CY Chemistry

Section 1: Physical Chemistry

Structure: Postulates of quantum mechanics. Operators. Commutation relations and expectations values; the role of the wave function and its absolute squares, time dependent and time independent Schrödinger equations. Born interpretation. Dirac bra-ket notation. Examples of model solvable quantum mechanical systems.

Particle in a Box: Solutions and interpretations for finite length and infinite potential barrier; concept of tunnelling; particle in 1D, 2D and 3D-boxes; applications.

Harmonic Oscillator: Exact solutions of wave functions, properties of Hermite polynomials. eigenvalues in one dimension. Calculation of expectation values for potential and kinetic energy, harmonic and anharmonic potentials.
Rotational Motion: Angular momentum operators (orbital and spin), spherical harmonics and their properties.

Hydrogen and Hydrogen-like Atoms: Atomic orbitals; radial and angular distribution functions and their probabilities; Atomic units, Multi-electron atoms: Orbital approximation; electron spin; Pauli exclusion principle; Slater determinants. Variational method and secular determinants; first order non-degenerate perturbation techniques.

Molecular Structure and Chemical Bonding: Born-Oppenheimer approximation; Valence bond theory treatment for hydrogen molecule and linear combination of atomic orbitals – molecular orbitals (LCAO-MO) theory. Concept of hybridization and hybrid orbitals. Applications of LCAO-MO theory to H_2^+, H_2; Molecular orbital theory (MOT) of homo- and heteronuclear diatomic molecules. Hückel theory, applications to simple molecules, small conjugated π-electron systems.

Group Theory: Symmetry elements and symmetry operations. Basic postulates of groups and group multiplication tables. Classes, reducible and irreducible representations of symmetry elements. Classification and labelling of molecular point groups. Symmetry based selection rules and their application to electronic and vibrational spectroscopy. Internal coordinates and symmetry labelling of vibrational modes; symmetry adapted linear combination of atomic orbitals (LCAO-MO); construction of hybrid orbitals using molecular point group symmetry.

Spectroscopy: Atomic spectroscopy; Russell-Saunders coupling; Term symbols and spectral details; origin of selection rules. Rotational, Vibrational, Electronic and Raman spectroscopy of diatomic and simple polyatomic molecules. Line broadening and line widths; simple properties of Gaussian and Lorentzian line shapes. Molecular spectroscopy: Absorbance, Beer- Lambert's law, Einstein's coefficient, Jablonski diagram. Relationship of transition moment integral with molar extinction coefficient and oscillator strength. Basic principles of Nuclear Magnetic Resonance: Gyromagnetic ratio; Chemical shift, nuclear coupling.

Equilibrium: Laws of thermodynamics. Standard states. Thermochemistry. Thermodynamic functions and their relationships: Gibbs-Helmholtz and Maxwell relations, Gibbs-Duhem equation, Van't Hoff equation. Criteria of spontaneity and equilibrium. Absolute entropy. Partial molar quantities. Thermodynamics of mixing. Chemical potential. Fugacity, Activity and Activity coefficient. Chemical equilibria. Dependence of equilibrium constant on temperature and pressure.

Solutions: Ideal and non-ideal solutions, Raoult's Law and Henry's Law.

Electrochemistry: Standard electrode potential and electrochemical cells. Nernst Equation and its application, relationship between electrode potential and thermodynamic quantities, Potentiometric and conductometric titrations. Ionic mobility and conductivity. Kohlrausch's law, Debye-Hückel limiting law. Debye-Hückel-Onsager equation.

Phase Equilibria: Phase rule. Clausius- Clapeyron equation. Phase diagram of one component system: CO_2, H_2O, S; two component systems: liquid-vapor, liquid-liquid and solid-liquid systems. Fractional distillation.

Azeotropes and Eutectics.

Statistical Thermodynamics: Micro-canonical, Canonical and Grand canonical ensembles, Boltzmann distribution, Partition functions and thermodynamic properties. Statistical mechanics of non-interacting systems, ideal monoatomic, diatomic gases, translational, rotational, vibrational and electronic partition functions.

