

VARDHMAN MAHAVEER OPEN UNIVERSITY, KOTA
M.Sc. CHEMISTRY
ENTRANCE EXAMINATION SYLLABUS

INORGANIC CHEMISTRY

Atomic Structure

Idea of De Broglie matter waves, Heisenberg's uncertainty principle, atomic orbitals, Schrodinger wave equation, significance of l and m^2 , quantum numbers, radial and angular wave function and probability distribution curves, shapes of s, p, d, orbitals, Aufbau and Pauli exclusion principles, Hund's multiplicity rule, electronic configurations of the elements, effective nuclear charge.

Periodic Properties

Atomic and ionic radii, ionization energy, electron affinity and electronegativity-definition, methods of determination or evaluation, trends in periodic table and applications in predicting and explaining the chemical behaviour.

Chemical Bonding

Covalent Bond: Valence bond theory and its limitations, directional characteristics of covalent bond, various types of hybridizations and shapes of simple inorganic molecules and ions. Valence shell electron pair repulsion (VSEPR) theory to NH_3 , H_3O^+ , SF_4 , ClF_3 , ICl_2 and H_2O ; MO theory, homonuclear and heteronuclear (CO and NO) diatomic molecules, multicenter bonding in electron deficient molecules, bond strength and bond energy, percentage ionic character from dipole moment and electronegativity difference.

Ionic Bond: Ionic structure, radius ratio effect and coordination number, limitations of radius ratio rule, lattice defects, semi-conductors, lattice energy and Born-Haber cycle, solvation energy and solubility of ionic solids, polarizing power and polarizability of ions, Fajan's rule.

Metallic bond: Free electron, valence bond and band theories.

Weak Interactions: Hydrogen bonding, van der Waals forces.

s-Block Elements

Comparative study, diagonal relationship, salient features of hydrides, solvation and complexation tendencies including their functions in biosystems, an introduction to alkyls and aryls of s-block elements.

Chemistry of Noble Gases

Chemical properties of Noble gases, chemistry of xenon, structure and bonding in xenon compounds.

p-Block Elements

Comparative study (including diagonal relationship) of groups 13-17 elements, compounds like hydrides, oxides, oxyacids and halides of groups 13-16.

Chemistry of Compounds

Hydrides of Boron: diborane and higher boranes, borazines, borohydrides, fullerenes, carbides, fluorocarbons, silicates (structural principle), tetrasulphur tetranitride, basic properties of halogens, interhalogens and polyhalides.

Chemistry of Elements of First Transition Series

Characteristics properties of d-block elements, properties of the elements of the first transition series, their binary compounds and complexes illustrating relative stability of their oxidation states, coordination number and geometry.

Chemistry of Elements of Second and Third Transition Series

General characteristics, comparative treatment with their 3d-analogues in respect to ionic radii, oxidation states, magnetic behaviour, spectral properties and stereochemistry.

Coordination Compounds

Werner's coordination theory and its experimental verification, effective atomic number concept, chelates, nomenclature of coordination compounds, isomerism in coordination compounds, valence bond theory of transition metal complexes.

Chemistry of Lanthanides

Electronic structure, oxidation states, ionic radii and lanthanide contraction, complex formation, occurrence and isolation, lanthanide compounds. Chemistry of Actinides: General features and chemistry of actinides, chemistry of separation of Np, Pu and Am from U, similarities between the later actinides and later lanthanides.

Acids and Bases

Arrhenius, Bronsted-Lowry, the Lux-Flood solvent system and Lewis concept of acids and bases. Non-aqueous Solvents: Physical properties of solvents, type of solvents and their general characteristics, reactions in liquid NH_3 and Liquid SO_2 . Oxidation and Reduction: Use of redox potential data-analysis of redox cycle, redox stability in water, Frost, Latimer and Pourbaix diagrams. Principle involved in the extraction of the elements.

Hard and Soft Acids and Bases (HSAB)

Classification of acids and bases as hard and soft. Pearson's HSAB concept, acid-base strength and hardness and softness. Symbiosis, theoretical basis of hardness and softness, electronegativity and hardness and softness.

