M.Sc

CHY

Sem. III

Paper –I

(P C 3061)

# (a) Applications of Spectroscopy, (b) Photochemistry, (c) Solid State Chemistry



#### Scheme of examination:

MM: 70

- 1. In Semester End Examination there will be 10 questions in all, 2 from each unit. Candidate has to answer any 5 questions, taking one from each unit.
- 2. Each question shall be of 14 marks.

# (a) Applications of Spectroscopy

#### UNIT-I

Vibrational Spectroscopy: Symmetry and shapes of AB<sub>2</sub>, AB<sub>3</sub>, AB<sub>4</sub>, AB<sub>5</sub> and AB<sub>6</sub>, mode of bonding of ambidentate ligands, ethylenediamine and diketonato complexes, application of resonance Raman spectroscopy particularly for the study of active sites of metalloproteins.

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 PH<sub>4</sub>, F<sub>2</sub> and (BH<sub>3</sub>).

# **Organic Chemistry**

#### UNIT - II

(a) 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 compounds. Steric effect in biphenyls.

(b) Optical Rotatory Dispersion (ORD) and Circular Dichroism

(CD): Definition, deduction of absolute configuration, octant rule for ketones.

#### UNIT - III

Infrared Spectroscopy: Instrumentation and Sample handling: Characteristic vibrational frequencies of alkanes, alkenes, alkynes, aromatic compounds, alcohols, ether's, 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 vibrational frequencies, overtones, combination bands and fermi resonance.

# (b) Photochemistry

#### **Unit-IV**

Photochemical Reactions: Interaction of electromagnetic radiation with matter, types of excitations, fate of excited molecule, quantum yield, transfer of excitation energy, actinometry.

# **Determination of Reaction Mechanism**

Classification, rate constants and life times of reactive energy state determination of rate constants of reactions. Effect of light intensity on the rate of photochemical reactions. Types of photochemical reactionsphoto dissociation, gas-phase photolysis.

Photochemistry of Alkene: Intramolecular reactions of the olefinic bond-geometrical isomerism, cyclisation reactions, rearrangement of 1,4and 1,5-dienes.

(c) SOLID STATE CHEMISTRY - 1

Solid State Reactions: General principles, experimental procedure, coprecipitation as a precursory to solid state reactions, kinetics of solid state reactions.

Crystal Defects and Non-Stoichiometry: Perfect and imperfect crystals, intrinsic and extrinsic defects-point defects, line and plane defects, vacancies-Schottky detects and Frenkel defects. Thermodynamics of Schottky and Frenkel defect formation, colour centres, non-stoichiometry and defects.

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

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# Bio-inorganic, Bio-organic and Bio-physical Chemistry

#### Scheme of examination:

MM: 52

- 1. In Semester End Examination there will be 10 questions in all, 2 from each unit. Candidate has to answer any 5 questions, taking one from each unit.
- 2. Question No. 1 shall be of 10 marks and remaining four questions of 10½ marks each.

#### UNIT-I

# (a) BIOINORGANIC CHEMISTRY

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

Bioenergetics and ATP Cycle: DNA polymerisation, glucose storage, metal complexes in transmission of energy; chlorophyll's, photosystem I and photosystem II in cleavage of water.

#### **Unit-II**

# (b): BIOORGANIC CHEMISTRY

**Introduction:** Basic considerations, Proximity effects and molecular adaption.

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 Koshalnd'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

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plots, reversible and irreversible inhibition.

#### UNIT - III

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 chemotrypsin, ribonuclease, lysozyme and carboxypeptidase.

Kinds 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 Isomerisations reactions,  $\beta$ -Cleavage and condensation, some isomerization and rearrangement reactions. Enzyme catalyzed carboxylation and decarboxylation.

#### Unit-IV

# (c): BIOPHYSICAL CHEMISTRY

Biological Cell and its Constituents: Biological cell, structure and functions of proteins, enzymes, DNA and RNA in living systems. Helix coils transition.

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

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Thermodynamics of Biopolymers 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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# Environmental Chemistry

#### Scheme of examination:

**MM: 35** 

- In Semester End Examination there will be 10 questions in all, 2 from each unit. Candidate has to answer any 5 questions, taking one from each unit.
- 2. Each question shall be of 7 marks.

#### 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. Calculation of Global mean temperature of the atmosphere. Pressure variation in atmosphere and scale height. Biogeochemical cycles of carbon, nitrogen, sulphure, phosphorus oxygen. Residence times.

#### **Unit-II**

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

#### Unit-III

Air Pollution: Air pollutants and their classifications. 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 SO2 and NOx. Acid rain control strategies.

Stratospheric Ozone Depletion: Mechanism of Ozone formation,

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Mechanism of catalytic Ozone depletion, Discovery of Antarctic Ozone hole and Role of chemistry and meteorology. Control Strategies.

#### Unit-IV

Aquatic Chemistry and Water Pollution: Redox chemistry in natural waters. Dissolved oxygen, biological oxygen demand, chemical oxygen demand, determination of DO, BOD and COD. Eutrophication, Sources of water pollution. Treatment of waste and sewage. Purification of drinking water, techniques of purification and disinfection.

