University of Kashmir
Syllabus for M.Sc. Entrance Test in Chemistry

Contents:

Unit- I

Atomic Structure Chemical Bonding and Periodic Properties: (04 Marks)

Wave Mechanical Concept of Atomic Structure: de- Broglie's wave equation; derivation; experimental verification.
Heisenberg's Uncertainty principle: Illustration of the principle & significance.
Schrödinger wave equation: significance of Ψ and $\Psi^{2.}$

Quantum numbers; Radial and Angular wave functions and Probability distribution curves. Shapes of s, p, & d orbitals.

Aufbau & Pauli's exclusion principles; Hund's multiplicity rule. Electron Configuration of Elements. Effective nuclear charge and its determination.

Chemical Bonding :
Ionic Solids: Ionic Structures; Radius ratio effect, Coordination number and limitations of radius ratio rule. Lattice defects; Lattice energy and Born Haber Cycle.
Solvation energy and solubility of ionic solids. Polarizing power and polarisibility of ions; Fajan's rules.
Metallic bond: Characteristics; comparison with ionic and covalent bonds & theories.

Valence bond theory: Directional Characteristics of Covalent bond; types of Hybridization and Shapes of simple molecules and ions. Limitations of VB theory.

Molecular Orbital Theory: LCAO, Energy level diagram of homo- & heteronuclear diatomic molecules like N_2, O_2 , F_2 ,CO, NO and HCI.

Multicentre bonding in electron deficient molecules; Bond strength and Bond energy.
Percent ionic character from dipole moment and electronegativity difference.

Week interactions: Hydrogen bonding (concept, types; effect on properties) and Vander Waal forces.

Periodic properties: Atomic, Ionic, Metallic and Vander Waal radii. Ionization Potentials, successive ionization potentials; Electronegativity and Electron affinity: Trends in Periodic table and Applications in predicting and explaining the Chemical behaviour.

Unit -II

S & P - Block Elements (04 Marks)

S – Block Elements:
General trends in Physical and Chemical properties of the Elements and their important classes of Compounds.
Lithium and Beryllium: Anomalous behaviour and diagonal relationship.
Hydrides: Classification and general properties.
Noble gases: Isolation and importance of Noble gases in theoretical Chemistry.
Clathrates: Types, preparation and stability.

Fluorides and Oxides of Xenon: Preparation, properties, structure and bonding (VB and MO treatment).

P – Block Elements:

Comparative study (including diagonal relationship and anomalous behaviour) of groups (13 -17). '

Boron Hydrides: Introduction, Nomenclature, Preparation, Properties, Structure and bonding in diborane (including higher boranes) Carboranes (Introductory idea)

Carbides: Classification, Preparation, Properties and Uses,Intercalation Compounds of graphite.

Nitrogen Compounds: Hydrazine, Hydroxylamine, Oxides and Oxyacids of nitrogen (Properties, Structure- bonding & Uses).Oxygen fluorides, Oxides and Oxyacids of Sulphur (Properties, Structure-bonding)

Halogens: General properties, Interhalogens; Polyhalides and Pseudohalogens, (Structure -bonding),

Unit -III

Transition & Inner Transition Elements (04 Marks)

Transition Elements:

Definition, Classification, Position in the Periodic table and the Electronic Configuration.

Physico-chemical properties: Atomic radii, Ionic radii, Metallic character and related properties. ' Ionization energies: Relation between the ionization energy and stability of a metal ion in a given oxidation state.

Variable oxidation states: Ionic! covalent character and Acidic/ basic character of compounds of a given transition metal in various oxidation states and stabilization of unusual oxidation states.

Spectral and Magnetic properties; calculation and uses of magnetic moment value.

Interstitial hydrides, carbides, nitrides and oxides of transition metals: Preparation, properties and uses (with respect to first transition series only).

Inner Transition Elements:

Lanthanoids: (At. No.58--); Introduction, Electronic configuration, Oxidation states, Magnetic properties & Complexing behaviour.

