

PGQP06 - M Sc Chemistry

Inorganic Chemistry

I. Atomic Structure

Evidence for the electrical nature of matter; discharge tube experiments; Thomson's atomic model; Rutherford model; Bohr's model of hydrogen atom; probability picture of electron; quantum numbers; Shapes of s, p, d, orbitals; Aufbau and Pauli exclusion principles, Hund's rule of maximum multiplicity; Electronic configurations of the elements; effective nuclear charge.

II. Chemical Bonding

Covalent bond – Valence Bond Theory (VBT) and its limitations, directional characteristics of covalent bond, various types of hybridization and shapes of simple inorganic molecules and ions. Valence Shell Electron Pair Repulsion Theory (VSEPR Theory) to NH_3 , H_3O^+ , SF_4 , ClF_3 , ICl_2^- and H_2O . Molecular Orbital Theory, homonuclear and heteronuclear diatomic molecules (CO and NO), multicenter bonding in electron deficient molecules, bond strength and bond energy, percentage ionic character from dipole moment and electronegativity difference.

III. 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.

IV. Acids, Bases and Non Aqueous Solvents:

Arrhenius Concept and Bronsted Theory. The Lux – Flood Solvent Systems. Lewis Concept of Acids and Bases. Physical Properties of a solvent. Types of Solvents and their general Characteristics. Reactions in non aqueous solvents with respect to liquid NH_3 and liquid SO_2 .

V. s – block elements: Comparative study including diagonal relationship of groups, salient features of Hydrides, solvation and complexation tendencies including their function in biosystems. An introduction to alkyls and aryls.

VI. p - block elements (A): Comparative study including diagonal relationship of groups 13 and 14. Group 13--- Hydrides of Boron, diborane, and higher boranes, borazine, borohydrides. Group 14 ---Fullerenes, carbides, fluorocarbons, silicates (structural principle)

VII. p - block elements (B): Comparative study including diagonal relationship of groups 15, 16 and 17. group 15- phosphazenes, group 16—tetra sulfur tetranitride, group 17—basic properties of halogens, interhalogens and polyhalides.

VIII. Chemistry of Noble Gases: Chemical properties of Noble Gases, Chemistry of Xenon, structure and bonding in Xenon compounds,

IX. Chemistry of the Elements of the First Transition Series.

Characteristic properties of the d-Block elements. Properties of the elements of the first transition series, their binary compounds, and complexes illustrating relative stability of their oxidation states, co-ordination number and geometry.

X. Co-ordination compounds

Werner's co-ordination theory and its experimental verification, effective atomic number concept, chelates, nomenclature of co-ordination compounds

XI. Oxidation and Reduction

Use of redox potential data-analysis of redox cycle, redox stability in water –frost, Latimer and pourbaix diagrams. Principles involved in the extraction of the elements.

XII. Chemistry of the Lanthanide Elements

Electronic structure, oxidation states and ionic radii and lanthanide contraction, complex formation, occurrence and isolation, lanthanide compounds.

XIII. Chemistry of the elements of the second and third transition series

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

XIV. Co-ordination Compounds

Isomerism in co-ordination compounds, valence bond theory of transition metal complexes

XV. Chemistry of Actinides

General features and chemistry of actinides, chemistry of separation of Np, Pu and Am from U, similarities between later actinides and later lanthanides.

XVI. Ionic Solids

Ionic structures, radius ratio effect and coordination number, limitation of radius ratio rule, lattice defects, semiconductors, lattice energy and Born-Haber cycle, salvation energy and solubility of ionic solids, polarizing power and polarizability of ions, Fajan's rule, metallic bond - free electron, valence bond and band theories.

XVII. Metal-Ligand Bonding in Transition Metal Complexes:

Limitations of Valence bond theory, Crystal field theory (CFT) splitting of d- orbitals in octahedral, tetrahedral and square planar complexes. Crystal Field Stabilization Energy (CFSE), Factors affecting 10 Dq, Spectrochemical series, Effect of crystal field splitting on properties of Octahedral complexes: Magnetic, Spectral.

