

ANUPGCET – 2018 :: 105-CHEMICAL SCIENCES (SYLLABUS)

Max. Marks: 100

INORGANIC CHEMISTRY

1. s-block elements: General characteristics of groups I & II elements, diagonal relationship between Li & Mg, Be & Al.

2. p-block elements:

General characteristics of elements of groups 13, 14, 15, 16 and 17

Group – 13: Synthesis and structure of diborane and higher boranes (B_4H_{10} and B_5H_9), boron-nitrogen compounds ($B_3N_3H_6$ and BN)

Group – 14: Preparation and applications of silanes and silicones, graphitic compounds.

Group – 15: Preparation and reactions of hydrazine, hydroxylamine, phosphazenes.

Group – 16: Classifications of oxides based on (i) Chemical behaviour and (ii) Oxygen content.

Group – 17: Inter halogen compounds and pseudo halogens

3. Organometallic Chemistry: Definition and classification of organometallic compounds, nomenclature, preparation, properties and applications of alkyls of 1, 2 and 13 group elements.

4. Chemistry of d-block elements: Characteristics of d-block elements with special reference to electronic configuration, variable valence, magnetic properties, catalytic properties and ability to form complexes. Stability of various oxidation states and e.m.f. Comparative treatment of second and third transition series with their 3d analogues. Study of Ti, Cr and Cu triads in respect of electronic configuration and reactivity of different oxidation states.

5. Chemistry of f-block elements: Chemistry of lanthanides – electronic structure, oxidation states, lanthanide contraction, consequences of lanthanide contraction, magnetic properties, spectral properties and separation of lanthanides by ion exchange and solvent extraction methods. Chemistry of actinides – electronic configuration, oxidation states, actinide contraction, position of actinides in the periodic table, comparison with lanthanides in terms of magnetic properties, spectral properties and complex formation.

6. Theories of bonding in metals: Valence bond theory, Explanation of metallic properties and its limitations, Free electron theory, thermal and electrical conductivity of metals, limitations, Band theory, formation of bands, explanation of conductors, semiconductors and insulators.

7. Metal carbonyls and related compounds – EAN rule, classification of metal carbonyls, structures and shapes of metal carbonyls of V, Cr, Mn, Fe, Co and Ni. Metal nitrosyls and metallocenes (only ferrocene).

8. Coordination Chemistry: IUPAC nomenclature, bonding theories – review of Werner's theory and Sidgwick's concept of coordination, Valence bond theory, geometries of coordination numbers 4-tetrahedral and square planar and 6-octahedral and its limitations, crystal field theory, splitting of d-orbitals in octahedral, tetrahedral and square-planar complexes – low spin and high spin complexes – factors affecting crystal-field splitting energy, merits and demerits of crystal-field theory. Isomerism in coordination compounds – structural isomerism and stereo isomerism, stereochemistry of complexes with 4 and 6 coordination numbers.

9. Spectral and Magnetic Properties of Metal Complexes: Electronic absorption spectrum of $[Ti(H_2O)_6]^{3+}$ ion. Types of magnetic behavior, spin-only formula, calculation of magnetic moments, experimental determination of magnetic susceptibility – Gouy method.

10. Reactivity of metal complexes: Labile and inert complexes, ligand substitution reactions – S_N^1 and S_N^2 , substitution reactions of square planar complexes – Trans effect and applications of trans effect.

11. Stability of Metal Complexes: Thermodynamic stability and kinetic stability, factors affecting the stability of metal complexes, chelate effect, determination of composition of complex by Job's method and mole ratio method.

12. Hard and soft acids bases (HSAB): Classification, Pearson's concept of hardness and softness, application of HSAB principles – Stability of compounds / complexes, predicting the feasibility of a reaction.

13. Bioinorganic Chemistry: Essential elements, biological significance of Na, K, Mg, Ca, Fe, Co, Ni, Cu, Zn and chloride (Cl). Metalloporphyrins – hemoglobin, structure and function, Chlorophyll, structure and role in photosynthesis.

ORGANIC CHEMISTRY

1. Structural theory in Organic Chemistry: Types of bond fission and organic reagents (Electrophilic, Nucleophilic, and free radical reagents including neutral molecules like H_2O , NH_3 & $AlCl_3$). Bond polarization: Factors influencing the polarization of covalent bonds, electro negativity – inductive effect. Application of inductive effect (a) Basicity of amines (b) Acidity of carboxylic acids (c) Stability of carbonium ions. Resonance or Mesomeric effect, application to (a) acidity of phenol, and (b) acidity of carboxylic acids. Hyper conjugation and its application to stability of carbonium ions, Free radicals and alkenes, carbanions, carbenes and nitrenes. Types of Organic reactions: Addition – electrophilic, nucleophilic and free radical. Substitution – electrophilic, nucleophilic and free radical. Elimination-Examples (mechanism not required).

