506. CHEMISTRY

UNIT – I

Symmetry of Molecules:

Concept of Symmetry in Chemistry – Symmetry Operations – Symmetry Elements : Rotational Axis of Symmetry and Types of Rotational Axes, Plane of Symmetry and types of Planes, Improper Rotational Axis of Symmetry , Inversion Center and Identity Element – More about Symmetry Elements – Molecular Point Groups: Definition and Notation of Point Groups, Classification Molecules in to C_1, C_s , C_i , C_n ,C_{nv} , C_{nh} , $C_{\infty v}$, D_n , D_{nh} , D_{nd} ,$D_{\infty h}$, S_n (n=even), T ,T_h , T_d , O , O_h , I, I_h , K_h Groups. Descent in Symmetry with Substitution – Exercises in Molecular Point Groups – Symmetry and Dipole moment – Symmetry criteria for Optical activity..

Bonding in metal complexes

Crystal Field Theory: Salient features of CFT. d-orbital splitting patterns in regular Octahedral, tetragonally distorted octahedral, Jahn-Tellar theorem-, tetrahedral, square planar, trigonal planar, and linear geometries. Factors influencing the magnitude of crystal field splitting in octahedral complexes – nature of metal ions, nature of ligands, geometry. Concept of weak field and strong fields. - Calculation of crystal field stabilization energies (CFSE's) in six and four coordinate complexes.

Types of magnetic behaviour – magnetic susceptibility – calculation of magnetic moment from magnetic susceptibility spin only formula ,- Quenching of orbital angular momentum – Determination of magnetic moment from Guoy's method . Applications of magnetic moment data for the determination of oxidation states, bond type and stereochemistry.

Free ion terms and Energy levels: Configurations,Terms,States and Microstates – Formula for the calculation of Microstates p^n and d^n configurations – L-S (Russel-Saunders) coupling scheme – j-j coupling scheme – Determination of terms for various p^n and d^n configurations of metal ins. Hole formalism – Energy ordering of terms (Hund's rules) Inter – electron repulsion Parameters (Racah parameters) – Spin-Orbital coupling parameters. Effect of weak cubic crystal fields on S,P,D and F terms- Orgel Diagrams.Jahn –Tellor theorem and its effects on terms.

Coordination Equilibria:

Solvation of metal ions- Binary complexes: Formation of binary Metal Complexes and their stability – types of Stability Constants – relation between them- trends in Step-wise Stability

Constants (Factors causing decrease and increase in Step-wise Stability) – Factors influencing the stability constants : (i) Ligand effects: Basicity , Substituent , Steric ,Chelate(size and number of chelate rings) , Macrocyclic and Cryptate effects- (ii) Metal ion effects: Ionic potential ,Effective Nuclear charge and Atomic Number (Irving-William's Order, geometry of Metal ion and Ligand) – Chelate effect and its Thermodynamic origin – Jahn-Tellar effect on Stability constants of Metal complexes – Pearson's Theory of Hard and Soft Acids and Bases (HSAB) , Applications of HSAB, Electronegetivity Vs Hardness and Softness. Symbiosis – Methods used for the determination of Stability constants (Basic Principles only): pH metric, Spectrophotometric and Polarographic methods.
Ternary Metal Complexes – definition – Formation of ternary metal complexes – Step-wise and simultaneous equilibria with simple examples.

Bio Coordination Chemistry:

Metal ions in Biological systems: Brief survey of metal ions in biological systems. Effect of metal ion concentration and its physiological effects. Basic principles in the biological selection of elements.
Oxygen transport and storage: Hemoglobin and Myoglobin: Geometric, electronic and magnetic aspects of Dioxygen binding, Oxygen adsorption isotherms and cooperativity in Hemoglobin and its physiological significance. Role of globin chain. Hemerythrin and Hemocyanin: Structure of deoxy forms, oxygen binding, Geometric, electronic and magnetic aspects. Comparison of Hemerythrin and Hemocyanin with hemoglobin.
Photosynthesis: Structural aspects of Chlorophyll. Photo system I and Photo system II.
Vitamin B_6 model systems: Forms of vitamin B_6 with structures. Reaction mechanisms of (1) Transamination (2) Decarboxylation and (3) Dealdolation in presence of metal ions.