XVIII. Bio-inorganic Chemistry

Overview, essential and trace elements in biological processes, Metalloporphyrins with special reference to haemoglobin and myoglobin. The role of Model systems, The alkali and alkaline earth metals, Metalloenzymes, Nitrogen fixation cycle.

XIX. Inorganic solid state chemistry

Introduction, Preparation of Nonmolecular solids, Band gaps, Metals, Insulators and Semi-conductors. Defects in Solids, Point defects: Schottky and Frenkel, Color center, extended defects. Non-stoichiometry.

XX. Organometallic chemistry

(A) Definition, nomenclature and classification of organometallic compounds, EAN rule, 18 electron rule. General methods of preparations and properties. Structure and bonding in mononuclear metal carbonyls: Ni(CO)₄, Fe(CO)₅ and Cr(CO)

(B) Polynuclear metal carbonyl: preparation and structures of Mn₂(CO)₁₀, Fe₂(CO)₉ and Fe₃(CO)₁₂ (Orbital diagram not expected)

(C) Sandwich compounds like Ferrocene: preparation, properties, reactions, structure and bonding.

(D) Preparation and properties of alkyl and aryls of Li, Al, Hg and Ti.

XXI. Electronic spectra of Transition Metal Complexes:

Introduction, Types of electronic transitions: The d-d transitions(d₁/d₉ and d₂/d₈), Charge transfer transitions and Ligand-ligand transitions, Selection rules (Laporte Orbital and Spin), Applications(Ligand field strength, Colour of complexes, Cis-trans isomerism and Geometry of complexes).

XXII. Industrial fuels and chemicals.

A) Industrial fuels like coal gas, producer gas and water gas.

B) Physico chemical principles involved in the manufacture of HNO₃ (Ostwald's method) and NH₃ (Haber's method).

XXIII. Air Pollution:

Introduction, classification of pollutants, sources, control, effect w.r.t. oxides of Nitrogen, Carbon and Sulphur, Photochemical smog, acid rain and Green House effect.

XXIV. Symmetry and Term symbols:

Symmetry elements: Centre of symmetry, Rotation axis, Mirror plane, rotation – reflection axis, Identity (Transdichloroethylene, H₂O and BCl₃)

XXV. Magnetic properties of transition metal complexes:

Types of magnetic behaviour, Methods of determining magnetic susceptibility(Gouy's method), spin only formula, application of magnetic moment data for 3d – metal complexes.

XXVI. Selected topics:

A) Nanochemistry: Introduction to nano particles, their properties and applications.

B) Solid acids: Introduction to zeolites, structure and applications.

C) Superconductors: Discovery, critical temperature, Meissner effect, Types: Conventional and High Temperature superconductors.

XXVII. Inorganic Polymers:

Definition, Properties, Glass transition temperature, Classification (Condensation, addition and coordination Polymers)

Silicones: Preparation, structure & bonding and applications.

XXVIII Thermodynamic and kinetic aspects of metal complexes:

A brief outline of thermodynamic stability of metal complexes and factors affecting the stability, substitution reactions of Octahedral complexes. Trans effect with respect to square planar complexes.

PHYSICAL CHEMISTRY

I Mathematical Concepts

Logarithmic relations, curve sketching, linear graphs and calculations of slopes differentiation of functions, maxima & minima, partial, differentiation & reciprocity relations. Integration of some useful/relevant functions

II Gaseous State

Postulates of kinetic theory of gases and deviation from ideal behaviour, Van der Waal's equation of state.

Critical phenomena; PV isotherms of real gases, continuity of states, the isotherms of van der Waal's equation, relationship between critical constants and van der Waal's constants, the law of corresponding states, reduced equation of state.

