



Department of Chemistry
University of Kashmir
(NAAC Accredited A++)

Entrance Test Syllabus
For Ph.D. Program in Chemistry

Unit 1:

Mechanisms of selected Complexation processes. d^n configuration and lability, Stability of uncommon oxidation states. Ligand preorganization, Complexes of Crown ethers and Cryptands, Tertiary phosphine as ligand. Jahn-Teller distortion, spectrochemical series.

Experimental Evidence in favor of Metal Ligand Orbital Overlap.

Molecular orbitals and energy level diagram for sigma bonded ML_6 and ML_4 systems. Effect of pi bonding (Pi donor and Acceptor Ligands).

Structure and bonding of mono- and poly-nuclear carbonyls. Spectroscopic characterization (Vibrational spectra) of metal carbonyls. Structure and bonding of transition metal nitrosyls, dinitrogen and dioxygen complexes. Conditional stability constant. Stereochemistry, Lipophilicity. HSAB theory and Plasma mobilizing index (PMI) of chelating drugs. Therapeutic index of different chelating drugs in metal ion detoxification.

Selected examples of lanthanide complexes with homo and hetero dinuclear coordination. Lanthanide Complexes as Sensory Probes, Lasers, NMR Shift Reagents and Contrast Agents in Magnetic Resonance Imaging (MRI). Lanthanide Single molecule magnets

Unit 2:

Energy profile of reactions, reaction intermediates and transition states. General reaction mechanism of square planar complexes, KS and KY pathways. Nature of entering group-Nucleophilicity and basicity, n_{pt} and n_{pt}° scales. Trans-effect theories and application in synthesis. Molecular rearrangements in 4-coordinate complexes. Empirical criteria to differentiate the mechanism of substitution reaction.

Classification of metal ions based on water exchange rates. Eigen-Wilkins mechanism. Anation reactions. Hydrolysis under acidic and basic conditions, Conjugate base (CB) mechanism.

Classification of Oxidation-Reduction reactions: Stoichiometric and Mechanistic.

Inner Sphere Electron Transfer Reaction Mechanism, Bridging Ligand Effects, Electron transfer through extended bridges, Double bridged Intermediates.

Outer Sphere Electron Transfer: Elementary steps. Chemical activation-Frank-Condon consideration. Marcus Cross Equation. Orbital symmetry considerations. Reactivity of organometallic compounds $C \equiv C$ vs $M-C$ bond. Effective atomic number rule and its applicability. Stability of Organometallic Compounds towards water and oxygen, Decomposition pathways. Structure, bonding and applications of Alkyls and aryls of Li, B and Al. Structure and bonding in Zeise's Salt. DCDM model of bonding in Pi organometallics. Homogenous Catalysis: Oxidative addition, Insertion reactions and water gas shift reaction (WGSR) and $C-H$ activation. Tolman Catalytic loop. Catalytic efficiency: TOF, TON and e.e.

Hydrogenation, Hydroformylation and Monsanto Acetic acid as industrial Catalytic processes.

Unit 3:

Ferritin and Transferrin: Structure, Metal binding sites; incorporation and release of iron; Haemoglobin and Myoglobin: Structure, oxygen saturation curves; Bohr Effect and cooperativity in haemoglobin. Dioxygen

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binding to Hemerythrin and Hemocyanin. Synthetic oxygen carrier model compounds: Vaska's iridium complex. Electron Carriers: Structure and biological role of Rubredoxin, Ferridoxin and Cytochromes.

Topology of Boron clusters, isolobal analogy, empirical rules for bonding in boron clusters, Selected examples of bonding in higher boranes. Bonding in Boron-Nitrogen, Phosphorous-Nitrogen compounds ((Borazine, Cyclophosphazenes, phosphonitrilic halides, and polythiazyls) Bent's rule applications.

Factors favoring metal-metal bond, bonding in di- and trinuclear metal clusters, cotton rationale and quadruple bonding, selected examples of bonding in dinuclear metal clusters.

Bonding in classical and non classical Hydrides.

Magnetic susceptibility and magnetic moment, correlation of μ_s and μ_{eff} values; orbital contribution to magnetic moments; applications of magnetic moment data in investigation of nature of bonding and stereochemistry of first row transition metal complexes. High spin- low spin crossover. Magnetic Properties of Inner transition compounds.

Theoretical aspects of d-d spectra, selection rules; spectral terms of d^1 - d^{10} metal ions.

Selected examples of d-d spectra. Charge transfer spectra (Factors affecting energies of LMCT and MLCT transitions).

