

Department of Chemistry

Ūniversity of Kashmir

(NAAC Accredited Grade-A+)

Hazratbal, Srinagar, 190006, J&K, India

P.G. Entrance Syllabus -2025

Unit 1:

Basic Inorganic Chemistry: Electronegativity. Effective nuclear charge. Fajan's rules. VSEPR theory of simple molecules. MO treatment of heteronuclear diatomic molecules (CO and NO). Multicenter bonding in electron deficient molecules. Acid base theories and applications.

Gravimetry: Introduction and Principle. Precipitation Reagents and Methods. Concentration, Super-saturation, Precipitation, Co-precipitation, Post precipitation, Digestion, Washing and Filtration. Gravimetric calculations. Complexometric Titrations, Metal ion Indicators, Titration Curves, Mixture Titrations: Masking and demasking. Back Titration, Precipitation Titrations.

Environmental Chemistry: Segments of Environment; Macro and Micronutrients in Soil. Acid. Water quality parameters: Dissolved oxygen, and Metals. Vertical profile of atmosphere, Reactions in Atmosphere. Molecular Symmetry: Molecular Symmetry - Symmetry elements and operations.

Unit 2:

s-Block Chemistry: Chemical reactivity of s-block elements towards water, oxygen, hydrogen, and halogens. Anomalous behavior and diagonal relationship. Chemical characteristics of the compounds of alkali and alkaline earth metals. Solutions of alkali metals in liquid ammonia, EDTA complexes of calcium and magnesium.

p-Block Elements: Boranes- classification, bonding in diborane. STYX convention, inert pair effect. Boron-Nitrogen (Borazine) and Nitrogen-Phosphorus compound (phosphonitrilic halides). Structure and bonding in silicates. Chemical behavior of oxides and oxoacids of phosphorus, sulphur and chlorine, peroxoacids of sulphur. Pseudohalogens, polyhalides, and interhalogen compounds. Structure and bonding in fluorides, oxides and oxyfluorides of xenon.

Ceramics and glasses: Definition and classification of ceramics. Applications of ceramics.

Unit 3:

Transition elements: variable oxidation states, anomalous electronic configurations. Trends in ionic radii, hydration and lattice energy of 3d series. Standard Electrode Potentials of M^{2+}/M and M^{3+}/M^{2+} systems. Complexing ability, Catalytic properties. Acidic/Basic character of transition metal compounds in various oxidation states. Stabilization of unusual oxidation states. Chemistry of selected transition metal compounds (Potassium ferricyanide and sodium nitroprusside).

Magnetic properties: calculation of magnetic moment value (spin only). Spectral properties (d-d bands and charge transfer transitions).

Chemistry of Inner-Transition Elements: Electronic configuration, oxidation states, f-orbital's. Complexing behavior of inner transition elements (Stereochemistry and stability). Spectral and Magnetic Properties (comparison with transition metals). Consequences of Lanthanide contraction (case studies). Separation of Lanthanides by ion–exchange and solvent extraction methods.

Selected examples of lanthanide complexes with nitrate, β -Diketonate, crown ether and porphyrin type ligands. Homo and hetero dinuclear coordination compounds, coordination polymers of lanthanide ions.

Unit 4:

Bioinorganic chemistry: Transport mechanism (uniport, symport and antiport). Siderophores and metallothionein. Ferritin and Transferrin: metal binding sites; incorporation and release of iron. Haemoglobin



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and Myoglobin: Structure, oxygen saturation curves. Representative synthetic oxygen carrier model compounds (Vaska type complexes).

Metalloenzymes: Structure, mechanism of action: Carbonic anhydrase, carboxypeptidase and Nitrogenase. Biological chemistry of Molybednum (Xanthine oxidase) and cobalt (Vit B12). Structure and biological role of Rubredoxin and Ferridoxin, Blue Copper proteins: (Oxidases and Plastocyanin). Cytochrome P450. Therapeutic applications of cis-platin, transition metal radio-isotopes (Tc) and MRI (Gd) agents. Toxicity of metals and chelation therapy (Therapeutic aspects of chelating drugs: conditional stability constant HSAB theory).

