University of Mysore

ENTRANCE TEST SYLLABUS FOR ADMISSION TO THE
M. Sc., COURSE IN ORGANIC CHEMISTRY

Chemistry Syllabus of B.Sc., Course under Semester Scheme

Unit – I

Elements of Quantum Mechanics: Schrodinger's wave equation – Explanation of the terms therein (no derivation). Quantum numbers and their significance (assigning Quantum numbers for n = 1, 2, 3 and 4). Pauli’s exclusion principle with example, Hund’s rule of maximum multiplicity with example, Effective nuclear charge, Screening effect – based on Slater’s rule (problems need not be worked out), (n+1) rule with examples, Aufbau principle, General energy level diagram of multi-electron atom (up to n=4 level), electronic configuration of 3d series elements, stability of completely filled, half filled and empty sub shells (Explain the concept of pairing energy promotional energy and symmetrical charge distribution).

Periodic Table and Periodicity: Atomic radius-covalent, ionic and van der Waal’s radii-explanation with examples, Variation of covalent radii in a group and in a period-explanation for the observed trends, Comparison of the size of atoms with the corresponding anions and cations, Variation of ionic radii in isoelectronic ions, Additive nature of covalent radii. Ionisation energy-explanation and the factors influencing ionisation energy, Variation of ionisation energy in a group and in a period, Effect of ionic size and electronic configuration on successive ionisation energies (to be illustrated with special reference to third period elements), Electron affinity explanation-variation in a group and in a period (observed trends in the values to be accounted for), Electronegativity-explanation-variation in a group and in a period (observed trends in the values to be accounted for) Pauling and Mulliken scales of electronegativity.
Statistical treatment of results of quantitative analysis: Classification of errors, Accuracy, precision, Minimization of errors (calibration of apparatus, running of blank determination, running parallel determination to be mentioned), significant figures and computation, Mean and standard deviation (explain with an example), distribution of random errors (explanation with the help of curve), Reliability of results (F-test and t-test). Sampling-basis of sampling, sampling procedure, sampling statistics, sampling and physical state, crushing and grinding, hazards in sampling.

Chemical Bonding – I

Ionic bonding: Factors that favour the formation of ionic bond. Lattice energy, Born-Haber cycle, setting up of Born-Haber cycle for NaCl, Role of lattice energy and hydration energy, Numerical calculation of lattice energy and electron affinity based on Born-Haber cycle for 1:1 solids.

Covalent bond: Factors favouring the formation of covalent bond (ionization energy, electron affinity, electro negativity, nuclear charge/inter nuclear distance and number of valence electrons), Valence bond approach- explanation with simple examples (H2, F2, HF, O2 and N2) to illustrate valence bond approach (no wave mechanical approach), Sigma and Pi bonds-explain by taking H2, O2 and N2 as examples.

Chemical Bonding – II

Concept of resonance-resonance energy, Resonance structures of CO, CO2, N2O, SO3²⁻ and CO3²⁻ Hybridisation directional property and geometry of sp, sp², sp³, sp³d and sp³d² hybrid orbitals taking BeCl₂, BF₃, SiC₄, PCl₅ and SF₆ as examples respectively, VSEPR theory with NH₃ and H₂O as examples.

Polarisation: Fajans rules of polarisation and their explanation, Bond length, bond order, bond energy and their significance, Polarity of covalent bond, Polar and non-polar molecules, Dipole moment and polarity of molecules to be explained by taking HCl, CO₂, NH₃, CC₄ and H₂O as examples.
**Molecular Orbital Theory**
An elementary account of MOT, Linear combination of atomic orbitals (no mathematical approach), Bonding and antibonding molecular orbitals, Conditions for the combination, Energy levels of molecular orbitals, Molecular orbital structures and bond orders of simple species like $\text{H}_2, \text{He}_2, \text{He}_2^+, \text{N}_2, \text{O}_2$ and $\text{F}_2$. Prediction of magnetic properties of these species.

**Coordinate bond:** Explanation with examples $\text{H}_2\text{O}^+$ and $\text{NH}_4^+$.

**Metallic bond:** Band theory, Explanation of electrical conductance of metals, Semiconductors (n and p types), Insulators and Superconductors (explanation arid applications with suitable examples).

**Hydrogen bonding:** Types of hydrogen bonding, Hydrogen bonding in $\text{HF}$, $\text{H}_2\text{O}$, $\text{NH}_3$, alcohols, carboxylic acids, nitrophenols, Appropriate anomalous properties like physical state, boiling point, solubility, nature and stereochemical rigidity due to hydrogen bonding in $\text{HF}$, $\text{H}_2\text{O}$, alcohols and nitrophenols, Structure of ice.

**s-block elements:** Comparative study of the properties of compounds of I group elements such as halides, carbonates, bicarbonates, hydroxides and nitrates, Explanation for the observed trends in the properties, Anomalous behaviour of lithium and its compounds, Diagonal relationship between lithium and magnesium, Causes for such relationship.

**Unit - II**

**Alkaline earth metals:** Comparative study of the properties of IIA group elements and their compounds such as oxides, halides, carbonates, hydroxides and sulphates. Explanation for the observed trends in the properties, Anomalous behavior of beryllium in the group and its diagonal relationship to aluminum.

