COURSE CURRICULUM FOR MASTER COURSES UNDER CHOICE BASED CREDIT SYSTEM



M.Sc. (CHEMISTRY)

DEPARTMENT OF CHEMISTRY

NETAJI SUBHAS UNIVERSITY, JAMSHEDPUR

First Semester				
Paper Name	Credit	Internal Marks	External Marks	Total Marks
INORGANIC CHEMISTRY-1	5	30	70	100
ORGANIC CHEMISTRY -1	5	30	70	100
PHYSICAL CHEMISTRY -1	5	30	70	100
PRACTICAL-1	6		100	100
TOTAL	21			400
Second	Semeste	r		
ANALYTICAL CHEMISTRY	5	30	70	100
GROUP THEORY & SPECTROSCOPY	5	30	70	100
PHYSICAL CHEMISTRY -2	5	30	70	100
PRACTICAL-2	6		100	100
TOTAL	21			400
	Semester			
APPLICATIONS OF SPECTROSCOPY	5	30	70	100
ENVIRONMENTAL CHEMISTRY	5	30	70	100
BIO-CHEMISTRY	5	30	70	100
PRACTICAL-3	6		100	100
TOTAL	21			400
Fourth Semester (Speciliz	ation, ch	oose any one grou	p)	
PHYSICAL-III	5	30	70	100
PHYSICAL-IV	5	30	70	100
PROJECT WORK	5			100
PRACTICAL-4A	6			100
TOTAL	21			400
INORGANIC-II	5	30	70	100
INORGANIC-III	5	30	70	100
PROJECT WORK	5			100
PRACTICAL-4B	6			100
TOTAL	21			400
ORGANIC-II	5	30	70	100
ORGANIC-III	5	30	70	100
PROJECT WORK	5			100
PRACTICAL-4C	6			100
TOTAL	21			400

SEMESTER I

I. Physical Chemistry – I

Unit-1: Chemical Thermodynamics

- (a) Partial molar properties in ideal gas mixture, Chemical Potential, its determination and variation with temperature and pressure, Gibb's Duhem equation.
- (b) Fugacity and activity its variation with 'T' and 'P', its determination. Fugacity of a gas mixture, Duhem, Margules equation and its application.

Unit-2: Statistical Thermodynamics

Partition function and its significance, Relationship with thermodynamic functions, Translational, Rotational, Vibrational and Electronic partition function. Its application in the case of monoatomic and diatomic molecules.

Unit-3: Surface Chemistry

Surface tension and Surface Free energy on liquids. Pressure difference across curved Surface (Laplace equation), Vapour pressure of droplets (Kelvin equation). Gibbs absorption isotherm, Estimation of surface area. (B.E.T equation), Unimolecular and bimolecular surface reations.

Unit-4: Chemical Kinetics

Mechanism and Kinetics of consecutive and opposing reactions. Activated complex theory of Uni-molecular reaction.

Mechanism and Kinetics of Photolysis of acetaldehyde and Photo dimerisation of Anthracene, Polymerization and Auto oxidation reaction. Homogeneous catalysis, Kinetic Enzyme catalysis, study of fast reactions by flow method

and relaxation methods.

Unit-5 Electro Chemistry

Electrode potential in terms of Chemical Potential and activity, Debye Huckle theory of conductance of electrolytic solution, its applications and limitations, Quantitative treatment of Debye Huckle Limiting law and its modification for finite size ions, effect of ion solvent interaction on activity coefficients, Butler-Volmer equation under equilibrium and non-equilibrium condition. Exchange current density Tafel Plot.

Unit-6: Macro Molecules

Types of Polymers, Kinetics and mechanism of Polymerization Molecular mass-number and mass average molecular mass, determinations of molecular mass by osmometry, viscosity and light scattering method.

INORGANIC CHEMISTRY-I

I. 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, the 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

II. Metal-Ligand Bonding

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

III. Electronic Spectra and Magnetic Properties of Transition Metal Complexes

IV. Spectroscopic ground states, correlation, Orgel and Tanabe-Sugano diagrams for transition metal complexes (d^1 - d^9 states), calculations of Dq, B and β 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 spincrossover.

V. Metal Clusters

Higher boranes, carboranes, metalloboranes and metallocarboranes. Metal carbonyl and halide clusters, compounds with metal-metal multiple bonds.

