

# SYLLABUS FOR CHEMISTRY

## PAPER-I

### Physical Chemistry

#### UNIT -I

**Solid State:** Laws of crystallography- Law of constancy of interfacial angle-explanation taking hexagonal crystal system as an example. Law of symmetry. Law of rationality of indices. Miller indices- Bravais lattices. X-ray diffraction by crystals. Derivation of Bragg's equation.

#### UNIT-II

**Gaseous State:** Maxwell's distribution of molecular velocities- Qualitative discussion of the collision number, mean free path and collision diameter. Critical Phenomena: P-V isotherms of real gases. Continuity of states-principals. Isotherms of van der Waals equation. Relationship between critical constants and van der Waals constants. Law of corresponding states.

**Liquid State:** Structure of liquids-qualitative description. Structural differences between solids, liquids and gases. Liquid crystals-Explanation, classification with examples. Application of liquid crystals in LCDs and thermal sensing.

**Solvents:**Physical properties of a solvent – density, dipole moment, specific conductance, dielectric constant, heats of fusion and vaporization. Reactions in aqueous and non aqueous solvents. Water and ammonia..

#### UNIT-III

**Colorimetry and Spectrophotometry:** Theory of colorimetry and spectrophotometry. Beer – Lambert's law instrumentation and applications of colorimetry and spectrophotometry.

**Ultraviolet absorption spectroscopy:** Absorption laws. Concept of molar absorptivity, energy level, types of electronic excitations, Frank-Condon principal (explanation about red shift and blue shift). Concept of chromophore and auxochrome. Bathochromic, hypsochromic, hyperchromic and hypochromic shifts. UV spectra of conjugated dienes and  $\alpha,\beta$ -unsaturated carbony compounds.

**IR spectroscopy:** Principles & applications.

**Nuclear Magnetic Resonance Spectroscopy:** Origin of spectra, instrumentation, solvents, nuclear shielding and deshielding, chemical shift spin-spin splitting, coupling constants, interpretation of PMR spectra.

## UNIT-IV

**Photoelectron spectroscopy:** Basic principles, valence and core binding energies, shifts in energies due to chemical forces photoelectron spectra.

**Mass spectrometry:** Principal and instrumentation of mass spectrometer. Applications in the determinations of Molecular mass and isotopic abundance. Nitrogen rule, even electron rule, Meclafferty rearrangement.

**Raman spectroscopy:** Classical and quantum theories of Raman effect. Concept of polarizability and polarzability ellipsoid. Rotations and vibrational Raman spectra. Selection rules.

## UNIT-V

**Thermodynamics:** First law of thermodynamics, Joule-Thomson effect. Bond dissociation energy and its calculation from thermo chemical data. Temperature dependence of enthalpy, Kirchhoff's equation. Second law of thermodynamics. Carnot's cycle. Thermodynamic scale of temperature. Concept of entropy. Third law of thermodynamics-its significance, unattainability of absolute zero. Gibbs function (G) and Helmholtz function (A) as thermodynamic quantities. A and G as criterion for thermodynamic equilibrium and spontaneity, their advantage over entropy change. Variation of G with P, V and T.

## UNIT-VI

**Surface chemistry:** Adsorption of gases on solids: Frandlich and Langmuir adsorption isotherm. Multilayer adsorption –BET equation. Determination of surface area and area of cross section of a molecule. Gibb's adsorption isotherm.

**Solutions, dilute solutions and colligative properties:** Ideal and non-ideal solutions, Methods of expressing concentrations-Activity and Activity coefficients. Colligative properties: Raoult's law of relative lowering of vapour pressure. Osmosis and laws of Osmotic pressure. Elevation of Boiling point and depression of freezing point.

**Physical properties and molecular structure:** Optical activity, polarization (Clausius-Mosotti equation), orientation of dipoles in an electric field, dipole moment.

**Refractometry:** Abbe's refractometer and its applications

## UNIT-VII

**Binary mixtures:** Liquid-liquid mixtures, completely miscible liquids, ideal liquid mixtures non-ideals systems showing positive and negative deviation from Raoult's law, Vapour pressure, Azeotropes, partially miscible liquids, Miscibility temperature and critical solution temperature

(CST). Effect of impurity on CST. Immiscible liquids, Steam distillation-principle and experimental details, Nernst Distribution law.

**Oxidation and Reduction:** Use of redox potential data thermodynamic feasibility using free energy, reducing and oxidizing tendency, Analysis of redox couple. Redox stability in water, Frost Latimer and Pourbaix diagrams.

