SYLLABUS

CHEMISTRY

B.Sc. PART-II

PAPER-I : INORGANIC CHEMISTRY

UNIT-I **CHEMISTRY OF TRANSITION SERIES ELEMENTS**

Transition Elements : Position in periodic table, electronic configuration, general characteristics, *viz.*, atomic and ionic radii, variable oxidation states, ability to form complexes, formation of coloured ions, magnetic moment μ_{so} (spin only) and μ_{eff} and catalytic behaviour. General comparative treatment of 4*d* and 5*d* elements with their 3*d* analogues with respect to ionic radii, oxidation states and magnetic properties.

UNIT-II **OXIDATION AND REDUCTION**

Redox potential, electrochemical series and its applications. Principles involved in extraction of the elements.

CO-ORDINATION COMPOUNDS

Werner's theory and its experimental verification, IUPAC nomenclature of co-ordination compounds, isomerism in co-ordination compounds. Stereochemistry of complexes with 4 and 6 co-ordination numbers. Chelates, polynuclear complexes.

UNIT-III **CO-ORDINATION CHEMISTRY**

Valence bond theory (inner and outer orbital complexes), electroneutrality principle and back bonding. Crystal field theory, crystal field splitting and stabilization energy, measurement of 10 D*q* (Δ_o), CFSE in weak and strong fields, pairing energies, factors affecting the magnitude of 10 D*q* (Δ_o, Δ_t). Octahedral Vs. tetrahedral co-ordination.

UNIT-IV **CHEMISTRY OF LANTHANIDE ELEMENTS**

Electronic structure, oxidation-states and ionic radii and lanthanide contraction, complex formation, occurrence and isolation, lanthanide compounds.

CHEMISTRY OF ACTINIDES

General features and chemistry of actinides, chemistry of separation of Np, Pu and Am from uranium, similarities between the later actinides and the later lanthanides.

UNIT-V **ACIDS-BASES**

Arrhenius, Bronsted-Lowry, conjugate acids and bases, relative strengths of acids and bases, the Lux-flood, solvent system and Lewis concepts of acids and bases.

NON-AQUEOUS SOLVENTS

Physical properties of a solvent, types of solvents and their general characteristics, reaction in non-aqueous solvents with reference to liquid ammonia and liquid sulphur dioxide, HF, H_2SO_4, ionic liquids.

PAPER-II : ORGANIC CHEMISTRY

UNIT-I **CHEMISTRY OF ORGANIC HALIDES**

Alkyl halides : Methods of preparation, nucleophilic substitution reactions - S_N1, S_N2 and S_Ni mechanisms with stereochemical aspects and effect of solvent etc.; nucleophilic substitution, elimination reactions.

Aryl halides : Preparation, including preparation from diazonium salts, nucleophilic aromatic substitution; S_NAr, benzyne mechanism. Relative reactivity of alkyl, allyl/ benzyl, vinyl and aryl halides towards nucleophilic substitution reactions.

UNIT-II **ALCOHOLS**

A. Alcohols : Nomenclature, preparation, properties and relative reactivity of 1°, 2°, 3° alcohols, Bouvaelt-Blanc reduction for the preparation of alcohols. **Dihydric alcohols :** Methods of formation, chemical reactions of vicinal glycols, oxidative cleavage [$Pb(OAc)_4$ and HIO_4] and pinacol-pinacolone rearrangement.

B. Trihydric alcohols : Nomenclature, methods of formation, chemical reactions of glycerol.

PHENOLS

A. Structure and bonding in phenols, physical properties and acidic character, comparative acidic strength of alcohols and phenols, acylation and carboxylation.

B. Mechanism of Fries rearrangement, Claisen rearrangement, Gatterman synthesis, Hauben-Hoesh reaction, Lederer-Manasse reaction and Reimer-Tiemann reaction.

UNIT-III **ALDEHYDES AND KETONES**

A. Nomenclature, structure and reactivity of carbonyl group. General methods of preparation of aldehydes and ketones.

Mechanism of nucleophilic addition to carbonyl groups : Benzoin, Aldol, Perkin and Knoevenagel condensation. Condensation with ammonia and its derivatives, Wittig reaction, Mannich reaction, Beckmann and Benzil- Benzilic rearrangement.

B. Use of acetals as protecting group, Oxidation of aldehydes, Baeyer-Villiger oxidation of ketones, Cannizzaro reaction, MPV, Clemmensen reduction, Wolff-Kishner reaction, $LiAlH_4$ and $NaBH_4$ reduction. Halogenation of enolizable ketones, an introduction to α,β-unsaturated aldehydes and ketones.

UNIT-IV **CARBOXYLIC ACIDS**

Preparation, structure and bonding, physical and chemical properties including, acidity of carboxylic acids, effects of substituents on acid strength, Hell-Volhard Zeilinsky reaction. Reduction of carboxylic groups, mechanism of decarboxylation.

Di carboxylic acids : Methods of formation and effect of heat and dehydrating agents. Hydroxyacids.