Bonding in Transition Metal Complexes

Limitations of valence bond theory, an elementary idea of crystal field theory, crystal field splitting in square planar, octahedral, tetrahedral and trigonal bipyramidal complexes, factors affecting the crystal field parameters, Jahn-Teller distortions, applications and limitations of crystal field theory. Magnetic Properties of Transition Metal Complexes: Types of magnetic behaviour, methods of determining magnetic susceptibility, spin-only formula, L-S coupling, correlation of n_s and n_{eff} and values, orbital contribution to magnetic moments, application of magnetic moment data for 3d-metal complexes.

Spectra of Transition Metal Complexes

Types of electronic transitions, selection rules for d-d transitions, spectroscopic ground states, spectrochemical series, Orgel-energy level diagram for d^1 and d^9 states, discussion of the electronic spectrum of $[(\text{Ti}(\text{H}_2\text{O})_6)]^{3+}$ complex.

Thermodynamic and Kinetic Aspects of Metal Complexes

A brief outline of thermodynamic stability of metal complexes and factors affecting the stability, substitution reactions of square planar complexes.

Organometallic Chemistry

Definition, nomenclature and classification of organometallic compounds; preparation and properties, bonding and applications of alkyl and aryls of Li, Al, Hg, Sn and Ti; a brief account of metal-ethylenic complexes and homogeneous hydrogenation; mononuclear carbonyls and the nature of bonding in metal carbonyls.

Bioinorganic Chemistry

Essential and trace elements in biological processes, metalloporphyrins with special reference to haemoglobin and myoglobin, biological role of alkali and alkaline earth metal ions with special reference to Ca^{+2} and Mg^{2+} . Nitrogen fixation. Silicones and Phosphazenes: Silicones and phosphazenes as examples of inorganic polymers. nature of bonding in triphosphazenes.

ORGANIC CHEMISTRY

Structure and Bonding

Hybridization, bond lengths and bond angles, bond energy, localized and delocalized chemical bonds, van der Waals interactions, inclusion compounds, clathrates, charge transfer complexes, resonance, hyperconjugation, inductive and field effects, hydrogen bonding.

Mechanism of Organic Reactions

Curved arrow notation, drawing electron movements with arrows, half headed and double headed arrow, homolytic and heterolytic bond breaking. Types of reagents- electrophiles and nucleophiles. Types of organic reactions, Energy considerations. Reactive Intermediates: Carbocations, carbanions, free radicals, carbenes, arynes and nitrenes (with examples). Assigning formal charges on intermediates and other ionic species. Methods of determination of reaction mechanism (product analysis, intermediates, isotope effects. Kinetic and stereochemical studies).

Stereochemistry of Organic Compounds

Concept of isomerism, types of isomerism. **Optical isomerism:** Elements of symmetry, molecular chirality enantiomers, stereogenic centre, optical activity, properties of enantiomers, chiral and achiral molecules with two stereogenic centres, diastereomers, threo and erythro diastereomers, meso compounds,

resolution of enantiomers, inversion, retention and racemization. Relative and absolute configuration: Sequence rules, D&L and R&S systems of nomenclature.

Geometric isomerism: Determination of configuration of geometric isomers, E&Z systems of nomenclature, geometric isomerism in oximes and alicyclic compounds.

Conformational isomerism: Conformational analysis of ethane and n-butane; conformations of cyclohexane, axial and equatorial bonds, conformation of mono substituted cyclohexane derivatives. Newmann projection and sawhorse formulae. Difference between configuration and conformation.

Alkanes and Cycloalkanes

Alkanes: IUPAC nomenclature of branched and unbranched alkanes, alkyl group, classification of carbon atoms in alkanes, isomerism in alkanes, sources, methods of preparation (with special reference to Wurtz reaction, Kolbe reactions, Corey-House reaction and decarboxylation of carboxylic acids), Physical properties and chemical reaction of alkanes. Mechanism of free radical halogenation of alkanes: orientation, reactivity and selectivity.

Cycloalkanes: Nomenclature, methods of preparation, chemical reactions, Baeyer's strain theory and its limitations, ring strains in small rings (cyclopropane and cyclobutane), theory of strainless rings. The case of cyclopropane ring: banana bonds.

