

CHEMICAL SCIENCE

PAPER-II

- (1) Structure and Bonding : Atomic orbitals, electronic configuration of atoms (L-S coupling) and the periodic properties of elements; ionic radii, ionisation potential, electron affinity, electronegativity; concept of hybridization. Molecular orbitals and electronic configuration of homonuclear and heteronuclear diatomic molecules. Shapes of polyatomic molecules; VSEPR, theory Symmetry elements and point groups for simple molecules. Bond lengths, bond angles, bond order and bond energies. Types of Chemical Bond (weak and strong) intermolecular forces, structure of simple ionic and covalent solids, lattice energy.
- (2) Acids and bases : Bronsted and Lewis acids and bases, pH and pK_a, acid-based concept in non-aqueous media; HSAB concept. Buffer solution.
- (3) Redox Reactions : Oxidation numbers. Redox potential. Electrochemical series. Redox indicators.
- (4) Energetics and Dynamics of Chemical Reactions : Law of conservation of energy.

Energy and enthalpy of reactions. Entropy, free-energy, relationship between free energy change and equilibrium. Rates of chemical reactions (first-and second-order reaction). Arrhenius equation and concept of transition state. Mechanisms, including S_N1 and S_N2 reactions, electron transfer reactions, catalysis. Colligative properties of solutions.
- (5) Aspects of s.p.d.f. Block Elements : General characteristics of each block. Chemical principles involved in extractions and purification of iron, copper, lead, zinc and aluminium. Coordination chemistry : structural aspects, isomerism, octahedral and

- tetrahedral crystal-field splitting of d-orbitals. CFSE, magnetism and colour of transition metal ions. Sandwich compounds, metal carbonyls and metal clusters. Rare gas compounds, non-stoichiometric oxides. Radio activity and transmutation of elements. Isotopes and their applications.
- (6) IUPAC Nomenclature of simple Organic and Inorganic Compounds :
 - (7) Concept of Chirality : Recognition of symmetry elements and chiral structures; R/S nomenclature, diastereoisomerism in acyclic and cyclic systems; E-Z isomerism. Conformational analysis of simple cyclic (chair and boat cyclohexanes) and acyclic systems. Interconversion of Fischer, Newman and Sawhorse projections.
 - (8) Common Organic Reactions and Mechanisms : Reactive Intermediates. Formation and stability of carbonium ions, carbanions, carbenes, nitrenes, radicals and arynes. Nucleophilic, electrophilic radical substitution, addition and elimination reactions. Familiar name reactions : Aldol, Perkin, Stobbe, Dieckmann condensation; Hofmann, Schmidt, Lossen Curtius, Beckmann and Fries rearrangements; Reimer-Tiemann, Reformatsky and Grignard reactions Diels-Alder Reactions; Claisen rearrangement; Fritzsche - Crafts reactions; Wittig reactions; and Robinson annulation. Routine functional group transformations and interconversions of simple functionalities. Hydroboration, Oppenauer oxidations; Clemmensen, Wolff-Kishner, Meerwein-Ponndorf-Verley and Birch reductions.
 - (9) Elementary principles and applications of electronic, vibrational, NMR, EPR and Mass Spectral techniques to simple structural problems.
 - (10) Data Analysis : Types of errors, propagation of errors, accuracy and precision, least squares analysis, average standard deviation.

PAPER-III

1. Quantum Chemistry : Planck's quantum theory, wave-particle duality. Uncertainty Principle. operators and commutation relations : postulates of quantum mechanics and Schrodinger equation free particle. particle in a box, degeneracy, harmonic oscillator, rigid rotator and the hydrogen atom. Angular momentum, including spin; coupling of angular momenta including spin-orbit coupling.
2. The variation method and perturbation theory. Application to the helium atom; antisymmetry and exclusion Principle, Slater determinantal wave functions. Terms symbols and spectroscopic states.
3. Born-Oppenheimer approximation. Hydrogen molecule ion. LCAO-MO and AB treatments of the hydrogen molecule; electron density. forces and their role in chemical binding. Hybridisation and valence Mos of H_2O , Ng_3 and CH_4 Huckel plelection theory and its applications to ethelene, butadience and benzene. Idea of self-consistent fields.
4. Group theoretical representations and quantum mechanics; vanishing of integrals, spectroscopic selection rules for vibrational, electronic, vibronic and Raman spectroscopy. MO treatment of large molecules with symmetry.
5. Spectroscopy : Theoretical treatment of rotational, vibrational and electronic spectroscopy. Principles of magnetic resonance, Mossbauer and photoelectron spectroscopy.
6. Thermodynamics : First law of thermodynamics, relation between C_p and C_v ; enthalpies of physical and chemical changes; temperature dependence of enthalpies. second law of thermo-