#### Unit-V

Soil: Soil composition, micro and macronutrients, soil pollution by fertilizers, plastic and metals. Methods of re-mediation of soil.

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(P C 3064) Sem. III Paper – IV M.Sc CHY Gr. I

# **Organotransition Metal Chemistry-I**

### Scheme of examination:

MM: 35

- 1. In Semester End Examination there will be 10 questions in all, 2 from each unit. Candidate has to answer any 5 questions, taking one from each unit.
- 2. Each question shall be of 7 marks.

#### 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 Bond-I alkylidenes, alkylidynes, low valent carbenes and carbynes-synthesis, nature of bond, structural characteristics.

#### Unit-III

Compounds of Transition Metal-Carbon Multiple Bond-II

Nucleophilic and electrophilic reactions on the ligands, role in organic synthesis.

#### Unit-IV

Transition Metal  $\pi$ -Complexes-I Unsaturated organic molecules, alkenes, alkynes, allyl preparation, Transition Metal  $\pi$  -Complexes with properties, nature of bonding and structural features. ar and the

Unit-V

# Transition Metal π-Complexes-II

Diene, dienyl, arene and trienyl complexes, preparation, properties, nature of bonding and structural features.

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# Bio-inorganic and supramolecular Chemistry-I

#### **Scheme of examination:**

MM: 35

- In Semester End Examination there will be 10 questions in all, 2 from each unit. Candidate has to answer any 5 questions, taking one from each unit.
- **2.** Each question shall be of 7 marks.

#### UNIT - I

# **Metal Storage and Transport**

Ferritin transferrin, 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.

#### Unit-IV

# Supramolecular Chemistry-I

Molecular recognition: Molecular receptors for different types of molecules including arisonic substrates, design and synthesis of co receptor molecules and multiple recognition.

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Supramolecular Chemistry-II

Supramolecular reactivity and catalysis.

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## Photo-inorganic Chemistry-I

#### Scheme of examination:

MM: 35

- 1. In Semester End Examination there will be 10 questions in all, 2 from each unit. Candidate has to answer any 5 questions, taking one from each unit.
- 2. Each question shall be of 7 marks.

### UNIT-I

## **Basics of Photochemistry-I**

Absorption, excitation, photochemical laws, quantum yield, electrically excited states-life times-measurements of the times. Flash photolysis.

#### **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**

# **Ligand Field Photochemistry-I**

Photosubstitution, photooxidation and photoreduction, lability and selectivity, zero vibrational levels of ground state and excited state.

#### **Unit-IV**

# Redox Reactions by Excited Metal Complexes-I

Energy transfer under conditions of weak interaction and strong interaction-exciplex formation; condition of the excited states to be useful as redox reactants.

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# Unit-V

# **Redox Reactions by Excited Metal Complexes-II**

Application of redox processes of electronically excited states for catalytic purposes, transformation of low energy reactants into high energy products, chemical energy into light.

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### Polymers - I

#### Scheme of examination:

MM: 35

- 1. In Semester End Examination there will be 10 questions in all, 2 from each unit. Candidate has to answer any 5 questions, taking one from each unit.
- 2. Each question shall be of 7 marks.

#### UNIT-I

Basics: Importance of polymers. 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.

#### Unit-II

## **Polymer Characterization**

Polydispersion-average molecular weight concept. Number, weight and viscosity average molecular weights. Polydispersity an molecular weight. distribution. The practical significance of molecular weight. Measurement of molecular-weights. End-group, viscosity, light scattering, osmotic and ultracentrifugation methods.

#### Unit-III

# (A) Structure, Properties and Applications of

Polymers based on boron-borazines, boranes and carboranes.

**UNIT-IV** 

(B) Structure, Properties and Applications of Polymers based on Phosphorous-Phosphazenes, Polyphosphates

**Unit-V** 

(C) Structure, Properties and Applications of: Metal clusters.

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# Organic Synthesis-I

## Scheme of examination:

MM: 35

- 1. In Semester End Examination there will be 10 questions in all, 2 from each unit. Candidate has to answer any 5 questions, taking one from each unit.
- 2. Each question shall be of 7 marks.

#### UNIT-I

# Organometallic Reagents-I

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.

### Unit-II

Oxidation – I: Introduction, Different oxidative processes.

Hydrocarbons-alkenes, aromatic rings, saturated C-H groups (activated and unactivated) Alcohols, diols, aldehyde's, ketones, ketals and carboxylic acids.

# **Unit-III**

Oxidation – II: Amines, hydrazines and sulphides. Oxidations with ruthenium tetraoxide, iodobenzene diacetate and thallium (III) Nitrate.

### **Unit-IV**

Rearrangements-I: General mechanistic considerations-nature of migration, migratory aptitude, memory effects. A detailed study of the following rearrangements. Pinacol-pinacolone, Wagner-Meerwein,

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Demjanov, Benzil-Benzillic acid. Favorskii, Arndt-Eister synthesis, Neber.