VI. Metal π -Complexes

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

VII. Isopoly and Heteropoly Acids and Salts

ORGANIC CHEMISTRY-I

1 Reaction Mechanism: Structure and Reactivity

Types of mechanisms, types of reactions, thermodynamic and kinetic requirements, kinetic and thermodynamic control, Hammond's postulate, Potential energy diagrams, transition states and intermediates, methods of determining mechanisms, isotope effects. Hard and soft acids and bases. 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.

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.

II Aliphatic Nucleophilic Substitution

The S_N2 , S_N1 , mixed S_N1 and S_N2 and SET mechanisms. Structural and electronic effects on S_N1 and S_N2 reactivity. Solvent effects. Kinetic isotope effects. Intramolecular assistance: Electrontransfer nature of S_N2 reaction.

The neighbouring group mechanism, neighbouring group participation by R and π -bonds, anchimeric assistance.

Classical and nonclassical carbocations, phenonium ions, norbornyl system, common carbocation rearrangements. Application of NMR spectroscopy in the detection of carbocations. The S_N i mechanism. Nucleophilic substitution at an allylic, aliphatic trigonal and a vinylic carbon. Reactivity effects of substrate structure, attacking nucleophile, leaving group and reaction medium, phase transfer catalysis and ultrasound, ambident nucleophile, regioselectivity.

III Aliphatic Electrophilic Substitution

Elecrophilic reactivity, general mechanism. 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.

Kinetic of SE2-Ar reaction. Structural effects on rates and selectivity.

IV Addition to Carbon-Carbon Multiple Bonds

Mechanistic and stereochemical aspects of addition reactions involving electrophiles, nucleophiles and free radicals, regio- and chemo-selectivity, orientation and reactivity. Addition to cyclopropane ring. Hydrogenation of double and triple bonds, hydrogenartion of aromatic rings. Hydroboration. Michael reaction. Sharpless asymmetric epoxidation.

V 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, Organozinc and Organolithium reagents to carbonyl and unsaturated carbonyl compounds. Mechanism of condensation reactions involving enolates- Aldol, Knoevenagel, Claisen, Mannich, Benzoin, Perkin and Stobbe reactions. Hydrolysis of esters and amides, ammonolysis of esters.

VI 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.

VII 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.

VIII 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), oxidation of aldehydes to carboxylic acids, auto-oxidation, coupling of alkynes and arylation of aromatic compounds by diazonium salts. Sandmeyer reaction. Free radical rearrangement. Hunsdiecker reaction.

PRACTICAL-I

INORGANIC CHEMISTRY

- 1. Cent per cent quantitative Analysis of Cement.
- 2. Estimation of the following:
 - (a) Magnesium by E.D.T.A. Methods (Volumetrically)
 - (b) Zinc by potassium ferrocyanide (Volumetrically)
 - (c) Nickel by Dimethylglyoxime (Gravimetrically)
 - (d) Managnese in steel by sodium bismuthate method.
- **3. A.** Separation and determination of two metal ions Cu-Ni, Ni-Zn, Cu-Fe etc. involving volumetric and gravimetric methods.
 - **B.** Separation of cations and anions by a) Paper chromatography b) Column Chromatography.
- 4. Preparation of inorganic compounds:
 - (i) [Cu(NH3)4]SO4.H2O
 - (ii) K3[Fe(C2O4)3]
 - (iii) Prussian Blue, Turnbull's Blue
 - (iv) [Ni(NH3)6]Cl2
 - (v) [Ni(dmg)2]

ORGANIC CHEMISTRY

5. Organic Qualitative

Identification of organic compounds containing one functional group using Chemical & Spectral Analysis

6. Separation, purification and identification of binary mixture (one liquid and one solid) involving TLC and Column Chronatography. Chemical tests and Functional group identification.

- 7 Preparation of organic compounds using methods not involving more than two steps. Some of the experiments listed below:
 - (i) Preparation of methyl Orange
 - (iv) Preparation of Martius yellow
 - (vi) Preparation of p-nitro aniline from acetanilide
 - (viii) Preparation of Cinnamic acid from Benzaldehyde
- **8** Estimation of Glucose

SEMESTER II

ANALYTICAL CHEMISTRY

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 preparations - dissolution and decompositions. Gravimetric techniques. Selecting and handling of reagents. Laboratory notebooks. Safety in the analytical laboratory.

II 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 errors and the effects upon the analytical results. Methods for reporting analytical data. Statistical evaluation of data-indeterminate errors. The uses of statistics.

III Food Analysis

Moisture, ash, crude protein, fat, crude fibre, 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.

