Department of Chemistry

School of Sciences

Islamic University of Science and Technology

Awantipora-192122, J&K

M. Sc. Chemistry

Entrance Test Syllabus

Unit-I: Atomic Structure, Periodic Properties and Chemical Bonding (04 Marks)

De Broglie wave equation, Heisenberg uncertainty principle, Schrodinger wave equation, significance of Ψ and Ψ^2, atomic orbitals, radial and angular wave functions and probability distribution curves, shapes of s, p and d orbitals, quantum numbers, Aufbau and Pauli exclusion principles, Hund's multiplicity rule, Electronic configurations of the elements, effective nuclear charge

Atomic/ionic radii, ionization energy, electron affinity, electronegativity, effective nuclear charge, Trends in periodic table, applications in predicting and explaining the chemical behaviour

Ionic Solids: ionic Structures; radius ratio effect, coordination number and limitations of radius ratio rule, lattice energy and Born Haber Cycle, solvation energy and solubility of ionic solids, polarizing power and polarizability of ions, Fajan's rules.

Metallic bond, comparison with ionic and covalent bonds ~~& theories~~, Valence bond theory and its limitations, directional characteristics of covalent bond, various types of hybridization and shapes of inorganic molecules and ions, Valence shell electron pair repulsion (VSEPR) theory, Molecular Orbital (MO) theory, LCAO, applications for homonuclear and heteronuclear diatomic molecules, multicenter bonding in electron deficient molecules, weak Interactions *viz.* hydrogen bonding, van der Waals forces

Unit-II: S & P - Block Elements (04 Marks)

Physical and Chemical properties of the s-block elements and their important classes of compounds, anomalous behavior, diagonal relationship, Hydrides, classification and general properties, commercially important compounds, isolation and importance of noble gases, clathrates, fluorides and oxides of Xenon

Physical and Chemical properties of the p-block elements and their important classes of compounds, anomalous behavior, diagonal relationship, boranes, carbides, nitrogen compounds, oxides and oxyacids of nitrogen, oxygen fluorides, oxides and oxyacids of sulphur and phosphorus, silicones and phosphazenes as inorganic polymers, general properties of halogens, Interhalogens, Polyhalides and Pseudohalogens, Various acid-base concepts, hard and soft acids and bases, non aqueous solvents

Unit-III: Transition & Inner Transition Elements (04 Marks)

Chemistry of elements of first transition series, characteristic properties of d-block elements, properties of the elements of the first transition series, their 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 of ionic radii, oxidation states, magnetic behavior, spectral properties and stereochemistry, variable oxidation states, standard electrode potentials of M^{2+}/M^{+} and M^{3+}/M^{2+} systems, stabilization of unusual oxidation states, spectral and magnetic properties (magnetic moment value), interstitial hydrides, carbides and oxides of first transition series

Lanthanoids, electronic configuration, oxidation states, magnetic properties & complexing behavior, ionic radii and lanthanide contraction, cause and consequences of lanthanide contraction, separation of lanthanoids, fractional crystallization, ion-exchange and solvent extraction methods.

Actinoids, introduction, electronic configuration, oxidation states, magnetic properties & comparison with lanthanoids, chemistry of separation of Np, Pu and Am from U.

Unit-IV: Coordination & Bioinorganic Chemistry (04 Marks)

Werner's coordination theory and its experimental verification, effective atomic number, concept and its significance, IUPAC nomenclature, stereochemistry of coordination numbers, isomerism in coordination compounds, valence bond and crystal field theories, magnetic and spectral properties in transition metal complexes (tetrahedral, square planar and octahedral), 10 Dq, factors affecting the magnitude of 10 Dq, pairing energy and CFSE in weak and strong field ligands, applications of coordination compounds in analytical chemistry

Abundance of elements in the living systems and the distribution of elements essential for life in the periodic table, natural selection of the elements, biochemical role of Li, Na, K, Ca, Mg, Fe and halogens in living systems, harmful effects of excess of metals in human body.

Unit-V: Qualitative and Quantitative Analyses (04 Marks)

Types of qualitative analysis, macro, semi micro; micro, ultra micro analyses, analysis of inorganic mixtures, group reagents, selective precipitation of ions, precipitation of sulphides and metal hydroxides, effect of acids, temperature and solvent upon the solubility of a precipitate, salt effect, reactions involved in separation and identification of cations and anions.

Underlying principles, common-ion effect, solubility product, relation between solubility and solubility product, Gravimetry, introduction, preparation of solution and precipitation methods, appearance, particle size and purity of precipitates, fractional precipitation, supersaturation, precipitate formation, co-precipitation and post precipitation, digestion, washing, ignition, gravimetric calculations.

Errors in chemical analysis: Terms and definitions - systematic errors. Random errors - statistical treatments - standard deviation of calculated results and reporting computed data - statistical data treatment and evaluation: Confidence intervals, statistical aids to hypothesis testing - analysis of variance and detection of gross errors.