# **Unit-V**

Rearrangements-II: Beckmann, Hofmann Curtius, Schmidt, Baeyer-

Villiger, Shapiro reaction.

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# Organic Synthesis M III

#### **Scheme of examination:**

MM: 35

- In Semester End Examination there will be 10 questions in all, 2 from each unit. Candidate has to answer any 5 questions, taking one from each unit.
- 2. Each question shall be of 7 marks.

#### UNIT-I

**Disconnection Approach-I:** An introduction to synthons and synthetic equivalents. Disconnection approach, functional group inter-conversions, the importance of the order of events in organic synthesis.

#### UNIT-II

**Disconnection Approach-II:** one group C-X and two group C-X disconnections, chemoselectivity, reversal of polarity, cyclisation reaction, amine synthesis.

#### **Unit-III**

**Protecting Groups:** Principle of protection of alcohol, amine, carbonyl and carboxyl groups.

#### **Unit-IV**

One Group C-C Disconnections-I: Alcohols and carbonyl compounds, regioselectivity.

Unit-V

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One Group C-C Disconnections-II: Alkene synthesis, use of acetylenes and aliphatic Nitro compounds in organic synthesis.

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## Heterocyclic Chemistry-I

## **Scheme of examination:**

**MM: 35** 

- 1. In Semester End Examination there will be 10 questions in all, 2 from each unit. Candidate has to answer any 5 questions, taking one from each unit.
- 2. Each question shall be of 7 marks.

#### UNIT - I

Nomenclature of Heterocycles: Replacement and systematic nomenclature (Hantzsch-Widman system) for monocyclic fused and bridged heterocycles.

#### **UNIT-II**

Aromatic Heterocycles: General chemical behaviour of aromatic heterocycles, classification (structural type), criteria of aromaticity (bond lengths, ring current and chemical shifts in <sup>1</sup>H-NMR-spectra. Empirical resonance energy, delocalization energy and Dewar resonance energy, diamagnetic susceptibility exaltations). Heteroaromatic reactivity and tautomerism in aromatic heterocycles.

#### Unit-III

Small Ring Heterocycles: Three-membered and four-membered heterocycles-synthesis and reactions of azirodines, oxiranes, thiranes, azetidines, oxetanes and thietanes.

**Unit-IV** 

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Six-Membered Heterocycles with one Heteroatom: Synthesis and reactions of pyrylium salts and pyrones and their comparison with pyridinium & thiopyrylium salts, phridones. Synthesis and reactions of quionlizinium and benzopyrylium salts, coumarins and chromones.

Six Membered Heterocycles with Two or More Heteroatoms

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

#### Unit-V

Seven-and Large-Membered Heterocycles Synthesis and reactions of azepines, oxepines, thiepines, diazepines thiazepines, azocines, diazocines, dioxocines and dithiocines.

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## **Chemistry of Natural Products-I**

#### **Scheme of examination:**

**MM: 35** 

- 1. In Semester End Examination there will be 10 questions in all, 2 from each unit. Candidate has to answer any 5 questions, taking one from each unit.
- 2. Each question shall be of 7 marks.

#### UNIT-I

Terpenoids-I: Clasification, nomenclature, occurrence, isolation, general methods of structure determination, isoprene rule. Structure determination, stereochemistry, biosynthesis and synthesis of the following representative molecules: Citral, Gerniol  $\alpha$ -Terpeneol.

#### **UNIT-II**

Terpenoids-I and and Carotenoids: Structure determination, stereochemistry, biosynthesis and synthesis of the following representative molecules: Menthol, Farnesol, Zingiberence, Santonin, Phytol, Abietic acid and b-Carotene.

#### **Unit-III**

Alkaloids-I: Definition, nomenclature and physiological action, occurrence, isolation, general methods of structure elucidation, degradation, classification based on nitrogen heterocyclic ring, role of alkaloids in plants.

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**UNIT-IV** 

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Alkaloids-II: Structure, stereochemistry, synthesis and biosynthesis of the following: Ephedrine, (+)- Conine, Nicotine, Atropine, Quinine and Morphine.

#### **Unit-V**

Prostaglandis: Occurrence, nomenclature, classification, biogenesis and physiological effects. Synthesis of  $PGE_2$  and  $PGF_{2\alpha}$ .

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# Analytical Chemistry-I

### Scheme of examination:

MM: 35

- In Semester End Examination there will be 10 questions in all, 2 from each unit. Candidate has to answer any 5 questions, taking one from each unit.
- 2. Each question shall be of 7 marks.

#### 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.

#### **Unit-II**

Errors and Evaluation-I: 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.

#### **Unit-III**

Errors and Evaluation-II: 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-IV

Food analysis: Moisture, ash, crude protein, fat crude fibre, carbohydrates, calcium, potassium, sodium and phosphate. Food adulteration-common adulteratnts in food, contamination of foods stuffs. Microscopic examination of foods for adulterants. Pesticide analysis in food prodeuts. Extraction and purification of sample. HPLC. Gas

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chromatogrphay for organophosphates. Thin-layer chromatography for identification of chlorinated pesticides in food products.

