

**SYLLABUS FOR LAB ASSISTANT (CHEMISTRY)****INORGANIC CHEMISTRY-I****UNIT I Atomic Structure:**

Bohr's theory, its limitations and atomic spectrum of hydrogen atom. Wave mechanics: de-Broglie equation, Heisenberg's Uncertainty Principle and its significance, Schrödinger's wave equation, significance of  $\psi$  and  $\psi^2$ . Quantum numbers and their significance. Sign of wave functions. Radial and angular wave functions for hydrogen atom. Radial and angular distribution curves. Shapes of *s*, *p*, *d* and *f* orbitals. Pauli's Exclusion Principle, Effective nuclear charge, shielding or screening effect, Slater rules, variation of effective nuclear charge in periodic table.

Hund's rule of maximum multiplicity, Aufbau's principle. Electronic configurations.

**UNIT II Periodicity of Elements:**

Modern periodic law; *s*, *p*, *d*, *f* block elements, the long form of periodic table. Detailed discussion of the following properties of the elements, with reference to *s* and *p*-block.

- Electropositive character
- Atomic and Ionic radii
- Covalent radii
- Ionization enthalpy; Successive ionization enthalpies and factors affecting ionization energy. Applications of ionization enthalpy.
- Electron gain enthalpy; trends of electron gain enthalpy.
- Electronegativity; Pauling's/ Mulliken's electronegativity scales. Variation of electronegativity with bond order, group electronegativity.
- Isoelectronic species.

**UNIT III Chemical Bonding:**

(i) *Ionic bond*: General characteristics, types of ions, size effects, radius ratio rule and its limitations. Born-Landé equation with derivation and importance of Kapustinskii expression for lattice energy. Derivation of Madelung constant, Born-Haber cycle and its applications, Solvation energy.

(ii) *Metallic Bond*: Qualitative idea of valence bond and band theories. Conductors, Semiconductors and insulators.

(iii) *Weak Chemical Forces*: van der Waals forces, ion-dipole forces, dipole-dipole interactions, induced dipole interactions, Instantaneous dipole-induced dipole interactions. Repulsive forces, Hydrogen bonding (theories of hydrogen bonding by valence bond treatment); Effects of melting, boiling points and solubility, energetics of dissolution process.

(iv) *Coordinate covalent bond*; General ideas.

**UNIT IV Chemical Bonding-II**

(ii) *Covalent bond*: Lewis structure, Valence Bond theory (Heitler-London approach). Hybridisation; types of hybridization. Energetics of hybridization, equivalent and nonequivalent hybrid orbitals, Resonance and resonance energy, Resonance structures of  $\text{CO}_3^{2-}$ ,  $\text{NO}_3^-$ ,  $\text{SO}_4^{2-}$ ,  $\text{SO}_2$ ,  $\text{SO}_3$ ,  $\text{CO}_2$  Molecular orbital theory. Molecular orbital diagrams of diatomic and simple polyatomic molecules  $\text{N}_2$ ,  $\text{O}_2$ ,  $\text{F}_2$ ,  $\text{CO}$ ,  $\text{NO}$ , and their ions; Formal charge, Valence shell electron pair repulsion theory (VSEPR), shapes of simple molecules and ions containing lone pairs and bond pairs of electrons,  $\text{BeF}_2$ ,

$\text{BF}_3$   $\text{H}_3\text{O}^+$ ,  $\text{NH}_3$ ,  $\text{H}_2\text{O}$ ,  $\text{H}_2\text{S}$ ,  $\text{O}_3$ ,  $\text{BO}_3^{3-}$ ,  $\text{PCl}_5$ ,  $\text{SF}_4$ ,  $\text{SF}_6$

## UNIT V Chemical Bonding-III and Oxidation-Reduction:

*Chemical Bonding:* Covalent character in ionic compounds, polarizing power and polarizability, consequences of polarization. Fajan's rule and its applications. Ionic character in covalent compounds: Dipole moment, Calculation of dipole moment, Percentage ionic character from dipole moment and electronegativity difference.

**[a] Oxidation-Reduction:** General concept, Electrochemical series and its applications, Hydrogen over voltage and oxygen over voltage, redox stability in water, Frost diagram (Nitrogen), Latimer diagram (chlorine in acidic and basic medium), disproportionation of  $\text{H}_2\text{O}_2$  into  $\text{O}_2$  and  $\text{H}_2\text{O}$  under acidic conditions and Pourbaix diagram (iron species in natural water).