Molecular Velocities: Root mean square, average and most probable velocities. Qualitative discussion of the Maxwell's distribution of molecular velocities, collision number, mean free path and collision diameter, liquifacation of gases (based on Joule – Thomson effect)

III Chemical Kinetics

Rate of reaction, factors influencing the rate of a reaction concentration, temperature, pressure, solvent, light, catalyst Concentration dependence of rates mathematical characteristics of simple chemical reaction. Zero order, first order, second order, pseudo order, half life & mean life. Determination of order of reaction: Differential method Integration method, Method of half life period & Isolation method.

Radioactive decay as a first order phenomenon.

Theories of Chemical Kinetics. Effect of temperature on the rate of reaction, Arrhenius equation and 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 & thermodynamic aspects.

IV Thermodynamics

Thermodynamic terms: System, surrounding, types of systems, intensive & extensive properties. State & path functions & their differentials. Thermodynamic process.

Concept of work & heat

First law of thermodynamics: statements and definitions of internal energy & enthalpy. Heat capacities at constant volume & pressure & their relationship. Joule's law, Joule-Thomson coefficient & inversion temperature. Calculation of w , q , dU , dH , for the expansion of ideal gases under isothermal & adiabatic conditions for reversible processes. Thermochemistry: standard state, standard enthalpy of formation. Hess's law of heat summation & its applications. Heat of reaction at constant pressure & at constant volume. Enthalpy of neutralization, bond dissociation energy & its calculation from thermochemical data. Temperature dependence of enthalpy. Kirchoff's equation.

V Solutions, Dilute Solutions and Colligative Properties

Ideal & non ideal solutions, methods of expressing concentrations of solutions, activity & activity coefficients.

Dilute solutions, colligative properties, Raoult's law, relative lowering of vapour pressure molecular weight determination. Osmosis: osmotic pressure & its measurement, depression of freezing point, thermodynamic derivation of relation between molecular weight and depression of freezing point. Elevation in boiling point thermodynamic derivation of relation between molecular weight and elevation in boiling point. Experimental methods for determining various colligative properties.

VI Liquid State and Applications

Intermolecular forces, structure of liquids (Qualitative description) Structural differences between solids, liquids and gases.

Liquid crystal: Difference between liquid crystals, solid and liquid. Classification, structure of nematic and cholesteric phases. Thermography and seven segment cell.

Surface between a liquid and vapour. Surface tension by capillary rise method, stalagmometer method. Viscosity of liquids, Poiseuille equation, use of Ostwald's Viscometer.

VII. Thermodynamics

Second law of thermodynamics: need for the law, different statements of the law. Carnot cycle and its efficiency, Carnot theorem. Thermodynamic scale of temperature.

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, entropy as a criteria of spontaneity and equilibrium. Entropy change in ideal gases and mixing of gases.

Third law of thermodynamics: Nernst heat theorem, statement and concept of residual entropy, evaluation of absolute entropy from heat capacity data. Gibbs and Helmholtz functions; Gibbs function (G) and Helmholtz function (A) as thermodynamic quantities, A & G as criteria for thermodynamic equilibrium and spontaneity, their advantages over entropy change. Variation of G and A with P , V & T .

VIII. Chemical Equilibrium

Equilibrium constant and free energy. Thermodynamic derivation of law of mass action. Le Chatelier's principle.

Reaction isotherm and reaction isochore – Clapeyron equation and Clausius – Clapeyron equation, applications

IX. 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,CO₂ and S systems.

Phase equilibria of two component system – solid –liquid equilibria, simple eutectic –Bi-Cd, Pb-Ag systems, desilverisation of lead.

Solid solutions –compound formation with congruent melting point (Mg-Zn) and incongruent melting point, (NaCl-H₂O), (FeCl₃-H₂O) and (CuSO₄-H₂O) system. Freezing mixtures, acetone – dry ice.

