

# University of Rajasthan Jaipur

# **SYLLABUS**

M.Sc. Chemistry (Annual Scheme)

**Previous Examination 2021** 

Final Examination 2022

Dy. Registrar (Acad.)
University of Rajasthan
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# M.Sc. (C(IRMISTRY) (Annual Scheme)

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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	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 Marks	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	CH-506	Elective Paper	03	50	18
Paper-VII	CH-507	Elective Paper	03	50	18
Seminar	CH-508	29		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.

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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-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, threo and erythro 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

- 1. 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

Polymer - 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.
- 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, 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[ $Cr(C_2O_4)_2(H_2O)_2$ ]
- Na[Cr(NH<sub>3</sub>)<sub>2</sub>(SCN)<sub>4</sub>]
- 5. [Mn(acac)<sub>2</sub>]
- 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

- Aniline → 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 covering all 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.
- 5. 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 20 Perform one of the quantitative analysis given in syllabus. (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 Viva 30

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