

CHEMISTRY OPTIONAL

Syllabus

Paper 1 :

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_2^+ , H_2 He_2^+ to Ne_2 , 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_2 ; 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 :

1. Work, heat and internal energy; first law of thermodynamics.
2. 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, C_p and C_v , 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 :

1. Debye-Huckel theory of strong electrolytes and Debye-Huckel limiting Law for various equilibrium and transport properties.
2. Galvanic cells, concentration cells; electrochemical series, measurement of e.m.f. of cells and its applications fuel cells and batteries.
3. 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. Bioinorganic 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 :

1. 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.
2. 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.
3. EAN rule, Synthesis structure and reactivity of metal carbonyls; carboxylate anions, carbonyl hydrides and metal nitrosyl compounds.
4. 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 2 :

1. Delocalised Covalent Bonding : Aromaticity, anti-aromaticity; annulenes, azulenes, tropolones, fulvenes, sydnones.

2.

- 1. Reaction mechanisms :** General methods (both kinetic and non-kinetic) of study of mechanisms or organic reactions : isotopies, method crossover experiment, intermediate trapping, stereochemistry; energy of activation; thermodynamic control and kinetic control of reactions.
- 2. Reactive intermediates :** Generation, geometry, stability and reactions of carbonium ions and carbanions, free radicals, carbenes, benzyne and nitrenes.
- 3. 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.
- 4. Elimination reactions :—** E1, E2 and E1cb mechanisms; orientation in E2 reactions—Saytzeff and Hoffmann; pyrolytic *syn* elimination—acetate pyrolysis, Chugaev and Cope eliminations.
- 5. Additional reactions :—** Electrophilic addition to C=C and C≡C; nucleophilic addition to C=O, C≡N, conjugated olefins and carbonyls.
- 6. Reactions and Rearrangements :—**
 - Pinacol-pinacolone, Hoffmann, Beckmann, Baeyer-Villiger, Favorskii, Fries, Claisen, Cope, Stevens and Wagner—Meerwein rearrangements.
 - 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.

- 1. Preparation and Properties of Polymers:** Organic polymers polyethylene, polystyrene, polyvinyl chloride, teflon, nylon, terylene, synthetic and natural rubber.
- 2. Biopolymers:** Structure of proteins, DNA and RNA.

5. Synthetic Uses of Reagents: OsO₄, HIO₄, CrO₃, Pb(OAc)₄, SeO₂, NBS, B₂H₆, Na-Liquid NH₃, LiAlH₄, NaBH₄, *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 :

1. **Rotational**—Diatomic molecules; isotopic substitution and rotational constants.
2. **Vibrational**—Diatomic molecules, linear triatomic molecules, specific frequencies of functional groups in polyatomic molecules.
3. **Electronic**—Singlet and triplet states. n and π transitions; application to conjugated double bonds and conjugated carbonyls Woodward-Fieser rules; Charge transfer spectra.
4. **Nuclear Magnetic Resonance (^1H NMR)**: Basic principle; chemical shift and spin-spin interaction and coupling constants.
5. **Mass Spectrometry** :—Parent peak, base peak, metastable peak, McLafferty rearrangement.



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