506. CHEMISTRY

Unit-1

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 s) – Spin-Orbital coupling parameters. Effect of weak cubic crystal fields on S,P,D and F terms- Orgel Diagrams.

Coordination Equilibria

Solvation of metal ions- Metal complex formation in solution-Binary metal complexes. Stability constants (types and relationships between them). – Factors influencing the stability constants: (i) Metal ion effects (charge/size, IP, crystal field effect, John-Teller effect, Pearson theory of hard and soft acids and bases (HSAB), elecronegativity and hardness and softness, symbiosis. (ii) Ligand effects (Basicity , Substituent effect , Steric , Chelate(size and number of chelate rings), Macrocyclic and Cryptate effects- crown ethers , crypton, size match selectivity or concept of hole size, limitations, Macrocycles with pendent groups– 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.

Ligational Aspects of Diatomic molecules

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 Os(II) dinitrogen complexes; Chemical fixation of dinitrogen.

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 – 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 $[Ni_5(CO)_{12}]$

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). Langford and Grey classification – A mechanism, D-Mechanism, I_a, I_d, and Intimate mechanism. 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.

Substitution reactions with out Breaking Metal-Ligand bond. Anation reaction

Ligand Substitution reactions in Square-Planar complexes: Mechanism of Substitution in Square-Planar complexes- Trans-effect, Trans-influence, 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. Factrors affecting direct electron transfer reactions, Cross reactions and Marcus-Hush theory.

Bio coordination chemistry.

Oxygen transport and storage: Hemoglobin (Hb) and Myoglobin (Mb) primary, secondary, tertiary and quarternary structures and non-covalent bonds present in them. Oxygenation equilibria for Mb and Hb. Factor effecting oxygenation equilibria. Cooperativity and its mechanism. Spin state of iron. Spatial and electronic aspects of dioxygen binding. Allosteric models (T and R states). Role of globin. Transport of NO and CO_2. Hemocynin (Hc) and Hemerythrin (Hr): Introduction-structure of active sites with oxygen and without oxygen. 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.

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: Axially chiral allenes,spiranes,alkylidene cycloalkanes, chiral biaryls, atropisomerism, planar chiral ansa compounds and trans- cyclooctene, helically chiral compounds and their configurational nomenclature

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

Racemisation and resolution techniques: Racemisation, 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.

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.

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, Cycloalky l groups , σ and π- bonds. Introduction to nonclassical carbocations.

Conformational analysis

Conformational isomerism: Introduction to the concept of dynamic stereochemistry. Conformational diastereoisomers and conformational enantiomers .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.

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

Pericyclic reactions

Introduction, Classification of pericyclic reactions,
Electrocyclic reactions: con rotation and dis rotation. Electrocyclic closure and opening in 4n and 4n+2 systems.
Cycloaddition reactions**:** suprafacial and antara facial additions in 4n and4n+2 cycloadditions.
Sigmatropic reactions**:** [i, j] shifts- suprafacial and antarafacial shifts, Cope and Claisen rearrangement reactions.
Approaches for the interpretation of mechanism of pericyclic reactions: Aromatic Transition States (ATS)/Perturbation Molecular Orbitals (PMO) approach-Concept of Huckel –Mobius aromatic and antiaromatic transition states. Framing Woodward-Hofmann selection rules for all the pericyclic reactions by ATS approach. Solving problems based on ATS approach.
Molecular orbitals: ethylene, 1, 3-butadiene, 1, 3, 5-hexatriene, allyl cation, allyl radical, pentadienyl cation, pentadienyl radical.
Frontier Molecular Orbital (HOMO-LUMO) approach-concept: Framing Woodward-Hofmann selection rules for all the pericyclic reactions by Frontier Molecular Orbital (FMO) approach. Solving problems based on FMO approach.
Conservation of orbital symmetry**:** (Correlation Diagrams) approach- for electrocylic and cycloadditions & cycloreversions.

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

Unit-III

Thermodynamics

Concept of Entropy, 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.

Thermodynamic relations. Gibbs equations. Maxwell relations.

Gibbs equations for non-equilibrium systems. . 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.. 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..

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

Statistical Thermodynamics:

Partition Functions: Concepts of distribution and probability, Boltzmann distribution law. Interpretation of partition functions- translational, rotational, vibrational and electronic partition functions. Relationship between partition functions and thermodynamic functions (only S & G).

Electrochemistry

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

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.

