DEPARTMENT OF CHEMISTRY

Syllabus for Ph.D Entrance Examination

Unit I

Reactive intermediates: Generation, stability and reactivity of carbocations, carbanions, carbenes, benzynes and nitrenes, Free radicals – configurations – identification by chemical and spectral methods – free radical halogenations

Electrophilic Substitution **:**Mechanism of aliphatic electrophilic substitution reaction – S_E1, S_E2, S_Ei reaction. Mechanism of aromatic electrophilic substitution reactions – complexes – nitration, halogenation, sulphonation, Friedel Craft alkylation and acylation – Reimer Tiemann reaction..

Addition reactions: Regio and stereochemistry of addition of halogens and halogens acids to carbon – carbon multiple bonds – hydroboration – addition to carbonyl bonds – mechanism of Aldol, Perkin, Stobbe, Dieckmann condensation, Reformatsky and Grignard reaction, Michael addition reaction and Mannich reaction – Formation and Synthetic application of enamics – Stork enamine reaction – Mechanism of ester hydrolysis.

Unit II

Rearrangements : Nucleophilic, electrophilic and free radical rearrangements – intramolecular and intermolecular – rearrangements – migratory aptitude – Wagner – Meerwin, pinacol – pinacolone, Benzil – Benzilic acid – Hofmann, Schmidt, Lossen, Curtius, Beckmann, Fries, Baeyer Villeger, Favorski, Stevens and Neber rearrangements.

Synthetic Reagents : Use of the following reagents in organic synthesis and functional group transformation – Dicyclohexylcarbodiimide, 1,3 dithiane (reactivity umpolung), trimethylsilyl, iodide, tri-n-butyl tin hydride, Woodward and Prevost hydroxylation, Osmium tetroxide, DDQ Wilkinson's Catalyst – Wittig reaction, Clemmenson reaction, Wolf Kishner reduction, Birch Reduction, Rosenmund reduction

Oxidation and Reduction: Oxidation of organic compounds with reagents based on peroxides, peracids, ozone, osmium, chromium, ruthenium, silver, dimethyl sulfoxide, iodine and selenium dioxide Reduction of organic compounds with reagents based on alkali and alkaline earth metals, boron, aluminium, hydrogen, hydrazine, formic acid and dissolving metals.

Unit III

Covalent Bonding

V.B. approach to bonding-Hitler-London, Pauling and Slater refinements, Concept of hybridization and structure of molecules, VSEPR theory shapes of molecules. M.O. approach to covalent bonding – symmetry and overlap of atomic orbitals – symmetry of molecular orbitals – sigma, pi and delta bondings – energy levels in homo and hetero nuclear diatomic systems – bond length, bond order and bond energy, Application to small molecules such as $BeCl_2$, BCl_3 and CCl_4, SF_4, ClF_3, BrF_3 , BrF_5 , IF_5, IF_7 etc – Bonding in Noble gas compounds – $XeCl_2$, XeF_4, $XeOF_4$, XeF_6., ionic character in a covalent bond. The concept of multicentre bonding. Bonding in simple planar triatomic systems. Structure and bonding di and trinuclear clusters of rhenium halides, diborane, and tetraborane.

Unit IV

Chemistry of Coordination Compounds

Brief review of the general characteristics of transition elements, nomenclature of coordination complexes, Isomerism in coordination compounds, types of ligands and chelate effect, stepwise and overall formation constants-determination of stability constant by Job's continuous variation method. Werner, Sidzwick, VB theory and CFT - Splitting of d-orbitals under different geometries – CFSE – evidence for CFSE-factors affecting CFSE – spectrochemical series – Jahn-Teller distortion- application of d-orbital splittings to explain magnetic properties, low spin and high spin complexes, – Site preferences - Limitations of CFT – Ligand field theory – MO theory – sigma – and pi-bonding in complexes – Nephelauxetic effect – The angular overlap model.

Unit V

Thermodynamics and Chemical Equilibrium

The second law of thermodynamics – Entropy – Disorder, Probability and entropy – The Third law of thermodynamics – Third law of entropies – thermodynamics of systems of variable compositions – partial molar quantities and their determination – chemical potential – Gibbs-Duhem equation – Fugacity and its determination – equilibrium constant and its temperature dependence

Chemical Kinetics

Collision theory of reaction rate – steric factor – theory of absolute reaction rates thermodynamic treatment – Unimolecular reactions – Lindemann, Hinshelwood, RRK, RRKM and Slater theories – Termolecular reactions – chain reactions – study of kinetics of chain reactions like H_2-Br_2 reaction, Decomposition of acetaldehyde and N_2O_5 explosive reactions – study of H_2O_2 reaction- ionic reactions in solution – factors influencing the reaction rate salt effect