Ligational Aspects of Diatomic molecules:

Metal Carbonyls:- Carbon monoxide as a ligand – Molecular orbitals of CO - Donor and Acceptor molecular orbitals of CO; Bonding modes of CO- Terminal and Bridging;
Evidence for multiple bonding from Bond lengths and Stretching frequencies;
18 Valence electron rule and its application.
Metal Nitrosyls: - NO as a ligand – Molecular orbitals of NO – Donor and Acceptor components; Bonding modes of NO – Terminal (Linear, Bent) and Bridging;
Structural aspects of $[IrCl(PPh_3)_2(CO)(NO)]^+$ and $[RuCl(PPh_3)_2(NO)_2]^+$.
Stereo chemical control of valence in $[Co(diars)_2(NO)]^{2+}$ and $[Co(diars)_2(NO)(SCN)]^+$.
Metal Dinitrogen complexes: - N_2 as aligand – Molecular orbitals of N_2; Bonding modes – Terminal and Bridging; Stretching frequencies; Structures of Ru (II) and Mo (0) dinitrogen complexes; Chemical fixation of dinitrogen.

Reaction mechanisms of transition metal complexes:

Ligand substitution reactions:

Energy profile of a reaction – Transition state or Activated Complex. Types of substitution reactions (SE,SN,SN^1,SN^2).

Ligand substitution reactions in octahedral complexes:

Aquation or Acid hydrolysis reactions, Factors effecting Acid Hydrolysis , Base Hydrolysis, Conjugate Base Mechanism, Evidences in favour of SN^1CB Mechanism.

Annation reactions.

Substitution reactions with out Breaking Metal-Ligand bond.

Ligand Substitution reactions in Square-Planar complexes: Mechanism of Substitution in Square-Planar complexes- Trans-effect, Grienberg's Polarization theory and π - bonding theory – Applications of Trans-effect in synthesis of Pt (II) complexes.

Electron Transfer Reactions (or Oxidation-Reduction Reactions) in Coordination compounds: Mechanism of One-electron Transfer Reactions: Atom (or group) Transfer or Inner Sphere Mechanism, Direct electron Transfer or Outer Sphere Mechanism.Marcus –Hush theory.

Metal Clusters:

Carbonyl clusters: Factors favouring Metal-Metal bonding – Classification of Clusters –
Low Nuclearity Clusters : M_3 and M_4 clusters , structural patterns in $M_3(CO)_{12}$ (M=Fe,Ru,Os) and $M_4(CO)_{12}$ (M=Co,Rh,Ir) Clusters-. Metal carbonyl scrambling – High Nuclearity clusters M_5,M_6,M_7,M_8 and M_{10} Clusters-, Polyhedral skeletal electron pair theory and Total Electron Count theory – Wades rules – Capping rule – Structural patterns in
$[Os_6(CO)_{18}]^{2-}$, $[Rh_6(CO)_{16}]$, $[Os_7(CO)_{21}]$, $[Rh_7(CO)_{16}]^{3-}$, $[Os_8(CO)_{22}]^{2-}$, $[Os_{10}C(CO)_{24}]^{2-}$ and $[Ni_5(CO)_{12}]^{2-}$.

Metal Halide clusters: Major structural types in Dinuclear Metal-Metal systems – Edge sharing Bioctahedra,Face sharing Bioctahedra,Tetragonal prismatic and Trigonal antiprismatic structures -. Structure and bonding in $[Re_2Cl_8]^{2-}$ and Octahedral halides of $[Mo_6(Cl)_8]^{4+}$ and $[Nb_6(Cl)_{12}]^{2+}$. Trinuclear halides of Re(III).Hoffman's Isolobal analogy and its Structural implications.

UNIT - II

Stereochemistry

Molecular representations: Wedge, Fischer, Newman and Saw-horse formulae, their description and interconversions.

Molecular Symmetry & Chirality: Symmetry operations and symmetry elements (Cn & Sn). Criteria for Chirality. Desymmetrization.

Axial, planar and helical chirality: Configurational nomenclature:Axially chiral allenes,spiranes,alkylidene cycloalkanes, chiral biaryls, atropisomerism.Planar chiral ansa compounds and trans- cyclooctene.Helically chiral compounds

Relative and absolute configuration: Determination of absolute configuration by chemical correlation methods.

Racemisation, racemates and resolution techniques: Resolutions by direct crystallization, diastereoisomer salt formation chiral chromatography and asymmetric transformation.