Acid base titrations, basic principles, preparation of standard solutions, primary and secondary standards, theory of visual titration of acids and bases including polybasic acids, indicator types, selection, preparation of indicator solutions, basic principles of precipitation titrations, detection of equivalence points, (Mohr, Volhard, Fajans, and Nephelometric methods), basic principles of redox titrations, balancing of redox equations, redox reagents and their equivalent weights, redox potentials and their applications in volumetric analyses, types and selection of redox indicators, analysis of redox cycle

Unit-VI: Fundamental concepts in Organic chemistry and Stereochemistry (04 Marks)

Bonding in Organic compounds, hybridisation. Electronic displacements; Inductive, Electrometric, Resonance and hyperconjugative effects. Aromaticity in organic compounds, criteria for aromaticity, Huckel's rule and its applications. Reactive intermediates; Structure, generation, and stability of Carbocations, Carbanions, Free radicals, Carbenes, Benzynes and Nitrenes. Methods of determination of reaction mechanism: Identification of Products, Isotope labelling, Stereochemical and Kinetic evidences.

Stereochemistry: Concept and types of stereoisomerism. Geometrical Isomerism: Configuration of geometrical isomers. E and Z system of nomenclature.Optical Isomerism: Elements of symmetry, molecular chirality, chiral and achiral molecules with two stereogenic centers.Enantiomers, diastereoisomers and Meso compounds.Relative and absolute configurations. D, L and R, S systems of nomenclature. Structure and Stereochemistry of Alkanes: Conformational analysis of n-butane and 1,2- dibromoethane using Newman, Sawhorse and Fischer Projection formulae. Conformations of cyclohexane and methylcyclohexane.

Unit-VII: Unsaturated hydrocarbons and alkyl halides (04 Marks)

Alkenes: Preparation of alkenes from alcohols and alkyl halides through elimination reaction. Hoffman and Saytzev's rules. Mechanistic and stereochemical details. Mechanistic details including regioselectivity and stereochemical implications of halogenation, hydrohalogenation, hydroboration, epoxidation, hydroxylation and ozonolysis.

Dienes: Structure of isolated, conjugated and cumulative dienes. 1,2 and 1,4-additions of 1,3- butadiene. Mechanism of Diels's-Alder reaction.

Alkynes: Structure and acidic character of alkynes. Mechanisms of addition of halogens, hydrogen, halides, hydration, hydroboration and catalytic and metal-ammonia reductions of alkynes.

Alkyl halides: Classification, preparation, and reactions of alkyl halides. Mechanistic details of SN1 and SN2 E1 and E2 reactions. Effects of structure of alkyl halides, nature of nucleophiles, leaving groups, solvent and stereo-chemical implications of SN reactions. Substitution versus Elimination.

Unit-VIII: Aromatic Compounds and Oxygen bearing compounds (04 Marks)

Aromatic Electrophilic Substitution Reactions: General mechanism of aromatic electrophilic substitution reactions. Formation of Sigma and pi-complexes with energy profile diagram. The second substitution-concept and role of activating and deactivating groups. Ortho and para ratio. Mechanisms of Fries and Claisen rearrangements and Gatterman, Huben-Hoesch, Veils-Meir-Haack and Riemer-Tieman reactions. Aromatic Nucleophilic Substitution Reactions: Aryl halides: Methods of preparation of aryl halides with mechanistic details of the reactions involved. Addition-Elimination and Elimination-Addition mechanisms of nucleophilic aromatic substitution reactions involving aryl halides. Mechanism of nucleophilic aromatic substitution reaction in nitroarenes.

Oxygen bearing compounds: Alcohols: Classification. Methods of formation of monohydric alcohols through reduction of aldehydes, ketones, carboxylic acids and esters using different reducing agents including mechanistic details of the reactions involved. Reactions of alcohols including Pinacole-Pinacolone rearrangement with mechanism. Methods of formation and the oxidative cleavage reactions of diols.

Aldehydes and Ketones: Structure and reactivity of carbonyl groups. Synthesis of aldehydes starting from acid chlorides and those of ketones from nitriles, carboxylic acids and 1,3- dithianes. Stereochemistry and mechanism of nucleophilic additions to carbonyl groups. Cram's rule. Mechanisms involved in Benzoin, Aldol/Cross Aldol, Perkin, Cannizzaro and Mannich condensations/reactions.

Ethers: Mechanisms involved in the synthetic procedures of ethers, their cleavage and autooxidation.