**p-block elements:** Boron trifluoride-preparation, electron acceptor character and uses, Boron hydrides dihorane-preparation (Electric discharge and chemical reduction method), properties, uses and structure.
Carbon - Fullerene (C_{60}), Silicon - Structure of silica, Silicates-types and structure with one example for each type.

Nitrogen-preparation (any two methods), properties, uses and structures of hydrazine, hydrazoic acid, hydroxylamine and nitrogen trichloride.

Halogens-Bleaching powder preparation, properties and structure.

Interhalogen compounds - preparation, properties and structures of ClF_{3}, BrF_{5} and IF_{7}.

Pseudo halogens - preparation, properties and structures of cyanogen and thiocyanogen (any one method of preparation and any three properties to be discussed).

Noble gases: Preparation, structure and applications of compounds of xenon and krypton (XeF_{2}, XeOF_{2}, XeO_{3}, KrF_{2}, KrF_{4}, KrO_{3}, xH_{2}O one method of preparation for each). Chemistry of radon (discovery, source and uses), clathrates (explanation with suitable examples, essential conditions for the formation and uses).

Non-aqueous solvents: Liquid ammonia - reasons for the solvent properties, typical reactions - solubility of alkali metals, acid-base, precipitation, ammonolysis, ionization of weak acids, advantages and disadvantages. Liquid sulphur dioxide - reasons for the solvent properties, typical reactions - acid-base, solvolysis, precipitation, amphoteric and redox.

Nuclear Chemistry: Fundamental particles of nucleus-nucleons, isotopes, isobars and isotones, (definition, with suitable examples), nuclear forces (brief explanation), nuclear stability-n/p ratio, mass defect, binding energy, inner structures of nucleus-liquid drop model, nuclear fission (definition with suitable examples), calculation of energy released in nuclear fission, modes of release of fission energy (uncontrolled and controlled).
Plutonium as a fissionable material (plutonium bomb), nuclear fusion and its advantages over nuclear fission reactions, hydrogen bomb, nuclear transmutation-artificial radioactivity, cyclotron, nuclear reactor, breeder reactor, Q-values of nuclear reactions, uses of radio isotopes-tracer technique, agriculture, medicine, food preservation and dating (explanation).

**d-Block elements:** Position in the periodic table, electronic configuration, general characteristics, atomic and ionic radii, ionization energy, variable oxidation states, spectral properties, redox potentials, colour and magnetic properties, catalytic activity, complex formation and interstitial compound formation.

**f-Block elements:** Electronic structure and position in the periodic table, oxidation states, spectral properties, magnetic properties, complex formation and ionic radii, lanthanide contraction-cause and its consequences, General survey of actinides-comparison with lanthanides, transuranic elements.

**Gravimetry:** Introduction to gravimetric analysis - precipitation methods (various steps involved to be discussed), advantages of gravimetric analysis, colloidal states (partial size, peptization to be discussed), super-saturation and precipitate formation (mechanism of precipitation - super-saturation, nucleation and crystal growth), purity of the precipitates, co-precipitation and post-precipitation, conditions of precipitations (mention the conditions), precipitation from homogeneous solutions (hydroxides and sulphates), washing and ignition of the precipitate (general discussions only).

**Organic precipitants:** Advantages of organic precipitants over inorganic precipitants, DMG, 8-hydroxyquinoline (oxine), Structure of Ni$^{2+}$ – DMG and Mg$^{2+}$–oxine complexes.

**Ion exchange:** Introduction, action of ion-exchange resins- cation exchange resins, anion exchange resins, exchange of inorganic ions, ion exchange capacity, separation of lanthanides by ion exchange method.
Unit – III

**Basic concepts of Co-ordination Chemistry:** Definition of the terms-molecular compounds (lattice and coordination compounds), ligands, co-ordination number, co-ordination sphere, classification of ligands, chelation, nomenclature of co-ordination compounds-physical methods in the study of complexes, change in conductance, colour and pH, stability of complex ions-stability constant, factors affecting the stability of a complex ion, polynuclear or bridged complexes, inner metallic complexes, isomerism in co-ordination compounds - (a) stereo isomerism - geometrical and optical isomerism exhibited by co-ordination compounds of co-ordination number 4 and 6. (b) structural isomerism - ionisation isomerism, hydrate isomerism, co-ordination isomerism, linkage isomerism, co-ordination position isomerism. Ligand isomerism. Role of Fe in haemoglobin and myoglobin, role of Mg in chlorophyll and Co in Vit B12.


**Crystal Field Theory (CFT):** Important features of crystal field theory, crystal field splitting of d-orbitals in tetrahedral and octahedral complexes, crystal field stabilisation energy (CFSE), factors affecting the magnitude of \(\Delta_C\) - (nature of the ligand, oxidation state of the metal ion, size of the orbitals, geometry of the complex), high spin (HS) and low spin (LS) complexes, magnetic properties of metal complexes based on crystal field theory; \([\text{Co(NH}_3)_6]^{3+}, [\text{CoFe}]^{3-}, [\text{Fe(CN)}_6]^{4+}, [\text{Fe(CN)}_6]^{3-}\) and \([\text{Ni(CN)}_6]^{2-}\).

