

PAPER-III

Physical Chemistry

Time-3 Hrs.

M.M. 50

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 half mark and the candidates are required to attempt all questions.

Total 5 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 5 marks.

Total 25 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 10 marks.

Total 20 marks

UNIT-I

Elementary Quantum Mechanics - Black-body radiation, Planck's radiation law, photoelectric effect, heat capacity of solids, Bohr's model of hydrogen atom (no derivation) and its defects, Compton effect.

Sinusoidal wave equation, Hamiltonian operator, Schrodinger wave equation and its importance, physical interpretation of the wave function, postulates of quantum mechanics, particle in one-dimensional box.

Schrodinger wave equation for H-atom, separation into three equations (without derivation), quantum numbers and their importance, hydrogen like wave functions, radial wave functions, angular wave function.

Molecular orbital theory, basic ideas- criteria for forming M. O. from A. O., construction of M. O's by LCAO- H_2^+ ion, calculation of energy levels from wave functions, physical picture of bonding and antibonding wave functions, concept of s, s^* , p, p^* orbitals and their characteristics. Hybrid orbitals- sp , sp^2 , sp^3 , calculation of coefficients of A.O's used in these hybrid orbitals.

Introduction to valence bond model of H_2 , M. O. and V. B. models.

UNIT-II

Spectroscopy - Introduction: electromagnetic radiation, regions of the spectrum, basic features of different spectrometers, statement of the Born- Oppenheimer approximation, degrees of freedom.

Rotational Spectrum - Diatomic molecules, energy levels of a rigid rotator (semi-classical principles), selection rules, spectral intensity, distribution using population distribution (Maxwell - Boltzmann distribution) determination of bond length, qualitative description of non-rigid rotor, isotope effect.

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Vibrational Spectrum - Infrared spectrum, energy level of simple harmonic oscillator, selection rules, pure vibrational spectrum, intensity, determination of force constant and qualitative relation of force constant and bond energies, effect of anharmonic motion and isotope on the spectrum, idea of vibrational frequencies of different functional groups.

Raman spectrum: Concept of polarizability, pure rotational and pure vibrational Raman spectra of diatomic molecules, selection rules.

Electronic Spectrum - Concept of potential energy curves for bonding and antibonding molecular orbitals, qualitative description of selection rules and Franck-Condon principle.

Qualitative description of s, p and n M.O., their energy levels and the respective transitions.

UNIT-III

Photochemistry - Interaction of radiation with matter, difference between thermal and photochemical processes, laws of photochemistry, Grotthus - Drapper law, Stark - Einstein law, Jablonski diagram depicting various processes occurring in the excited state, qualitative description of fluorescence, phosphorescence, non-radiative process (internal conversion, intersystem crossing), high and low quantum yields, photosensitization, photochemical equilibrium, photolization, photodimerisation of anthracene, photoinhibition, chemical actinometry.

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Solutions, Dilute Solutions and Colligative Properties

- Ideal and non-ideal solutions, methods of expressing concentrations of solutions, activity and activity coefficient. Dilute solution: colligative properties, Raoult's law, relative lowering of vapour pressure, molecular weight determination. Osmosis, law of osmotic pressure and its measurement.

Determination of molecular weight from osmotic pressure, elevation of boiling point and depression of freezing point, thermodynamic derivation of relation between molecular weight and elevation in boiling point and depression in freezing point, experimental methods for determining various colligative properties, abnormal molar mass, degree of dissociation and association of solute, Vant-Hoff factor.

UNIT-IV

Ionic Conductance - Electrical transport, conduction in metal and electrolytes, solutions, specific conductance, equivalent conductance and molecular conductance, effect of dilution on conductance, migration of ions, Kohlraush's law and its applications, transport numbers and its determination by Hittorf's method and moving boundary methods, ionic mobility, application of conductivity measurement, conductometric titrations.

UNIT-V

Chemical Kinetics and Catalysis - Rate of reaction, factors influencing the rate of reaction, concentration,

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temperature, pressure, solvent, light and catalysis, order of a reaction, zero-order, first order and second order reaction, half life and mean life, conductometric, potentiometric, polarimetric and spectrophotometric methods of determination of order of reactions, method of integration, half life method and isolation method, experimental methods of kinetics, elementary idea about opposing, parallel, consecutive and chain reaction, effect of temperature on reaction rates. Arrhenius equation, concept of activation energy and its measurement, simple collision's theory (hard sphere model), transition state theory (equilibrium hypothesis) limitations.

Theory of unimolecular reactions, catalysis, theory and mechanism, classification of catalysis, enzyme catalysis and its mechanism.

1. Principle of Physical chemistry: B. R. Puri Sharma and M. S. Pathania.
2. A Text Book of Physical Chemistry: A. S. Negi and S.C. Anand.
3. A Text Book of Physical Chemistry: Kundu and Jain.
4. Physical Chemistry (Hindi Ed.): Suresh Ameta, Khandelwal, Ameta and Vardia.

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