

CHEMISTRY(CY)

SYLLABUS FOR GENERAL APTITUDE (GA)

Verbal Ability: English grammar, sentence completion, verbal analogies, word groups, instructions, critical reasoning and verbal deduction.

Numerical Ability: Numerical computation, numerical estimation, numerical reasoning and data interpretation.

Section 1: Physical Chemistry

Structure:

Postulates of quantum mechanics. Time dependent and time independent Schrödinger equations. Born interpretation. Particle in a box. Harmonic oscillator. Rigid rotor. Hydrogen atom: atomic orbitals. Multi-electron atoms: orbital approximation. Variation and first order perturbation techniques. Chemical bonding: Valence bond theory and LCAO-MO theory. Hybrid orbitals. Applications of LCAO-MOT to H_2^+ , H_2 and other homonuclear diatomic molecules, heteronuclear diatomic molecules like HF, CO, NO, and to simple delocalized π -electron systems. Hückel approximation and its application to annular π -electron systems. Symmetry elements and operations. Point groups and character tables. Origin of selection rules for rotational, vibrational, electronic and Raman spectroscopy of diatomic and polyatomic molecules. Einstein coefficients. Relationship of transition moment integral with molar extinction coefficient and oscillator strength. Basic principles of nuclear magnetic resonance: nuclear g factor, chemical shift, nuclear coupling.

Equilibrium:

Laws of thermodynamics. Standard states. Thermochemistry. Thermodynamic functions and their relationships: Gibbs-Helmholtz and Maxwell relations, van't Hoff equation. Criteria of spontaneity and equilibrium. Absolute entropy. Partial molar quantities. Thermodynamics of mixing. Chemical potential. Fugacity, activity and activity coefficients. Chemical equilibria. Dependence of equilibrium constant on temperature and pressure. Non-ideal solutions. Ionic mobility and conductivity. Debye-Hückel limiting law. Debye-Hückel-Onsager

equation. Standard electrode potentials and electrochemical cells. Potentiometric and conductometric titrations. Phase rule. Clausius-Clapeyron equation. Phase diagram of one component systems: CO₂, H₂O, S; two component systems: liquid-vapour, liquid-liquid and solid-liquid systems. Fractional distillation. Azeotropes and eutectics. Statistical thermodynamics: microcanonical and canonical ensembles, Boltzmann distribution, partition functions and thermodynamic properties.

Kinetics:

Transition state theory: Eyring equation, thermodynamic aspects. Potential energy surfaces and classical trajectories. Elementary, parallel, opposing and consecutive reactions. Steady state approximation. Mechanisms of complex reactions. Unimolecular reactions. Kinetics of polymerization and enzyme catalysis. Fast reaction kinetics: relaxation and flow methods. Kinetics of photochemical and photophysical processes.

Surfaces and Interfaces:

Physisorption and chemisorption. Langmuir, Freundlich and 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:

Hydrides, halides, oxides, oxoacids, nitrides, sulfides – shapes and reactivity. Structure and bonding of boranes, carboranes, silicones, silicates, boron nitride, borazines and phosphazenes. Allotropes of carbon. Chemistry of noble gases, pseudohalogens, and interhalogen compounds. Acid-base concepts.

Transition Elements:

Coordination chemistry – structure and isomerism, theories of bonding (VBT, CFT, and MOT). 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 diagrams,

charge-transfer spectra. Magnetic properties of transition metal complexes. Reaction mechanisms: kinetic and thermodynamic stability, substitution and redox reactions.

Lanthanides and Actinides:

Recovery. Periodic properties, spectra and magnetic properties.

Organometallics:

18-Electron rule; metal-alkyl, metal-carbonyl, metal-olefin and metallocenes. Fluxionality in organometallic complexes. Types of organometallic reactions. Homogeneous catalysis - Hydrogenation, hydroformylation, acetic acid synthesis, metathesis and olefin oxidation. Heterogeneous catalysis - Fischer-Tropsch reaction, Ziegler-Natta polymerization.

Radioactivity:

Decay processes, half-life of radioactive elements, fission and fusion processes.

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, structures of AX , AX_2 , ABX_3 type compounds, spinels, band theory, metals and semiconductors.

Instrumental Methods of Analysis:

UV-visible spectrophotometry, NMR and ESR spectroscopy, mass spectrometry. Chromatography including GC and HPLC. Electroanalytical methods- polarography, cyclic voltammetry, ion-selective electrodes. Thermoanalytical methods.

Section 3: Organic Chemistry

Stereochemistry:

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

Reaction Mechanisms:

Basic mechanistic concepts – kinetic versus thermodynamic control, Hammond's postulate and Curtin-Hammett principle. Methods of determining reaction mechanisms through identification of products, intermediates and isotopic labeling. Nucleophilic and electrophilic substitution reactions (both aromatic and aliphatic). Addition reactions to carbon-carbon and carbon-heteroatom (N,O) multiple bonds. Elimination reactions. Reactive intermediates – carbocations, carbanions, carbenes, nitrenes, arynes and free radicals. Molecular rearrangements involving electron deficient atoms.

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 and Si based reagents in organic synthesis. Carbon-carbon bond formation through coupling reactions - Heck, Suzuki, Stille and Sonogoshira. Concepts of multistep synthesis - retrosynthetic analysis, strategic disconnections, synthons and synthetic equivalents. 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. Carbon-carbon bond forming reactions through enolates (including boron enolates), enamines and silyl enol ethers. Michael addition reaction. Stereoselective addition to C=O groups (Cram and Felkin-Anh models).

Pericyclic Reactions and Photochemistry: Electrocyclic, cycloaddition and sigmatropic reactions. Orbital correlations - FMO and PMO treatments. Photochemistry of alkenes, arenes and carbonyl compounds. Photooxidation and photoreduction. Di- π -methane rearrangement, Barton reaction.

Heterocyclic 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, structural features of proteins, nucleic acids, steroids, terpenoids, carotenoids, and alkaloids.

Spectroscopy:

Applications of UV-visible, IR, NMR and Mass spectrometry in the structural determination of organic molecules.