phenol iii) Aniline iv) Aspirin (titrimetry) v) Ibuprofen (titrimetry)

B) Isolation of the following compounds

i) Caffeine from tea leaves (solvent extraction) ii) Piperine from pepper (Soxhlet extraction)

ii) Lycopene from tomato

Books Suggested :

1 A text book of practical Organic chemistry by A.I. Vogel, ELBS and Longman group.

2. Practical Organic chemistry by Mann and Saunders, ELBS and Longman group

3. Laboratory Manual of Organic Chemistry by Raj K Bansal

ANDHRA UNIVERSITY  
DEPARTMENT OF INORGANIC AND ANALYTICAL CHEMISTRY

M.Sc. (PREVIOUS)  
(SCHOOL OF CHEMISTRY)

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I SEMESTER

PAPER I: GENERAL CHEMISTRY:

QUANTUM CHEMISTRY-I AND MOLECULAR SPECTROSCOPY

BASIC QUANTUM CHEMISTRY:

UNIT I:

Wave equation-interpretation of wave function-properties of wave function-normalisation and orthogonalisation, Operators- linear and non-linear- commutators of operators. Postulates of quantum mechanics, Setting up of operators observables- Hermitian operator- Eigen values of Hermitian operator

UNIT II:

Wave mechanics of simple systems with constant potential energy, particle in one dimensional box - factors influencing colour-transition - dipole integral, Symmetry arguments in deriving the selection rules - the concept of tunneling - particle in a three dimensional box. Rigid rotor, Wave mechanics of systems with variable potential energy- simple harmonic oscillator - solution of wave equation - selection rules

MOLECULAR SPECTROSCOPY:

UNIT III:

Rotational spectra of diatomic molecules- Rigid rotor-Selection Rules-Calculation of bond length-isotopic effect, Second order Stark effect and its applications, Infrared spectra of diatomic molecules-harmonic and anharmonic oscillators- Selection rules-overtone-combination bands-Calculation of force constant, anharmonicity constant and zero point energy. Fermi resonance, Simultaneous vibration-rotation spectra of diatomic molecules

UNIT IV:

Raman effect- Classical and Quantum mechanical explanations- Rotational Raman and Vibrational Raman spectra, Electronic spectra of diatomic molecules- Vibrational coarse structure-intensity of spectral lines- Franck Condon principle- applications, Rotational fine structure-band head and band shading, Charge transfer spectra.

**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 ( $\text{PtCl}_4^{2-}$ ) and Octahedral complexes ( $\text{CoF}_6^{3-}$ ,  $\text{Co}(\text{NH}_3)_6^{3+}$ ).

Walsh diagram for  $\text{H}_2\text{O}$  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 ( $\text{S}_4\text{N}_4$ ,  $(\text{SN})_x$ ) 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  $\beta$  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)

DEPARTMENT OF INORGANIC AND ANALYTICAL CHEMISTRY

List of Experiments for M.Sc., previous Inorganic chemistry practicals CH-105

**Semester – I**

**I. Inorganic Synthesis:** Preparation of

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

**II. Semimicro qualitative analysis of six radical mixtures**

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

**Anions:**  $\text{CO}_3^{2-}$ ,  $\text{S}^{2-}$ ,  $\text{SO}_3^{2-}$ ,  $\text{Cl}^-$ ,  $\text{Br}^-$ ,  $\text{I}^-$ ,  $\text{NO}_3^-$ ,  $\text{SO}_4^{2-}$ ,  $\text{CH}_3\text{COO}^-$

$\text{C}_2\text{O}_4^{2-}$ ,  $\text{C}_4\text{H}_4\text{O}_6^{2-}$ ,  $\text{PO}_4^{3-}$ ,  $\text{CrO}_4^{2-}$ ,  $\text{AsO}_4^{3-}$ ,  $\text{F}^-$ ,  $\text{BO}_3^{3-}$

**Cations :** Ammonium ( $\text{NH}_4^+$ )

1<sup>st</sup> group: Hg, Ag, Pb, Tl, W

2<sup>nd</sup> group: Hg, Pb, Bi, Cu, Cd, As, Sb, Sn, Mo

3<sup>rd</sup> group: Fe, Al, Cr, Ce, Th, Ti, Zr, V, U, Be

4<sup>th</sup> group: Zn, Mn, Co, Ni

5<sup>th</sup> group: Ca, Ba, Sr

6<sup>th</sup> group: Mg, K, Li

**SYLLABUS FOR M.Sc CHEMISTRY**

**Organic Chemistry**

Specialisations (1) Organic Chemistry and (2) Chemistry and Analysis of Foods, Drugs and Water,- of the Department of Organic Chemistry, and Chemistry and Analysis of Foods, Drugs and Water, Andhra University, Visakhapatnam - 530 003.

