

M.Sc. II Year (Final)

Paper-I : CH-501

Applications of Spectroscopy, Photochemistry and Solid State Chemistry

(4 hrs. or 6 periods / week)

Exam Duration : 3 Hrs.

Max. Marks: 100

Unit-I

Ultraviolet and Visible Spectroscopy

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

Infrared Spectroscopy

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

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

Unit-II

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

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

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

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

Unit-III

NMR Spectroscopy : FT NMR- Fourier transform technique.

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

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

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

Mass Spectrometry

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

Unit-IV

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

on the rate of photochemical reactions. Types of photochemical reactions, photo-dissociation, gas-phase photolysis.
Photochemistry of Alkenes :Intramolecular reactions of the olefinic bond - geometrical isomerism, cyclisation reactions, rearrangement of 1,4- and 1,5-dienes. **Photochemistry of Carbonyl Compounds** :Intramolecular reactions of carbonyl compounds - saturated, cyclic and acyclic, β , γ -unsaturated and α,β -unsaturated compounds, cyclohexadienones. Intermolecular cycloaddition reactions - dimerisations and oxetane formation.
Photochemistry of Aromatic Compounds :Isomerisations, additions and substitutions.

Unit-V

Solid State Reactions : General principles, experimental procedure, co-precipitation as a precursor 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 defects and Frenkel defects. Thermodynamics of Schottky and Frenkel defect formation, colour centres, non-stoichiometry and defects.

Electronic Properties and Band Theory :Metals, insulators and semiconductors, electronic structure of solids, band theory, band structure of metals, insulators and semiconductors, Intrinsic and extrinsic semiconductors, doping semiconductors, p-n junctions, super conductors.

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

Books Suggested

UNIT I, II and III

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

UNIT IV

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

UNIT V

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

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Exam Duration: 3 hrs.

Max. Marks: 75

Unit-I

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

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

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

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

Unit-II

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

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

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

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

Unit-III

Co-enzyme Chemistry :Cofactors as derived from vitamins, coenzymes, prosthetic groups, apoenzymes. Structure and biological functions of coenzyme A, thiamine pyrophosphate, pyridoxal phosphate, NAD^+ , $NADP^+$, FMN, FAD, lipoic acid, vitamin B_{12} . Mechanisms of reactions catalyzed by the above cofactors.

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

Unit-IV

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

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

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

Unit-V

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

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

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

Books Suggested

1. Principles of Bioinorganic Chemistry, S.J. Lippard and J.M. Berg, University Science Books.
2. Bioinorganic Chemistry, I. Bertini, H.B. Gray. S.J. Lippard and J.S. Valentine, University Science books.
3. Inorganic Biochemistry vols. I and II, ed. G.L. Eichhom, Elsevier.
4. Progress in Inorganic Chemistry, Vols 18 and 38 ed. J.J. Lippard, Wiley.
5. Principles of Biochemistry, A. L. Lehninger. Worth Publishers.
6. Bioorganic Chemistry : A Chemical Approach to Enzyme Action, Hermann Dugas and C. Penny, Springer Verlag.
7. Understanding Enzymes, Trevor Palmer, Prentice Hall.
8. Enzyme Chemistry: Impact and Applications, Ed. Collin J Suckling, Chemistry.
9. Enzyme Mechanisms, Ed. M.I. Page and A. Williams, Royal Society of Chemistry.
10. Fundamentals of Enzymology, N.C. Price and L. Stevens, Oxford University Press.
11. Immobilized Enzymes : An Introduction and Applications in Biotechnology, Michael I.D. Trevan, John Wiley.
12. Enzymatic Reaction Mechanisms. C, Walsh, W.H. Freeman.
13. Enzyme Structure and Mechanism. A. Fersht, W.H. Freeman.
14. Biochemistry : The Chemical Reactions of Living Cells, D.E. Metzler. Academic Press.
15. Biochemistry, L. Stryer, W.H. Freeman.
16. Biochemistry, J. David Rawn. Neil Patterson.
17. Biochemistry. Voet and Voet, John Wiley.
18. Outlines of Biochemistry, E.E. Conn and P.K. Stumpf. John Wiley.
19. Bioorganic Chemistry : A Chemical Approach to Enzyme Action. H Dugas and C. Penny, Springer-Verlag.
20. Macromolecules : Structure and Function. F Wold. Prentice Hall.

Paper-III : CH-503

Environmental Chemistry

(2 Hrs. or 3 period / week)

Exam Duration : 3 hrs.