Liquids –liquid mixtures – ideal liquid mixtures, Raoult's and Henry's law. Non –ideal system – azeotropes- HCl-H₂O and ethanol – water systems

Partially miscible liquids –phenol –water, trimethylamine –water, nicotine –water systems.

Lower and upper consolute temperature. Effect of impurity on consolute temperature. Immiscible liquids, steam distillation.

Nernst distribution law – thermodynamic derivation, applications.

X. 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's dilution law its uses and limitations . Debye –Huckel-Onsager's equation for strong electrolytes (elementary treatment only). Transport number, definition and determination by Hittorf method and moving boundary method.

Applications of conductivity measurements :determination of degree of dissociation , determination of K_a of acids , determination of solubility product of a sparingly soluble salt, conductometric titrations .

XI. Solid State

Defination of space lattice, unit cell.

Laws of crystallography –(i) law of constancy of interfacial angles

(ii) law of rationality of indices (iii) law of symmetry elements in crystals.

X-ray diffraction by crystals .derivation of Bragg equation. Determination of crystal structure of NaCl, KCl and CsCl (Laue's method and powder method).

XII. Colloidal State

Definition of colloids, classification of colloids .

Solids in liquids (sols): properties –kinetic, optical and electrical; 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

XIII. Quantum Chemistry:

De Broglie hypothesis, the Heisenberg's uncertainty principle, sinusoidal wave equation, Hamiltonian operator, Schrödinger wave equation and its importance, physical interpretation of the wave function, postulates of quantum mechanics, particle in one dimensional box.

Schrödinger wave equation for H-atom, separation into three equations (without derivation), quantum numbers and their importance, hydrogen like wave function, radial wave functions, angular wave functions.

XIV. Electrochemistry:

Electrolytic and galvanic cells; reversible and irreversible cells, conventional representation of electrochemical cells; types of reversible electrodes; gas-metal ion, metal-metal ion, metal-insoluble salt-anion and redox electrodes, electrode reaction; Nernst equation; derivation of cell E.M.F. and single electrode potential, reference electrodes, standard hydrogen electrode; calomel electrodes; standard electrodes potential, sign convention, electrochemical series and its applications. EMF of a cell and its measurements; Concentration cells (both electrodes and electrolytes) with and without transport; liquid junction potential and its measurement; Application of concentration cell; determination of ionic product of water; transport number of ions; solubility and solubility product. Polarization; elimination of polarization; decomposition potential, measurement of decomposition potential; factor affecting decomposition potential over voltage and types of over voltage; measurement of over voltage; factor affecting over voltage

XV. Molecular Structure:

Optical activity and molecular structure; polarization (Mosotti-Clausius 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.

XVI. Nuclear Chemistry:

Composition of the nucleus. Nuclear binding forces, binding energy, stability, nucleon-nucleon forces and their equality, characteristics and theory of nuclear forces. Nuclear models, the shell model, liquid drop model and its merits. Theory of radioactive disintegration, rate of disintegration half, average life of radio element, units of radioactivity, definition and characteristics of artificial radioactivity. Determination and measurements of radioactivity: Ionisation current measurements; saturation collection; multiplicative ion collection; the Geiger-Muller Counter, characteristics of an ideal Geiger-Muller Counter, proportional counter. methods based on photon collection, Scintillation counter, characteristics of a suitable Scintillator

XVII. Molecular structure and molecular spectra:

Introduction to electromagnetic radiation; regions of the spectrum; statement of the Born-Oppenheimer approximation; degrees of freedom.

Rotational Spectrum: Diatomic molecules, energy level of a rigid rotor (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.

XVIII Quantum Chemistry:

Molecular orbital theory, basic ideas-criteria for forming M.O from A.O, construction of M.O's by LCAO- H_2^+ ion, calculation of energy levels from wave functions, physical picture of bonding and antibonding wave functions.

