GROUP - (B) ELECTIVE PAPER
PAPER VI. PHYSICAL ORGANIC CHEMISTRY

M.M. - 75 | 60 Hrs. (2 Hrs./Week)

Units	Topics
I	**Concepts in Molecular Orbital (MO) and Valence Bond (VB) Theory** — **10 Hrs.** Introduction to Huckel Molecular Orbital (HMO) method as a means to explain modern thecretical methods. Advanced techniques in PMO and FMO theory. Molecular mechanics, semi empirical methods and ab inito and density functional methods. Scope and limitations of several computational programmes. Quantitative MO theory - Huckel Molecular Orbital (HMO) method as applied to ethene, allyl and butadiene. Qualitative MO theory-ionisation potential. Electron affinities. MO energy levels. Orbital symmetry. Orbital interaction diagrams. MO of simple organic systems such as ethene, allyl, butadiene, methane and methyl group. Conjugation and hyperconjugation. Aromaticity. Valence Bond (VB) configuration mixing diagrams. Relationship between VB configuration mixing and resonance theory. Reaction profiles. Potential energy diagrams. Curvecrossing model-nature of activation barrier in chemical reactions.
II	**Principles of Reactivity** — **5 Hrs.** Mechanistic significance of entropy, enthalpy and Gibb's free energy. Arrhenius equation. Transition state theory. Uses of activation parameters, Hammond's postulate. Bell-Evans-Polanyi principle. Potential energy surface model. Marcus theory of electron transfer. Reactivity and selectivity principles. **Kinetic Isotope Effect** — **4 Hrs.** Theory of isotope effects. Primary and secondary kinetic isotope effects. Heavy atom isotope effects. Tunneling effect. Solvent effects. **Structural Effects on Reactivity** — **6 Hrs.** Linear Free Energy Relationships (LFER). The Hammett equation, substituent constants, theories of substituent effects. Interpretation of σ-values. Reaction constant ρ. Deviations from Hammett equation. Dual-parameter correlations, inductive substituent constant. The Taft model, σ_1,- and σ_R - scales.
III	**Solvation and Solvent Effects** — **6 Hrs.** Qualitative understanding of solvent-solute effects on reactivity. Thermodynamic measure of solvation. Effects of solvation on reaction rates and equilibria. Various empirical indexes of solvation based on physical properties, solvent-sensitive reaction rates, spectroscopic properties and scales for specific solvation. Use of solvation scales in mechanistic studies. Solvent effects from the curve-crossing model. **Acids, Bases, Electrophiles, Nucleophiles and Catalysis** — **6 Hrs.** Acid-base dissociation. Electronic and structural effects, acidity and basicity. Acidity functions and their applications. Hard and soft acids and bases. Nucleophilicity scales. Nucleofugacity. The α-effect. Ambivalent nucleophiles. Acid-base catalysis - specific and general catalysis. Bronsted catalysis. Nucleophilic and electrophilic catalysis. Catalysis by non-covalent binding-micellar catalysis. **Steric and Conformational Properties** — **6 Hrs.** Various type of steric strain and their influence on reactivity. Steric acceleration. Molecular measurements of steric effects upon rates. Steric LFER. Confiromational barrier to bond rotation-spectroscopic detection of individual conformers. Acyclic and monocyclic systems. Rotation around partial double bonds. Winstein - Holness and Curtin-Hammett Principle.

IV	**Nucleophilic and Electrophilic Reactivity**	**6 Hrs.**
	Structural and electronic effects on S_N1 and S_N2 reactivity. Solvent effects. Kinetic isotope effects. Intramolecular assistance. Electron transfer nature of S_N2 reaction. Nucleophilicity and S_N2 reactivity based on curve-crossing model. Relationship between polar and electron transfer reactions. $S_{RN}1$ mechanism. Electrophilic reactivity, general mechanism. Kinetic of S_E2-Ar reaction. Structural effects on rates and selectivity. Curve-crossing approach to electrophilic reactivity.	
	Radical and Pericyclic Reactivity	**6 Hrs.**
	Radical stability, polar influences, solvent and steric effects. A curve crossing approach to radical addition, factors effecting barrier heights in additions, regioselectivity in radical reactions.	
	Reactivity, specificity and perselectivity in pericyclic reactions.	
V	**Supra molecular Chemistry**	**5 Hrs.**
	Properties of convalent bonds - bond length, inter-bond angles, force constant, bond and molecular dipole moments. Molecular and bond polarizability, bond dissociation enthalpy, entropy. Intermolecular forces, hydrophobic effects. Electrostatic, induction, dispersion and resonance energy. Magnetic interactions, magnitude of interaction energy, forces between macroscopic bodies, medium effects. Hydrogen bond.	
	Principles of molecular association and organization as exemplified in biological macromolecules like enzymes, nucleic acids, membranes and model systems like micelles and vesicles. Molecular receptors and design principles. Crytands, cyclophanes, calixeranes, cyclodextrines. Supramolecular reactivity and catalysis. Molecular channels and transport processes. Molecular devices and nanotechnology.	