Nuclear Chemistry: Stability of nucleus: n/p ratio, binding energy, packing fraction, structure of nucleus- Shell model and Liquid drop model. Types of nuclear reactions, nuclear cross section, isotope separation methods. Radioactivity: natural and induced. Radioactive decay. Application of radioisotopes in chemical reactions, and medicine. Carbon dating.

Unit 5:

Coordination Chemistry: Werner's Theory. Geometrical and optical isomerism. Bonding models in coordination complexes: Limitations of VBT, Crystal field theory of octahedral tetrahedral and square planar complexes. Factors affecting magnitude of Δ . CFSE calculations of weak and strong field ligands.

Stability of coordination compounds and factors affecting stability. Chelate and Macrocyclic effect. Spectrochemical series. Magnetic properties of transition metal complexes. Limitations of Crystal field theory. Analytical applications of coordination compounds.

Organometallic compounds: Definition and classification. Hapticity concept, Applications of 18-electron rule. Stability of organometallic compounds. Preparation, structure and bonding in Zeise's salt. Homogenous and heterogenous catalysis.

pi-Acid Complexes of Transition Metals: Transition Metal Carbonyls: Carbon Monoxide as ligand; synthesis, and bonding in mononuclear carbonyls (synergistic bonding). Spectral analysis of metal carbonyl compound (FTIR).

Unit 6:

Aromaticity: Requirements of aromaticity. Huckel's rule and its significance. Homo and Antiaromaticity, Aromaticity of non-benzenoid compounds like pyrrole, thiophene, furan and aromatic ions (3, 5 and 7-membered rings).

Aromatic electrophilic substitution: General mechanism. The second substitution: role of activating and deactivating groups, orientation of benzene. Mechanisms of Gattermann, Huben-Hoesch, Veils-Meir Haack and Riemer-Tieman reactions. Aromatic nucleophilic substitution: Discussion of SN–unimolecular, SN₂Ar and benzyne mechanisms.

Conformations with respect to ethane, butane and cyclohexane. Interconversion of Wedge Formula, Newmann, Sawhorse and Fischer representations. Concept of chirality (upto two carbon atoms). Configuration: Geometrical and Optical isomerism; Enantiomerism, Diastereomerism and Meso compounds). Threo and Erythro; D and L; cis – trans nomenclature; CIP Rules: R/S (for upto 2 chiral carbon atoms) and E/Z Nomenclature (upto two C=C systems).

Reactive intermediates: Structure, generation and stability of Carbocations, Carbanions, Free radicals, Carbenes, Benzynes and Nitrenes.



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Unit 7:

Methods of formation of Alkenes, Saytzeff rule, Hoffman rule. Electrophilic and free radical additions. Marknwnikov's rule, anti Markownikov's addition of HBr, hydroboration, ozonolysis. 1,2 and 1,4 addition in conjugated dienes. Diel's Alder reaction. Acidity of alkynes, Mechanism of electrophilic and nucleophilic addition reactions of Alkynes. Mechanism of nucleophilic substitution reactions of alkyl and benzyl halides: SN_1 , SN_2 and SN_i reactions.

Alcohols: Synthesis of 1, 2 diols and trihydric alcohols (Glycerol), Periodic acid and Lead tetra acetate oxidations of 1,2-diols. Phenols: Comparative study of acidic character of substituted phenol. Nitration and sulphonation on α and β napthols, Mechanisms of Kolbe's–Schmidt reactions, Fries and Claisen rearrangements.

Unit-8:

Substitution and elimination reactions of alkyl halides and alcohols: Mechanistic details of SN_1 and SN_2 ; E_1 and E_2 reactions. Hoffman and Saytzev's rules, Effects of structure of alkyl halides/ alcohols, nature of nucleophiles, leaving groups and effect of solvent. Substitution versus Elimination. Mitsunobu reaction.