Determination of configuration in E,Z-isomers: Spectral and Chemical methods of configuration determination of E,Z isomers. Determination of configuration in aldoximes and ketoximes.

Conformational analysis

Introduction to conformational isomerism and the concept of dynamic stereochemistry.Study of conformations in ethane and 1,2-disubstituted ethane derivatives like butane, dihalobutanes, halohydrin, ethylene glycol, butane-2, 3-diol amino alcohols and 1,1,2,2-tetrahalobutanes. Klyne-Prelog terminology for conformers and torsion angles Conformations of unsaturated acyclic compounds-Propylene,

1-Butene, Acetaldehyde, Propionaldehyde and Butanone. Conformational diastereoisomers and conformational enantiomers -. Factors affecting the conformational stability and conformational equilibrium – Attractive and repulsive interactions. Use of Physical and Spectral methods in conformational analysis.

Conformational affects on the stability and reactivity of acyclic diastereoisomers – steric and stereoelectronic factors-examples.Conformation and reactivity: The Winstein-Holness equation and the Curtin – Hammett principle

Reaction mechanism

Electrophilic addition to carbon carbon double bond: Stereoselective addition to carbon carbon double bond ; *anti* addition- Bromination and epoxidation followed by ring opening. *Syn* addition of OsO_4 and $KMnO_4$.

Elimination reactions Elimination reactions E2, E1, E1CB mechanisms. Orientation and stereoselectivity in E2 eliminations. Pyrolytic *syn* elimination and α-elimination, elimination Vs substitution.

Determination of reaction mechanism: Determination of reaction mechanism: Energy profiles of addition and elimination reactions, transition states, product isolation and structure of intermediates, use of isotopes, chemical trapping, crossover experiments. Use of IR and NMR in the investigation of reaction mechanism.

Nucleophilic Aromatic substitution: Aromatic Nucleophilic substitution: $S_N1(Ar)$, S_N2 (Ar), and benzyne mechanisms; evidence for the structure of benzyne. Von Richter rearrangement. Definition and types of ambident nucleophiles.

Neighbouring group participation : Criteria for determining the participation of neighbouring group. Enhanced reaction rates, retention of configuration, isotopic labeling and cyclic intermediates. Neighbouring group participation involving Halogens, Oxygen, Sulphur, Nitrogen, Aryl, Cycloalkyl groups, σ and π- bonds. Introduction to nonclassical carbocations.

Electrophilic substitution at saturated carbon and single electron transfer reactions.

Mechanism of aliphatic electrophilic sustitution. S_E1, S_E2, and S_Ei. SET mechanism.

Reactive intermediates and Molecular rearrangements.

Reactive Intermediates: Generation, detection, structure, stability and reactions of carbocations, carbanions, carbenes, nitrenes and free radicals.

Molecular rearrangements: Definition and classification. Molecular rearrangements involving 1) electron deficient carbon: Wagner- Meerwein, Pinacol-Pinacolone, Allylic and Wolf rearrangement. 2) electron deficient Nitrogen: Hofmann, Lossen, Curtius, Schmidt and Beckmann rearrangements 3) electron deficient Oxygen: Baeyer-Villiger oxidation. 4) Base catalysed rearrangements: Benzilic acid , Favourski , Transannular , Sommlett-Hauser and Smiles rearrangement

Carbohydrates and Proteins

Carbohydrates: Determination of the relative and absolute configuration in D (+) glucose and D (-) fructose.Proof for the chair conformation of D (+) glucose. Occurence, importance and synthesis of monosaccharides containing functional groups such as amino, halo and sulphur. Structure elucidation and synthesis of sucrose.Conformational structures of D(+)ribose, 2-deoxyD-ribose, sucrose, lactose maltose and cellobiose. Structural features of starch, cellulose and chitin.

Proteins: Acid and enzymatic hydrolysis of proteins.Determination of the amino acid sequence in polypeptides by end group analysis.Chemical synthesis of di and tripeptides. Merrifield's solid phase synthesis.

Heterocyclic compounds

Importance of heterocyclic compounds as drugs. Nomenclature of heterocyclic systems based on ring size,number and nature of hetero atoms.Synthesis and reactivity of indole, benzofuran, benzothiophene, quinoline, isoquinoline, coumarin, chromone, carbazole and acridine.