2. Acyclic Hydrocarbons:

Alkanes– IUPAC Nomenclature of Hydrocarbons. Methods of preparation: Hydrogenation of alkynes and alkenes, Wurtz reaction, Kolbe's electrolysis, Corey- House reaction. Chemical reactivity – inert nature, free radical substitution mechanism. Halogenation example- reactivity, selectivity and orientation.

Alkenes – Preparation of alkenes (a) by dehydration of alcohols (b) by dehydrohalogenation of alkyl halides (c) by dehalogenation of 1,2 dihalides (brief mechanism), Saytzev's rule. Properties: Addition of hydrogen – heat of hydrogenation and stability of alkenes. Addition of halogen and its mechanism. Addition of HX, Markonikov's rule, addition of H_2O , HOX, H_2SO_4 with mechanism and addition of HBr in the presence of peroxide (anti – Markonikov's addition). Oxidation – hydroxylation by $KMnO_4$, OsO_4 , peracids (via epoxidation) hydroboration, Dienes – Types of dienes, reactions of conjugated dienes – 1,2 and 1,4 addition of HBr to 1,3 – butadiene and Diel's – Alder reaction.

Alkynes – Preparation by dehydrohalogenation of dihalides, dehalogenation of tetrahalides, Properties; Acidity of acetylenic hydrogen (formation of Metal acetylides). Preparation of higher acetylenes, Metal ammonia reductions Physical properties. Chemical reactivity – electrophilic addition of X_2 , HX, H_2O (Tautomerism), Oxidation with $KMnO_4$, OsO_4 , reduction and Polymerisation reaction of acetylene.

3. Alicyclic hydrocarbons (Cycloalkanes): Nomenclature, Preparation by Freund's methods, heating dicarboxylic metal salts. Properties – reactivity of cyclopropane and cyclobutane by comparing with alkanes, Stability of cycloalkanes – Baeyer's strain theory, Sachse and Mohr predictions and Pitzer's strain theory. Conformational structures of cyclobutane, cyclopentane, cyclohexane.

4. Benzene and its reactivity: Concept of resonance, resonance energy. Heat of hydrogenation, heat of combustion of Benzene, mention of C-C bond lengths and orbital picture of Benzene. Concept of aromaticity – aromaticity (definition), Huckel's rule – application to Benzenoid (Benzene, Naphthalene) and Non – Benzenoid compounds (cyclopropenyl cation, cyclopentadienyl anion and tropylium cation) Reactions – General mechanism of electrophilic substitution, mechanism of nitration. Friedel Craft's alkylation and acylation. Orientation of aromatic substitution – Definition of ortho, para and meta directing groups. Ring activating and deactivating groups with examples (Electronic interpretation of various groups like NO_2 and Phenolic). Orientation of (i). Amino, methoxy and methyl groups (ii). Carboxy, nitro, nitrile, carbonyl and Sulfonic acid groups. (iii). Halogens (Explanation by taking minimum of one example from each type).

5. Polynuclear Hydrocarbons - Structure of naphthalene and anthracene (Molecular Orbital diagram and resonance energy) any two methods of preparation of naphthalene and reactivity. Reactivity towards electrophilic substitution. Nitration and sulfonation as examples.

6. Halogen compounds: Nomenclature and classification of alkyl (into primary, secondary, tertiary), aryl, aralkyl, allyl, vinyl, benzyl halides. Chemical Reactivity, formation of RMgX Nucleophilic aliphatic substitution reaction- classification into S_N^1 and S_N^2 . Energy profile diagram of S_N^1 and S_N^2 reactions. Stereochemistry of S_N^2 (Walden Inversion) S_N^1 (Racemisation). Explanation of both by taking the example of optically active alkyl halide – 2-bromobutane. Ease of hydrolysis – comparison of alkyl, benzyl, allyl, vinyl and aryl halides.

