SUBJECT : CHEMISTRY

SYLLABUS

INORGANIC CHEMISTRY

Unit I

Chemical Periodicity: Modern periodic law – Periodicity in properties, the trend in the atomic and ionic radii, ionization potential and electron affinity along the period. Effective nuclear charge – Slater rules and its uses.

Structure and bonding in homo – and hetero-nuclear molecules, including shapes of molecules. (VSEPR Theory): Linear combination of AOs in hybridization, Stereochemistry of the hybrid orbitals, Calculation of s & p characters of equivalence and non-equivalence of hybrid orbitals.

MO theory: MO diagram for the homo-nuclear diatomic molecules, hetero-nuclear diatomic molecules and triatomic molecules.

Concepts of acids and bases: HSAB concept – theory, classification, characteristics of hard and soft species – symbiosis. Bronsted-Lowry concept – conjugate acid-base theory – relative strength of acids and bases, applications. Lewis concept-characteristic features of the Lewis theory.

Non-Aqueous Solvents: Classification of solvents –characteristics of a solvent/ ionizing solvent. Advantages and disadvantages of the following non-aqueous solvents: NH_3, HF, HCN, acetic acid, H_2SO_4. Molten salts as solvents and ionic liquids, supercritical fluids in inorganic chemistry.

Nature of bonding of Main group elements: Alkali and alkaline earth metal complexes: ligands – alkylamines, alkoxides, b-diketones and crown ethers. Electron rich and electron deficient compound of main group elements. Allotropes of carbon.

Transition elements and coordination compounds: Structure, bonding theories, spectral and magnetic properties, reaction mechanisms. Transition Elements – General group trends, Stability of various oxidation states. Difference between the first, second and third transition series. Types of transitions, selection rules for electronic transitions, ground states, correlation diagrams, Orgel and Tanabe Sugano diagrams.

Coordination compounds: Crystal field theory – splitting of d orbitals under different geometries – CFSE – Spectrochemical series – Jahn Teller distortion – Limitations of CFT – MO theory – sigma and pi-bonding in complexes.

Inner transition elements: Spectral, magnetic, redox properties and its applications.

Unit II **Organometallic Compounds:** synthesis, structure of bonding and important types of reactions of organometallic compounds – oxidative addition, reductive elimination. Catalysis – Hydrogenation, Hydroformylation, Monsanto and Wacker processes, alkene polymerization.

Cages and clusters: Chemistry and molecularity of metal clusters such as binuclear and trinuclear metal clusters, metal carbonyl, halide type clusters, Borazines and phosphazenes.

Bioinorganic Chemistry: Structures and biological importance of porphyrin ring system, metalloporphyrin, haemoglobin, myoglobin and chlorophyll. Iron-sulphur proteins, Metalloenzymes, Photosynthesis – photosystem-I and photosystem-II. Metal storage and transport – Fe, Cu and Zn storage and transport.

Nuclear chemistry: Nuclear fission and fusion reactions, radio-analytical techniques and activation analysis. Decay modes, types of nuclear reaction – threshold energy, energy barrier, Q-value, nuclear cross section, photonuclear reaction, nuclear fission, spallation, fragmentation and fusion. Fission as a chain reaction – nuclear fuels: fertile and fissile isotopes, radiation hazards – nuclear reactors in India.

PHYSICAL CHEMISTRY

Unit III **Basic principles of quantum mechanics:** Planck's quantum hypothesis and black body radiation; photoelectric effect – classical theory and Einstein's quantum theory. Bohr's theory of hydrogen atom; failure of Bohr's model. Postulate of quantum chemistry; Heisenberg's uncertainty principle; Davison and Germer experiment. Operator algebra; linear, differential and Hermitian operator; Hamiltonian operator; angular momentum; eigen values and eigen functions. Wave equation – time-independent and time-dependent Schrodinger's wave equation. Particle–in–a–box (1D & 3D); rigid rotator; harmonic oscillator and hydrogen atom, including shapes of atomic orbitals; orbital and spin-angular momenta; tunnelling.

Approximation method of quantum mechanics: Variational principle and its application to hydrogen molecule. Perturbation theory up to second order in energy and its applications.

Atomic structure and Spectroscopy: Term symbols, RS and jj coupling, spectra of hydrogen, many electron systems and anti-symmetry principle.

Chemical bonding in diatomic: Elementary concepts of MO and VB theories, Huckel theory conjugated pi electron system (ethylene, butadiene and benzene).

Chemical applications group theory: Symmetry elements, symmetry operations, point groups, their symbols, character tables (C2v, C2h, C3v and C4v), reducible and irreducible representation, great orthogonality theorem and its consequences. Applications of group theory in vibrational spectroscopy, symmetry aspects of molecular vibrations, symmetry selection rules for IR and Raman spectra. Determining symmetries of normal modes of vibration. Symmetry applied to MO theory and orbital hybridization.