- dynamics, entropy. Gibbs-Helmholtz equation. Third law of thermodynamics and calculation of entropy.
7. Chemical Equilibrium : Free energy and entropy of mixing, partial molar quantities, Gibbs-Duhem equation. Equilibrium constant. temperature-dependence of equilibrium constant, phase diagram of one and two-component systems, phase rule.
 8. Ideal and Non-ideal solutions. excess functions, activities, concept of hydration number : activities in electrolytic solutions; mean ionic activity coefficient; Debye-Huckel treatment of dilute electrolyte solutions.
 9. Electrochemistry : Electrochemical cell reactions, Nernst equation, Electrode Kinetics, electrical double layer, electrode/electrolyte interface, Batteries, primary & secondary Fuel cells, corrosion and corrosion prevention.
 10. Surface Phenomena : Surface tension,adsorption on solids, electrical phenomena at interphases, including electrokinetic, micelles and reverse micelles : solubilization, micro-emulsions. Application of photoelectron spectroscopy. ESCA and Auger spectroscopy to the study of surfaces.
 11. Statistical Thermodynamics : Thermodynamic probability and entropy : Maxwell-Boltzmann, Bose-Einstein and Fermi-Dirac statistics. Partition function: rotational translational, vibrational and electronic partition functions for diatomic molecules : calculations of thermodynamic functions and equilibrium constants. Theories of specific heat for solids.
 12. Non-equilibrium Thermodynamics : Postulates and methodologies, linear laws, Gibbs equation, Onsager reciprocal theory.
 13. Reaction Kinetics : Methods of determining rate laws. Mechanisms of photochemical, chain and oscillatory reactions. Collision theory of reaction rates; steric factor, treatment of unimolecular reactions. Theory of absolute reaction rates,

- comparison of results with Eyring and Arrhenius equations. Ionic reaction : salt effect. Homogeneous catalysis and Michaelis-Menten kinetics; heterogeneous catalysis.
14. Fast Reaction : Luminescence and Energy transfer processes. Study of kinetics by stoppedflow technique, realization method, flash photolysis and magnetic resonance method.
 15. Macromolecules : Number-average and weight average molecular weights; determination of molecular weights. Kinetics of polymerisation. Stereochemistry and mechanism of polymerisation.
 16. Solids : Dislocation in solids, schottky and Frenkel defects, Electrical properties; Insulators and semiconductors; superconductors; band theory of solids, Solid-state reactions.
 17. Nuclear Chemistry : Radioactive decay and equilibrium. Nuclear reactions; Q value, cross sections, types of reactions, Chemical effects of nuclear transformations; fission and fusion, fission products and fission yields. Radioactive techniques; tracer technique, neutron activation analysis, counting techniques such as G.M. ionization and proportional counter.
 18. Chemistry of Non-transition Elements : General discussion on the properties of the nontransition elements; special features of Individual elements; synthesis, properties and structure of their halides and oxides, polymorphism of carbon, phosphorus and sulphur. Synthesis, properties and structure of boranes, Carboranes, borazines, silicates carbides, silicones, phosphazenes, sulphurnitrogen compounds : peroxo compounds of boron, carbon and sulphur; oxy acids of nitrogen, phosphorous, sulphur and halogens, interhalogens pseudohalides and noble gas compounds.
 19. Chemistry of Transition Elements : Coordination chemistry of transition metalions; Stability constants of complexes and their

