8. CHEMISTRY

PAPER-I

SECTION-A: PHYSICAL CHEMISTRY

Unit-I:

Classical thermodynamics

Brief resume of concepts of law of thermodynamics – free energy, chemical potential and entropies – Partial molar properties – partial molar free energy – partial molar volume and partial molar heat content and their significances – concept of fugacity and determination of fugacity – activity – activity coefficient – Third law of thermodynamics,

Unit-II:

Chemical dynamics

Empirical rate laws – Theories of reaction rates – Determination of reaction mechanism – Reaction in solutions – catalysed reaction kinetics

Electrochemistry

Electrochemistry of solutions – Debye – Huckel – Onsager treatment and its extension, Ion association – Thermodynamics of electrified interfaces – Lipmann equation – Butler Volumer equation – theory of double layer at interfaces and semiconductor – corrosion and prevention methods.

Unit-III:

Surface chemistry

Adsorption – Surface tension, Capillary action – pressure difference across curved surface isotherm – BET equation – surface films on liquids.

Polymers : Definition, type of polymers – kinetie of polymerization – mechanism of polymerization –Solid state chemistry : Structural classification of solids of binary and ternary compounds – defects in solids – Electrical properties : Metals, insulator, semiconductor, super conductors – band theory of solids.

Phase equilibria: Thermodynamic derivation of phase rule – Three component systems and their application.

Unit-IV

Quantum Mechanics

Postulates – Particle in box, rigid rotator – harmonic oscillator – variation principles, first order perturbation principle – angular momentum

SECTION – B : INORGANIC CHEMISTRY

Unit-I

Periodic properties and chemical bondChemical periodicity, VSEPR theory for different types of molecules, Walsh diagram (tri- and penta – atomic molecules), dπ-pπ bond, bent rule and energetic of hybridization some simple reactions of covalently bonded molecules.

Acid-base concept and Non-aqueous solvents

Hard-soft acid base concept – acid base strength – theoretical basis of hardness and softness. Non aqueous solvents: types and characteristics – reactions in non-aqueous solvents.

Symmetry and Group Theory in Chemistry

Symmetry elements and symmetry operations – definitions of group, subgroup, cosets relation between orders of a finite group and its subgroup – Conjugacy relation and classes. Point symmetry group – Stoneflies symbols – representations of groups by matrices (representation for the Cn, Cnv, Cnh, Dnh groups) – Character of a representation – The great Orthogonality theorem (without proof)

Unit-II

Chemistry of transition and inner transition elements: General characteristics of 1st row transition elements and inner transition elements with special reference to electronic structure, ionic radii, oxidation states, complex formation, magnetic behaviour and spectral properties.

Coordination compounds

Nomenclature and isomerism of coordination compounds – valence bond theory and its limitations – Crystal field theory and its applications to octahedral, tetrahedral and square planer complexes – Limitations of crystal field theory – Molecular orbital theory: sigma bonding and energy level diagram in octahedral, tetrahedral and square planar complexes: bonding and energy level diagram in octahedral complexes.

Unit-III

Metal – Ligand Equilibria in Solution

Stepwise and overall formation constants and their interrelation, factors affecting the stability of metal complexes – chelate effect and its thermodynamic origin

Reaction mechanism of transition metal complexes

Energy profile of a reaction – Thermodynamic and kinetic stability of metal complexes – Kinetic application of valence bond and crystal field theories.

Substitution reactions of octahedral complexes: acid hydrolysis – base hydrolysis: conjugate base mechanism and the direct/indirect evidences – Substitution reactions in square planar complexes: the trans effect and its application to synthesis of complexes – theories of trans effect – mechanism and factors affecting the substitution reactions

Nuclear chemistry

Radioactive disintegrations, radio isotopes and their applications, nuclear reactions, fission and fusion, radio analytical techniques and activation analysis.

Unit-IV

Metal π complexes

Metal carbonyls: synthesis, structure and bonding – vibrational, spectra of metal carbonyls for bonding and structural elucidation – EAN concept and application to metal carbondyOrganometallic Chemistry

Organometallic Chemistry

Preparation, properties and applications alkyl and aryls of group-I and II metal (Li, Mg, Zn) and transition metals (Ti, Ni,. Cu and Pd).