#### **Unit-V**

Analysis of Water Pollution-I: Origin of Waste water, types, water pollutants and their effects. Sources of water pollution-domestic, industrial, agriculatural soil and radioactive wastes as sources of pollution. Objectives of analysis-parameter for analysis-colour, turbidity, total solids, conductivity, acidity, alakalinity, hardness, chloride, sulphate, fluoride, silica, phosphates and different forms of nitrogen.

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# Physical Organic Chemistry-I

#### Scheme of examination:

**MM: 35** 

- 1. In Semester End Examination there will be 10 questions in all, 2 from each unit. Candidate has to answer any 5 questions, taking one from each unit.
- 2. Each question shall be of 7 marks.

#### HNIT - I

Concepts in Molecular Orbital (MO) and Valence Bond (VB) Theory : Introduction to Huckel molecular orbital (MO) method as a mean to explain mdoern theoretical methods. Advanced techniques in PMO and FMO theory. Molecular mechanics, semi empirical methods and abinito and density functional methods. Scope and limitations of several computational programmes.

Quanitative 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 interaction diagrams. MO of simple organic systems such as ethene, allyl, butadiene, methane and methyo group. Conjugation and hypeconjugation. Aromaticity.

Valence bond (VB) configuration mixing diagrams. Relationship between VB configuration mixing and resonance theory. Reaction profiles.

al.) Potential energy diagrams. Curve-crossing model-nature of activation

barrier in chemical reactions.

Unit-II

Principles of Reactivity: Mechanistic significance of entropy, enthalphy and Gibb's free energy. Arrrhenius 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.

#### **Unit-III**

**Kinetic Isotope Effect:** Theory of isotope effects. Primary and secondary kinetic isotope effects. Heavy atom isotope effects. Tunneling effect. Solvent effects.

#### **Unit-IV**

Structural Effects on Reactivity: Linear free energy relationships (LFER). The Hammett equation, substitutent constants, theories sof substitutent effects. Interpretation of  $\sigma$ -values. Reaction constantp. Deviations from Hammett equation. Dualparameter correlatins, inductive substituent constant. The Taft model,  $\sigma$  1 and  $\sigma$  R scales.

#### Unit-V

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.

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## **Chemical Dynamics-I**

#### **Scheme of examination:**

**MM: 35** 

- 1. In Semester End Examination there will be 10 questions in all, 2 from each unit. Candidate has to answer any 5 questions, taking one from each unit.
- 2. Each question shall be of 7 marks.

#### UNIT-I

Atmospheric Reactions-I: Physical structure of the atmosphere, chemical composition of the atmosphere, Kinetic and mechanism of NOx, CIOx cycles and H<sub>2</sub>+O<sub>2</sub> reaction. Mechanism of general methane oxidation.

#### Unit-II

# **Atmospheric Reactions-II:**

- (a)Kinetics and mechanism of low temperature oxidation of methane. Concept of global warming.
- (b) Oscillatory Reactions: Autocatlysis and oscilatory reactions, Kinetics and mechanism of Belousov-Zhabotinski (B-z) reactions.

#### Unit-III

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

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**Unit-IV** 

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

#### Unit-V

Dynamics of Gas-surface Reactions: Adsorption/desorption kinetics and transitin 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 imporance of heterogeneous catalysis.

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## Electrochemistry-I

#### Scheme of examination:

MM: 35

- 1. In Semester End Examination there will be 10 questions in all, 2 from each unit. Candidate has to answer any 5 questions, taking one from each unit.
- 2. Each question shall be of 7 marks.

#### UNIT - I

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 outputs.

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.

#### **Unit-II**

Electrochemical Energy Storage: Properties of Electrochemical energy stores: Measure of battery performance, Charging and discharging of a battery, Storage Density, Energy Density. Classical Batteries: (i) Lead Acid (ii) Nickel-Cadmium. Modern Batteries: (i) Zinc-Air (ii) Nickel-Metal Hydride, (iii) Lithium Battery, Future Electricity storers: Storage in (i) Hydrogen, (ii) Alkali Metals, (iii) Non aqueous solutions.

#### Unit-III

**Irreversible Electrode processes :** Criteria of irreversibility, informatino from irreversible wave.

Methods of determining kinetic parameters for quasi-rversible and

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irreversible waves: Koutecky's methods, Meits Israel Method, Gellings method.

#### **Unit-IV**

Electrocatalysis: Chemical catalysts and Electrochemical catalysts with special reference to purostates, porphyrin oxides of rare earths.

Electrocatalysis in simple redox reactions, in reaction involving adsorbed species. Influence of various parameters.

#### Unit-V

Kinetic of Electrode Process: Essentials of Electrode reaction. Current Density, Overpotential, Tafel Equation, Butler Volmer equation. Standard rate constant (K<sup>0</sup>) and Transfer coefficient (α), Exchange Current.