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Natural products

Importance of natural products as drugs. Isolation of natural products by steam distillation, solvent extraction and chemical methods. General methods in the structure determination of terpenes. Isoprene rule. Structure determination and synthesis of

α-terpeniol and camphor. Biogenesis of monoterpenes. Structure determination and synthesis of β-carotene. General methods of structure determination of alkaloids. Structure determination and synthesis of papaverine and quinine.

UNIT – III

Thermodynamics

Brief review of concepts of I and II laws of thermodynamics. Concept of entropy. Entropy as a state function. Calculation of entropy changes in various processes. Entropy changes in an ideal gas. Entropy changes on mixing of ideal gases. Entropy as a function of V and T. Entropy as a function of P and T. Entropy change in isolated systems- Clausius inequality. Entropy change as criterion for spontaneity and equilibrium.

Third law of thermodynamics. Evaluation of absolute entropies from heat capacity data for solids, liquids and gases. Standard entropies and entropy changes of chemical reactions. Helmholtz and Gibbs free energies (A and G). A and G as a criteria for equilibrium and spontaneity. Physical significance of A and G. Driving force for chemical reactions- relative signs of ΔH and ΔS.

Thermodynamic relations. Gibbs equations. Maxwell relations. Temperature dependence of G. Gibbs- Helmholtz equation. Pressure dependence of G.

Chemical potential: Gibbs equations for non-equilibrium systems. Material equilibrium. Phase equilibium. Clapeyron equation and Clausius-Clapeyron equation .

Conditions for equilibrium in a closed system. Chemical potential of ideal gases. Ideal-gas reaction equlibrium-derivation of equilibrium constant. Temperature dependence of equilibrium constant-the van't Hoff equation.

Solutions: Specifiying the Solution composition. Partial molar poperties-significance. Relation between solution volume and partial molar volume. Measurement of partial molar volumes- slope and intercept methods. The chemical potential. Variation of chemical potential with T and P. Gibbs-Duhem equation-derivation and significance

Ideal solutions. Thermodynamic properties of ideal solutions. Mixing quantities. Vapour pressure-Raoult's law. Thermodynamic properties of ideally dilute solutions. Vapour pressure- Henry's law.

Nonideal systems. Concept of fugacity, fugacity coefficeient. Determination of fugacity. Non ideal solutions. Activities and activity coefficients. Standard-state conventions for non ideal solutions. Determination of activity coefficients from vapour pressure measurements. Activity coefficients of nonvolatile solutes using Gibbs-Duhem equation.

Multicomponent phase equilibrium: Vapour pressure lowering, freezing point depression and boiling point elevation

Quantum Chemistry

Black body radiation-Planck's concept of quantization-Planck's equation, average energy of an oscillator (derivation not required). Wave particle duality and uncertain principle-significance of these for microscopic entities. Emergence of quantum mechanics. Wave mechanics and Schroedinger wave equation.

Operators-operator algebra. Commutation of operators, linear operators.Complex functions. Hermitian operators. Operators ∇ and ∇^2 . Eigenfunctions and eigenvalues. Degeneracy.

Linear combination of eigenfunctions of an operator. Well behaved functions. Normalized and orthogonal functions.

Postulates of quantum mechanics. Physical interpretation of wave function. Observables and operators. Measurability of operators. Average values of observables. The time dependent Schrodinger equation. Separation of variables and the time-independent Schrodinger equation..

Theorems of quantum mechanics. Real nature of the eigen values of a Hermitian operator-significance. Orthogonal nature of the eigen values of a Hermitian operator-significance of orthogonality. Expansion of a function in terms of eigenvalues. Eigen functions of commuting operators-significance. Simultaneous measurement of properties and the uncertainty principle.

Particle in a box- one dimensional and three dimensional. Plots of ψ and ψ^2-discussion. Degeneracy of energy levels. Comparison of classical and quantum mechanical particles. Calculations using wave functions of the particle in a box-orthoganality, measurability of energy, position and momentum, average values and probabilities. Application to the spectra of conjugated molecules.

Cartesian, Polar and spherical polar coordinates and their interrelations

Schrodinger equation for the hydrogen atom- separation into three equations. Hydrogen like wave functions. Radial and angular functions. Quantum numbers n, l and m and their importance. The radial distribution functions. Hydrogen like orbitals and their representation. Polar plots, contour plots and boundary diagrams.