Alkenes, Cycloalkenes, Dienes and Alkynes

Alkenes : Nomenclature of alkenes, methods of preparation, mechanisms of dehydration of alcohols and dehydrohalogenation of alkyl halides, regioselectivity in alcohol dehydration, the Saytzeff rule, Hofmann elimination, physical properties and relative stabilities of alkenes. Chemical reactions of alkenes-Mechanisms involved in hydrogenation, electrophilic and free radical additions, Markownikof's rule, hydroboration-oxidation, oxymercuration-reduction, epoxidation, ozonolysis, hydration, hydroxylation and oxidation with KMnO_4 , polymerization of alkenes. Substitution at the allylic and vinylic positions of alkenes. Industrial applications of ethylene and propene.

Cycloalkenes: Methods of formation, conformation and chemical reactions of cycloalkenes.

Dienes: Nomenclature and classification of dienes: isolated, conjugated and cumulated dienes. Structure of allenes and butadiene, methods of preparation, polymerization. Chemical reactions-1,2- and 1,4-additions, Diels-Alder reaction.

Alkynes: Nomenclature, structure and bonding in alkynes. Methods of preparation. Chemical reactions of alkynes, acidity of alkynes. Mechanism of electrophilic and

nucleophilic addition reactions, hydroboration-oxidation, metal-ammonia reduction, oxidation and polymerization.

Arenes, Aromaticity, Alkyl and Aryl Halides

Arenes and Aromaticity: Nomenclature of benzene derivatives. The aryl group. Aromatic nucleus and side chain. Structure of benzene: Molecular formula and Kekule structure, stability and carbon-carbon bond lengths of benzene, resonance structure and MO picture. Aromaticity: the Huckle's rule, aromatic ions. Aromatic electrophilic substitution: General pattern of the mechanism, role of π - and σ -complexes. Mechanism of nitration, halogenation, sulphonation, mercuration and Friedel Crafts reaction, energy profile diagrams. Activating & deactivating substituents, orientation and otho/para ratio. Side chain reactions of benzene derivatives. Birch reduction. Methods of formation of alkylbenzene, alkynyl benzene and biphenyl.

Alkyl and Aryl Halides: Nomenclature and classes of alkyl halides, methods of preparation, chemical reactions. Mechanism of nucleophilic substitution reactions of alkyl halides, SN^2 and SN^1 reactions with energy profile diagrams. Polyhalogen compounds: chloroform and carbon tetrachloride. Methods of preparation of aryl halides, nuclear and side chain reactions. The addition, elimination and the elimination-addition mechanism of nucleophilic aromatic substitution reactions. Relative reactivities of alkyl halides vs allyl, vinyl and aryl halides. Synthesis and use of D.D.T. and B.H.C.

Alcohols and Phenols

Classification and nomenclature. **Monohydric alcohols:** Nomenclature, method of preparation by reduction of aldehydes, ketones, carboxylic acids and esters. Hydrogen bonding. Acidic nature. Reactions of alcohols. **Dihydric alcohols:** Nomenclature, methods of preparation, chemical reaction of vicinal glycols, oxidative cleavage [$Pb(OAc)_4$ and HIO_4] and pinacol-pinacolone rearrangement.

Trihydric alcohols: Nomenclature and methods of preparation, chemical reactions of glycerol.

Phenols: Nomenclature, structure and bonding, preparation of phenols, physical properties and acidic character. Comparative acidic strengths of alcohols and phenols, resonance stabilization of phenoxide ion. Reactions of phenols: electrophilic aromatic substitution, acylation and carboxylation. Mechanism of Fries rearrangement, Claisen rearrangement, Gatterman synthesis, Hauben-Hoesch reaction, Lederer-Manasse reaction and Reimer-Tiemann reaction.

Aldehydes and Ketones

Nomenclature and structure of the carbonyl group. Synthesis of aldehydes and ketones with particular reference to the synthesis of aldehydes from acid chlorides,

synthesis of aldehydes and ketones using 1,3-dithianes, synthesis of ketones from nitriles and from carboxylic acids, Physical properties, Mechanism of nucleophilic additions to carbonyl group with particular emphasis on benzoin, aldol, Perkin and Knoevenagel condensations. Condensation with ammonia and its derivatives. Wittig reaction, Mannich reaction. Use of acetals as protecting group. Oxidation of aldehydes, Baeyer-Villiger oxidation of ketones, Cannizzaro's reaction, Meerwein-Ponndorf-Verley, Clemmensen, Wolff-Kishner, LiAlH_4 and NaBH_4 reductions. Halogenation of enolizable ketones. An introduction to α,β -unsaturated aldehydes and ketones.