Mechanistic details including regioselectivity and stereochemical implications of halogenation, hydrohalogenation, hydroboration, epoxidation, Prevost and Woodward hydroxylation. Acidic character, hydration and catalytic/ metal-ammonia reductions of alkynes. Heterogeneous and homogeneous hydrogenation of double bonds and aromatic rings. Hydroboration of alkene, Electrophilic and nucleophilic epoxidation of alkene. Regioselectivity of epoxide ring opening. Sharpless asymmetric epoxidation. Addition to dienes. Mechanism, stereochemistry and regio-chemistry of Elimination reactions in cyclic systems.

UNIT 9:

Nucleophilic additions to carbonyls and stereochemical aspects through various models (Cram, Cram chelation) for acyclic systems. Stereochemical control in addition of nucleophiles to cyclic carbonyl compounds. Formation and stability of enolates and enamines. Addition of Phosphorus and sulfur ylids. Wittig-Horner reaction. Michael addition.

Need for Green Chemistry and the role of chemists. Principles of Green Chemistry. E-Factor. Tools of Green Chemistry: Selection of starting materials, Catalysts, Alternative Solvents: Supercritical carbon dioxide, H₂O, Ionic Liquids, green reagents, atom economy. Alternative energy sources: Microwaves, Sonication, Mechanical and Visible light.

UNIT 10:

Principles of Ultra Violet Spectroscopy, Electronic transitions in organic molecules, Woodward-Fieser rules for calculation of λ_{max} of organic compounds. Principles of Infrared spectroscopy, The Infrared spectrum, the functional group and fingerprint regions, Characteristic IR absorption bands, Intensity and position of absorption bands. Structural features effecting vibrational frequency. Application of IR spectroscopy in structural elucidation of organic compounds.

NMR: Basic concepts, Chemical shift and its measurements for various classes of compounds. One bond coupling, two bond coupling, three bond coupling, second order spectra. Proton exchange, deuterium exchange, Peak broadening exchange. Nuclear Overhouser Effect (NOE). Applications of ¹H NMR in structural elucidation of simple molecules.



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UNIT 11:

Gaseous State: Kinetic molecular theory of gases, Root mean square, average and most probable velocities; qualitative discussion of Maxwell's distribution of molecular velocities.

Deviation of gases from ideal behaviour, van der Waal's equation of state. PV isotherms of real gases, continuity of states, van der Waal's equation isotherms. Relationship between critical constants and van der Waal's constants, the law of corresponding states, reduced equation of state.

Liquid State: Viscosity and surface tension of liquids, factors affecting viscosity and surface tension

Solid State: General characteristics of solids, Symmetry elements in crystals, Crystal lattice and unit cell, number of atoms in the unit cell, close-packed structures, packing efficiency, and Characteristic structures of ionic solids (NaCl, CaF₂, ZnS).

X-Ray Diffraction by Solids: Laws of Crystallography, Lattice Planes and Miller indices; Interplanar distance, Bragg equation, Debye-Scherrer method of X-ray structural analysis of crystals, Systematic absences, identification of cubic unit cells from systematic absences in diffraction pattern. Structure factor and its relation to intensity. Calculation of structure factor for Rock salt, and Cesium chloride structures.

Unit 12:

First Law of thermodynamics: Heat capacity, heat capacities at constant volume and constant pressure and their relationship. Joule's law, Joule-thomson coefficient and inversion temperature. Calculation of w, q, $\Delta U \& \Delta H$ for the expansion of ideal and non-ideal (van der Waals) gases under isothermal and adiabatic conditions for reversible. Bond dissociation energy and its calculation from thermo-chemical data. Kirchhoff's equation.

Second law of thermodynamics: Different statements of the law. Carnot cycle and its efficiency, carnot theorem. Concept of entropy, entropy as a state function, entropy as a function of V&T and P&T, entropy change in physical processes. Clausius inequality, entropy as a criteria of spontaneity and equilibrium. Entropy change in ideal gas expansion and entropy of mixing of ideal gases. Gibb's paradox, Maxwell's relations and thermodynamic equations of state.