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M.Sc CHY Sem. IV Paper -I (P C 4061)

#### (a) Applications of Spectroscopy, (b) Photochemistry, (c) Solid State Chemistry

#### **Scheme of examination:**

**MM: 70** 

- 1. In Semester End Examination there will be 10 questions in all, 2 from each unit. Candidate has to answer any 5 questions, taking one from each unit.
- 2. Each question shall be of 14 marks.

# (a) Applications of Spectroscopy

#### UNIT-I

# **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 <sup>195</sup>Pt and <sup>119</sup>Sn NMR.

# **Mossbauer Spectroscopy:**

Basic principles, spectral parameters and spectrum display. Application of the technique to the studies of (1) bonding and structures of Fe<sup>+2</sup> and Fe<sup>+3</sup> compounds including those of intermediate spin, (2) Sn<sup>+2</sup>, Sn<sup>+4</sup> compounds nature of M-L bond, coordination number, structure and (3) detection of oxidation state and inequivalent MB atoms.

#### **UNIT II**

Nuclear Magnetic Resonance Spectroscopy: General introduction and definition, chemical shift, spin-spin interaction, shielding mechanism, mechanism of measurement, 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 &

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mercapto), chemical exchange, effect of duteration, complex spin-spin interaction between two, three, four and five nuclei (first order spectra), stereochemistry, hindered rotation, Karplus curve-variation of coupling constant with dihedral angle. Simplification of complex spectra nuclear magnetic double resonance, NMR shift reagents, solvent effects, Fourier transform technique, Nuclear Overhauser Effect (NOE).

Carbon-13 NMR Spectroscopy: General considerations, chemical shift (aliphatic, olefinic, alkyne, aromatic, heteroaromatic and carboynl carbon), coupling constants. Two dimension NMR spectroscopy-COSY, NOESY, DEPT, INEPT, APT and INADEQUATE techniques.

#### UNIT III

Mass Spectroscopy: 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. Mc Lafferty rearrangement. Nitrogen rule. High resolution mass spectroscopy. Example of mass spectral fragmentation of organic compounds with respect to their structure determination.

# (b) Photochemistry

#### **UNIT IV**

Photochemistry of Carbonyl Compounds: Intramolecular reactions of carbonyl compounds-saturated, cyclic and acyclic, β, γ unsaturated and α, β unsaturated compounds, cyclohexadienones. Intermolecular cyloaddition reactions-dimerisations and oxetane formation.

Photochemistry of Aromatic Compounds: Isomerisations, additions and substitutions.

Miscellaneous Photochemical Reactions: Photo-Fries reactions of

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anilides, Photo-Fries rearrangement. Barton reaction. Singlet molecular Oxygen reaction. Photochemical formation of smog. Photo degradation of polymers. Photochemistry of vision.

## (c) SOLID STATE CHEMISTRY:

#### **UNIT V**

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 semiconductors, p-n junctions, super conductors.

Optical properties: Application of optical and electron microscopy.

Magnetic Properties: Classification of materials: Effect of temperature, calculation of magnetic moment, mechanism of ferro and anti ferromagnetic ordering super exchange.

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# Bio-inorganic, Bio-organic and Bio-physical Chemistry

Paper –II

#### Scheme of examination:

MM: 52

- 1. In Semester End Examination there will be 10 questions in all, 2 from each unit. Candidate has to answer any 5 questions, taking one from each unit.
- 2. Question No. 1 shall be of 10 marks and remaining four questions of 10½ marks each.

#### UNIT - I

# (a) Bio-inorganic Chemistry:

# **Transport and Storage of Dioxygen:**

Heam proteins and oxygen uptake, structure and function of haemoglobin, mygolobin, haemocyanin and hemerythrin, model synthetic complexes of iron, cobalt and copper.

Electron Transfer in Biology: Structure and function of metal of proteins in electron transport process, cytochromes and ion-sulphure proteins, synthetic models.

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

## **UNIT II**

# (b) Bio-organic Chemistry

reactions catalyzed by the above cofactors.

Co-Enzyme Chemistry: Cofactors as derived from vitamines, 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>. Mechanism of

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

## **UNIT III**

**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 cheesemaking, syrups from corn starch, enzymes as targets for drug design. Clinical uses of enzymes, enzyme therapy, enzymes and recombinant DNA Technology.

#### UNIT IV

# (c) Bio-physical chemistry

Bioenergetics: Standard free energy change in biochemical reactions, exergonic, endergonic. Hydrolysis of ATP, synthesis of ATP from ADP. Biopolymer Interactions: Forces involved in biopolymer interactions, hydrophobic forces, dispersion force interactions. Multiple equilibria and various types of binding processes in biological systems. Hydrogen ion titration curves.

#### **IINIT** V

Biopolymers and their molecular Weights: Evaluation of size, shape, molecular weight and extent of hydration of biopolymers by various

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experimental techniques. Sedimentation equilibrium, hydrodynamic methods, diffusion, sedimentation velocity, viscosity, electrophoresis and rotational motions.