IV 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 as sources of pollution. Objectives *of* analysis-parameter for analysis-colour, 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. Measurements of DO, BOD and COD. Pesticides as water pollutants and analysis. Water pollution laws and standards.

V Analysis of Soil, Fuel, Body Fluids and Drugs

- (a) Analysis of soil: moisture, pH, total nitrogen, phosphorus, silica, lime, magnesia, manganese, sulphur and alkali salts.
- (b) Fuel analysis: solid, 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.

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

PHYSICAL CHEMISTRY-II

Unit-1: Solid state chemistry

Perfect and imperfect crystals, intrinsic and extrinsic defects, line defects, plane defects, Vaccancies-schottky and Frenkel defect. Non-stochiometric defects.

Unit-3: Introduction of Quantum mechanics

The Schrodinger equation and the postulates of quantum mechanics. Particle in three dimensional box, Hermitian operators, properties of operators, Angular momentum operator, their Eigen function and Eigen values, Theorem of operators.

Unit-4: Exactly Soluble System

Linear Harminic oscillator, Harmonic Vibration Hermit differential equation and its solution through recursion relation, Hermit polynomial. H-like atoms, separation of r, θ , ϕ equation. Laguerre and associated Laguerre polynomial. Legendre polynomial equation and their solution. the rigid rotor.

-5 Approximate Method

Variation method, Linear application to Harmonic oscillator, perturbation method, first order perturbation, Application to He-atom.

Huckle theory of conjugated systems, bond order and charge density-its calculation. Application to ethylene and butadiene.

GROUP THEORY & SPECTROSCOPY

I Symmetry and Group Theory in Chemistry

Symmetry elements and symmetry operation, definitions 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 matrices (representation for the Cn, Cnv, Cnh. Dnh etc. groups to be worked out explicitly). Character of a representation. The great orthogonality theorem (without proof) and its importance. Character tables and their use; spectroscopy.

II 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.

III Vibrational Spectroscopy

A. Infrared Spectroscopy

Review of linear harmonic oscillator, vibrational energies of diatomic molecules, zero point energy, force constant and bond strengths; anharmonicity, Morse potential energy diagram, vibration-rotation spectroscopy, P,Q,R branches. Breakdown of Oppenheimer approximation; vibrations of polyatomic molecules. Selection rules, normal modes of vibration, group frequencies, overtones, hot bands, factors affecting the band positions and intensities, far IR region, metal-ligand vibrations, normal co-ordinate analysis,

B. 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 anti Stokes Raman spectroscopy (CARS).

IV Magnetic Resonance Spectroscopy

A. Nuclear Magnetic Resonance Spectroscopy

Nuclear spin, nuclear resonance, saturation, shielding of magnetic nuclei, chemical shift, deshielding, spin-spin interactions, factors influencing coupling constant "j" Classification (AXB, AMX, ABC, A2B2 etc.), spin decoupling; basic ideas about instrument, NMR studies of nuclei other than proton-¹³C, ¹⁹F and ³¹P. FT NMR, advantages of FT NMR.

B. Nuclear Quadrupole Resonance Spectroscopy

Quadrupole nuclei, quadrupole moments, electric field gradient, coupling constant, splitting. Applications.

C. Electron Spin Resonance Spectroscopy

Basic principles, zero field splitting and Kramer's degeneracy, factors affecting the 'g' value. Isotropic and anisotropic hyperfine coupling constants, spin Hamiltonian, spin densities and Mc Connell relationship, measurement techniques, applications.

V Electronic Spectroscopy

A. Atomic Spectroscopy

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

B. 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.

VI X-ray Diffraction

Bragg condition, -Miller indices, Laue method, Bragg 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, Ramchandran diagram.

PRACTICAL-II

1. Measurement of density of gases and vapours

- (a) Victor Meyer's Method Determination of Molecular weight of Acetone, Chloroform, Benzene, (Mixture).
- (b) Duma's Method Determination of molecular weight of acetone, Carbon-Tetrachloride.

2. Determination of Molecular weight of substances

- (a) Beckmann's freezing point Method
- (b) Beckmann's Boiling point method.

3. Viscosity of liquids and solution by ostwald tube

Determination of percentage composition of a mixture of two liquids.

4. Surface Tension of liquids and solutions

- (a) Study of the effect of conc. on surface tension of acetic acid and Sodium chloride solutions.
- (b) Determination of Parachor.

