

# Entrance Exam for Ph.D Syallabus (Chemistry)

## INORGANIC CHEMISTRY

**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 di-atomic 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 pKa, 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 SN1 and SN2 reactions, electron transfer reactions, catalysis. Colligative properties of solutions.

**5. Aspects of s.p.d.f. Block Elements**

**6. IUPAC Nomenclature of simple Inorganic Compounds**

**7. Chemistry of Non-transition Elements**

**8. Chemistry of Transition Elements**

**9. Chemistry of Lanthanides and Actinides:** Spectral and magnetic properties; Use of lanthanide compounds as shift reagents.

**10. Organometallic chemistry of Transition Elements:** Synthesis, structure and bonding, organometallic reagents in organic synthesis and in homogeneous catalytic reactions (hydrogenation, hydroformylation, isomerisation and polymerisation);  $\pi$ -acid metal complexes, activation of small molecules by coordination.

**11. Bioinorganic Chemistry**

**12. Data Analysis:** Types of errors, propagation of errors, accuracy and precision, least squares analysis, average standard deviation.

## **PHYSICAL CHEMISTRY**

**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. 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

**3. Spectroscopy :** Theoretical treatment of rotational, vibrational and electronic spectroscopy. Principles of magnetic resonance, Mossbauer and photoelectron spectroscopy.

**4. 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 thermodynamics, entropy. Gibbs-Helmholtz equation. Third law of thermodynamics and calculation of entropy.

**5. 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.

**6. 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.

**7. Electrochemistry :** Electrochemical cell reactions, Nernst equation, Electrode Kinetics, electrical double layer, electrode/electrolyte interface, Batteries, primary & secondary Fuel cells, corrosion and corrosion prevention.

**8. Surface Phenomena :** Surface tension, adsorption on solids, electrical phenomena at interfaces, including electrokinetic, micelles and reverse micelles : solubilization, micro-emulsions. Application of photoelectron spectroscopy. ESCA and Auger spectroscopy to the study of surfaces.

**9. 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.

**10. Fast Reaction :** Luminescence and Energy transfer processes. Study of kinetics by stopped flow technique, relaxation method, flash photolysis and magnetic resonance method.

**11. Macromolecules :** Number-average and weight average molecular weights; determination of molecular weights. Kinetics of polymerisation. Stereochemistry and mechanism of polymerisation.

**12. Solids :** Dislocation in solids, Schottky and Frenkel defects, Electrical properties; Insulators and semiconductors; superconductors; band theory of solids, Solid-state reactions.

**13. 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.

**14. 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. Electroanalytical techniques : voltammetry, cyclic voltammetry, polarography, amperometry, coulometry and conductometry ion-selective electrodes, anodic stripping voltammetry : TGA, DTA, DSC and online analysers.

## **ORGANIC CHEMISTRY**

**1 IUPAC Nomenclature of simple Organic compounds, Aromaticity :** Huckel's rule and concept of aromaticity (n) annulenes and heteroannulenes, fullerenes (C<sub>60</sub>)

**2. Stereochemistry and conformational Analysis :** Newer method of asymmetric synthesis (including enzymatic and catalytic), enantio and diastereo selective synthesis. Effects of conformation on reactivity in acyclic compounds and cyclohexanes.

**3. Selective Organic Name Reactions**

**4. Mechanisms of Organic Reaction :** Labelling and Kinetic isotope effects, Hammett equation, (sigma-rho) relationship, non-classical carbonium ions, neighbouring group participation.

**5. Pericyclic Reactions :** Selection rules and stereochemistry of electrocyclic reactions, cycloaddition and sigmatropic shifts, Sommelet, Hauser, Cope and Claisen rearrangements.

**6. Heterocyclic Chemistry :** Synthesis and reactivity of furan thiophene, pyrrole, pyridine, quinoline, isoquinoline and indole; Skraup synthesis, Fischer indole synthesis.

**7. 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-nbutyltin 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.

**8. Chemistry of Natural products :** Familiarity with methods of structure elucidation and biosynthesis of alkaloids, terpenoids, steroids, carbohydrates and proteins.

**9. Bioorganic Chemistry :** Elementary structure and function of biopolymers such as proteins and nucleic acids.

**10. Photochemistry :** Cis-trans isomerization, Paterno-Buchi reaction, Norrish Type I and II reactions, photoreduction of ketones, pinacol rearrangement, photochemistry of arenes.

**11. Spectroscopy :** Applications of mass, UV-VIS, IR and NMR spectroscopy for structural elucidation of compound.