7. Hydroxy compounds: Nomenclature and classification of hydroxy compounds. Alcohols: Preparation with hydroboration reaction, Grignard synthesis of alcohols. Phenols: Preparation i) from diazonium salt, ii) from aryl sulphonates, iii) from cumene. Physical properties- Hydrogen bonding (intermolecular and intramolecular). Effect of hydrogen bonding on boiling point and solubility in water. Chemical properties:

- acidic nature of phenols.
- formation of alkoxides/phenoxides and their reaction with RX.
- replacement of OH by X using PCl_5 , PCl_3 , PBr_3 , $SOCl_2$ and with HX/ $ZnCl_2$.
- esterification by acids (mechanism).
- dehydration of alcohols.
- oxidation of alcohols by CrO_3 , $KMnO_4$.
- special reaction of phenols: Bromination, Kolb-Schmidt reaction, Reimer-Tiemann reaction, Fries rearrangement, azocoupling. Identification of alcohols by oxidation with $KMnO_4$, ceric ammonium nitrate, Lucas reagent and phenols by reaction with $FeCl_3$. Polyhydroxy compounds: Pinacol-Pinacolone rearrangement.

8. Carbonyl compounds: Nomenclature of aliphatic and aromatic carbonyl compounds, structure of the carbonyl group. Synthesis of aldehydes from acid chlorides, synthesis of aldehydes and ketones using 1,3-dithianes, synthesis of ketones from nitriles and from carboxylic acids. Physical properties: absence of hydrogen bonding, keto-enol tautomerism, reactivity of carbonyl group in aldehydes and ketones. Nucleophilic addition reaction with a) $NaHSO_3$, b) HCN, c) RMgX, d) NH_2OH , e) $PhNHNH_2$, f) 2,4-DNPH. g) Alcohols-formation of hemiacetal and acetal. Halogenation using PCl_5 with mechanism. Base catalysed reactions: a) Aldol, b) Cannizzaro reaction, c) Perkin reaction, d) Benzoin condensation, e) Haloform reaction, f) Knoevenagel reaction. Oxidation of aldehydes- Baeyer-Villiger oxidation of ketones. Reduction: Clemmensen reduction, Wolf-Kishner reduction, MPV reduction, reduction with $LiAlH_4$ and $NaBH_4$. Analysis of aldehydes and ketones with a) 2,4-DNT test, b) Tollen's test, c) Fehling test, d) Schiff test, e) Haloform test (with equation).

9. Carboxylic acids and derivatives: Nomenclature, classification and structure of carboxylic acids. Methods of preparation by a) hydrolysis of nitriles, amides and esters. b) carbonation of Grignard reagents. Special methods of preparation of aromatic acids by a) oxidation of side chain. b) hydrolysis by benzotrichlorides. c) Kolbe reaction. Physical properties: Hydrogen bonding, dimeric association, acidity-strength of acids with examples of trimethyl acetic acid and trichloroacetic acid. Relative differences in the acidities of aromatic and aliphatic acids. Chemical properties: Reactions involving H, OH and COOH groups- salt formation, anhydride formation, acid chloride formation, amide formation and esterification (mechanism). Degradation of carboxylic acids by Hunsdiecker reaction, decarboxylation by Schmidt reaction, Arndt-Eistert synthesis, halogenation by Hell-Volhard-Zelinsky reaction. Derivatives of carboxylic acids: Reaction of acid chlorides, acid anhydrides, acid amides, esters (mechanism of the hydrolysis of esters by acids and bases).

10. Active methylene compounds: Acetoacetic esters: preparation by Claisen condensation, keto-enol tautomerism. Acid hydrolysis and ketonic hydrolysis. Preparation of a) monocarboxylic acids. b) dicarboxylic acids. Reaction with urea Malonic ester: preparation from acetic acid. Synthetic applications:

Preparation of

a) monocarboxylic acids (propionic acid and n-butyric acid).

b) dicarboxylic acids (succinic acid and adipic acid).

c) α , β -unsaturated carboxylic acids (crotonic acid). Reaction with urea.

11. Exercises in interconversion

12. Nitrogen compounds

13. Nitro hydrocarbons: Nomenclature and classification – nitro hydrocarbons – structure. Tautomerism of nitroalkanes leading to aci and keto form. Preparation of Nitroalkanes. Reactivity – halogenation, reaction with HONO (Nitrous acid), Nef reaction and Mannich reaction leading to Michael addition and reduction. Amines (Aliphatic and Aromatic): Nomenclature, Classification into 1^o, 2^o, 3^o Amines and Quarternary ammonium compounds. Preparative methods - 1. Ammonolysis of alkyl halides 2. Gabriel synthesis 3. Hoffman's bromamide reaction (mechanism). 4. Reduction of Amides and Schmidt reaction. Physical properties and basic character – Comparative basic strength of Ammonia, methyl amine, dimethyl amine, trimethyl amine and aniline – comparative basic strength of aniline, methylaniline and N,N-dimethyl aniline (in aqueous and non-aqueous medium), steric effects and substituent effects. Use of amine salts as phase transfer catalysts. Chemical properties: a) Alkylation b) Acylation c) Carbylamine reaction d) Hinsberg separation e) Reaction with Nitrous acid of 1^o, 2^o, 3^o (Aliphatic and aromatic amines). Electrophilic substitutions of Aromatic amines – Bromination and Nitration. oxidation of aryl and 3^o Amines. Diazotization Cyanides and isocyanides: Nomenclature (aliphatic and aromatic) structure. Preparation of cyanides from a) Alkyl halides b) from amides c) from aldoximes. Preparation of isocyanides from Alkyl halides and Amines. Properties of cyanides and isocyanides, a) hydrolysis b) addition of Grignard reagent iii) reduction iv) oxidation.