5. Thermochemistry

- (a) Determination of water equivalent of a calorimeter
- (b) Determination of the Heat of Neutralization of :
 - (i) Strong acid and strong base (HCl and NaOH)
 - (ii) Weak acid and strong base (NaOH and CH3COOH).
- (c) Determination of Heat of solution of Potassium Nitrate
- (d) Determination of basicity of succinic Acid by Thermochemical Method.

6. Order of Reaction

- (a) Determination of the rate constant of hydrolysis of an ester with an acid (Methyl acetate and HCl).
- (b) Determination of the rate constant of saponification of ethyl acetate by NaOH.

7. Partition Co-efficient

- (a) Determination of partition coefficient of:
 - (i) Benzoic acid between water and Benzene
 - (ii) Iodine between water and carbon tetrachloride

9. Conductivity

- (a) Determination of cell constant
- (b) Determination of equivalent conductivity of weak acid (acetic and succinic acid) at several concentrations and calculation of the dissociation constant of the acid
- (c) Determination of the basicity of an acid (citric acid and oxalic acid)
- (d) Titration of:
 - (i) strong acid and strong base (HCl and NaOH)
 - (ii) weak acid and strong base (CH₃COOH and NaOH)

SEMESTER III

BIO-CHEMISTRY

GROUP-A (Bioinorganic Chemistry)

I Metal Ions in Biological Systems

Essential and trace metals. Na⁺/K⁺ Pump Role of metals ions in biological processes,

II Bioenergetics and ATP Cycle

DNA polymerisation, glucose storage, metal complexes in transmission of energy; chlorophylls, photosystem I and photosystem II in cleavage of water. Model systems.

III Transport and Storage of Dioxygen

Heme proteins and oxygen uptake, structure and function of hemoglobin, myoglobin, hemocyanins and hemerythrin, model synthetic complexes of iron, cobalt and copper.

IV Electron Transfer in Biology

Structure and function of metalloproteins in electron transport processes - cytochromes and ion-sulphur proteins, synthetic models

V Nitrogenase

Biological nitrogen fixation, molybdenum nitrogenase, spectroscopic and other evidence, other nitrogenases model systems.

GROUP-B (Bioorganic Chemistry)

I Enzymes and Mechanism of Enzyme Action

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 Koshtand's induced fit hypothesis, concept and identification of active site by the use of inhibitors, affinity labeling and enzyme modification by site-directed mutagenesis. Enzyme kinetics, Michaelis-Menten and Lineweaver-Burk plots, 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 A.

II Kinds of Reactions Catalysed by Enzymes

Nucleophilic displacement on a phosphorus atom, multiple displacement reactions and the coupling of ATP cleavage to endergonic processes. Addition and elimination reactions, enolic intermediates in isomerization reactions, p-cleavage and condensation, some isomerization and rearrangement reactions. Enzyme catalyzed carboxylation and decarboxylation.

III Co-Enzyme Chemistry

Enzyme Models. Cofactors as derived from vitamins, coenzymes, prosthetic groups, apoenzymes.

Structure and biological functions of coenzyme A, thiamine pyrophosphate, pyridoxal phosphate, NAD^+ , $NADP^+$ FMN, FAD, lipolc acid, vitamin B_{12} . Mechanisms of reactions catalyzed by the above cofactors.

IV Biotechnological Applications of Enzymes

Large-scale production and purification of enzymes, techniques and methods of immobilization of enzymes, effect of immobilization on enzyme activity, application of immobilized enzymes, use of enzymes in food and drink industry-brewing and cheese- making, syrups from corn starch, enzymes as targets for drug design. Clinical uses of enzymes, enzyme therapy, enzymes and recombinant DNA technology.

ENVIRONMENTAL CHEMISTRY

I Environment

Introduction. Composition of atmosphere, vertical temperature, heat budget of the earth atmospheric system, vertical stability atmosphere. Biogeochemical cycles of C, N, P, S and 0. Biodistribution of elements.

II Hydrosphere

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

III Soils

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

IV Atmosphere

Chemical composition of atmosphere - particles, ions and radicals and their formation. Chemical and photochemical reactions in atmosphere, smog formation, oxides of N, C, S, 0 and their effect, pollution by chemicals, petroleum, minerals, chlorofluorohydrocarbons. Green-house effect, acid rain, air pollution controls and their chemistry. Analytical methods for measuring air pollutants. Continuous monitoring instruments.

V Industrial Pollution

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

VI Environmental Toxicology

Chemical solutions to environmental problems, biodegradability, principles of decomposition, better industrial processes. Bhopal gas tragedy, Chernobyl, Three mile island, Sewozo and Minamata disasters.

