Chemistry

PAPER-I

1. Atomic Structure :

Heisenberg's uncertainty principle Schrodinger wave equation (time independent); Interpretation of wave function, particle in one- dimensional box, quantum numbers, hydrogen atom wave functions; Shapes of s, p and d orbitals.

2. Chemical bonding :

Ionic bond, characteristics of ionic compounds, lattice energy, Born-Haber cycle; covalent bond and its general characteristics, polarities of bonds in molecules and their dipole moments; Valence bond theory, concept of resonance and resonance energy; Molecular orbital theory (LCAO method); bonding H2 +, H2 He2 + to Ne2, NO, CO, HF, CN–, Comparison of valence bond and molecular orbital theories, bond order, bond strength and bond length.

3. Solid state :

Crystal systems; Designation of crystal faces, lattice structures and unit cell; Bragg's law; X-ray diffraction by crystals; Close packing, radius ratio rules, calculation of some limiting radius ratio values; Structures of NaCl, ZnS, CsCl, CaF2; stoichiometric and nonstoichiometric defects, impurity defects, semiconductors.

4. The gaseous state and Transport Phenomenon :

Equation of state for real gasses, intermolecular interactions, and critical phenomena and liquefaction of gasses; Maxwell's distribution of speeds, intermolecular collisions, collisions on the wall and effusion; Thermal conductivity and viscosity of ideal gasses.

5. Liquid State :

Kelvin equation; Surface tension and surface energy, wetting and contact angle, interfacial tension and capillary action.

6. Thermodynamics :

Work, heat and internal energy; first law of thermodynamics.

Second law of thermodynamics; entropy as a state function, entropy changes in various processes, entropy-reversibility and irreversibility, Free energy functions; Thermodynamic equation of state; Maxwell relations; Temperature, volume and pressure dependence of U, H, A, G, Cp and Cv, and ; J-T effect and inversion temperature; criteria for equilibrium, relation

between equilibrium constant and thermodynamic quantities; Nernst heat theorem, introductory idea of third law of thermodynamics.

7. Phase equilibria and solutions :

Clausius-Clapeyron equation; phase diagram for a pure substance; phase equilibria in binary systems, partially miscible liquids—upper and lower critical solution temperatures; partial molar quantities, their significance and determination; excess thermodynamic functions and their determination.

8. Electrochemistry :

Debye-Huckel theory of strong electrolytes and Debye-Huckel limiting Law for various equilibrium and transport properties.

Galvanic cells, concentration cells; electrochemical series, measurement of e.m.f. of cells and its applications fuel cells and batteries.

Processes at electrodes; double layer at the interface; rate of charge transfer, current density; overpotential; electroanalytical techniques : amperometry, ion selective electrodes and their use.

9. Chemical kinetics:

Differential and integral rate equations for zeroth, first, second and fractional order reactions; Rate equations involving reverse, parallel, consecutive and chain reactions; Branching chain and explosions; effect of temperature and pressure on rate constant. Study of fast reactions by stop-flow and relaxation methods. Collisions and transition state theories.

10. Photochemistry:

Absorption of light; decay of excited state by different routes; photochemical reactions between hydrogen and halogens and their quantum yields.

11. Surface phenomena and catalysis:

Adsorption from gasses and solutions on solid adsorbents; Langmuir and B.E.T. adsorption isotherms; determination of surface area, characteristics and mechanism of reaction on heterogeneous catalysts.

12. Bio-inorganic chemistry:

Metal ions in biological systems and their role in ion-transport across the membranes (molecular mechanism), oxygen-uptake proteins, cytochromes and ferredoxins.

13. Coordination chemistry :

(i) Bonding in transition of metal complexes. Valence bond theory, crystal field theory and its modifications; applications of theories in the explanation of magnetism and electronic spectra of metal complexes.

(ii) Isomerism in coordination compounds; IUPAC nomenclature of coordination compounds; stereochemistry of complexes with 4 and 6 coordination numbers; chelate effect and polynuclear complexes; trans effect and its theories; kinetics of substitution reactions in square-planar complexes; thermodynamic and kinetic stability of complexes.

(iii) EAN rule, Synthesis structure and reactivity of metal carbonyls; carboxylate anions, carbonyl hydrides and metal nitrosyl compounds.