**Gaseous fuels:** Definition of fuels - Classification with eg. - Characteristics, calorific value and advantages, compressed natural gas (CNG), water gas, producer gas and LPG- their production, composition and applications.
**Propellants:** Definition, Characteristics, classification and application. Abrasives: Definition, Classification with examples - hardness, manufacture and applications of carborundum, alundum and tungsten carbide.

**Refractories:** Definition, properties, classification with examples and applications.

**Ceramics:** Definition and examples, Raw materials and their role, varieties of clay, production of ceramic wares, glazing and insulators-uses.

**Metallurgy:** Types of metallurgy: Pyrometallurgy: Extraction of Nickel from sulphide ore, general metallurgy followed by Mond's process (purification), Manganese from oxide ores-reduction by the alumino - thermite process - refining by electrolytic process. **Hydrometallurgy:** Extraction of gold from native ore by cyanide process and refining by quartation process. **Electrometallurgy:** extraction of lithium by fusion method followed by electrolysis of lithium chloride.

**Powder metallurgy:** Importance, metal powder production and application, production of tungsten powder. Extraction of (1) Thorium from monazite sand - purification by iodine method, (2) Uranium from pitch lende production of U₃O₈ by carbonate method, U₃O₈ to UO₂ by hydrogen reduction, UO₂ to U by fluoride method and (3) Plutonium from burnt nuclear fuel.

**Steel:** Production, properties and applications of ferro alloys. 1. ferro silicon 2. Ferrochrome 3. Ferro manganese.

**Alloy Steels:** Influence of Si, Mn, Cr, Ni, Ti, V, Mo and W on the properties of steel. Heat treatment of steel gardening case hardening carbidng and nitriding, tempering and annealing.
**ISO 9000:** History perspective, scope, definitions, ISO 9000 series - 9001, 9002, 9003 and 9004, twenty elements of ISO 9000 series registration, documentation of process and implementation processes.

**Unit – IV**

**Introduction to organic chemistry:** Definition-Importance of Organic compounds to life and applications in food, fuels, textiles, dyes, drugs, cosmetics etc., with examples.

**Classification of organic compounds:** Into aliphatic (saturated and unsaturated compounds) with examples, - cyclic (homocyclic, alicyclic and heterocyclic) and aromatic with one example each.

**Nomenclature:** IUPAC and trivial names upto 6 carbon atoms of organic compounds - aliphatic hydrocarbons, alcohols, acids, aldehydes, ketones, amines, halogen compounds, hydroxy acids and amines.

**Principles of purification of organic compounds:**
Crystallisation, fractional crystallisation, distillation, fractional distillation, distillation under reduced pressure, steam distillation and sublimation. Brief procedure for the principles of all the methods of purification is to be given.

**Electronic effects and reactive intermediates:**
Homolytic bond cleavage - definition – free radicals-definition with examples.
Heterolytic bond cleavage – definition with examples.
Stability of primary, secondary and tertiary carbonium ions, carbanions and carbon free radicals.

**Reactive Intermediates:**
Electrophiles and Nucleophiles – definitions and their nature with examples,
Inductive effect - definition (+I effect and -I effect) explanation with examples by taking halogen derivatives and halogenated acids upto 4 carbon atoms.

Resonance effect - definition-explanation with examples by taking aromatic carboxylic acids

Hyperconjugation - definition-explanation by taking CH$_3$ as an example.

Influence of these on the properties of molecules

**Aliphatic Hydrocarbons:**

**Alkenes:** Free radical mechanism of chlorination of methane.

**Alkenes:** Synthesis from alcohols (dehydration) and alkyl halides (dehydrohalogenation) Mechanism of Markownikoff’s and Anti-Markownikoff’s rule Oxidation of alkenes with KMnO$_4$ (dilute and concentrated). Ozonolysis and its importance.

**Alkynes:** Acidity of alkynes - terminal alkynes and non-terminal alkynes. Metal acetylidic (copper and silver) comparison of acidity of alkynes with alkanes and alkenes.

**Dienes:** Types-isolated, conjugated and cumulative dienes with examples, synthesis of 1,3 butadiene from 1,4-Butanediol. Addition of halogen to 1,3 butadiene, Diels-Alder reaction with one example.

Detection of C, H (combustion method), N, S and halogens (Lassaignes1 method). Estimation of sulphur and halogen by Carius method and nitrogen by Kjeldhals method (Problems to be worked out).

**Organic Reagents:** One method of preparation and applications of the reagents-acetic anhydride, benzy chloride, dimethyl sulphate, Raney nickel and sodium ethoxide.
**Cycloalkanes** - Definition and examples. Reactions- hydrogenation and halogenation, Comparison of the stabilities of cycloalkanes Baeyer’s-Strain theory-postulates and limitations, Sasche-Mohr’s theory of strainless rings, Chair and boat conformation of cyclohexane and their stability by taking methyl groups as substituents at equatorial and axial positions.