Ethers and Epoxides

Nomenclature of ethers and methods of preparation, physical properties. Chemical reactions: cleavage and autoxidation. Ziesel's method. Synthesis of epoxides. Acid and base catalyzed ring opening of epoxides, orientation of epoxide ring opening. Reactions of Grignard and organolithium reagents with epoxides.

Carboxylic Acids

Nomenclature, structure and bonding, physical properties, acidity of carboxylic acids, effect of substituents on acid strength. Preparation of carboxylic acids. Reactions of carboxylic acids. Hell-Volhard-Zelinsky reaction. Synthesis of acid chlorides, esters and amides. Reductions of carboxylic acids. Mechanism of decarboxylation. Methods of formation, chemical reactions of haloacids. Hydroxyacids: malic, tartaric and citric acids. Methods of formation and chemical reactions of unsaturated monocarboxylic acids. Dicarboxylic acids: Methods of synthesis and effect of heat and dehydrating agents.

Carboxylic Acid Derivatives

Structure and nomenclature of acid chlorides, esters, amides and acid anhydrides. Relative stability and reactivity of acyl derivatives. Physical properties, interconversion of acid derivatives by nucleophilic acyl substitution. Preparation of carboxylic acid derivatives and chemical reactions. Mechanism of esterification and hydrolysis (acidic and basic).

Organic Compounds of Nitrogen

Preparation of nitroalkanes and nitroarenes. Chemical reactions of nitroalkanes. Mechanism of nucleophilic substitution in nitroarenes and their reduction in acidic, neutral and alkaline media. Picric acid. Halonitroarenes: reactivity. Alkyl and Aryl Amines: Reactivity, structure and nomenclature of amines, physical properties, stereochemistry of amines. Separation of a mixture of primary, secondary and tertiary amines. Structural features effecting basicity of amines. Amine salts as phase transfer catalysts. Preparation of alkyl and aryl amines (reduction of nitro

compounds and nitriles). Reductive amination of aldehydic and ketonic compounds. Gabriel-phthalimide reaction, Hofmann bromamide reaction. Reactions of amines, electrophilic aromatic substitution in arylamines, reactions of amines with nitrous acid. Synthetic transformations of aryldiazonium salts, azo coupling.

Spectroscopy

Ultra-violet (UV) Spectroscopy: Absorption laws (Beer-Lambert's law), molar absorptivity, presentation and analysis of UV spectra, types of electronic transitions, effect of conjugation. Concept of chromophore and auxochrome. Bathochromic, hypsochromic, hyperchromic and hypochromic shifts. UV spectra of conjugated dienes and enones.

Infrared (IR) Spectroscopy: Molecular vibrations, Hooke's law, selection rules, intensity and position of IR bands, measurement of IR spectrum, fingerprint region, characteristic absorptions of various functional groups and interpretation of IR spectra of simple organic compounds.

Nuclear Magnetic Resonance (NMR) Spectroscopy: Nuclear shielding and deshielding, chemical shift and molecular structure, spin-spin splitting and coupling constant, areas of signals. Interpretation of PMR spectra of simple organic molecules such as ethyl bromide, ethanol, acetaldehyde, 1,1,2-tribromoethane, ethyl acetate, toluene and acetophenone. Problems pertaining to the structure elucidation of simple organic compounds using UV, IR and PMR spectroscopic techniques.

Organometallic Compounds

Organomagnesium Compounds: The Grignard reagents-formation, structure and chemical reactions. **Organozinc Compounds:** Formation and chemical reactions. **Organolithium compounds:** Formation and chemical reactions.

Organosulphur compounds

Nomenclature, structural features, methods of formation and chemical reactions of thiols, thioethers, sulphonic acids, sulphonamides and sulphaguanidine.

Heterocyclic Compounds

Introduction, Molecular orbital picture and aromatic characteristics of pyrrole, furan, thiophene and pyridine. Methods of synthesis and chemical reactions with particular emphasis on the mechanism of electrophilic substitution. Mechanism of nucleophilic substitution reactions in pyridine derivatives. Comparison of basicity of pyridine, piperidine and pyrrole. Introduction to condensed five and six-membered heterocycles. Preparation and reactions of indole, quinaline and isoquinoline with special reference to Fisher-indole synthesis, Skraup's synthesis

and Bischler-Napieralski synthesis. Mechanism of electrophilic substitution reactions of indole, quinoline and isoquinoline.