I - SEMESTER

Course/Paper - III: Organic Chemistry - 1

UNIT - I

Structure and reactivity: Localised and delocalised covalent bond - Concept of resonance and aromaticity - Huckel's rule for aromaticity in benzenoid and non-benzenoid compounds, anti-aromaticity and homo-aromaticity. Nature of reaction energy and kinetic considerations - types of organic reactions - reagents - reactive intermediates. Their formation and stabilization - inductive and mesomeric effects.

UNIT - II

Stereochemistry and stereoisomerism. Conformational isomerism and analysis in acyclic and simple cyclic systems - substituted ethanes, cyclopentane, cyclohexane cycloheptane, cyclo octane and decalins, optical isomerism - optical activity - molecular dissymmetry and chirality - elements of symmetry.

Fisher's projection D,L. and R,S. configurations - relative and absolute configurations optical isomerism due to asymmetric carbon atoms - optical isomerism in biphenyls, allenes and spirans

- optical isomerism of nitrogenous compounds racemisation and resolution - geometrical isomerism and E,Z configurations, properties of geometrical isomers.

### UNIT - III

Chemistry of heterocyclic compounds, synthesis and reactivity of the following systems

-  
Pyridine, quinoline, Isoquinoline, Indole, Benzofuran, Benzothiophene - Pyrazole, Imidazole, Oxazole, Isoxazole, Thiazole, Isothiazole, Pyridazine, pyrimidine and Pyrazine.

### UNIT - IV

Chemistry of some typical natural products. A study of the following compounds involving their isolation, structure elucidation, synthesis and biogenesis - flavonoids - quercetin, cyanidin and genestein, terpenoids,  $\alpha$ - terpineol  $\alpha$  - pinene, camphor, farnesol.

## First SEMESTER

### PRACTICAL IIP: ORGANIC CHEMISTRY PRACTICAL -I CH106

synthesis of Aspirin, benzoic acid, p-nitroaniline from aniline, methyl, 2-naphthyl ether, Anthranilic acid, 2,4-dinitro phenyl hydrazine, Sym- Tribromo benzene, Benzanilide.

## ANDHRA UNIVERSITY-SCHOOL OF CHEMISTRY

### I Semester

### CH-104 PHYSICAL CHEMISTRY-I

(Effective from the admitted batch of 2011-12)

#### UNIT-I:

Thermodynamics: Chemical equilibrium- effect of temperature on equilibrium constant-Van't Hoff equation. Partial molar quantity- different methods of determination of partial molar quantity. Chemical potential- Phase rule and its derivation, Gibbs-Duhem equation, Duhem-Margules equation, Clausius-Clapeyron equation. Nernst heat theorem. Third law of thermodynamics- Determination of the absolute entropy- Apparent exceptions to Third law of thermodynamics.

#### UNIT-II:

Micelles and Macromolecules: 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.

Polymers- Definition, types of polymers, electrically conducting, fire resistant, liquid crystal polymers, kinetics of polymerization. Molecular mass- Number and mass average molecular mass, molecular mass determination- Osmometry, viscometry, diffusion and light scattering methods. Sedimentation, chain configuration of macromolecules, calculation of average dimensions of various structures.

#### 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. 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. 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 isomerization reactions with examples.

**Text 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 K.L. Kapoor

**Reference Books:**

1. Thermodynamics for Chemists, Samuel Glasstone
2. Chemical Kinetics by K.J.Laidler, McGraw Hill Pub.
3. Photochemistry, R.P. Kundall and A. Gilbert, Thomson Nelson.
4. Introduction to Polymer Science, V.R. Gowriker, N.V.Viswanadhan and J. Sreedhar., Wiley Easter.
5. Micelles, Theoretical and applied aspects, V.Moroi, Plenum publishers.

**First SEMESTER**

**PRACTICAL IIIP: PHYSICAL CHEMISTRY PRACTICAL –I CH107**

1. Critical Solution Temperature of partially miscible liquids phenol-water System.
2. Effect of electrolyte (NaCl) on miscibility temperature.
3. Determination of cell constant.
4. Determination of  $P_k$ , value of acetic acid by conductometric method.
5. Conductometric titration of strong acid with strong base (HCL vs NaOH)
6. Conductometric titration of a weak acid strong base (HOAc vs NaOH)

- Books suggested:
9. Practical Experiments in Physical Chemistry by Alexander Finallay.
  10. Experiments in Chemistry by D.V. Jahagirdan. Himalaya Pub. House, 2003.
  11. Physical chemistry experiments by P. Ghosh.