14. Heterocyclic Compounds

15. Introduction and definition: Simple 5 membered ring compounds with one hetero atom Ex. Furan. Thiophene and pyrrole. Importance of ring system – presence in important natural products like hemoglobin and chlorophyll. Numbering the ring systems as per Greek letter and Numbers. Aromatic character – 6- electron system (four- electrons from two double bonds and a pair of non-bonded electrons from the hetero atom). Tendency to undergo substitution reactions. Resonance structures: Indicating electron surplus carbons and electron deficient hetero atom. Explanation of feebly acidic character of pyrrole, electrophilic substitution at 2 or 5 position, Halogenation, Nitration and Sulphonation under mild conditions. Reactivity of furan as 1,3 -diene, Diels Alder reactions (one example). Sulphonation of thiophene purification of Benzene obtained from coal tar). Preparation of furan, Pyrrole and thiophene from 1,4,- dicarbonyl compounds only, Paul-Knorr synthesis, structure of pyridine, Basicity – Aromaticity – Comparison with pyrrole – one method of preparation and properties – Reactivity towards Nucleophilic substitution reaction – chichibabin reaction.

16. Carbohydrates: Monosaccharides: All discussion to be confined to (+) glucose as an example of aldo hexoses and (-) fructose as example of ketohexoses. Chemical properties and structural elucidation: Evidences for straight chain pentahydroxy aldehyde structure (Acetylation, reduction to n-hexane, cyanohydrin formation, reduction of Tollen's and Fehling's reagents and oxidation to gluconic and saccharic acid). Number of optically active isomers possible for the structure, configuration of glucose based on D-glyceraldehyde as primary standard (no proof for configuration is required). Evidence for

cyclic structure of glucose (some negative aldehydes tests and mutarotation). Cyclic structure of glucose. Decomposition of cyclic structure (Pyranose structure, anomeric Carbon and anomers). Proof for the ring size (methylation, hydrolysis and oxidation reactions). Different ways of writing pyranose structure (Haworth formula and chair conformation formula). Structure of fructose: Evidence of 2 – ketohexose structure (formation of penta acetate, formation of cyanohydrin its hydrolysis and reduction by HI to give 2-Carboxy-n-hexane). Same osazone formation from glucose and fructose, Hydrogen bonding in osazones, cyclic structure for fructose (Furanose structure and Haworth formula). Interconversion of Monosaccharides: Aldopentose to aldo hexose – eg: Arabinose to D-Glucose, DMannose (Kiliani - Fischer method). Epimers, Epimerisation – Lobry de bruyn van Ekenstein rearrangement. Aldohexose to Aldopentose eg: D-glucose to D-arabinose by Ruff's degradation. Aldohexose (+) (glucose) to ketohexose (-) (Fructose) and Ketohexose (fructose) to aldohexose (Glucose)

17. Amino acids and proteins: Introduction: Definition of Amino acids, classification of Amino acids into alpha, beta, and gamma amino acids. Natural and essential amino acids – definition and examples, classification of alpha amino acids into acidic, basic and neutral amino acids with examples. Methods of synthesis: General methods of synthesis of alpha amino acids (specific examples – Glycine, Alanine, valine and leucine) by following methods: a) from halogenated carboxylic acid b) Malonic ester synthesis c) strecker's synthesis. Physical properties: Optical activity of naturally occurring amino acids: L-configuration, irrespective of sign rotation, Zwitterion structure – salt like character - solubility, melting points, amphoteric character, definition of isoelectric point. Chemical properties: General reactions due to amino and carboxyl groups – lactams from gamma and delta amino acids by heating peptide bond (amide linkage). Structure and nomenclature of peptides and proteins.