XIX. Applied Electrochemistry

Definition of pH, pOH, pK_a , and pK_b ; introduction to potentiometer; determination of pH using hydrogen, quinhydrone and glass electrodes by potentiometric method; Buffer solution, types, buffer action, buffer capacity, mechanics of buffer action, Henderson-Hasselbalch equation. Corrosion-Types, theories - electrochemical and chemical. Energy sources: Acid and alkaline battery. Ni-Cd cell fuel cells, solar cells. Secondary batteries

XX. Nuclear Chemistry

Nuclear fission, energy released in fission and fission products, neutron emission in fission, nuclear energy, classification of reactors, the breeder reactor, nuclear reactors in India. Chain reaction and conditions for its control; reprocessing of spent fuels; units of radiation energy; applications of radioactive isotopes; radioisotopes as tracers; biological effects of radiation.

XXI. Photochemistry:

Interaction of radiation with matter, differences between thermal and photochemical processes, laws of photochemistry: Grothuss- Drapper law, Stark-Einstein law, Jablonski diagram; depicting various processes occurring in the excited state, quantum yield and its measurements qualitative description of fluorescence, phosphorescence, non-radiative processes (internal conversion, inter system crossing), photosensitized reactions-energy transfer processes (simple examples).

XXII. Spectroscopy:

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, effect of an- harmonic motion and isotope on the spectrum, 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.

ORGANIC CHEMISTRY

I. Structure and Bonding:

Hybridization, C-C bond lengths and bond angles, bond energy, localized and delocalized chemical bonds, Definition and examples of Van der Waals interactions, resonance, hyperconjugation, inductive and field effects, intramolecular and intermolecular hydrogen bonding.

II. Fundamentals of Organic Chemistry:

Curved arrow notation, drawing electron movement with arrows, half and double headed arrows, homolytic and heterolytic bond breaking. Types of reagents – electrophiles and nucleophiles with examples. Types of Organic Reactions: Addition, Elimination, Substitution, Oxidation, Reduction and Rearrangement-one example of each. Energy profile diagrams for exothermic and endothermic reactions, single step and two step reactions. Reactive intermediates – Carbocations, carbanions, free radicals, carbenes, arynes and nitrenes; examples, shape and ways of formation. Assigning formal charges on intermediates and other ionic species. Methods of determination of reaction mechanisms (one example each of product analysis, intermediates, isotope effects, kinetic and stereochemical studies). Theory of acids and bases: Lewis concept; Bronsted and Lowry concept

III. Alkanes and cycloalkanes:

IUPAC nomenclature of alkanes. General methods of formation (with special reference to Wurtz reaction, Kolbe reaction, Corey-House reaction & decarboxylation of carboxylic acids). Physical properties and chemical reactions of alkanes: halogenation, combustion and pyrolysis. Mechanism of free radical halogenation of alkanes: orientation, reactivity and selectivity with propane as an example. Cycloalkanes – nomenclature, general methods of formation, Baeyer strain theory and its limitations. Ring strain in small rings (cyclopropane and cyclobutane), theory of strainless rings. The case of cyclopropane ring: banana bonds.

IV. Alkenes, dienes and alkynes:

IUPAC nomenclature of alkenes, general methods of formation, mechanisms of dehydration of alcohols and dehydrohalogenation of alkyl halides, regioselectivity in alcohol dehydration. The Saytzeff rule, Hoffmann elimination, physical properties and relative stabilities of alkenes. Chemical reactions of alkenes – Epoxidation, ozonolysis, hydration, hydroxylation and oxidation with KMnO_4 . Mechanisms involved in hydrogenation, electrophilic and free radical additions, Markownikoff's rule, hydroboration-oxidation, oxymercuration-reduction. Polymerization of alkenes. Substitution at the allylic and vinylic positions of alkenes. Industrial applications of ethene and propene. Nomenclature and classification of dienes, isolated, conjugated and cumulated dienes. Structure and stereochemistry of allenes, methods of formation of butadiene, polymerization. Chemical reactions – 1,2- and 1,4-additions, Diels-Alder reaction. Nomenclature, structure and bonding in alkynes. General methods of formation. Chemical

reactions of alkynes, acidity of alkynes. Mechanism of electrophilic and nucleophilic addition reactions, metal-ammonia reduction and polymerization.

