

University of Kashmir

Syllabus for M.Sc. Entrance Test in Chemistry

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Unit- I

Atomic Structure Chemical Bonding and Periodic Properties:

(04 Marks)

Quantum numbers; Radial and Angular wave functions and Probability distribution curves. Shapes of s, p and d orbitals. Aufbau and 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 polarisability of ions; Fajan's rules.

Metallic bond: Characteristics; comparison with ionic and covalent bonds and theories.

Valence bond theory: Directional Characteristics of Covalent bond; types of Hybridization. Limitations of VB theory. VSEPR theory: Assumptions; prediction of shapes of molecules

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

Multicentre bonding in electron deficient molecules; Bond strength and Bond energy.

Percent ionic character from dipole moment and electronegativity difference.

Weak 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 behavior.

Unit -II

S and P - Block Elements

(04 Marks)

S – Block Elements:

Lithium and Beryllium: Anomalous behavior 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 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, Structure and bonding in diborane (including higher boranes), empirical rules for bonding and structure in boranes, Introductory idea of isolobal analogy and Polyhedral skeletal electron pair theory.

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

Nitrogen Compounds: Hydrazine, Hydroxylamine, Oxides and Oxyacids of nitrogen (Structure-bonding and Uses). Oxygen fluorides, Oxides and Oxyacids of Sulphur (Properties, Structure-bonding). Properties and Bonding in Boron Nitrogen $(BN)_n$, Sulfur Nitrogen $(SN)_n$ and Nitrogen Phosphorus $(PN)_n$ compounds

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

Noble Gas Compounds: Structure and Bonding.

Unit -III

Transition and Inner Transition Elements

(04 Marks)

Transition Elements: Definition, Classification, 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. Metal metal bonding in dinuclear clusters

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

Inner Transition Elements:

Comparative account of transition and inner transition elements, d vs f orbitals. Lanthanoids: (At. No.58); Electronic configuration, Oxidation states, Magnetic properties and Complexing behaviour. Cause and Consequences of lanthanide contraction

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

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

Chemistry of Separation of Np, Pu and Am from U.

Application of Inner Transition element compounds as Sensory Probes, Lasers, NMR Shift Reagents and Contrast Agents in Magnetic Resonance Imaging (MRI). Lanthanide based Single molecule magnets

Unit -IV

Coordination and 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: the distribution of elements essential for life in the periodic table. Criteria of essentiality of a metal ion, Biochemical role of Li, Na, K, Ca, Mg, Fe and halogens in living systems.

Harmful effects of excess of metals on human body.

Chelation Therapy: Therapeutic index of different chelating drugs in metal ion detoxification. Limitations and Hazards of Chelation therapy

Unit -V

Qualitative and 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 cations;

Precipitation as 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. .

Quantitative Analysis:

Gravimetry: Introduction, Preparation of Solution and Precipitation methods.

Physical properties of precipitates: Appearance, particle size and purity. Fractional precipitation. Colloidal State: Super saturation; 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 standards, 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: 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. Markownikov'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. Oppenauer 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 deshielding 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 hormones 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,

Liquid State: Liquefaction of gases (based on Joule-Thomson effect) and adiabatic expansion. Intermolecular forces, structure of liquids (a qualitative description).

Solid State: Symmetry elements in crystals, Lattice planes and Miller indices. X-ray diffraction by crystals, derivation of Bragg's equation and its application. Interplanar distances in terms of miller indices. Determination of crystal structure by Laue's method and powder method. Systematic absence of diffraction lines in the X-ray pattern of cubic crystals with reference to NaCl, KCl & CsCl.

Unit XII:

Chemical Kinetics & Photochemistry

(04 marks)

Order of reaction; derivation of rate equations for second (two reactants) and third order reactions. Determination of order of reaction by differential rate, integration, half-life period and isolation methods.

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

Theories of chemical kinetics: Simple collision theory based on hard sphere model, evaluation of rate constants of atomic reactions, extension to molecular reactions, limitations. Brief idea of transition state theory (equilibrium hypothesis).

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.

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, photosensitized reactions, energy transfer processes (simple examples).

Unit XIII:

Laws of Thermodynamics and Chemical Equilibria (05 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 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 ($FeCl_3-H_2O$ 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 (ΔG , ΔH and K). Concentration cells, valency of ions, solubility product and activity coefficient. Potentiometric titrations.

Unit XV:

Spectroscopy

(03 marks)

Spectroscopy: Electromagnetic radiation, regions of the spectrum, basic features of different spectrometers. Statement of Born-Oppenheimer approximation.

Rotational spectrum: Moment of inertia, classification of molecules on the basis of moment of inertia. Energy of a rigid diatomic rotor, selection rules for rotational transition and associated spectrum, relative population of rotational levels and spectral intensity, determination of bond length.

Vibrational Spectrum: Classical and quantum mechanical (qualitative) treatment of simple harmonic oscillator, selection rules for vibrational transition, pure vibrational spectrum of a diatomic molecule, determination of force constant, relation of force constant with bond length and bond energy, vibrational degrees of freedom, idea of vibrational frequencies of different functional groups and selection rules.

Ultraviolet Spectroscopy: The electromagnetic spectrum. Beer-Lambert law, molar absorptivity, presentation and analysis of electronic spectra. Types of electronic excitations.