(iv) Complexes with aromatic systems, synthesis, structure and bonding in metal olefin complexes, alkyne complexes and cyclopentadienyl complexes; coordinative unsaturation, oxidative addition reactions, insertion reactions, fluxional molecules and their characterization; Compounds with metal—metal bonds and metal atom clusters.

14. Main Group Chemistry:

Boranes, borazines, phosphazenes and cyclic phosphazene, silicates and silicones, Interhalogen compounds; Sulphur—nitrogen compounds, noble gas compounds.

15. General Chemistry of 'f' Block Element:

Lanthanides and actinides: separation, oxidation states, magnetic and spectral properties; lanthanide contraction.

PAPER-II
1. Delocalised covalent bonding :

Aromaticity, anti-aromaticity; annulenes, azulenes, tropolones, fulvenes, sydnones.

2. (i) Reaction mechanisms : General methods (both kinetic and non-kinetic) of study of mechanisms or organic reactions : isotopes, method crossover experiment, intermediate trapping, stereochemistry; energy of activation; thermodynamic control and kinetic control of reactions.

(ii) Reactive intermediates : Generation, geometry, stability and reactions of carbonium ions and carbanions, free radicals, carbenes, benzynes and nitrenes.

(iii) Substitution reactions :—SN 1, SN 2, and SN i, mechanisms ; neighbouring group participation; electrophilic and nucleophilic reactions of aromatic compounds including heterocyclic compounds—pyrrole, furan, thiophene and indole.

(iv) Elimination reactions :—E1, E2 and E1cb mechanisms; orientation in E2 reactions—Saytzeff and Hoffmann; pyrolytic syn elimination—acetate pyrolysis, Chugaev and Cope eliminations.

(v) Addition reactions :—Electrophilic addition to C=C and C≡C; nucleophilic addition to C=O, C≡N, conjugated olefins and carbonyls.

(vi) Reactions and Rearrangements :—(a) Pinacol-pinacolone, Hoffmann, Beckmann, Baeyer Villiger, Favorskii, Fries, Claisen, Cope, Stevens and Wagner—Meerwein rearrangements.

(b) Aldol condensation, Claisen condensation, Dieckmann, Perkin, Knoevenagel, Witting, Clemmensen, Wolff-Kishner, Cannizzaro and von Richter reactions; Stobbe, benzoin and acyloin condensations; Fischer indole synthesis, Skraup synthesis, Bischler-Napieralski, Sandmeyer, Reimer-Tiemann and Reformatsky reactions.

3. Pericyclic reactions :—Classification and examples; Woodward-Hoffmann rules—electrocyclic reactions, cycloaddition reactions [2+2 and 4+2] and sigmatropic shifts [1, 3; 3, 3 and 1, 5], FMO approach.

4. (i) Preparation and Properties of Polymers: Organic polymers polyethylene, polystyrene, polyvinyl chloride, teflon, nylon, terylene, synthetic and natural rubber.

(ii) Biopolymers: Structure of proteins, DNA and RNA.

5. Synthetic Uses of Reagents:

OsO_4, HIO_4, CrO_3, $Pb(OAc)_4$, SeO_2, NBS, B_2H_6, Na-Liquid NH_3, $LiAlH_4$, $NaBH_4$, n-BuLi, MCPBA.

Photochemistry :—Photochemical reactions of simple organic compounds, excited and ground states, singlet and triplet states, Norrish-Type I and Type II reactions.
Spectroscopy:
Principle and applications in structure elucidation :

(i) Rotational—Diatomic molecules; isotopic substitution and rotational constants.

(ii) Vibrational—Diatomic molecules, linear triatomic molecules, specific frequencies of functional groups in polyatomic molecules.

(iii) Electronic—Singlet and triplet states. n→π* andπ→π* transitions; application to conjugated double bonds and conjugated carbonyls Woodward-Fieser rules; Charge transfer spectra.

(iv) Nuclear Magnetic Resonance (1HNMR): Basic principle; chemical shift and spin-spin interaction and coupling constants.

(v) Mass Spectrometry :—Parent peak, base peak, metastable peak, McLafferty rearrangement.