

Department of Chemistry
Syllabus for M. Sc. Chemistry Entrance Examination for Session 2023-24

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INORGANIC CHEMISTRY

1. Atomic Structure

Idea of de Broglie matter waves, Heisenberg uncertainty principle, atomic orbitals, quantum numbers, radial and angular wave functions and probability distribution curves, shapes of s, p and d orbitals. Aufbau and Pauli exclusion principles, Hund's multiplicity rule. Electronic configurations of the elements, effective nuclear charge, Slater's rules.

2. Covalent Bond

Valence bond theory and its limitations, directional characteristics of covalent bond, various types of hybridization and shapes of simple inorganic molecules and ions (BeF_2 , BF_3 , CH_4 , PF_5 , SF_6 , IF_7 , SO_4^{2-} , ClO_4^-), Valence shell electron pair repulsion (VSEPR) theory to NH_3 , H_3O^+ , SF_4 , ClF_3 , ICl_2 and H_2O . MO theory of heteronuclear (CO and NO) diatomic molecules, bond strength and bond energy, percentage ionic character from dipole moment and electronegativity difference.

3. Ionic bonding

Lattice energy (mathematical derivation excluded) and Born - Haber cycle, solvation energy and its relation with solubility of ionic solids, polarizing power and polarisability of ions, Fajan's rule.

4. Periodic Properties

Atomic and ionic radii, ionization energy, electron affinity and electronegativity – definition, methods of determination or evaluation, trends in periodic table (in s & p block elements).

5. s - Block Elements

Comparative study of the elements including, diagonal relationships, salient features of hydrides (methods of preparation excluded), solvation and complexation tendencies including their function in biosystems.

6. p - Block Elements

Emphasis on comparative study of properties of p-block elements (including diagonal relationship and excluding methods of preparation).

Boron family (13th group)

Diborane – properties and structure (as an example of electron-deficient compound and multicentre bonding), Borazene – chemical properties and structure, Trihalides of Boron – Trends in Lewis acid character, structure of aluminium (III) chloride.

Carbon Family (14th group)

Catenation, p π – d π bonding (an idea), carbides, fluorocarbons, silicates (structural aspects), silicon – general methods of preparations, properties and uses.

Nitrogen Family (15th group)

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Oxides – structures of oxides of N, P. Oxyacids – structures and relative acid strengths of oxyacids of Nitrogen and phosphorus. Structures of white, yellow and red phosphorus.

Oxygen Family (16th group)

Oxyacids of sulphur – structures and acidic strength, H_2O_2 – structure, properties and uses.

Halogen Family (17th group)

Basic properties of halogen, interhalogens types properties, hydro and oxyacids of chlorine – structure and comparison of acid strength.

7. Chemistry of Noble Gases

Chemical properties of the noble gases with emphasis on their low chemical reactivity, chemistry of xenon, structure and bonding of fluorides, oxides & oxyfluorides of xenon.

8. Chemistry of d-Block Elements (3d series)

Definition of transition elements, position in the periodic table, General group trends with reference to electronic configuration, variable valency, color, magnetic and catalytic properties. Preparation & properties of some compounds of transition elements – peroxocompounds of Cr, $\text{K}_2\text{Cr}_2\text{O}_7$, KMnO_4 and $\text{K}_4[(\text{Fe}(\text{CN})_6)]$.

9. Chemistry of f - block elements

Lanthanides

Electronic configuration, oxidation states, color and magnetic properties, lanthanide contraction, separation of lanthanides by ion-exchange method.

Actinides

General features and chemistry of actinides, Comparison of properties of Lanthanides and Actinides.

10. Coordination Compounds

Nomenclature of coordination compounds, isomerism in coordination compounds, valence bond theory of transition metal complexes.

11. Metal - ligand Bonding in Transition Metal Complexes

Limitations of valence bond theory, an elementary idea of crystal-field theory, crystal field splitting in octahedral, tetrahedral and square planar complexes, factors affecting the crystal-field parameters.

12. Acids and Bases, HSAB Concept

Arrhenius, Bronsted–Lowry, Lux–Flood, Solvent system and Lewis concepts of acids & bases, relative strength of acids & bases, Concept of Hard and Soft Acids & Bases.

13. Theory of Qualitative and Quantitative Inorganic Analysis

Chemistry of analysis of various groups of basic and acidic radicals, Chemistry of identification of acid radicals in typical combinations, Chemistry of interference of acid radicals including their removal in

the analysis of basic radicals. Theory of precipitation, co-precipitation, Postprecipitation, purification of precipitates.

14. Organometallic Chemistry

Definition, nomenclature and classification of organometallic compounds. Preparation, properties, and bonding of alkyls of Li, metal-ethylenic complexes, mononuclear carbonyls and the nature of bonding in metal carbonyls, EAN rule applied to metal carbonyls.