### UNIT -VIII

**Chemical Kinetics:** Concentration dependence of rates, differential rate laws of simple chemical reactions, zero, first, second, nth and pseudo first order reaction.

Derivation of rate constants for second order and nth order reactions with equal initial concentrations Determination of order of a reaction –Differential, Integration, Half life period and Isolation methods. Transition state theory-Derivation of relationship between rate constant and equilibrium constant thermodynamic aspects of activation.

**Catalysis:** Role of catalyst in altering reaction rate, Acid base catalysis, specific and general acid base catalysis mechanism and kinetics, Enzyme catalysis, Derivation of Michaelis-Menten equation.

### UNIT-IX

**Chemical Equilibrium:** Derivation of relationship between equilibrium constant and free energy equation. Thermodynamic derivation of law of mass action, Le Chatelier's Principle Van't Hoff's reaction isotherm and reaction isochore (Van't Hoff equation)

**Phase Equilibrium:** Phase rule. Derivation of phase rule from phase equilibrium of one and two component system with examples.

### UNIT-X

**Electrochemistry:** Transport number strong and weak electrolytes. Debye-Huckel-Onsager equation for strong electrolytes(no derivation). Applications of conductivity measurements. Reference electrodes, Calomel, Quinhydrone, Ag-AgCl and glass electrode (Construction, Electrode reaction, Nernst equation), E.MF of cells and its measurements by potentiometric method, calculation of electrode potential, computation of cell EMF, relation between  $G$  and  $K$  for a cell reaction, Concentration cells: liquid junction potential Determination of pH using hydrogen electrode, Quinhydrone electrode and glass electrode by potentiometric methods. Decomposition potential polarization and over voltage. Applications of hydrogen over voltage.

Electrical double layer and its Thermodynamics. A brief survey of Helmholtz – Perrin, Gouy – Chapman and Stern electrical double layer. Electrochemical energy sources- Batteries, Classification characteristics, Primary, secondary and Fuel cells.

Corrosion & its prevention.

## UNIT-XI

**Irreversible Electrode Process:** Reversible and irreversible electrodes, Polarization, Ohmic overvoltage concentration Overvoltage, activation overvoltage. Oxygen over Voltage. Effect of temperature, current density and pH on over voltage. Experimental determination of over voltage. Energy barrier and electrode kinetics, Buttlur-Volmer equation, Tafel equation.

## UNIT-XII

**Quantum Mechanics:** Wave- particle duality of material particles, deBroglie equation, Heisenberg uncertainty principle. Concept of operators (operator-operand), algebra of operators. Commutative and non-commutative operators, linear operators, Laplacian operator, Hamiltonian operator, Eigen value, Eigen function, Hermitian operator, turn over rule, atomic units. Wave equation for stretched rings Schrodinger wave equation wave equation for particles. Postulates of quantum mechanics. Application of Schrodinger equation to a free particles and to particle trapped in a potential field (one dimension & three dimension). Degeneracy, wave equation for H-atom separation and solution of R, and  $\Theta$  equations. Application of Schrodinger equation to rigid rotator and harmonic oscillator. Approximate methods-necessity of approximate methods, perturbation method, the theory of perturbation method –first order and second order correction, application to HE- atom (first order correction only)- calculation of first ionization potential and binding energy. Variation theorem statement and proof.

**Elementary Quantum Mechanics:** Quantum theory of radiation (Black body radiation), Planck's radiation law, Heat capacities of solids, Photoelectric effect, Compton effect. Quantum numbers and their importance.

## UNIT-XIII

**Photochemistry:** Introduction, quantum yield and its determination, factors affecting quantum yield, actinometry. Term symbols and significance, Photosensitization: Photodegradation: Photocatalyst-ZnO, TiO<sub>2</sub>, principal, application of ZnO/TiO<sub>2</sub> in the Photodegradation of dyes(IC), pesticides(DDT) and in industrial effluents. Effect of Photodegradation on COD value.

**Nuclear Chemistry:** nuclear reactions, fission, and fusion, radio analytical techniques and activation analysis.

# PAPER-II

## Inorganic Chemistry

### UNIT I

**Periodic Properties:** Methods of determination of Atomic properties – Atomic size, ionization energy, Electron affinity and Electronegativity, Effective nuclear charge-shielding effect, Slater's rule and its applications, Ionic radii.

### UNIT II

**Chemistry of s-Block Elements:**Hydrides and Complex hydrides, Comparative study of lattice energy, enthalpy of formation, enthalpy of hydration and solubility's of alkali metal and alkaline earth metal halides, hydroxides and sulphates. Complexation tendencies of alkali metals with crown ether. Boranes, Silicates & Phosphorous acids.