Organic Synthesis via Enolates

Acidity of α -hydrogens. alkylation of diethyl malonate and ethyl acetoacetate. Synthesis of ethyl acetoacetate: the Claisen condensation. Keto-enol tautomerism of ethyl acetoacetate. Alkylation of 1,3-dithianes. Alkylation and acylation of enamines.

Carbohydrates

Classification and nomenclature, monosaccharides: mechanism of osazone formation, interconversion of glucose and fructose, chain lengthening and chain shortening of aldoses, configuration, erythro and threo diastereomers, conversion of glucose into mannose, formation of glycosides, ethers and esters, determination of ring size, cyclic structure of D(+) glucose, mechanism of mutarotation, structure of ribose and deoxyribose. An introduction to disaccharides (maltose, sucrose and lactose) and polysaccharides (starch and cellulose) without involving structure determination.

Amino Acids, Peptides, Proteins and Nucleic Acids

Classification, structure and stereochemistry of amino acids. Acid-base behaviour, isoelectric point and electrophoresis. Preparation and reactions of α -amino acids. Structure and nomenclature of peptides and proteins. Classification of proteins. Peptide structure determination, end group analysis, selective hydrolysis of peptides. Classical peptide synthesis, solid-phase peptide synthesis. Structures of peptides and proteins, Levels of protein structure, Protein denaturation/renaturation. Introduction to constituents of nucleic acids. Ribonucleosides and ribonucleotides. The double helical structure of DNA.

Fats, Oils and Detergents

Natural fats, edible and industrial oils of vegetable origin, common fatty acids, glycerides, hydrogenation of unsaturated oils. Saponification value, iodine value, acid value, soaps, synthetic detergents, alkyl and aryl sulphonates.

Synthetic Polymers

Addition or chain-growth polymerization. Free radical vinyl polymerization, ionic vinyl polymerization, Ziegler-Natta polymerization and vinyl polymers. Condensation or step growth polymerization. Polyesters, polyamides, phenol-formaldehyde resins, urea-formaldehyde resins, epoxy resins and polyurethanes. Natural and synthetic rubbers. Synthetic Dyes: Colour and constitution (electronic

concept), classification of dyes. Synthesis of methyl orange, Congo red, malachite green, crystal violet, phenolphthalein, fluorescein, Alizarin and Indigo

PHYSICAL CHEMISTRY

Mathematical Concept and Computers

Logarithmic relations, curve sketching, linear graphs and calculations of slopes differentiation of functions like kx , ex , x^n , $\sin x$, $\log x$; maxima and minima, partial differentiation and reciprocity relations, integrations of some useful / relevant functions: Permutations and combinations. Factorials. Probability. Computers: General introduction to computers, different components of a computer, hardware and software input output devices; binary numbers and arithmetic; introduction to computer languages. Programming, operating systems.

Gaseous States

Postulates of kinetic theory of gases, deviation from ideal behaviour, van der Waals equation of state. Critical Phenomena: PV isotherms of real gases, continuity of states, the isotherms of van der Waals equation, relationship between critical constants and van der Waals constants, the law of corresponding states, reduced equation of state. Molecular Velocities: Root mean square, average and most probable velocities. Qualitative discussions of the Maxwell's distribution of molecular velocities, collision number, mean free path and collision diameter. Liquefaction of gases (based on Joule-Thomson effect).

Liquid State

Intermolecular forces, structure of liquids (a qualitative description). Structural differences between solids, liquids and gases. Liquid Crystals: Difference between liquid crystal, solid and liquid. Classification, structure of nematic and cholestric phases. Thermography and seven segment cell.

Colloidal State

Definition of colloids, classification of colloids. Solids in liquids (sols): kinetic, optical and electrical properties; stability of colloids. Protective action, Hardy-Schulze law, gold number. Liquids in liquids (emulsions): types of emulsions, preparation, emulsifier. Liquids in solids (gels): classification, preparation and properties, inhibition, general applications of colloids.

