

# UNIVERSITY OF RAJASTHAN JAIPUR

# **SYLLABUS**

# M.SC. CHEMISTRY

# **Annual Scheme**

M.Sc. (Previous)Examination 2020

M.Sc. (Final) Examination 2021

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(Academic)
University of Rejesthan

Syllabus: M.Sc. Chemistry

# M.Sc. (CHEMISTRY) (Annual Scheme)

### SCHEME OF EXAMINATION

Each Theory Paper: 3 Hrs. Duration

Dissertation/Thesis/ Survey Report: Field Work, if any.

- The number of papers and the maximum marks for each paper/ practical shall be shown in the syllabus for the subject concerned. It will be necessary for a candidate to pass in the theory part as well as in practical part (wherever prescribed) of a subject/paper separately.
- A candidate for a pass at each of the Previous and the Final Examinations shall be required to obtain:
  - 1) Atleast 36% marks in the aggregate of all the papers prescribed for the examination, and
  - 2) Atleast 36% marks in practical(s) wherever prescribed at the examination, provided that if a candidate fails to secure atleast 25% marks in each individual paper at the examination and also in the dissertation/Survey report/field work, wherever prescribed, he shall be deemed to have failed at the examination notwithstanding his having obtained the minimum percentage of marks required in the aggregate for that examination. No division will be awarded at the Previous and the Final Examination. Division shall be awarded at the end of the Final Examination on the combined marks obtained at the Previous and the Final Examination taken together, as noted below :

First Division

60% of the aggregate marks taken together of the

Second Division

48% Previous and the Final Examination.

All the rest will be declared to have passed the examination.

- 3. If a candidate clears any Paper(s)/ Practical(s)/ Dissertation prescribed at the Previous and/or Final Examination after a continuous period of three years, then for the purpose of working out his division the minimum pass marks only viz. 25% (36% in the case of practical) shall be taken into account in respect of such Paper(syPractical(syDissertation as are cleared after the expiry of the aforesaid period of three years: provided that in case where a candidate required more than 25% marks in order to reach the minimum aggregate as many marks out of those actually secured by him will be taken into account as would enable him to make up the deficiency in the requisite minimum, aggregate.
- 4. The Thesis/Dissertation/Survey Report/Field Work shall be typewritten and submitted in triplicate so as to reach the office of the Registrar atleast 3 weeks before the commencement of the theory examinations. Only such candidates shall be permitted to offer Dissertation! Field Work/Survey Report/Thesis (if provided in the scheme of examination) in lieu of a paper as have secured atleast 55% marks in the aggregate of all the papers prescribed for the previous examination in the case of annual scheme irrespective of the number of papers in which a candidate actually appeared at the examination.

N.B. Non-collegiate candidates are not eligible to offer dissertation as per provisions of O. 170-A

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### M.Sc. Chemistry (Two Year Course)

Note: In each question paper 10 questions will be set. Candidates have to answer 5 questions selecting at least one question from each unit.

MSc. I Year (Previous)

Paper	Course No.	Course	Exam Duration (Hours)	Max Marks	Min Marks
Paper-l	CH-401	Inorganic Chemistry	03	100	36
Paper-II	CH-402	Organic Chemistry	03	100	36
Paper-III	CH-403	Physical Chemistry	03	100	36
Paper-IV	CH-404	Spectroscopy and Diffraction Methods	03	50	18
Paper-V	per-V CH-405 Green and Sustainable Chemistry		03	50	18
Paper-VI	CH-406	Analytical Techniques	03	50	18
Practical	CH-407		14	200	72
			Total Marks	650	

# M.Sc. II Year (Final)

Paper	Course No.	Course	Exam Duration Hours	Max Manks	Min Marks
Paper-I	CH-501	Applications of Spectroscopy, Photochemistry and Solid State Chemistry	03	100	36
Paper-II	CH-502	Bioinorganic Chemistry Bioorganic Chemistry Biophysical Chemistry	03	75	27
Paper-III	CH-503	Environmental Chemistry	03	50	18
Paper-IV	CH-504	Elective Paper	03	50	18
Paper-V	CH-505	Elective Paper	03	50	18
Paper-VI	er-VI CH-506 Elective Paper		03	50	18
Paper-VII	CH-507	Elective Paper	03	50	18
Seminar	CH-508			25	9
Practical	CH-509		14	200	72
<del></del>	M.Sc. I	Year (Previous) & II Year (Final)	Total Marks Grand Total	650 1300	

The following alternative groups of elective papers are approved for M.Sc. II Year course. College / department having more than 30 seats has to offer minimum two elective groups.

Group-I	CH-504	Organotransition Metal Chemistry
	CH-505	Bioinorganic and Supramolecular Chemistry
	CH-506	Photoinorganic Chemistry
	CH-507	Polymers
Group-II	CH-504	Organic Synthesis-I
	CH-505	Organic Synthesis-II
	CH-506	Heterocyclic Chemistry
	CH-507	Chemistry of Natural Products
Group-III	CH-504	Analytical Chemistry
	CH-505	Physical Organic Chemistry
	CH-506	Chemical Dynamics
	CH-507	Electrochemistry

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# M.Sc. I YEAR (PREVIOUS)

# Paper I: CH - 401 Inorganic Chemistry (4 hrs. or 6 periods / week)

Exam Duration: 3 hrs.

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Max. Marks: 100

#### Unit-I

#### Symmetry and Group Theory in Chemistry

Symmetry elements and symmetry operation, definition of group, subgroup, relation between orders of a finite group and its subgroup. Conjugacy relation and classes. Point symmetry group. Schonflies symbols, representations of groups by metrics (representation for the  $C_n$ ,  $C_{nv}$ ,  $D_{nh}$ , etc., groups to be worked out explicitly). Character of a representation. The great orthogonality theorem (without proof) and its importance. Character tables and their uses; spectroscopic derivation of character table for  $C_{2v}$  and  $C_{3v}$  point group. Symmetry aspects of molecular vibrations of  $H_2O$  molecule.

#### Unit-II

# Stereochemistry and Bonding in Main Group Element Compounds

VSEPR, Walsh diagram [tri-atomic (AH<sub>2</sub> type) and penta-atomic (CH<sub>3</sub>I) molecules].  $d\pi$ -p $\pi$  bond. Bent rule and energetics of hybridization, some simple reactions of covalently bonded molecules.

Metal-Ligand bonding: Limitations of crystal field theory. Molecular orbital theory: octahedral, tetrahedral and square planar complexes and  $\pi$ -bonding complexes.

Metal Clusters: Higher boranes, carboranes, metalloboranes and metallocarboranes, compounds with metal-metal multiple bonds.

#### Unit-III

# Electronic Spectra and Magnetic Properties of Transition Metal Complexes

Spectroscopic ground states, correlation. Orgel and Tanabe-Sugano diagrams for transition metal complexes ( $d^1-d^9$  states), calculations of D $\alpha$ , B and  $\beta$  parameters, charge transfer spectra, spectroscopic method of assignment of absolute configuration in optically active metal chelates and their stereochemical information, anomalous magnetic moments, magnetic exchange coupling and spin crossover.

#### Unit-IV

#### Reaction Mechanism of Transition Metal Complexes

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

#### Unit-V

### Nuclear and Radiochemistry:

Laws of radioactive decay; Detection of radiations; Geiger-Nuttal rule; GM tubes and their characteristics; Ionization chamber, Proportional counters, Scintillation counters; Solid state detectors; Calibration of counting equipments; Determination of absolute disintegration rates.

Activation analysis: Principles; Various methods of activation; Methodology; Advantages, limitations and applications.

#### Books Suggested:

1. Chemical Applications of Group Theory. F A. Cotton.

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- 2. Advanced Inorganic Chemistry, F.A. Cotton and Wilkinson, John Wiley.
- 3. Inorganic Chemistry, J.E. Huheey, Harper & Row.
- 4. Chemistry of the Elements. N.N. Greenwood and A. Earnshow, Pergamon.
- norganic Electronic Spectroscopy, A.B.P. Lever, Elsevier.
- 6. Magnetochemistry, R.I. Carlin, Springer Verlag.
- 7. Comprehensive Coordination Chemistry, Eds. G. Wilkinson. R.D. Gillars and J.A. McCleverty, Pergamon.
- 8. Nuclear and Radiochemistry; G. Friedlander, J. W. Kennedy, E. S. Macias and J. M. Miller; 3<sup>rd</sup>Edn., Wiley: NY, 1981.
- 9. Essentials of Nuclear Chemistry, H. J. Arnikar, 4<sup>th</sup>Edn., New Age International: N Delhi, India, 2011.
- 10. Nuclear and Radiochemistry: Fundamental and Applications, 2 Vols., Jens-Volker Kratz and Karl Heinrich Lieser; 3<sup>rd</sup>Edn., John Wiley & Sons: UK, 2013.

# Paper II: CH -402 Organic Chemistry (4 hrs. or 6 periods / week)

Exam Duration: 3 hrs.

Max. Marks: 100

#### Unit-I

#### Nature of Bonding in Organic Molecules

Delocalized chemical bonding - conjugation, cross conjugation, resonance, hyperconjugation, bonding in fullerenes, tautomerism.

Aromaticity in benzenoid and non-benzenoid compounds, alternant and non-alternant hydrocarbons. Huckel's rule, energy level of  $\pi$ -molecular orbitals. Annulenes, anti-aromaticity, homo-aromaticity. PMO approach.

#### Stereochemistry

Conformational analysis of cycloalkanes, decalins, effect of conformation on reactivity, conformation of sugars, strain due to unavoidable crowding. Elements of symmetry, chirality, molecules with more than one chiral centre, three and erythre isomers, methods of resolution, optical purity. Enantiotopic and diastereotopic atoms, groups and faces. Stereospecific and stereoselective synthesis. Asymmetric synthesis. Optical activity in the absence of chiral carbon (biphenyls, allenes and spiranes), chirality due to helical shape. Stereochemistry of the compounds containing nitrogen, sulphur and phosphorus.

#### Unit-II

#### Reaction Mechanism: Structure and Reactivity

Types of mechanisms, types of reactions, thermodynamic and kinetic requirements, kinetic and thermodynamic control, Hammond's postulate, Curtin-Hammett principle. Potential energy diagrams, transition states and intermediates. Methods of determining mechanisms, isotope effects. Generation, structure, stability and reactivity of carbocations, carbanions, free radicals, carbenes and nitrenes.

Effect of structure on reactivity, resonance and field effects, steric effect, quantitative treatment. The Hammett equation and linear free energy relationship, substituent and reaction constants, Taft equation.

#### Aliphatic Nucleophilic Substitution

The  $S_N2$ ,  $S_N1$ , mixed  $S_N1$ - $S_N2$  and SET mechanisms.

The neighbouring group mechanism, neighbouring group participation by  $\pi$  and  $\sigma$  bonds, anchimeric assistance. Classical and nonclassical carbocations, phenonium ions, norbornyl system, common carbocation rearrangements. The  $S_N$ i mechanism. Nucleophilic substitution at the allylic, aliphatic trigonal and a vinylic carbon.

Reactivity effects of substrate structure, attacking nucleophile, leaving group and reaction medium, phase transfer catalysis and ultrasound. Ambident nucleophile, regioselectivity.

#### Unit-III

#### Aliphatic Electrophilic Substitution

Bimolecular mechanisms -  $S_E2$  and  $S_Ei$ . The  $S_E1$  mechanism - electrophilic substitution accompanied by double bond shifts. Effect of substrates, leaving group and the solvent polarity on the reactivity.

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#### Aromatic Electrophilic Substitution

The arenium ion mechanism, orientation and reactivity, energy profile diagrams. The ortho/para ratio, ipso attack, orientation in other ring systems. Quantitative treatment of reactivity in substrates and electrophiles. Diazonium coupling, Vilsmeir reaction, Gattermann-Koch reaction.

#### Aromatic Nucleophilic Substitution

The  $S_NAr$ ,  $S_N1$ , benzyne and  $S_{RN}1$  mechanisms. Reactivity - effect of substrate structure, leaving group and attacking nucleophile. The von Richter, Sommelet-Hauser and Smiles rearrangements.

#### Free Radical Reactions

Types of free radical reactions, free radical substitution mechanism, mechanism at an aromatic substrate, neighbouring group assistance. Reactivity for aliphatic and aromatic substrates at a bridgehead. Reactivity in the attacking radicals. The effect of solvents on reactivity. Allylic halogenation (NBS), coupling of alkynes and arylation of aromatic compounds by diazonium salts. Sandmeyer reaction. Free radical rearrangement, Hunsdiecker reaction.