APPLICATIONS OF SPECTROSCOPY

Inorganic Chemistry

I Electronic Spectroscopy

Electronic Spectral Studies for d¹- d⁹ systems in octahedral, tetrahedral and square planer complexes,

II Vibrational Spectroscopy

Symmetry and shapes of AB2, AB3, AB4, AB5 and AB6, mode of bonding of ambidentate ligands, nitrosyl, ethylenediamine and diketonato complexes, application of resonance. Raman spectroscopy and its applications.

III Electron Spin Resonance Spectroscopy

Hyperfine coupling, spin polarization for atoms and transition metal ions, spin-orbit coupling and significance of g-tensors, application to transition metal complexes (having one unpaired electron) including biological systems and to inorganic free radicals such as PH₄, F₂⁻and [BH₃]⁻.

IV Nuclear Magnetic Resonance of Paramagnetic Substances in Solution

The contact and Pseudo contact shifts, factors affecting nuclear relaxation, some applications including biochemical systems, an overview of NMR of metal nuclide with emphasis on ¹⁹⁵Pt and ¹¹⁹Sn NMR.

V Mössbauer 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 intermediatespin, (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.

Organic Chemistry

I Ultraviolet and Visible Spectroscopy

Various electronic transitions (185-800 nm), Beer—Lambert law, effect of solvent on electronic transitions, ultraviolet bands for carbonyl compounds, unsaturated carbonyl compounds, dienes,

conjugated polyenes. Fieser-Woodward rules for conjugated dienes and carbonyl compounds, ultraviolet spectra of aromatic and heterocyclic compounds.

II 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). Effect of hydrogen bonding and solvent effect on vibrations frequencies, overtones, combination bands and Fermi resonance. FT IR. IR of gaseous, solids and polymeric materials.

III Nuclear Magnetic Resonance Spectroscopy

PMR Spectroscopy

General introduction and definition, chemical shift, spin-spin interaction, shielding mechanism, 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), chemical exchange, effect of deuteration, solvent effects. Fourier transform technique.

Carbon-13 NMR Spectroscopy

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.

IV Mass Spectrometry

Introduction, ion production - El, Cl, 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.

PRACTICAL-III

1. Experiments-I (Lab-work)

Group-A: Estimation of following in water

- (a) Ca (b) Fe (c) Mg
- (d) Chemical oxygen demand (COD)
- (e) Biochemical oxygen demand (BOD) &
- (f) Dissolved oxygen (DO)

<u>Group-B:</u> Analysis of soil for the followings

- (a) Ca (b) Mg (c) Total nitrogen
- (d) Carbonate (e) Organic matter (f) Ammonia & (g) Nitrate nitrogen

2. Experiments-II (Field-work)

Group-C: Field work consist of

- 1. Visit to some nearby areas (river, villages, industrial area) for collection of water & soil samples
- 2. Analysis of sample with reference to pollution and
- 3. Submission of report of field work
- 3. Note book and attendance
- 4. viva-voce

SEMESTER IV

I. GENERIC/DISCIPLINE CENTRIC ELECTIVE

INORGANIC-II

I Alkyls and Aryls of Transition Metals

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

II Compounds of Transition Metal-Carbon Multiple Bonds

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

III Transition Metal π -Complexes

Transition metal π -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 to organic synthesis

IV Transition Metal Compounds with Bonds to Hydrogen

Transition Metal Compounds with Bonds to Hydrogen.

V Homogeneous Catalysis

Stoichiometric reactions for catalysis, homogeneous catalytic hydrogenation, Zeigler-Natta polymerization of olefins, catalytic reactions involving carbon monoxide such as hydrocarbonylation of oletins (oxo reaction), oxopalladation reactions, activation of C-H bond.

VI Fluxional Organometalilc Compounds

Fluxionality and dynamic equilibria in compounds such as h^2 - olefin, h^3 allyl and dienyl complexes

GENERIC/DISCIPLINE CENTRIC ELECTIVE:

ORGANIC-II

I Curve Crossing Model to Chemical Reactions

Valence bond(VB) configuration mixing diagrams. Relationship between VB configuration mixing and resonance theory. Reaction profiles. Rules for constructing Valance Bond Correlation Diagram. Reactivity pattern based on Valance Bond State Correlation Diagram (VBSCD model). Curve crossing model-nature of activation barrier in chemical reactions.

V.B. Correlation diagram for

One Bond Reactions: V.B. Configuration of Ionic Bond. Heterolysis of Polar Covalent bond in solutions.