Molecular spectroscopy: Spectrum, electromagnetic radiation and its properties, regions of electromagnetic spectrum and their uses, rotational and vibrational spectra of diatomic, Born-Oppenheimer approximation. UV-Visible spectroscopy – principle, Beer-Lambert's law, instrumentation, types of electronic transitions, chromophore and auxochromes. Absorption bands and intensity, factors governing absorption maximum and intensity. UV-VIS spectra of simple organic compounds such as alkenes, phenols, anilines, carbonyl compounds and 1,3-diketones.

IR spectroscopy: Principle, regions of IR, selection rule of IR, modes of vibration of diatomic, triatomic linear (CO_2) and nonlinear molecules (H_2O); types of molecular vibration, application of IR spectroscopy, overtones, IR regions of alcohols, aldehyde, ketones. Raman spectroscopy – Principle, types of stokes and anti–stokes lines. Raman shift – difference between Raman and IR spectroscopy, mutual exclusion principle, vibrations of CO_2 molecule, dipole moment and polarizability.

Electronic spectra: Theory of ESR spectra, position of ESR absorption, g and A factor, hyperfine structure, ESR spectra of simple carbon centered free radicals – CH_3, CD_3 electronic spectra of diatomic molecule – Morse function and Frank Condon principle and basic principles of magnetic resonance spectroscopy.

Chemical thermodynamics: Scope and limitations of thermodynamic system, surroundings and boundary – types of system, extensive and intensive properties; thermodynamic processes – state functions, enthalpy, entropy and internal energy; concept of work and heat, heat capacity, molar heat capacity, first law of thermodynamics and its mathematical expressions. Hess's law of constant heat summation – enthalpies of bond dissociation, combustion, formation, atomization, sublimation, phase transition, hydration, ionization and solution.

Reversible and irreversible process: Spontaneity of processes, criteria for spontaneity with respect to ΔS of the universe and ΔG of the system. Second law of thermodynamics, Clausius's statement and Kelvin – Planck's statement. Third law of thermodynamics and zeroth law of thermodynamics. Joule – Thomson effect, Inversion temperature, Maxwell's relations, Carnot theorem, Gibbs free energy and Helmholtz work function and Nernst heat theorem.

Unit IV

Classical thermodynamics: Partial molar properties, chemical potential, Gibb's-Duhem equation. Determination of partial molar quantities, Thermodynamics of real gases, fugacity – determination of fugacity by graphical and equation of state methods, dependence of temperature, pressure and composition, Thermodynamics of ideal and non-ideal mixtures. Activity and activity coefficients.

Statistical thermodynamics: Concepts of statistical thermodynamics, distinguishable and non-distinguishable particles. Assemblies, ensembles, canonical particles. Boltzmann distribution, Bose-Einstein, Fermi-Dirac statistics, comparison and application; kinetic theory of gases, partition function and their relation to thermodynamic quantities, calculation for model systems.

Phase Rule: Phase, degree of freedom, component, One component system, water system – triple point – two components system, reduced phase rule – eutectic temperature – lead & silver system – congruent and incongruent melting point – Zn & Mg system – NaCl & Water system – CST – Phenol & water system. Henry's law – Raoult's law – Nernst distribution law – solvent extraction – steam distillation – fractional crystallization – Parke's process.

Colloids and Surfaces: Stability and properties of colloids, gold number, types of adsorption, Freundlich's and Langmuir's adsorption isotherms and surface area; heterogeneous catalysis.

Unit V

Chemical kinetics: Empirical rate laws and temperature dependence, Rate of reaction, order of a reaction, examples and rate equations for zero order, first order, second order and third order reaction. Molecularity of a reaction – unimolecular and bimolecular reaction, half-life period. Theories of reaction rates – collision theory, kinetics of collision theory, failure of collision theory, modification of collision theory, Lindeman theory, Hinshelwood theory and transition state theory/absolute reaction rate theory (ARRT). Potential energy surfaces and reaction coordinates. Study of complex reactions – kinetics of reversible, parallel, consecutive and chain reactions, photochemical reactions (H_2-Br_2), steady-state approximation, Stern-Volmer equation. Reactions in solutions – cage effect, primary and secondary salt effects, kinetic isotropic effect, linear free energy relationships, Hammett and Traft equation. Kinetic methods of analysis – flow techniques, stopped-flow and continuous-flow techniques, pulse methods, flash photolysis and pulse radiolysis. Relaxation theory and relaxation technique – kinetic of relaxation methods (T-jump and P-jump). Ionic liquids and its applications. Catalysis – homogeneous catalysis, acid-base catalysis, protolytic and prototropic mechanism, acidity function. enzyme catalysis – Michaelis-Menten kinetics, types of inhibitor in enzyme catalysis.