## PHYSICAL CHEMISTRY-I

### UNIT I Gaseous state-I:

Kinetic molecular model of a gas: postulates and derivation of the kinetic gas equation; collision frequency; collision diameter; mean free path and viscosity of gases, including their temperature and pressure dependence, relation between mean free path and coefficient of viscosity, calculation of  $\sigma$  from  $\eta$ ; variation of viscosity with temperature and pressure. Maxwell distribution and its use in evaluating molecular velocities (average, root mean square and most probable) and average kinetic energy, law of equipartition of energy, degrees of freedom and molecular basis of heat capacities

### UNIT II Gaseous state-II and Liquid state:

**[a] Gaseous state:** van der Waals equation of state, its derivation and application in explaining real gas behaviour, Behaviour of real gases: Deviations from ideal gas behaviour, compressibility factor,  $Z$ , and its variation with pressure for different gases. Causes of deviation from ideal behaviour. Isotherms of real gases and their comparison with van der Waals isotherms, continuity of states, critical state, relation between critical constants and van der Waals constants, law of corresponding states. **[b] Liquid state:** Qualitative treatment of the structure of the liquid state; physical properties of liquids; vapour pressure, surface tension and viscosity, and their determination (Iostenioscopic method, drop weight method, Capillary rise method and the Ostwald visocometer method). Effect of addition of various solutes on surface tension and viscosity.

### UNIT III Solid state:

Nature of the solid state, law of constancy of interfacial angles, law of rational indices, Miller indices, elementary ideas of symmetry, symmetry elements and symmetry operations, qualitative idea of point and space groups, seven crystal systems and fourteen Bravais lattices; X-ray diffraction, Bragg's law, determination of crystal structure (Laue's and powder pattern method). Defects in crystals. Glasses and liquid crystals.

**UNIT IV Ionic equilibria-I:**

Strong, moderate and weak electrolytes, degree of ionization, factors affecting degree of ionization, ionization constant and ionic product of water. Ionization of weak acids and bases, pH scale, common ion effect; dissociation constants of mono-, di- and triprotic acids (exact treatment). Different types of salt; Salt hydrolysis-calculation of hydrolysis constant, Relation between  $K_a$ ,  $K_b$  and  $K_w$ , degree of hydrolysis and pH for different salts; of (1) strong acid and weak base (2) weak acid and strong base.  
(Numerical problems on relevant topics)

**UNIT V Ionic equilibria-II**

Qualitative treatment of acid – base titration curves. Theory of acid–base indicators; selection of indicators and their limitations. Buffer solutions; derivation of Henderson equation and its applications; buffer capacity, buffer range, buffer action and applications of buffers in analytical chemistry and Bio-chemical processes in the human body. Solubility and solubility product of sparingly soluble salts – applications of solubility product principle.

**ORGANIC CHEMISTRY- I  
(Basic & Hydrocarbon)****UNIT I Basics of Organic Chemistry:**

*Organic Compounds:* Classification, and Nomenclature, Hybridization, Shapes of molecules, Influence of hybridization on bond properties.

*Electronic Displacements:* Inductive, electromeric, resonance and mesomeric effects, hyperconjugation and their applications; Dipole moment; Homolytic and Heterolytic fission with suitable examples; Electrophiles and Nucleophiles; Nucleophilicity and basicity; Types, shape and their relative stability of Carbocations, Carbanions, Free radicals and Carbenes. Introduction to types of organic reactions and their mechanism: Addition, Elimination and Substitution reactions.

**UNIT II Stereochemistry:**

Fischer Projection, Newmann and Sawhorse Projection formulae and their interconversions; Geometrical isomerism: cis–trans and, syn-anti isomerism E/Z notations with C.I.P rules.

*Optical Isomerism:* Optical Activity, Specific Rotation, Chirality/Asymmetry, Enantiomers, Molecules with two or more chiral-centres, Distereoisomers, meso structures, Racemic mixture and resolution. Relative and absolute configuration: D/L and R/S designations.

**UNIT III Chemistry of Aliphatic Hydrocarbons:****[a] Carbon-Carbon sigma bonds**

Chemistry of alkanes: Formation of alkanes, Wurtz Reaction, Wurtz-Fittig Reactions, Free radical substitutions:

**[b] Carbon-Carbon pi bonds:**

Formation of alkenes and alkynes by elimination reactions, Mechanism of E1, E2, reactions. Saytzeff and Hofmann eliminations.

*Reactions of alkenes:* Electrophilic additions their mechanisms (Markownikoff/ Anti Markownikoff addition), mechanism of oxymercuration-demercuration,

hydroborationoxidation, ozonolysis, reduction (catalytic and chemical) 1,2- and 1,4-addition reactions in conjugated dienes and, Diels-Alder reaction; Allylic and benzylic bromination and mechanism, e.g. propene, 1-butene, toluene, ethylbenzene.

#### **UNIT IV Alkynes, Cycloalkanes and Conformational Analysis**

**[a]** Reactions of alkynes: Acidity, Electrophilic and Nucleophilic additions. Hydration to form carbonyl compounds, Alkylation of terminal alkynes

**[b]** Types of cycloalkanes and their relative stability, Baeyer strain theory, Conformation analysis of alkanes: Relative stability: Energy diagrams of cyclohexane:

**[c]** Chair, Boat and Twist boat forms; Relative stability with energy diagrams.

#### **UNIT V Aromatic Hydrocarbons**

*Aromaticity:* Hückel's rule, aromatic character of arenes, cyclic carbocations/carbanions and heterocyclic compounds with suitable examples. Electrophilic aromatic substitution: halogenation, nitration, sulphonation and Friedel-Craft's alkylation/acylation with their mechanism. Directing effects of the groups.