Ionic radii and Lanthanide contraction: Cause and Consequences of lanthanide contraction

Separation of lanthanoids: Fractional Crystallization, Ion-exchange and Solvent extraction methods.

Actinoids: (At. No.90-103); Introduction, Electronic configuration, Oxidation states, Magnetic properties & Comparison with lanthanoids. .

Chemistry of Separation ofNp, Pu and Am from U.

Unit -IV

Coordination & Bioinorganic Chemistry (04 Marks)

Coordination Compounds:

Introduction, Werner's Coordination Theory and its experimental verification.

Effective atomic number: Concept and its significance.
IUPAC Nomenclature and Stereochemistry of Coordination numbers (2-6) Isomerism in **Coordination Compounds** : (including geometrical and optical) Valence bond and Crystal field theories to explain, structure, bonding, 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.

Bioinorganic Chemistry :

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

Unit -V

Qualitative & Quantitative Analyses (04 Marks)

Qualitative Analysis:

Underlying principles- Common-ion effect, Solubility product, Relation between Solubility and Solubility product.

Types of Qualitative Analysis: - Macro, Semi micro; Micro; Ultra micro Analyses.

Analysis of Inorganic Mixtures; - Group reagents, Selective precipitation of captons; 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 C!ltions and anions. .

Quantitative Analysis:

Gravimetry: Introduction, Preparation of Solution and Precipitation methods.
Physical properties of precipitates: Appearance, particle size and purity. Fractional precipitation. Colloidal State: Supersaturation; Precipitate formation, Co-precipitation and post - precipitation. Digestion, Washing, Ignition, and Gravimetric calculations.

Titrimetry:

Acid - Base Titrations: Basic principles; preparation of standard solutions; primary and secondary stapdards, theory of Visual titration of acids and bases including polybasic acids. .

Indicators: Types, Selection, and Preparation of indicator solutions.
Precipitation titrations: Basic principles; Detection of Equivalence points, (Mohr, Volhard, Fajans, and Nephelometric methods).
Redox titrations: Basic principles; Balancing of redox equations, Redox reagents and their Equivalent weights.
Redox potentials and their applications in Volumetric analyses.
Redox indicators: Types, selection and analysis of redox cycle

Unit VI:

Fundamentals of Organic Chemistry & Isomerism (04 Marks)

Hybridization, Inductive, Electrometric, Resonance and hyperconjugative effects. Requirements of aromaticity, Huckel's rule and its significance.
Carbocations, Carbanions and Free radicals (Structure and stability) Carbenes, Benzynes and Nitrenes. Methods for determination of reaction mechanism.

Concept of stereo isomerism: elements of symmetry, molecular chirality, enantiomers and diastereomers, Inversion, retention and racemisation.Sequence rules. R,S-System of nomenclature. Geometrical isomers, E, Z-system of nomenclature.
Conformations of n-butane, ethylene glycol and 1 ,2-dibromoethane, cyclohexane and its monosubstituted derivative, Axial and equatorial bonds. Baeyer's strain theory and its limitations. Ring strain in smaller rings with respect to cyclopropane ring.

Unit- VII:

Hydrocarbons and their Halogen Derivatives (04 Marks)

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: S_N1, S_N2 and S_Ni reactions.
Aromatic Electrophilic substitutions: General pattern of the mechanism of nitration, halogenation Sulphonation and Friedal Craft's reaction. Activating and deactivating substituents, orientation and ortho/para ratio. Birch reduction.
Addition - Elimination and Elimination Addition mechanisms of nucleophilic aromatic substitution reactions.

Unit-VIII

Nitrogen and Oxygen bearing Functional Groups: (04 Marks)

Mechanism of nucleophilic substitution in nitroarenes. Reduction of nitrocompounds.
Preparation, properties and factors affecting basicity of amines. Mechanism of Electrophilic aromatic substitution in arylamines. Reaction of aryl amines with nitrous acid and reactions of arenediazonium salts. Azo coupling.