#### Unit-IV

#### Addition to Carbon-Carbon Multiple Bonds

Mechanistic and stereochemical aspects of addition reactions involving electrophiles, nucleophiles and free radicals. Regio- and chemoselectivity. Orientation and reactivity. Addition to cyclopropane ring. Hydrogenation of double and triple bonds, hydrogenation of aromatic rings. Hydroboration. Michael reaction. Sharpless asymmetric epoxidation.

### Addition to Carbon-Hetero Multiple Bonds

Mechanism of metal hydride reduction of saturated and unsaturated carbonyl compounds, acids, esters and nitriles. Addition of Grignard reagents, organozine and organolithium reagents to carbonyl and unsaturated carbonyl compounds. Wittig reaction.

Mechanism of condensation reactions involving enolates - Aldol, Knoevenagel, Claisen, Mannich, Benzoin, Perkin and Stobbe reactions. Hydrolysis of esters and amides, ammonolysis of esters.

#### **Elimination Reactions**

The E2, El and ElcB mechanisms and their spectrum. Orientation of the double bond. Reactivity - effects of substrate structures, attacking base, the leaving group and the medium. Mechanism and orientation in pyrolytic elimination.

#### Unit-V

#### **Pericyclic Reactions**

Molecular orbital symmetry, Frontier orbitals of ethylene, 1,3-butadiene, 1,3,5-hexatriene and allyl system. Classification of pericyclic reactions. Woodward-Hoffmann correlation diagrams. FMO and PMO approach. Electrocyclic reactions - conrotatory and disrotatory motions. 4n, 4n+2 and allyl systems. Cycloadditions - antarafacial and suprafacial additions. 4n and 4n+2 systems, 2+2 addition of ketenes. 1,3-dipolar cycloadditions and chelotropic reactions.

Sigmatropic rearrangements - Suprafacial and antarafacial shifts of H, sigmatropic shifts involving carbon moieties. 3,3- and 5,5-sigmatropic rearrangements. Claisen, Cope and aza-Cope rearrangements. Fluxional tautomerism. Ene reaction.

### Books Suggested

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

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# Paper III: CH-403 Physical Chemistry (4 hrs. or 6 periods / week)

Exam Duration: 3 hrs.

Max. Marks: 100

#### Unit-I

#### Quantum Chemistry

Introduction to Exact Quantum Mechanical Results: The Schrodinger equation and the postulates of quantum mechanics. Discussion of the solutions of the Schrodinger equation to some model systems viz., particle in a box, the harmonic oscillator, the rigid rotor, the hydrogen atom.

Approximate Methods: The variation theorem, linear variation principle. Perturbation theory (up to second order and non-degenerate). Applications of variation method and perturbation theory to Helium atom.

Angular Momentum: Ordinary angular momentum, generalized angular momentum, eigen functions for angular momentum, eigen values of angular momentum, operator using ladder operators, addition of angular momenta, tunneling, spin, antisymmetry and Pauli's exclusion principle.

Molecular Orbital Theory: Huckel theory of conjugated systems, bond and charge density calculations. Applications to ethylene, butadiene, cyclopropenyl radical, cyclobutadiene etc. Introduction to extended Huckel theory.

#### Unit-II

#### Thermodynamics

Classical Thermodynamics:Brief resume of concepts of laws of thermodynamics, free energy, chemical potential and entropies. Partial molar properties, partial molar free energy, partial molar volume and partial molar heat content and their significances. Determinations of these quantities. Concept of fugacity and determination of fugacity.

Non-ideal systems: Excess functions for non-ideal solutions. Activity, activity coefficient, Debye Huckel theory for activity coefficient of electrolytic solutions; determination of activity and activity coefficients, ionic strength. Application of phase rule to three component systems, second order phase transitions.

Statistical Thermodynamics: Concept of distribution, thermodynamic probability and most probable distribution. Ensemble averaging, postulates of ensemble averaging. Canonical, grand canonical and micro canonical ensembles, corresponding distribution laws (using Lagrange's method of undetermined multipliers). Partition functions-Translation, rotational, vibrational and electronic partition functions, calculation of thermodynamic properties in terms of partition functions Application of partition functions.

Heat capacity behaviour of solids-chemical equilibria and equilibrium constant in terms of partition functions, Fermi-Dirac statistics, distribution law and applications to metal. Bose-Einstein statistics, distribution Law and application to helium.

#### Unit-III

#### **Chemical Dynamics**

Methods of determining rate laws, collision theory of reaction rates, steric factor, activated complex theory, Arrhenius equation and the activated complex theory; ionic reactions, kinetic salt effects, steady state kinetics, kinetic and thermodynamic control of reactions, treatment of unimolecular reactions.

Dynamic chain reactions (hydrogen-bromine reaction, pyrolysis of acetaldehyde, decomposition of ethane), photochemical reactions (hydrogen-bromine and hydrogen-chlorine) and homogeneous catalysis, kinetics of enzyme reactions, Michaelis-Menten and Lineweaver-Burk plots, general features of fast reactions, study of fast reactions by flow method, relaxation method, flash photolysis and the nuclear magnetic resonance method, dynamics of unimolecular reactions (Lindemann Hinshelwood and Rice-Ramsperger-Kassel- Marcus [RRKM] theories of unimolecular reactions).

#### Unit-IV

#### Surface Chemistry

Adsorption: Surface tension, capillary action, pressure difference across curved surface (Laplace equation), vapour pressure of droplets (Kelvin equation). Gibbs adsorption isotherm, estimation of surface area (BET equation), surface films on liquids (Electro-kinetic phenomenon).

Micelles: 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,

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thermodynamics of micellization-phase separation and mass action models, solubilization, micro emulsion, reverse micelles.

#### Macromolecules

Potenter - definition, types of polymers, electrically conducting, fire resistant, liquid crystal polymers, kinetics of polymerization, mechanism 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 dimension of various chain structures.

#### Unit-V

#### Electrochemistry

Electrochemistry of solutions. Debye-Huckel-Onsager treatment and its extension, ion solvent interactions. Debye-Huckel-Jerum mode. Thermodynamics of electrified interface equations. Derivation of electro capillarity, Lippmann equations (surface excess), methods of determination. Structure of electrified interfaces. Guoy-Chapman, Stern, Graham Devanathan-Mottwatts, Tobin, Bockris, Devanathan models, Overpotentials, exchange current density, derivation of Butler-Volmer equation, Tafel plot.

Quantum aspects of charge transfer at electrodes-solution interfaces, quantization of charge transfer, tunneling. Polarography theory, llkovic equation, half wave potential and its significance.

#### **Books Suggested**

- 1. Physical Chemistry. P.W. Atkins, ELBS.
- 2. Introduction to Quantum Chemistry, A.K. Chandra, Tata McGraw Hill.
- 3. Quantum Chemistry. Ira N. Levine, Prentice Hall.
- 4. Coulson's Valence. R. McWeeny, ELBS.
- 5. Chemical Kinetics. K.J. Laidler, McGraw-Hill.
- 6. Kinetics and Mechanism of Chemical Transformation. J. Rajaraman and J. Kuriacose. McMillan.
- 7. Micelles, Theoretical and Applied Aspects, V. Moroi, Plenum.
- 8. Modern Electrochemistry Vol. I and Vol. II, J.O'M. Bockris and A.K.N. Reddy, Plenum.
- 9. Introduction to Polymer Science, V.R. Gowarikar, N.V. Vishwanathan and J. Sridhar, Wiley Eastern.

# Paper IV: CH - 404 Spectroscopy and Diffraction Methods (2 hrs. or 3 periods / week)

Exam Duration: 3 hrs.

Max. Marks:50

#### Unit-I

#### **Unifying Principles**

Electromagnetic radiation, interaction of electromagnetic radiation with matter - absorption, emission, transmission, reflection, refraction, dispersion, polarisation and scattering. Uncertainty relation and natural line width and natural line broadening, transition probability, results of the time dependent perturbation theory, transition moment, selection rules, intensity of spectral lines.

Microwave Spectroscopy Classification of molecules, rigid rotor model, effect of isotopic substitution on the transition frequencies, intensities, non-rigid rotor, Stark effect, nuclear and electron spin interaction and effect of external field. Applications.

#### Unit-II

#### Vibrational Spectroscopy

Infrared Spectroscopy: Review of linear harmonic oscillator, vibrational energies of diatomic molecules, zero point energy, force constantand bond strengths; anharmonicity, Morse potential energy diagram, vibration-rotation spectroscopy. PQR branches. Breakdown of Oppenheimer approximation, Selection rules, group frequencies, overtones, hot bands, far IR region, metal-ligand vibrations, normal co-ordinate analysis.

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Raman Spectroscopy: Classical and quantum theories of Raman effect. Pure rotational, vibrational and vibrational-rotational Raman spectra, selection rules, mutual exclusion principle. Resonance Raman spectroscopy, coherent antistokes Raman spectroscopy (CARS).

#### Unit-III

### Electronic Spectroscopy

Atomic Spectroscopy: Energies of atomic orbitals, vector representation of momenta and vector coupling, spectra of hydrogen atom and alkali metal atoms.

Molecular Spectroscopy: Energy levels, molecular orbitals, vibronic transitions, vibrational progressions and geometry of the excited states. Franck-Condon principle, electronic spectra of polyatomic molecules Emission spectra; radiative and non-radiative decay, internal conversion, spectra of transition metal complexes, charge-transfer spectra. Photoelectron Spectroscopy: Basic principles; photo-electric effect, ionization process. Koopman's theorem. Photoelectron spectra of simple molecules, ESCA, chemical information from ESCA. Auger electron spectroscopy - basic idea.

#### Unit-IV

#### Magnetic Resonance Spectroscopy

Nuclear Magnetic Resonance Spectroscopy: General introduction, Nuclear spin, auclear resonance. *Proton NMR spectroscopy*: shielding mechanism, chemical shift and its measurements, factors influencing chemical shift, deshielding. Chemical shift values and correlation for protons bonded to carbon (aliphatic, olefinic, aldehydic and aromatic) and other nuclei (alcohols, phenols, enols, carboxylic acids, amines, amides &mercapto). Spin-spin interactions, coupling constant 'J', factors influencing coupling constant. Complex spin-spin interaction between two, three, four and five nuclei (ABX, AMX, ABC, A<sub>2</sub>B<sub>2</sub>, etc.). Spin decoupling, chemical exchange, effect of deuteration. Simplification of complex spectra: nuclear magnetic double resonance, NMR shift reagents, solvent effects. NMR of Paramagnetic substances in solution, the contact and pseudocontact shifts, factors affecting nuclear relaxation. Nuclear Overhauser effect (NOE).

Electron Spin Resonance Spectroscopy: Basic principles, zero field splitting and Kramer's degeneracy, Isotropic and anisotropic Hyperfine coupling, spin-orbit coupling and significance of g-tensors, factors affecting the 'g' value, application to transition metal complexes; spin Hamiltonian, spin densities and McConnell relationship, applications: spin polarization for atoms and transition metal ions.

#### Unit-V

X-ray Diffraction: Bragg's condition, Miller indices, Laue Method, Bragg's method. Debye Scherrer method of X-ray structural analysis of crystals, index reflections, identification of unit cells from systematic absences in diffraction pattern. Structure of simple lattices and X-ray intensities, structure factor and its relation to intensity and electron density, phase problem. Description of the procedure for an X-ray structure analysis, absolute configuration of molecules.

Electron Diffraction: Scattering intensity vs. scattering angle, Wierl equation, measurement technique, elucidation of structure of simple gas phase molecules. Low energy electron diffraction and structure of surfaces.

Neutron Diffraction: Scattering of neutrons by solids, measurements techniques. Elucidation of structure of magnetically ordered unit cell.

#### Books suggested

- 1. Modern Spectroscopy, J.M. Hollas, John Wiley.
- 2. Applied Electron Spectroscopy for Chemical Analysis, Ed. H Windawi& F.L. Ho, Wiley Interscience.
- 3. NMR, NQR, EPR and Mossbauer Spectroscopy in Inorganic Chemistry, R.V. Parish, Ellis Harwood.
- 4. Physical Methods in Chemistry, R.S. Drago, Saunders College.
- 5. Introduction to Molecular Spectroscopy, G.M. Barrow, McGraw Hill.
- Basic Principles of Spectroscopy, R. Change, McGraw Hill.
- 7. Theory and Application of UV Spectroscopy, H.H. Jaffe and M. Orchin, IBH-Oxford.
- 8. Introduction to Photoelectron Spectroscopy, P.K. Ghosh, John Wiley.
- 9. Introduction to Magnetic Resonance, A Carrington and A.D. Maclachalan, Harper & Row.

