Paper-III CHN-403 Physical Chemistry

Unit I : Quantum Chemistry 15 Hrs

Introduction to Exact Quantum Mechanical Results

The Schrödinger equation and the postulates of quantum mechanics. Discussion of solutions of the Schrödinger equation to some model systems viz., particle in a box, the harmonic oscillator, the rigid rotor, the hydrogen atom.

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.

Unit II Quantum Chemistry

Angular Momentum

Ordinary angular momentum, generalized angular momentum, eigenfunctions for angular momentum, eigenvalues of angular momentum, operator using ladder operators, addition of angular momenta, spin, antisymmetry and Pauli exclusion principle.

Electronic Structure of Atoms and Molecular Orbital Theory

Electronic configuration, Russell-Saunders terms and coupling 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. Huckel theory of conjugated systems, Applications to ethylene, butadiene. Introduction to extended Huckel theory.

Unit III Thermodynamics – I 11 Hrs

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 significances. Determinations of these quantities. Concept of fugacity and determination of fugacity.

Non-ideal systems: Excess functions for non-ideal solutions. Activity, activity coefficient. Debye-Hückel 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.

Unit IV Thermodynamics – II 11 Hrs

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 Lagrange's method of undetermined multipliers).

Partition functions – translational, rotational, vibrational and electronic partition functions, calculation of thermodynamic properties in terms of partition functions. Applications of partition functions.

Non Equilibrium Thermodynamics 8 Hrs

Thermodynamic criteria for non-equilibrium states, entropy production and entropy flow, entropy balance equations for different irreversible processes (e.g. heat flow, chemical reaction etc.) transformations of the generalized fluxes and forces, non equilibrium stationary states, phenomenological equations.