Kinetics and Reaction Dynamics: Elementary, parallel, opposing, and consecutive reactions. Steady state approximation. Mechanism of complex reactions. Unimolecular reactions. Potential energy surface and classical trajectories, Concept of saddle points, Transition state theory: Eyring equation, thermodynamic aspects. Kinetics of polymerization. Catalysis concepts and enzyme catalysis. Kinetic isotope effects. Fast reaction kinetics: relaxation and flow methods. Diffusion controlled reactions. Kinetics of unimolecular and bimolecular photophysical processes, Quantum yield calculation, static and dynamic quenching.

Surfaces and Interfaces: Physisorption and chemisorption. Langmuir, Freundlich and Brunauer-Emmett-Teller (BET) isotherms. Surface catalysis: Langmuir-Hinshelwood mechanism. Surface tension, viscosity, Self-assembly/ physical chemistry of colloids, micelles and macromolecules.

Section 2: Inorganic Chemistry

Main Group Elements: Shapes and structures of molecules using VSEPR postulates, Hydrides, halides, oxides, oxoacids, nitrides, sulfides - shapes and reactivity. Structure and bonding of boranes, carboranes, silicones, silicates, boron nitride, borazine and phosphazenes: electron counting in polyhedral boranes, isolobal analogy. Allotropes of carbon, phosphorus and sulfur. Industrial synthesis of compounds of main group elements such as NH_3, H_2SO_4 and HNO_3. Chemistry of noble gases and interhalogen compounds. Acid-base concepts and principles (Lewis, Brønsted, HSAB and acid-base catalysis).

Transition Metals: Coordination chemistry – structure and isomerism, theories of bonding (VBT, CFT, and MOT). Metal-metal multiple bonds. Energy level diagrams in various crystal fields, CFSE, applications of CFT, Jahn-Teller distortion. Electronic spectra of transition metal complexes: spectroscopic term symbols, selection rules, Orgel and Tanabe-Sugano diagrams, nephelauxetic effect and Racah parameter, charge-transfer spectra. Magnetic properties of transition metal complexes. Ray-Dutt and Bailar twists, Reaction mechanisms: kinetic and thermodynamic stability, associative, dissociative substitution and redox reactions.

Lanthanides and Actinides: Recovery. Periodic properties, spectral and magnetic properties.

Organometallics: 18-Electron rule; metal-alkyl, metal-carbonyl, metal-olefin and metal-carbene complexes and metallocenes. Fluxionality in organometallic complexes. Types of organometallic reactions. Homogeneous catalysis – Hydrogenation, hydroformylation, methanol to acetic acid process, olefin metathesis and Wacker oxidation. Heterogeneous catalysis – Fischer-Tropsch reaction, Ziegler-Natta polymerization.

Bioinorganic Chemistry: Ion (Na^+ and K^+) transport, oxygen binding, transport and utilization, electron transfer reactions, nitrogen fixation, metalloenzymes containing magnesium, molybdenum, iron, cobalt, copper and zinc.

Solids: Crystal systems and lattices, Miller planes, crystal packing, crystal defects, Bragg's law, ionic crystals, structure of AX, AX_2, ABX_3 type compounds, spinels, band theory, metals and semiconductors, Zeolites and their applications.

Instrumental Methods of Analysis: UV-visible, fluorescence and FT-IR spectrophotometry, NMR and ESR spectroscopy, mass spectrometry, atomic absorption spectroscopy, Mössbauer spectroscopy (Fe and Sn) and X-ray crystallography. Electroanalytical methods – cyclic voltammetry, ion-selective electrodes. Thermo-analytical methods: TGA, DTA and DSC.

Section 3: Organic Chemistry

General Concepts: Structure dependence on properties such as basicity and acidity. Role of aromatic stability on physical properties of organic compounds.

Stereochemistry: Chirality and symmetry of organic molecules with or without chiral centres and determination of their absolute configurations and optical purity. Relative stereochemistry in compounds having more than one stereogenic centre. Homotopic, enantiotopic and diastereotopic atoms, groups and faces. Conformational analysis of acyclic and cyclic compounds. Geometrical isomerism and optical isomerism. Configurational and conformational effects, atropisomerism, and neighbouring group participation on reactivity and selectivity/specificity. Stereoselective and stereospecific synthesis. Enantiomeric excess.

Reaction Mechanisms: Basic mechanistic concepts and energy profile diagrams - kinetics versus thermodynamic control, Hammond's postulate and Curtin-Hammett principle. Methods of determining reaction mechanisms through kinetics, identification of products, intermediates and isotopic labelling. Solvent effects in substitution and elimination reactions. Linear free-energy relationship – Hammett and Taft equations.

