PAPER-III
PHYSICAL CHEMISTRY

Time: 3 Hrs. **M.M. 100**

Note: The paper will be divided into THREE sections.

Section-A : Ten questions (short type answer) two from each Unit will be asked. Each question will be of one mark and the candidates are required to attempt all questions. **Total 10 marks**

Section-B : Five questions (answer not exceeding 250 words) one from each Unit with internal choice will be asked and the candidates are required to attempt all questions. Each question will be of 10 marks.
Total 50 marks

Section-C : Four questions may be in parts covering all the five Units (answer not exceeding 500 words) will be asked. The candidates are required to attempt any TWO questions. Each question will be of 20 marks.
Total 40 marks

UNIT-I

Quantum chemistry - The Schrodinger equation and the postulates of quantum mechanics, solutions of the Schrodinger equation to some model system viz.. particle in a box, the harmonic oscillator.

Approximate methods - The variation theorem and its applications, hydrogen atom.

Angular momentum - Ordinary angular momentum, generalized angular momentum, eigen functions and eigen values of angular momentum, operators, algebra of operators, ladder operators, addition of angular momenta, spin, antisymmetry and Pauli's exclusion principle.

Electronic structure of atoms - Electronic configuration, Russell-Saunder's terms and coupling schemes, molecular orbital theory, Huckel theory of conjugated systems, bond order and charge density calculations, application to ethylene and butadiene.

UNIT-II

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.

Non-ideal systems - excess function for non-ideal solutions, activity, activity coefficient.

Debye-Huckel theory for activity coefficient of electrolyte solutions, determination of activity and activity coefficients, ionic strength.

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 function, translational, rotational, vibrational and electronic partition functions, calculation of thermodynamic properties in terms of partition functions, applications of partition functions.

Chemical equilibrium and equilibrium constant in terms of partition functions, Fermi-Dirac statistics, Bose-Einstein statistics, distribution law.

Non-equilibrium thermodynamics - 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, microscopic reversibility and Onsager's reciprocity relations.

UNIT-III

Chemical dynamics - 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, chain reactions, photochemical reactions (Hydrogen-bromine and hydrogen-chlorine reactions) oscillatory reactions, (Belousov-Zhabotinsky reaction), homogeneous catalysis, kinetics of enzyme reactions, general features of fast reactions.

UNIT-IV

Surface adsorption chemistry - Surface tension, Gibbs adsorption isotherm, estimation of surface area (BET equation), surface films on liquids (Electrokinetic phenomenon), catalytic activity at surfaces.

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, solubilization, micro-emulsion, reverse micelles.

Macromolecules - Definition, types of polymers, electrically conducting, fire resistant and 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.

UNIT-V

Electrochemistry - Debye-Huckel-Onsager treatment and its extension, ion-solvent interactions, Debye-Huckel-Jerum mode, derivation of electro-capillarity, Lippmann equations (surface excess), methods of determination, structure of electrified interfaces,