Solid State

Classification of solids, definition of space lattice, lattice points, crystal lattice and unit cell. Seven crystal systems. Symmetry elements in crystals. Types of solid

crystals: Ionic, covalent, molecular and metallic. Laws of crystallography (i) Law of constancy of interfacial angles (ii) Law of rationality of indices (iii) Law of symmetry. X-ray diffraction by crystals. Derivation of Bragg's equation Determination of crystal structure of NaCl, KCl and CsCl (Laue's method and powder method).

Chemical Kinetics and Catalysis

Chemical kinetics and its scope, rate of a reaction, factors influencing the rate of a reaction: concentration, temperature, pressure, solvent, light, catalyst. Concentration dependence of rates, mathematical characteristics of simple chemical reactions-zero order, first order, second order, pseudo order, half life and mean life. Determination of the order of reaction: differential method, method of integration, method of half life period and isolation method. Radioactive decay as a first order phenomenon. Experimental methods of chemical kinetics: conductometric, potentiometric, optical methods, polarimetry and spectrophotometry. Theories of Chemical Kinetics: Effect of temperature on rate of reaction, Arrhenius concept of activation energy. Simple collision theory based on hard sphere model, transition state theory (equilibrium hypothesis). Expression for the rate constant based on equilibrium constant and thermodynamic aspects. Catalysis, characteristics of catalysed reactions, classification of catalysis, miscellaneous examples

Thermodynamics

Definition of thermodynamic terms: System, surroundings, etc. Types of systems, intensive and extensive properties. State and path functions and their differentials. Thermodynamic process, concept of heat and work. First Law of Thermodynamics: Statement, definition of internal energy and enthalpy. Heat capacity, heat capacities at constant volume and pressure and their relationship. Joule's law, Joule-Thomson coefficient and inversion temperature. Calculation of w , q , dU & dH for the expansion of ideal gases under isothermal and adiabatic conditions for reversible process.

Second Law of Thermodynamics: Need for the law, different statements of the law. Carnot's cycle and its efficiency, Carnot theorem. Concept of Entropy: Entropy as a state function, entropy as a function of V & T , Entropy as a function of P & T , entropy change in physical change, Clausius inequality and entropy as a criteria of spontaneity and equilibrium. Entropy change in ideal gases and mixing of gases. Third Law of Thermodynamics: Nernst's heat theorem. Statement and concept of residual entropy, evaluation of absolute entropy from heat capacity data. Gibbs and Helmholtz function: Gibbs function (G) & Helmholtz function (A) as thermodynamic quantities, A & G as criteria for thermodynamic equilibrium and

spontaneity, their advantage over entropy change. Variation of G & A with P , V & T .

Thermochemistry

Standard state, standard enthalpy of formation-Hess's law of heat summation and its applications. Heat of reaction at constant pressure and at constant volume. Enthalpy of neutralization. Bond dissociation energy and its calculation from thermo-chemical data, temperature dependence of enthalpy. Kirchhoff's equation.

Chemical Equilibrium

Equilibrium constant and free energy. Thermodynamic derivation of law of mass action. Le chatelier's principle. Reaction isotherm and reaction isochores, isochore-Clapeyron equation and Clausius-Clapeyron equation. Applications.

Phase Equilibrium

Statement and meaning of the terms: Phase, component and degree of freedom. derivation of Gibbs phase rule, phase equilibria of one component system-water, CO_2 and S systems. Phase equilibria of two component system-solid-liquid equilibria, simple eutectic Pb-Ag system. Solid solutions-compound formation with congruent melting point (Mg-Zn) and incongruent melting point ($NaCl-H_2O$) system. Freezing mixtures: acetone-dry ice. Partially miscible liquids: Phenol-water and nicotine-water systems. Lower and upper consolute temperature. Effect of impurity on consolute temperature.

Electrochemistry

Electrical transport: conduction in metals and in electrolyte solutions, specific conductance and equivalent conductance, measurement of equivalent conductance, variation of equivalent and specific conductance with dilution. Migration of ions and Kohlrausch law, Arrhenius theory of electrolyte dissociation and its limitations, weak and strong electrolytes, Ostwald dilution law its uses and limitations. Debye-Huckle-Onsager's equation for strong electrolytes (elementary treatment only). Transport number: definition and determination by Hittorf's method and moving boundary method. Applications of conductivity measurements: Determination of degree of dissociation, determination of K_a of acids, conductometric titrations.