Two Bond Process: Covalent Bond: Radical Exchange Reactions, Nucleophilic Exchange Reactions, Nucleophilicity and S_N 2 reactivity based on curve- crossing model.

Electrophilic Exchange Reactions. Curve-crossing approach to electrophilic reactivity; Ionic Bond.

II Principals of Reactivity

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

III Kinetic Isotope Effect

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

IV Structural Effects on Reactivity

Linear free energy relationships (LFER). The Hammett equation, substituentS constants, theories of substituent effects. Interpretation of σ -values. Reaction constant ρ . Deviations from Hammett equation. Dual-parameter correlations, inductive substituent constant. The Taft model, σ_L -and σ_R scales.

V Supramolecular Chemistry

Properties of covalent bonds - bond length, inter-bond angles, force constant, bond and molecular dipole moments. Molecular and bond polarizability, bond dissociation enthalpy, entropy.

Intermolecular forces, hydrophobic effects. Electrostatic, induction, dispersion and resonance energy, magnetic interactions, magnitude of interaction energy, forces between macroscopic bodies, medium effects. Hydrogen bond.

Principles of molecular association and organization as exemplified in biological macromolecules like enzymes, nucleic acids, membranes and model systems like micelles and vesicles. Molecular receptors and design principles. Cryptands, cyclophanes, calixeranes, cyclodextrines. Supramolecular reactivity and catalysis. Molecular channels and transport processes. Molecular devices and nanotechnology.

VI Terpenoids and Carotenoids

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

VII Alkaloids

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

VIII Steroids

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

GENERIC/ DISCIPLINE CENTRIC ELECTIVE

PHYSICAL-III

I Diffraction of X-rays by crystals

Debye Scherrer mechod, indexing powder pattern for cubic and tetragonal crystals, rotating crystal method, Fourier transform and reciprocal lattices, Bragg equation in reciprocal lattice, neutron diffraction.

II Metallic bonds

Free electron theory, band theory, Fermi level, Brillouin zone, wave function for electrons in solids, metallic conductors, insulator, semiconductors (intrinsic & extrinsic), properties of junctions.

III Polymer

Polymer solution, thermodynamics of polymer solutions, molar mass and molar mass distribution, methods of measuring molar masses, micelle formation and hydrophobic interaction.

IV Electrically conducting polymers

Electrically conducting polymers electrochemical polymerization, band structure of polymers, mechanism of conduction in polymers, doping of polymers, application of conduction polymers.

V Potential Energy Surfaces

Mechanism of activation, potential energy surface for three atom reaction, Potential energy curve for successive reactions, Properties of potential energy surfaces, Inter conversion of translational and vibrational energies, Combination of atoms, Orthopara conversion, Activated state of three atom and four atom reactions, Potential energy profile, reaction co-ordinate, Transmission coefficient, non-adiabatic reaction.

VI Study of Fast Reactions

Photo physical Chemistry-Flash Photolysis, Relaxation technique, Nuclear Magnetic Resonance Method, Molecular Beam and Shock-tube Kinetics, Flow method. Reactions of Protons, Electrons metal ions.

II. GENERIC/DISCIPLINE CENTRIC ELECTIVE

INORGANIC-III

I Metal Storage Transport and Biomineralization

Ferritin, transferrin, and siderophores

II Calcium in Biology

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

III Metalloenzymes

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

IV Metal-Nucleic Acid Interactions

Metal ions and metal complex interactions. Metal complexes - nucieic acids

V Metals in Medicine

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

VI Supramolecular Chemistry

Concepts and language.

- (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.
- (C) Transport processes and carrier design.
- (D) Supramolecular devices. Supramolecular photochemistry, supramolecular electronic, ionic and switching devices. Some example of self-assembly in supramolecular chemistry

GENERIC/DISCIPLINE CENTRIC ELECTIVE:

ORGANIC-III

I Pericyclic Reactions

Radical stability, polar influences, solvent and steric effects. A curve crossing approach to radical addition, factors effecting barrier heights in additions, regioselectivity in radical reactions, Reactivity, specificity and periselectivity in pericyclic reactions.

Molecular orbital symmetry, Frontier orbitals of ethylene, 1,3-butadiene, 1,3,5-hexatriene and allyl system. Classification of periycyclic 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 cheleotropic reactions.

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

II Heterocycles:

Nomenclature & Classification

Replacement and systematic nomenclature (Hantzs MCH-Widman system) for monocyclic fused and bridged heterocycles.