15. Bioinorganic Chemistry

Essential and trace elements in biological processes, Biological role of alkali and alkaline earth metal ions, Na/K pump, role of Ca^{2+} in blood clotting.

16. Silicones and Phosphazenes

Silicones and phosphazenes as examples of inorganic polymers, nature of bonding in triphosphazenes.

PHYSICAL CHEMISTRY

17. Gaseous States

Maxwell's distribution of velocities and energies (derivation excluded), Calculation of root mean square velocity, average velocity and most probable velocity. Collision diameter, collision number, collision frequency and mean free path. Deviation of Real gases from ideal behaviour. Derivation of Vander Waal's Equation of State, its application in the calculation of Boyle's temperature (compression factor), Explanation of behaviour of real gases using Vander Waal's equation. Critical temperature, Critical pressure, critical volume and their determination.

18. Liquid States

Structure of liquids. Properties of liquids – surface tension, viscosity, vapour pressure and optical rotations and their determination.

19. Solid State

Classification of solids, Laws of crystallography – (i) Law of constancy of interfacial angles (ii) Law of rationality of indices (iii) Law of symmetry. Symmetry elements of crystals. Definition of unit cell & space lattice. Bravais lattices, crystal system. X-ray diffraction by crystals. Derivation of Bragg equation. Determination of crystal structure of NaCl, KCl. Liquid crystals: Difference between solids, liquids and liquid crystals, types of liquid crystals. Applications of liquid crystals.

20. Kinetics

Rate of reaction, rate equation, factors influencing the rate of a reaction – concentration, temperature, pressure, solvent, light, catalyst. Order of a reaction, integrated rate expression for zero order, first order, second and third order reaction. Half life period of a reaction. Methods of determination of order of reaction, effect of temperature on the rate of reaction – Arrhenius equation. Theories of reaction rate –

Simple collision theory for unimolecular and bimolecular collision. Transition state theory
Bimolecular reactions.

21. Thermodynamics

Definition of thermodynamic terms: system, surrounding, etc. Types of systems, intensive and extensive properties. State and path functions and their differentials. Thermodynamic process. Concept of heat and work. Zeroth Law of thermodynamics, 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 for ideal gas and real gas: and inversion temperature. Calculation of w, q, dU & dH for the expansion of ideal gases under isothermal and adiabatic conditions for reversible process, Temperature dependence of enthalpy, Kirchhoff's equation. Bond energies and applications of bond energies. Second law of thermodynamics, need for the law, different statements of the law, entropy as a criterion of spontaneity and equilibrium. Entropy change in ideal gases and mixing of gases. Third law of thermodynamics: Nernst heat theorem, evaluation of absolute entropy from heat capacity data.

22. Chemical Equilibrium

Equilibrium constant and free energy, concept of chemical potential, Thermodynamic derivation of law of chemical equilibrium. Temperature dependence of equilibrium constant, Le-Chatelier's principle and its applications, Clapeyron equation and Clausius-Clapeyron equation, its applications.

23. Phase Equilibrium

Statement and meaning of the terms – phase component and degree of freedom, thermodynamic derivation of Gibbs phase rule, phase equilibria of one component system – Example – water and Sulphur systems. Phase equilibria of two component systems solid-liquid equilibria, simple eutectic – Example – Pb-Ag system.

24. Electrochemistry

Electrolytic conduction, factors affecting electrolytic conduction, specific conductance, molar conductance, equivalent conductance and relation among them, their variation with concentration. Arrhenius theory of ionization, Ostwald's Dilution Law. Debye-Huckel Onsager's equation for strong electrolytes (elementary treatment only), Transport number, definition and determination by Hittorf's methods (numerical included), Kohlrausch's Law, calculation of molar ionic conductance and effect of viscosity, temperature & pressure on it. Application of Kohlrausch's Law in calculation of conductance of weak electrolytes at infinite dilution. Applications of conductivity measurements: determination of degree of dissociation, determination of K_a of acids, determination of solubility product of sparingly soluble salts, conductometric titrations. Definition of pH and pKa, Buffer solution, Buffer action, Henderson-Hasselbalch equation, Buffer mechanism of buffer action. Electrolytic and Galvanic cells – reversible & irreversible cells, conventional representation of electrochemical cells. EMF of cell and its measurement, Weston standard cell, activity and activity coefficients. Calculation of thermodynamic quantities of cell reaction (ΔG , ΔH & ΔS). Types of reversible electrodes – metal-metal ion gas electrode, metal – insoluble salt-anion and redox electrodes. Electrode reactions, Nernst equations,

derivation of cell EMF and single electrode potential. Standard Hydrogen electrode, reference electrodes, standard electrodes potential, sign conventions, electrochemical series and its applications. Concentration cells with and without transference, liquid junction potential, application of EMF measurement i.e. valency of ions, solubility product activity coefficient, potentiometric titration (acid-base and redox). Determination of pH using Hydrogen electrode, Quinhydrone electrode and glass electrode by potentiometric methods.