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# Scheme of examination:

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MM: 35

- 1. In Semester End Examination there will be 10 questions in all, 2 from each unit. Candidate has to answer any 5 questions, taking one from each unit.
- 2. Each question shall be of 7 marks.

# UNIT - I

Tropospheric Photochemistry: Mechanism of Photochemical decomposition of NO2 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. Reaction of OH radicals with SO<sub>2</sub> and NO<sub>x</sub>. Formation of Nitrate radical and its reactions. Photochemical smog meteorological conditions and chemistry of its formation.

### UNIT II

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

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

#### UNIT III

**Environmental Toxicology-I:** 

(a) Toxic heavy metals: Mercury, lead, arsenic and cadmium. Causes of toxicity. Bioaccumulation, sources of heavy metals. Chemical

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speciation of Hg, Pb, As, and Cd. Biochemical and damaging effects.

(b) Toxic Organic Compounds: Pesticides, classification, properties and uses of organochlorine and organophosphorous pesticides. detection and damaging effects.

## UNIT IV

# **Environmental Toxicology-II:**

- Polychlorinated biphenyls: Properties, use and environmental (a) contamination and effects.
- (b) Polynuclear Aromatic Hydrocarbons: Source, structures and as pollutants.

# **UNIT V**

# **Environmental Disaster-II**

Bhopal gas tragedy, Chernobyl, three mile island, Minimtata Disease, Sevoso (Italy), London smog.

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# Organotransition Metal Chemistry-II

# **Scheme of examination:**

MM: 35

- 1. In Semester End Examination there will be 10 questions in all, 2 from each unit. Candidate has to answer any 5 questions, taking one from each unit.
- 2. Each question shall be of 7 marks.

## UNIT-I

Transition Metal  $\pi$  - Complexes – II: Important reactions relating to nucleophilic and electrophilic attack on ligands and organic synthesis.

## **UNIT II**

Transition metal compounds with bonds to hydrogen.

### **UNIT III**

# Homogeneous Catalysis-I

Homogeneous Catalysis, Stoichiometric reactions for catalysis, hydrogenation, Zeigler-Natta polymerization of olefins.

#### **UNIT IV**

# Homogeneous Catalysis-II

Catalytic reactions involving carbon monoxide, oxoreaction, oxopalladation reaction, activation of C-H bond.

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UNIT V

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# Fluxional Organometallic Compounds

Fluxionality and dynamic equilibria in compounds such as  $\eta^2$  - olefine,  $\eta^3$ -allyl and dienyl complexes.

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# Bio-inorganic and supramolecular Chemistry-II

# **Scheme of examination:**

MM: 35

- 1. In Semester End Examination there will be 10 questions in all, 2 from each unit. Candidate has to answer any 5 questions, taking one from each unit.
- 2. Each question shall be of 7 marks.

### UNIT - I

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

### UNIT II

**Metalloenzymes-II:** Copper enzymes-superoxide dismutase.

Molybdenum oxatransferase enzymes-xanthine oxidase. Coenzyme vitamin B12.

## **UNIT III**

Metal-Nucleic Acid Complexes: Metal ions and metal complex interactions. Metal complex nucleic acids.

### UNIT IV

Supramolecular Chemistry-II(A): Transport processes and carrier design.

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UNIT V

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# **Supramolecular Chemistry-II(B):**

Supramolecular devices. Supramolecular photochemistry, supramolecular electronic, ionic and switching devices.

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# Photo-inorganic Chemistry-II

# **Scheme of examination:**

MM: 35

- 1. In Semester End Examination there will be 10 questions in all, 2 from each unit. Candidate has to answer any 5 questions, taking one from each unit.
- 2. Each question shall be of 7 marks.

# UNIT-I

Basics of Photochemistry-II: Energy dissipation by radiative and nonradiative processes, absorption spectra, Frank-Condon principle, photochemical stages-primary and secondary processes.

# UNIT II

# **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 III

Ligand Field Photochemistry – II: Energy content of excited state, zero-zero spectroscopic energy, development of the equations for redox potentials of the excited states.

#### UNIT IV

Redox Reactions by Excited Metal Complexes – III: Excited electron transfer, metal complexes as attractive candidates, (2,2-bipyridine and 1,10-phenanthroline complexes), illustration of reducing and oxidising

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character of Ruthenium (Ru<sup>+2</sup>) (bipyridal complex), comparison with Fe (bipy)<sub>3</sub>; role of spin-orbit coupling-life time of these complexes.

## **UNIT V**

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

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# Polymers - II

# Scheme of examination:

MM: 35

- In Semester End Examination there will be 10 questions in all, 2 from each unit. Candidate has to answer any 5 questions, taking one from each unit.
- 2. Each question shall be of 7 marks.

# UNIT-I

Polymer Characterization – II: Analysis and testing of polymerschemical 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 II

**Inorganic Polymers:** A general survey and scope of Inorganic Polymers special characteristics, classification, homo and hetero atomic polymers.

