U.P. EDUCATION SERVICE SELECTION COMMISSION, PRAYAGRAJ

Syllabus

CHEMISTRY
(Assistant Professor-Higher Education)
(Subject Code-70)

UNIT-1

- **Structure and Bonding :** Molecular orbitals and electronic configuration of homonuclear and heteronuclear diatomic molecules. Shapes of polyatomic molecules and ions; VSEPR Theory.
- Symmetry elements and point groups for simple molecules, character tables and its application; Symmetry consideration in coordination compounds and symmetry aspects of molecular orbital and ligand field theories.
- spectroscopy of Inorganic Compounds PMR,^{13}C, ^{31}PNMR and ^{19}F NMR of inorganic compounds: splitting pattern of compounds containing two or more than two types of NMR active nucler. Identification of fluxional molecules .
- ESR spectroscolony: g- value, factor affecting g-value. Number of fine components in the e.s.r. spectrum due to Zero field splitting, hyperfine structure. number of hyperfine lines and Super hyperfine splitting, number of hyperfine lines and their intensities in metal complexes.
- Mossbauer spectroscopy: Isomer shift, number of Mosbauer singnals.
- Electronic spectroscopy: charge transfer transitions and charge transfer spectra in transition metal complexes.

UNIT-2

- **Chemistry of Non-transition Elements :** General discussion on the properties of the non-transitional elements; special features of individual elements; preparation, properties and structure of their halides, oxides etc. Polymorphism of carbon, phosphorus and sulphur. Synthesis, properties and structure of boranes, carboranes, borazines, silicates, carbides, silicones, phosphazenes, sulphur -nitrogen compounds, peroxo compounds of boron, carbon and sulphur, oxy acids of nitrogen, phosphorus, sulphur and halogens, interhalogens, pseudohalides and noble gas compounds.
- **Bio inorganic chemistry :** Metal ions in biology, molecular mechanism of ion-transport across membranes, oxygen uptake proteins, cytochromes and ferridoxins.

UNIT-3

- **Chemistry of Transition Elements :** Co-ordination chemistry of transition metal ions; structural aspects, isomerism, octahedral, tetrahedral and square planner crystal field splitting of d-orbitals, CFSE, magnetism and colour of transition metal ions, John-Teller effect, spectrochemical series, nephelauxetic series, quenching of orbital angular moment, spin orbit coupling. Stereochemistry of coordination compounds, stability constants of complexes and their determination, stabilization of unusual oxidation states.
- **Mechanism of Inorganic Reactions :** Substitution reactions, trans effect, electron transfer reactions. Fluxional molecules, palladium catalysed reactions.
- **Organometallic Chemistry :** Synthesis, structure and bonding, organometallic reagents in organic synthesis and in homogeneous catalytic reactions (hydrogenation, hydroformulation, isomerisation and polymerisation) π- metal complexes.

- **Ligand Field and Molecular Orbital Theories :** M.O. energy level diagrams of octahedral, tetrahedral and square planner complexes, Effect of π bonding on the energy of t_{2g} orbitals and on Dq. experimental evidences for metal-ligand orbital overlap.