Max. Marks : 50

Unit-I

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

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

Tropospheric Photochemistry: Mechanism of photochemical decomposition of NO_2 and formation of ozone. Formation of oxygen atoms, hydroxyl, hydroperoxy and organic radicals and hydrogen peroxide. Reactions of hydroxyl radicals with methane and other organic compounds. Reactions of OH radicals with SO_2 and NO_x . Formation of nitrate radical and its reactions. Photochemical smog, meteorological conditions and chemistry of its formation.

Unit-II

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

Acid Rain : Definition, acid rain precursors and their aqueous and gas phase atmospheric oxidation reactions. Damaging effects on aquatic life, plants, buildings and health. Monitoring of SO_2 and NO_x - Acid rain control strategies.

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

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

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

Unit-III

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

Unit-IV

Environmental Toxicology

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

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

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

Polynuclear Aromatic Hydrocarbons - Sources, structures and as pollutants.

Unit-V

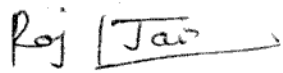
Soil and Environmental Disasters

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

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

Books Suggested:

1. Environmental Chemistry. Colin Baird, W.H. Freeman Co. New York. 1998.
2. Chemistry of Atmospheres. R.P. Wayne. Oxford.
3. Environment Chemistry, A.K. De, Wiley Eastern, 2004.
4. Environmental Chemistry, S.E. Manahan, Lewis Publishers.
5. Introduction to Atmospheric Chemistry, P.V. Hobbs, Cambridge.


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ELECTIVE PAPERS

Group I

- CH-504 : Organotransition Metal Chemistry
- CH-505 : Bioinorganic and Supramolecular Chemistry
- CH-506 : Photoinorganic Chemistry
- CH-507 : Polymers.

Group II

- CH-504 : Organic Synthesis-I
- CH-505 : Organic Synthesis-II
- CH-506 : Heterocyclic Chemistry
- CH-507 : Chemistry of Natural Products

Group III

- CH-504 : Analytical chemistry
- CH-505 : Physical Organic Chemistry
- CH-506 : Chemical Dynamics
- CH-507 : Electrochemistry

ELECTIVE PAPER-1 (CH-504, Group-I) Organotransition Metal Chemistry (2 Hrs. or 3 period/week)

Exam Duration : 3 hrs.

Max. Marks: 50

Unit-I

Alkyls and Aryls of Transition Metals

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

Unit-II

Compounds of Transition Metal-Carbon Multiple Bonds

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

Unit-III

Transition Metal 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 organic synthesis. **Transition metal compounds with bonds to hydrogen**

Unit-IV

Homogeneous Catalysis

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

Unit-V

Fluxional Organometallic Compounds

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

Books Suggested

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

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

Exam Duration: 3 hrs.

Max. Marks: 50

Unit-I

Metal Storage and Transport

Ferritin transferring and siderophores

Unit-II

Calcium in Biology

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

Unit-III

Metalloenzymes

Zinc enzymes - carboxypeptidase and carbonic anhydrase. Iron enzymes - catalase, peroxidase and cytochrome P-450. Metallo enzyme-II Copper enzymes - superoxide dismutase. Molybdenum oxatransferase enzymes-xanthine oxidase. Coenzyme vitamin B12.

Unit-IV

Metal-Nucleic Acid Complexes

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

Metals in Medicine

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

Unit-V

Supramolecular Chemistry-I

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

(B.) Supramolecular reactivity and catalysis.

Supramolecular Chemistry-II

(A.) Transport processes and carrier design.

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

Books Suggested

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

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

Exam Duration: 3 hrs.

Max. Marks: 50

Unit-I

Basics of Photochemistry

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

Unit-II

Properties of Excited States

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

Unit-III

Excited States of Metal Complexes

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

Unit-IV

Ligand Field Photochemistry

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

Unit-V

Redox Reactions by Excited Metal Complexes

Energy transfer under conditions of weak interaction and strong interaction-exciplex formation; condition of the excited states to be useful as redox reactants, excited electron transfer, metal complexes as attractive candidates, (2,2'-bipyridine and 1,10-phenanthroline complexes), illustration of reducing and oxidising character of $[\text{Ru}(\text{bpy})_3]^{2+}$ complex, comparison with $[\text{Fe}(\text{bpy})_3]^{3+}$; role of spin-orbit coupling - life time of these complexes. Application of redox processes of electronically excited states for catalytic purposes, transformation of low energy reactants into high energy products, chemical energy into light.

Metal Complex Sensitizers

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

Books Suggested

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

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

Exam Duration : 3 hrs.