### **PHYSICAL CHEMISTRY- II (Thermodynamic and its Application)**

#### **UNIT I Chemical Thermodynamics-I:**

Intensive and extensive variables; state and path functions; isolated, closed and open systems; zeroth law of thermodynamics.

*First law:* Concept of heat,  $q$ , work,  $w$ , internal energy,  $U$ , and statement of first law; enthalpy,  $H$ , relation between heat capacities, calculations of  $q$ ,  $w$ ,  $U$  and  $H$  for reversible, irreversible and free expansion of gases (ideal and van der Waals) under isothermal and adiabatic conditions.

*Second Law:* Concept of entropy; thermodynamic scale of temperature, statement of the second law of thermodynamics; molecular and statistical interpretation of entropy. Calculation of entropy change for reversible and irreversible processes.

#### **UNIT II Chemical Thermodynamics-II:**

*Third Law:* Statement of third law, concept of residual entropy, calculation of absolute entropy of molecules.

*Thermochemistry:* Heats of reactions: standard states; enthalpy of formation of molecules and ions and enthalpy of combustion and its applications; Hess law of constant summation, 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.

**UNIT III Free Energy Functions and Systems of Variable Composition:**

**[a]**Free Energy Functions: Gibbs and Helmholtz energy; variation of  $S$ ,  $G$ ,  $A$  with  $T$ ,  $V$ ,  $P$ ; Free energy change and spontaneity. Relation between Joule-Thomson coefficient and other thermodynamic parameters; inversion temperature; Gibbs-Helmholtz equation; Maxwell relations; thermodynamic equation of state.

**[b]**Systems of Variable Composition: Partial molar quantities; Gibbs-Duhem equation, chemical potential of ideal mixtures, change in thermodynamic functions in mixing of ideal gases.

**UNIT IV 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. Equilibrium constants and their quantitative dependence on temperature, pressure and concentration. Free energy of mixing and spontaneity; thermodynamic derivation of relations between the various equilibrium constants  $K_p$ ,  $K_c$  and  $K_x$ . Le Chatelier principle (quantitative treatment);

**Solutions and Colligative Properties:**

**UNIT V** Dilute solutions; lowering of vapour pressure, Raoult's and Henry's Laws and their applications. Thermodynamic criteria for ideal solution. Thermodynamic derivation using chemical potential to derive relations between the four colligative properties [(i) relative lowering of vapour pressure, (ii) elevation of boiling point, (iii) Depression of freezing point, (iv) osmotic pressure] and amount of solute. Applications in calculating molar masses of normal, dissociated and associated solutes in solution.

**INORGANIC CHEMISTRY-II****(s- & p- Blocks elements)****UNIT I General Principles of Metallurgy:**

Chief modes of occurrence of metals based on standard electrode potentials. Ellingham diagrams for reduction of metal oxides using carbon and carbon monoxide as reducing agent. Electrolytic Reduction, Hydrometallurgy. Methods of purification of metals: Electrolytic process, Parkering process, van Arkel-de Boer process and Mond's process, Zone refining, oxidative process, Amalgamation process, Poling process.

**UNIT II Acids and Bases:**

Arrhenius concept of acids and bases, Brønsted-Lowry concept of acids-bases, LuxFlood concept of acids –bases, solvent systems, relative strength of acids, types of acid-base reactions, levelling solvents, Lewis acid-base concept and its limitations, Pearsons classification of Lewis acids and Lewis bases, Hard and Soft Acids and Bases (HSAB) Principle and applications.

**UNIT III Chemistry of s and p Block Elements:**

Inert pair effect, Relative stability of different oxidation states, diagonal relationship and anomalous behaviour of first member of each group. Allotropy, catenation, isomorphism. Complex formation tendency of  $s$  and  $p$  block elements. Hydrides and their classification-ionic, covalent and interstitial.

#### **UNIT IV Chemistry of *s* and *p* Block Elements:**

Study of the following compounds with emphasis on structure, bonding, preparation, properties and uses: Boric acid and borates, boron nitrides, borohydrides (diborane), silanes, Oxides and oxoacids of nitrogen, Phosphorus and chlorine, Peroxo acids of sulphur, interhalogen compounds, polyhalide ions, pseudohalogens and properties of halogens

#### **UNIT V Noble Gases and Inorganic Polymers:**

Occurrence and uses, rationalization of inertness of noble gases, Clathrates; preparation, properties and structures of XeF<sub>2</sub>, XeF<sub>4</sub>, XeF<sub>6</sub>, XeO<sub>3</sub>, XeOF<sub>4</sub> and XeOF<sub>2</sub>; Nature of bonding in noble gas compounds (Valence bond treatment and MO treatment for XeF<sub>2</sub> and XeF<sub>4</sub>). Molecular shapes of noble gas compounds (VSEPR theory).