### UNIT III

Structure, Properties and Applications of Polymers based on Silicon, silicones, polymetalloxanes and polymetallosiloxanes, silazanes.

# UNIT IV

Structure, Properties and Applications (D): Polymers based on Sulphur-

Tetrasulphur tetranitride and related compounds.

**UNIT V** 

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Structure, Properties and Applications (E): Co-ordination and metal chelate polymers.

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# Organic Synthesis-II

# Scheme of examination:

**MM: 35** 

- 1. In Semester End Examination there will be 10 questions in all, 2 from each unit. Candidate has to answer any 5 questions, taking one from each unit.
- 2. Each question shall be of 7 marks.

### UNIT-I

# Organometallic Reagents - II:

Principle precipitation, properties and applications of the following in organic synthesis with mechanistic details. Transition metals. Cu, Pd, Ni, Fe, Co, Rh, Cr, and Ti compounds. Other elements S, Si, B and I compounds.

### UNIT II

**Reduction - I:** Introduction, Different reductive processes. Alkanes, alkenes, alkynes, and aromatic rings. Carbonyl compounds-aldehydes, ketones, acids and their derivatives.

#### UNIT III

**Reduction - II:**Epoxides, Nitro, nitroso, azo and oxime groups. Hydrogenolysis.

## UNIT IV

Metallocenes, Nonbenzenoid Aromatics Compounds and Polycyclic

Compounds – I: General consideration. Synthesis and reactions of some representative compounds. (Tropone, tropolone, azulene.)

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# UNIT V

Metallocenes, Nonbenzenoid Aromatics Compounds and Polycyclic Compounds – II: General consideration. Synthesis and reactions of some representative compounds. (Ferrocene, phenanthrene, fluorine and

indene).

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# **Organic Synthesis-IV**

# Scheme of examination:

MM: 35

- 1. In Semester End Examination there will be 10 questions in all, 2 from each unit. Candidate has to answer any 5 questions, taking one from each unit.
- 2. Each question shall be of 7 marks.

### UNIT-I

Two Group C-C Disconnections-I: Diels-Alder Reaction, 1,3-difunctionalised compounds,  $\alpha$ ,  $\beta$ - unsaturated carbonyl compounds, control in carbonyl condensations.

# **UNIT II**

# Two Group C-C Disconnections-II:

1,5-difunctionalised compounds. Micheal addition and Robinson annelation.

### **UNIT III**

**Ring Synthesis:** Saturated heterocycles, synthesis of 3,4,5 and 6 membered rings. aromatic heterocycles in organic synthesis.

## **UNIT IV**

Synthesis of Some Complex Molecules – I: Application of the above in the synthesis of following compounds: Camphor, Longifoline, Cortsone, Reserpine.

**UNIT V** 

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UNII V

Synthesis of Some Complex Molecules – II: Vitamin D, Juvabione,

Aphidicolin and Fredericamycin A.

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# Heterocyclic Chemistry-II

### Scheme of examination:

MM: 35

- In Semester End Examination there will be 10 questions in all, 2 from each unit. Candidate has to answer any 5 questions, taking one from each unit.
- 2. Each question shall be of 7 marks.

### UNIT-I

Non-aromatic Heterocycles: Strain-bond angle and torsional strains and their consequences in small ring heterocycles. Conformatino 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.

### UNIT II

Heterocyclic Synthesis: Principles of heterocyclic synthesis involving cyclization reactions and cycloaddition reactions.

### **UNIT III**

# **Meso-ionic Heterocycles**

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

**UNIT IV** 

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Benzo-Fused Five-Membered Heterocycles

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

## **UNIT V**

Heterocyclic Systems Containing P: 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, reactivity and special characteristics of 3-, 5- and 6-membered ring system.

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

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# **Chemistry of Natural Products-II**

### **Scheme of examination:**

MM: 35

- In Semester End Examination there will be 10 questions in all, 2 from each unit. Candidate has to answer any 5 questions, taking one from each unit.
- 2. Each question shall be of 7 marks.

# UNIT-I

Steroids – I: Occurrence, nomenclature, classification, basic skeleton, Diel's hydrocarbon and stereochemistry, Isolation, structure, determination and synthesis of Cholesterol and Bile acids.

#### UNIT II

**Steroids** – **II:** Structure, determination and synthesis of Androsterone, Testosterone, Estrone, Progestrone, Aldosterone, Biosynthesis of Steroids.

### UNIT III

Plant Pigments – I: Occurrence, nomenclature and general methods of structure determination. Isolation and synthesis of Apigenin, Luteolin Quercetin, Myrcetin, Quereentin, β-glucoside and Vitexin.

Plant Pigments – II: Occurrence, nomenclature and general methods of structure determination, isolation and synthesis of Diadzein, Buttein, Ireusin Cyanidin-7, arabinoside, Cyanidin, Esutidin, Biosynthesis of flavonoids: Acetate pathway and Shikimic acid pathway.

### **UNIT IV**

Prophyrins: Structure and synthesis of Haemoglobin and Chlorphyll.