Unit 4:

Aromaticity: Huckel rule and concept of aromaticity, Molecular orbital diagram of annulenes, Frost diagram. Relation between NMR and aromaticity. Anti and Homoaromaticity Aromaticity in fused ring systems.

Reactive Intermediates: Generation, Structure, fate and stability of Carbocations (Classical and Non-Classical), Carbanions, Free radicals, Carbenes, Nitrenes, Arynes and Radical ions.

Aliphatic Nucleophilic Substitutions: Mechanism, stereochemical implications and comparison of S_N2 , S_N1 , S_Ni and NGP reactions. Factors affecting rates of S_N1 and S_N2 reactions. Nucleophilic substitution at allylic, benzylic, aliphatic trigonal and vinylic carbons. Mitsunobu reactions. Nucleophilic substitutions on elements other than carbon. Examples of nucleophilic substitutions in biological systems.

Elimination reactions: Mechanism and stereochemical implications of $E1$, $E2$, $E1cB$ and $E2C$ elimination reactions. Factors affecting these reactions. Competition between substitution and elimination reactions. Elimination in cyclic systems and vinyl halides. Mechanism and orientation in pyrolytic eliminations, Shapiro reaction.

Aromatic Nucleophilic substitution: Discussion of different mechanisms (S_N1 , S_NAr , Benzyne and $S_{RN}1$). Mechanisms of Von- Richter, Sommelet-Hauser and Smiles rearrangements and Chichibabin reaction.

Free Radical Substitution: Free radical substitution mechanisms. Neighbouring Group Assistance in free radical reactions. Factors affecting radical substitutions. Auto-oxidation, coupling of alkynes and arylation of aromatic compounds by diazonium salts, Sandmeyer and Hunsdiecker reactions.

Stereoisomerism: Classification, molecules with one, two or more chiral centres; Configuration nomenclature, D L, R S and E Z nomenclature. Axial and planar chirality and helicity (P & M); Stereochemistry and configurations of allenes, spiranes, alkylidene cycloalkanes, adamantanes, catenanes, biphenyls (atropisomerism), bridged biphenyls, ansa compounds and cyclophanes. Racemic modification.

Unit 5:

Addition Reactions:

Addition to Carbon-Oxygen double bond: Nucleophilic additions to carbonyls and stereochemical aspects through various models (Cram, Cram chelation and Felkin-Anh models), Review of mechanisms of addition



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of water, hydrogen cyanide, alcohols, amines, organometallic reagents and hydrides to aldehydes and ketones. Mechanism and stereochemical aspects of Aldol reactions (Controlling aldol reactions, intramolecular Aldol reaction and Cross Aldol condensation), Knoevenagel reaction, Robinson annulation, Claisen and cross Claisen ester condensation. Dickman and Stobbes reactions. Addition of Phosphorus, nitrogen and sulfur ylids. Wittig-Horner reaction.

Rearrangements:

General mechanistic treatment of nucleophilic, electrophilic and free radical rearrangements. Nature of migration and migratory aptitude, and memory effect. Detailed mechanistic and stereochemical implications involved in the following rearrangements: Wagner-Meerwein, Pinacol, Semipinacol, Demjanov, Benzil-Benzilic acid, Favorskii, Arndt-Eistert, Neber, Hofmann, Curtius, Lossen, Schmidt, Beckmann, Baeyer-Villiger, Pyne and Dienone - phenol rearrangements.

Photochemistry:

Photochemical reactions of alkenes (Geometrical isomerization) and 1,3, 1,4 and 1,5 dienes.

Photochemistry of Carbonyl compounds: Photochemical reactions of acyclic and cyclic saturated carbonyl compounds (Norrish type I and II reactions), α , β - and β,γ - unsaturated ketones, cyclohexenones and cyclohexadienones. Intermolecular cycloaddition reactions (Paterno- Buchi reaction).

Photoisomerizations of benzenes and its alkyl derivatives. Nucleophilic photosubstitutions in aromatic compounds. Photo-Fries rearrangements of aryl esters and anilides. Barton and Hoffmann-Loefer-Freytag reactions.

Pericyclic reactions:

Molecular orbital symmetry, Frontier orbitals of ethene, 1,3- butadiene, 1,3,5-hexatriene and allylic systems. HOMO, LUMO concept, FMO approach. Classification of Pericyclic reactions. Woodward Hofmann rules for conservation of symmetry.

Cycloadditions: Thermal and Photochemical 2+2 and 4+2 cycloadditions. Regioselectivity in 2 + 2 and Diels Alder reactions. Alder-Ene reaction and 1,3 dipolar cycloadditions. Suprafacial and Antarafacial cycloadditions.