V. Stereochemistry of organic compounds:

Newman and saw horse formulae, Fischer and flying wedge formulae. Concept of isomerism. Types of isomerism. Conformational isomerism – Conformational analysis of ethane and n-butane; conformations of cyclohexane, axial and equatorial bonds, conformation of mono-substituted cyclohexane derivatives.

Optical isomerism – elements of symmetry, molecular chirality, definition and examples of enantiomers, stereogenic centre, optical activity, properties of enantiomers, chiral and achiral molecules with two stereogenic centers, diastereomers, threo and erythro diastereomers, meso compounds, resolution of enantiomers, inversion, retention and racemization. Specification of configuration at chiral centers: Sequence rules and R:S system of nomenclature.

Geometric Isomerism - Determination of configuration of geometric isomers.

E and Z system of nomenclature, geometric isomerism in oximes and alicyclic compounds.

Difference between configuration and conformation.

VI. Arenes and Aromaticity

Nomenclature of benzene derivatives. Structure of benzene: molecular formula and Kekule structure. Stability and C–C bond lengths of benzene, resonance structure, MO picture. Aromaticity: The Huckel's rule, aromatic ions, anti-aromaticity. Aromatic electrophilic substitution – general pattern of the mechanism role of σ - and π - complexes. Mechanism of nitration, halogenation, sulphonation and Friedel-Crafts reaction. Activating and deactivating substituents, orientation and ortho/para ratio. Side chain reactions of benzene derivatives. Birch reduction. General methods of formation and chemical reactions of alkyl benzenes – reduction, oxidation, ring and side chain substitution.

VII. Alkyl and aryl halides:

Nomenclature and classes of alkyl halides, general methods of formation, chemical reactions. Mechanism and stereochemistry of nucleophilic substitution reactions of alkyl halides, S_N2 and S_N1 reactions with energy profile diagrams, solvent effect. The addition – elimination (bimolecular displacement) and the elimination – addition (benzyne) mechanisms of nucleophilic aromatic substitution reactions. Relative reactivities of alkyl halides vs. allyl, vinyl and aryl halides.

VIII. Electromagnetic Spectrum: Absorption Spectra

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 auxochromes, Bathochromic, hypsochromic, hyperchromic and hypochromic shifts. UV spectra of conjugated dienes and enones, Woodward-Fieser rules for calculation of UV maxima of the above two systems. Numerical problems on above.

Infra Red (IR) absorption spectroscopy – Molecular vibrations, Hooke's law, selection rules, Intensity and position of IR bands, measurement of IR spectrum, Finger print region and its use to establish identity, Applications to determine purity, to study progress of chemical reactions and hydrogen bonding. Characteristic absorptions of various functional groups and interpretation of IR spectra of simple organic compounds. Simple problems in structure elucidation using UV and IR spectroscopy.

IX. Alcohols

Classification and nomenclature. Monohydric alcohols – Methods of preparations by reduction of carbonyl compounds, carboxylic acids, and esters, using Grignard reaction. Hydrogen bonding, acidic nature. Reactions of alcohols – esterification, oxidation and dehydration.

Dihydric alcohols – Nomenclature, methods of preparation by hydroxylation of alkenes and acid catalyzed opening of epoxides. Reactions of vicinal glycols – pinacol-pinacolone rearrangement with mechanism

X. Ethers and Epoxides

Nomenclature of ethers and methods of preparation by Williamson synthesis, from alcohols by use of diazomethane and by use of H_2SO_4 . Physical properties. Chemical reactions: cleavage with HI.

Synthesis of epoxides by reaction of alkenes with peracids and by elimination from vicinal halohydrins. Acid and base catalyzed ring opening of epoxides, orientation of ring opening, reactions of Grignard and organolithium reagents with epoxides.