*Inorganic Polymers:* Types of inorganic polymers, comparison with organic polymers, synthesis, structural aspects and applications of silicones and siloxanes. Borazines, silicates and phosphazenes.

### **ORGANIC CHEMISTRY-II (Oxygen containing functional groups)**

#### **UNIT I Chemistry of Halogenated Hydrocarbons:**

*Alkyl halides:* Methods of preparation, nucleophilic substitution reactions – SN<sub>1</sub>, SN<sub>2</sub> mechanisms with stereochemical aspects and effect of solvent etc.; nucleophilic substitution vs. elimination.

*Aryl halides:* Preparation, including preparation from diazonium salts. nucleophilic aromatic substitution; S<sub>N</sub>Ar. Relative reactivity of alkyl, allyl/benzyl, vinyl and aryl halides towards nucleophilic substitution reactions. Organometallic compounds of Mg and Li – Use in synthesis of organic compounds.

#### **UNIT II Alcohols, Phenols:**

*Alcohols:* preparation, properties and relative reactivity of 1°, 2°, 3° alcohols; Preparation and properties of glycols: Oxidation by periodic acid and lead tetraacetate, Pinacol-Pinacolone rearrangement;

*Phenols:* Preparation and properties; Acidity and factors effecting it, Ring substitution reactions, Reimer–Tiemann and Kolbe’s–Schmidt Reactions, Fries and Claisen rearrangements with mechanism.

#### **UNIT III Ethers, Epoxides and Sulphur containing compounds:**

*Ethers:* Preparation and reactions with acids

*Epoxides:* Reactions of epoxides with alcohols, ammonia derivatives and LiAlH<sub>4</sub>  
Preparation and reactions of thiols, thioethers and sulphonic acids.

#### **UNIT IV Carbonyl Compounds:**

Structure, reactivity and preparation; Nucleophilic additions, Nucleophilic addition-elimination reactions with ammonia derivatives with mechanism; Mechanisms of Aldol and Benzoin condensation, Knoevenagel condensation, Claisen-Schmidt, Perkin, Cannizzaro and Wittig reaction,  $\alpha$ -substitution reactions, oxidations and reductions (Clemmensen, Wolff-Kishner, LiAlH<sub>4</sub>, NaBH<sub>4</sub>, MPV. Addition reactions of unsaturated carbonyl compounds: Michael addition.

**UNIT V Carboxylic Acids and their Derivatives:**

Preparation, physical properties and reactions of monocarboxylic acids: Preparation and reactions of acid chlorides, anhydrides, esters and amides; Comparative study of nucleophilic substitution at acyl group -Mechanism of acidic and alkaline hydrolysis of esters, Claisen condensation, Dieckmann and Reformatsky reactions, Simple reactions of dicarboxylic acids and hydroxy acids; maleic and fumaric acids.

**PHYSICAL CHEMISTRY-III****(Phase Equilibria and Chemical Kinetics)****UNIT I Phase Equilibria-I**

Concept of phases, components and degrees of freedom, derivation of Gibbs Phase Rule for nonreactive and reactive systems; Clausius-Clapeyron equation and its applications to solid-liquid, liquid-vapour and solid-vapour equilibria, Reduced phase rule (definition), phase diagram for one component systems, ( $H_2O$  system) with applications. Phase diagrams for systems of solid-liquid equilibria involving eutectic, KI- $H_2O$  system congruent Mg-Zn system and incongruent melting points. NaCl- $H_2O$  system

**UNIT II Phase Equilibria-II**

Two component system of solid solution (Pb-Ag) Three component systems, waterchloroform-acetic acid system, triangular plots.

*Binary solutions:* Gibbs-Duhem-Margules equation, its derivation and applications to fractional distillation of binary miscible liquids (ideal and nonideal), azeotropes, Lever rule, partial miscibility of liquids, CST, miscible pairs, steam distillation. Nernst distribution law: its derivation and applications.

**UNIT III Chemical Kinetics:**

Order and molecularity of a reaction, factors affecting rate of reaction, determination of rate laws, derivation of integrated rate law expression upto second order reactions. Determination of order of reaction (integrated, differential, graphical and half life period method) up to first order reactions, experimental methods of the determination of rate laws.

**UNIT IV Chemical Kinetics**

Kinetics of complex reactions; Opposing reactions, parallel reactions, consecutive reactions and their differential rate equations (steady-state approximation in reaction mechanisms), chain reactions. Temperature dependence of reaction rates; Arrhenius equation; activation energy. Collision theory of reaction rates, Activated complex Theory (Eyring equation)

**UNIT V Catalysis and Surface chemistry:**

**[a]** Types of catalyst, specificity and selectivity, mechanisms of catalyzed reactions at solid surfaces; effect of particle size and efficiency of nanoparticles as catalysts.