Many electron systems. Approximate methods. The variation method-variation theorem and its proof. Trial variation function and variation integral. Examples of variational calculations. Paricle in a box. Construction of trial function by the method of linear combinations. Variation parameters. Secular equations and secular determinant..

Bonding in molecules. Molecular orbital theory-basic ideas. Construction of MOs by LCAO , H_2^+ ion. The variationan integral for H_2^+ ion. Detailed calculation of Wave functions and energies for the bonding and antibonding MOs. Physical picture of bonding and antibonding wave functions. Energy diagram. The MO and VB wave functions for H_2 molecule and their comparision.

Electrochemistry

Electrochemical Cells : Derivation of Nernst equation – problems. Chemical and concentration cells (with and without transference). Liquid junction potential – derivation of the expression for LJP – its determination and elimination**.** Applications of EMF measurements : Solubility product, potentiometric titrations, determination of transport numbers, equilibrium constant measurements.

Decomposition potential and its significance. Electrode polarization – its causes and elimination. Concentration overpotential.

Concept of activity and activity coefficients in electrolytic solutions. The mean ionic activity coefficient. Debye-Huckel theory of electrolytic solutions. Debye-Huckel limiting law (derivation not required). Calculation of mean ionic activity coefficient. Limitations of Debye-Huckel theory. Extended Debye-Huckel law.
Theory of electrolytic conductance. Derivation of Debye-Huckel-Onsager equation – its validity and limitations.
Concept of ion association – Bjerrum theory of ion association (elementary treatment) - ion association constant – Debye-Huckel-Bjerrum equation.

Chemical Kinetics

Theories of reaction rates : Collision theory, steric factor. Tranition state theory. Reaction coordinate, activated complex and the transition state. Thermodynamic formulation of transition state theory. Activtion parameters and their significance. The Eyring equation. Unimolecular reactions and Lindamann's theory.
Complex reactions- Opposing reactions, parallel reactions and consecutive reactions(all first order type). Chain reactions-general characteristics, steady state treatment. Example- H_2-Br_2 reaction. Derivation of rate law.
Effect of structure on reactivity- Linear free energy relationships. Hammett and Taft equations-substituent(σ and σ^*) and reaction constant (ρ and ρ^*)with examples. Deviations from Hammett correlations. reasons- Change of mechanism, resonance interaction. Taft four parameter equation. Correlations for nucleophillic reactions. The Swain – Scott equation and the Edward equation.
The reactivity-selectivity principle and the isoselectivty rule. The intrinsic barrier and Hammond's postulate.

Photochemistry

Electronic transitions in molecules. The Franck Condon principle. Electronically excited molecules- singlet and triplet states. Radiative life times of excited states-theoretical treatment. Measured lifetimes. Quantum yield and its determination. Actinomety-ferrioxalate and uranyl oxalate actinometers-problems.
Derivation of fluorescence and phosphorescence quantum yields. E-type delayed fluorescence- evaluation of triplet energy splitting(ΔE_{ST}). Photophysical processes-photophysical kinetics of unimolecular reactions. Calculation of rate constants of various photophysical processes-problems, State diagrams
Photochemical primary processes. Types of photochemical reactions- electron transfer, photodissociation, addition, abstraction, oxidation and isomerization reactions with examples. Effect of light intensity on the rates of photochemical reactions. Photosensitization. Quenching-Stern Volmer equation. Experimental set up of a photochemical reaction. Introduction to fast reactions- Principle of flash photolysis.

Solid state chemistry

Magnetic properties of solids- classification of magnetic materials, Magnetic susceptibility, Langevin diamagnetism, Weiss theory of para magnetism

Electronic properties of metals, insulators and semi conductors: Electronic structure of solids, Band theory, band structure of metals, insulators and semiconductors. Electrons, holes and Excitons. The temperature dependence of conductivity of extrinsic semi conductors. Photo conductivity and photovoltaic effect-p-n junctions.

Superconductivity. Occurrence of superconductivity. Destruction of superconductivity by magnetic fields-Meisner effect. Types of superconductors. Theories of super conductivity-BCS theory.

High temperature superconductors. Structure of defect perovskites. High T_c superconductivity in cuprates. Phase diagram of Y-Ba-Cu-O system. Crystal structure of $YBa_2Cu_3O_{7-x}$. Preparation of 1-2-3 materials. Origin of high T_c superconductivity.