- determination; stabilization of unusual oxidation states. Stereochemistry of coordination compounds, Ligandfield theory, splitting of d-orbitals in low-symmetry environments. Jahn-Teller effect; Interpretation electronic spectra including charge transfer spectra; spectrochemical series, nephelauxetic series Magnetism: Diapara ferro and antiferromagnetism, quenching of orbital angular moment, spinorbit copling; inorganic reaction mechanisms; substitution reactions, trans effect and electron transfer reactions, photochemical reactions of chromium and ruthenium complexes. Fluxional molecules iso-and heteropolyacids, metal clusters. Spin corssover in coordination compounds.
20. Chemistry of Lanthanides and Actinides : Spectral and magnetic properties; Use of lanthanide compounds as shift reagents.
 21. Organometallic chemistry of Transition Elements : Synthesis, structure and bonding, organometallic reagents in organic synthesis and in homogeneous catalytic reactions (hydrogenation, hydromaylation, isomerisation and polymerisation); Pi-acid metal complexes, activation of small molecules by coordination.
 22. Topics in Analytical Chemistry : Adsorption partition, exclusion electrochromatography. Solvent extraction and ion exchange methods. Application of atomic and molecular absorption and emission spectroscopy in quantitative analysis Light scattering techniques including nephelometry and Raman spectroscopy. Electronalytical techniques : voltammetry, cyclic, voltammetry, polarography, amperometry, colometry and conductometry ion-elective electrodes, annodic stripping voltammetry : TGA, DTA, DSC and online analysers.
 23. Bionorganic Chemistry : Metal ions in Biology, Molecular machanism of ion transport across membranes; ionophores. Photosynthesis. PSL, PSH; nitrogen fixation, oxygen uptake pro-

- teins, cytochromes and ferredoxins.
24. Aromaticity : Huckel's rule and concept of aromaticity (n) annulenes and heteroannulenes, fullerenes (C₆₀)
 25. Stereochemistry and conformational Analysis : Newer method of asymmetric synthesis (including enzymatic and catalytic nexus), enantio and diastereo selective synthesis. Effects of conformation on reactivity in acyclic compounds and cyclohexanes.
 26. Selective Organic Name Reactions : Favorskii reaction; Stork enamine reaction; Michael addition; Sharpless asymmetric epoxidation; Ene reaction, Barton reaction, Hofmann-Löffler-Freytag reaction, Shapiro reaction, Baeyer-Villiger reaction, Chichibabin reaction.
 27. Mechanisms of Organic Reaction : Labelling and Kinetic isotope effects, Hammett equation, (sigma-rho) relationship, non-classical carbonium ions, neighbouring group participation.
 28. Pericyclic Reactions : Selection rules and stereochemistry of electrocyclic reactions, cycloaddition and sigmatropic shifts, Sommelet, Hauser, Cope and Claisen rearrangements.
 29. Heterocyclic Chemistry : Synthesis and reactivity of furan, thiophene, pyrrole, pyridine, quinoline, isoquinoline and indole; Skraup synthesis, Fischer indole synthesis.
 30. Reagents in Organic Synthesis : Use of the following reagents in organic synthesis and functional group transformations; Complex metal hydrides, Gilman's reagent, lithium dimethylcuprate, lithium diisopropylamide (LDA), dicyclohexylcarbodiimide, 1,3-dithiane (reactivity umpolung), trimethylsilyl iodide, tri-n-butyltin hydride, Woodward and Prevost hydroxylation, osmium tetroxide, DDQ, selenium dioxide, phase transfer catalysis, crown ethers and Merrifield resin, Peterson's synthesis, Wilkinson's catalyst, Baker yeast.

31. Chemistry of Natural products : Familiarity with methods of structure elucidation and biosynthesis of alkaloids, terpenoids, steroids, carbohydrates and proteins.
 32. Bioorganic Chemistry : Elementary structure and function of biopolymers such as proteins and nucleic acids.
 33. Photochemistry : Cis-trans isomerization, Paterno-Buchi reaction, Norrish Type I and II reactions, photoreduction of ketones, diphenyl ethane rearrangement, photochemistry of arenes.
 34. Spectroscopy : Applications of mass, UV-VIS, IR and NMR spectroscopy for structural elucidation of compounds.
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