**Aromatic hydrocarbons**: Modern concept of structure of benzene including molecular orbital theory, aromaticity, Resonance energy, Electrophilic substitution reactions of benzene with mechanism (chlorination, sulphonation, nitration, Friedel-Craft’s reaction- (alkylation and acylation). Electronic interpretation of orientating influence of electron donating groups (CH₃, -Cl, -NH₂, -OH) and electron withdrawing groups (-NO₂, -SO₂H, -COOH-CHO) on electrophilic substitution reactions, Resonance structures of naphthalene, anthracene and phenanthrene.

**Alkyl halides**: Classification, nucleophilic substitution reaction: SN¹ and SN² with mechanism (taking examples of hydrolysis of t-butyl bromide, methyl bromide) – characteristics of SN¹ and SN² reactions.

**Elimination reaction**: Dehydrohalogenation, Saytzeff’s rule, Mechanism. of E₁ and E₂ reactions (taking the examples of t-butyl bromide and ethyl bromide).

**Organo metallic compounds**: Definition with examples. Grignard’s reagent preparation of C₂H₅MgI and synthetic applications (conversion to alkanes, 1°, 2° and 3° alcohols, aldehydes, ketones and acids).

**Organo lithium compounds**: Preparation, properties [reaction with water ethylene oxide, aldehydes including HCHO, ketones and CO₂] and application of CH₃ Li.
Unit - V

**Alcohols:** Definition - Classification with examples.

**Monohydric alcohols:** Preparation of alcohols by hydroborotan method, Distinguishing tests between 1<sup>°</sup>, 2<sup>°</sup> and 3<sup>°</sup> alcohols (oxidation and Victor Meyer’s method). Conversion of primary to secondary; secondary to tertiary and primary to tertiary alcohols. Dehydration of 1<sup>°</sup>, 2<sup>°</sup> and 3<sup>°</sup> alcohols and comparison of their rates.

**Dihydric alcohols:** Glycol Preparation from vicinal dihalides and uses.

**Pinacols:** Pinacol-pinacolone rearrangement and Mechanism.

**Trihydric alcohols:** Glycerol-synthesis from propene, Reactions with cone. HNO<sub>3</sub> cone. H<sub>2</sub>SO<sub>4</sub>, oxalic acid and HI, Uses of glycerol.

**Phenols:** Definition-Classification with examples. Acidity of phenols-effect of substituents on acidity. Mechanism of Reirner-Tiemann’s and Koe1be-Schmidt reactions. Frie’s rearrangement. [no mechanism]

**Carbonyl compounds:** Nomenclature, addition reaction with HCN, NaHSO<sub>3</sub>, condensation reactions with 2, 4-DNP, NH<sub>2</sub>OH, Knoevenagel reaction with mechanism, Aldol condensation, Perkin’s reaction, Cannizzaro’s reaction, C1aisn condensation, conversion of HCHO to sugar during photo synthesis (mechanisms for all reactions).

**Carboxylic acids:** Definition - Classification with examples, Synthesis by Arndt-Eistert reaction, Acidity of carboxylic acids - resonance structure of carboxylate ion and its stability, Effect of substituents on acidity (both aliphatic and aromatic carboxylic acids).

**Hydroxy acids:** Synthesis of lactic, citric and tartaric acid - one method each and their importance, effect of heat on α, β, γ, hydroxyl acids.
**Amines:** Definition - Classification with examples, Separation of amines mixture by Hinsberg's method using toluene sulphonyl chloride. Distinction tests for 1°, 2° and 3° amines [acylation and Hoffmann's exhaustive methylation]. Action of nitrous acid on different amines (both aliphatic and aromatic 1° 2° and 3° amines), Basicity of amines, Effect of substituents on basicity of aliphatic and aromatic amines, Hoffmann-Martius rearrangement.

**Diazonium Compounds:** Preparation, mechanism of preparation and synthetic applications of benzene diazonium chloride (conversion to phenol, halobenzene, azobenzene, phenyl hydrazine and coupling reaction).

**Carbohydrates:** Definitions, Importance, Classification based on composition with examples (including definition) reducing and non-reducing sugars.

**Monosaccharides:** Glucose: Reactions of glucose with NH₂OH, HCN, C₆H₅NHNH₂ Br₂-water, conc. HNO₃, complete reduction with H₂/Red P, CH₃OH/dry HCl, acetic anhydride and reduction reactions.

**Structural elucidation of glucose:** Open chain structure, configuration (no elucidation - assume). Drawbacks of open chain structure (including muta rotation). Ring structure - Fischer and Haworth's structure. Determination of ring size by methylation method.

**Fructose:** Reactions of fructose (with NH₂OH, HCN, C₆H₅NHNH₂ Br₂-water, conc. HNO₃, complete reduction with H₂/Red P, CH₃OH/dry HCl, Acetic anhydride, Reduction reactions).

**Structural elucidation of fructose:** Open chain structure, configuration (no elucidation - assume). Ring structure- Fischer and Haworth's structure – both pyranose form and furanose form.

**Conversion reactions:** (1) Ascending (Kiliáni's synthesis), (2) descending (Wohl's degradation), (3) aldose to ketose and (4) ketose to aldose, (5) Epimerisation.
**Disaccharides:** Structural elucidation of sucrose. Structural formulae of maltose and lactose (Haworth’s structure).