UNIT-4

- **Stereochemistry:** Element of symmetry, chiral and aehiral molecules, R, S nomenclature, diastereomerism in acyclic compounds. Methods of asymmetric synthesis. Stereospecific and stereo-selective reactions. Interconversion of Fischer, Newman flying wadge and Sawhorse projections. E, Z isomerism, conformational analysis of mono and disubstituted cyclohexanes.
- **Reaction Mechanism :**
  - **(a) General Organic Chemistry: Hypercoryugation, resonance, Aromaticity: Benzenoid and non-benzenoid aromatic compounds and ions.**
  - **(b) Reaction Intermediates :** generation, geometry, stability and reactions of carbocations, carbanions, free radicals, carbenes & NHC, benzynes and non classical carbocations.
  - **(c) Substitution reaction :** SN1, SN2, SNi, SN1' and SN2' mechanisms, Neighbouring group participation in aliphatic nucleophilic substitutions. Electrophilic and nucleophilic aromatic subtitution reactions.
  - **(d) Elimination reactions :** E1, E2 and E1 cb mechanisms. orientation in E2 reaction (Saytezeff and Hofmann), Pyrrolytic syn-elimination. Stereochemistry of elimination reaction.
  - **(e) Addition Reactions:** Electrophilic addition to carbon-carbon multiple bond and its stereochemistry. Nucleophilic addition to carbon-oxygen double bond and activated Carbon-carbon double bond. (Michael addition)
  - **(f) Common Organic Reaction and Mechanism :**
    - (i) Aldol, Perkin, Dieckmann condensation, Reformatsky, Benzoin, Wittig, Reimer-Tiemann, Diels-Alder, Robinson annulation, Ene, Barton reaction, Hofmann-Loffor-Freytage reactions, Shapiro reaction, Sharpless epoxidation reaction, Mannich reaction, Stetter reaction and Baylis-Hillman reaction.
    - (ii) Rearrangements : Pinacol-Pinacolone, Wagner-Meerwein, Demjanove, Beckmann, Hofmann, Curtius, Schmidt, Lossen, Sommelet-Hauser, Favoroskii and Baeyer-Villiger rearrangement.

UNIT-5

- **Reagents in Organic Synthesis :**
  Use of following reagents in organic synthesis and functional group transformation:
  - (i) **Complex metal hybrids :** $LiAlH_4$, $NaBH_4$, Sia_2BH, mono and dialkyl boranes, disobutylaluminium hydride and tri-n-butyltin hydride.
  - (ii) **Organometallic Compounds :** Grignard reagents, Lithium dialkylcadmium, alkyllitrhium and Trimethyl silyl iodide
  - (iii) 1, 3-Dithiane, lithium diisopropylamide, DDQ, SeO_2.

- **Pericyclic Reactions :** Classification and examples, Woodward-Hofmann's Rule, Elcetrocyclic reaction, Cycloaddition reaction ([2+2] and [4+2] only) and sigmatropic shifts {[1,3] -shift, [1,5]-shift and [3,3]-shift (Cope rearrangement and Claisen Rearrangement)}, FMO approach only.
- **Photochemistry :**
  - **(a)** Photochemistry processes, Jablonski diagram, exciplexes, photosensitisations.
  - **(b)** Photochemistry of alkenes (cis-trans isomerisation), Photochemical addition reactions of 1,3: 1,4 and 1,5-dienes, dimerisations.
  - **(c)** Photochemistry of Carbonyl compounds : Norrish Type-I and Norrish Type-II of cyclic and acyclic ketones, Paterno-Buchi reaction, Photoreduction.

(d) Rearrangement given by β, γ- unsaturated ketones, cyclohexenons and 2,5-cyclohexadienones.

(e) Photochemistry of aromatic compounds, skeletal isomerisation.

(2) Structure determination of organic compounds by UV, IR, NMR(Proton and ^{13}C) and mass spectroscopic techniques.

UNIT-6

- **Electro -chemistry :** Redox potential, electrochemical series, redox indicators. Kohlrausch's law of independent migration of ions. Transport number and its determination, Hydrolysis of salts, pH and buffer solutions, type of single electrodes and elctrode potentials, concentration cell with and without transference, liquid junction potential, fuel cell.
- **Nuclear Chemistry :** Radioactive decay and equilibrium. Nuclear reactions; fission and fusion, mass defect, fission products and yields. Radioactive techniques; tracer technique, neutron activation analysis, counting techniques such as G.M. ionisation and proportional counter.
- **Solids :** Cubic Crystal Systems, Dislocations in solids, Schottky and Frenkel Defects, electrical properties, insulators and semiconductors, superconductors, band theory of solids, solid –state reactions.