Types of Reactions: Nucleophilic and electrophilic substitution reactions (both aromatic and aliphatic). Addition reactions to carbon-carbon and carbon-heteroatom (N and O) multiple bonds. Elimination reactions. Reactive intermediates – carbocation, carbanion, carbenes, nitrenes, arynes and free radicals. Molecular rearrangements. Barton decarboxylation and Barton-McCombie reaction, Hunsdiecker reaction.

Organic Synthesis: Synthesis, reactions, mechanisms and selectivity involving the following classes of compounds – alkenes, alkynes, arenes, alcohols, phenols, aldehydes, ketones, carboxylic acids, esters, nitriles, halides, nitro compounds, amines and amides. Uses of Mg, Li, Cu, B, Zn, P, S, Sn and Si based reagents in organic synthesis. Carbon-carbon bond formation through coupling reactions – Heck, Suzuki, Stille, Sonogashira, Negishi, Kumada, Hiyama, Tsuji-Trost reactions; olefin metathesis, McMurry coupling and Buchwald-Hartwig amination reactions. Baylis-Hillman, Henry, Ritter, Sakurai, Tebbe olefination, Pauson-Khand and Nazarov cyclization reactions. Concepts of multistep synthesis – retrosynthetic analysis, strategic disconnections, synthons and synthetic equivalents. Atom economy and green chemistry, Umpolung reactivity – formyl and acyl anion equivalents. Selectivity in organic synthesis – chemo-, regio- and stereoselectivity. Protection and deprotection of functional groups. Concepts of asymmetric synthesis – resolution (including enzymatic), desymmetrization and use of chiral auxiliaries, organocatalysis. Carbon-carbon and carbonheteroatom bond forming reactions through enolates (including boron enolates), enamines and silyl enol ethers. Stereoselective addition to C=O groups (Cram, Prelog and Felkin-Anh models). Asymmetric aldol reactions – Evans reaction and proline catalyzed reaction.

Oxidation: Oxidation of alcohols involving metal and non-metal-based (chromium, manganese, DMSO, and hypervalent iodine) reagents. Peracid oxidation of alkenes and carbonyls. Alkenes to diols (manganese and osmium-based reagents), alkenes to carbonyls with bond cleavage (ozonolysis), and alkenes to alcohols/carbonyls without bond cleavage (hydroboration-oxidation). Asymmetric epoxidations (Sharpless and Jacobsen) and Sharpless asymmetric hydroxylation.

Reduction: Catalytic homogeneous and heterogeneous hydrogenation. Metal based reductions using Li/Na in liquid ammonia, magnesium, zinc, titanium, and samarium. Hydride transfer reagents: $NaBH_4$, L-selectride, K-selectride, Luche reduction, $LiAlH_4$ and DIBAL-H.

Pericyclic Reactions and Photochemistry: Electrocyclic, cycloaddition and sigmatropic reactions. Diels-Alder reaction, Claisen and Cope rearrangements and their applications in organic synthesis. FMO method of analysis. Woodward-Hoffmann rules. Photochemistry of alkenes, arenes and carbonyl compounds. Photo-oxidation and photo-reduction. Di-π-methane rearrangements, Norrish type-I and II reactions. Paternó-Büchi reaction, Photo-Curtius and Wolff rearrangements. Barton and Hofmann-Löffler-Freytag reactions.

Heterocyclic Compounds: Nomenclature of mono- and bicyclic, as well as mono- and di-heteroatomic compounds, Structure, preparation, properties and reactions of furan, pyrrole, thiophene, pyridine, indole, quinoline and isoquinoline.

Biomolecules: Structure, properties and reactions of mono- and di-saccharides, physicochemical properties of amino acids, chemical synthesis of peptides, chemical structure determination of peptides and proteins, structural features of proteins, nucleic acids, lipids, steroids, terpenoids, carotenoids, and alkaloids.

Experimental Techniques in Organic Chemistry: Optical rotation (polarimetry). Application of various chromatographic techniques such as thin-layer, column, HPLC and GC. Applications of UV-visible, IR, NMR spectroscopy and Mass spectrometry in the structural determination of organic molecules.