Oxidative cleavage of Alcohols with $Pb(OAc)_4$ and HIO_4 and Pinacole- Pinacolone rearrangement Electrophilic Aromatic substitutions: Mechanism of Fries and Claisen rearrangements, Gatterman, Huben-Hoesch and Reimer Tieman reactions. Acidic character of phenols.
Methods of formation of ethers and epoxides Acid and base catalysed ring opening and reactions of Grignard and organolithium reagents with epoxides.
Stereochemistry and mechanism of nucleophilic addition to Carbonyl group (Cram's rule). Benzoin, Aldol, Perkin, Knoevenagal & Mannich reactions. Condensation with Ammonia and amines. $LiAlH_4$ and $NaBH_4$ reduction, Meerwein-pondroff verley reduction. Oppenaner oxidation. Cannizzaro's reaction. Baeyer-villiger oxidation, Clemmenson reduction, Wolf-Kishner reductions.

Factors affecting acid strength of carboxylic acids. Preparation of carboxylic acids (using Grignard's reagent and from nitriles). HVZ reaction, conversion of acids to acid chlorides, esters,anhydrides and amides, their relative stabilities and interconversion by nucleophilic acyl substitutions. Reduction of carboxylic acids.

Unit-IX

Spectroscopy: (04 Marks)

Types of electronic excitations, chromophore and auxochrome. Bathochromic and hypsochromic shifts. UV spectra of conjugated enes and enones. Prediction of λ-max of enes and enones using Woodward rules.
Infrared spectroscopy: Infrared region, Molecular vibrations, Hooks law (No derivation), selection rules, the infrared spectrum, Finger Print region, effect of resonance, Inductive effect, H-bonding electronegativity on IR spectra. Characteristic absorption of the following functional groups- Alkanes, Alkenes, Alkynes, Alcohols, ethers, carbonyl compounds, amines and carboxylic acids. Interpretation of IR spectra of simple molecules.
Nuclear Magnetic resonance (NMR) spectroscopy: Basic principles, Proton magnetic resonance (^1H NMR). Shielding and deshilding of - protons, chemical shift and equivalent and nonequivalent protons, spin-spin splitting and coupling constants for vicinal, geminal and long range coupling. Areas of signals.
Interpretation of NMR spectra of simple organic molecules such as ethyl bromide, ethanol, acetaldehyde, ethyl acetate and acetophenone.

Unit-X

Biomolecules: **(04 Marks)**

Carbohydrates: Introduction, classification Determination of ring size. Mechanism of osazone formation, glycoside formation, acetylation and methylation, chain lengthening and chain shortening of aldoses. Interconversion of glucose and fructose and conversion of glucose into Mannose, Mechanism of mutarotation.
Proteins: Introduction, classification, structure and stereochemistry of amino acids. Acid base behaviour and isoelectric points, the peptide bond, primary secondary and tertiary structure of proteins.
Lipids: Definition, natural fats and oils, structural features of triglycerides, common fatty acids. Hydrogenation of oils. Saponification, iodine and acid values.
Introduction to steroidal compounds (Cholesterol, sex harmones and cortisone). Introduction, classification and importance of terpenoids and Alkaloids. Structural features of their representative examples.

Unit XI:

States of Matter **(04 marks)**

Gaseous State: Deviation of gases from ideal behavior, PV isotherms of real gases, continuity of states, the isotherms of vander Waal's equation, relationship between critical constants and vander Waal's constants, the law of corresponding states, reduced equation of state. Root mean square, average and most probable velocities. 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). Dipole moment, induced dipole moment, Measurement of dipole moment (temperature method and refractivity method), Dipole moment and structure of molecules.

Liquid crystals: Classification & structure of nematic, smectic and cholesteric phases. Liquid crystal displays and Thermography.