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# PaperV: CH-405 GREEN AND SUSTAINABLE CHEMISTRY (2 hrs. or 3 periods / week)

Exam Duration: 3 hrs.

Max. Marks: 50

#### UNIT-I

Introduction, principle and concepts of Green Chemistry

Need for green chemistry; Inception and evolution of green chemistry; Twelve principles of green chemistry with their explanations and examples; Designing a green synthesis using these principles; Green chemistry in day to day life.

#### UNIT - II

Non-traditional greener alternative approaches

Different approaches to green synthesis: (a) Uses of green reagents in organic synthesis - Dimethyl carbonate, polymer supported reagents - peracids and chromic acid; (b) Green catalysts, role of catalysis in sustainable development, homogeneous and heterogeneous catalysts; Introduction, advantages and applications of - (i) Nanocatalysts, (ii) Phase transfer catalysts, (iii) Biocatalysts, (iv) Organocatalysts, in organic synthesis.

#### UNIT - III

Applications of non-conventional energy sources

Introduction of microwave induced synthesis: Microwave activation, equipment, time and energy benefits, limitations. Organic transformations under microwaves - Fries rearrangement, Diels-Alder reaction, decarboxylation, saponification of ester, alkylation of reactive methylene compounds; Heterocyclic synthesis - β-Lactams, pyrrole, quinoline.

Introduction of ultrasound assisted green synthesis: Instrumentation, physical aspects, applications in organic transformations.

Electrochemical synthesis: Introduction, synthesis of sebacic acid and adiponitrile.

#### UNIT-IV

**Environmentally Benign Solutions to Organic Solvents** 

lonic liquids as green solvents: Introduction, properties and types of ionic liquids. Synthetic applications - Diels-Alder reaction, epoxidation and Heck reaction.

Aqueous phase reactions: Enhancement of selectivity, efficiency. Synthetic applications - 1,3-Dipolar Cycloadditions, Carbon-Carbon bond-forming processes and bromination reactions.

Fluorous solvents in green chemistry: Scope, definition and their synthetic applicability.

Role of supercritical carbon dioxide in green chemistry.

Ethyl lactate as a renewable green solvent: Properties and applications.

#### UNIT -V

**Synthesis of Nanomaterials** 

Greener synthesis of Nanomaterials— Microwaveassisted synthesis of Quantum Dots (QD) in aqueous medium, Magnetic Nanoparticles, MW-assisted Nano Catalysis in water.

Synthesis of Nanoparticles using Bacteria, Yeast, Algae and Fungus.

#### SUGGESTED BOOKS AND REFERENCES:

- 1. P.A.G. Blackie, Organic synthesis in water, Springer.
- 2. P.T. Anastas, J.C. Warner, Green Chemistry, theory and practice, Oxford University Press.
- 3. M. Lancaster, Green Chemistry: An introductory text, Royal Society of Chemistry.
- 4. V. Polshettiwar, T. Asefa, G. Hutchings, Nanocatalysis: Synthesis and applications, Wiley.
- 5. M.A. Ryan, M. Tinnesand, Introduction to Green Chemistry, American Chemical Society.
- 6. P.T. Anastas, Handbook of Green Chemistry, John Wiley and Sons.
- 7. V.K. Ahluwalia, MKidwai, New Trends in Green Chemistry, Springer.
- 8. Paul T Anastas, Innovations in Green Chemistry and Green Engineering, Springer.

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#### Paper VI: CH - 406 ANALYTICAL TECHNIQUES

#### (2 hrs. or 3 periods / week)

Exam Duration: 3 hrs.

Max. Marks: 50

#### UNIT I

#### **Statistics - Introduction to Chemometrics**

Limitations of analytical methods, Errors and classification, Determinant, constant and indeterminate, accuracy, precision, minimization of errors, significant figures and computation rules, mean and standard deviation, distribution of random errors, variance and confidence interval, paired *t*-test, least square method, correlation and regression, linear regression.

#### UNIT II

#### Sampling in analysis

Definition, theory, basis and techniques of sampling, sampling statistics, sampling and physical state, crushing and grinding, hazards in sampling, techniques of sampling of gases, fluid, solids, and particulates, minimization of variables, transmission and storage of samples, high pressure ashing techniques (HPAT), particulate matter, its separation in gas stream, filtering and gravity separation, analysis of particulate matter like asbestos, mica, dust and aerosols etc.

Solvent extraction method in analysisPrinciple, classification, theory, instrumentation and applications.

#### UNIT III

#### Conductometry:

Important laws, definitions, relations, effect of dilution on conductivity, measurement of conductivity, types of conductometric titrations, its applications and limitations.

#### Potentiometry:

Principle, instrumentation, types of potentiometric titrations and its applications, pH measurements, determination of pH, ion selective electrodes, instrumentation and applications.

#### UNIT - IV

#### Coulometry:

Introductions, principle, experimental details of coulometry at constant current and constant potential, titrational applications.

#### Atomic Absorption Spectroscopy

Introduction, principle, Grotrian Diagram, Instrumentation, applications, detection limit, sensitivity and disadvantages

#### UNIT- V

#### Food Analysis

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

#### SUGGESTED BOOKS AND REFERENCES

- 1. Mendham J., Denney R.C., Barnes J. D., Thomas M.J.K., Vogels' text book of quantitative chemical analysis, 6<sup>th</sup> edition, Prentice Hall, 2000.
- 2. Skoog Douglas A., Holler F. James, Nieman Timothy A., Principles of instrumental analysis, Saunders College Pub., 1998.
- 3. Day R. A and A. L. Underwood, Quantitative analysis, Prentice Hall, 1999.
- 4. Drago R. S., Physical methods in Chemistry, Saunders, 1999.
- 5. Peters D.G, J. M. Hayes and G. M. Hefige, A brief introduction to Modern chemical analysis, Philadelphia: Saunders, 1976.
- 6. Ebsworth E.A.V, DWA Rankin and C. Craddock, Structural methods in inorganic chemistry, ELBS.
- 7. Elan JAD Butter Worth, Photoelectron spectroscopy.

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- 8. Eliel E.L, Stereochemistry of carbon compounds, Tata-McGraw-Hill
- G.D. Christian, P.K. Dasgupta, K.A. Schug, Analytical Chemistry, Wiley, 7<sup>th</sup>edn., 2013.
- 10. D.A. Skoog, D.M. West and F.J. Hooler, S.R. Crouch, Fundamentals of Analytical Chemistry, 9th edn., 2014.
- 11. J.H. Kennedy, Analytical Chemistry Principles, Saunders College Publishing, New York, 2<sup>nd</sup>edn., 1990.
  - 12. L.G. Hargis, Analytical Chemistry Principles and Techniques, Prentice Hall, 1988.
  - 13. R.A. Day, Jr. and A.L. Underwood, Quantitative Analysis, 6th edn., Prentice Hall, 1991.
  - 14. S.M. Khopkar, Environmental Solution, Wiley Eastern.
  - 15. S.M. Khopkar, Basic Concepts of analysis Chemistry, New Age International, 1998.
  - 16. Alka L. Gupta, Analytical Chemistry, Pragati Publication, 2014.
  - 17. D C Das, Analytical Chemistry, Prentice Hall India Learning Private Limited, 2010.

#### CH-407: M.Sc. (Prev.) PRACTICAL

(9 hrs. / week)

Practical Exam Duration 14 hrs. (spread over 2 days)

Max. Marks: 200

#### INORGANIC CHEMISTRY

Qualitative Analysis of mixture containing 8 radicals including -

- a) Less common metal ions Tl, Mo, W, Ti, Zr, Th, V, U (two metal ions in cationic/anionic forms)
- b) Insolubles oxides, sulphates and halides.

#### Quantitative Analysis

- a) Separation and determination of two metal ions Cu-Ni, Ni-Zn, Cu-Fe involving volumetric and gravimetric methods.
- b) Chromatographic Separation of cations and anions by
- a) Paper Chromatography
- b) Column Chromatography

Preparation of selected inorganic compounds(10 out of following) and their studies by IR spectra, Handing of air and moisture sensitive compounds.

- 1. [VO(acac)<sub>2</sub>]
- 2. TiO(C<sub>9</sub>H<sub>8</sub>NO)<sub>2</sub>.2H<sub>2</sub>O
- 3. cis-K[ $Cr(C_2O_4)_2(H_2O)_2$ ]
- 4. Na[Cr(NH<sub>3</sub>)<sub>2</sub>(SCN)<sub>4</sub>]
- 5.  $[Mn(acac)_2]$
- 6.  $K_3[Fe(C_2O_4)_3]$
- 7. Prussian Blue, Turnbull's Blue.
- 8. [Co(NH<sub>3</sub>)<sub>6</sub>] [CO(NO<sub>2</sub>)<sub>6</sub>]
- 9. cis-[Co(trien)(NO<sub>2</sub>)<sub>2</sub>]Cl.H<sub>2</sub>O
- 10.  $[Co(Py)_2Cl_2]$
- 11. [Ni(NH<sub>3</sub>)<sub>6</sub>]Cl<sub>2</sub>
- 12.  $[Ni(dmg)_2]$
- 13. [Cu(NH<sub>3</sub>)<sub>4</sub>]SO<sub>4</sub>.H<sub>2</sub>O

#### ORGANIC CHEMISTRY

# Qualitative Analysis

Separation, purification and identification of compounds of binary mixture of one liquid and one solid using distillation, chemical tests. IR spectra to be used for functional group identification.

#### Organic Synthesis (at least six to be carried out)

# a) One step Preparations:

1. Acetylation: Acetylation of cholesterol

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- 2. Oxidation: Adipic acid by chromic acid oxidation of cyclohexanol / cyclohexene.
- 3. Aldol condensation : Dibenzal acetone from benazaldehyde.

#### b) Two step Preparations

- LaAniline → Sym. Tribromoaniline → Sym. Tribromobenzene
- 2. Benzoin →Benzil→ Dibenzyl
- 3. Aniline → Dibenzoaminobenzene → p-Aminoazobenzene
- 4. Nitrobenzene → m-Dinitrobenzene → m-Nitroaniline
- 5. Phthalic anhydride → Fluorescein → Eosin

The products may be characterised by Spectral Techniques.

# Quantitative Analysis (At least 2 to be performed)

- 1. Determination of the percentage or number of hydroxyl groups in an organic compound by acetylation method.
- 2. Estimation of amines / phenols using bromate bromide solution or acetylation method.
- 3. Determination of Iodine number and Saponification value of an oil sample.
- 4. Determination of DO, COD and BOD of water sample.

#### PHYSICAL CHEMSITRY

A list of minimum 20 experiments to be selected coveringall headings given below. At least two typical experiments are to be selected from each heading.

### Phase Equilibria

- (i) Determination of congruent composition and temperature of a binary system (e.g., diphenylamine-benzophenone system)
- (ii) Determination of glass transition temperature of a given salt (e.g. CaCl<sub>2</sub>) conductometrically.
- (iii) To construct the phase diagram for three component system (e.g. chloroform acetic acid water).

#### Chemical Kinetics

- (i) Determination of the effect of (a) Change of temperature (b) Change of concentration of reactant and catalyst and (c) Ionic strength of the media on the velocity constant of hydrolysis of an ester/ionic reactions.
- (ii) Determination of the velocity constant of hydrolysis of an ester/ ionic reaction in micellar media.
- (iii) Determination of the rate constant for the oxidation of iodide ions by hydrogen peroxide studying the kinetics as an iodine clock reaction.
- (iv) Determination of the primary salt effect on the kinetics of ionic reactions and testing of the Bronsted relationship (iodide ion is oxidized by persulphate ion).

#### Solutions

- (i) Determination of molecular weight of non-volatile and non-electrolyte / electrolyte by cryoscopic method and to determine the activity coefficient of an electrolyte.
- (ii) Determination of the degree of dissociation of weak electrolyte and to study the deviation from ideal behaviour that occurs with a strong electrolyte.

### Conductometry

- (i) Determination of the velocity constant, order of the reaction and energy of activation for saponification of ethyl acetate by sodium hydroxide conductometrically.
- (ii) Determination of solubility and solubility product of sparingly soluble salts (e.g., PbSO<sub>4</sub>, BaSO<sub>4</sub>) conductometrically.
- (iii) Determination of the strength of strong and weak acids in a given mixture conductometrically.
- (iv) To study the effect of solvent on the conductance of AgNO<sub>3</sub> / acetic acid and to determine the degree of dissociation and equilibrium constant in different solvents and in their mixtures (DMSO, DMF, dioxane, acetone, water) and to test the validity of Debye-Huckel-Onsager theory.
- (v) Determination of the activity coefficient of zinc ions in the solution of 0.002 M zinc sulphate using Debye Huckel's limiting law.