Bioinorganic Chemistry

Essential and trace metals in biological processes – role of alkali and alkaline earch metal jons - Na+- K+ Pump – metalloporphyrins with special reference to hemoglobin and myoglobin, Metal complexes in transmission of energy – chlorophylix, photosystem-I and photosystem-II in cleavage of water - ATP as energy currency in biological system.

Structure and function of metalloproteins in electron transport processes – cytochromes and ferrodoxin.

Biological nitrogen fixation, molybdenum nitrogenase, spectroscopic and other evidences – Metal complexes in medicine.

PAPER-II

SECTION-A : ORGANIC CHEMISTRY

Unit-I

Stereochemistry, structure and reactivity

Conformational analysis of cycloalkanes, decalins, effect of conformation on reactivity, conformation of sugars, steric strain due to unavoidable crowding. Elements of symmetry, chirality, molecules with more than one chiral center, threo and erythro isomers, methods of resolution, optical purity, enantiopticanddiasterotopic atoms, groups and faces, sterospecific and steroselective synthesis – Asymmetric synthesis – Optical activity in the absence of chiral carbon (biphenyls, allenes and spiranes), chirality due to helical shape.

Types of mechanisms, types of reactions, thermodynamic and kinetic requirements, kinetic and thermodynamic control, Potential energy diagrams, transition states and intermediates, methods of determining mechanisms, isotope effects.

Aliphatic nucleophilic substitution

The SN2, SN1, mixed SN1 and SN2 and SET mechanisms. The neighbouring group mechanism, neighbouring group participation by p and s bonds, anchimeric assistance

The SN1 mechanism.

Nucleophilic substitution at an allylic, aliphatic trigonal and a vinylic carbon.Reactivity effects of substrate structure, attacking nucleophile, leaving group and reaction medium, phase transfer catalysis and ultrasound, ambident nucleophile, leaving group and reaction medium, phase transfer catalysis and ultrasound, ambident nucleophile, regioselectivity.

Aliphatic electrophilic substitution

Bimolecular mechanisms – SE2 and SEi. The SE1 mechanism, electrophilic substitution accompanied by double bond shifts. Effect of substrates, leaving ground and the solvent polarity on the reactivity.

Unit-II

Aromatic Electrophilic Substitution

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

Aromatic Nucleophilic Sustitution TheSNAr, SN1, benzyne and SRN1 mechanisms. Reactivity – effect of substrate structure, leaving group and attacking nuleophile. The von Richter, Sommelet – Hauser, and Smiles rearrangements.

Free radical reactions

Types of free radical reactions, free radical substitution mechanism, mechanism at an aromatic substrate, neighbouring group assistance – Reactivity for aliphatic and aromatic sustrates at a bridgehead.Reactivity in the attacking radicals – The effect of solvents on ractivity. Allylic halogenation (NBS), oxidation of aldehydes to carboxylic acids auto-oxidation, coupling of alkynes and arylation of aromatic compounds by diazonium salts. Sandmeyer reaction. Free radical rearrangement. Hunsdiecker reaction.

Addition to Carbon – Carbon Multiple Bonds

Mechanism and stereochemical aspects of addition reactions involving electrophies, nucleophiles and free radicals, regio – and chemo selectivity, orientation and reactivity. Addition to cyclopropane ring – Hydrogenation of double andtriple bonds, hydrogenationof aromatic rings. Hydroboration – Michael reaction

Addition to Carbon – Hetero Multiple Bonds.

Mechanism of metal Hydride reduction of saturated and unsaturated carbony1 compounds, acids, esters and nitriles. Addition of Grignard reagents,organozinc and organolithium reagents tocarbony1 and unsaturated carbony1 compounds. Witting reaction – Mechanism of condensation

reactions involving enolates – Aldol, Knoevenagel, Claisen, Mannich, Benzoin, Perkin and Stobbe reactions.

Elimination Reactions

The E2, E1 and E1CB mechanisms and their spectrum –Orientation of the double bond Reactivity – effect of substrate structures, attacking base, the leaving and the medium.Mechanism and orientation in pyrolytic elimination.