**Polysaccharides:** Partial structural formulae of starch, cellulose and their uses.

**Unit – VI**

**Stereochemistry:** Introduction - definition, elements of symmetry (plane, centre, simple axes and alternative axes), asymmetry and dissymmetry. Chiral carbon atom. Designation of configuration of R-S notation. Optical activity explanation - cause of optical activity (non super impossability, enantiomers, diastereomers. Optical isomerism in tartaric acid and biphenyls. Racemisation, resolution, methods of resolution (Biochemical and chemical methods), Walden inversion, Asymmetric synthesis (partial and absolute).

**Geometrical Isomerism:** Definition with examples, Designation of cis-trans, E-Z notations with examples. Geometrical isomerism of oximes (aldoximes and ketoximes), Beckmann rearrangement.

**Conformational Isomerism**

**Conformation of ethane:** Staggered, elliptical and skew conformations. Newmann projection formula. Stability of different conformations, plot of potential energy of ethane molecule as a function of rotation about C-C bond.

**Active methylene compounds:** Definition- Ethyl acetoacetate. Preparation (one method) Keto-enol tautomerism in ethyl acetoacetate - its evidence. Synthetic applications (acid hydrolysis, ketonic hydrolysis - mono carboxylic acids, dicarboxylic acids-succinic acids, adipic acids- antipyrine, uracil, acetyl acetone, crotonic acid and cinnamic acid).

**Detergents and soaps:** Definition, examples, merits and demerits of syndets in relation to soaps, Cleansing action of soaps.
**Waxes:** Definition - classification - Animal and plant waxes (one example each).

**Natural pigments:** Structural formulae and their importance of anthocyanin, β-carotene, haemoglobin.

**Dyes:** Colour and constitution, chromophore-auxochrome theory, Classification of dyes based on applications with examples, Synthesis of malachite green and indigo, Structural elucidation of alizarin and its synthesis.

**Terpenes:** Definition - Isoprene rule, Classification, isolation (solvent extraction, steam distillation), structural elucidation of citral and its synthesis, Structural formulae of β-tcpineol, camphor and menthol.

**Heterocyclic compounds:** Definition, Classification with examples, synthesis of furan, thiophene, pyrrole, pyridine, indole (Fischer method), quinoline (Skraup's synthesis), isoquinoline, pyrimidine (one method each). Aromaticity and basicity of pyrrole and pyridine.

**Uric acid:** Elucidation of structure and synthesis by Fischer's method, conversion of uric acid to purine and caffeine, Synthesis of guanine and theobromine.

**Alkaloids:** Definition, classification based on heterocyclic rings - isolation, Synthesis and structural elucidation of nicotine, Structural formulae of quinine, atropine, piperine, cocaine and morphine. Physiological importance of alkaloids.

**Vitamins:** Definition, Classification, structural elucidation and synthesis of vitamin-A, synthesis of vitamin - C, structural formulae of vitamins B1, B2, B6, calciferol, E and K- and their importance.

**Hormones:** Definition, classification, synthesis of adrenaline, thyroxine, Structural formulae of estradiol, progesterone and testosterone.- and their importance.
**Drugs:** Chemotherapy and chemotherapeutic agents, Definition of drugs, types of drugs: antipyretics, analgesics, anaesthetics, sedatives, Narcotics, antiseptics. Antibacterials, antibiotics, antimalarials, sulphadrugs with examples, Synthesis of paracetamol, sulphanilamide, sulphaguanidine.

**Insecticides, Fungicides and Herbicides:** Definition, Classification, synthetic organic insecticides and Fungicides, structural formulae and their importance of aldrin, BHC, Lindane, malathion.

**Herbicides:** Definition structural formulae and their importance of Diuren, 2, 4-D [2,4-dichlorophenoxy acetic acid] and their importance.

**Wood protectants:** Definition, importance of creosote oil, pental chlorophenols.

**Unit – VII**

**Gases:** Maxwell-Boltzmann distribution of molecular velocities (no derivation-assume equation) explanation of effect of temperature on distribution of molecular velocities using distribution curve (graph), Boltzmann factor (definition and equation), Energy distribution as a function of temperature, Types of molecular velocities - average (\(U_{av}\)) root mean square (\(U_{rms}\)) - most probable (\(U_{mp}\)) - their definition and equations (no derivation)- Relation between probable, average and root mean square velocities of molecules and their calculations (based on temperature dependence).

**The critical phenomenon** - Andrew's experiments on carbon dioxide, Critical constants \(T_c\), \(P_c\) and \(V_c\) - definitions-experimental determination of critical temperature and critical pressure by using Cagniard-de la Tour's apparatus-critical volume by Cailletes and Mathias method — van der Waal's equation-relation with vander Waal's constants 'a' and 'b' and critical constants \(T_c\), \(P_c\) and \(V_c\) to be derived-using isotherm of \(CO_2\) Law of corresponding states and reduced equation of state (to be derived).