18. Mass Spectrometry: Basic principles – Molecular ion / parent ion, fragment ions / daughter ions. Theory – formation of parent ions. Representation of mass spectrum. Identification of parent ion, (M+1), (M+2), base peaks (relative abundance 100%) Determination of molecular formula – Mass spectra of ethylbenzene, acetophenone, n-butyl amine and 1-propanol.

PHYSICAL CHEMISTRY

1. Gaseous state: Compression factors, deviation of real gases from ideal behavior. Van der Waal's equation of state. P-V Isotherms of real gases, Andrew's isotherms of carbon dioxide, continuity of state. Critical phenomena. The van der Waal's equation and the critical state. Relationship between critical constants and van der Waal's constants. The law of corresponding states and reduced equation of states. Joule Thomson effect. Liquefaction of gases: i) Linde's method and ii) Claude's method.

2. Liquid state: Intermolecular forces, structure of liquids (qualitative description). Structural differences between solids, liquids and gases. Liquid crystals, the mesomorphic state. Classification of liquid crystals into Smectic and Nematic. Differences between liquid crystal and solid/liquid. Application of liquid crystals as LCD devices.

3. Solid state: Symmetry in crystals. Law of constancy of interfacial angles. The law of rationality of indices. The law of symmetry. Definition of lattice point, space lattice, unit cell. Bravais lattices and crystal systems. X-ray diffraction and crystal structure. Bragg's law. Determination of crystal structure by Bragg's method and the powder method. Indexing of planes and structure of NaCl and KCl crystals. Defects in crystals. Stoichiometric and non-stoichiometric defects. Band theory of semiconductors. Extrinsic and intrinsic semiconductors, n- and p-type semiconductors and their applications in photo electrochemical cells.

4. Solutions: Liquid-liquid - ideal solutions, Raoult's law. Ideally dilute solutions, Henry's law. Non-ideal solutions. Vapour pressure – composition and vapour pressure-temperature curves. Azeotropes-HCl-H₂O, ethanol-water systems and fractional distillation. Partially miscible liquids-phenol-water, trimethylamine-water, nicotine-water systems. Effect of impurity on consolute temperature. Immiscible liquids and steam distillation. Nernst distribution law. Calculation of the partition coefficient. Applications of distribution law.

5. Colloids and surface chemistry: Definition of colloids. Solids in liquids (sols), preparation, purification, properties -kinetic,optical,electrical. Stability of colloids, Hardy-Schulze law, protective colloid. Liquids in liquids (emulsions) preparation, properties, uses. Liquids in solids (gels) preparation, uses. Adsorption: Physical adsorption, chemisorption. Freundlich, Langmuir adsorption isotherms. Applications of adsorption.

6. Phase rule: Concept of phase, components, degree of freedom. Derivation of Gibbs phase rule. Phase equilibrium of one component – water system. Phase equilibrium of two-component system, solid-liquid equilibrium. Simple eutectic diagram of Pb-Ag system, desilverisation of lead. Solid solutions compound with congruent melting point- (Mg-Zn) system, compound with incongruent melting point – NaCl- water system. Freezing mixtures.

7. Dilute solutions: Colligative properties. Raoult's law, relative lowering of vapour pressure, its relation to molecular weight of non-volatile solute. Elevation of boiling point and depression of freezing point. Derivation of relation between molecular weight and elevation in boiling point and depression in freezing point. Experimental methods of determination. Osmosis, osmotic pressure, experimental determination. Theory of dilute solutions. Determination of molecular weight of non-volatile solute from osmotic pressure. Abnormal Colligative properties. Van't Hoff factor, degree of dissociation and association.

8. Electrochemistry: Specific conductance, equivalent conductance, measurement of equivalent conductance. Variation of equivalent conductance with dilution. Migration of ions, Kohlrausch's law. Arrhenius theory of electrolyte dissociation and its limitations. Ostwald's dilution law. Debye-Huckel-Onsagar's equation for strong electrolytes (elementary treatment only). Definition of transport number, determination by Hittorf's method. Application of conductivity measurements-determination of dissociation constant (K_a) of an acid, determination of solubility product of sparingly soluble salt, conductometric titrations. Types of reversible electrodes- the gas electrode, metal-metal ion, metalinsoluble salt and redox electrodes. Electrode reactions, Nernst equation, single electrode potential, standard Hydrogen electrode, reference electrodes, standard electrode potential, sign convention, electrochemical series and its significance. Reversible and irreversible cells, conventional representation of electrochemical cells. EMF of a cell and its measurements. Computation of cell EMF. Applications of EMF measurements, Calculation of thermodynamic quantities of cell reactions (ΔG , ΔH and K). Determination of pH using quinhydrone electrode, Solubility product of AgCl. Potentiometric titrations.