Max. Marks : 50

Unit-I

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

Unit-II

Polymer Characterization

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

Unit-III

Inorganic Polymers

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

Unit-IV

Structure, Properties and Applications of

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

Structure, Properties and Applications of

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

Unit-V

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

Books Suggested:

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

ELECTIVE PAPER-1
(CH-504, Group-II) Organic Synthesis-I
(2Hrs. or 3 periods/week)

Exam Duration : 3 hrs.

Max. Marks : 50

Unit-I

Organometallic Reagents

Principle, preparations, properties and applications of the following in organic synthesis with mechanistic details.
Group I and II metal organic compounds. Li, Mg, Hg, Cd, Zn and Ce compounds.
Transition metals : Cu, Pd, Ni, Fe, Co, Rh, Cr, and Ti compounds.

Unit-II

Oxidation

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

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

Oxidations with ruthenium tetroxide, iodobenzene diacetate and thallium(III) nitrate.

Unit-III

Reduction

Introduction. Different reductive processes.

Alkanes, alkenes, alkynes and aromatic rings. Carbonyl compounds - aldehydes, ketones, acids and their derivatives.

Epoxides. Nitro, nitroso, azo and oxime groups. Hydrogenolysis.

Unit-IV

Rearrangements

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

Unit-V

Metalloenes, Nonbenzenoid Aromatics and Polycyclic Aromatic Compounds

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

Books Suggested:

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

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

Exam Duration : 3 hrs.

Max. Marks : 50

Unit-I

Disconnection Approach

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

Unit-II

Protecting Groups

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

One Group C-C Disconnections

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

Unit-III

Two Group C-C Disconnections

Diels-Alder reaction, 1,3-difunctionalised compounds, α,β -unsaturated carbonyl compounds, control in carbonyl condensations, 1,5-difunctionalised compounds. Michael addition and Robinson annelation.

Unit-IV

Two Group C-C Disconnections

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

Unit-V

Ring Synthesis

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

Books Suggested:

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

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ELECTIVE PAPER-3
(CH-506, Group II) Heterocyclic Chemistry
(2Hrs. or 3 periods/week)

Exam Duration : 3 hrs.

Max. Marks : 50

Unit-I

Nomenclature of Heterocycles

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

Aromatic Heterocycles

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

Unit-II

Non-aromatic Heterocycles

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

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

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

Heterocyclic Synthesis

Principles of heterocyclic synthesis involving cyclization reactions and cycloaddition reactions.

Unit-III

Small Ring Heterocycles

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

Benzo-Fused Five-Membered Heterocycles

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

Unit-IV

Meso-ionic Heterocycles

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

Six-Membered Heterocycles with one Heteroatom

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

Unit-V

Six Membered Heterocycles with Two or More Heteroatoms

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

Heterocyclic Systems Containing P, As, Sb and B

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

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

Books Suggested:

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

ELECTIVE PAPER 4
(CH-507, Group -II) Chemistry of Natural Products
(2Hrs. or 3 periods/week)

Max. Marks : 50

Exam Duration : 3 hrs.

Unit-I

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, Geraniol, α -Terpeneol, Menthol, Farnesol, Zingiberene, Santonin, Phytol, Abietic acid and β -Carotene.

Unit-II

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 and Morphine.

Unit-III

Steroids

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

Unit-IV

Plant Pigments

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

Porphyrins

Structure and synthesis of Haemoglobin and Chlorophyll.

Unit-V

Prostaglandins : Occurrence, nomenclature, classification, biogenesis and physiological effects. Corey's Synthesis of PGE₂ and PGF_{2 α}

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

Books Suggested

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

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ELECTIVE PAPER-1
(CH-504, Group -III) Analytical Chemistry
(2Hrs. or 3 periods/week)

Exam Duration : 3 hrs.

Max. Marks : 50

Unit-I

Introduction

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

Errors and Evaluation

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

Unit-II

Food Analysis

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

Unit-III

Analysis of Water Pollution

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

Unit-IV

Analysis of Soil and Fuel

Analysis of soil : moisture pH, total nitrogen, phosphorus, silica, lime, magnesia, manganese, sulphur and alkali salts.

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

Unit-V

Analysis of Body Fluids and Drugs

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

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

Books Suggested

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

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

Exam Duration : 3 hrs.

Max. Marks : 50

Unit-I

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

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

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

Unit-II

Principles of Reactivity

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

Kinetic Isotope Effect

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

Unit-III

Structural Effects on Reactivity

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

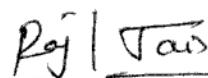
Solvation and Solvent Effects

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

Unit-IV

Acids, Bases, Electrophiles, Nucleophiles and Catalysis

30


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

Steric and Conformational Properties

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

Unit-V

Nucleophilic and Electrophilic Reactivity

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

Radical and Pericyclic Reactivity

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

Reactivity, specificity and periselectivity in pericyclic reactions.

