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. Determination of absolute entropy of solids, liquids and gases. Residual entropy, Thermodynamics of mixing of gases (ΔS_{mix}, ΔG_{mix}, ΔH_{mix}).

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 Ionic Strength – Debye – Huckel – Onsager treatment and its extension, Ion association – Thermodynamics of electrified interfaces – Lipmann equation – Butler Volmer equation – theory of double layer at interfaces and semiconductor – corrosion and prevention methods. Appication of EMF – Determination of solubility, degree of dissociation, hydrolysis constant and pH.

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 – Electrodensity, delocalization energy, bond order and charge density calculations – application to ethylene – butadiene – cyclopropylene radical, cyclobutadiene

Electronic structure of atoms

Electronic configuration, L-S coupling – term symbol d^2 – d^{10} & ground state of module– 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, dπ-pπ bond, Bent rule of 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. Super acids and Hammet acidity function.

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– 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.

Electronic spectra of transition metal complexes

Types of electronic transitions, selection rule – Spectrochemical, series –
Spectroscopic ground states, correlation – Orgel diagrams for transition metals complexes (d^1 to d9 states), Nephelauxetic series calculations of 10 Dq, B and β – parameters, charge transfer spectra MLCT, LMCT.

Unit - III

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. **S**ubstitution reactions of octahedral complexes: Dissociative (D),Associative (A) and interchange mechanism acid hydrolysis Anation 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 and inner sphere reactions.

Nuclear chemistry; Mass defect 7 Binding energy

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

Unit-IV

Metal л complexes

Alkyls and aryls of transition metals, compounds having metal carbon multiple bond, transition metal π – complexes. Metal carbonyls: Preparation, properties and structure. 18 electron rule and its basis. Homogeneous catalysis, Reactions of organometallic compounds.

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, enantiotopic and 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 reaction mechanisms, isotope effects.

Aliphatic nucleophilic substitution

The S_N2, S_N1, mixed S_N1 and S_N2 and SET mechanisms. The neighbouring group mechanism, neighbouring group participation by sigma and pi - bonds, anchimeric assistance. Classical and non-classical carbocations, phenonium ions, norborny1 system, common carbocations rearrangements.

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 – S_E2 and S_Ei. 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 attack, orientation in other ring systems – Quantitative treatment of reactivity in substrates and electrophiles – Diazonium coupling – Vilsmeir reaction, Gattermann - Koch reaction.

Aromatic Nucleophilic Sustitution

The S_NAr, S_N1, benzyne and SR_N1 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.

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. Hydrogenation of double and triple bonds, hydrogenation of 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 to carbony1 and unsaturated carbony1 compounds. Witting reaction – Mechanism of condensation reactions involving enolates – Aldol, Knoevenagel, Claisen, Mannich, Benzoin.

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.

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 amines. 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.

Nuclear Magnetic Resonance Spectroscopy

Principles, chemical shift, spin-spin interaction, shielding mechanism, chemical shift, factors affecting chemical shift . Stereochemistry, hindered 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.

SECTION-E: GENERAL CHEMISTRY

Unit-I

Surface chemistry

Adsorption: Freundlich adsorption isotherm, Langmuir adsorption isotherm, Gibb's adsorption isotherm, BET equation, surface tension, capillary action – pressure difference across curved surface, surface films on liquids.

Micelles : Surface active agents and their classifications – Structure of micelles – CMC – hermodynamics 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).

Unit-II

Bioinorganic Chemistry

Essential and trace metals in biological processes – role of alkali and alkaline earth metal ions, - Na+- K+ Pump, metalloporphyrins with special reference to hemoglobin and myoglobin, Metal complexes in transmission of energy – chlorophyll, photosystem-I and photosystem-II in cleavage of water - ATP as energy currency in biological system. Metalloenzymes: Carbonic anhydrase, carboxypetidase.

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.

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 – IV

Supramolecular Chemistry :

(i) Receptors/Hosts on molecular recognition of different types of guests and biological supramolecular systems.

(ii) Chemistry of crown ethers, calixarenes and cyclodextrines.