9. Chemical kinetics: Rate of reaction, factors influencing the rate of a reaction-concentration, temperature, pressure, solvent, light, catalyst. Experimental methods to determine the rate of reaction. Definition of order and molecularity. Derivation of rate constants for first, second, third and zero order reactions and examples. Derivation for time half change. Methods to determine the order of reactions. Kinetics of complex reactions (first order only): opposing reactions, parallel reactions, consecutive reactions and chain reactions. Effect of temperature on rate of reaction, Arrhenius equation, concept of activation energy. Theories of reaction rates- collision theory-derivation of rate constant for bimolecular reaction. The transition state theory (elementary treatment).

10. Photochemistry: Difference between thermal and photochemical processes. Laws of photochemistry - Grothus-Draper's law and Stark-Einstein's law of photochemical equivalence. Quantum yield. Errioxalate actinometry. Photochemical hydrogen- chlorine, hydrogen-bromine reaction. Jablonski diagram depicting various processes occurring in the excited state, qualitative description of fluorescence,phosphorescence, non-radiative processes (internal conversion, intersystem crossing). Photosensitized reactions- energy transfer processes (simple example)

11. Thermodynamics: The first law of thermodynamics-statement, definition of internal energy and enthalpy. Heat capacities and their relationship. Joule's law-Joule-Thomson coefficient. Calculation of w , q , dU and dH for the expansion of perfect gas under isothermal and adiabatic conditions for reversible processes. State function. Temperature dependence of enthalpy of formation-Kirchoff's equation. Second law of thermodynamics. 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 changes in cyclic, reversible, and irreversible processes and reversible phase change. Calculation of entropy changes with changes in V & T and P & T . Entropy of mixing inert perfect gases. Entropy changes in spontaneous and equilibrium processes. The Gibbs (G) and Hlmholtz (A) energies. A & G as criteria for thermodynamic equilibrium and spontaneity-advantage over entropy change. Gibbs equations and the Maxwell relations. Variation of G with P , V and T .

Chemistry and Industry

Physico Chemical methods of analysis

1. Separation techniques

1. Solvent extraction: Principle and process, Batch extraction, continuous extraction and counter current extraction. Application – Determination of Iron (III)

2. Chromatography: Classification of chromatography methods, principles of differential migration adsorption phenomenon, Nature of adsorbents, solvent systems, R_f values, factors effecting R_f values.

a. Paper Chromatography: Principles, R_f values, experimental procedures, choice of paper and solvent systems, developments of chromatogram – ascending, descending and radial. Two dimensional chromatography, applications.

b. Thin layer Chromatography (TLC): Advantages. Principles, factors effecting R_f values. Experimental procedures. Adsorbents and solvents. Preparation of plates. Development of the chromatogram. Detection of the spots. Applications.

c. Column Chromatography: Principles, experimental procedures, Stationary and mobile Phases, Separation technique. Applications

d. High Performance Liquid Chromatography (HPLC): Principles and Applications.

e. Gas Liquid Chromatography (GLC): Principles and Applications

2. Spectrophotometry: General features of absorption – spectroscopy, Beer-Lambert's law and its limitations, transmittance, Absorbance, and molar absorptivity. Single and double beam spectrophotometers. Application of Beer-Lambert law for quantitative analysis of

1. Chromium in $K_2Cr_2O_7$

2. Manganese in manganous sulphate Iron (III) with thiocyanate.

3. Molecular Spectroscopy

(i) Electronic Spectroscopy: Interaction of electromagnetic radiation with molecules and types of molecular spectra. Potential energy curves for bonding and antibonding molecular orbitals. Energy levels of molecules (σ, δ, n). Selection rules for electronic spectra. Types of electronic transitions in molecules effect of conjugation. Concept of chromophore.

(ii) Infra red spectroscopy: Energy levels of simple harmonic oscillator, molecular vibration spectrum, selection rules. Determination of force constant. Qualitative relation of force constant to bond energies. Anharmonic motion of real molecules and energy levels. Modes of vibrations in polyatomic molecules. Characteristic absorption bands of various functional groups. Finger print nature of infrared spectrum.

(iii) Raman spectroscopy: Concept of polarizability, selection rules, pure rotational and pure vibrational Raman spectra of diatomic molecules, selection rules.