Books Suggested :

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

ELECTIVE PAPER - 3

(CH-506, Group-III) Chemical Dynamics

(2 Hrs. or 3 period/week)

Exam Duration : 3 hrs.

Max. Marks : 50

Unit-I

Atmospheric Reactions

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

Unit-II

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

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

Micelles catalysis and inhibition : Kinetics and mechanism of micelle catalyzed reactions (1st order and second order) Various type of micelle catalyzed reactions. Micelle inhibited reactions.

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

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Unit-III

Radiation Chemistry and Photochemistry

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

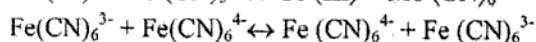
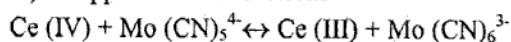
Transition State

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

Unit-IV

Substitution reactions.

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



Bridged outer-sphere electron transfer mechanism.

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

Unit-V

Metal ion catalysis and induced phenomena

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

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

Books Recommended

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

ELECTIVE PAPER-4
(CH-507, Group-III) Electrochemistry
(2 Hrs. or 3 period/week)

Exam Duration : 3 hrs.

Max. Marks : 50

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 output.

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

Electrochemical Energy Storage :

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

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

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

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

Unit-II

Corrosion and Stability of Metals :

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

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

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

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

Unit-III

Bioelectrochemistry:

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

Unit-IV

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

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

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

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

Unit-V

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

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

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

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

Book Suggested:

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

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

Exam Duration 15 minutes/student

Max Marks 25

Seminar to be conducted in presence of External examiner.

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Exam Duration: (14 hrs in 2 days)

Max. Marks: 200

Inorganic Chemistry

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

Selection can be made from the following:

1. Sodium amide, Inorg. Synth., 1946, 2, 128.
2. Synthesis and thermal analysis of group II metal oxalate hydrate, J. Chem. Ed., 1988, 65, 1024.
3. $[\text{PhBCl}_2]$ Dichlorophenylborane. Synthesis in vacuum line.
4. Preparation of Tin (IV) iodide, Tin (IV) chloride and Tin (II) iodide. Inorg. Synth., 1953, 4, 119.
5. Relative stability of Tin (IV) and Pb (IV). Preparation of ammonium hexachlorostannate $(\text{NH}_4)_2[\text{SnCl}_6]$; ammonium hexachloroplumbate $(\text{NH}_4)_2[\text{PbCl}_6]$.
6. Hexabis (4-nitrophenoxy) cyclotriphosphazene.
7. Synthesis of trichlorodiphenylantimony (V) hydrate, Inorg. Synth., 1985, 23, 194.
8. Sodium tetrathionate, $\text{Na}_2\text{S}_4\text{O}_6$.
9. Metal complexes of dimethylsulfoxide and their IR: $\text{CuCl}_2 \cdot \text{DMSO}$; $\text{PdCl}_2 \cdot 2\text{DMSO}$; $\text{RuCl}_2 \cdot 4\text{DMSO}$, J. Chem. Educ., 1982, 59, 57.
10. Synthesis of metal acetylacetonate: IR, Inorg. Synth., 1957, 5, 130; 1963, 1, 183.
11. Bromination of $[\text{Cr}(\text{acac})_3]$, J. Chem. Edu, 1986, 63, 90.
12. $[\text{Cu}(\text{acac})_2] \cdot \text{H}_2\text{O}$.
13. *cis*- and *trans*- $[\text{Co}(\text{en})_2\text{Cl}_2]^+$.
14. *cis*- $[\text{Co}(\text{en})_2\text{Cl}_2]\text{Cl}$, J. Chem Soc., 1960, 4369.
15. Cr(III) complexes. $[\text{Cr}(\text{H}_2\text{O})_6]\text{NO}_3 \cdot 3\text{H}_2\text{O}$; $[\text{Cr}(\text{H}_2\text{O})_4\text{Cl}_2]\text{Cl} \cdot 2\text{H}_2\text{O}$; $[\text{Cr}(\text{en})_3]\text{Cl}_3$; $[\text{Cr}(\text{acac})_3]$, Inorg, Synth., 1972, 13, 184.
16. Preparation of *N,N*-bis(salicylaldehyde)ethylenedimine, salen H_2 ; $[\text{CO}(\text{salen})]$, J. Chem. Educ., 77, 54, 443; 1973, 50, 670.
17. Preparation of Fe(II) chloride (use it as Friedel-Craft chlorination source), J. Org. Chem., 1978, 43, 2423; J. Chem. Edu., 1984, 61, 645; 1986, 63, 361.
18. Reaction of Cr(III) with a multidentate ligand; a kinetics experiment (visible spectra Cr-EDTA complex), J. A. C. S., 1953, 75, 5670.
19. Preparation of $[\text{Co}(\text{phenanthroline-5, 6-quinone})]$.
20. Preparation and use of Ferrocene, J. Chem Edu., 1966, 43, 73; 1976, 53, 730.
21. Preparation of copper glycine complex. *cis*- and *trans*- bis(glycinato)copper (II), J. Chem. Soc. Dalton, 1979, 1901; J. Chem. Edu. 1982, 59, 1052.
22. Preparation of phosphine (Ph_3P) and its transition metal complexes.
23. Any other experiment such as conversion of *p*-xylene to terephthalic acid catalyzed by CoBr_2 (homogeneous catalysis).