Indicators: Definition, types (acid-base, redox, adsorption indicators) examples for each type. Theory of indicators - Ostwald’s theory and Quinonoid theory - indicator constant, action of phenolphthalein and methyl orange in acid-base solutions - pH titration curves for: - strong acid Vs strong base - weak acids strong base - weak base vs strong acid - choice of indicators in these types of titrations - colour change and pH range - Universal indicator definition.


Liquid mixtures: Classification of binary mixtures into - partially miscible, completely miscible and completely immiscible pairs of liquids (explanation with examples for each type), Raoult’s law, definition of ideal and non-ideal solutions based on Raoult’s law.

Partially miscible liquids: Critical solution temperature (C.S.T.) - types, phenol-water system, triethylamine water system, nicotine-water system (mutual solubility temperature - M.S.T vs composition curves to be drawn). Effect of addition of non-volatile solute on C.S.T

Binary mixtures of completely miscible liquids: Vapour Pressure - definition, Vapour pressure composition diagrams, and vapour pressure - temperature diagrams,
classification into types - obeying Raoult’s Law (type I), showing positive deviation from 
Raoult’s law (type II) and showing negative deviation from Raoult’s law (type III) - 
examples for each type.

Principles of fractional distillation, fractional distillation of type I, type II, and type III liquid 
mixtures (with examples), azeotropic mixtures - definition.

Binary mixtures of completely immiscible liquids (with examples), weight fraction of 
distillates (no derivation), principles of distillation, applications, (numerical problems on 
weight fractions of components).

**Colligative properties:** Concept of vapour pressure, variation of vapour pressure with 
temperature, Definition of boiling point and freezing point, effect of dissolution of solute on 
the vapour pressure of the solvent, lowering of vapour pressure, Raoult’s Law-Relation 
between relative lowering of vapour pressure and molar mass (to be derived). 
Determination of relative molar mass of solute by dynamic method, Elevation of boiling 
point and its relation to lowering of vapour pressure, and molar mass (to be derived). 
Ebullioscopic constant of the solvent and its relation to the boiling point (only equation), 
determination of molar mass of the solute by Walker-Lumsden’s method. Depression in 
freezing point and its relation to lowering of vapour pressure and molar mass (to be 
derived). Cryoscopic constant and its relation to the melting point (equation). 
Determination of molar mass of a non-volatile solute by Beckmann’s method. (Problems to 
be worked out).

**Semipermeable membrane:** Natural and artificial, preparation of copper ferrocyanide 
membrane by Morse-Frazer method, definition of osmosis, osmotic pressure (mention 
applications), determination of osmotic pressure by Berkely-Hartleys method, laws of 
osmotic pressure-analogy with gas law, molar mass from osmotic, pressure measurement 
(relation to be derived), isotonic solutions, plasmolysis, abnormal molecular weights-
causes-Van’t Hoff’s factor. (Problems to be worked out).

Properties of colloidal system: Optical properties-Tyndall effect, kinetic properties- Brownian movement, Electrical properties-zeta potential, electrophoresis, electro osmosis, coagulation of colloids, Hardy-Schultz rule and coagulation value-mutual coagulation, protective action of lyophilic sols, gold number.


Unit – VIII


Buffer Solutions: Introduction, Definition, Types with examples, Henderson’s and Hassel Bach’s equation (both to be derived), Role of buffer in pH maintenance in industry (sugar, paper and beverage). Numerical problems on - activity co-efficient, ionic strength (H+), pH, pOH and buffers.
**Distribution law:** Nernst distribution law in liquid-liquid systems, Distribution coefficient, Statement of Nernst distribution law-verification of distribution law taking distribution of I$_2$ in H$_2$O and CCl$_4$ - limitations of the Law. Conditions for the validity of distribution law, association of the solute in one of the solvents, dissociation of solute in one of the solvents. Application of distribution law with respect to solvent extraction process (Numerical problems).

**Thermodynamics:** Introduction - Definition - Scope - Limitations - definition of thermodynamic terms with examples, processes isothermal, adiabatic, isochoric, isobaric and cyclic. Difference between isothermal and adiabatic processes.

**Concept of thermodynamic reversible and irreversible processes:** Thermodynamic reversible and irreversible processes their definitions, differences with examples, state function - definition with examples, work and heat - definitions and explanation, inter conversion of work and heat — Joule- mechanical equivalent, units of heat, new sign convention of heat and work, maximum work, maximum work done during an isothermal-reversible expansion of an ideal gas $W = -2.303 \, \text{nRT} \, \log \left( \frac{V_2}{V_1} \right)$ or $[W = -2.303 \, \text{nRT} \, \log \left( \frac{P_1}{P_2} \right)]$ to be derived. Numerical problems to be worked out.

**First law of thermodynamics:** Statements, mathematical expression $q = dE + w$ to be derived, enthalpy of a system (definition, $H=E+PV$), heat capacity - heat capacity of gases - types, heat capacity at constant pressure $C_p$, and heat capacity at constant volume $C_v$ and their definitions, relation between $C_p$ and $C_v$ (derivation using thermodynamic concept), ratio and molecular complexity.

