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

Thermodynamics –I : Definition of thermodynamic terms, system, surrounding, etc., types of systems, intensive and extensive properties, state and path functions, their differentials, thermodynamics process, concept of heat

work.

First law of Thermodynamics - Statement, definition of internal energy and enthalpy, heat capacity, heat capacities at constant volume and pressure and their relationship, Joule' s law, Joule-Thomson coefficient and inversion temperature, calculation of w, q, dU and dH for the expansion of ideal gases under isothermal and adiabatic conditions for reversible process.

Thermochemistry: Standard state, standard enthalpy of formation, Hess's law of heat summation and its applications, Heat of reaction at constant pressure and at constant volume, Enthalpy of neutralization, bond dissociation energy and its calculation from thermochemical data, temperature dependence of enthalpy, Kirchhoff' s equation.

UNIT-II

Thermodynamics - II : Second law of thermodynamics: need for the law, different statements of the law, Carnot cycle and its efficiency, Carnot theory, thermodynamic scale of temperature.

Concept of entropy: Entropy as a state function, entropy as a function of V and T, entropy as a function of P and T; entropy change in physical change, Clausius inequality, entropy as a criteria of spontaneity and equilibrium, entropy change in ideal gases and mixing of gases.

Third Law of Thermodynamics - Nernst heat theorem,

statement and concept of residual entropy, evaluation of absolute entropy from heat capacity data. Gibbs and Helmholtz function, Gibbs function (G) and Helmholtz function (A) as thermodynamic quantities, A & G as criteria for thermodynamic equilibrium and spontaneity, their advantage over entropy change, variation of G and A with P, V and T.

Chemical Equilibrium - Equilibrium constant and free energy, thermodynamic derivation of law of mass action, distribution law and phase rule, Le Chatelier's principle, Nernst's distribution law for solute, principle of extraction of solute from solution and washing of precipitates.

Reaction isotherm and reaction isochore - Clapeyron equation and Clausius - Clapeyron equation, applications, partial molar quantities, partial molar volume and its distribution, chemical potential and its physical significance, Gibbs-Duhem equation.

UNIT-III

Macromolecules - Nomenclature, classification, properties of polymer, mass of macromolecules, number average and weight average molecular mass, determination of molecular weight by osmotic pressure, viscosity and light scattering and sedimentation (ultra centrifuge) methods.

Surface Chemistry - Sorption at surfaces, physical and chemical adsorption, Freundlich, Langmuir and Gibbs adsorption isotherms and their derivation, Streaming

potential electrophoresis and electrosmosis.

UNIT-IV

Phase Equilibrium - Statement and meaning of the terms - phase, component and degree of freedom, derivation of Gibb's phase rule, phase equilibrium of one component system- water, CO_2 and S - system.

Phase equilibria of two component system - Solid - liquid equilibria, simple eutectic, Bi-Cd, Pb-Ag systems, desilverization of lead.

Solid solutions - Compound formation with congruent melting point (Mg - Zn) and incongruent melting point, (NaCl - H_2O), ($FeCl_3$ - H_2O) and ($CuSO_4$ - H_2O) systems, freezing mixtures, acetone - dry ice.

Liquid - liquid mixtures: Ideal liquid mixtures, Raoult's and Henry's law, Non -ideal system, azeotropes: HCl - H_2O and ethanol - water systems.

Partially miscible liquids: phenol - water, trimethylamine - water, nicotine - water systems, lower and upper consolute temperature, effect of impurity on consulate temperature.

Immiscible liquids, steam distillation.

UNIT V

Electrochemistry : Types of reverse electrode : gas - metal ion, metal-metal ion, metal-insoluble salt - anion and redox electrodes, electrode reactions, Nernst equation, derivation of cell E.M.F. and single electrode

potential, standard hydrogen electrode-reference electrodes-standard electrode potential, sign conventions, electrochemical series and its significance, electrolytic and Galvanic cells- reversible and irreversible cells, conventional representation of electrochemical cells. EMF of a cell and its measurements, computation of cell EMF. Calculation of thermodynamic quantities of cell reactions (ΔG, ΔH and K) polarization, over potential and hydrogen over voltage. Concentration cell with or without transport, liquid junction potential, application of concentration cells, valency of ions, solubility product and activity coefficient, potentiometric titrations.

Ionic Equilibria - Arrhenius theory of electrolyte and its application, Ostwald's dilution law, its uses and limitations. Debye - Huckle theory of strong electrolytes, asymmetric, electrophoretic, Debye- Falkenhagen and Wein effects, Activity coefficient, mean activity coefficient, ionic strength, Debye- Huckel limiting law.

Books Recommended:

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 , R.C.Khandelwal, R. Ameta and J. Vardia.