AND HRA UNIVERSITY  
DEPARTMENT OF INORGANIC AND ANALYTICAL CHEMISTRY

II SEMESTER

M.Sc. (PREVIOUS)

(SCHOOL OF CHEMISTRY)

II SEMESTER

PAPER I: GENERAL CHEMISTRY — II

QUANTUM CHEMISTRY-II, SYMMETRY- GROUP THEORY AND  
ELEMENTS OF COMPUTER PROGRAMMING.

UNIT I:

Hydrogen atom-solution of  $R(r)$ ,  $\Phi(\phi)$  and  $\Theta(\theta)$  equations-probability density in orbitals- shapes of orbitals. Perturbation theory- time independent perturbation (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:

Valence bond approach- directed valence- hybridization- covalent bond- calculation of ionic and covalent bond contributions in hydrogen molecule. Molecular orbital theory - LCAO approximation - hydrogen molecule ion - hydrogen molecule (fundamental concepts only)- The electronic transitions in the hydrogen molecule.

MOLECULAR SYMMETRY AND GROUP THEORY

UNIT III:

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 Transformation and classes- Representations- reducible and irreducible representations, Mulliken symbols, Orthogonality theorem and its implications, Character table and its anatomy.

ELEMENTS OF COMPUTER PROGRAMMING:

UNIT IV:

Basic components of Computers, higher and lower level languages, Microsoft Fortran: constants, variables and operators, arithmetic expressions, assignment and replacement statements, Input and Output statements- Format free and Format directed I/O statements- Iw, Fw.d, Ew.d and Gw.d format specifications, conditional and unconditional statements- Logical IF, Block IF and Go To statements, Do statement- syntax and rules.

Application to Chemical Problems:

Flowcharts and Programs for

M.Sc. Previous Chemistry Syllabus, Semester - II  
**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.

$\text{Re}_2\text{Cl}_8^{2-}$ ,  $\text{Mo}_2\text{Cl}_8^{4-}$ ,  $\text{Re}_2(\text{RCOO})_4\text{X}_2$ ,  $\text{Mo}_2(\text{RCOO})_4(\text{H}_2\text{O})_2$ ,  $\text{Cr}_2(\text{RCOO})_4(\text{H}_2\text{O})_2$ ,  $\text{Cu}_2(\text{RCOO})_4(\text{H}_2\text{O})_2$ ,  $\text{Cr}_2\text{Cl}_9^{3-}$ ,  $\text{Mo}_2\text{Cl}_9^{3-}$ ,  $\text{W}_2\text{Cl}_9^{3-}$ ,  $\text{Re}_3\text{Cl}_9$ ,  $\text{Re}_3\text{Cl}_{12}^{3-}$ ,  $\text{Mo}_6\text{Cl}_8^{4+}$ ,  $\text{Nb}_6\text{X}_{12}^{2+}$  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,  $\text{CH}_3$ ,  $\text{Mn}(\text{CO})_5$ ; S,  $\text{CH}_2$ ,  $\text{Fe}(\text{CO})_4$ ; 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 valence bond and crystal field theories.

**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.

DEPARTMENT OF INORGANIC AND ANALYTICAL CHEMISTRY

List of Experiments for M.Sc., previous Inorganic chemistry practicals CH-205

**Semester –II**

**III Quantitative analysis:**

- a) **Volumetric** : i) Determination of Ferric iron by photochemical reduction

- ii) Determination of Nickel by EDTA
- iii) Determination of Calcium and Magnesium in a mixture by EDTA
- iv) Determination of Ferrocyanide by Ceric sulphate
- v) Determination of Copper(II) in presence of iron(III)

- b) Gravimetric:**
- i) Determination of Zinc as Zinc pyrophosphate
  - ii). Determination of Nickel from a mixture of Copper and Nickel.

Course/Paper - III: Organic Chemistry - 2 ,

UNIT - I

Aromatic substitution reactions - electrophilic, nucleophilic and through benzyne - radical substitution of arenes - orientation of nucleophilic substitution at a saturated carbon, SN1, SN2, SNi reactions -effect of structure, nucleophile, leaving group, solvent. Additions involving electrophiles, nucleophiles and free radicals.

Elimination reactions - E1, E1CB, E2 reactions – elimination versus substitution reactions.

