23. CHEMISTRY - (The examination for this Subject will be held at Chennai only)

PHYSICAL CHEMISTRY

Chemical Thermodynamics: Concepts of temperature (zeroth law), Exact and Inexact differentials, First law of thermodynamics, Reversible and irreversible processes, concept of entropy, Clausius inequality, entropy change accompanying specific processes, Free energy and criteria for spontaneity. Fundamental equations of Thermodynamics, Gibbs Helmholtz equation, Maxwell's relations, Chemical potential, partial molar properties, Gibbs-Duhem equation, van't Hoff equation. Chemical and Phase equilibria: Chemical equilibrium, interrelations between Kp, Kc and Kx, the effect of temperature and pressure on equilibrium constant, Le Chatelier's principle, Raoult's law: Ideal and non-ideal solutions, Gibbs phase rule, Clausius-Clapeyron equation, one component phase diagram of water. Two-component phase diagrams- vapour pressure diagrams, temperature- composition diagrams, Liquid-liquid solutions, liquid-solid solutions, Activity and activity coefficients, colligative properties. Concepts on Thermo and Electro Chemistry: Activity of electrolytes, Ionic mobility and conductivity, Kohlrausch law, Debye-Hückel limiting law. DebyeHückel-Onsager equation. Standard electrode potentials and electrochemical cells. EMF and Nernst Equation, relationship between Electrode potential and thermodynamic quantities, Basic process at electrode and electrode-electrolyte interface. Concepts of quantum chemistry and spectroscopy: Black-body radiation, photoelectric and Compton effects, line spectra of atoms, Bohr model of the hydrogen atom, Young's double slit experiment, and Wave-particle duality. Time-dependent and time-independent Schrödinger equations (TISE), Hamiltonian, Operators, eigenvalues and eigen functions, commutation relations, Heisenberg uncertainty principle. Angular momentum (orbital & spin), commutation relations. Rotational Spectroscopy: Rigid rotor energy level, pure rotational spectra of diatomic rigid rotors – rotational transitions, intensities & selection rules. Vibrational Spectroscopy (IR and Raman): Harmonic and anharmonic oscillators, vibration of diatomic molecules, vibrational-rotational couplings in diatomic molecules. Raman scattering, vibrational Raman lines & selection rules, vibrational Raman spectra of diatomic molecules. Concepts of photochemistry: Definition of photochemical reactions, comparative study of thermal and photochemical reactions. Laws of photochemistry: Lambert and Beer law. Grotthus–Draper law, Stark – Einstein law, Photophysical process: fluorescence, phosphorescence and other deactivating processes. Jablonski diagram. Photosensitization: chemiluminescence, bioluminescence.

INORGANIC CHEMISTRY

Main Group Elements: Hydrides, halides, oxides, oxoacids, nitrides, sulfides – properties, shapes and reactivity. Structure and bonding of boranes, carboranes, silicones, silicates, boron nitride, borazines and phosphazenes. Chemical properties of the noble gases with emphasis on their low chemical reactivity, chemistry of xenon, structure and bonding of fluorides, oxides & oxyfluorides of xenon. Acid-base concepts and principles (Lewis, Bronsted, HSAB and acid-base catalysis). Transition Elements: Coordination chemistry – structure, nomenclature and isomerism, theories of bonding (VBT, CFT, and MOT). Energy level diagrams in various crystal fields, CFSE, applications of CFT, Jahn-Teller distortion and EAN rule applied to metal carbonyls. Various types of hybridization and shapes of