UNIT-IV

Techniques of Chromatography

i. Introduction, Classification of chromatographic techniques, differential migration rates, partition ratio, retention time, relation between partition ratio and retention time, capacity factor, selectivity factor. Efficiency of separation- resolution, diffusion, plate theory and rate theory.

ii. **GC:** Principle, instrumentation, detectors- TCD, FID, ECD. Derivatisation techniques, PTGC.

iii. **HPLC:** Principle, instrumentation, detectors- UV detectors, Photodiode array detector, fluorescence detector.

iv. Applications: Methods of quantitation for GC and HPLC: GC analysis of hydrocarbons in a mixture, GC assay of methyl testosterone in tablets, atropine in eye drops. HPLC assy of paracetamol and asprin in tablets.

NMR spectroscopy

^{1}H NMR spectroscopy: Magnetic properties of nuclei, Principles of NMR. Instrumentation, CW and pulsed FT instrumentation, equivalent and non equivalent protons, enantiotopic and diastereotopic protons, Chemical shifts, factors affecting the chemical shifts, electronegativity

and anisotropy, shielding and deshielding effects,Signal integration, Spin-spin coupling: vicinal,germinal and long range, Coupling constants and factors affecting coupling constants.

Applications of ^{1}H NMR spectroscopy: Reaction mechanisms (cyclic bromonium ion,electrophilic and nucleophilic substitutions, carbocations and carbanions),E,Z isomers,conformation of cyclohexane and decalins, keto-enol tautomerism, hydrogen bonding, proton exchange processes (alcohols, amines and carboxylic acids), C-N rotation. Magnetic resonance imaging(MRI). ^{1}H NMR of organic molecules and metal complexes: ethyl acetate, 2- butanone, mesitylene, paracetamol, asprin, ethylbenzoate, benzyl acetate, 2-chloro propionic acid, $[HNi(OPEt_3)_4]^+$, $[HRh(CN)_5]$ Rh I=1/2, $[Pt(acac)_2]$.

^{1}H,^{19}F,^{31}P and solid state NMR spectroscopy: First order and non first order spectra e.g.,AX,AX_2,AX_3, A_2X_3,AMX and AB,ABC, Simplification of complex spectra: increased field strength, deuterium exchange,Lanthanide shift reagents and double resonance techniques. Discrimination of enantiomers by use of chiral NMR solvents (CSAs), chiral lanthanide shift reagents and Mosher's acid. Nuclear Overhauser enhancement (NOE). Fluxional molecules- bullvalene, $[\eta^5\text{-}C_5H_5M]$, $[\eta^5\text{-}(C_5H_5)_2$ Ti $\eta^1\text{-}(C_5H_5)_2]$ and $[\eta^4C_8H_8Ru(CO)_3]$.

^{19}F NMR spectroscopy: ^{19}F chemical shifts, coupling constants. Applications of ^{19}F NMR involving coupling with ^{19}F,^{1}H and ^{31}P: 1,2 dichloro-1,1 difluoro ethane, BrF_5, SF_4, PF_5, ClF_3, IF_5, HF_2^-.

^{31}P NMR spectroscopy: ^{31}P chemical shifts, coupling constants. Applications of ^{31}P NMR involving coupling with ^{31}P , ^{19}F, ^{1}H and ^{13}C: ATP, Ph_3PSe, P_4S_3, $P(OCH_3)_3$, H_3PO_4, H_3PO_3, H_3PO_2, HPF_2, PF_6^-, PH_3,[Rh $(PPh_3)Cl_3$] Rh I=1/2

Introduction to solid state NMR: Magic angle spinning (MAS).Applications of solid state NMR

<u>Rotational and Vibrational spectroscopy</u>

a). Microwave Spectroscopy: Classification of molecules based on moment of inertia. Diatomic molecule as rigid rotator and its rotational energy levels. Selection rules (derivation not required). Calculation of bondlengths from rotational spectra of diatomic molecules. Isotope effect on rotational spectra. Calculation of atomic mass from rotational spectra. Brief description of microwave spectrometer.

b). Vibrational Spectroscopy. Vibrational energy levels of diatomic molecules, selection rules (derivation not required). Calculation force constant from vibrational frequency. Anharmonic nature of vibrations. Fundamental bands, overtones and hot bands, Fermi Resonance. Vibration-rotation spectra diatomic molecules. Vibrations of poly atomic molecules. Normal modes of vibration, concept of group frequencies. Characteristics of vibrational frequencies of functional groups; Stereochemical effects on the absorption pattern in carbonyl group, cis-trans isomerism and hydrogen bonding. Isotopic effect on group frequency. IR spectra of metal coordinated NO_3^-, SO_4^{2-} and CO_3^{2-} ions.