#### Potentiometry and pH metry

(i) Determination of strengths of halides in a mixture potentiometrically.

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- (ii) Determination of the strength of strong and weak acids in a given mixture using a potentiometer/pH meter.
- (iii) Determination of temperature dependence of EMF of a cell.
- (iv) Determination of the formation constant of silver-ammonia complex and stoichiometry of the complex potentiometrically.
  - (v) Acid-base titration in a non-aqueous media using a pH meter.
  - (vi) Determination of activity and activity coefficient of electrolytes.
  - (vii) Determination of the dissociation constant of acetic acid in DMSO, DMF, acetone and dioxane by titrating it with KOH.
  - (viii) Determination of the dissociation constant of monobasic/dibasic acid by Albert-Serjeant method.
  - (ix) Determination of thermodynamic constants.  $\Delta G$ ,  $\Delta S$ , and  $\Delta H$  for the reaction by e.m.f. method. Zn  $H_2SO_4 \rightarrow ZnSO_4 + 2H$

#### Polarimetry

- (i) Determination of rate constant for hydrolysis/inversion of sugar using a polarimeter.
- (ii) Enzyme kinetics inversion of sucrose.

#### Reference Books:

- Vogel's Textbook of Quantitative Analysis, revised, J. Bassett. R.C. Denney, G.H. Jeffrey and J. Mendham, ELBS.
- 2. Synthesis and Characterization of Inorganic Compounds, W.L. Jolly. Prentice Hall.
- 3. Experiments and Techniques in Organic Chemistry, D.P. Pasto. C. Johnson and M. Miller, Prentice Hall.
- 4 Macroscale and Microscale Organic Experiments, K.L. Williamson, D.C. Health.
- Systematic Qaulitatitve Organic Analysis, H. Middleton. Adward Arnold.
- Handbook of Organic Analysis-Qualitative and Quantitative. H. Clar. Adward Arnold.
- Vogel's Textbook of Practical Organic Chemistry. A.R. Tatchell. John Wiley.
- 8. Practical Physical Chemistry, A.M. James and F.E. Porichard, Longman.
- 9. Findley's Practical Physical Chemistry, B.P. Levitt, Longman.
- 10. Experimental Physical Chemistry, R.C. Das and B. Behera, Tata-McGraw Hill.

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# INSTRUCTIONS TO THE EXAMINERS CH-407: M.Sc. (Previous) Chemistry Practical

Min. Marks: 72 Max. Marks: 200 Exam Duration: 14 hrs (spread over 2 days) **Inorganic Chemistry** (i) Analysis of mixture containing 8 radicals including one radical of rare elements. 30 Separation and determination of two metal ions Cu-Ni, Ni-Zn, Cu-Fe involving volumetric and gravimetric method. (Both these exercises should be given in equal ratio by lots.) (ii) Separation of cations and anions by paper chromatography or column chromatography. 20 Preparation of one selected inorganic compound and its study by IR. Organic Chemistry (i) Separation, purification and identification of compounds of binary mixture (one liquid and one solid) using distillation, chemical tests. IR spectra to be used for functional group determination. (ii)Perform one of the 8 organic syntheses as mentioned in the syllabus and may be characterized by spectral techniques. Or Perform one of the quantitative analysis given in syllabus. 20 (Both these exercises should be given in equal ratio by lots.) **Physical Chemistry** (i) One minor physical experiment. 20 (ii) One major physical experiment 30

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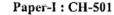
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#### M.Sc. II Year (Final)



# Applications of Spectroscopy, Photochemistry and Solid State Chemistry (4 hrs. or 6 periods / week)

Exam Duration: 3 Hrs.

Max. Marks: 100

#### Unit-I

#### Ultraviolet and Visible Spectroscopy

Various electronic transitions (185-800 nm), Beer-Lambert law, effect of solvent on electronic transitions, ultraviolet spectra of carbonyl compounds, unsaturated carbonyl compounds, dienes, conjugated polyenes, Fieser-Woodward rules for conjugated dienes and carbonyl compounds, ultraviolet spectra of aromatic compounds. Steric effect in biphenyls.

#### Infrared Spectroscopy

Instrumentation and sample handling, Characteristic vibrational frequencies of alkanes, alkenes, alkynes, aromatic compounds, alcohols, ethers, phenols and amines. Detailed study of vibrational frequencies of carbonyl compounds (ketones, aldehydes, esters, amides, acids, anhydrides, lactones, lactams and conjugated carbonyl compounds). Factors affecting the band positions and intensities, Effect of hydrogen bonding and solvent effect on vibrational frequencies, overtones, combination bands and Fermi resonance.

Applications of Vibrational Spectroscopy: Symmetry and shapes of  $AB_2$ ,  $AB_3$ ,  $AB_4$ ,  $AB_5$  and  $AB_6$ , mode of bonding of ambidentate ligands, ethylenediamine and diketonato complexes, application of resonance Raman spectroscopy particularly for the study of active sites of metalloproteins.

#### Unit-II

**Mossbauer Spectroscopy**: Basic principles, spectral parameters and spectrum display. Application of the technique to the studies of (1) bonding and structures of  $Fe^{+2}$  and  $Fe^{+3}$  compounds including those of intermediate spin,(2)  $Sn^{+2}$  and  $Sn^{+4}$  compounds, nature of M-L bond, coordination number, structure and (3) detection of oxidation state and inequivalent MB atoms.

Electron Microscopy: Basic principles of Electron Microscopy: SEM, TEM, AFM; and their applications in structural analysis.

Optical Rotatory Dispersion (ORD) and Circular Dichroism (CD) Definition, deduction of absolute configuration, octant rule for ketones.

Magnetic Properties of Transition Metal Complexes Spectroscopic method of assignment of absolute configuration in optically active metal chelates and their stereochemical conformation, anomalous magnetic moments, magnetic exchange coupling and spin crossover.

#### Unit-III

NMR Spectroscopy: FT NMR-Fourier transform technique.

NMR active nuclei other than proton - 19F and 31P.

Carbon-13 NMR- General considerations, chemical shift (aliphatic, olefinic, alkyne, aromatic, heteroaromatic and carbonyl carbon), coupling constants.

Two dimension NMR spectroscopy - COSY, NOESY, DEPT, INEPT, APT and INADEQUATE techniques.

#### Mass Spectrometry

Introduction, ion production – EI, CI, FD and FAB, factors affecting fragmentation, ion analysis, ion abundance. Mass spectral fragmentation of organic compounds, common functional groups, molecular ion peak, metastable peak. McLafferty rearrangement. Nitrogen rule. High resolution mass spectrometery. Examples of mass spectral fragmentation of organic compounds with respect to their structure determination.

#### Unit-IV

Photochemical Reactions: Fate of excited molecule. *Determination of Reaction Mechanism*: Classification, rate constants and life times of reactive energy states - determination of rate constants of reactions. Effect of light intensity

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on the rate of photochemical reactions. Types of photochemical reactions, photo-dissociation, gas-phase photolysis. cotochemistry of Alkenes: Intramolecular reactions of the olefinic bond - geometrical isomerism, cyclisation reactions, rearrangement of 1,4- and 1,5-dienes. Photochemistry of Carbonyl Compounds :Intramolecular reactions of carbonyl compounds - saturated, cyclic and acyclic,  $\beta$ ,  $\gamma$ -unsaturated and  $\alpha$ ,  $\beta$ -unsaturated compounds, cyclohexadienones. Intermolecular cycloaddition reactions - dimerisations and oxetane formation.

Photochemistry of Aromatic Compounds: Isomerisations, additions and substitutions.

Solid State Reactions: General principles, experimental procedure, co-precipitation as a precursor to solid state

Crystal Defects and Non-Stoichiometry: Perfect and imperfect crystals, intrinsic and extrinsic defects - point defects, line and plane defects, vacancies - Schottky defects and Frenkel defects. Thermodynamics of Schottky and

Frenkel defect formation, colour centres, non-stoichiometry and defects. Electronic Properties and Band Theory : Metals, insulators and semiconductors, electronic structure of solids, band theory, band structure of metals, insulators and semiconductors, Intrinsic and extrinsic semiconductors, doping

Organic Solids: Electrically conducting solids, organic charge transfer complex, organic metals, new superconductors.

# Books Suggested

# UNIT I, II and III

- 1. Physical Methods for Chemistry, R.S. Drago. Saunders Company
- 2. Structural Methods in Inorganic Chemistry. E.A.V. Ebsworth D.W.H. Rankin &S.Cradock, ELBS.
- 3. Infrared and Raman Spectra: Inorganic and Coordination Compounds. K. Nakamoto, Wiley.
- 4. Progress in Inorganic Chemistry vol. 8. ed., I.Cotton.Vol. 15. ed. S.J. Lippard. Wiley.
- 5. Transition Metal Chemistry ed. R.L. Carlin vol. 3 Dekker.
- 6. Inorganic Electronic Spectroscopy. A.P.B. lever. Elsevier.
- 7. NMR, NQR, EPR and Mossbauer Spectroscopy in Inorganic Chemistry R.V. Parish. EllisHorwood.
- 8. Practical NMR Spectroscopy, M. L. Martin, J.J. Delpeuch and G.J. Martin, Heyden.
- 9. Spectrometric Identification of Organic Compounds, R.M. Silverstein. G.C. Bassler and T.C. Morrill. John Wiley.
- 10. Introduction to NMR Spectroscopy, R.J. Abraham. J. Fisher and P. Loftus, Wiley.
- 11. Application of Spectroscopy of Organic Compounds. J.R. Dyer, Prentice Hall.
- 12. Spectroscopic Methods in Organic Chemistry D. H. Williams. I. Fleming. Tata McGraw-Hill.

- 1. Fundamentals of Photochemistry, K.K. Rohtagi-Mukherji, Wiley-Eastern.
- 2. Essentials of Molecular photochemistry, A Gilbert and J. Baggott, Blackwell Scientific Publication.
- 3. Molecular Photochemistry. N. J. Turro, W.A. Benjamin.
- 4. Introductory Photochemistry. A. Cox and T. Camp, McGraw-Hill.
- 5. Photochemistry, R.P. Kundall and A. Gilbert. Thomson Nelson.
- 6. Organic Photochemistry, J. Coxon and B. Halton, Cambridge University Press.

- 1. Solid State Chemistry and its Applications, A.R West. Plenum.
- 2. Principles of the Solid State, H.V. Keer, Wiley Eastern.
- 3. Solid State Chemistry, N.B. Hannay.
- 4. Solid State Chemistry, D.K. Chakrabarty, New Wiley Eastern.

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#### Paper-II: CH-502

# Bioinorganic Chemistry, Bioorganic Chemistry and Biophysical Chemistry (4 hrs or 6 period/ week)

Exam Duration; 3 hrs.

Max. Marks: 75

#### Unit-I

Metal Ions in Biological Systems: Bulk and trace metals with special reference to Na, K, Mg, Ca, Fe, Cu, Zn, Co and  $K^+/Na^+$  pump.

Transport and Storage of Dioxygen: Haem proteins and oxygen uptake, structure and function of haemoglobin, myoglobin, haemocyanin and hemerythrin, model synthetic complexes of iron, cobalt and copper.

Electron Transfer in Biology: Structure and function of metalloproteins in electron transport processes cytochromes and iron-sulphur proteins, synthetic models.

Nitrogen fixation: Biological nitrogen fixation and its mechanism, nitrogenase. Chemical nitrogen fixation.

#### Unit-II

Bioorganic Chemistry: Introduction, Basic considerations. Proximity effects and molecular adaptation.

Enzymes :Introduction and historical perspective, chemical and biological catalysis, remarkable properties of enzymes like catalytic power, specificity and regulation, Nomenclature and classification, extraction and purification. Fischer's lock and key and Koshland's induced fit hypothesis, concept and identification of active site by the use of inhibitors, affinity labeling and enzyme modification by site-directed mutagenesis. reversible and irreversible inhibition.

Mechanism of Enzyme Action: Transition-state theory, orientation and steric effect, acid-base catalysis, covalent catalysis, strain or distortion. Examples of some typical enzyme mechanisms for chymotrypsin. ribonuclease, lysozyme and carboxypeptidase.