**Second law of thermodynamics:** Limitations of first law of thermodynamics - Need for II law of thermodynamics, spontaneous, non-spontaneous and equilibrium processes (definitions and examples for each), different methods of stating II law, heat engine (explanation with example), Carnot cycle - definition - efficiency of cagnot cycle definition efficiency of carnot cycle (derivation), concept of entropy - definition and physical
significances of entropy - criteria of spontaneity in terms of entropy change, statements of II law in terms of entropy numerical problems to be worked out on entropy calculations and efficiency of Carnot engine).

**Free energy:** Helmholtz and Gibb's free energy - their definitions and their relationship, Gibb's-Helmholtz equation at constant pressure and volume (derivations) thermodynamic criteria of equilibrium and spontaneity, variation of free energy with temperature and pressure, Clausius-Clapeyron equation (differential form to be derived). Integrated form of Clausius-Clappeyron equation (to be assumed) and its applications - (enthalpy of vapourisation, boiling point and freezing point at different temperatures, numerical problems on these applications), Van't Hoff's reaction isotherms and isochore equations (to be derived).

**Physical properties and chemical constitution:** Additive and constitutive properties, properties of liquids viscosity, definition of coefficient of viscosity, factors affecting viscosity-temperature, size, weight, shape of molecules, intermolecular forces, determination of viscosity of liquids by Ostwald's method.

**Surface tension:** Definition, effect of temperature on surface tension, effect of solute on surface tension, determination of surface tension of liquids using stalgmometer.

**Parachor:** Definition - Sugden equation, calculation of parachor and its application with respect to structural elucidation of benzene and quinone - numerical problems based on surface tension and viscosity and parachor applications.

**Polarisation:** Induced orientation and. molar polarisation - their definition, Clausius-Mosotti equation (no derivation) and its importance.

**Crystallography:** Elements of symmetry-plane, axis and centre, elements of symmetry in cubic crystals, law of rational indices-Weiss and Miller indices, lattice planes in cubic crystals, crystal lattice and unit cell, types of lattice-Bravais lattices, X-ray diffraction and
Bragg’s law (to be derived), determination of crystal structure of rock salt by rotating crystal method using Bragg’s spectrometer, application of X-ray studies-distance between lattice planes, density of crystals, determination of Avogadro number (Numerical problems on applications).

**Liquid crystals:** Definition, classification of thermotropic liquid crystals into smectic and nematic with examples, molecular arrangement of these and their uses.

**Unit - IX**

**Spectrophotometry and Photochemistry:** Lambert-Beer’s law - statement and mathematical form (to be derived) molar extinction coefficient - definition-spectrbphotometer construction and working and its application, Laws of photochemistry-Grotthus-Draper law of photochemical activation and Einstein’s law of photochemical equivalence. Quantum efficiency, reasons for low yield (taking HBr decomposition as example) and high quantum yield (HCl formation as example), actinometry-uranyl oxalate actinometer.

**Photophysical processes:** Definition with examples - Photosensitization (eg photosynthesis in plants), photo- inhibition, fluorescence, phosphorescence, chemiluminescence and bioluminescence with examples. Determination of absorbed intensity-schematic diagram of the apparatus used. Detectors-thermopile, photoelectric cell and actinometer (Uranyl oxalate).

**Radiation Chemistry:** Definition, primary and secondary stages in radiochemical reactions, ionic yield, energy yield, comparison with photochemistry, units of radiation-rad, gray and roentgen, Dosimeter-Fricke-dosimeter. Theories of radiolysis-Lind’s and EHT theories. Radiolysis of water vapour, benzene and acetic acid.

**Phase Equilibria:** Phase rule-statement, Gibb’s phase rule-definition of the terms with examples, application to one Component systems (water system), reduced phase rule-
statement, reduced systems, two component system- simple eutectic type KI-water system, freezing mixtures, Pb-Ag system, (desilverisation of argentiferous lead).

**Electrochemistry-I:** Introduction. conductance - specific conductance, equivalent conductance and molar conductance their definitions and SI units. Conductance cell 1 and cell constant. Determination of equivalent conductance by meter-bridge method, ionic mobility, ionic conductance, Kohlrausch’s law and its significance determination of equivalent conductance at infinite dilution for weak electrolyte.

**Transport number:** Definition and explanation, anomalous transport number - explanation with examples - relationship between ionic conductance and transport number (to be derived), determination of transport number by moving boundary method - transport number of H+ using CdCl₂ as supporting electrolyte. (Numerical problems on equivalent conductance, transport numbers and Kohlrausch’s law.

**Electrochemistry-II**

**Application of conductance measurements:** (a) solubility and solubility product of sparingly soluble salt, (b) ionic product of water, (c) degree of ionization of weak electrolyte. Numerical problems, for the applications of a, b and c to be worked out.

**Conductometric titration:** Strong acid Vs strong base, weak acid Vs strong base, strong acid Vs weak base, weak acid Vs weak base, with suitable examples for each.

**Hydrolysis of salts:** Derivation of hydrolysis constant and degree of hydrolysis of the salt of weak acid and weak base (ammonium acetate), effect of temperature on degree of hydrolysis.