Enzyme catalysis, Michaelis-Menten mechanism, acid-base catalysis.

**[b]** Surface chemistry: Physical adsorption, chemisorption, adsorption isotherms. nature of adsorbed state. Factors affecting adsorption, Freundlich adsorption isotherm derivation, Langmuir adsorption (eliminating idea only)

## INORGANIC CHEMISTRY-III (Coordination Chemistry)

### UNIT I Coordination Chemistry-I

IUPAC nomenclature of coordination compounds, isomerism in coordination compounds. Stereochemistry of complexes with 4 and 6 coordination numbers. Chelate effect, polynuclear complexes, Labile and inert complexes. Werner's theory, valence bond theory (inner and outer orbital complexes), electroneutrality principle and back bonding.

### UNIT II Coordination Chemistry:

Crystal field theory, measurement of  $10 Dq$  ( $\Delta_o$ ), CFSE in weak and strong fields, pairing energies, factors affecting the magnitude of  $10 Dq$  ( $\Delta_o$ ,  $\Delta_t$ ). Octahedral vs. tetrahedral coordination, tetragonal distortions from octahedral geometry Jahn-Teller theorem, square planar geometry. Qualitative aspect of Ligand field and MO Theory.

### UNIT III Transition Elements:

General group trends with special reference to electronic configuration: atomic and ionic radii, colouration, variable valency, magnetic, catalytic properties, ability to form alloys, interstitial compounds and ability to form complexes. Differences between the first, second and third transition series. Chemistry of Ti, V, Cr, Mn, Fe and Co in various oxidation states (excluding their metallurgy)

### UNIT IV Lanthanoids and Actinoids:

Introduction, Electronic configuration, oxidation states, ionic radii, colour, complex formation tendency, spectral and magnetic properties, lanthanide contraction: Causes and consequences, separation of lanthanides (ion-exchange method and from monazite sand). Comparison of lanthanides and actinides, chemistry of separation of Np, Pu and Am from U. Preparation, reactions, structure and uses of uranium hexafluoride.

### UNIT V Bioinorganic Chemistry:

Essential and trace elements in biological system. Sodium/Potassium pump, carbonic anhydrase and carboxypeptidase. Excess and deficiency of some trace metals. Toxicity of metal ions (Hg, Pb, Cd and As), reasons for toxicity, Use of chelating agents in medicine. Iron and its application in bio-systems; Storage and transfer of iron. Metalloporphyrins (chlorophyll), heme-proteins (Haemoglobin, Myoglobin) and crownethers. Biological role of alkaline earth metal ions with reference to  $Ca^{+2}$ .

## ORGANIC CHEMISTRY-III (Heterocyclic Compound)

### UNIT I Nitrogen Containing Functional Groups:

Preparation and important reactions of nitro and compounds, nitriles and isonitriles  
Amines: Effect of substituent and solvent on basicity; Preparation and properties: Gabriel phthalimide synthesis, Carbylamine reaction, Mannich reaction, Hoffmann's exhaustive methylation, Hofmann-elimination reaction; Distinction between 1°, 2° and 3° amines with Hinsberg reagent and nitrous acid. Diazonium Salts: Preparation and their synthetic applications

### UNIT II Polynuclear Hydrocarbons:

Reactions of naphthalene phenanthrene and anthracene Structure, Preparation and structure elucidation and important derivatives of naphthalene and anthracene.

**UNIT III Heterocyclic Compounds:**

Classification and nomenclature, Structure, aromaticity in 5-numbered and 6-membered rings containing one heteroatom; Synthesis, reactions and mechanism of substitution reactions of: Furan, Pyrrole (Paal-Knorr synthesis, Knorr pyrrole synthesis, Hantzsch synthesis), Thiophene, Pyridine (Hantzsch synthesis), Pyrimidine, Structure elucidation of indole, Fischer indole synthesis and Madelung synthesis), Structure elucidation of quinoline and isoquinoline, Skraup synthesis, Knorr quinoline synthesis, Bischler-Napieralski reaction,

**UNIT IV Alkaloids:**

Natural occurrence, General structural features, Isolation and their physiological action Hoffmann's exhaustive methylation, Emde's modification, Structure elucidation and synthesis of Hygrine and Nicotine. Medicinal importance of Nicotine, Hygrine, Quinine, Morphine, Cocaine, and Reserpine.

**UNIT V Terpenes:**

Occurrence, classification, isoprene rule; Elucidation of structure and synthesis of Citral, Neral and  $\alpha$ -terpineol.