Types of Reactions Catalysed by Enzymes: Nucleophilic displacement on a phosphorus atom, multiple displacement reactions and the coupling of ATP cleavage to endergonic processes. Transfer of sulphate, addition and elimination reactions, enolic intermediates in isomerization reactions. β-Cleavage and condensation, some isomerization and rearrangement reactions. Enzyme catalyzed carboxylation and decarboxylation.

#### Unit-III

Co-enzyme Chemistry: Cofactors as derived from vitamins, coenzymes, prosthetic groups, apoenzymes. Structure and biological functions of coenzyme A, thiamine pyrophosphate, pyridoxal phosphate, NAD<sup>+</sup>, NADP<sup>+</sup>, FMN, FAD, lipoic acid, vitamin B<sub>12</sub>. Mechanisms of reactions catalyzed by the above cofactors.

Enzyme Models: Host-guest chemistry, chiral recognition and catalysis, molecular recognition, molecular asymmetry and prochirality. Biomimetic chemistry, crown ether, cryptates. Cyclodextrins, cyclodextrin-based enzyme models, calixarenes, ionophores, micelles, synthetic enzymes or synzymes.

#### Unit-IV

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

Statistical Mechanics in Biopolymers: Chain configuration of macromolecules, statistical distribution end to end dimensions, calculation of average dimensions for various chain structure. Polypeptide and protein structures, introduction to protein folding problem.

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

#### Unit-V

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

Cell Membrane and Transport of Ions: Structure and functions of cell membrane, ion transport through cell membrane, irreversible thermodynamic treatment of membrane transport. Nerve conduction.

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

Books Suggested

1. Principles of Bioinorganic Chemistry, S.J. Lippard and J.M. Berg, University Science Books.

2. Bioinorganic Chemistry, I. Bertini, H.B. Gray. S.J. Lippard and J.S. Valentine, University Science books.

3. Inorganic Biochemistry vols. I and II, ed. G.L. Eichhom, Elsevier.

4. Progress in Inorganic Chemistry, Vols 18 and 38 ed. J.J. Lippard, Wiley.

5. Principles of Biochemistry, A. L. Lehninger. Worth Publishers.

 Bioorganic Chemistry: A Chemical Approach to Enzyme Action, Hermann Dugas and C. Penny, Springer Verlag.

7. Understanding Enzymes, Trevor Palmer, Prentice Hall.

- 8. Enzyme Chemistry: Impact and Applications, Ed. Collin J Suckling, Chemistry.
- 9. Enzyme Mechanisms, Ed. M.I. Page and A. Williams, Royal Society of Chemistry.

10. Fundamentals of Enzymology, N.C. Price and L. Stevens, Oxford University Press.

11. Immobilized Enzymes: An Introduction and Applications in Biotechnology, Michael I.D. Trevan, John Wiley.

12. Enzymatic Reaction Mechanisms. C, Walsh, W.H. Freeman.

- 13. Enzyme Structure and Mechanism. A. Fersht, W.H. Freeman.
- 14. Biochemistry: The Chemical Reactions of Living Cells, D.E. Metzler. Academic Press.
- 15. Biochemistry, L. Stryer, W.H. Freeman.
- 16. Biochemistry, J. David Rawn. Neil Patterson.
- 17. Biochemistry. Voet and Voet, John Wiley.

18. Outlines of Biochemistry, E.E. Conn and P.K. Stumpf. John Wiley.

19. Bioorganic Chemistry: A Chemical Approach to Enzyme Action. H Dugas and C. Penny, Springer-Verlag.

20. Macromolecules: Structure and Function. F Wold. Prentice Hall.

Paper-III: CH-503 Environmental Chemistry (2 Hrs. or 3 period / week)

Exam Duration: 3 hrs.

Max. Marks: 50

#### Unit-I

Atmosphere: Atmospheric layers. Vertical temperature profile, heat radiation, budget of the earth atmosphere systems. Properties of troposphere, thermodynamic derivation of lapse rate. Temperature inversion. Calculations of Global mean temperature of the atmosphere. Pressure variation in atmosphere and scale height. Biogeochemical cycles of carbon, nitrogen, sulphur, phosphorus and oxygen. Residence times.

Atmospheric Chemistry: Sources of trace atmospheric constituents: nitrogen oxides, sulphur dioxide and other sulphur compounds, carbon oxides, chlorofluorocarbons and other halogen compounds, methane and other hydrocarbons.

Tropospheric Photochemistry: Mechanism of photochemical decomposition of NO<sub>2</sub> and formation of ozone. Formation of oxygen atoms, hydroxyl, hydroperoxy and organic radicals and hydrogen peroxide. Reactions of hydroxyl radicals with methane and other organic compounds. Reactions of OH radicals with SO<sub>2</sub> and NOx. Formation of nitrate radical and its reactions. Photochemical smog, meteorological conditions and chemistry of its formation.

#### Unit-II

Air Pollution : Air pollutants and their classification. Aerosols - sources, size distribution and effect on visibility, climate and health.

Acid Rain: Definition, acid rain precursors and their aqueous and gas phase atmospheric oxidation reactions. Damaging effects on aquatic life, plants, buildings and health. Monitoring of SO<sub>2</sub> and NOx - Acid rain control strategies.

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Stratospheric Ozone Depletion: Mechanism of ozone formation, Mechanism of catalytic ozone depletion. Discovery of Antarctic ozone hole. Instrumental methods for detection of ozone depletion gases.

Green House Effect: Terrestrial and solar radiation spectra. Major green house gases and their sources and Global verming potentials. Climate change and consequences.

Urban Air Pollution: Exhaust emissions, damaging effects of carbon monoxide. Monitoring of CO. Control strategies.

#### Unit-III

Aquatic Chemistry and Water Pollution: Redox chemistry in natural waters. Dissolved oxygen, biological oxygen demand, chemical oxygen demand, determination of DO, BOD and COD. Aerobic and anaerobic reactions of organic sulphur and nitrogen compounds in water, acid-base chemistry of fresh water and sea water. Aluminum, nitrate and fluoride in water. Eutrophication. Sources of water pollution. Treatment of waste water and sewage. Purification of drinking water, techniques of purification and disinfection.

#### Unit-IV

#### **Environmental Toxicology**

Toxic Heavy Metals - Mercury, lead, arsenic and cadmium. Causes of toxicity. Bioaccumulation, sources of heavy metals. Chemical speciation of Hg, Pb, As and Cd. Biochemical and damaging effects.

Toxic Organic Compounds - Pesticides, classification, properties and uses of organochlorine and organophosphorus pesticides, detection and damaging effects.

Polychlorinated Biphenyls - Properties, uses and environmental contamination and effects.

Polynuclear Aromatic Hydrocarbons - Sources, structures and as pollutants.

#### Unit-V

#### Soil and Environmental Disasters

Soil composition, micro and macronutrients. soil pollution by fertilizers, plastic and metals. Methods of remediation of soil.

Bhopal gas tragedy, Chernobyl, Three mile island, Minamata Disease, Sevoso (Italy), London smog.

#### Books Suggested:

- 1. Environmental Chemistry. Colin Baird, W.H. Freeman Co. New York. 1098.
- 2 Chemistry of Atmospheres. R.P. Wayne. Oxford.
- 3 Environment Chemistry, A.K. De, Wiley Eastern, 2004.
- 4 Environmental Chemistry, S.E. Manahan, Lewis Publishers.
- 5. Introduction to Atmospheric Chemistry, P.V. Hobbs, Cambridge.

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#### Group I

CH-504 : Organotransition Metal Chemistry

CH-505: Bioinorganic and Supramolecular Chemistry

CH-506: Photoinorganic Chemistry

CH-507 :Polymers.

#### Group II

CH-504 : Organic Synthesis-I CH-505 : Organic Synthesis-11

CH-506 : Heterocyclic Chemistry

CH-507: Chemistry of Natural Products

#### Group III

CH-504: Analytical chemistry

CH-505: Physical Organic Chemistry

CH-506 : Chemical Dynamics CH-507 : Electrochemistry

#### **ELECTIVE PAPER-1**

# (CH-504, Group-I) Organotransition Metal Chemistry (2 Hrs. or 3 period/week)

Exam Duration: 3 hrs.

Max. Marks: 50

#### Unit-I

# Alkyls and Aryls of Transition Metals

Types, routes of synthesis, stability and decomposition pathways, organocopper in organic synthesis.

#### Unit-II

# Compounds of Transition Metal-Carbon Multiple Bonds

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

#### Unit-III

Transition Metal  $\pi$ -complexes: Transition metal  $\pi$ -Complexes with unsaturated organic molecules, alkenes, alkynes, allyl, diene, dienyl, arene and trienyl complexes, preparations, properties, nature of bonding and structural features. Important reactions relating to nucleophilic and electrophilic attack on ligands and organic synthesis. Transition metal compounds with bonds to hydrogen

#### Unit-IV

#### Homogeneous Catalysis

Stoichiometric reactions for catalysis, homogeneous catalytic hydrogenation, Ziegler-Natta polymerizaton of olefins, catalytic reactions involving carbon monoxide such as hydrocarbonylation of olefins (oxo reaction). Oxopalladation reactions, activation of C-H bond.

#### Unit-V

# Fluxional Organometallic Compounds

Fluxionality and dynamic equilibria in compounds such as □-olefin, □'-allyl and dienyl complexes.

#### **Books Suggested**

- 1. Principles and Application of Organotransition Metal Chemistry. J.P. Collman, L.S. Hegsdus, J.R. Norton and R.G. Finke. University Science Books.
- 2. The Organometallic Chemistry of the Transition Metals. R.H. Crabtree. John Wiley.
- 3. Metallo-organic Chemistry. A.J. Pearson, Wiley
- 4. Organometallic Chemistry, R.C. Mehrotra and A. Singh, New Age International.

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# (CH-505, Group-I) Bioinorganic and Supramolecular Chemistry (2 Hrs. or 3 periods/week)

Exam Duration: 3 hrs.

Unit-1

Max. Marks: 50

Metal Storage and Transport

Ferritin transferring and siderophores

Unit-II

Calcium in Biology

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

Unit-III

Metalloenzymes

Zinc enzymes - carboxypeptidase and carbonic anhydrase. Iron enzymes - catalase, peroxidase and cytochrome P-450. Metallo enzyme-II Copper enzymes - superoxide dismutase. Molybdenum oxatransferase enzymes-xanthine oxidase. Coenzyme vitamin Bl2.

Unit-IV

Metal-Nucleic Acid Complexes

Metal ions and metal complex interactions. Metal complex-nucleic acids.

Metals in Medicine

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

Unit-V

Supramolecular Chemistry-I

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

(B.) Supramolecular reactivity and catalysis.

Supramolecular Chemistry-II

(A.) Transport processes and carrier design.

(B.) Supramolecular photochemistry. Supramolecular devices - electronic, ionic and switching devices.

Books Suggested

1. Principles of bioinorganic Chemistry. S.J. Lippard and J.M. Berg, University Science Books.

- 2. Bioinorganic Chemistry. I. Bertini. H.B. Gray. S.J. Lippard and J.S. Valentine, University Science Books.
- 3. Inorganic Biochemistry Vols. I and II Ed. G.L. Eichhorn, Elsevier.
- 4. Progress in Inorganic Chemistry. Vols. 18 Ed. J.J. Lippard. Wiley
- 5. Supramolecular Chemistry, J.M. Lehn. VCH.

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# (CH-506, Group-I) Photoinorganic Chemistry (2 Hrs. or 3 period/ week)

Sam Duration: 3 hrs.

Unit-I

Max. Marks: 50

#### Basics of Photochemistry

Absorption, excitation, photochemical laws, quantum yield, electronically excited states-life times-measurements of the times. Flash photolysis. Energy dissipation by radiative and non-radiative processes, absorption spectra. Frank-Condon principle, photochemical stages - primary and secondary processes.

Unit-II

#### **Properties of Excited States**

Structure, dipole moment, acid-base strengths, reactivity. Photochemical kinetics - calculation of rates of radiative processes. Bimolecular deactivation - quenching.

Unit-III

#### **Excited States of Metal Complexes**

Excited states of metal complexes: comparison with organic compounds, electronically excited states of metal complexes, charge transfer spectra, charge transfer excitations.

#### Unit-IV

#### Ligand Field Photochemistry

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

#### Unit-V

# Redox Reactions by Excited Metal Complexes

Energy transfer under conditions of weak interaction and strong interaction-exciplex formation; condition of the excited states to be useful as redox reactants, excited electron transfer, metal complexes as attractive candidates, (2,2'-bipyridine and 1,10-phenanthroline complexes), illustration of reducing and oxidising character of [Ru(bpy)3]2+complex, comparison with [Fe(bpy)3]3+; role of spin-orbit coupling - life time of these complexes. Application of redox processes of electronically excited states for catalytic purposes, transformation of low energy reactants into high energy products, chemical energy into light.