(iv) Proton magnetic resonance spectroscopy (¹H-NMR) Principles of nuclear magnetic resonance, equivalent and non-equivalent protons, position of signals. Chemical shift, NMR splitting of signals – spin-spin coupling, coupling constants. Applications of NMR with suitable examples – ethyl bromide, ethanol, acetaldehyde, 1,1,2-tribromo ethane, ethyl acetate, toluene and acetophenone.

(v) Spectral interpretation: Interpretation of IR, UV-Visible, ¹H-NMR and mass spectral data of the following compounds 1. Phenyl acetylene 2. Acetophenone 3. Cinnamic Acid 4. Paranitro aniline.

Drugs, formulations, pesticides and green chemistry

1. Drugs

1. Introduction: Drug, disease (definition), Historical evolution, Sources – Plant, Animal synthetic, Biotechnology and human gene therapy
2. Terminology: Pharmacy, Pharmacology, Pharmacophore, Pharmacodynamics, Pharmacokinetics (ADME, Receptors – brief treatment) Metabolites and Anti metabolites.
3. Nomenclature: Chemical name, Generic name and trade names with examples
4. Classification: Classification based on structures and therapeutic activity with one example each.
5. Synthesis: Synthesis and therapeutic activity of the following drugs., L-Dopa, Chloroquin, Omeprazole, Albuterol and ciprofloxacin.
6. Drug Development: Pencillin, Separation and isolation, structures of different pencillins
7. HIV-AIDS: Immunity – CD-4 cells, CD-8 cells Retrovirus, replication in human body. Investigation available, prevention of AIDS. Drugs available – examples with structures: PIS: Indinavir (Crixivan), Nelfinavir (Viracept), NNRTIS: Efavirenz (Susrtiva), Nevirapine (Viramune) NRTIs: Abacavir (Ziagen), Lamivudine (Epiriv, 3TC) Zidovudine (Retravir, AZT, ZDV)
8. Monographs of drugs: Eg Paracetamol, Sulpha methoxazole (Tablets)

2. Formulations

1. Need of conversion of drugs into medicine. Additives and their role (brief account only)
2. Different types of formulations

3. Pesticides

1. Introduction to pesticides – types – Insecticides, Fungicides, Herbicides, Weedicides, Rodenticides plant growth regulators, Pheromones and Hormones. Brief discussion with examples, Structure and uses.
2. Synthesis and present status of the following.
DDT, BHC, Malathion, Parathion, Endrin, Baygon, 2,4-D and Endo-sulphon

4. Green Chemistry

Introduction: Definition of green Chemistry, need of green chemistry, basic principles of green chemistry

Green Synthesis: Evaluation of the type of the reaction i) Rearrangements (100% atom economic), ii) Addition reaction (100% atom economic), Pericyclic reactions (no by-product). Selection of solvent:

i) Aqueous phase reactions ii) Reactions in ionic liquids iii) Solid supported synthesis iv) Solvent free reactions (solid phase reactions)

ii) Green catalysts: i) Phase transfer catalysts (PTC) ii) Biocatalysts

Microwave and Ultrasound assisted green synthesis:

1. Aldol condensation
2. Cannizzaro reaction
3. Diels-Alder reactions
4. Strecker synthesis
5. Willaimson synthesis
6. Dieckmann condensation

Macromolecules, materials Science and catalysis

1. Macromolecules: Classification of polymers, chemistry of polymerization, chain polymerization, step polymerization, coordination polymerization – tacticity. Molecular weight of polymers-number average and weight average molecular weight, degree of polymerization, determination of molecular weight of polymers by viscometry, Osmometry and light scattering methods. Kinetics of free radical polymerization, derivation of rate law. Preparation and industrial application of polyethylene, PVC, Teflon, polyacrylonitrile, terelene and Nylon66. Introduction to biodegradability.

2. Materials science: Superconductivity, characteristics of superconductors, Meissner effect, types of superconductors and applications. Nanomaterials- synthetic techniques, bottom-up-sol-gel method, top-down- electro deposition method. Properties and applications of nano-materials. Composites definition, general characteristics, particle reinforce and fiber reinforce composites and their applications.

3. Catalysis Homogeneous and heterogeneous catalysis, comparison with examples. Kinetics of specific acid catalyzed reactions, inversion of cane sugar. Kinetics of specific base catalyzed reactions, base catalyzed conversion of acetone to diacetone alcohol. Acid and base catalyzed reactions- hydrolysis of esters, mutarotation of glucose. Catalytic activity at surfaces. Mechanisms of heterogeneous catalysis. Langmuir-Hinshelwood mechanism. Enzyme catalysis: Classification, characteristics of enzyme catalysis. Kinetics of enzyme catalyzed reactions-Michaelis Menton law, significance of Michaelis constant (K_m) and maximum velocity (V_{max}). Factors affecting enzyme catalysis- effect of temperature, pH, concentration and inhibitor. Catalytic efficiency. Mechanism of oxidation of ethanol by alcohol dehydrogenase.