simple inorganic molecules and ions. Electronic spectra of transition metal complexes: spectroscopic term symbols, selection rules, Orgel and Tanabe-Sugano diagrams, nephelauxetic effect and Racah parameter, charge-transfer spectra. Lanthanides and Actinides: Recovery. Periodic properties, spectra and magnetic properties. Organometallics: 18-Electron rule; metal-alkyl, metal-carbonyl, metal-olefin and metal- carbene complexes and metallocenes. Preparation & properties of transition complexes. Types of organometallic reactions. Homogeneous catalysis – Hydrogenation, hydroformylation, acetic acid synthesis, metathesis, olefin oxidation and cross coupling reactions. Heterogeneous catalysis – Fischer- Tropsch reaction, Ziegler-Natta polymerization. Radioactivity: Detection of radioactivity, Decay processes, half-life of radioactive elements, fission and fusion processes. Solids: Crystal systems and lattices, Miller planes, crystal packing, crystal defects, Bragg's law, ionic crystals, structures of AX, AX2, ABX 3 type compounds, spinels, band theory, metals and semiconductors. Biological role of alkali and alkaline earth metal ions. Nuclear Chemistry: Mass defect and binding energy, nuclear reactions, fission and fusion, nuclear reactor and breeder reactors, radiodating. Solid State chemistry and defects. Errors in chemical analysis: Terms and definitions - systematic errors. Random errors – statistical treatments - standard deviation of calculated results and reporting computed data. Separation techniques: Solvent extraction, chromatography - thin layer chromatography, ion exchange chromatography, HPLC, Gas chromatography.

ORGANIC CHEMISTRY

Concept of isomerism. Types of isomerism. Optical isomerism - elements of symmetry, molecular chirality, enantiomers, stereogenic centre, optical activity, properties of enantiomers, chiral and achiral molecules with two stereogenic centres, diastereomers, threo and erythro diastereomers, mesocompounds, resolution of enantiomers, inversion, retention and racemization. Relative and absolute configuration, sequence rules, R & S systems of nomenclature. Geometric isomerism – determination of configuration of geometric isomers. E & Z system of nomenclature. Conformational isomerism - conformational analysis of ethane and n-butane, conformations of cyclohexane, axial and equatorial bonds. Newman projection and Sawhorse formula. Difference between configuration and conformation. Stereoselective and stereospecific synthesis. Aromaticity: the Huckel rule, aromatic ions, annulenes up to 10 carbon atoms, aromatic, antiaromatic and non-aromatic compounds. Activating, deactivating substituents and orientation. Reaction Mechanisms: Nucleophilic and electrophilic substitution reactions (both aromatic and aliphatic). Types of reagents electrophiles and nucleophilcs. Reactive intermediates - carbocations, carbanions, free radicals, carbenes (formation, structure & stability). Addition reactions to carbon-carbon and carbon-heteroatom (N and O) multiple bonds. Elimination reactions. Chemical reactions of alkenes - mechanisms involved in hydrogenation, electrophilic and free radical additions, Markownikoffs rule, hydroboration, oxidation, oxymercuration reduction, ozonolysis, hydration, and hydroxylation. Chemical reactions of alkynes, acidity of alkynes. Molecular rearrangements: Pinacol-Pinacolane, Cannizzaro, Wager–Meerwein, Fries, Claisen, Cope, Beckman, Hofmann, Curtius, Schotten-Baumann, Gattermann-Koch and Benzil-Benzilic acid rearrangements. Oxidation and Reduction: Mn & Cr reagents; Per-acid; $LiAlH_4$, $NaBH_4$. H_2/Pd-C Catalyst; Clemmensen, Wolf-Kishner & Rosenmund reduction. Application of UV, IR, NMR and Mass for structure determination (up to C10). Pericyclic Reactions and

Photochemistry: Electrocyclic, cycloaddition and sigmatropic reactions. Orbital correlations – FMO and PMO treatments, Woodward-Hoffmann rule. Photochemistry of alkenes, arenes and carbonyl compounds. Photooxidation and photoreduction. Di-π-methane rearrangement, Barton McCombie reaction, Norrish type-I and II cleavage reaction. Heterocyclic Compounds: Structure, preparation, properties and reactions of furan, pyrrole, thiophene, pyridine, indole, quinoline and isoquinoline. Carbohydrate Chemistry. Natural products: Terpenes and alkaloids.