CHEMISTRY

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, excess functions for non ideal solutions

Unit-II:

Chemical dynamics

Empirical rate laws – Theories of reaction rates – Determination of reaction mechanism – Reaction in solutions – catalysed reaction kinetics – Techniques for fast reactions viz. flow method, relaxation method, flash photolysis, NMR method.

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

Quantum Mechanics

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

Molecular orbital theory

Huckel theor of conjugated systems – Free valence index, bond order and charge density calculations – application to ethylene – butadiene – cyclopropylene radical, cyclobutadiene

Electronic structure of atoms

Electronic configuration, L-S coupling – term separation of energies of pn and dn configurations – spin orbit coupling – Zeeman splitting.

SECTION – B : INORGANIC CHEMISTRY

Unit-I

Periodic properties and chemical bonding

Chemical periodicity, VSEPR theory for different types of molecules, Walsh diagram (tri- and penta – atomic molecules), dп-pп 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.

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 and Metal – Ligand Bonding

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.

Electronic spectra of transition metal complexes

Types of electronic transitions, selection rule – Spectrochemical, series – Spectroscopic ground states, correlation – Orgel and Tanabe-Sugano diagrams for transition metals complexes (d^1 to d9 states), calculations of Dq, B and b parameters – charge transfer spectra.

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.

Redox reactions: Outersphere reactions, Marcus theory for outerasphere reaction – inner sphere reactions.

Nuclear chemistry

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

Unit-IV

Metal л complexes

Metal carbonyls: synthesis, structure and bonding – vibrational, spectra of metal carbonyls for bonding and structural elucidation – EAN concept and application to metal carbondyls – important reactions OF METAL CARBONYIS – Preparation, bonding, structure and important reactions of transition metal nitrosyl, dinitrogen and dioxygen complexes – tertiary phosphine as ligand.

SECTION-C : 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, enantiopticand diasterotopic 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, Hammond's postulate, Curtin-Hammett principle. 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 Classical and non-classical carbocations, phenonium ions, norbormy1 system, common carbocations rearrangements – Application of NMR spectroscopy in the detection of carbocations.

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

The SNAr, 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 chemoselectivity, orientation and reactivity. Addition to cyclopropane ring – Hydrogenation of double andtriple bonds, hydrogenation of aromatic rings. Hydroboration – Michael reaction – Sharpless asymmetric epoxidation.

Addition to Carbon – Hetero Multiple Bonds.

Mechanism of metal Hydride reduction of saturated and unsaturated 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.

SECTION-D: ANALYTICAL CHEMISTRY

Unit-I

Introduction to analytical chemistry and data processing

Role of analytical chemistry, classification of analytical methods, types of instrumental analysis – Errors of analysis, classification, source and minimization of errors, absolute and relative errors, accuracy and precision, significant figures, mean value and deviation, average and standard deviation, median value, range, confidence intervals. Sampling in analysis. Definition, theory of sampling, technique of sampling, statistical criteria of good sampling, stratified sampling, transmission and storage of samples.

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 compoiunds, 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

Principles, Ion production – EI, CI, FD and FAB – factors affecting fragmentation, ion analysis and abundance – Mass spectral fragmentation of organic compounds, common functional groups – Molecular ion peak – Metastable peak, Mc Lafferty rearrangement. Nitrogen rule – High resolution mass spectrometry – Examples of mass spectral fragmentation of simple organic compounds with respect to their structure determination.

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

Chromatographic methods

Basic principles and applications of chromatographic techniques (Paper, TLC, Ion Exchange, HPLC, GLC).

Spectroscopic methods

Atomic adsorption spectroscopy : Principles and application of AAS in chemical analysis.

Flame photometric methods : Principles – Interference in flame photometry – Application in quantitative analysis.

Nephelometric method: Principle and applications in analysis.

X-ray diffraction method : Wiese indices, Miller indices, Laue method, Bragg's law and applications in determination of crystal structure.

SECTION-E: GENERAL CHEMISTRY

Unit-I

Surface chemistry

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

Micelles : Surface active agents and their classifications – Structure of micelles – CMC – Thermodynamics of micellizations – Solubilization –micro emulsion – reverse micelle.
Polymers : Definition, type of polymers – kinetie of polymerization – mechanism of polymerization – Molecular mass and its determination (Osmometry, Viscometry, diffusion and light scattering methods).
Phase equilibria : Thermodynamic derivation of phase rule – Three component systems and their application.

Unit-II

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.
Metalloenzymes: Carbonic anhydrase, carboxypetidase.
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.

Unit-III

Photo chemistry

Different laws, quantum yield, fluorescence, phosphorescenc, chemiluminiscence, photolysis, photo synthesis, photosensitiser, photoinhibitor

Photochemical Reactions

Interaction of electromagnetic radiation with matter, type of excitations, fate of excited molecule, 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.
Miscellaneous Photochemical Reactions: Photo-Fries reactions of anilides. Photo-Fries rearrangement. Barton reaction. Singlet molecular oxygen reactions. Photochemical formation of smog.

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.)