**UNIT V** 

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Pyrethroids and Rotenones: Synthesis and reactions of Pyrethroids and Rotenones. (For structure educidation, emphasis is to be placed on the use of spectral parameters wherever possible).

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# **Analytical Chemistry-II**

# Scheme of examination:

**MM: 35** 

- In Semester End Examination there will be 10 questions in all, 2 from each unit. Candidate has to answer any 5 questions, taking one from each unit.
- 2. Each question shall be of 7 marks.

# UNIT-I

Introduction: Sample separation-dissolution and decompositions.

Gravimetric techniques. Selecting and handling of reagents. Laboratory notebooks. Safety in the analytical laboratory.

### **UNIT II**

# **Analysis of Water Pollution – II:**

Heavy metal pollution-public health significance of cadmium, chromium, copper, lead, zinc, managanese, mercurry 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.

#### **UNIT III**

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

(b) Fuel analysis: liquid and gas. Ultimate and proximate analysisheating values-grading of coal. Liquid fuels-flash point, aniline point, octane number and carbon residue. Gaseous fuels-producer gas and water gas-calcorific value.

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### UNIT IV

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

# **UNIT V**

Drug analysis: Narcotics and dangerous drugs. Classification of drugs.

Screeing by gas and hing-layer chromatography and spectrophotometric

measurements.

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# Physical Organic Chemistry-II

### Scheme of examination:

MM: 35

- 1. In Semester End Examination there will be 10 questions in all, 2 from each unit. Candidate has to answer any 5 questions, taking one from each unit.
- 2. Each question shall be of 7 marks.

### UNIT-I

Acids, Bases, Electrophiles, Nucleophiles and Catalysis: 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 a-effect. Ambivalent nucleophiles. Acid-base catalysis-specific and general catalysis. Bronsted catalysis, Nuceophilic and electrophilic catalysis. Catalysis by noncovalent binding-micellar catalysis.

### UNIT II

Steric and Conformation Properties: Various type of steric strain and their influence on reactivity. Steric acceleration. Molecular measurements of steric effects upon rates. Steric LFET, 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 III

Nucleophilic and Electrophilic Reactivity: Structural and electronic effects on SN1 and SN2 reactivity. Solvent effect Kinetic isotope effects. Intromolecular assistance. Electron transfer nature of SN2 reaction.

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Nucleophilicity and SN2 reactivity based on curvedcrossing mode.

Relationshiop between polar and electron transfer reactions SRN1 mechanism. Electrophilic reactivity, general mechanism. Kinetic of SE2 Ar reaction. Structural effects on rates and selectivity. Curve-crossing approach to electrophilic reactivity.

#### UNIT IV

Radical and Pericyclic Reactivity: Radical stability, polar influences, 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.

### **UNIT 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. Princples of molecular association and organization as exemplified in biological macromolecules like enzymes, nucleic acids, membranes and model system like micelles and vesicles. Molecular receptors and design principles. Cryptands, cyclophanes, calixeranes, cyclodextrines. Supramolecular reactivity and catalysis. Molecular channels and trnasport processes, Molecular devices and nanotechnology.

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# **Chemical Dynamics-II**

# **Scheme of examination:**

MM: 35

- 1. In Semester End Examination there will be 10 questions in all, 2 from each unit. Candidate has to answer any 5 questions, taking one from each unit.
- 2. Each question shall be of 7 marks.

#### UNIT - I

Radiation Chemistry: 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. Holeconcept in the presence of semiconductor type photocatalysis. Kinetics and mechanism of electron transfer reaction in the presence of visible light. Kinetics of exchange reactions (Mathematical analysis).

#### UNIT II

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

#### UNIT III

Substitution Reactions – I: 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

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and mechanism. Various types of inner sphere bridges, adjustment and remote attack. Linkage isomerism.

#### UNIT IV

Substitution Reactions – I: Chemical and resonance mechanism.

Marcus-Cross relation in outersphere reactions (no mathematical derivation). Its application in reactions: Ce(IV) + Mo(CN)<sub>6</sub><sup>4-</sup> —>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> 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 cyclodextrines. Considering one full case study, Nucleophilic and electrophilic catalyst 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.

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# **Electrochemistry-II**

### Scheme of examination:

**MM: 35** 

- 1. In Semester End Examination there will be 10 questions in all, 2 from each unit. Candidate has to answer any 5 questions, taking one from each unit.
- 2. Each question shall be of 7 marks.

## UNIT-I

Corrosion and Stability of Metals: Civilization and Surface mechanism of the corrosion of the metals; Thermodynamics and the stability of metals, Potential -pH (or Pourbaix) Diaphragmal; uses and abuses, Corrosion current and corrosion potential -Evans diagrams. Measurement of corrosion rate: (i) Weight Loss method, (ii) Electrochemical Method.

### **UNIT II**

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.

### **UNIT III**

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

UNIT IV

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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.

# **UNIT V**

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

Stripping analysis: anodic and Cathodic modes, Pre electrolysis and Stripping steps, applications of Stripping Analysis.

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