25. Quantum Mechanics-I

Black-body radiation, Planck's radiation law, photoelectric effect, heat capacity of solids, Compton effect, wave function and significance of wave function, postulates of quantum mechanics, quantum mechanical operator, commutation relations, Hamiltonian operator and Hermitian operator. Role of operators in quantum mechanics, to show quantum mechanically that position and momentum cannot be predicated simultaneously, Determination of wave function & energy of a particle in one dimensional box, Pictorial representation and its significance.

26. Spectroscopy

Introduction: Electromagnetic radiation, regions of spectrum, basic features of spectroscopy, statement of Born-oppenheimer approximation, Degrees of freedom.

Rotational Spectrum

Diatomic molecules. Energy levels of rigid rotator (semi-classical principles), selection rules, spectral intensity distribution using population distribution (Maxwell-Boltzmann distribution), determination of bond length, qualitative description of non-rigid rotor; isotope effect.

Vibrational spectrum

Infrared spectrum: 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, effects of anharmonic motion and isotopic effect on the spectra., idea of vibrational frequencies of different functional groups.

Raman Spectrum

Concept of polarizability, pure rotational and pure vibrational Raman spectra of diatomic molecules, selection rules.

Electronic Spectrum

Concept of potential energy curves for bonding and antibonding molecular orbitals, qualitative description of selection rules and Franck-Condon principle. Qualitative description of sigma and pi and n molecular orbital (MO) their energy level and respective transitions.

27. Photochemistry

Interaction of radiation with matter, difference between thermal and photochemical processes. Laws of photochemistry: Grotthus-Draper law, Stark-Einstein law (law of photochemical equivalence) 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).

28. Solutions, Dilute Solutions and Colligative Properties

Ideal and non-ideal solutions, methods of expressing concentrations of solutions, activity and activity coefficient. Dilute solution, Colligative properties, Raoult's law, 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 of freezing point, Thermodynamic derivation of relation between molecular weight and elevation in boiling point and depression in freezing point. Experimental methods for determining various colligative properties. Abnormal molar mass, degree of dissociation and association of solutes.

ORGANIC CHEMISTRY

29. Structure and Bonding

Localized and delocalized chemical bond, van der Waals interactions. Resonance and hyperconjugation. Inductive effect, Electromeric effect & their comparison.

30. 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, R & S systems of nomenclature. Geometric isomerism – determination of configuration of geometric isomers. E & Z system of nomenclature. Conformational isomerism – conformational analysis of ethane and n-butane, conformations of cyclohexane, axial and equatorial bonds. Newman projection and Sawhorse formula. Difference between configuration and conformation.

31. Mechanism of Organic Reactions

Curved arrow notation, drawing electron movements with arrows, half-headed and double-headed arrows, homolytic and heterolytic bond breaking. Types of reagents – electrophiles and nucleophiles. Reactive intermediates – carbocations, carbanions, free radicals, carbenes (formation, structure & stability).

32. Alkanes

IUPAC nomenclature of branched and unbranched alkanes, the alkyl group, classification of carbon atoms in alkanes. Isomerism in alkanes, sources, methods of formation (with special reference to Wurtz reaction, Kolbe reaction, Corey-House reaction and decarboxylation of carboxylic acids), physical properties. Mechanism of free radical halogenation of alkanes: reactivity and selectivity.

33. Alkenes

Nomenclature of alkenes, mechanisms of dehydration of alcohols and dehydrohalogenation of alkyl halides. 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, Markownikoff's rule, hydroboration-oxidation, oxymercuration-reduction, ozonolysis, hydration, hydroxylation and oxidation with KMnO_4 .

34. Arenes and Aromaticity

Nomenclature of benzene derivatives: Aromatic nucleus and side chain. Aromaticity: the Huckel rule, aromatic ions, annulenes up to 10 carbon atoms, aromatic, antiaromatic and non-aromatic compounds. Aromatic electrophilic substitution – general pattern of the mechanism, mechanism of nitration, halogenation, sulphonation and Friedel-Crafts reaction. Activating, deactivating substituents and orientation.

35. Alkynes

Nomenclature, structure and bonding in alkynes. Methods of formation. Chemical reactions of alkynes, acidity of alkynes. Mechanism of electrophilic and nucleophilic addition reactions, hydroboration-oxidation of alkynes.