#### Metal Complex Sensitizers

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

#### **Books Suggested**

- 1. Concepts of Inorganic Photochemistry, A.W. Adamson and P.D. Fleischauer, Wiley.
- 2. Inorganic Photochemistry, J. Chem. Educ. vol. 60 no. 10, 1983.
- 3. Progress in Inorganic Chemistry, vol. 30 ed. S.J. Lippard, Wiley.
- 4. Coordination Chem. Revs., vol. 15, p 321, 1975; vol. 39, p 121, 1981; vol. 97, p 313, 1990.
- 5. Photochemistry of Coordination Compounds, V. Balzari and V. Carassiti. Academic Press.
- 6. Elements in Inorganic Photochemistry, G.J. Ferraudi, Wiley.

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# ELECTIVE PAPER-4 (CH-507, Group-I) Polymers (2Hrs. or 3 periods/week)

Exam Duration: 3 hrs.

Max. Marks: 50

#### Unit-I

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

#### Unit-II

# **Polymer Characterization**

Poly dispersion - average molecular weight concept number, weight and viscosity average molecular weights. Poly dispersity and molecular weight distribution. The practical significance of molecular weight. Measurement of molecular-weights. End group, viscosity, light scattering, osmotic and ultracentrifugation methods. Analysis of polymers - chemical analysis of polymers, spectroscopic methods, X-ray diffraction study, microscopy. Thermal analysis and physical testing - tensile strength. Fatigue, impact tear resistance. Hardness and abrasion resistance.

#### Unit-III

# **Inorganic Polymers**

A general survey and scope of inorganic polymers, special characteristics, classification, homo and hetero atomic polymers.

#### Unit-IV

# Structure, Properties and Applications of

- a) Polymers based on boron borazines, boranes and carboranes.
- b) Polymers based on silicon, silicones polymetalloxanes and polymetallosiloxanes, silazenes.

# Structure, Properties and Applications of

- a) Polymers based on phosphorous phosphazenes, polyphosphates.
- b) Polymers based on sulphur tetrasulphurtetranitride and related compounds.

#### Unit-V

Structure, Properties and Applications of - (a) Metal clusters, (b) Co-ordination and metal chelate polymers.

#### Books Suggested:

- 1. Inorganic Chemistry, J.E. Huheey, Harper Row.
- 2. Developments in Inorganic polymer Chemistry. M.F Lappert and G. J. Leigh
- 3. Inorganic polymers, N.H. Ray.
- 4. Inorganic polymers, Graham and Stone.
- 5. Inorganic Rings and Cages, D.A. Armitage.
- 6. Textbook of Polymer Science, F.W. Billmeyer, Jr. Wiley.
- 7. Contemporary Polymer Chemistry, H.R. Alcock and F.W. Lambe. Prentice Hall.

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# (CH-504, Group-II) Organic Synthesis-I (2Hrs. or 3 periods/week)

Exam Duration: 3 hrs.

Max. Marks: 50

Unit-I

#### Organometallic Reagents

Principle, preparations, properties and applications of the following in organic synthesis with mechanistic details. Group I and II metal organic compounds. Li, Mg, Hg, Cd, Zn and Ce compounds.

Transition metals: Cu, Pd, Ni, Fe. Co, Rh, Cr, and Ti compounds.

#### Unit-II

#### Oxidation

Introduction. Different oxidative processes. Hydrocarbons – alkenes, aromatic rings, saturated C-H groups (activated and unactivated).

Alcohols, diols, aldehydes, ketones, ketals and carboxylic acids Amines, hydrazines, and sulphides.

Oxidations with ruthenium tetraoxide, lodobenzene diacetate and thallium(III) nitrate.

Unit-III

#### Reduction

Introduction. Different reductive processes.

Alkanes, alkenes, alkynes and aromatic rings. Carbonyl compounds - aldehydes, ketones, acids and their derivatives. Epoxides. Nitro, nitroso, azo and oxime groups. Hy drogenolysis.

#### Unit-IV

#### Rearrangements

General mechanistic considerations - nature of migration, migratory aptitude, memory effects. A detailed study of the following rearrangements: Pinacol-pinacolone, Wagner-Meerwein, Demjanov, Benzil-Benzillic acid, Favorskii, Arndt-Eistert synthesis, Neber, Beckmann, Hofmann, Curtius, Schmidt, Baeyer-Viliger, Shapiro and Schimdt reaction.

#### Unit-V

# Metallocenes, Nonbenzenoid Aromatics and Polycyclic Aromatic Compounds

General considerations, synthesis and reactions of some representative compounds, (tropone, tropolone. Azulene, ferrocene, phenanthrene, fluorene and indene).

#### Books Suggested:

- 1. Modern Synthetic Reactions H.O. House. W.A. Benjamin.
- 2. Some modern Methods of Organic Synthesis. W Carruthers. Cambridge Univ. Press.
- 3. Advanced Organic Chemistry, Reactions Mechanisms and Structure J. March. John Wiley.
- 4. Principles of Organic synthesis. R.O.C Norman and J.M. Coxon. Blackie Academic & Professional.
- 5. Advanced Organic Chemistry Part B. F A Carey and R.J. Sundberg. Plenum Press.
- 6. Rodd's Chemistry of Carbon Compounds. Ed. S Coffey, Elsevier.

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# (CH-505, Group-II) Organic Synthesis-II (2Hrs. or 3 periods/week)

Exam Duration: 3 hrs.

#### Unit-I

Max. Marks: 50

#### Disconnection Approach

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

#### Unit-II

#### **Protecting Groups**

Principle of protection of alcohol, amine, carbonyl and carboxyl groups.

# One Group C-C Disconnections

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

#### Unit-III

#### Two Group C-C Disconnections

Diels-Alder reaction, 1,3-difunctionalised compounds,  $\alpha,\beta$ -unsaturated carbonyl compounds, control in carbonyl condensations, 1,5-difunctionalised compounds. Michael addition and Robinson annelation.

#### Unit-IV

### Two Group C-C Disconnections

Use of 1,2-; 1,4- and 1,6-difunctionalised compounds in ring synthesis.

#### Unit-V

#### Ring Synthesis

Special methods for Saturated heterocycles, synthesis of 3-, 4-, 5- and 6-membered rings, aromatic heterocycles in organic synthesis. Use of Ketene, pericyclic reactions and photochemical reactions.

#### Books Suggested:

- 1. Designing Organic Synthesis, S. Warren, Wiley.
- 2. Organic Synthesis Concept, Methods and Starting Materials, J. Fuhrhop.
- 3. Some Modern Methods of Organic Synthesis. W. Carruthers, Cambridge Univ. Press.
- 4. Modern Synthetic Reactions H O. House, W.A. Benjamin
- 5. Advanced Organic Chemistry: Reactions, Mechanisms and Structure, J. March, Wiley.
- 6. Principles of Organic Chemistry Part B. F A. Carey and R.J. Sundberg. Plenum Press.

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# (CH-506, Group II) Heterocyclic Chemistry

(2Hrs. or 3 periods/week)

Exam Duration: 3 hrs.

Unit-I

Max. Marks: 50

Nomenclature of Heterocycles

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

Aromatic Heterocycles

General chemical behaviour of aromatic heterocycles. classification (structural type), criteria of aromaticity (bond lengths, ring current and chemical shifts in lH NMR spectra. Empirical resonance energy, delocalization energy and Dewar resonance energy, diamagnetic susceptibility exaltations).

Heteroaromatic reactivity and tautomerism in aromatic heterocycles.

Non-aromatic Heterocycles

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

Conformation of six-membered heterocycles with reference to molecular geometry, barrier to ring inversion, pyramidal inversion and 1,3-diaxial interaction.

Stereo-electronic effects anomeric and related effects, Attractive interactions - hydrogen bonding and intermolecular nucleophilic electrophilic interactions.

Heterocyclic Synthesis

Principles of heterocyclic synthesis involving cyclization reactions and cycloaddition reactions.

Unit-III

Small Ring Heterocycles

Three-membered and four-membered heterocycles - synthesis and reactions of aziridines, oxiranes, thiiranes, azetidines, oxetanes and thietanes.

Benzo-Fused Five-Membered Heterocycles

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

Unit-IV

Meso-ionic Heterocycles

General classification, chemistry of some important meso-ionic heterocycles of type-A and B and their applications.

Six-Membered Heterocycles with one Heteroatom

Synthesis and reactions of pyrylium salts and pyrones and their comparison with pyridinium & thiopyrylium salts and pyridones. Synthesis and reactions of quinolizinium and benzopyrylium salts, coumarins and chromones.

Unit-V

Six Membered Heterocycles with Two or More Heteroatoms

Synthesis and reactions of diazines, triazines, tetrazines and thiazines.

Heterocyclic Systems Containing P, As, Sb and B

Introduction and nomenclature of 5- and 6-membered Heterocyclic rings systems containing phosphorusphosphorinanes, phosphorines, phospholanes and phospholes; containing As and Sb.

Introduction and spectral characteristics of 3-, 5- and 6-memberedHeterocyclic rings containing Boron.

Books Suggested:

- 1. Heterocyclic Chemistry Vol. 1-3. R.R. Gupta. M. Kumar and V. Gupta. Springer India.
- 2. The Chemistry- of Heterocycles. T Eicher and S. Hauptmann. Thieme.
- 3. Heterocyclic Chemistry, J.A. Joule. K. Mills and G.F Smith. Chapman and Hall.
- 4. Heterocyclic Chemistry, T.L. Gilchrist, Longman Scientific Technical.
- 5. Contemporary Heterocyclic Chemistry. G.R. Newkome and W W. Paudler. Wiley-InterScience.
- 6. An Introduction to the Heterocyclic Compounds. R.M. Acheson. John Wiley.
- 7. Comprehensive Heterocyclic Chemistry, A.R. Katrizky and C.W. Rees. eds. Pergamon Press.

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# (CH-507, Group -II) Chemistry of Natural Products (2Hrs. or 3 periods/week) Max. Marks: 50

Exam Furation: 3 hrs.

Unit-I

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

Unit-II

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

Quinine and Morphine.

Unit-III

Occurrence, nomenclature, basic skeleton. Diel's hydrocarbon and stereochemistry. Isolation, structure determination and synthesis of Cholesterol, Bile acids, Androsterone, Testosterone, Estrone, Progestrone, Aldosterone. Biosynthesis of steroids.

Unit-IV

Occurrence, nomenclature and general methods of structure determination. Isolation and synthesis of Apigenin, Luteolin, Quercetin, Diadzein, Cyanidin, Hirsutidin, Biosynthesis of flavonoids: Acetate pathway and Shikimic acid pathway.

**Porphyrins** 

Structure and synthesis of Haemoglobin and Chlorophyll.

Unit-V

Prostaglandins: Occurrence, nomenclature, classification, biogenesis and physiological effects. Corey's Synthesis of PGE2 and PGF2a

Pyrethroids and Rotenones: Synthesis and reactions of Pyrethroids and Rotenones.

- 1. Natural Products: Chemistry and Biological Significance, J. Mann. R.S. Davidson, J.B. Hobbs, D.V. Banthrope **Books Suggested** and J B Harbome, Longman. Essex.
- 2. Organic Chemistry: Vol. 2. I.L. Finar. ELBS.
- 3. StereoselectiveSynthesis: A Practical Approach, M. Norgradi. VCH.
- 4. Rodd's Chemistry of Carbon Compounds, Ed. S. Coffey, Elsevier.
- 5. Chemistry. Biological and Pharmacological Properties of Medicinal Plants from the Americas, Ed. Kurt Hostettmann, M P. Gupta and A. Marston. Harwood Academic Publishers.
- 6. Introduction to Flavonoids, B.A. Bohm. Harwood Academic Publishers.
- 7. New Trends in Natural Product Chemistry, Atta-ur-Rahman and M.I.Choudhary, Harwood Academic Publishers.
- 8. Insecticides of Natural Origin, Sukh Dev. Harwood Academic Publishers.

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# (CH-504, Group -III) Analytical Chemistry (2Hrs. or 3 periods/week)

Exam Duration: 3 hrs.