Unit-IX: Spectroscopy (04 Marks)

The electromagnetic spectrum. Beer-Lambert law, molar absorptivity, presentation and analysis of electronic spectra. Types of electronic excitations. Effects of conjugation and solvents on absorption. Chromophores and auxochromes. Bathochromic and hypsochromic shifts. Ultraviolet spectra of enes and enones. Prediction of maxima of enes and enones using Woodward's rules. Infrared spectroscopy: The infrared region, Molecular vibrations, significance of Hook's law and selection rules. The infrared spectrum. Fingerprint region and its significance. Effect of resonance, inductive effect and H-bonding on infrared absorptions. Characteristic absorptions of Alkanes, alkenes, alkynes, alcohols, ethers, carbonyl compounds, amines and carboxylic acids and their derivatives. Nuclear Magnetic Resonance Spectroscopy: Basic principles of NMR spectroscopy. Shielding and deshielding of protons. The chemical shift; Equivalent and non-equivalent protons. Spin-spin splitting, coupling constants for vicinal, geminal and long range couplings. Characteristic functional group NMR absorptions. The NMR spectra of ethyl bromide, ethanol, acetaldehyde, ethyl acetate, methyl propionate, toluene and acetophenone.

Unit X: Biomolecules (04 Marks)

Carbohydrates: Introduction, classification, D&L-system of Nomenclature, and Cyclisation of Monosaccharides. Determination of ring size of D-glucose. Mechanisms of formation of osazones, glycosides, acetates and methyl ethers of monosacchrides. Chain lengthening and shortening processes of aldoses. Mechanism of Mutarotation. Chemistry of sucrose, maltose and lactose.

Nucleic Acids: Introductions, structural features of Nucleosides, Nucleotides, RNA and DNA.

Amino acids, Peptides & Proteins: Introduction, classification, structure and stereochemistry of amino acids. Acid-base behaviour and isoelectric points. Methods of formation and reactions of alpha-amino acids. Structure determination of dipeptides through end group analysis and selective hydrolysis and their classical and solid phase syntheses. Primary, Secondary, Tertiary and Quaternary structures of proteins.

Unit XI: States of Matter (04 Marks)

Gaseous State: Deviation of gases from ideal behavior, van der Waal's equation of state. Critical Phenomenon: PV isotherms of real gases, continuity of states, the isotherms of vander-Waal's equation. Relationship between critical constants and van der Waal's constants, the law of corresponding states, reduced equation of state. Molecular velocities: Maxwell's distribution of molecular velocities. Root mean square, average and most probable velocities; collision number, mean free path and collision diameter. Kinetic theory of gases and equipartition theorem.

Liquid State: Vapour pressure, Viscosity and Surface tension of liquids. Solid State: Symmetry elements in crystals, lattice planes and Miller indices. Bragg's equation and derivation. Interplanar distances in terms of Miller indices.

Unit XII: Chemical Thermodynamics(04 Marks)

State and path functions. Heat capacity, heat capacities at constant pressure and volume, Mayers relationship, Joule-Thomson effect, Calculation ofw, q, ΔU & ΔH for the expansion of ideal gases under isothermal and adiabatic conditions. Kirchhoff's equation

Different statements of the second law. Carnot cycle and its efficiency, Carnot theorem. Concept of entropy. Clausius inequality; entropy as criteria for spontaneity and equilibrium. Entropy change in physical processes, Entropy change during ideal gas expansion and mixing of ideal gases.

Gibb's (G) and Helmholtz (A) functions, Gibbs-Helmholtz equation, Variation of G and A with P, V and T. Nernst heat theorem, third law of thermodynamics.

Unit XIII: Chemical and Phase Equilibria (04 Marks)

Equilibrium: Relationship between equilibrium constant and free energy change. Thermodynamic derivation of law of mass action. Clausius-Clapeyron equation and its applications.

Phase Equilibria: Meaning of the terms: phase, component and degree of freedom, Phase rule. Phase diagrams of one component systems – water and sulphur systems.

Phase equilibria of two component system: Solid-liquid equilibria, simple eutectic system (Pb-Ag), desilverisation of lead.

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

Unit XIV: Chemical Kinetics (04 Marks)

Order and rate of reaction, derivation of integrated rate equations for first, second and third order reactions. Determination of order of reaction by different methods. Arrhenius equation, concept of activation energy. Steady state and equilibrium approximation. Collision and transition state theory of reaction rates.

Unit XV: **Electrochemistry (04 Marks)**

Arrhenius theory of electrolyte dissociation and its limitations. Kohlrausch's law. Debye-Huckel-Onsager's equation for strong electrolytes (elementary treatment without derivation). Transport number, definition and determination by Hittorf's and moving boundary methods. Application of conductivity measurements: determination of degree of dissociation and dissociation constants of acids, solubility product of a sparingly soluble salt, conductometric titrations.

Conductivity of electrolytes- Specific, molar and equivalent conductivity, Electrochemical reaction and electrode potential, Nernst equation and its use for estimation of equilibrium electrode potential Reversible electrode and its types, Different types of reference electrodes. Electrochemical series and its significance. Concentration cells and its types.