Third law of thermodynamics: Nernst heat theorem, statement of third law, concept of residual entropy, The calorimetric measurement of entropy, residual entropy. Gibbs function (G) and Helmholtz function (A) as criteria for thermodynamic equilibrium and spontaneity. Variation of G and A with P, V, T and composition Equilibrium constant and free energy change. Reaction isotherm and reaction isochore, Clapeyron equation and Clausius-Clapeyron equation, applications. Activity and activity coefficient.

UNIT 13:

Thermodynamics of multicomponent systems: Chemical potential, temperature and pressure dependence. Thermodynamic mixing functions of ideal and nonideal solutions, Excess thermodynamic functions of non-ideal solutions.

Phase Equilibria: phase, component and degree of freedom. Gibbs phase rule, Phase diagrams of onecomponent systems (water and sulphur) and two-component systems involving eutectics, congruent and incongruent melting points (lead-silver, FeCl₃-H₂O and Na-K only).

Partially miscible liquids: Lower and upper consolute temperatures, (examples of phenol-water, trimethylaminewater, nicotine-water systems). Nernst distribution law- applications.

Surfactants: Introduction, types, cmc and micellization, vesicles and bilayers.



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Solid surfaces: Adsorption at solid surfaces, adsorption models; Langmuir adsorption isotherm, BET adsorption isotherm and its use in estimation of surface area. Adsorption on porous solids.

Unit 14:

Basic Concepts in Kinetics: Molecularity and Order of reaction, rate equations for first, second (two reactants) and third order reactions. Determination of order of reaction by differential rate, integration, half-life and isolation methods.

Temperature dependence of reaction rates: -Arrhenius equation, concept of activation energy.

Reaction Rate Theories: Simple collision theory based on hard sphere model, evaluation of rate constants of atomic reactions, extension to molecular reactions, limitations.

Catalysis: Characteristics of catalyzed reactions, Acid-Base catalysis with examples Kinetics of photochemical reactions: Photochemical decomposition of hydrogen iodide.

Hydrogen-chlorine and hydrogen-bromine reactions, Comparison with thermal decomposition reactions. Enzyme Catalysis: Introduction to enzyme-catalyzed reactions, Michaelis-Menton equation, effect of temperature and pH. Enzyme inhibition.

Photochemistry: Interaction of radiation with matter, difference between thermal and photochemical processes. Laws of photochemistry. Grothus-Drapper law, Stark-Einstein law, Jablonski diagram depicting various processes occurring in the excited state, qualitative description of fluorescence, phosphorescence, non-radiative processes (internal conversion, intersystem crossing) quantum yield, photosensitized reactions, energy transfer processes (simple examples). Kinetics of photochemical reactions: Photochemical decomposition of hydrogen iodide. Hydrogen-chlorine and hydrogen-bromine reactions, Comparison with thermal decomposition.

Unit-15:

Ionic conductors: molar and specific conductance of electrolyte solutions, empirical relations, Migration of ions and Kohlrausch law, ionic mobility, Debye-Huckel-Onsager's equation for strong electrolytes (basic approximations). Transport number, definition and determination by Hittorf's method and moving boundary method.

Application of conductivity measurements: determination of degree of dissociation and dissociation constants of acids; determination of solubility product of a sparingly soluble salt, conductometric titrations.

Types of reversible electrodes: gas-metal-ion, metal-metal ion, metal-insoluble salt-anion and redox electrodes. Electrode potential, standard electrode potential, standard hydrogen electrode, reference electrodes, sign conventions. Electrode reactions, Nernst equation, determination of cell E.M.F, electrochemical series and its significance.

Electrolytic and Galvanic cells, reversible and irreversible cells, conventional representation of an electrochemical cell. Measurement of EMF of a cell.

Applications of emf Measurements: Calculation of thermodynamic functions of cell reactions (Δ G, Δ H and K.). Concentration cells, valency of ions, solubility product and activity coefficient. Potentiometric titrations.