B.Sc. II Paper – III

Physical Chemistry

Unit I
(Thermodynamics & Chemical Equilibrium)

I Thermodynamics – I

Definition of thermodynamic terms:

System, surroundings etc. Types of systems, intensive and extensive properties. State and path functions and their differentials. Thermodynamic process. Concept of heat and 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 & 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 thermo-chemical data, temperature dependence of enthalpy. Kirchhoff's equation.

II Chemical Equilibrium

Equilibrium constant and free energy. Thermodynamic derivation of law of mass action. Le Chatelier's principle.

Reaction isotherm and reaction isochore – Clapeyron-clausius equation and its applications.

Unit II

III Thermodynamics – II

Second law of thermodynamic:

Need for the law, different statements of the law. Cornot's cycle and its efficiency, Carnot's theorem. Thermodynamic scale of temperature.

Concept of entropy:

Entropy as a state function, entropy as a function of V & T, entropy as a function of P & T, entropy change in physical change, Clausius inequality, entropy as a criteria of sopntaneity and equilibrium. Equilibrium change in ideal gases and mixing of gases.

Gibbs and Helmholtz functions:

Gibbs function (G) and Helmhotz 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.

Third law of thermodynamics:

Nernst heat theorem, statement and concept of residual entropy.

Nernst distribution law – thermodynamic derivation, applications.

Unit III
(Electrochemistry – I & solutions)

IV Electrochemistry – I:

Electrical transport – conduction in metals and in electrolyte solutions, specific conductance and equivalent conductance, measurement of equivalent conductance, variation of equivalent and specific conductance with dilution.

Migration of ions and Kohlrausch's law, Arrhenius theory of electrolyte dissociation and its limitations, weak and strong electrolytes , Ostwald's dilution law its uses and limitations. Debye-Huckel-Onsager's equation for strong electrolytes (elementary treatment only). Transport number, definition and determination by Hittorf's method and moving boundary method.

Applications of conductivity measurements: determination of degree of dissociation, determination of K_a of acids, determination of solubility product of a sparingly soluble salt, conductometric titrations.

V Solutions:

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. Immiscible liquids, steam distillation.

Unit IV
(Electrochemistry – II & Phase Equilibrium)

VI Electrochemistry – II:

Types of reversible electrodes – gas-metal ion, 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 ($\triangle G$, $\triangle H$ and K)

Concentration cell with and without transport, liquid junction potential, application of concentration cells, valency of ions, solubility product and activity coefficient, potentiometric titrations.

Definition of pH and pK_a, determination of pH using hydrogen, quinhydrone and glass electrodes, by potentiometric methods.

Buffers – mechanism of buffer action, Henderson-Hazel equation. Hydrolysis of salts.

VII Phase Equilibrium:

Statement and meaning of the terms – phase, component and degree of freedom, derivation of Gibb's phase rule, phase equilibria of one component system – water, CO_2 and S systems.

Phase equilibria of two component system - solid liquid equilibria, simple eutectic – Bi-Cd, Pb-Ag systems, desilverisation of lead.

Solid solutions – compound formation with congruent melting point (Mg-Zn) and incongruent melting point, ($FeCl_3$-H_2O) and ($CuSO_4$-H_2O) system