### UNIT III

**Chemistry of d- and f-block elements:** Electronic configuration, stabilities of oxidation states and complexing ability. Magnetic property, Expression for magnetic moment, Comparative treatment of 4d and 5d series with their 3d analogues, Lanthanide contraction, Comparison between lanthanides and actinides, Extraction of metals and Ellingham diagram.

**Alloys:** Principles and purpose of alloying, effect of alloying, Stainless steel and inverse steel-constituents, properties and applications.

**Nano Chemistry:** General methods of synthesis, characterization techniques, preparation of nano particle by chemical method, application of nano materials.

### UNIT IV

**Chemical Bonding:** Ionic bonding and covalent bonding, Valence band theory, Concept of hybridization, Valence Shell Electron Pair Repulsion (VSEPR) theory, Basic principle of Molecular orbital theory, Molecular orbital diagrams of homo and heteronuclear species, Solvation and Solubility of ionic solids, Polarising power and Polarisability of ions. Fajan's rule diagonal relationship. Metallic bond-Application of Band theory for explaining the electrical and thermal conductance.

### UNIT V

**Theories of acids and bases:** Bronsted and Lewis acids and bases, Lux-Flood theory, solvent leveling effects, HSAB concept, super acids. Reactions in non-aqueous media: Reactions in molten salts.

## UNIT VI

**Co-ordination Compounds:** Nomenclature, Isomerism in coordination compounds.

**Metal-ligand Bonding in Transition Metal Complexes:** Valence bond theory-examples for  $sp^3$ ,  $dsp^2$ ,  $dsp^3$ ,  $d^2sp^3$ , and  $sp^3d^2$  hybridisation, Explanation for magnetic properties, Crystal field theory-important concepts of CFT, Crystal fields splitting in octahedral, tetrahedral and square planar complexes, crystal field stabilization energy. Calculation of CFSE, spectrochemical series, Factors affecting the crystal field splitting, Limitation of CFT.

**Spectral Properties of Metal Complexes:** Term symbols, selection rules for electronic transitions-spin selection rule, the Laportic selection rule, Orgel diagrams, Tanabe-Sugano diagrams, stereo isomerism, chirality, CD, ORD, Cotton effect and magnetic circular dichroism, absolute configuration.

**Metal-Ligand Equilibria in Solution:** Step-wise and over-all formation constant and their relationships, trends in step wise constant, kinetic and thermodynamic stability of metal complexes, determination of binary formation constants by PH meter, spectrophotometry, polarography, and by ion exchange methods.

**Kinetics and Mechanism of Reactions of Coordination Compounds:** Inert and labile complexes, Mechanism of substitution reactions, classification of ligand substitution reactions in octahedral and square planar complexes, molecular rearrangements of four and six coordinated complexes.

**Electron Transfer Reaction (Redox Reactions):** Inner and outer sphere mechanisms, one electron, two electron, complimentary and non complimentary electron-transfer reactions.

## UNIT VII

### **Bio-inorganic Chemistry:**

**Metal Ions in Biological Systems:** Essential and trace metals, active transport of cations, ionophores, metalloproteins as enzymes carboxy peptidase, (catalases, peroxidases, cytochrome P450, copper oxidases) super oxide dismutase, vitamin B12, coenzyme, enzyme action inhibition and poisoning. Metals in medicine- Metal deficiency, chelation therapy and metal complexes as drugs. Chlorophyll and its role in photosynthesis.

## UNIT VIII

**Group Theory and Symmetry:** Symmetry elements and Symmetry operations, groups, subgroups, molecular point groups, Schoenflies notations, matrix representations of symmetry operation, matrix representations of groups, Reducible and Irreducible representations, characters

of representations, The great orthogonality theorem, character tables and their construction (C<sub>2v</sub>, C<sub>2h</sub>, C<sub>3v</sub>)- Mullikan symbols, molecular models. Determination of vibration modes, hybridization, molecular orbitals on the basis of group theory.

## UNIT IX

### Analytical Chemistry

**Errors and Sampling:** Limitations of analytical methods, errors, accuracy and precision, mean and standard deviation, Paired t-test, correlation and regression, linear regression, Quality control and quality assurance. The basis of sampling.

#### Titrimetric and Gravimetric analysis:

**Acid base titrations:** Titration curves determination of equivalence point – theory, acid base indicators, colour change, range of indicators.

**Complexometric Titrations:** Titration curves, EDTA titrations, titrations of mixtures, masking and demasking agents, metal ion indicators.