GENERAL CHEMISTRY

1. Atomic Structure and elementary quantum mechanics: Blackbody radiation, Planck's radiation law, photoelectric effect, Compton effect, de Broglie's hypothesis, Heisenberg's uncertainty principle. Postulates of quantum mechanics. Schrodinger wave equation and a particle in a box, energy levels, wave functions and probability densities. Schrodinger wave equation for H-atom. Separation of variables, Radial and angular functions, hydrogen like wave functions, quantum numbers and their importance.

2. Chemical Bonding: Valence bond theory, hybridization, VB theory as applied to ClF_3 , BrF_4 , $Ni(CO)_4$, XeF_2 . Dipole moment – orientation of dipoles in an electric field, dipole moment, induced dipole moment, dipole moment and structure of molecules. Molecular orbital theory – LCAO method, construction of M.O. diagrams for homo-nuclear and hetero-nuclear diatomic molecules (N_2 , O_2 , HCl , CO and NO). Comparison of VB and MO theories.

3. Stereochemistry of carbon compounds: Molecular representations- Wedge, Fischer, Newman and Saw-Horse formulae. Stereoisomerism, Stereoisomers: enantiomers, diastereomers- definition and examples. Conformational and configurational isomerism- definition. Conformational isomerism of ethane and n-butane. Enantiomers: Optical activity- wave nature of light, plane polarised light, interaction with molecules, optical rotation and specific rotation. Chiral molecules- definition and criteria- absence of plane, center, and S_n axis of symmetry- asymmetric and disymmetric molecules. Examples of asymmetric molecules (Glyceraldehyde, Lactic acid, Alanine) and isymmetric molecules (trans -1,2-dichloro cyclopropane). Chiral centers: definition- molecules with similar chiral carbon (Tartaric acid), definition of mesomers- molecules with dissimilar chiral carbons (2,3-dibromopentane). Number of enantiomers and mesomers- calculation. D,L and R,S configuration for asymmetric and disymmetric molecules. Cahn-Ingold-Prelog rules. Racemic mixture- racemisation and resolution techniques. Diastereomers: definition- geometrical isomerism with reference to alkenes- cis, trans and E,Z- configuration.

4. General Principles of Inorganic qualitative analysis: Solubility product, common ion effect, characteristic reactions of anions, elimination of interfering anions, separation of cations into groups, group reagents, testing of cations.

5. Molecular symmetry: Concept of symmetry in chemistry-symmetry operations, symmetry elements. Rotational axis of symmetry and types of rotational axes. Planes of symmetry and types of planes. Improper rotational axis of symmetry. Inversion centre. Identity element. The symmetry operations of a molecule form a group. Flow chart for the identification of molecular point group.

6. Theory of quantitative analysis

a) Principles of volumetric analysis. Theories of acid-base, redox, complexometric, iodometric and precipitation titrations, choice of indicators for these titrations.

b) Principles of gravimetric analysis: precipitation, coagulation, peptization, coprecipitation, post precipitation, digestion, filtration and washing of precipitate, drying and ignition, precipitation from homogenous solutions, requirements of gravimetric analysis.

7. Evaluation of analytical data.: Theory of errors, idea of significant figures and its importance, accuracy – methods of expressing accuracy, error analysis and minimization of errors, precision – methods of expressing precision, standard deviation and confidence limit.

8. Introductory treatment to:

a. Pericyclic Reactions Concerted reactions, Molecular orbitals, Symmetry properties HOMO, LUMO, Thermal and photochemical pericyclic reactions. Types of pericyclic reactions – electrocyclic, cycloaddition and sigmatropic reactions – one example each.

b. Synthetic strategies Terminology – Disconnection (dix), Symbol (), synthon, synthetic equivalent (SE), Functional group interconversion (FGI), Linear, Convergent and Combinatorial syntheses, Target molecule (TM). Retrosynthesis of the following molecules

1. acetophenone 2. cyclohexene 3. phenylethylbromide

c. Asymmetric (Chiral) synthesis Definitions-Asymmetric synthesis, enantiomeric excess, diastereomeric excess. stereospecific reaction, definition, example, dehalogenation of 1,2-dibromides by I⁻. stereoselective reaction, definition, example, acid catalysed dehydration of 1-phenylpropanol.