**PHYSICAL CHEMISTRY-IV****(Electrochemistry-I, Quantum Chemistry-I & Spectroscopy-I)****UNIT I Conductance-I:**

Arrhenius theory of electrolytic dissociation and its limitations. Conduction in metals and in electrolyte solutions, electrolysis, Conductivity, equivalent and molar conductivity and their variation with dilution for weak and strong electrolytes. Molar conductivity at infinite dilution. Measurement of conductance, Kohlrausch law of independent migration of ions. Ostwald's dilution law, its uses and limitations, Debye-Hückel-Onsager equation. Ionic velocities, mobilities and their determinations, transference numbers and their relation to ionic mobilities, determination of transport numbers using Hittorf and Moving Boundary methods.

**UNIT II Electrochemistry-I:**

Quantitative aspects of Faraday's laws of electrolysis, rules of oxidation/reduction of ions based on half-cell potentials, applications of electrolysis in metallurgy and industry. Electrolytic and Galvanic cells, reversible and irreversible cells with examples. Electromotive force of a cell and its measurement, Nernst equation; Standard electrode (reduction) potential and its application to different kinds of half-cells. Polarization, decomposition potential, overvoltage, polarography, corrosion.

**UNIT III Quantum Chemistry-I:**

Postulates of quantum mechanics, quantum mechanical operators, Schrödinger equation and its application to free particle and "particle-in-1 D-box" quantization of energy levels, zero-point energy and Heisenberg Uncertainty principle; wave functions, probability distribution functions, Qualitative treatment of hydrogen atom and hydrogen-like ions: setting up of Schrödinger equation in spherical polar coordinates, radial part, quantization of energy (only final energy expression). Average and most probable distances of electron from nucleus.

#### **UNIT IV Molecular Spectroscopy-I:**

Interaction of electromagnetic radiation with molecules and various types of spectra; Born-Oppenheimer approximation.

Rotation spectroscopy: Selection rules, intensities of spectral lines, determination of bond lengths of diatomic and linear tri-atomic molecules, isotopic substitution.

Vibrational spectroscopy: Classical equation of vibration, computation of force constant, amplitude of diatomic molecular vibrations, anharmonicity, Morse potential, dissociation energies, fundamental frequencies, overtones, hot bands, degrees of freedom for polyatomic molecules, modes of vibration, concept of group frequencies.

Vibration-rotation spectroscopy: diatomic vibrating rotator, P, Q, R branches.

Raman spectroscopy: Qualitative treatment of Rotational Raman effect; Stokes and anti-Stokes lines; their intensity difference, rule of mutual exclusion.

#### **UNIT V Electrical & Magnetic Properties of Atoms and Molecules:**

Basic ideas of electrostatics, Electrostatics of dielectric media, Clausius-Mosotti equation, Lorenz-Laurentz equation, Debye equation, dependence of polarizability on frequency, bond moments Dipole moment, molecular polarizabilities and their measurements. Dielectric polarization and dielectric constant, electric polarization of molecules, determination of dielectric constant, determination of dipole moments, molar refraction and molar polarization. Diamagnetism, paramagnetism, magnetic susceptibility and its measurement, molecular interpretation.

### **ORGANIC CHEMISTRY-IV**

#### **(Biomolecules)**

##### **UNIT I Nucleic Acids:**

Components of nucleic acids, Nucleosides and nucleotides; Structure, synthesis: Adenine, Guanine, Cytosine, Uracil and Thymine; Structure of polynucleotides.

##### **UNIT II Amino Acids, Peptides and Proteins:**

Amino acids, Peptides and their classification.  $\alpha$ -Amino Acids - Synthesis, ionic properties and reactions. Zwitterions,  $pK_a$  values, isoelectric point and electrophoresis; Study of peptides: determination of their primary structures-end group analysis, methods of peptide synthesis. Synthesis of peptides using Nprotecting, C-protecting and C-activating groups -Solid-phase synthesis

##### **UNIT III Enzymes:**

Introduction, classification and characteristics of enzymes. Salient features of active site of enzymes. Mechanism of enzyme action (taking trypsin as example), factors affecting enzyme action, coenzymes and cofactors and their role in biological reactions, specificity of enzyme action (including stereospecificity), enzyme inhibitors and their importance, phenomenon of inhibition (competitive, uncompetitive and noncompetitive inhibition including allosteric inhibition).

##### **UNIT IV Lipids:**

Introduction to oils and fats; common fatty acids present in oils and fats, Hydrogenation of fats and oils, Saponification value, acid value, iodine number. Rancidity.

##### **UNIT V Pharmaceutical Compounds: Structure and Importance:**

Classification, structure and therapeutic uses of antipyretics: Paracetamol (with synthesis), Analgesics: Ibuprofen (with synthesis), Antimalarials: Chloroquine (with

synthesis). An elementary treatment of Antibiotics and detailed study of chloramphenicol, Medicinal values of vitamin C and antacid (ranitidine).

