



# CHEMISTRY

## SYLLABUS

### UPSC (Optional) - Mains

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**CHEMISTRY****SYLLABUS****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  $H_2$ ,  $He_2$ ,  $NO$ ,  $CO$ ,  $HF$ ,  $CN^-$ , 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, semi-conductors.
- 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  $U$ ,  $H$ ,  $A$ ,  $G$ ,  $C_p$  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.

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- 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 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

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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; Compound 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: 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, 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.

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- (v) **Addition reactions:** —Electrophilic addition to  $C=C$  and  $C \equiv C$ ; nucleophilic addition to  $C=O$ ,  $C \equiv N$ , 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.
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**—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.  $n$  and transitions; application to conjugated double bonds and conjugated carbonyls Woodward-Fieser rules; Charge transfer spectra. (iv) Nuclear Magnetic Resonance ( $^1H$  NMR): Basic principle; chemical shift and spin-spin interaction and coupling constants.
- (iv) **Mass Spectrometry:** —Parent peak, base peak, metastable peak, McLafferty rearrangement