UNIT-7

- **Spectroscopy :** Basic principles and applications of IR, Ramam, ESR, NMR, Massbauer and Photoelectron spectroscopy in structural elucidation of simple inorganic and coordination compounds including F & P containing inorganic compounds. Elementary principles and application of electronic (UV), vibrational (IR), PMR, C-13 NMR and Mass spectral techniques for structural elucidation of organic compounds and Compounds Containing F.
- **Topics in Analytical Chemistry:** Adsorption partition, exclusion electrochromatography, solvent extraction and ion exchange methods, electroanalytical techniques, voltammetry, cyclic voltammetry, polarography, amperometry, coulometry and conductometry, ion selective electrodes, annodic stripping voltammetry, TGA, DTA etc.
- **Data Analysis:** Mean and standard deviation, absolute and relative errors, linear regression; covariance and correlation coefficient.

UNIT-8

- **Thermodynamics :** Variation of internal energy with temperature and volume, Enthalpy as a function of temperature and pressure, relation between C_p and C_v, Kirchoff's equation, Joule-Thompson coefficient, Inversion temperature, Important thermodynamic quantities (w, q, ΔE, ΔH) in an isothermal expansion of an ideal gas and adiabatic expansion of an ideal gas, Spontaneous processes, Carnot cycle, Statement of second law, concept of entropy, Thermodynamic equation of state (Energy as a function of T and V, enthalpy as a function of T and P), Variation of entropy with Temperature and Volume, Helmholtz and Gibbs free energy, Gibbs-Helmholtz equation, Thermodynamic criteria of equilibrium, Clapeyron and Claucious equation, Hoff equation, Thermodynamic derivation of Phase Rule and distribution law, Partial molar Quantities, Chemical potential and other thermodynamic functions, Effect of Temperature and Pressure on chemical potential; chemical potential of real gas and fugacity of real gas. Nernst heat theorem and its application to non-condensed system, statements of third law, The relationship between entropy constant and Nernst Chemical constant, Determination of entropy from the third law.

- **Chemical Kinetics and Catalysis :** Differential and integral rate equations for zero, first, second and third order reactions, Half-life period, Kinetics of first order opposing, consecutive and parallel reactions, Effects of temperature on reaction rate, energy of activation and collision theory of bimolecular gaseous reactions. Steady-State approximation, Lindemann's theory of reaction rates. Thermodynamic formulation of rate constant, comparision of collision and absolute reaction rate theory, calculation of transmission co-efficient, Primary and Secondary salt effects, kinetics of homogenious, acid -base and enzyme catalysis, heterogenious catalysis.

UNIT-9

- **Chain reactions and Photochemistry :** Chain reaction, free radical chains (Rice-Herzfeld mechanism for the decomposition of ethane), Einstein's law of Photochemical equivalence, Quantum efficiency, Kinetics of some photochemical reactions (Decompositions of acetaldehyde, dimerization of anthracene).
- **Statistical Thermodynamics :** Degeneracy of energy levels. Probability and most probable distribution, translational, rorational, vibrational and electronic partition function. Internal energy and heat capacity in terms of partition function. Thermodynamic function for gaseous system, Molar heat capacity of gases, Heat capacity of monoatomic crystal. The Einstein model, Debye's theory of solid heat capacities of Crystal at very low temperatures, Calorimetric entropy, spectroscopic entropies, expression for equilibrium constant in terms of partition functions, Base-Einstein statistics, Fermi-Dirac statistics, Comparision of M-B, B-E and F-D statistics.

UNIT-10

- **Fast Reaction:** Luminescence and energy transfer processes. Study of Kinetic by stopped flow technique, relaxation method, flash photolysis and magnetic resonance method.
- **Non-equilibrium Thermodynamics :** Postulates and methodologies, linear laws, Gibbs equation, Onsager reciprocal theory.
- **Macromolecules :** Number- average and weight average molecular weights; determination of molecular weights. Kinetics of polymerization. Stereochemistry and mechanism of polymerisation.