Electrochemistry: Faraday's laws of electrolysis; specific, equivalent and molar conductance, measurement of conductance. Variation of conductance with dilution for strong and weak electrolytes. Kohlrausch law and its applications. Ostwald's dilution law, transport number and its determination by Hittorf method and moving boundary method. Debye-Huckel theory. Electrochemical cells – cells types, galvanic cells, reversible and irreversible cells, electrode potential, oxidation potential, reduction potential, Nernst equation, redox systems.

Ion-ion interaction and activity coefficient – concept of ionic atmosphere, derivation of Debye-Huckel limiting law, verification and experimental validity. Ion-transport in solution – electrolytic conductance, derivation of Debye-Huckel-onsagar equation and experimental validity, first and second Wien effect. Ion-association – Bjerrum treatment of ion association, factors influencing ion association, effect of ion association on conductivity and activity coefficient of electrolytes in solution and triple ion formation.

Electrodics – electrode-electrolyte interface, electrical double layer – Helmoltz-Perrin, Gouy-Chapman and stern models and its comparison. Electrocapillary phenomena and electrocapillary curves, Lippmann equation, electrocapillary maximum, electrokinetic phenomena, Zeta potential and its applications. Electrode kinetics Bulter-Volmer equation for one-step electron transfer, high field approximation, Tafel equation, high and low over potential limits, ionic equilibria, conductometric and potentiometric titrations. Electrochemical energy systems – primary and secondary cells, fuel cells, types of fuel cells, batteries – primary and secondary batteries, lead acid storage battery, liquid lithium-ion batteries, solid-state sodium-ion batteries.

Solid state: Classification of solids, isotropic and anisotropic crystals, unit cell and space lattice, Miller indices for lattice planes, crystal structures, diffraction of X-rays by crystals, Bragg's law and its applications. Defects of crystals and band structure of solids.

Polymer chemistry: Polymerization – types of polymerization, mechanism of free radical, anionic and cationic polymerization. Polymers molecular weight determination. Preparation, properties, uses of thermoplastic and thermosetting polymers. Elastomers, vulcanization and molding methods of polymers.

ORGANIC CHEMISTRY

Unit VI

IUPAC nomenclature: Organic molecules including regio and stereoisomers.

Principles of stereochemistry: Configurational and conformational isomerism in acyclic and cyclic compounds, stereogenicity, stereoselectivity, enantioselectivity, diastereo selectivity and asymmetric induction. Geometrical isomerism resulting from double bonds – E, Z system of nomenclature, monocyclic compounds and fused ring systems, stereo specific and stereo selective reactions with examples.

Aromaticity: Benzenoid and non-benzenoid compounds, generation and reactions.

Organic reactive intermediates: Generation, stability and reactivity of carbocations, carbanions, free radicals, carbenes, benzynes and nitrenes. Organic reaction mechanisms involving the addition, elimination and substitution reactions with the electrophilic, nucleophilic or radical species. Reaction pathways determination.

Common named reactions and rearrangements – Still Coupling, Heck reaction, Pusond-Kahn Reaction, Suzuki Coupling, Mitsunobu reaction, Baylis-Hillman reaction, Mukiayama’s reaction, Metathesis reaction. Nef reaction, Henry reaction, Ritter reaction. Pinacol-Pinacolone, Wagner-Meerwein, Demjanov, dienone-phenol, Favorskii, Baeyer-Villiger, Wolff, Wittig, Neber, Stevens, Hofmann, Lossen, Curtius, Beckmann, Benzidine and Von Richter rearrangements. Applications in organic synthesis.

Polarimetry: Circular dichroism, Optical Rotatory Dispersion, principles and applications.

Unit VII

Organic transformations and reagents: Functional group inter-conversion including oxidations and reductions. Common catalysts and reagents (organic, inorganic, organometallic and enzymatic), organic transformations in Chemo, regio and stereo selective reactions.

Concepts in organic synthesis: Retro-synthesis, disconnection, synthons, linear and convergent synthesis, umpolung of reactivity and protecting groups. Regioselectivity and chemoselectivity. Alkene synthesis-uses of acetylenes. Two group C-C disconnections in 1,2; 1,3; 1,4; 1,5 difunctional substituents, Diels-Alder reactions, Regio and stereo control in carbonyl condensation, Michael addition and Robinson annulations.

Asymmetric synthesis: Chiral auxiliaries, methods of asymmetric induction, substrate, reagent and catalyst controlled reactions, determination of enantiomeric and diastereomeric excess. Enantiomeric discrimination, resolution, kinetics and optical studies.