**Precipitation Titrations:** Precipitation reactions, titration curves, factors influencing the sharpness of end points, chemical indicators for precipitation titrations, applications of precipitation titration analysis.

**Oxidation – Reduction Titrations:** Redox process, titration curves, redox indicators and applications.

**Gravimetric analysis:** Requirements & conditions of precipitations, co-precipitation, post precipitation, nature of the precipitate, super saturation, precipitation from homogeneous solution and effect of excess of precipitant, temperature, PH and complex formation of completeness of precipitation.

**Organic Reagents in Inorganic Analysis:** Organic precipitants, general properties, reagents as precipitants.

**Conductometry:** Theory-Measurement of Conductivity – Basis for Conductometric titrations.

**Potentiometry:** Principles – Reference electrodes – indicator electrodes, selective electrodes – measurement of cell emf – potentiometric titrations.

**Voltametry:** Polarography – Direct current Polarography – Theory – Dropping Mercury Electrode – Quantitative technique – Measurement of Wave Heights – Pulse Polarography – Rapid Scan Polarography – Stripping Voltametry – Cyclic Voltametry.

**Amperometry:** Principles, amperometric titrations

**Electrogravimetry:** Theory, completeness and nature of the deposit, instrumentation, electrolytic separation of metals and applications.

#### UNIT X

##### **Chromatographic Techniques:**

Separation Techniques - Solvent extraction, Principles, classifications and theory of chromatographic separation. This layer chromatography, column chromatography, size exclusion chromatography, Ion exchange chromatography, Paper chromatography, Gas Chromatography and HPLC

#### UNIT XI

**Industrial Chemistry:** Silicones & Fluorocarbons and Phosphonitrile halides, Fuels: Composition, production and applications of natural gas, water gas, producer gas, LPG and bio gas, Propellants: characteristics and applications.

**Glasses:** Types, composition and uses of glasses, Raw materials manufacture, Cement, Ceramics, Insulators: superconductors. Paints: Constituents of paints and their functions, Manufacture of white lead and lithopone.

#### UNIT XII

**Air Pollution:** Types and sources of air pollutants; concentrations of air pollutants; principles and methods of sampling; causes, consequences of air pollution and their remedies.

**Radioactive Pollution:** Sources of pollutants; effect of vegetation and health. Detection and monitoring of radioactive pollutants. Methods of safe disposal of radioactive waste.

**Water Pollution:** Types of water pollutants and their effects; sources of water pollution; Objectives of analysis, Parameters of analysis.

#### UNIT XIII

##### **Biochemistry**

**Carbohydrates:** Introduction, Ring size determination of monosaccharides, configuration and conformations of monosaccharides, anomeric effect, Hudson's rules, epimerization and mutarotation.

Synthesis, industrial and biological importance of glycosides, amino sugars, sucrose, maltose and lactose.

**Polysaccharides:** General methods of structure elucidation. Industrial importance and biological importance of cellulose, starch, glycogen, dextran, hemicelluloses, pectin, agar-agar. Biosynthesis of carbohydrates.

**Lipids:** Nomenclature, classification, purification, synthesis of lipids, phospholipids, sphingolipids, biological importance of lipids: Lecithin, sphingolipids, oils and fats.

**Prostaglandins:** Introduction, classification and biological importance, constitution of PGEL

**Amino acids, Peptides and Proteins:** General methods of preparation, properties and reactions of amino acids. Peptide bond; Proteins; biological importance, classification based on structure and composition, primary structure of proteins and its determinations; Denaturation and renaturation, Biosynthesis of peptides.

**Vitamins:** Biological importance and synthesis of Vitamin A, Vitamin B<sub>6</sub>, Vitamin C and Vitamin E, Vitamin K, Vitamin H & Vitamin E (tocopherol).

#### UNIT XIV

**Nucleic acids:** Purine and pyrimidine bases, Structure of nucleosides and nucleotides. Methods of formation of internucleotide bonds Structure of DNA and RNAs. Biological importances of DNA and RNAs. Protein-nucleic acid interaction chromatin and viral nuclear capsid.

**Hormones:** Classification, sex hormones, Non-steroidal oestrogens, and their clinical applications, Synthesis and mode of action of hormones.

## Organic chemistry

### Unit I

IUPAC nomenclature of organic compounds: Alkanes, alkenes, alkynes, alkyl halides, alcohols, carboxylic acids, aldehydes, ketones. Aromatic hydrocarbons and heterocyclic compounds. Concept of resonance, inductive and hyper conjugation effect, hydrogen bonding.