Electrocyclic Reactions: Thermal and Photo-induced Electrocyclic reactions of $4n$ and $4n + 2$ systems and their stereochemistry. Conrotatory and disrotatory motions.

Sigmatropic rearrangements: Introduction, classification and mechanistic details of [1,3], [1,5], [1,7], [2,3] and [3,3] sigmatropic shifts. Cope and Claisen rearrangements. Suprafacial and Antarafacial shifts of hydrogen atom.

Unit 6:

Spectroscopy:

UV-IR: Principles and applications of Ultra Violet and Infra-Red Spectroscopy in structural elucidation of organic compounds.

Mass Spectrometry: Time-of-Flight. Determination of molecular formula, Role of Isotopes, Nitrogen Rule, Metastable Peak. Fragmentation pattern like Stevenson rule, initial ionization event, α -cleavage, inductive cleavage, two bond cleavage, Retro-Diels. Alder cleavage, McLafferty Rearrangements. Fragmentation pattern of alkanes, alkenes, alcohols, phenols, aldehydes, ketones, Carboxylic acids, Amines, Problems based on Mass Spectrometry.

NMR: Basic concepts, Mechanism of Measurements, Chemical shift values for various classes of compounds. Fourier Transform (FT), Techniques and advantages, Nuclear overhauser effect (NOE). One bond coupling, two bond coupling, three bond coupling, second order spectra A2, AB, AX, AB2, ABX, AX2, A2B2. Proton exchange, deuterium exchange, Peak broadening exchange C-13 NMR: Carbon 13-chemical shifts, proton coupled and decoupled spectra. Off-Resonance De-coupling, A quick dip into DEPT-45, DEPT-90, DEPT-135. Introduction to two-dimensional spectroscopy methods, Cosy techniques, HETCOR technique, OESY.

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Unit 7:

Quantum Mechanics:

Time-independent and time-dependent Schrodinger equation. Postulates of quantum mechanics. Operator concept, quantum mechanical operators in Cartesian and Spherical polar co-ordinate systems, some properties of quantum mechanical operators. Review of particle in a box problem. The solution of problems of harmonic oscillator & the rigid rotator. Tunneling effect. Solution of the Hydrogen-like atom problem, radial and angular wave functions.

General theory of angular momentum. Eigen functions and Eigen values of angular momentum operators. Ladder operators. Spin angular momentum, antisymmetry and Pauli's principle. Atomic term symbols, term separation of pn and dn configurations, spin-orbit coupling, Zeeman splitting. Approximation methods: The Variation theorem, linear variation principle, application to hydrogen atom and helium atom. Chemical Bonding: LCAO-MO approximation, H_2^+ molecular ion, brief introduction to H_2 . Molecular term symbols. Valence bond treatment of hydrogen molecule, comparison of MO and VB methods in the light of hydrogen molecule.

Hybridization of orbitals (sp , sp^2 & sp^3). Huckel's Pi-MO theory: Application to linear and cyclic polyenes. Pi-electron charge and bond-order. Alternant hydrocarbons, Naphthalene, heteroatomic conjugated systems. Limitations of Huckel theory.

Hamiltonian and wave function for multi-electron systems. Electronic Hamiltonian, antisymmetrized wave function, Slater determinant

Unit 8:

Chemical Kinetics:

Overview of basic concepts: Macroscopic and microscopic kinetics, kinetic analysis of experimental data, Differential method, integration method.

Fast reactions: General features of fast reactions, study of fast reactions by flow method, relaxation method and flash photolysis.

Theories of Chemical Reactions: Overview of Arrhenius and Collision theory, Activated complex theory of reaction rates, statistical & thermodynamic formulations, comparison with collision theory.

Unimolecular reactions: Lindman, Hinshelwood.

Structure Reactivity Relationships: Quadratic Free-Energy Relationships (QFER), Hammett and Taft relationships.

Surface Reactions: Unimolecular & bimolecular surface reactions [Langmuir-Hinshelwood & Langmuir-Riedel mechanism], classical & statistical treatments.

Reactions in solutions: Effect of solvent on reaction rates, Diffusion controlled reactions (partial & full microscopic diffusion control), Ionic Reactions; Single & double sphere models of ionic reactions, effect of ionic strength.

Enzyme catalyzed Reactions: Kinetics of enzyme catalyzed reactions, Effect of substrate concentration, temperature and pH. Enzyme inhibition.

Electrochemistry:

Ion solvent Interactions: Non structural (Born) treatment and an introduction to structural (Ion-dipole, Ion-quadrupole) treatments of ion-solvent interactions.