Aromatic Heterocycles

Criteria of aromaticity including ring current and chemical shifts in 1H NMR spectra.

Non-aromatic Heterocycles

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

Heterocyclic Synthesis: Princples of heterocyclic synthesis involing cyclization reactions and cycloaddition reactions.

III Small ring Heterocycles

Three, Four & Five membered heterocycles including medicinal applications of benzopyrroles, benzofurans and benzothiophenes

IV 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 benzopyryliumsalts, coumarins and chromones.

V Six-Membered Heterocycles with Two or More Heteroatoms

Synthesis and reactions of diazines, triazines, tetrazines and thiazines

VI Seven- and Large-Membered Heterocycles

Synthesis and reactions of azepines, diazepines.

VII Heterocyclic Systems Containing P, As, Sb & B

Heterocyclic rings containing phosphorus: introduction, nomenclature, Synthesis and characteristics of 5- and 6-membered ring systems-phosphorinanes, phosphorines, phospholanes and phospholes.

Heterocyclic rings containing As and Sb: Introduction, synthesis and characteristics of 5- and 6-membered ring systems.

Heterocyclic rings containing B: Introduction, synthesis reactivity and spectral characteristics of 3-5- and 6- membered ring system.

VIII Vitamins

Determination and Synthesis of Vit. A, B,, B_Z, B₆, Vit. C and Vit. D.

GENERIC/ DISCIPLINE CENTRIC ELECTIVE

PHYSICAL-IV

I Super conductivity

Super conductivity meissner effect, microscopic theory of superconductivity, conventional organic and high temp, superconductors, fullerenes, applications of superconductors.

Transformation in crystals - thermodynamics of transformation, order-disorder transitions, martensitic transition, polymorphic transformation

II Specific heat of solids

Specific heat of solids classical theory, quantum theory of specific heats-Einstein and Debye theories, characteristic temp and its calculation, T-law. Solid state reactions, laws governing nucleation, homogeneous and heterogeneous nucleation, thermodynamic barrier.

III Polymer liquid crystal

Polymer liquid crystal nematic, cholesteric and smectic phases, liquid crystalline order of the main chain and of the side groups in polymers, synthesis and properties of polymer liquid crystals, liquid crystalline order in biological materials.

IV Surface chemistry

Surface chemistry surface films, BET isotherm for, multilayers & its derivation, kinetics of surface processes, unimolecular and bimolecular surface reactions, electrocapillarity, electrokinetic effects, statistical mechanics of adsorption, Colloids.

V Kinetics of Condensed Phase Reactions

Rate determining steps in diffusion controlled reactions and activation controlled reactions, Stokes-Einstein equation and dependence of rate constant on co-efficient of viscosity of medium, Kinetics of ionic reactions in solution-electrostatic contribution to free energy in single and double spherical models of activated complex, entropy of activation for ion-ion reactions; Kinetics of dipole-dipole reaction, ion-dipole reaction, dependence of rate constant on ionic strength and dielectric constant of medium, Bronsted-Bjerrum equation.

III. <u>GE/DC PRACTICAL:</u>

INORGANIC PRACTICAL -IV

- 1. Qualitative separation and determination of the following pairs of metal ion using gravimetric and volumetric methods
 - a. $Ag^+(g)$ and $Cu^{2+}(v)$
 - b. $Cu^{2+}(g)$ and $Zn^{2+}(v)$
 - c. $Fe^{3+}(g)$ and $Ca^{2+}(v)$
 - d. $Mg^{2+}(g)$ and $Ca^{2+}(v)$
- 2. Quantitative Analysis
 - a. Analysis of alloys (brass, type metal, solder, gun metal) cement, steel using conventional chemical analysis/and physical techniques (if possible).

(Preferably one alloy and cement analysis may be carried out).

3. Chromatographic Separations

- a. Cadmium and zinc
- b. Zinc and magnesium.
- c. Thin-layer / Paper chromatography-separation of nickel, manganese, cobalt and zinc.Determination of Rf values.

4. Synthesis and characterization of following metal complexes:

- a. Sodium tetrathionate Na2S4O6.
- b. Metal complex of dimethyl sulfoxide: CuCl2.2DMSO
- c. Synthesis of metal acetylacetonate
- d. Synthesis of copper and nickel Schiff base complexes.
- e. Synthesis of copper and nickel dithiocarbamates
- f. [Co(NH₃)₅ Cl] Cl₂
- g. (ii) [Co(NH₃)₅ NO₂] Cl₂
- h. (iii)[Co(NH₃)₅ ONC] Cl₂

GE/DC PRACTICAL:

ORGANIC PRACTICAL -IV

1. Characterization of organic compounds

It is expected to carry out separation, purification and identification of the components of a mixture of three organic compounds (three solids or two liquids and on solid, two solids and one liquid). Student should also check the purity of the separated components on TLC plates.