U.NIT - II

Mechanism of some name reactions: Aldol, Perkin, Benzoin, Cannizzaro, Wittig, Grignard, Reformatsky - Meerwein, Hoffmann Claisen and Favorsky rearrangements. Hydroboration - openauer oxidation, clemmensen reduction - Meerwein - Ponderf and verley and Birch reductions. Stork enamine reactions, Michael addition, Mannich Reaction, Diels - Alder reaction, Ene - reaction, Bayer - Villiger Reaction.

UNIT - III

Spectra and structure - application of organic spectroscopy UV, IR, <sup>1</sup>HNMR and Mass spectral data.

UNIT - IV

Isolation, structure elucidation and synthesis of alkaloids; atropine, nicotine, and quinine. Purines - Caffeine configuration and ring structures of glucose and fructose, anomeric effects.

Text books:

1. Organic Chemistry Vol. I (Sixth Edn.) and Vol. II (Fifth Ed.,) by I.L. Finar ELBS.
2. Organic Chemistry (fifth Edn., ) by Morrison and Boyd, PHI, India.
3. Organic Chemistry (fifth edition) by Francis A. Carey Tata Mc Graw Hill publishing company Limited, New Delhi.
4. Reaction Mechanism in Organic Chemistry by Mukherjee Sirigh, NTerniitarr, Indiar
5. A guide book to mechanism in Organic Chemistry by Peter Sykes, ELBS.

REFERENCE BOOKS:

Advanced organic chemistry by Jerry March (4th Edition)Wiley

Eastern. .

Chemistry of Natural Products, K.W.Bentley by stereochemistry of carbon compounds by E.Eliel, John Wiley & Sons, Inc.

Stereochemistry of Organic compounds by D. Nasipuri.

Chemistry of Natural products by R.S. Kalsi Kalyani Publishers. 1983.

## **Second SEMESTER**

### **PRACTICAL IIP: ORGANIC CHEMISTRY PRACTICAL –II CH-206**

#### **Practical-II: Organic analysis**

Identification of the compounds by a systematic study of the physical characteristics (mp/bp), extra elements (nitrogen, halogens and sulfur), solubility, functional groups, preparation of crystalline derivatives and identification by referring to literature. A minimum of 6 Compounds should be analyzed by these procedures.

## **SCHOOL OF CHEMISTRY ANDHRA UNIVERSITY** **II Semester** **CH-204 PHYSICAL CHEMISTRY-II** **(Effective from the admitted batch of 2011-12)**

#### **UNIT-I:**

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

#### **UNIT-II:**

Electron Spin Resonance: Principle and experimental technique- g-factor, line shapes and line widths- hyperfine interactions- applications of ESR studies to the structure of free radicals, metal complexes and biological systems.

#### **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. Activity coefficient from EMF data. Primary and secondary cells, batteries examples. Fuel cells.

#### **UNIT-IV:**

Electrochemistry II: The electrode-electrolyte interface. The electrical double layer. The Helmholtz-Perrin parallel-plate model, the Gouy-Chapman diffuse-charge model and the Stern model. Electrode reactions: Charge transfer reactions at the electrode-electrolyte interface.

Exchange current density and overpotential. Derivation of Butler-Volmer equation. High field approximation, Tafel equation, Low field equilibrium, Nernst equation. Voltammetry-Concentration polarization, experimental techniques.

**Text Books:**

4. Physical Chemistry by Peter Atkins and Julio de Paula, Oxford University Press.
5. Physical Chemistry by G.W. Castellon, Narosha Publishing House
6. Physical chemistry by K.L. Kapoor

**Reference Books:**

6. Introduction to Electrochemistry, S.Glasstone.
7. Fundamentals of Molecular Spectroscopy, Banwell
8. Spectroscopy by Barrow.

**II SEMESTER**

**PRACTICAL IIIP: PHYSICAL CHEMISTRY PRACTICAL – II CH207**

1. Determination of composition of cuprammonium cation.
2. Determination of equilibrium constant of the reaction:  $KI + I_2 = KI_3$
3. Conductometric titration of mixture of a strong acid and weak acid weak acid with a strong base (HCl + HOAc) vs NaOH.
4. Potentiometric titration of iron (II) with  $K_2Cr_2O_7$
5. Determination of relative strength of acids (HCl) by ester hydrolysis
6. Polarimetric determination of relative strength of acids by hydrolysis of sucrose.

**Books suggested:** 1. Practical Experiments in Physical Chemistry by

Alexander Finallay

2. Experiments in Chemistry by D.V. Jahagirdan.

Himalaya pub. House, 2003.

3. Physical chemistry experiments by P. Ghosh.