Raman Spectroscopy- Quantum theory of Raman effect, Rotational raman and Vibrational Raman spectra, Stokes and anti- Stokes lines. Complementary nature of IR and Raman spectra.

Electronic spectroscopy

Electronic spectroscopy: Electronic spectra: Elementary energy levels of molecules-selection rules for electronic spectra; types of electronic transitions in molecules. Chromophores: Congugated dienes, trienes and polyenes, unsaturated carbonyl compounds, benzene and its derivatives, Woodward-Fieser rules. Polynuclear aromatic hydrocarbons and diketones. Solvent and structural influences on absorption maxima, stereochemical factors. Cis-trans isomers, and cross conjugation. Beer's law application to mixture analysis and dissociation constant of a weak acid.

Electro Analytical Techniques

a) Types and Classification of Electro analytical Methods.

i) Potentiometry- Types of electrodes, Hydrogen gas, Calomel, Quin hydrone and glass electrodes. Determination of pH. Potentiometric titrations.

ii) Conductometry – Definition of terms – conductivity, specific conductivity, cell constant. Mobility of ions, Conductometric titrations.

b) D.C Polarography :. Dropping mercury electrode- Instrumentation-polarogram. Types of Currents : Residual, Migration, Limiting. Two and Three electrode assemblies. Ilkovic equation (derivation not necessary) and its consequences. Types of limiting Currents : Adsorption, Diffusion, Kinetic. Applications of polarography in qualitative and quantitative analysis. Analysis of mixtures. Application to inorganic and organic compounds. Determination of stability constants of complexes.

c) Brief account of following techniques and their advantages over conventional d.c.polargraphy.

(i) A.C.polarography (ii) Square-wave polarography (iii) Pulse polarography (iv) Differential pulse polarography

d) Amperometric titrations :Principle, Instrumentation. Types and applications of amperometric titrations. Determination of SO_4^{2-}, metal ions viz., Mg^{2+}, Zn^{2+}, Cu^{2+} and other substances.

e) Cyclic Voltammetry : Principle, instrumentation, reversible and irreversible cyclic voltammograms. Applications. Cyclic voltammetric study of insecticide parathion.

Mass spectrometry

Origin of mass spectrum, principles of EI mass spectrometer. Types of fragments: odd electron and even electron containing neutral and charged species (even electron rule), Nitrogen rule, isotopic peaks, determination of molecular formula, metastable ion peaks. High resolution mass spectrometry. Salient features of fragmentation pattern of organic compounds including β-cleavage, Mclafferty rearrangement, retro Diels – Alder fragmentation and ortho

effect. Principle of EI, CI, Fast Atom Bombardment (FAB), Secondary Ion Mass Spectrometry (SIMS), Electrospray (ESI) ionization and Matrix Assisted Laser Desorption Ionization (MALDI) methods. Introduction to principle and applications of Gas Chromatography-Mass Spectrometry (GC-MS) and Liquid chromatography-Mass Spectrometry (LC-MS) techniques.

Photoelectron & ESR sprectroscopy

Photoelectron Spectroscopy

Principle and Instrumentation, Types of Photoelectron Spectroscopy – UPS & XPS
Binding Energies, Koopman's Theorem, Chemical Shifts.
Photoelectron Spectra of Simple Molecules: N_2, O_2, F_2, , CO, HF, NH_3 and H_2O - Vibrational Structure of PES Bands, Potential energy curves, Interpretation of Vibrational spectral data for ionized (M^+) species, Prediction of Nature of Molecular Orbitals. ESCA in qualitative analysis, Principles of Auger electron spectroscopy.

Electron Spin Resonance

Introduction, principle, instrumentation, selection rules, interpretation of Lande's factor 'g'. Hyperfine and super hyperfine Coupling. Anisotropy in 'g' values and hyperfine coupling constants. Zero field splitting, Kramer's degeneracy, quadrupolar interactions.
Study of free radicals and transition metal complexes. Evidence for covalency in complexes, ex. Cu(II) Bissalcylaldimine, Bis-acetylacetanatovanadyl(II) and hexachloroiridium(IV) complexes.