

## **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 H<sub>2</sub> +, H<sub>2</sub> He<sub>2</sub> + to Ne<sub>2</sub>, 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, CaF<sub>2</sub>; stoichiometric and nonstoichiometric defects, impurity defects, semiconductors.

#### **4. The gaseous state and Transport Phenomenon :**

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

#### **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,  $\Delta H$  and  $\Delta S$ ; 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-Hückel theory of strong electrolytes and Debye-Hückel 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 gases 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, sydrones.

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

(ii) **Reactive intermediates** : Generation, geometry, stability and reactions of carboniumions and carbanions, free radicals, carbenes, benzyne and nitrenes.

(iii) **Substitution reactions** :— $S_N\ 1$ ,  $S_N\ 2$ , and  $S_N\ i$ , 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, Wittig, 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 polymerspolyethylene, polystyrene, polyvinyl chloride, teflon, nylon, terylene, synthetic and natural rubber.

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

**5. Synthetic Uses of Reagents:**

OsO<sub>4</sub>, HIO<sub>4</sub>, CrO<sub>3</sub>, Pb(OAc)<sub>4</sub>, SeO<sub>2</sub>, NBS, B<sub>2</sub>H<sub>6</sub>, Na-Liquid NH<sub>3</sub>, LiAlH<sub>4</sub>, NaBH<sub>4</sub>, *n*-BuLi, MCPBA.

6. **Photochemistry** :—Photochemical reactions of simple organic compounds, excited and ground states, singlet and triplet states, Norrish-Type I and Type II reactions.

7. **Spectroscopy:**

Principle and applications in structure elucidation :

- (i) **Rotational**—Diatom molecules; isotopic substitution and rotational constants.
- (ii) **Vibrational**—Diatom molecules, linear triatomic molecules, specific frequencies of functional groups in polyatomic molecules.
- (iii) **Electronic**—Singlet and triplet states.  $n\pi\pi^*$  and  $\pi\pi\pi^*$  transitions; application to conjugated double bonds and conjugated carbonyls Woodward-Fieser rules; Charge transfer spectra.
- (iv) **Nuclear Magnetic Resonance ( $^1\text{H}\text{NMR}$ )**: Basic principle; chemical shift and spin-spin interaction and coupling constants.
- (v) **Mass Spectrometry** :—Parent peak, base peak, metastable peak, McLafferty rearrangement.