Spectrophotometric Determinations

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

Flame Photometric Determinations

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

c) Cadmium and Magnesium in tap water.

Quantitative determinations of a three component mixture:

One Volumetrically and two Gravimetrically

a) Cu^{+2} , Ni^{+2} , Zn^{+2}

b) Cu^{+2} , Ni^{+2} , Mg^{+2}

Chromatographic Separations

a) Cadmium and zinc

b) Zinc and magnesium

c) Thin-layer chromatography-separation of nickel, manganese, cobalt and zinc, Determination of R_f values.

d) Separation and identification of the sugars present in the given mixture of glucose, fructose and sucrose by paper chromatography and determination of R_f values.

Organic Chemistry

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

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

i) Photochemical reaction:

(Benzophenone \rightarrow Benzpinacol \rightarrow Benzpinacolone)

ii) Beckman Rearrangement: Benzanilide from benzene

(Benzene \rightarrow Benzophenone \rightarrow Benzophenone oxime \rightarrow Benzanilide)

iii) Benzilic acid rearrangement: Benzilic acid from benzoin

(Benzoin \rightarrow Benzil \rightarrow Benzilic acid).

iv) Synthesis of heterocyclic compounds

a) Skraup synthesis: Preparation of quinoline from aniline

b) Fisher Indole synthesis: Preparation of 2-phenylindole from phenylhydrazine.

v) Diazocoupling: Phthalic anhydride \rightarrow Phthalamide \rightarrow anthranilic acid \rightarrow methyl red.

Extraction of Organic Compounds from Natural Sources

a) Isolation of caffeine from tea leaves.

b) Isolation of casein from milk (the students are required to try some typical colour reactions of proteins)

c) Isolation of lactose from milk (purity of sugar should be checked by TLC and PC and R_f values reported).

d) Isolation of chlorophyll a & b from spinach / spirulina.

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

Spectroscopy: Identification of organic compounds by the analysis of their spectral data (UV, IR, ^1HMR , ^{13}CMR & MS).

Spectrophotometry (UV/VIS) Estimations

a) Amino acids

b) Proteins

c) Carbohydrates

d) Cholesterol

e) Ascorbic acid

f) Aspirin

g) Caffeine

Physical Chemistry

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

A. Thermodynamics

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

B. Spectroscopy

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

C. Polarography

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

D. Chemical Kinetics

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

Books Suggested:

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

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INSTRUCTIONS TO THE EXAMINERS
CH-509: M.Sc. (Final) Chemistry Practical
Duration of Exam: 14 hrs. (Spread over 2 days)

Max. Marks: 200

Min. Marks 72

Inorganic Chemistry

1. Preparation of one of the selected inorganic compounds as mentioned in the syllabus and its study by IR, electronic spectra, Mossbauer, ESR and magnetic susceptibility. Handling of air and moisture sensitive compounds involving vacuum lines.

or

Quantitative determination of a three component mixture by volumetric & gravimetric methods. 25

2. Spectrophotometric determination of one of the 5 exercises given in the syllabus.

or

Flame Photometric determinations (one exercise) 15

3. Chromatographic separation of two metal ions. 10

Organic Chemistry

1. Qualitative Analysis

Separation, purification and identification of the components of a mixture of three organic compounds (three solids or two liquids and one solid, two solid and one liquid), using TLC for checking the purity of the separated compounds.

Chemical analysis, IR, ¹HMR and Mass spectral data. 30

2. Multi-step synthesis of Organic Compounds

Perform one of the multi-step synthesis of organic compounds. 20

or

Spectroscopy

Identification of Organic Compounds by the analysis of their spectral data

Physical Chemistry

From the Experiments listed in syllabus

1. Perform one Major physical experiment 30

2. Perform one Minor physical experiment 20

Viva

30

Record

20