



NATIONAL INSTITUTE OF TECHNOLOGY TIRUCHIRAPPALLI - 620015

DEPARTMENT OF CHEMISTRY SYLLABUS FOR WRITTEN TEST

Structure

Postulates of quantum mechanics. Operators. Time dependent and time independent Schrödinger equations. Born interpretation. Dirac bra-ket notation. Particle in a box: infinite and finite square wells; concept of tunnelling; particle in 1D, 2D and 3D-box; applications. Harmonic oscillator: harmonic and anharmonic potentials; Hermite polynomials. Rotational motion: Angular momentum operators, Rigid rotor. Hydrogen and hydrogen-like atoms: atomic orbitals; radial distribution function. Multi-electron atoms: orbital approximation; electron spin; Pauli exclusion principle; Slater determinants. Approximation Methods: Variation method and secular determinants; first order perturbation techniques. Atomic units. Molecular structure and Chemical bonding: Born-Oppenheimer approximation; Valence bond theory and linear combination of atomic orbitals – molecular orbital (LCAO-MO) theory. Hybrid orbitals. Applications of LCAO-MO theory to H_2^+ , H_2 ; orbital theory (MOT) of homo- and heteronuclear diatomic molecules. Hückel approximation and its application to annular π – electron systems.

Spectroscopy

Atomic spectroscopy; Russell-Saunders coupling; Term symbols and spectral details; origin of selection rules. Rotational, vibrational, electronic and Raman spectroscopy of diatomic and polyatomic molecules. Line broadening. Einstein's coefficients. Relationship of transition moment integral with molar extinction coefficient and oscillator strength. Zeeman Effect - Frank Condon principle- Vibronic transitions- selection rules- polarization of transitions- Transition dipole moment and Fermi's Golden Rule- Instrumentation and sampling - Fluorescence Spectroscopy – Jablonski Diagram- Kasha's rules- Quenching. Basic principles of nuclear magnetic resonance: gyromagnetic ratio; chemical shift, nuclear coupling.

Kinetics

Elementary, parallel, opposing and consecutive reactions. Steady state approximation. Mechanisms of complex reactions. Unimolecular reactions. Potential energy surfaces 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 photochemical and photo physical processes. Basic principles of electron spectroscopy, classification - electron energy analysis-photon sources - UV, X-ray, synchrotron, theory, angular dependence-cross section and its determination-valence and core photoemission - Koopmans' theorem.

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.

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 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, substitution and redox reactions. Metal-metal multiple bond.

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. 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. C-C Heck & Suzuki coupling reactions, Olefin Metathesis – ADMET- metathesis polymerization – Hartwig-Buchwald amination

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, AX₂, ABX₃ type compounds, spinels, band theory, metals and semiconductors.

Instrumental Methods of Analysis

UV-visible, fluorescence and FTIR spectrophotometry, NMR and ESR spectroscopy, mass spectrometry, atomic absorption spectroscopy, Mössbauer spectroscopy (Fe and Sn) and X-ray crystallography. Chromatography including GC and HPLC. Electroanalytical methods- polarography, cyclic voltammetry, ion-selective electrodes. Thermoanalytical methods.

Stereochemistry

Chirality and symmetry 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 and optical isomerism. Configurational and conformational effects, atropisomerism, 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 kinetics, identification of products, intermediates and isotopic labelling. Linear free-energy relationship – Hammett and Taft equations. 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 — carbocations, carbanions, carbenes, nitrenes, arynes and free radicals. Molecular rearrangements.

Mössbauer spectroscopy

Gamma ray emission – recoil – recoilless resonance absorption – Debye model – Instrumentation and techniques- hyperfine interaction - Isomer shift – quadrupolar splitting - magnetic interactions –impact of Zeeman effect - applications to iron and tin compounds – Fe-S proteins -

Mass spectroscopy

Methods of desorption and ionization (EI, CI, ESI, MALDI, FAB, TOF), instrumentation, magnetic sector analysis, quadrupole analyser, ion cyclotron resonance (FT), meta stable ions, study of fragmentation pattern, bond cleavage, McLafferty rearrangement, retro Alder fragmentation, applications in organic chemistry, isotope distribution analysis.

Experimental Techniques in Organic Chemistry

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