### Unit II

**Stereochemistry:** Principles of stereochemistry, projection formula, chirality, D/L and R/S notations, optical isomerism, geometrical isomerism, E/Z notations, enantiomers, diastereoisomers, epimers and racemization. Configuration and conformation. Effect of conformation on reactivity. Regio-, stereo-, diastereoselective and chemo-selective reactions.

### Unit III

**Reaction mechanism I:** Classification, methods of determination (kinetic and non-kinetic methods), Hammett equation.

**Chemistry of reactive intermediates:** carbocations, carbanions, free radicals, carbenes, nitrenes, benzyne and ylides.

#### Unit IV

**Reaction mechanisms II:** Substitution reactions- aliphatic electrophilic and nucleophilic substitution reactions, aromatic electrophilic and nucleophilic substitution reactions.

#### Unit V

**Elimination reactions :** E1, E2, E1Cb and syn eliminations.

**Addition reactions:** addition across carbon-carbon and carbon-hetero atom multiple bonds

Formation and hydrolysis of esters, decarboxylation reactions and free radical reactions.

**Condensation reactions:** Claisen, Dieckmann, Perkin, Knoevenongel, Stobbe, Benzoin and Darzen's reactions.

#### Unit VI

**Rearrangement reactions:** Pinacole-pinacolone, Hoffmann, Curtius, Lossen, Beckmann, Wagner-Meerwein, Fries, Claisen, Cope, Demroth, and Steven rearrangement. Baeyer-Villegier reaction

#### Unit VII

**Name reactions:** Clemenson & Wolf-Kishner reduction, Remier-Tiemann reaction, Reformatsky reactions, Kolbe's electrolysis, Barton reaction, Hoffmann- Lofter-Freytag reaction, Mitsunobu reaction, Suzuki coupling reaction, Heck reaction, Stork-enamine reaction, Stille-Kelley coupling, Barton decarboxylation, Sharpless assymmetric epoxidation, Woodward-Prevost hydroxylation and Peterson reaction.

#### Unit VIII

**Photochemistry and pericyclic reactions:** Jablonski diagram, Norrish type-I and II reaction, photochemistry of alkenes, carbonyl compounds, aromatic hydrocarbons, Di-pi rearrangement, photoreduction and autooxidation.

**Pericyclic reactions :** Classification, Woodward-Hoffmann rules for electrocyclic, cycloaddition reactions and sigmatropic rearrangements (FMO approach and correlation diagram)

#### Unit IX

**Oxidations:** Oxidation with chromium and manganese salts, lead tetraacetate, periodic acid, SeO<sub>2</sub>, chloramine-T, OsO<sub>4</sub>, ozone, peracids, H<sub>2</sub>O<sub>2</sub>.

**Reductions:** Dissolving metal reduction, Catalytic reduction, Complex metal hydride reductions, dibrane (hydroboration).

### Unit X

**Synthetic reagents:** NBS, AIBN, benzoyl peroxide, DDQ, DCC, trimethyl silane, trimethyl silyl chloride/ iodide / cyanide, Fenton's reagent, dithiane, acyl anion equivalents, n-butyl lithium, Gilman reagents, PPA, Zeigler-Natta catalyst, organo tin and organoaluminium reagents.

### Unit XI

Protection and deprotection of functional groups, asymmetric synthesis, retrosynthesis.

### Unit XII

**Heterocyclic compounds:** Chemistry of furan, pyrrole, thiophene, indole, pyridine, coumarins, pyrazoles, oxazoles, sydnone, thiazoles, quinolines and isoquinolines.

### Unit XIII

**Medicinal Chemistry:** Modern theories of drug action, concept of receptors, computer aided drug design, quantitative and qualitative SAR. Sulfa drugs, analgesics, antibiotics, anti-inflammatory, anticancer, antidiabetic, antiviral and antihypnotic drugs.

**Agrochemicals:** Pesticides, herbicides, insecticides and pheromones.

**Food additives:** Edible colours, flavours, sweeteners, antioxidants and preservatives.

### Unit XIV

Chemistry of alkaloids and terpenoids.

**Chemistry of synthetic polymers:** Polyethylene, poly vinyl chloride, Teflon, terylenes, nylons, urethans, polystyrene, poly carbamate and synthetic resins. Synthetic and natural rubbers, biodegradable polymers, conducting polymers.

### Unit XV

**Green chemistry:** Principles and applications, microwave and solvothermal reactions, solvent free synthesis, phase transfer catalysts and reactions involving ionic liquids.

### Unit XVI

Joint applications of UV, IR, NMR ( $^1\text{H}$  and  $^{13}\text{C}$ -) and mass spectroscopy.