Unit-III

Pericyclic Reactions

Molecular orbital symmetry, frontier orbitals of ethylene, 1, 3- butadiene, 1,3,5 – hexatriene and ally1 system. Classification of pericyclic reactions. Woodward – Hoffmann correlation diagrams. FMO and PMO approach. Electrocyclic reactions – conrotatory and disrotatory motions – antrafacial and suprafacial additions, 4n and 4n+2 systems, 2+2 addition of ketenes, 1,3 dipolar cycloadditions and chelotropic reactions.

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

Photochemical Reactions

Interaction of electromagnetic radiation with matter, type of excitations, fate of excited molecule, quantum yield, transfer of excitation energy, actinometry.

Photochemistry of Alkenes : Intramolecular reactions of the olefinic bond – geometrical isomerism, cyclisation reactions, rearrangement of 1,4- and 1.5- dienes.

Photochemistry of Carbony1 Compounds : Intramolecular reactions of carbony1 compounds – saturated, cyclic and acyclic, β,γ-unsaturated and α, β- unsaturated compounds, cyclohexadienones

Photochemistry of Aromatic Compounds :Isomerisations, additions and substitutions.

Photochemical formation of smog.

Unit-IV

Disconnection approach

An introduction to synthons and synthetic equivalents, disconnection approach, functional group inter-conversion, 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 and amine synthesis.

Protecting groups : Principle of protection of alcohol, amine, carbony1 and carboxy1 groups.

SECTION-B: ANALYTICAL CHEM

Unit-I

Introduction to analytical chemistry and data processing -Role of analytical chemistry, classification of analytical methods, types of instrumental analysis

Environmental samples and their analyses

Aquatic pollution: Inorganic, organic, pesticides, agricultural, industrial etc.-Water qualify parameters: dissolved oxygen, biochemical oxygen demand, solids, metals, content of chlorides, fluoride, sulfate, phosphate, nitrate.

Analytical methods for measuring BOD, DO, COD, fluoride, nitrate (As, Cd, Cr, Hg, Pb, Se etc.)

Unit-II

Ultraviolet and Visible Spectroscopy

Various electronic transitions, Beer-Lambert's Law, effect of solvent on electronic transitions, ultraviolet bands for carbony1 compounds, unsaturated carbony1 compounds, dienes, conjugated polyenes.Fieser – Woodward rules for conjugated dienes and carbony1 compounds, ultraviolet spectra of aromatic compounds

Infrared Spectroscopy

Principles – Vibrational frequencies of alkanes, alkenes, alkynes, aromatic compounds, alcohols, ethers, phenols, ary1 aminers. Detailed study of vibrational frequencies of carbony1 compounds (Ketones, aldehydes), esters, amides, acids, anhydrides, lactones, lactams and conjugated carbony1 compounds. H-bonding and solvent effect on vibrational frequencies, overtones, combination bands and Fermi resonance.

Nuclear Magnetic Resonance Spectroscopy

Principles, chemical shift, spin-spin interaction, shielding mechanism, chemical shift values and correlation for protons bonded to carbon (Aliphatic, olefinic, enols, carboxylic acids, amines, amides &mercapto) chemical exchange, effect of deuteration, complex spin-spin interaction between two, three, four and five nuclei (first order spectra), virtual coupling. Stereochemistry, hindred rotation, Karplus curve-variation of coupling constant with dihedral angle.Simplification of complex spectra nuclear magnetic double resonance, chemical shift reagents, solvent effects.

Mass Spectrometry-analysis and abundance – Mass spectral fragmentation of organic compounds, common functional groups – Molecular ion peak – Metastable peak, Mc Lafferty rearrangement.

Problems relating to elucidation of structure of simple organic molecules using UVVIS, IR, NMR and Mass spectral data.

Unit-III

Solvent Extraction and ion exchange

Solvent Extraction: Principles, classification of extraction, mechanism of extraction, extraction equilibria, techniques of extraction, applications in analytical chemistry.

Ion exchange: Type of ion exchange resins, synthesis and characteristics of ion exchange resins, action of ion exchange resins, ion exchange equilibria, technique of ion exchange, application of ion exchange in analytical chemistry.

Unit-IV

Electron spin resonance

Principles zero filed splitting and Kramer's degeneracy, factors affecting the g value, hyperfine splitting and applications to sample radicals.