36. Alkyl and Aryl Halides

Nomenclature and classes of alkyl halides, methods of formation, chemical reactions. Mechanisms and stereochemistry of nucleophilic substitution reactions of alkyl halides, $\text{S}_{\text{N}}1$ and $\text{S}_{\text{N}}2$ reactions with energy profile diagrams. Methods of formation and reactions of aryl halides. Addition-elimination and the elimination-addition mechanisms of nucleophilic aromatic substitution reactions. Relative reactivities of alkyl halides vs allyl, vinyl and aryl halides.

37. Alcohols

Monohydric alcohols – nomenclature, methods of formation by reduction of aldehydes, ketones, carboxylic acids and esters. Hydrogen bonding. Acidic nature. Reactions of alcohols- Pinacol-Pinacolone rearrangement.

38. 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, Mechanisms of Fries rearrangement, Claisen rearrangement, Reimer-Tiemann reaction, Kolbe's reaction, Schotten-Baumann reaction and Gattermann-Koch reaction.

39. Carboxylic Acids & Acid Derivatives

Nomenclature of carboxylic acids, structure and bonding, physical properties, acidity of carboxylic acids, effects of substituents on acid strength. Preparation of carboxylic acids. Reactions of carboxylic acids. Hell-Volhard-Zelinsky reaction. Reduction of carboxylic acids. Mechanism of decarboxylation. Structure, nomenclature and preparation of acid chlorides, esters, amides and acid anhydrides. Relative stability of acyl derivatives. Interconversion of acid derivatives by nucleophilic acyl substitution. Mechanisms of esterification and hydrolysis (acidic and basic), Reformatsky reaction and Perkin reaction.

40. Amines

Structure and nomenclature of amines, physical properties. Separation of a mixture of primary, secondary and tertiary amines. Structural features affecting basicity of amines. Preparation of alkyl and aryl amines (reduction of nitro compounds, nitriles, reductive amination of aldehydic and ketonic compounds. Gabriel phthalimide reaction, Hofmann bromamide reaction. Electrophilic aromatic substitution in aryl amines, reactions of amines with nitrous acid.

41. Diazonium Salts

Mechanism of diazotisation, structure of benzene diazonium chloride, Replacement of diazo group by H, OH, Halogens (F, Cl, Br, I), NO_2 and CN groups, coupling reaction and its synthetic applications.

42. 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, advantage of oxidation of alcohols with chromium trioxide (Sarett reagent) pyridinium chlorochromate (PCC) and pyridinium dichromate. Physical properties. Comparison of reactivities of aldehydes and ketones. 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, Oxidation of aldehydes, Baeyer-Villiger oxidation of ketones, Cannizzaro reaction, and Meerwein-Ponndorf-Verley (MPV), Clemmensen, Wolff-Kishner, LiAlH_4 and NaBH_4 reductions.

43. Carbohydrates

Classification and nomenclature. Monosaccharides, mechanism of osazone formation, interconversion of glucose and fructose, chain lengthening and chain shortening of aldoses. Configuration of monosaccharides. Erythro and threo diastereomers. Conversion of glucose into mannose. Formation of glycosides, ethers and esters. Determination of ring size of glucose and fructose. Open chain and cyclic structure of D-(+)-glucose & D-(-)-fructose. Mechanism of mutarotation. Structures of ribose and deoxyribose. An introduction to disaccharides (maltose, sucrose and lactose) and polysaccharides (starch and cellulose) without involving structure determination.

44. 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.

45. Amino Acids, Peptides & Proteins

Classification of amino acids. Acid-base behavior, isoelectric point and electrophoresis. Preparation 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: primary, secondary, tertiary and quaternary structures.

46. 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.

47. Organic Synthesis via Enolates

Acidity of α -hydrogens, alkylation of diethyl malonate and ethyl acetoacetate. Synthetic uses of ethyl acetoacetate, Claisen condensation and Keto-enol tautomerism

48. Ultraviolet (UV) absorption spectroscopy

Absorption laws (Beer-Lambert 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 enes and enones, Woodward-Fieser rules, calculation of λ_{\max} of simple conjugated dienes and α , β -unsaturated ketones. Applications of UV Spectroscopy in structure elucidation of simple organic compounds.

49. Infrared (IR) absorption 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. Applications of IR spectroscopy in structure elucidation of simple organic compounds.

50. NMR Spectroscopy

Principle of nuclear magnetic resonance, the PMR spectrum, number of signals, peak areas, equivalent and nonequivalent protons, positions of signals and chemical shift, shielding and deshielding of protons, proton counting, splitting of signals and coupling constants, magnetic equivalence of protons. Discussion of PMR spectra of the molecules: ethyl bromide, n-propyl bromide, isopropyl bromide, 1,1-dibromoethane, 1,1,2-tribromoethane, ethanol, acetaldehyde, ethyl acetate, toluene, benzaldehyde and acetophenone. Simple problems on PMR spectroscopy for structure determination of organic compounds.

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