Types of reversible electrodes: Gas-metal ion, metal-metal ion, metal-insoluble salt anion and redox electrodes. Electrode reactions, Nernst's equation, derivation of cell EMF and single electrode potential, standard hydrogen electrode, reference

electrodes, standard electrode potential, sign conventions, electrochemical series and its significance. Electrolyte and Galvanic Cells: Reversible and irreversible cells, conventional representation of electrochemical cells. EMF of a cell and its measurements. Computation of cell EMF. Calculation of thermodynamic quantities of cell reactions (ΔG , ΔH and K), polarization, over-potential and hydrogen over-voltage. Concentration cell with and without transport, liquid-junction potential, application of concentration cells, valency of ions. Solubility product and activity coefficient, determination of solubility product of a sparingly soluble salt. Definition of pH and pKa. Determination of pH using hydrogen electrode by potentiometric titrations. Buffers: mechanism of buffer action, Henderson-Hasselbalch equation, hydrolysis of salts.

Elementary Quantum Mechanics

Black-body radiation, Planck's radiation law, photoelectric effect, heat capacity of solids, Bohr's model of hydrogen atom (no derivation) and its defects. Compton effect. De Broglie hypothesis, Heisenberg's uncertainty principle, Sinusoidal wave equation, Hamiltonian operator, Schrodinger wave equation and its importance, physical interpretation of the wave function, postulates of quantum mechanics, particle in a one dimensional box. Schrodinger wave equation for H-atom. separation into three equations (without derivation), quantum numbers and their importance, hydrogen like wave functions, radial wave functions, angular wave functions.

Molecular Orbital Theory

Basic ideas, criteria for forming MO from AOs, construction of MO's of H_2^+ ion by LCAO, calculation of energy level from wave functions, physical picture of bonding and anti-bonding wave functions, concept of σ , σ^* , π , π^* orbitals and their characteristics. Hybrid orbitals- sp , sp^2 , sp^3 . calculation of coefficients of AO's used in these hybrid orbitals. Introduction to valence bond model of H_2 , comparison of MO and VB models.

Spectroscopy

Introduction, electromagnetic radiation, spectrum, basic features of different spectrometers, statement of the Born-Openheimer approximation, degrees of freedom.

Rotational Spectroscopy: Diatomic molecules, energy levels of a rigid rotator (semi-classical principles), selection rules, spectral intensity, using population distribution (Maxwell-Boltzmann distribution) determination of bond length, qualitative description of non-rigid rotator, isotope effect.

Vibrational (Infrared) Spectroscopy: Energy levels of simple harmonic oscillator, selection rules, pure vibrational spectrum, intensity, determination of force constant and qualitative relation of force constant and bond energies. effect of anharmonic motion and isotope on the spectrum, idea of vibrational frequencies of different functional groups.

Raman Spectroscopy: Concept of polarizability, pure rotational and pure vibrational Raman spectra of diatomic molecules, selection rules. **Electronic Spectroscopy:** Concept of potential energy curves for bonding and anti-bonding molecular orbitals, qualitative description of selection rules and Frank-Condon principle. qualitative description of σ , π and n MO, their energy levels and the respective transitions.

Photochemistry

Interaction of radiation with matter, difference between thermal and photochemical processes. Laws of photochemistry: Grothus-Draper 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, actinometry, photosensitized reactions-energy transfer processes (simple examples).

Physical Properties and Molecular Structure

Optical activity, polarization (Cauchy-Mossotti equation), orientation of dipoles in an electric field, dipole moment, induced dipole moment, measurement of dipole moment- temperature method and refractivity method. dipole moment and structure of molecules. magnetic properties-paramagnetism, diamagnetism and ferromagnetics.

Solutions

Dilute Solutions and Colligative Properties: Ideal and non-ideal solutions and their properties, methods of expressing concentrations of solutions, activity and activity coefficient. Raoult's and Henry's laws, Azeotropes-ethanol-water system. Nernst Distribution law-Thermodynamic derivation, applications. Dilute solution, colligative properties, relative lowering of vapour pressure, molecular weight determination. Osmosis, law of osmotic pressure and its measurement, determination of molecular weight from osmotic pressure. Elevation of boiling point and depression in freezing point. Experimental methods for determining various colligative properties. Abnormal value and abnormal molar mass, degree of dissociation and association of solutes.