2. Extraction of Organic compounds from Natural Sources

- a. Isolation of Caffeine from Tea Leaves (Ref. Experimental Organic Chemistry H Dupon Durst. George W.Gokel, p.464 McGraw Hall Book Co., New York).
- b. Isolation of Casein from milk (Some typical colour reactions of proteins).
- c. Isolation of lactose from milk (purity of sugar should be checked by LC and PC and Rf values reported).
- d. Isolation of Nicotine dipicrate from tobacco
- e. Isolation of piperine from black pepper
- f. Isolation of Lycopene from tomatoes
- g. Isolation of β -carotene from carrots
- h. Isolation of Oleic acid from olive oil
- i. Isolation of Eugenol from cloves
- j. Isolation of (+)Limonine from citrus rinds

3. Multistep Synthesis of Organic Compounds

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

- a. Beckman rearrangement: Benzanilide from benzene
 - Benzene → Benzophenone → Benzophenone oxime → Benzanilide
- b. Benzilic acid rearrangement: Benzilic acid from benzoin
 - Benzoin \rightarrow Benzil \rightarrow Benzilic acid
- c. Synthesis using microwaves
 - Alkylation of diethyl malonate with benzyl chloride
- d. Synthesis using phase transfer catalyst
 - Alkylation of diethyl malonate or ethyl acetoacetate with an alkyl halide

4. Some illustrative exercises are given below:

- a. Estimation of phenol / aniline using bromate bromide solution/or acetylation method
- b. Estimation of carbonyl group by using 2,4-dinitrophenyl hydrazine
- c. To determine the percentage or number of phenolic groups in the given sample by the acetylation method.

5. Identification of organic compounds

By the analysis of their spectral data (UV, IR PMR, CMR & MS).

6. Spectrophotometric (UV/VIS) Estimations

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

GE/DC PRACTICAL:

PHYSICAL PRACTICAL -IV

1. Conductometry

- a. To determine the solubility and solubility product of a sparingly soluble salt
- b. To verify Onsager equation for a uni-univalent electrolyte in aqueous solution
- c. To titrate a mixture of HCl, CH₃COOH and CuSO₄ with NaOH
- d. To determine the rate constant of saponification of an ester by NaOH.

2. Determination of Equivalence conductance of following strong electrolyte:

- a. KCl
- b. NaCl
- c. AgNO3
- d. HCl
- e. KNO3

3. Potentiometry

- a. To determine the solubility and solubility product of AgCl in water
- b. To determine the E^0 of Zn/Zn^{++} , Cu/Cu^{++} electrodes.
- c. To determine the basicity of a polybasic acid and its dissociation constant.
- d. To investigate the complex formed between CuSO₄ and NH₃.

4. Polarography

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

5. Chemical Kinetics

- a. Determination of relative strengths of HCl and H2SO4 (k_1 / k_2) for the hydrolysis of methylacetate.
- b. Determination of relative strengths of HNO3 and H2SO4 (k_1 / k_2) for the hydrolysis ofmethyl acetate.

- c. To study the kinetics of alkaline hydrolysis of an ester in aquo-organic solvent system with respect to effect of solvent composition and dielectric constant on rate constant.
- d. To determine the rate constant of the reaction between K₂S₂O₈ and KI at two different temp, and hence to determine the energy of activation of the reaction.

6. Thermochemistry

- a. Determination of basicity of a polybasic acid.
- b. Determination of heat of displacement of Cu by Zn from Cu^{2+} salt solution.
- c. Determination of heat of hydration of Na₂SO₄ to Na₂SO₄, 10 H₂O.

7. Distribution law

- a. Determination of Composition of Cupric-ammine sulphate formed between CuSO₄ and NH₃
- b. Determination of equilibrium constant for the reaction KI+I₂=KI₃

8. Viscosity and Surface Tension

- a. To determine the radius of a molecule from viscosity measurement.
- b. To determine the parachor of CH₂, C and H

IV. <u>CORE COURSE (PROJECT)</u>:

PROJECT WORK

Each student has to submit the dissertation work duly forwarded by the HOD of Department concerned.