**UNIT I Conductance-II:**

Theory of strong electrolytes, Relaxation effect, Electrophoretic effect, Wien effect, Debye-Falkenhagen effect, Walden's rules. Activity coefficients of electrolytes, Mean Ionic activity coefficients, Ionic strength, Concentration cells with and without transference, liquid junction potential; Applications of conductance measurement: (i) degree of dissociation of weak electrolytes, (ii) ionic product of water (iii) solubility and solubility product of sparingly soluble salts, (iv) conductometric titrations, and (v) hydrolysis constants of salts.

**UNIT II Electrochemistry-II:**

Types of electrodes: Metal-metal ion electrodes, metal-metal insoluble salt electrodes, metal-amalgam electrodes, redox electrodes, calomel-electrode. Application of EMF measurements in determining (i) free energy, enthalpy and entropy of a cell reaction, (ii) equilibrium constants, and (iii) pH values, using hydrogen, quinone-hydroquinone, glass electrodes, Qualitative discussion of potentiometric titrations (acid-base, redox, precipitation). The structures of electrified interfaces, The Helmholtz-Perrin model, Stern model; Electrocatalysis.

**UNIT III Quantum Chemistry-II:**

Setting up of Schrödinger equation for many-electron atoms (He, Li). Need for approximation methods. Statement of variation theorem and application to simple systems; Chemical bonding: Covalent bonding, valence bond and molecular orbital approaches, LCAO-MO treatment of  $H_2^+$ . Bonding and antibonding orbitals. Qualitative extension to  $H_2$ . Comparison of LCAO-MO and VB treatments of  $H_2$ .

**UNIT IV Molecular Spectroscopy-II:**

Electronic spectroscopy: Franck-Condon principle, electronic transitions, singlet and triplet states, fluorescence and phosphorescence, dissociation and pre-dissociation, calculation of electronic transitions of polyenes using free electron model. Nuclear Magnetic Resonance (NMR) spectroscopy: Principles of NMR spectroscopy, Larmor precession, chemical shift and low resolution spectra, different scales, spin-spin coupling and high resolution spectra, interpretation of PMR spectra of organic molecules. Electron Spin Resonance (ESR) spectroscopy: Its principle, hyperfine structure, ESR of simple radicals.

**UNIT V Photochemistry:**

Characteristics of electromagnetic radiation, Lambert-Beer's law and its limitations, physical significance of absorption coefficients. Laws, of photochemistry, quantum yield, actinometry, examples of low and high quantum yields, photochemical equilibrium and the differential rate of photochemical reactions, photosensitised reactions, quenching. Role of photochemical reactions in biochemical processes, photostationary states, chemiluminescence.

## INORGANIC CHEMISTRY-IV

### (Organometallic Chemistry)

#### UNIT I Theoretical Principles in Qualitative Analysis (H<sub>2</sub>S Scheme):

Basic principles involved in analysis of cations and anions and solubility products, common ion effect. Principles involved in separation of cations into groups and choice of group reagents. Interfering anions (fluoride, borate, oxalate and phosphate) and need to remove them after Group II.

#### UNIT II Organometallic Compounds:

Definition and classification of organometallic compounds on the basis of bond type. Concept of hapticity of organic ligands. Metal carbonyls: 18 electron rule, electron count of mononuclear, polynuclear and substituted metal carbonyls of 3d series. General methods of preparation (direct combination, reductive carbonylation, thermal and photochemical decomposition) of mono and binuclear carbonyls of 3d series. Structures of mononuclear and binuclear carbonyls of Cr, Mn, Fe, Co and Ni using VBT. pi-acceptor behaviour of CO (MO diagram of CO to be discussed).

#### UNIT III Organometallic Compounds:

*Zeise's salt*: Preparation and structure, evidences of synergic effect and comparison of synergic effect with that in carbonyls.

*Metal Alkyls*: Important structural features of methyl lithium (tetramer) and trialkylaluminium (dimer), concept of multicentre bonding in these compounds. Role of triethylaluminium in polymerisation of ethene (Ziegler – Natta Catalyst). Species present in ether solution of Grignard reagent and their structures.

*Ferrocene*: Preparation and reactions (acetylation, alkylation, metallation, Mannich Condensation). Structure and aromaticity. Comparison of aromaticity and reactivity with that of benzene.

#### UNIT IV Reaction Kinetics and Mechanism:

Introduction to inorganic reaction mechanisms. Substitution reactions in square planar complexes, Trans- effect, theories of trans effect, Mechanism of nucleophilic substitution in square planar complexes, Thermodynamic and Kinetic stability, Kinetics of octahedral substitution, Ligand field effects and reaction rates, Mechanism of substitution in octahedral complexes.

