MC-03
PHYSICAL CHEMISTRY

(Question will be set from each unit/section with internal choice)

Marks - 100 **120 Hrs. (4Hrs/Week)**

Units	Topics
I	**Quantum Chemistry** **30 Hrs.**
	A. **Introduction to Exact Quantum mechanical Results:** The Schrodinger equation and the postulates of quantum mechanics. Discussion of solutions of the Schrodinger equation to some model systems viz. particle in a box, the harmonic oscillator, the rigid rotor, the hydrogen atom.
	B. **Approximate Methods**: The variation theorem, linear variation principle. Perturbation theory (first order and non-degenerate). Applications of variation method and perturbation theory to the Helium atom.
	C. **Angular Momentum:** Ordinary angular momentum, generalized angular momentum, eigen functions for angular momentum, eigenvalues of angular momentum, operator using ladder operators, addition of angular momenta, spin, antisymmetry and Pauli exclusion principle.
	D. **Electronic Structure of Atoms:** Electronic configuration, Russell-Saunders terms and copuling schemes, Slater-Condon parameters, term separation energies of the p^n configuration, term separation energies for the d^n configurations, magnetic effects: spin-orbit coupling and Zeeman splitting, introduction to the methods of self-consistent field the virial theorem.
	E. **Molecular Orbital Theory:** Huckel theory of conjugated systems, bond order and charge density calculations. Applications to ethylene, butadiene, cyclopropenyl radical, cyclobutadiene etc. Introduction to extended Huckel theory.
II	**Thermodynamics :** **30 Hrs.**
	A. Classical Thermodynamics: Brief resume of concepts of laws of thermodynamics, free energy, chemical potential and entropies. Partial molar properties; partial molar free energy, partial molar volume and partial molar heat content and their significance. Determinations of these quantities. Concept of fugacity and determination of fugacity.
	Non-ideal systems: Excess function for non-ideal solution. Activity coefficient debye-Huckel theory for activity coefficient of electrolytic solutions; determination of activity and activity coefficients; ionic strength.
	Application of phase rule to three component systems; second order phase transitions.
	B. **Statistical Thermodynamics:** Concept of distribution, thermodynamic probability and most probable distribution. Ensemble averaging, postulates of ensemble averaging. Canonical, grand canonical and microcanonical ensembles, corresponding distribution laws (using lagranges' method of undetermined multipliers).
	Partition functions - translational, rotational, vibrational and electronic partition functions. Calculation of thermodynamic properties in terms of partition functions. Application of partition functions.
	Heat capacity behaviour of solids - chemical equilibria and equilibrium constant in terms of partition functions, Fermi-Dirac statistics, distribution law and applications to metal. Bose-Einstein statistics distribution law and application to helium.

C. **Non Equilibrium Thermodynamics:** Thermodynamic criteria for non-equilibrium states, entropy production and entropy flow, entropy balance equations for different irreversible process (e.g., heat flow, chemical reaction etc.) transformation of the generalized fluexe and forces, non equilibrium stationary states, phenomenological equations, microscopic reversibility and Onsager's reciprocity relations, electrokinetic phenomena, diffusion, electric conduction, irreversible thermodynamics for biological systems, coupled reactions.

III **Chemical Dynamics** **20 Hrs.**

Methods of determining rate laws, collision theory of reaction rates, steric factor, activated complex theory, Arrhenius equation and the activated complex theory; ionic reactions, kinetic salt effects, steady state kinetics, kinetic and thermodynamic control of reactions, treatment of unimolecular reactions.

Dynamic chain (hydrogen-bromine reaction, pyrolysis of acetaldehyde, decomposition of ethane) photochemical (hydrogen-bromine and hydrogen-chlorine reactions) and oscillatory reactions (Belousov - Zhabotinsky reactions), Homogeneous catalysis, kinetics of enzyme reactions, general features of fast reactions, study of fast reactions by flow method, relaxation method, flash photolysis and the nuclear magnetic resonance method.

Dynamics of molecular motions, probing the transition state, dynamics of barrierless chemical reactions in solution, dynamics of unimolecular reactions (Lindemann - Hinshelwood and Rice-Ramsperger - Kassel - Marcus (RRKM) theories of unimolecular reactions).

IV **Surface Chemistry**

A. **Adosorption:** Surface tension, capillary action, pressure differences across curved surface (Laplace equation), vapour pressure of droplets (Kelvin equation), Gibbs adsorption isotherm, estimation of surface area (BET equation), surface films on liquids (Electro-kinetic phenomenon), catalytic activity at surfaces.

B. **Micelles:** Surface active agents, classification of surface active agents, micellization, hydrophobic interaction, critical micellar concentration (CMC), factors affecting the CMC of surfactants, counter ion binding to micelles, thermodynamics of micellization - phase separation and mass action models, solubilization, micro emulsion, reverse micelles.

C. **Macromolecules:** Polymer - definition, types of polymers, electrically conducting, fire resistant, liquid crystal polymers, kinetics of polymerization, mechanism of polymerization.

Molecular mass, number and mass average molecular mass, molecular mass determination (osmometry, viscometry, diffusion and light scattering methods), sedimentation, chain configuration of macromolecules, calculation of average dimensions of various chain structures.

V **Electrochemistry** **20 Hrs.**

Electrochemistry of solutions. Debye-Huckel - Onsager treatment and its extension, ion solvent interactions. Debye-Huckel-Jerum mode. Thermodynamics of electrified interface equations. Derivation of electro-capillarity, Lippmann equations (surface excess), methods of determination. Structure of electrified interfaces. Guoy - Chapman, Strern, Graham - Devanathan - Mottwatts, Tobin, Bockris, Devanathan models.

Over potentials, exchange current density, derivation of Butler - Volmer equation, Tafel plot.

Quantum aspects of charge transfer at electrodes-solution interfaces, quantization of charge transfer, tunneling.

Semiconductor interfaces - theory of double layer at semiconductor, electrolyte solution interfaces, structure of double layer interfaces. Effect of light at semiconductor solution interface.

Electrocatalysis - influence of various parameters. Hydrogen electrode.

Bioelectrochemistry, threshold membrane phenomena, Nernst-Planck equation, Hodges - Huxley equations, core conductor models, electrocardiography.

Palarography theory, Ilkovic equation; half wave potential and its significance.

Introduction to corrosion, homogenous theory, forms of, corrosion, corrosion monitoring and prevention methods.