

CHEMISTRY

PART - A : RESEARCH METHODOLOGY

- 1. Errors and Evaluation** : Definition of terms in mean and median. Precision-standard deviation, relative standard deviation. Accuracy-absolute error, relative error. Types of error in experimental data determinates (systematic), indeterminate (or random) and gross. Sources of errors and the effects upon the analytical results. Methods for reporting analytical data.
- 2. Electroanalytical Methods** : *Conductometric* - Discussion of the nature of curves in acid-base (including mixtures of acids), precipitation and complexometric titrations; *Potentiometric* - Different types of electrodes, discussion of the nature of curves for oxidation-reduction and acid-base titrations, comparison with the conductometric method; *Polarographic* - Polarographically active species, concept of residual, diffusion and limiting currents and half wave potential, Ilkovic equation and factors affecting diffusion current.
- 3. Thermoanalytical Methods** : *Thermogravimetric* - Apparatus, factors affecting TGA, interpretation of TG curves of $\text{CaC}_2\text{O}_4 \cdot \text{H}_2\text{O}$ and $\text{MgC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ and in the analysis of their mixtures; *Differential Thermal Analysis and Differential Scanning Calorimetry* - Apparatus, factors affecting DTA/DSC curves with special reference to heating rate, particle size and packing, measurements of heats of transition or heat of reaction and heat of dehydration of metal salt hydrates.
- 4. Separation Techniques** : *Principle, Technique and Analytical Applications of the Following*: Solvent extraction; Chromatography (Paper, Thin Layer and Column); Ion exchange; and Structure elucidation of spectral data (IR and UV).

PART - B : CHEMISTRY

- 1. Fundamental Concepts of Quantum Chemistry** : De Broglie hypothesis, the Heisenberg's uncertainty principle, Sinusoidal wave equation, Hamiltonian operator, Schrodinger wave equation and its importance, Physical interpretation of the wave function, postulates of quantum mechanics, Particle in one dimension, particle in a one dimensional box; Schrodinger wave equation for H-atom, separation into three equations (without derivation), hydrogen like wave functions, radial wave functions, angular wave functions.
- 2. Quantum Mechanical Treatment of a Harmonic Oscillator** : One dimensional harmonic oscillator (classical and quantum mechanical treatment).
- 3. Thermodynamics and Electrochemistry** : The Joule Thomson's effect, The Gibbs Helmholtz equation and its applications, The Maxwell's relations, Thermodynamic equations of state (Relationship between E or H and P, V, T); Chemical potential and variation of chemical potential with temperature and pressure, The Gibbs-Duhem equation, Fugacity and variation of fugacity with temperature and pressure, concept of activity and activity coefficient; Debye-Falkenhagen effects, Wein effect, Ionic association, Basic concept of the electrical double layer and electrokinetic phenomena.
- 4. Stereochemistry and Bonding in Main Group Compounds** : VSEPR, Walsh diagram, $d\pi - p\pi$ bonds, Bent's rule, Energetics of hybridization, Some simple reactions of covalently bonded molecules.
- 5. Preparation, structure, bonding and technical applications of polyether complexes of alkali and alkaline earth metals, polyphosphazenes, thiazyl and its polymers, tetrasulphur dinitride; Structures of silicones and silicates.**

6. Preparation properties, structure and applications of alkyls and aryls of lithium, beryllium, magnesium, aluminium.
7. **Structures of 2 to 8 Coordinate Metal Complexes** : Cation-anion ratio in various polyhedra, Hybrid orbitals and preferred conditions of formation of the complexes of following geometries : C.N.2 – Linear; C.N.3 - Trigonal planar, Trigonal pyramidal; C.N.4 - Tetrahedral, Square planar; C.N.5 - Trigonal bipyramidal, square pyramidal, pentagonal; C.N.6 - Octahedral, Trigonal prism; C.N.7 - Pentagonal bipyramidal, Capped octahedral, Capped trigonal prism; C.N.8 - Cubic, Tetragonal antiprismatic, Dodecahedral, Hexagonal bipyramidal, and Bicapped trigonal prism,
8. Stereoisomerism in six coordinate octahedral complexes (Ma_3bcd , Ma_2bcde , $Mabcde$ and complexes containing bi-and terdentate ligands) Intermolecular and intramolecular (rearrangements Bailar and Ray Dutta Twist only), mechanism of racemisation in tris (chelate) octahedral complexes. Methods of resolution of optical isomers.
9. Kinetics and mechanism of substitution reactions in octahedral Co (III) and square planar Pt (II) Complexes; *Electron transfer reactions* : Mechanism of one electron transfer reactions (Inner and outer sphere mechanisms), factors affecting the rates of direct electron transfer reactions and the Marcus equation; Two electron transfer reactions.
10. **Metal Ligand Equilibria in Solution** : Step wise and overall formation constants and their relations, Factors affecting the stability of metal complexes with reference to the nature of metal ions and ligands, determination of stability constants by pH-metric and spectrophotometric methods.
11. **Organic Reaction Mechanism** : *Substitution Reactions*: Aliphatic nucleophilic, substitution (SN^1 , SN^2 , SN^i , mixed SN^1 and SN^2 , and SET mechanisms). Role of substrate structure, attacking reagents, leaving groups and solvents on SN^1 and SN^2 mechanisms. Neighbouring group participation by α and π bonds, anchimeric assistance. Stereochemistry of SN^1 and SN^2 reactions; Aromatic electrophilic substitution (nitration, halogenation, sulfonation, Friedel-Craft's alkylation and Friedel-Craft's acylation). Reactivity and orientation in electrophilic aromatic substitution. Hammett equation (sigma and rho). The effects of multiple substitutions. Nucleophilic aromatic substitution (The addition- elimination and Elimination - addition mechanisms). *Elimination Reactions*: Mechanism and orientation of $E1$, $E2$, $E1_{CB}$ reactions. The factors affecting $E1$, $E2$, $E1_{CB}$ reactions. $E1-E2-E1_{CB}$ spectrum. Factors affecting substitution versus elimination. Hofmann and saytzeff like eliminations. Stereochemistry of elimination reactions. Pyrolytic eliminations; *Addition Reactions*: (a) Addition of halogens and halogen acids to alkenes. 1,2-Bishydroxylation, epoxidation and hydroboration-oxidation reactions to alkenes. Mechanism and stereochemistry of electrophilic addition reactions. Sharpless asymmetric epoxidation. Nucleophilic addition to alkenes; (b) Addition to carbon-oxygen double ($C=O$) bonds, Cram's rule, Mechanisms of Aldol, Perkin, Knoevenagel, Claisen and Cannizzaro reactions.
12. General methods for the determination of structures of Alkaloid and ~~Peptides~~ *Peptides* *HEAD 2012*
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