Solid State: Definition of space lattice, unit cell and it's dimensions, crystal systems. Laws of crystallograhy:- (i) Law of constancy of interfacial angles (ii) Law of rational indices (iii) Law of symmetry. Symmetry elements in crystals, Lattice planes and Miller indices. X-ray diffraction by crystals.

Unit XII:

Chemical Kinetics & Photochemistry (04 marks)

Determination of order of reaction by differential, integration, half life period and isolation methods. Techniques for kinetic investigation: Conductometry, Potentiometry, Polarimetry and Spectrophotometry.

Effect of temperature on rate of reaction, Arrhenius equation, concept of activation energy. Theories of chemical kinetics: Simple Collision theory – Basic approximations, evaluation of rate constant for atomic reactions, extension to molecular reactions and limitations.

Photochemical decomposition of hydrogen iodide. Photochemical combination of Hydrogen-chlorine and hydrogen-bromine reactions.

Photochemistry:

Interaction of radiation with matter, difference between thermal and photochemical processes. Laws of photochemistry. Lambert-Beer law, Grothus-Drapper law, Stark-Einstein law, Jablonski diagram - fluorescence, phosphorescence, non-radiative processes (internal conversion, intersystem crossing) quantum yield, photosensitized reactions.

Unit XIII:

Laws of Thermodynamics and Chemical Equilibria (04 marks)

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, dU & dH 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.

Third law of thermodynamics: Nernst heat theorem, statement of third law, concept of residual entropy, evaluation of absolute entropy from heat capacity data. Gibbs function (G) and Helmholtz function (A) as criteria for thermodynamic equilibrium and

spontaneity. Variation of G and A with P, V and T.

Equilibrium constant and free energy change. Reaction isotherm and reaction isochore, Clapeyron equation and Clausius-Clapeyron equation, applications. Thermodynamics of elevation in .boiling point and depression in freezing point. Activity and activity coefficient. Thermodynamic mixing functions of ideal and nonideal solutions, Excess thermodynamic functions of non-ideal solutions.

Statement and meaning of the terms: phase, component and degree of freedom. Gibbs phase rule, phase equilibria of one component svstem - 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 ($FeCl_3$-H_2O systems). Partially miscible liquids: Lower and upper consolute temperature, (examples of Phenol-water, trimethylamine-water, nicotine-water systems).
Nernst distribution law- applications.

Unit-XIV:

Electrochemistry (04 marks)

Migration of ions and Kohlrausch law, Debye-Huckel-Onsager's equation for strong electrolytes (elementary treatment only). 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. Calculation of thermodynamic functions of cell reactions (□G, □H and K.). Concentration cells, valency of ions, solubility product and activity coefficient. Potentiometric titrations.

Unit XV:

Quantum Chemistry & Spectroscopy (04 marks)

Limitation of Classical mechanics: Black-body radiation, Planck's radiation law, photoelectric effect, heat capacity of solids and atomic spectra. De Broglie hypothesis, the Heisenberg's uncertainty principle. Introduction to operators and operator algebra. Hermitian operator, Hamiltonian operator, Schrodinger wave equation and its importance, physical interpretation of the wave function, postulates of quantum mechanics, Quantum mechanical treatment of particle in a one dimensional box. Quantum numbers and their importance, hydrogen like wave functions, radial wave functions, angular wave functions.

Spectroscopy:

Electromagnetic radiation, regions of the spectrum and associated spectroscopies.

Rotational spectroscopy: Moment of inertia, classification of molecules on the basis of moment of inertia, classical treatment of rotation of rigid diatomic molecules, quantization of angular momentum, quantization of energy levels of rigid diatomic molecules, selection rules for transitions and associated spectrum, intensity of spectral lines, determination of bond length.

Vibrational Spectroscopy: Classical and quantum (qualitative) treatments of harmonic vibrations of diatomic molecules. Pure vibrational spectrum of diatomic molecules, selection rules, determination of force constant. vibrational degrees of freedom, idea of vibrational frequencies of different functional groups.