Pericyclic reactions: Electrocyclisation, cycloaddition, sigmatropic rearrangements and other related concerted reactions. Principles and applications of photochemical reactions in organic chemistry.

Synthesis and reactivity of common heterocyclic compounds containing one or two heteroatoms: Furan, thiophene, pyrrole, pyridine, quinoline, isoquinoline, indole, flavins and anthocyanins. Chemistry of natural products – Carbohydrates (Maltose, Starch, Cellulose) proteins and peptides, fatty acids, nucleic acids, terpenes, steroids (Chloesterol, Oestrone, Progresterone) and alkaloids (Reticulene, Reserpine, Morphine). Biogenesis of terpenoids (Zingiberene, Squalene, Lanosteroal).

Biopolymers: Structure and functions of proteins and Nucleic acids. Mechanism of Enzyme action on DNA and RNA.

Theory and spectral interpretations – Structure determination of organic compounds by IR, UV-Vis, ^{1}H & ^{13}C NMR and Mass spectroscopic techniques.

ANALYTICAL CHEMISTRY

Unit VIII

Data analysis: Nature of quantitative measurements and treatment of data. Mean, median, precision and accuracy, standard deviation, significant figures, Gaussian distribution curves, Null Hypothesis, Confidence interval of mean, Rejection of data (Q test), Student's t, F tests. Errors – absolute and relative errors, linear regression, covariance and correlation coefficient.

Sampling: Principles of sampling methods for solid, liquids and gases. Gross sampling, Sampler's responsibility and pitfalls, hazards of sampling.

Separation Techniques: Classical forms of chromatography – Introduction, principle and applications of column, thin layer chromatography and paper chromatography, Gas and High-Performance Liquid Chromatography.

Thermo analytical techniques: Principles and applications of TGA, DTA and DSC.

Unit IX

Instrumental Analysis: Fluorimetry – Principles of fluorescence, Instrumentation and its Applications. Turbidimetry and Nephelometry – Theory, instrumentation and its applications.

Emission spectrometry: Principle, instrumentation and interferences, determination of alkali metals and iron in non-ferrous alloys. Flame Photometry – Theory, Instrumentation and a few important applications, Emission Techniques – Theory, techniques of excitation, electrodes and their shapes, flame and plasma emission spectrometry – instrumentation and its applications. Atomic Absorption Spectrometry – Theory, instrumentation (flame and flameless atomization) and its applications.

Mossbauer spectroscopy: Introduction, principle, instrumentation, recoil energy, Doppler effect, number of MB signals, isomer shift, quadrupole splitting, magnetic hyperfine splitting applications.

NMR spectroscopy: Nuclear spin states, NMR active nuclei, nuclear magnetic moment, Larmor equation. Absorption of energy and resonance, population density of nuclear spin states, saturation phenomena, relaxation mechanisms, Bloch equation (only significance and derivation, not required). Comparison of CW and FT NMR instrument. Chemical shift – Standards in NMR, Shielding and De-shielding, Spin-spin coupling, splitting origin and rules – factors affecting coupling constant.

Unit X

Nano Chemistry: Basics, nanoparticles and nanomaterials, types of nanoparticles, preparation, properties and uses of nanoparticles. Carbon nanomaterials – nanotubes, nanorods and nanofibre. Porous solids – nanowires, nanomachines and quantum dots. Methods of nanomaterials synthesis.

Chemical Microscopy: Microscope – parts and optical path application and qualitative study. Electron Microscopy – Principle, Microscope and its operation, sample preparations, applications to analysis, electron probe analyzer, ion microscopy, SEM, TEM, EDS. Fluorescence microscopy – Confocal, Phase contrast SPM, AFM, STM, MFM, EFM. XPS – Electron spectroscopy for Chemical Analysis (ESCA), Principle, Instrumentation, Auger electron spectroscopy – Theory, Principle, instrumentation and general applications – qualitative analysis and depth profiling of solid surfaces.

Green chemistry: Principles and Concepts of Green Chemistry, green solvents, super critical CO_2. Waste minimization techniques Green catalysis.

Environmental Chemistry: Scope and importance, renewable resources, solar, wind, hydrothermal and tidal energies. Polymers, plastics and its harmful environment effects. Pollution effects on human health.

Supramolecular Chemistry: Nature of supramolecular interaction, host-guest interaction, molecular recognition and its types, self assembly, cation binding hosts, cation, anion and neutral receptors, crown ethers, clathrates and its applications.

Medicinal chemistry: Drug and drug metabolism, mechanism of different types of drug actions, common disease, disorders and their treatment methods. Blood and clinical tests – estimation of blood urea, cholestral, sugar, Fe protein, cholesterol, albumin, vitamins and minerals. Medicinally important compounds and disease caused by deficiency of vitamins.