#### UNIT V Catalysis by Organometallic Compounds:

Study of the following industrial processes and their mechanism:

1. Alkene hydrogenation (Wilkinsons Catalyst)
2. Hydroformylation (Co salts)
3. Wacker Process
4. Synthetic gasoline (Fischer Tropsch reaction)
5. Synthesis gas by metal carbonyl complexes

## ORGANIC CHEMISTRY-V

### (Organic spectroscopy)

#### UNIT I Organic Spectroscopy-I:

*UV Spectroscopy*: Types of electronic transitions,  $\lambda$  max, Chromophores and Auxochromes, Bathochromic and Hypsochromic shifts, Intensity of absorption; Application of Woodward Rules for calculation of  $\lambda$  max for the following systems:  $\alpha$ ,  $\beta$  unsaturated aldehydes, ketones, carboxylic acids and esters; Conjugated dienes:

alicyclic, homoannular and heteroannular; Extended conjugated systems (aldehydes, ketones and dienes).

*IR Spectroscopy:* Fundamental and non-fundamental molecular vibrations; IR absorption positions of O, N and S containing functional groups; Effect of H-bonding, conjugation, resonance and IR absorptions; Fingerprint region and its significance; application in functional group analysis.

## UNIT II Organic Spectroscopy-II:

*NMR Spectroscopy:* Basic principles of Proton Magnetic Resonance, chemical shift and factors influencing it; Spin – Spin coupling and coupling constant; Anisotropic effects in alkene, alkyne, aldehydes and aromatics, Interpretation of NMR spectra of simple compounds.

## UNIT III Carbohydrates:

Occurrence, classification and their biological importance. Monosaccharides: Constitution of glucose and fructose, epimers and anomers, mutarotation, determination of ring size of glucose, Haworth projections and conformational structures; Interconversions of aldoses and ketoses; Killiani-Fischer synthesis and Ruff degradation; Disaccharides – Structure elucidation of maltose and sucrose. Polysaccharides – Elementary treatment of starch, cellulose.

## UNIT IV Dyes:

Classification, Colour and constitution; Mordant and Vat Dyes; Synthesis and applications of: Azo dyes – Methyl Orange and Congo Red (mechanism of Diazo Coupling); Triphenyl Methane Dyes -Malachite Green, Rosaniline and Crystal Violet; Phthalein Dyes – Phenolphthalein and Fluorescein; Natural dyes –structure elucidation and synthesis of Alizarin and Indigotin.

## UNIT V Polymers:

Number average molecular weight, Weight average molecular weight, Polydispersity Index. Polymerisation reactions -Addition and condensation -Mechanism of cationic, anionic and free radical addition polymerization; Metallocene-based Ziegler-Natta polymerisation of alkenes; Preparation and applications of plastics – thermosetting (phenol-formaldehyde, Polyurethanes) and thermosoftening (PVC, polythene); Fabrics – natural and synthetic (acrylic, polyamido, polyester); Rubbers – natural and synthetic: Buna-S, Chloroprene and Neoprene; Vulcanization; Polymer additives; Biodegradable with examples.

## ORGANIC CHEMISTRY-V

### ANALYTICAL METHODS IN CHEMISTRY

#### Qualitative and quantitative aspects of analysis:

evaluation of analytical data, errors, accuracy and precision, methods of their expression, normal law of distribution if indeterminate errors, statistical test of data; F, Q and t test, rejection of data.

#### Optical methods of analysis:

Origin of spectra, interaction of radiation with matter, fundamental laws of spectroscopy and selection rules, validity of Beer-Lambert's law.

*UV-Visible Spectrometry:* Basic principles of instrumentation (choice of source, monochromator and detector) for single and double beam instrument;

*Infrared Spectrometry:* Basic principles of instrumentation (choice of source, monochromator & detector) for single and double beam instrument; sampling techniques. Structural illustration through interpretation of data, Effect and importance of isotope substitution.

*Flame Atomic Absorption and Emission Spectrometry:* Basic principles of instrumentation (choice of source, monochromator, detector, choice of flame and Burner designs. Techniques of atomization and sample introduction, Techniques for the quantitative estimation of trace level of metal ions from water samples.

**Thermal methods of analysis:**

Theory of thermogravimetry (TG), basic principle of instrumentation. Techniques for quantitative estimation of Ca and Mg from their mixture.

**Electro analytical methods:**

Classification of electroanalytical methods, basic principle of pH metric, potentiometric and conductometric titrations. Techniques used for the determination of equivalence points. Techniques used for the determination of pKa values.

**Separation techniques:**

Solvent extraction: Classification, principle and efficiency of the technique.

Mechanism of extraction: extraction by solvation and chelation.

Technique of extraction: batch, continuous and counter current extractions.

Qualitative and quantitative aspects of solvent extraction: extraction of metal ions from aqueous solution, extraction of organic species from the aqueous and nonaqueous media.

Chromatography: Classification, principle and efficiency of the technique.

Mechanism of separation: adsorption, partition & ion exchange.

Development of chromatograms: frontal, elution and displacement methods.

Qualitative and quantitative aspects of chromatographic methods of analysis: IC, GLC, GPC, TLC and HPLC.

Stereoisomeric separation and analysis: Measurement of optical rotation, calculation of Enantiomeric excess (ee)/ diastereomeric excess (de) ratios and determination of enantiomeric composition using NMR.