**Electromotive force-I:** Electrolytic and electro chemical cells, electrode reaction of Daniel cell, single electrode potential, sign of electrode potential-convention (reduction potential to be adopted). Convention of representing a cell, EMF and standard EMF of a cell, cell reaction, reversible and irreversible cells, Nernst equation (to be derived) and calculation
of electrode potential, standard hydrogen gas electrode, reference electrodes-calomel and
Ag-AgCl electrode-construction and working, electrochemical series and its significance,
equilibrium constant and free energy cell reaction, spontaneity of a cell reaction,
concentration cells.

**EMF of concentration cells:** Definition with explanation - with transference and without
transference concentration cells - with examples. Liquid junction potential and salt bridge.

Numerical problems on Nerst equation and EMF calculation.

**Fuel cells:** Working of H₂-O₂ fue 1 cell and its importance.

**Chemical Kinetics:** Introduction-differential and integrated rate equations for second
order kinetics, derivation of second order rate equation when a=b and a≠b, unit of rate
constant, half-life period, experimental verification of second order reactions-study of
kinetics of saponification of an ester, determination of the order of reaction- differentional
and time for half-change method, Experimental methods of chemical kinetics,
conductometric- example saponification of esters, potentioniometric-example- kinetics of
brornination of N,N-di-methyl aniline and spectrophotometric—example –colorimetric
study of kinetics of oxidation of Indigocarmine by chloramine-T.

**Application of kinetic studies:** Arriving at the mechanism of urea formation from
ammonium cyanate.

**Unit – X**

**Inorganic polymers:** Definition - examples, differences between inorganic and organic
polymers, glass transition temperature (Tg).

**Fluorocarbons:** Definition examples - Preparation, properties and uses of Freon 12, Freon
22, PTFE and polyperfluorvinyl chloride.
**Phosphorous based polymers:** Phosphazenes - Definition - types and structures, crystalline polymeta phosphates - Maddrell's salts, Kuroll's salts- properties and uses, applications of phosphorous based polymers.

**Sulphur based polymers:** Polymeric sulpharinitride (SN)\textsubscript{n} and chalcogenide glasses-preparation, properties, structure and applications.

**Silicon based polymers:** Types - preparation, properties and uses of silicone rubbers or elastomers, and silicone resins.

**Polymers:** Definition, Polymerization, types.

**Synthetic rubbers:** synthesis of butyl rubber, Neoprene, Buna-S.

**Synthetic fibers:** partial structural formulae of Nylon 66, saran, orlon and vinyon.

**Synthetic plastics:** thermoplastics and thermosetting resins with examples, synthesis of polystyrene, urea formaldehyde, polyurethane, phenol-formaldehyde resins.

**Chromatography:**

**Paper chromatography:** Definition. Introduction to ascending, descending and circular chromatography Rf value and its application.

**Thin layer chromatography (TLC):** Introduction, Determination of aspirin, phenacetin and caffeine in a mixture. The recovery of separated substances by elution techniques.

**Column chromatography:** Introduction-principle, brief experimental details and applications.

High performance chromatography (HPLC): Introduction, Schematic diagram - instrumentation and application.

Molecular Spectroscopy: Regions of spectra, types of spectra, microwave spectra-rotational spectra of diatomic molecules, moment of inertia (expression to be derived) expression for rotational energy, selection rule and transition, calculation of bond length, IR-Spectra-vibrational spectra of diatomic molecules-force constant (no derivation) expression for vibrational energy, zero point energy, selection rule and transitions.

Vibrational modes of polyatomic molecules taking H₂O and CO₂ molecules as examples. Applications of IR spectroscopy (Mention).

NMR Spectroscopy: Introduction-spin number, chemical shift, instrumentation, NMR spectra of ethyl alcohol- simple and high resolution, applications (Mention).

Spectroscopic applications to organic compounds: Elucidation of the structure of organic compounds from.

UV-spectroscopy: Absorption maxima values for simple organic molecules and their calculation.

IR-spectroscopy: Absorption frequencies for functional groups in simple organic molecules.

NMR-spectroscopy: Introduction-chemical shift (δ-scale), spin-spin coupling, coupling constant, application to simple organic molecules. For all the spectroscopic methods, ethyl
alcohol, ethane, propane, ethylene, methylamine, aniline, benzene, toluene, acetone, acetophenone, methyl cyanide and other simple molecules are considered (the students are to be familiarized in identifying the structure from the above data).

**Electromotive force – II:**

**Application of EMF measurements:** (a) Determination of pH of a solution using quinhydrone electrode and glass electrode (using dip type Calomel electrode) - Explanation with Principle and procedure. (b) Potentiometric titration – principle, location of end points in (1) Neutralization reactions [NaOH Vs HCl] (2) Oxidation-reduction, reactions, [K₂Cr₂O₇ Vs FAS] (3) Precipitation reaction [KCl Vs Ag NO₃] and (4) Complexation reactions- (ZnSO₄ Vs K₃[Fe (CN)₆]).

**Polarisation:** Decomposition potential, over voltage, determination of H₂-over voltage, factors affecting over voltage, importance.

**Corrosion:** Definition-electrochemical theory, protective measures (surface coating, alloying, cathodic protection).

**Energy sources:** Dry cell, storage cells-acid, solar cells-construction, working and their importance.