506. CHEMISTRY

UNIT – I
Symmetry of Molecules:

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.


Coordination Equilibria:
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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.


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<sub>1</sub>, SN<sub>2</sub>).

**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<sub>1</sub>CB Mechanism.
Annotation reactions.

**Substitution reactions without 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<sub>3</sub> and M<sub>4</sub> clusters, structural patterns in M<sub>3</sub>(CO)<sub>12</sub> (M=Fe,Ru,Os) and M<sub>4</sub>(CO)<sub>12</sub> (M=Co,Rh,Ir) Clusters-. Metal carbonyl scrambling – High Nuclearity clusters M<sub>5</sub>, M<sub>6</sub>, M<sub>7</sub>, M<sub>8</sub> and M<sub>10</sub> Clusters-. Polyhedral skeletal electron pair theory and Total Electron Count theory – Wades rules – Capping rule – Structural patterns in [Os<sub>8</sub>(CO)<sub>18</sub>]<sup>2-</sup>, [Rh<sub>6</sub>(CO)<sub>16</sub>], [Os<sub>7</sub>(CO)<sub>21</sub>] , [Rh<sub>7</sub>(CO)<sub>18</sub>]<sup>3-</sup>, [Os<sub>8</sub>(CO)<sub>22</sub>]<sup>2-</sup>, [Os<sub>10</sub>C(CO)<sub>24</sub>]<sup>2-</sup> and [Ni<sub>5</sub>(CO)<sub>12</sub>]<sup>2-</sup>. Metal Halide clusters: Major structural types in Dinuclear Metal-Metal systems – Edge sharing Biocahedra, Face sharing Biocahedra, Tetragonal prismatic and Trigonal antiprismatic structures -. Structure and bonding in [Re<sub>2</sub>Cl<sub>8</sub>]<sup>2-</sup> and Octahedral halides of [Mo<sub>6</sub>(Cl)<sub>16</sub>]<sup>4+</sup> and [Nb<sub>6</sub>(Cl)<sub>12</sub>]<sup>2+</sup>. 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.


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 OsO₄ and KMnO₄

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: S₅1(Ar), S₅2 (Ar), and benzyne mechanisms; evidence for the structure of benzyne. Von Richter rearrangement. Definition and types of ambident nucleophiles.


Electrophilic substitution at saturated carbon and single electron transfer reactions.
Mechanism of aliphatic electrophilic substitution. S₂E₁, S₂E₂, and S₂Ei. SET mechanism.

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


**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. Occurrence, 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.

**Natural products**


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**UNIT – III**

**Thermodynamics**


**Quantum Chemistry**

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


*Particle in a box*- one dimensional and three dimensional. Plots of $\psi$ and $\psi^2$-discussion. Degeneracy of energy levels. Comparison of classical and quantum mechanical particles. Calculations using wave functions of the particle in a box-orthogonality, 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.


*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**


Concept of ion association – Bjerrum theory of ion association (elementary treatment) - ion association constant – Debye-Huckel-Bjerrum equation.

**Chemical Kinetics**


Unimolecular reactions and Lindamann’s theory.


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 nucleophilic reactions. The Swain – Scott equation and the Edward equation.

The reactivity-selectivity principle and the isoselectivity rule. The intrinsic barrier and Hammond’s postulate.

**Photochemistry**


**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.


**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.


**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

$^1$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$_2$X$_3$, 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, [$\eta^5$-C$_5$H$_5$M], [$\eta^5$-(C$_5$H$_5$)$_2$ Ti $\eta^1$-(C$_5$H$_5$)$_2$] and [$\eta^4$C$_8$H$_8$Ru(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$_6$, 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$_3$PSe, P$_3$S$_3$, P(OCH$_3$)$_3$, H$_3$PO$_4$, H$_3$PO$_3$, H$_3$PO$_2$, HPF$_2$, PF$_6^-$, PH$_3$.$^+$[Rh (PPh$_3$)$_3$Cl$_3$] Rh $I=1/2$

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

**Rotational and Vibrational spectroscopy**

**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.

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


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.


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...
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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 spectroscopy

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, CO, HF, NH₃ and H₂O - 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
Study of free radicals and transition metal complexes. Evidence for covalency in complexes, ex. Cu(II) Bissalcyldimine, Bis-acetylacetanatovanadyl(II) and hexachloroiridium(IV) complexes.