Max. Marks: 50

#### Unit-I

#### Introduction

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

#### **Errors and Evaluation**

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

#### Unit-II

#### Food Analysis

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

#### Unit-III

#### **Analysis of Water Pollution**

Origin of waste water, types, water pollutants and their effects. Sources of water pollution - domestic, industrial, agricultural, soil and radioactive wastes. Objectives of analysis, parameter for analysis - color, turbidity; total solids, conductivity, acidity, alkalinity, hardness, chloride, sulphate, fluoride, silica, phosphates and different forms of nitrogen. Heavy metal pollution - public health significance of cadmium, chromium, copper, lead, zinc, manganese, mercury and arsenic. General survey of instrumental technique for the analysis of heavy metals in aqueous systems. Measurement of DO, BOD and COD. Pesticides as water pollutants and analysis. Water pollution laws and standards.

#### Unit-IV

#### Analysis of Soil and Fuel

Analysis of soil: moisture pH, total nitrogen, phosphorus, silica, lime, magnesia, manganese, sulphur and alkali salts. Fuel analysis: liquid and gas. Ultimate and proximate analysis - heating values - grading of coal. Liquid fuels - flash point, aniline point, octane number and carbon residue. Gaseous fuels - producer gas and water gas - calorific value.

#### Unit-V

#### Analysis of Body Fluids and Drugs

Clinical chemistry: Composition of blood-collection and preservation of samples. Clinical analysis. Serum electrolytes, blood glucose, blood urea nitrogen, uric acid, albumin, globulins, barbiturates, acid and alkaline phosphatases. Immunoassay: principles of radio immunoassay (RIA) and applications. The blood gas analysis, trace elements in the body.

Drug analysis: Narcotics and dangerous drugs. Classification of drugs. Screening by gas and thin-layer chromatography and spectrophotometric measurements.

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#### Books Suggested

- 1. Analytical Chemistry. G.D. Christian. John Wiley.
- 2. Fundamentals of Analytical Chemistry. D A. Skoog. D M. Westand F.J. Hooler. W.B Saunders.
- 3 Analytical Chemistry Principles. J.H. Kennedy. W.B. Saunders.
- 4. Analytical Chemistry Principles and Techniques. L.G. Hargis. Prentice Hall.
- 5. Principles of Instrumental analysis D A. Skoog and J.L. Loary. W.B Saunders.
- 6. Principles of Instrumental Analysis D A. Skoog W.B. Saunders.
- 7. Quantitative Analysis. R.A. Day, Jr. and A.L Underwood, Prentice Hall.
- 8. Environmental Solution. S.M. Khopkar, Wiley Eastern.
- 9. Basic Concepts of Analysis Chemistry. S.M. Khopkar, Wiley Eastern.
- 10. Handbook of Instrumental Techniques for Analytical Chemistry, F. Settle. Prentice Hall.

# ELECTIVE PAPER-2 (CH-505, Group-III) Physical Organic Chemistry (2Hrs. or 3 periods/week)

Exam Duration: 3 hrs.

Max. Marks: 50

#### Unit-I

#### Concepts in Molecular Orbital (MO) and Valence Bond (VB) Theory

Introduction to Huckel molecular orbital (MO) method as a mean to explain modern theoretical methods. Advanced techniques in PMO and FMO theory. Molecular mechanics, semi-empirical methods and ab inito and density functional methods. Scope and lmitations of several computational programmes.

Quantitative MO theory - Huckel molecular orbital (HMO) method as applied to ethene, allyl and butadiene. Qualitative MO theory - ionisation potential. Electron affinities. MO energy levels. Orbital symmetry. Orbital interactiondiagrams. MO of simple organic systems such as ethene, allyl, butadiene, methane and methyl group. Conjugation and hyperconjugation. Aromaticity. Valence bond (VB) configuration mixing diagrams. Relationship between VB configuration mixing and resonance theory. Reaction profiles. Potential energy diagrams. Curve-crossing model - nature of activation barrier in chemical reactions

#### Unit-II

#### Principles of Reactivity

Mechanistic significance of entropy, enthalpy and Gibb's freeenergy. Arrhenius equation. Tansition state theory. Use of activation parameters, Hammond's postulate, Bell-Evans-Polanyi principle. Potential energy surface model. Marcus theory of electronic transfer. Reactivity and selectivity principles.

#### **Kinetic Isotope Effect**

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

#### Unit-III

#### Structural Effects on Reactivity

Linear free energy relationships (LFER). The Hammett equation, substituent constants, theories of substituent effects. Interpretation of  $\sigma$ -values. Reaction constant  $\rho$ . Deviations from Hammett equation. Dualparameter correlations, inductive substituent constant. The Taft model,  $\sigma$ -order of  $\sigma$ -values.

#### Solvation and Solvent Effects

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

Unit-IV

Acids, Bases, Electrophiles, Nucleophiles and Catalysis

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

#### Steric and Conformational Properties

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

#### Unit-V

#### Nucleophilic and Electrophilic Reactivity

Structural and electronic effects on  $S_N1$  and  $S_N2$  reactivity Solvent effect. Kinetic isotope effects. Intramolecular assistance. Electron transfer nature of  $S_N2$  reaction. Nucleophilicity and  $S_N2$  reactivity based on curve crossing model. Relationship between polar and electron transfer reactions.  $S_{RN}1$  mechanism Electrophilic reactivity, general mechanism. Kinetics of  $S_E2$ -Ar reaction Structural effects on rates and selectivity. Curve-crossing approach to electrophilic reactivity.

#### Radical and Pericyclic Reactivity

Radical stability, polar influence, solvent and steric effects. A curve crossing approach to radical addition, factors effecting barrier heights in addition, regioselectivity in radical reactions.

Reactivity, specificity and periselectivity in pericyclic reactions.

#### Books Suggested:

- 1. Molecular Mechanics. U. Burkert and N.L Alinger. ACS Monograph 177, 1982.
- 2. Organic Chemists. Book of Orbitals : L. Salem and W.L. Jorgensen, Academic Press.
- 3. Mechanism and Theory in Organic Chemistry. T.H. Lowry and K.C. Richardson. Harper and Row.
- 4. Introduction to Theoretical Organic Chemistry and Molecular Modeling.
- 5. Physical Organic Chemistry, N.S. Isaacs, ELBS/Longman.
- 6. The Physical Basis of Organic Chemistry: H. Maskill, Oxford University Press.

# ELECTIVE PAPER - 3 (CH-506, Group-III) Chemical Dynamics (2 Hrs. or 3 period/week)

Exam Duration: 3 hrs.

**Atmospheric Reactions** 

Unit-I

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Physical structure of the atmosphere, chemical composition of the atmosphere. Kinetics and mechanism of NOx, CIOx cycles and  $H_2 + O_2$  reaction. Mechanism of general methane oxidation. Kinetics and mechanism of low temperature oxidation of methane. Concept of global warming.

#### Unit-II

Oscillatory Reactions: Autocatalysis and oscillatory reactions, Kinetics and mechanism of Belousov-Zhabotinski (B-Z) reaction.

Enzymes and Inhibitions: Kinetics of one enzyme - Two substrate systems and their experimental characteristics. Enzyme inhibitors and their experimental characteristics. Kinetics of enzyme inhibited reactions.

Micelles catalysis and inhibition: Kinetics and mechanism of micelle catalyzed reactions (Ist order and second order) Various type of micelle catalyzed reactions. Micelle inhibited reactions.

Dynamics of Gas-surface reactions: Adsorption/desorption kinetics and transition state theory Dissociative adsorption and precursor state. Mechanism of Langimur's adsorption of the oxidation of carbon monoxide to carbon dioxide. True and apparent activation energies. Industrial importance of heterogeneous catalysis.

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Max. Marks: 50

#### Unit-III

#### Radiation Chemistry and Photochemistry

Radiation chemistry of water and aqueous solutions. Hydrogen atom and hydroxyl radical - oxidizing and reducing conditions. Kinetics and mechanism of photochemical and photosensitized reactions (One example in each case). Stern-Volmer equation and its application. Hole-concept in the presence of semi-conductor type photocatalysts. Kinetics and mechanism of electron transfer reaction in the presence of visible light. Kinetics of exchange reactions (mathematical analysis).

#### **Transition State**

A brief aspect of statistical mechanics and transition state theory, application in calculation of the second order rate constant for reactions with collision for (1) atom + atom (2) atom + molecule (3) molecule + molecule reactions. Static solvent effects and thermodynamics formulations. Adiabatic electron transfer reactions, energy surfaces.

#### Unit-IV

#### Substitution reactions.

Substitution reactions. Classification of ligand substitution mechanism. Anation and base catalyzed kinetics of anation reactions Aquation and acid catalyzed kinetics of aquation reactions (octahedral complexes). Inner-sphere electron transfer reactions and mechanism. Various types of inner sphere bridges, adjustment and remote attack Linkage isomerism. Chemical and resonance mechanisms. Marcus-Cross relation in outer sphere reactions (no mathematical derivation) Its application in reactions-

Ce (IV) + Mo (CN)<sub>5</sub><sup>4</sup> 
$$\leftrightarrow$$
 Ce (III) + Mo (CN)<sub>6</sub><sup>3</sup>·  
Fe(CN)<sub>6</sub><sup>3</sup>· + Fe(CN)<sub>6</sub><sup>4</sup>·  $\leftrightarrow$  Fe (CN)<sub>6</sub><sup>4</sup>· + Fe (CN)<sub>6</sub><sup>3</sup>·

Bridged outer-sphere electron transfer mechanism.

Kinetics of reactions in the presence of cyclodextrins. Considering one full case study, nucleophilic and electrophilic catalysts and their mode of action.

#### Unit-V

#### Metal ion catalysis and induced phenomena

Metal ion catalyzed reactions, their kinetics and reaction mechanism in solutions. Induced reactions, their characteristics. Mechanism of - (i) Fe(II) induced oxidation of iodine by Cr(VI). (ii) As(III) induced oxidation of Mn(II) by chromate in acid solutions.

Kinetics and mechanism of induced reactions in metal complexes (octahedral complexes of Cobalt(III) only). Kinetics of hydroformylation reaction.

#### **Books Recommended**

- 1. Progress in Inorganic Chemistry, Vol. 30, 1967.
- 2. R. Lumry and R.W. Raymond, Electron Transfer Reactions, Interscience.
- 3. N.L. Bender, Mechanism of Homogeneous Catalysis from protein to protein, Wiley.
- 4. A.G. Sykes, Kinetics of Inorganic reactions, Pergamon.
- 5. S.W. Benson, Mechanism of Inorganic Reactions, Academic Press.
- 6. Physical Chemistry Vol. 2, Ed. Prof. YaGrasimov, Mir publisher.
- 7. Basolo and Pearson, Inorganic Reaction Mechanism, Wiley.
- 8. H. Taube, Electron Transfer Reactions, Oxford Press.

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# (CH-507, Group-III) Electrochemistry (2 Hrs. or 3 period/week)

Exam Duration: 3 hrs.

Unit-I

Max. Marks: 50

# Conversion and storage of Electrochemical Energy

Present status of energy consumption: Pollution problem. History of fuel cells, Direct energy conversion by electrochemical means. Maximum intrinsic efficiency of an electrochemical converter.

Physical interpretation of the Carnot efficiency factor in electrochemical energy converters. Power output.

Electrochemical Generators (Fuel cells): Hydrogen oxygen cells, Hydrogen Air cell. Hydrocarbon air cell, alkaline fuel cell. Phosphoric and fuel cell, direct NaOH fuel cells, applications of fuel cells.

# Electrochemical Energy Storage:

Properties of electrochemical energy storers: measure of battery performance. Charging and discharging of a battery, storage density, energy density.

Classical Batteries: (i) Lead Acid (ii) Nickel-Cadmium, (iii) Zinc-Manganese dioxide

Modern Batteries: (i) Zinc-Air, (ii) Nickel-Metal Hydride, (iii) Lithium Battery.

Future Electricity Storage: in (i) Hydrogen, (ii) Alkali Metals, (iii) Non aqueous solutions.

#### Unit-II

### Corrosion and Stability of Metals:

Surface mechanism of the corrosion of the metals. Thermodynamics and the stability of metals. Potential-pH (or Pourbaix) Diagrams. Corrosion current and corrosion potential - Evans diagrams.

Measurement of corrosion rate: (i) Weight Loss Method (ii) Electrochemical Method.

Inhibiting Corrosion: Cathodic and Anodic Protection, (i) Inhibition by addition of substrates to the electrolyte environment, (ii) by charging the corroding method from external source, anodic Protection. Organic inhibitors. The Fuller Story Green inhibitors.

Passivation: Structure of Passivation films, Mechanism of Passivation. Spontaneous Passivation: Nature's method for stabilizing surfaces.