XI. Aldehydes and Ketones:

Nomenclature and structure of the carbonyl group. Synthesis of aldehydes by oxidation of alcohols and reduction of acid chlorides, synthesis of ketones by oxidation of alcohols, from nitriles by Grignard reaction and from carboxylic acids. Physical properties. Mechanism of nucleophilic additions to carbonyl group with particular emphasis on benzoin, aldol, Perkin and Knoevenagel condensations, reaction with ammonia and its derivatives, Wittig reaction and Mannich reaction. Halogenation of enolizable ketones. Mechanisms and one application each of the above reactions.

XII. Phenols

Nomenclature, structure and bonding. Preparation of phenols by alkali fusion of aromatic sulphonic acids, Dow's process from chlorobenzene and from Cumene through hydroperoxide rearrangement with mechanism. Physical properties and acidic character. Comparative acid strengths of alcohols and phenols, resonance stabilization of the phenoxide ion. Reaction of phenols – Electrophilic aromatic substitution, acylation and carboxylation. Mechanisms of Fries rearrangement, Claisen rearrangement, Gattermann synthesis and Riemer-Tiemann reaction.

XIII. Oxidation and Reduction reactions of carbonyl compounds

Oxidation of aldehydes, Baeyer-Villiger oxidation of ketones, Cannizzaro reaction, Meerwein-Ponndorf-Verley, Clemmensen, Wolff-Kischner, LiAlH_4 and NaBH_4 reduction. Mechanisms and one application each of the above reactions

XIV. Carboxylic Acids

Nomenclature, structure and bonding. Physical properties, acidity and effects of substituents on acid strength. Preparation of carboxylic acids by oxidation of carbonyl compounds, carbonation of Grignard reagent, hydrolysis of cyanides, preparation of aromatic acids by oxidation of alkyl benzenes. Reactions of carboxylic acids. Hell-Volhard-Zelinsky reaction, synthesis of acid chlorides, esters and amides. Reduction of carboxylic acids. Mechanism of decarboxylation.

Dicarboxylic acids: Methods of preparation and effect of heat and dehydrating agents with reference to malonic acid only.

XV. Carboxylic Acids Derivatives

Structure and nomenclature of acid chlorides, esters, amides and acid anhydrides. Physical properties. Methods of preparation from carboxylic acids and interconversion of acid derivatives by nucleophilic acyl substitution. Mechanisms of esterification and acidic and basic hydrolysis of esters with evidences.

XVI. Organic Compounds of Nitrogen

Preparation of nitroalkanes and nitroarenes. Chemical reactions of nitroalkanes. Mechanisms of nucleophilic substitution in nitroarenes and their reductions in acidic, neutral and alkaline media. Picric acid – preparation and properties.

Structure and nomenclature of amines, physical properties. Stereochemistry of amines. Separation of a mixture of primary, secondary and tertiary amines. Structural features affecting basicity of amine. Amine salts as phase-transfer catalysts. Preparation of alkyl and aryl amines by reduction of nitro compounds and nitriles, reductive amination of carbonyl compounds, Gabriel phthalimide reaction and Hofmann bromamide reaction.

XVII. Spectroscopy:

Proton Magnetic Resonance (^1H NMR) spectroscopy, theory, nuclear shielding and deshielding, chemical shift and molecular structure, spin-spin splitting and coupling constants, intensity of peaks, interpretation of PMR spectra of simple organic molecules. ^{13}C Magnetic Resonance: Number of signals, splitting of signals – proton coupled and decoupled spectra, off resonance decoupled spectra. ^{13}C MR chemical shifts – identification of hybridization of carbons and nature of functionalization. Mass Spectrometry: Simple idea of instrumentation, Definitions of parent or molecular ion peak and base peak. Isotope effect with respect to alkyl halides, Fragmentation of ketones – α cleavage and Mc Lafferty rearrangement.