Ion-Ion Interactions: Activity and activity co-efficient. Debye-Huckel theory of activity coefficients of electrolyte solutions; derivation of Debye-Huckel limiting law, validity and extension to high concentrations; ion-pair formation-Bjerrum model.



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Electrified Interface: Metal-electrolyte electrified interface, concept of surface excess, thermodynamics of electrified interface, Lippman equation, electrocapillary curves. Methods for determination of surface excess.

Structural models of metal-electrolyte interface: Helmholtz-Perrin, Gouy-Chapman and Stern models, Structure of semiconductor/electrolyte interface.

Theories of Heterogeneous Electron Transfer: Electron transfer at electrified interface at and away from equilibrium. Butler-Volmer equation, low and high field approximations.

Unit 9:

Statistical Mechanics

Basics of Probability theory: Probability, Fundamental counting principle, Permutations, Configurations, Concept of distribution, thermodynamic probability and most probable distribution. Sterling approximation. Boltzmann, Bose-Einstein and Fermi-Dirac distribution laws.

Partition function & its significance. Translational, rotational, vibrational and electronic partition functions. Relation between partition function and thermodynamic functions.

Application to Chemical Systems:

Calculation of thermodynamic properties in terms of partition functions, application to ideal monoatomic & diatomic gases. Equilibrium constant in terms of partition functions with application to isomerization and atomization reactions.

Nuclear spin statistics: symmetry and nuclear spin, Ortho and Para nuclear spin states, Ortho and Para Hydrogen and Deuterium, CO.

Statistical mechanics of solids: Einstein and Debye models (Partition function, Average energy and heat capacity), limitations of the models.

Surface Chemistry:

Liquid Surface: Surface tension, pressure difference across curved surfaces (Laplace equation), vapor pressure of droplets (Kelvin equation), Capillary condensation.

Thermodynamics of Interfaces: Surface excess, surface tension and thermodynamic parameters, Gibbs adsorption isotherm.

Solid liquid interface: Contact angle, Young's equation, wetting, Wetting as contact angle phenomena.

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.

Surfactants: Classification of Surfactants, Solubility of Surfactants: Kraft temperature and cloud point, Micellization of surfactants: critical micelle concentration (cmc), aggregation number, counterion binding, factors affecting cmc in aqueous media. Thermodynamics of micellization: pseudophase model and mass action models. Structure and shape of micelles: geometrical consideration of chain packing, variation of micellar size and shape transitions with surfactant concentration, temperature and pH.

Unit 10:

Spectroscopy:

Interaction of light with matter, transition probability, transition moment integral, derivation of selection rules. Intensity of spectral lines; Einstein's treatment of absorption and emission processes. Beer-Lambert Law: Transmittance, Absorbance, Molar Integrated Intensity, Oscillator strength. Natural spectral.

Vibrational spectroscopy: Linear harmonic oscillator- classical and quantum treatment of vibrations, vibrational energies of diatomic molecules, zero point energy, force constant and bond strength, anharmonicity, Morse potential energy levels. Fundamental bands, overtones and hot bands. Vibration-rotation spectra of diatomic molecules; P, Q and R branches;

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Raman spectroscopy: Molecular polarizability, rotational, vibrational, and vibrational-rotational Raman spectra. Selection rules; rule of mutual exclusion. Applications.

Electronic Spectroscopy: Vibronic transitions. Intensity of spectra—the Franck-Condon principle. Electronic spectra of organic molecules, chromophores. Effects of solvent, electron withdrawing and electron donating groups, conjugation and extended conjugation on the position of spectral bands.

NMR: Basic principles, Nuclear spin, spin angular momentum, quantization of angular momentum. Nuclear magnetic moment, precessional (Larmor) frequency, energy levels in a magnetic field, resonance absorption of radio frequency radiation. Population of energy levels, Relaxation processes (T_1 , T_2). Shielding and deshielding of magnetic nuclei. Chemical shift, its measurement and factors influencing chemical shifts; local paramagnetic and diamagnetic shielding, neighboring group anisotropy and ring currents in aromatic systems Spin-Spin coupling, coupling constants. Examples.

Symmetry:

Symmetry elements and assignment of point groups (Recapitulation). Combination and matrix representation of symmetry operations. The Great Orthogonality Theorem: Elementary idea and consequences. Reducible and Irreducible representations: Irreducible representations - Properties, proof and illustration of properties, Mulliken symbols. Character tables: Construction (C_{2v} , C_{3v} , C_{4v} and D_4 groups), structure of character table, linear and rotational functions (elementary idea), binomial and other polynomial functions (elementary idea). Reducible representations - Construction and reduction using the standard reduction formula.