CARBOXYLIC ACID DERIVATIVES

Structure of acid chlorides, esters, amides and acid anhydrides, Relative stability of acyl derivatives. Physical properties, inter-conversion of acid derivatives by nucleophilic acyl substitution. Mechanism of acid and base catalyzed esterification and hydrolysis.

UNIT-V **ORGANIC COMPOUNDS OF NITROGEN**

A. Preparation of nitroalkanes and nitroarenes. Chemical reactions of nitroalkanes. Mechanism of nucleophilic substitution in nitroarenes and their reduction in acidic, neutral and alkaline medium.

B. Reactivity, structure and nomenclature of amines, physical properties. Stereochemistry of amines. Separation of mixture of primary, secondary and tertiary amines. Structural features affecting basicity of amines. Preparation of alkyl and aryl amines (reduction of nitro compounds and nitriles), reductive amination of aldehydic and ketonic compounds. Gabriel-Phthalimide reaction, Hofmann-Bromamide reaction, reactions of amines, electrophilic aromatic substitution of aryl amines, reaction of amines with nitrous acid. Synthetic transformations of aryl diazonium salts, Azo coupling.

PAPER-III : PHYSICAL CHEMISTRY

UNIT-I **THERMODYNAMICS-I**

A. Intensive and extensive variables; state and path functions; isolated, closed and open systems; Zeroth law of thermodynamics. First law : Concept of heat, work, internal energy and statement of first law; enthalpy, relation between heat capacities, calculations of q, w, U and H for reversible, irreversible and free expansion of gases under isothermal and adiabatic conditions. Joule-Thomson expansion, inversion temperature of gases, expansion of ideal gases under isothermal and adiabatic condition.

B. THERMO CHEMISTRY

Thermochemistry, laws of thermochemistry, heats of reactions, standard states; enthalpy of formation of molecules and ions and enthalpy of combustion and its applications; calculation of bond energy, bond dissociation energy and resonance energy from thermochemical data, effect of temperature (Kirchhoff's equations) and pressure on enthalpy of reactions, Adiabatic flame temperature, explosion temperature.

UNIT-II **THERMODYNAMICS-II**

A. Second Law of Thermodynamics : Spontaneous process, second law, statement of Carnot cycle and efficiency of heat engine, Carnot's theorem, thermodynamic state of temperature. Concept of entropy : Entropy change in a reversible and irreversible process, entropy change in isothermal reversible expansion of an ideal gas, entropy change in isothermal mixing of ideal gases, physical signification of entropy, molecular and statistical interpretation of entropy.

B. Gibbs and Helmholtz free energy, variation of G and A with pressure, volume, temperature, Gibbs-Helmholtz equation, Maxwell relations, elementary idea of Third law of thermodynamics, concept of residual entropy, calculation of absolute entropy of molecule.

UNIT-III **CHEMICAL EQUILIBRIUM**

Criteria of thermodynamic equilibrium, degree of advancement of reaction, chemical equilibria in ideal gases. Concept of Fugacity, Thermodynamic derivation of relation between Gibbs free energy of reaction and reaction quotient. Coupling of exergonic and endergonic reactions. Equilibrium constants and their quantitative dependence on temperature, pressure and concentration. Thermodynamic derivation of relations between the various equilibrium constants K_p, K_c and K_x. Le-Chatelier principle (quantitative treatment). Equilibrium between ideal gas and a pure condensed phase.

IONIC EQUILIBRIA

Ionization of weak acids and bases, pH scale, common ion effect; dissociation constants of mono protic acids (exact treatment). Salt hydrolysis-calculation of hydrolysis constant, degree of hydrolysis and pH for different salts. Buffer solutions; derivation of Henderson equation and its applications. Solubility and solubility product of sparingly soluble salts-applications of solubility product principle.

UNIT-IV **PHASE EQUILIBRIUM**

A. Phase rule, phase, component and degree of freedom, derivation of Gibbs phase rule, Clausius-Clapeyron equation and its applications to Solid-Liquid, Liquid-Vapour and Solid-Vapour, limitation of phase rule, applications of phase rule to one component system; water system and sulphur system. Applications of phase rule to two component system : Pb-Ag system, desilverization of lead, Zn-Mg system. Ferric chloride-water system, congruent and incongruent, melting point and eutectic point. Three component system : Solid solution liquid pairs.

B. Nernst distribution law, Henry's law, application, solvent extraction.

UNIT-V **PHOTOCHEMISTRY**

Characteristics of electromagnetic radiation, interaction of radiation with matter, difference between thermal and photochemical processes, Lambert-Beer's law and its limitations, physical significance of absorption coefficients. Laws of photochemistry : Grothus-Drapper law, Stark-Einstein law, quantum yield, actinometry, examples of low and high quantum yields, photochemical equilibrium and the differential rate of photochemical reactions, quenching, role of photochemical reaction in biochemical process. Jablonski diagram depicting various process occurring in the excited state, qualitative description of fluorescence, phosphorescence, non-radiative processes (internal conversion, intersystem crossing), photosensitized reactions, energy transfer processes (simple examples), photostationary states, chemiluminescence.