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 life times. Quantum yield and its determination. Experimental set up of a photochemical reaction. Actinometry-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

Photochemistry: Photochemistry of π-π^* transitions: Excited states of alkenes, cis-trans isomerisation, and photo stationary state. Photochemistry of 1,3-butadiene Electrocyclisation and sigmatropic rearrangements, di-π methane rearrangement. Intermolecular reactions, photocycloadditions, photodimeriastion of simple and conjugated olefins. Addition of olefins to α, β-unsaturated carbonyl compounds. Excited states of aromatic compounds,

Photoisimerisation of benzene Photochemistry of (n-π^*) transitions: Excited states of carbonyl compounds, hemolytic cleavage of α- bond, Norrish type I reactions in acyclic and cyclic ketones and strained cycloalkane diones.

Intermolecular abstraction of hydrogen: photoreduction-influence of temperature, solvent, nature of hydrogen donor and structure of the substrate.

Intramolecular abstraction of hydrogen: Norrish type II reactions in ketones, esters and 1,2 diketones, Addition to carbon-carbon multiple bonds, Paterno-Buchi reaction,

Photochemistry of nitrites-Barton reaction.

Quantum Chemistry

A brief review of 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 Schrödinger wave equation.

Operator**s**- 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. 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 pots 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.

Chemical Kinetics

Theories of reaction rates: Collision theory, steric factor. Transition state theory. Thermodynamic formulation of transition state theory. Potential energy surface diagram, Reaction coordinate, Activated complex. Activation 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. Reactions in solutions: Primary and secondary salt effects.

The reactivity-selectivity principle – Isokinetic temperature -Isoselectivty rule, Intrinsic barrier and Hammond's postulate.

Solid state chemistry

Electronic properties of metals, insulators and semi-conductors: Electronic structure of solids, Band theory, band structure of metals, insulators and semi-conductors. 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 – Meissner 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 $YBa_2Cu_3O_{7-x}$. Prepartion of 1-2-3 materials. Origin of high T_c superconductivity.

Nanoparticles:
Introduction to nanoparticles. Reduced dimensionality in solids – zero dimensional systems, fullerenes, quantum dots. One dimensional systems, carbon nano tubes, preparation of nano particles –top down and bottom up methods. Preparation of nanomaterials- – sol gel methods, and chemical vapour deposition method; thermolysis.

Unit-IV

Techniques of Chromatography

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.

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

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

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. ^{1}H NMR of organicmolecules

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 moleculesbullvalene, [$\eta5$-C_5H_5M], [$\eta5$-$(C_5H_5)_2$ Ti $\eta1$-$(C_5H_5)_2$] and [$\eta4C_8H_8Ru(CO)_3$].

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

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 bond lengths from rotational spectra of diatomic molecules. Isotope effect on rotational spectra. Calculation of atomic mass from rotational spectra. *Brief description of microwave spectrometer.*

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. Vibrationrotation 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.

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

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, mono substituted derivative (Ph-R), di substituted derivative (R-C_6H_4-R′) and substituted benzene derivatives (R-C_6H_4-COR′), Woodward-Fieser rules. Polynuclear aromatic compounds (Biphenyl, stilbene, naphthalene, anthracene, phenanthrene and pyrene). Heterocyclic systems. Absorption spectra of charge transfer complexes. Solvent and structural influences on absorption maxima, stereochemical factors. Cis-trans isomers, and cross conjugation.

Electro and thermal Analytical Techniques

I: Types and Classification of Electro analytical Methods:

a) D.C Polarography:. Instrumentation - Dropping mercury electrode- -polarogram. Types of Currents: Residual, Migration, Limiting. Two and Three electrode assemblies. Ilkovic equation (derivation not necessary) and its consequences..

b) 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

c) Amperometric titrations: Principle, Instrumentation. Types and applications of amperometric titrations.

d) Cyclic Voltammetry: Principle, instrumentation, Applications. Cyclic voltammetric study of insecticide parathion.

II: Thermal Analysis: Thermal techniques-Introduction, types of thermo analytical methods. Thermogravimetry principle and applications of thermogravimetry, differential thermal analysis- principle and applications of DTA. Differential scanning calorimetry. DSC: Principle, and application of DSC.

Photoelectron Spectroscopy

Principle and Instrumentation, Types of Photoelectron Spectroscopy – UPS & XPS. Binding Energies, Koopman's Theorem, Chemical Shifts. Photoelectron Spectra of Simple Molecules: N2, O2, F2, - Vibrational Structure of PES Bands, 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 and quadrupolar interactions.

***