#### Unit-III

#### Bioelectrochemistry:

Bioelectrodics, Membrane Potentials, Simplistic theory, Modern theory. Electrical conductance in biological organisms. Electronic. Protonic electrochemical mechanism of nervous systems, enzymes as electrodes.

#### Unit-IV

Kinetics of Electrode Process: Essentials of electrode reaction current density, overpotential, Tafel Equation, Butler Volmer equation. Standard rate constant (K°) and transfer coefficient (a), exchange current.

Irreversible Electrode processes: criteria of irreversibility, information from irreversible wave.

Methods of determining kinetic parameters for quasi-reversible and irreversible waves: Koutecky's method. Meits Israel method. Gelling's method.

Electrocatalysis: Chemical catalysts and electrochemical catalysts with special reference to purostates, porphyrin oxides of rare earths. Electro-catalysis in simple redox reactions and reaction involving adsorbed species. Influence of various parameters.

#### Unit- V

Potential Sweep Method: Linear sweep voltammetry, cyclic voltammetry, theory and applications. Diagnostic criteria of cyclic voltammetry.

Controlled current microelectrode techniques: comparison with controlled potentials methods, chronopotentiometry, theory and applications.

Bulk Electrolysis Methods: Controlled potential coulometry. Controlled coulometry. Electroorganic synthesis and its important applications.

Stripping analysis: Anodic and cathodic modes. Preelectrolysis and stripping steps, applications of stripping analysis.

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#### Book Suggested:

- 1. Modern Electrochemistry Vol. I, IIA, IIB JO'M Bockris and A.K.N. Reddy, Plenum Publication. New York.
- 2. Polarographic Techniques by L. Meites. Interscience.
- "Fuel cells; Their electrochemistry" McGraw Hill Book Company. New York.
- 4. Modern Polarographic Methods by A.M. Bond and Marcel Dekker
- 5. Polarography and allied techniques By K. Zutshi, New Age International publication, New Delhi.
- 6. Electroanalytical Chemistry by Basil H. Vessor& Galen W., Wiley Interscience.
- 7. Topics in Pure and Applied Chemistry. Ed. S.K. Rangrajan. SAEST Publication, Karaikudi (India)

CH-508: M.Sc. (Final) Seminar (1hr/week)

Exam Duration 15 minutes/student Seminar to be conducted in presence of External examiner.

Max Marks 25

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# CH-509: M.Sc. (Final) Chemistry Practical (9 Hrs. /week)

Exam Duration: (14 hrs in 2 days)

Max. Marks: 200

### **Inorganic Chemistry**

Preparation: Preparation of selected inorganic compounds and their study by IR spectra. Handling of air and moisture sensitive compounds involving vacuum lines.

Selection can be made from the following:

- 1. Sodium amide, Inorg. Synth., 1946, 2, 128.
- 2. Synthesis and thermal analysis of group II metal oxalate hydrate, J. Chem. Ed., 1988, 65, 1024.
- 3. [PhBCl<sub>2</sub>] Dichlorophenylborane. Synthesis in vacuum line.
- 4 . Preparation of Tin (IV) iodide, Tin (IV) chloride and Tin (II) iodide. Inorg. Synth., 1953, 4, 119.
- 5. Relative stability of Tin (IV) and Pb (IV). Preparation of ammonium hexachlorostannate ( $NH_4$ )<sub>2</sub>[SnCl<sub>6</sub>]; ammonium hexachloroslumbate ( $NH_4$ )<sub>2</sub>[PbCl<sub>6</sub>].
- 6. Hexabis (4-nitrophenoxy) cyclotriphosphazene.
- 7. Synthesis of trichlorodiphenylantimony (V) hydrate, Inorg. Synth., 1985, 23, 194.
- 8. Sodium tetrathionate, Na<sub>2</sub>S<sub>4</sub>O<sub>6</sub>.
- 9. Metal complexes of dimethylsulfoxide and their IR: CuCl<sub>2</sub>.DMSO; PdCl<sub>2</sub>.2DMSO; RuCl<sub>2</sub>.4DMSO, J. Chem. Educ., 1982, 59, 57.
- 10. Synthesis of metal acetylacetonate: IR, Inorg. Synth., 1957, 5, 130; 1963, 1,183.
- 11. Bromination of [Cr(acac)<sub>3</sub>], J. Chem. Edu, 1986, 63, 90.
- 12 [Cu(acac)<sub>2</sub>]. H2O.
- 13. cis- and trans- [Co(en)<sub>2</sub>Cl<sub>2</sub>]<sup>+</sup>.
- 14. cis-[Co(en)<sub>2</sub>Cl<sub>2</sub>]Cl, J. Chem Soc., 1960, 4369.
- 15. Cr(III) complexes. [Cr(H<sub>2</sub>O)<sub>6</sub>]NO<sub>3</sub>.3H<sub>2</sub>O; [Cr(H<sub>2</sub>O)<sub>4</sub>,Cl<sub>2</sub>]Cl.2H<sub>2</sub>O; [Cr(en)<sub>3</sub>]Cl<sub>3</sub>; [Cr(acac)<sub>3</sub>], Inorg, Synth., 1972,
- 13, 184.
- 16. Preparation of N,N-bis(salicyladehyde)ethylenedimine, salen H<sub>2</sub>; [CO(salen)], J. Chem. Educ., 77, 54, 443; 1973, 50, 670.
- 17. Preparation of Fe(II) chloride (use it as Friedel-Craft chlorination source), J. Org. Chem., 1978, 43, 2423; J. Chem. Edu., 1984, 61, 645; 1986, 63, 361.
- 18. Reaction of Cr(III) with a multidentate ligand; a kinetics experiment (visible spectra Cr-EDTA complex), J. A. C. S., 1953,75,5670.
- 19. Preparation of [Co(phenanthroline-5, 6-quinone)].
- 20. Preparation and use of Ferrocene, J. Chem Edu., 1966, 43, 73; 1976, 53, 730.
- 21. Preparation of copper glycine complex. cis- and trans- bis(glycinato)copper (II), J. Chem. Soc. Dalton, 1979, 1901; J. Chem. Edu. 1982, 59, 1052.
- 22. Preparation of phosphine (Ph<sub>3</sub>P) and its transition metal complexes.
- 23. Any other experiment such as conversion of p-xylene to terephathalic acid catalyzed by CoBr<sub>2</sub> (homogeneous catalysis).

#### Spectrophotometric Determinations

- a) Manganese/Chromium/Vanadium in steel sample.
- b) Nickel/Molybdenum/Tungsten/Vanadium/Uranium by extractive spectrophotometric method.
- c) Fluoride/Nitrite/Phosphate.
- d) Iron-phenanthroline compelexes: Job's method of continuous variations.
- e) Zirconium-alizarin Red-S complex: Mole-ratio method.
- f) Copper ethylenediamine complex: Slope-ratio method.

#### Flame Photometric Determinations

- a) Sodium and potassium when present together.
- b) Lithium/Calcium/Barium/Strontium.

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e) Cadmium and Magnesium in tap water.

# Quantitative determinations of a three component mixture:

One Volumetrically and two Gravimetrically

a) Cu<sup>+2</sup>, Ni<sup>+2</sup>, Zn<sup>+2</sup>

b) Cu<sup>+2</sup>, Ni<sup>+2</sup>, Mg<sup>+2</sup>

# Chromatographic Separations

- a) Cadmium and zinc
- b) Zinc and magnesium
- c) Thin-layer chromatography-separation of nickel, manganese, cobalt and zinc, Determination of Rf values.
- d) Separation and identification of the sugars present in the given mixture of glucose, fructose and sucrose by paper chromatography and determination of Rf values.

# **Organic Chemistry**

Qualitative Analysis: Separation, purification and identification of the components of three organic compounds (three solids or two liquids and one solids or two solids and one liquid), using for checking the purity of the separated compounds, chemical analysis, IR, PMR and mass spectral data.

Multi-step Synthesis of Organic Compounds: The exercises should illustrate the use of organic reagents and may involve purification of the products by chromatographic techniques.

i) Photochemical reaction:

(Benzophenone → Benzpinacol → Benzpinacolone)

ii) Beckman Rearrangement: Benzanilide from benzene

(Benzene → Benzophenone → Benzophenone oxime → Benzanilide)

iii) Benzilic acid rearrangement: Benzilic acid from benzoin

(Benzoin → Benzil → Benzilie acid).

- iv) Synthesis of heterocyclic compounds
  - a) Skraup synthesis: Preparation of quinoline from aniline
  - b) Fisher Indole synthesis: Preparation of 2-phenylindole from phenylhydrazine.
- v) Diazocoupling: Phthalic anhydride → Phthalamide → anthranilic acid → methyl red.

# **Extraction of Organic Compounds from Natural Sources**

- a) Isolation of caffeine from tea leaves.
- b) Isolation of casein from milk (the students are required to try some typical colour reactions of proteins)
- c) Isolation of lactose from milk (purity of sugar should be checked by TLC and PC and Rf values reported).
- d) Isolation of chlorophyll a & b from spinach / spirulina.

Paper Chromatography: Separation and identification of the sugars present in the given mixture of glucose, fructose and sucrose by paper chromatography and determination of Rf values.

Spectroscopy: Identification of organic compounds by the analysis of their spectral data (UV, IR, 1HMR, 13CMR &

# Spectrophotometry (UV/VIS) Estimations

- a) Amino acids
- b) Proteins
- c) Carbohydrates
- d) Cholesterol
- e) Ascorbic acid
- f) Aspirin
- g) Caffeine

Physical Chemistry

A list of experiments under different headings are given below. Typical experiments are to be selected from each type.

A. Thermodynamics

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- (i) Determination of partial molar volume of solute (e.g. KCI) and solvent in a binary mixture.
- (ii) Determination of the temperature dependence of the solubility of a compound in two solvents having similar intramolecular interactions (benzoic acid in water and in DMSO-water mixture) and calculate the partial molar heat of solution.

# B. Spectroscopy

- (i) Determination of pKa of an indicator (e.g. methyl red) in (a) aqueous and (b) micellar media.
- (ii) Determination of stoichiometry and stability constant of Ferricisothiocyanation complex ion in solution
- (iii) Determination of rate constant of alkaline bleaching of Malachite green and effect of ionic strength on the rate of

# C. Polarography

- (i) Identification and estimation of metal ions such as Cd2+, Pb2+, Zn2+ and Ni2+ etc. polarographically.
- (ii) Study of a metal ligand complex polarographically (using Lingane's Method).

# D. Chemical Kinetics

- (i) Determination of rate constant and formation constant of intermediate complex in the reaction of Ce(IV) and Hypophosphorous acid at ambient temperature.
- (ii) Determination of energy and enthalpy of activation in the reaction of KMnO4 and benzyl alcohol in acid medium.
- (iii) Determination of energy of activation and entropy of activation from a single kinetic run.
- (iv) Kinetics of an enzyme catalyzed reaction.

# Books Suggested:

- 1. Inorganic Experiments, J. Derek Wooings, VCH.
- 2. Microscale Inorganic Chemistry, Z. Szafran, R.M Pike and M.M. Singh, Wiley.
- 3. Practical Inorganic Chemistry, G. Marr and B. W. Rockett. Van Nostrad.
- 4. The Systematic Identification of Organic Compounds, R.L Shriner and D.Y. Curlin.

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# INSTRUCTIONS TO THE EXAMINERS

# CH-509: M.Sc. (Final) Chemistry Practical

Duration of Exam: 14 hrs. (Spread over 2 days)

Max. Marks: 200 Min. Mark	ks 72
Inorganic Chemistry	
1. Preparation of one of the selected inorganic compounds as mentioned in the syllabus and its study spectra. Mossbaur, ESR and magnetic susceptibility. Handling of air and moisture sensitive compound lines.	by IR, electronic counds involving
or	
Quantitative determination of a three component mixture by volumetric & gravimetric methods.	25
2. Spectrophotometric determination of one of the 5 exercises given in the syllabus.	
or	
Flame Photometric determinations (one exercise)	15
3. Chromatographic separation of two metal ions.	10
Organic Chemistry  1. Qualitative Analysis  Separation, purification and identification of the components of a mixture of three organic compound two liquids and one solid, two solid and one liquid), using TLC for checking the purity of the separate Chemical analysis, IR, <sup>1</sup> HMR and Mass spectral data.  2. Multi-step synthesis of Organic Compounds	ed compounds.
Perform one of the multi-step synthesis of organic compounds.	20
Spectroscopy Identification of Organic Compounds by the analysis of their spectral data	
Physical Chemistry	
From the Experiments listed in syllabus	
1. Perform one Major physical experiment	30
2. Perform one Minor physical experiment	20
Viva	30
Record	20

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