Problems pertaining to the structure elucidation of simple organic molecules using spectroscopic techniques (UV, IR, PMR, CMR and MS). Types of problems to be specified. UV and IR to be used as supporting data. Types of CMR and Mass spectroscopy problems to be specified.

XVIII. Alkaloids:

Structure elucidation and synthesis of Nicotine, Atropine and Papaverine

XIX. Stereochemistry of Reactions:

Mechanism and stereochemistry of (i) Addition of halogens and halogen acids to open chain alkenes. Markownikoff's and anti- Markownikoff's addition. (ii) $\text{S}_{\text{N}}1$, $\text{S}_{\text{N}}2$, $\text{S}_{\text{N}}\text{i}$, substitutions and (iii) E_1 , E_2 and $\text{E}_{1\text{cb}}$ elimination reactions.

XX. 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 5 and 6 membered heterocycles. Preparation and reactions of indole, quinoline and isoquinoline with special reference to Fischer indole synthesis, Skraup synthesis and Bischler-Napieralski synthesis. Mechanism of electrophilic substitution reactions of indole, quinoline and isoquinoline.

XXI. Vitamins and Hormones:

Vitamins: Importance and classification. Structure elucidation and synthesis of Vitamins A and C.

Hormones: Important hormones and their uses. Structure elucidation and synthesis of Thyroxine and Adrenaline.

XXII. Amino acids, Peptides, Proteins and Nucleic Acids:

Classification, structure and stereochemistry of amino acids. Acid-base behavior, 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 methods of peptide synthesis, solid-phase peptide synthesis. Structures of peptides and proteins. Levels of protein structures. Protein denaturation/renaturation. Nucleic acids: Introduction. Hydrolysis of nucleic acids. Ribonucleosides and ribonucleotides. General idea of the double helical structure of DNA glucose. Mechanism of mutarotation. Formation of glycosides, ethers and esters. Structure elucidation of sucrose.

XXIII. Terpenes:

Classification. General methods of structure elucidation. Chemistry and synthesis of citral and its conversion to ionones. Chemistry and synthesis of α -terpineol, camphor. Chemistry of α -pinene. Chemistry of zingiberene.

XXIV. Organic synthesis via Enolates:

Acidity of α -hydrogens, Synthesis of ethyl acetoacetate by Claisen condensation, keto-enol tautomerism in ethyl acetoacetate. Alkylation of diethyl malonate and ethyl acetoacetate. Alkylation of 1,3-dithianes. Alkylation and acylation of enamines.

XXV 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 and acid value of oils. Soaps, synthetic detergents, alkyl and aryl sulphonates.

XXVI. Synthetic Polymers:

Addition or chain-growth polymerization. Free radical vinyl polymerization, ionic vinyl polymerization, Zeigler-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.

XXVII. Synthetic Dyes:

Color and constitution (electronic concept). Classification of dyes. Chemistry and synthesis of methyl orange, Congo Red, Malachite Green, Crystal Violet, Phenolphthalein, Fluorescein, Alizarin and Indigo.

XXVIII. Synthetic Drugs:

Classification according to use. One compound with name and structure from all classes of pharmacodynamic agents and chemotherapeutic agents. Synthesis and uses of the following drugs: Phenobarbital, Chlorpheniramine, Atenolol, Ibuprofen, Naproxen, Methyldopa, Chloramphenicol, Metronidazole and Ethambutol.

XXIX. Organosulphur and Organophosphorus Compounds:

Nomenclature, structural features. Methods of formation and chemical reactions of thiols, thioethers, sulphonic acids. General reactions only. Introduction to organophosphorus compounds. General methods of preparation of phosphines and phosphonium salts. Wittig reaction and its applications.

XXX. Photochemistry:

General idea of photochemical reactions. Electronic transitions and transition states. Jablonskii diagram. Norrish type I and Norrish type II cleavage of ketones.