# 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 electronegetivity.

**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 NaC1, 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 ($H_2$, $F_2$, HF, $O_2$ and $N_2$) to illustrate valence bond approach (no wave mechanical approach), Sigma and Pi bonds-explain by taking $H_2$, $O_2$ and $N_2$ as examples.

**Chemical Bonding – II**

Concept of resonance-resonance energy, Resonance structures of CO, $CO_2$, $N_2O$, $SO_3^{2-}$ and $CO_3^{2-}$. Hybridisation directional property and geometry of sp, $sp^2$, $sp^3$, $sp^3d$ and $sp^3d^2$ hybrid orbitals taking $BeCl_2$, $BF_3$, $SiC1_4$, $PCl_5$ and $SF_6$ as examples respectively, VSEPR theory with $NH_3$ and $H_2O$ 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, $CO_2$, $NH_3$, $CC1_4$ and $H_2O$ 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 $H_2$, $He_2$, $He_2^+$, $N_2$, $O_2$ and $F_2$, Prediction of magnetic properties of these species.

**Coordinate bond:** Explanation with examples $H_3O^+$ and $^+NH_4$.

**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 HF, $H_2O$, $NH_3$, alcohols, carboxylic acids, nitrophenols, Appropriate anomalous properties like physical state, boiling point, solubility, nature and stereochemical rigidity due to hydrogen bonding in HF, $H_2O$, 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 trifluride-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 - Stiucture 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 $IF_7$.

**Pseudohalogens** - preparation, properties and. structures of eyanogen 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 ($XeF_2$, $XeOF_2$, $XeO_3$, $KrF_2$, $KrF_4$, $KrO_3$. $xH_2O$ 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-ordinaflon Chemistry:** Definition of the terms-mo1ecu1ar. 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 isomeñsm - 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 $B_{12}$.

**Valence Bond Tleory (VBT):** Formation of octahedral complexes on the basis of VBT, Outer and inner orbital octahedral complexes; $[Fe(CN)_6]^{4-}$, $[Fe(CN)_6]^{3-}$, $[Co(CN)_6]^{3-}$, $[CoF_6]^{3-}$ and $[Cr(H_2O)_6]^{3+}$. Formation of tetrahedral and square planar complexes on the basis of VBT-$[Ni(CN)_4]^{2-}$, $[Cu(NH_3)_4]^{2+}$, and $[Ni(CO)_4]$, Limitations of VBT.

**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 $\Delta_o$– (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; $[Co(NH_3)_6]^{3+}$, $[CoF_6]^{3-}$, $[Fe(CN)_6]^{4-}$, $[Fe(CN)_6]^{3-}$ and $Ni(CN)_6]^{2-}$.

**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 $U_3O_8$ by carbonate method, $U_3O_8$ to $UO_2$ by hydrogen reduction, $UO_2$ 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 carbiding 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 acetylides (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 l,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 Rcagents:** 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 cycloa1kanes 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:** Modem 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 ($CH_3$, -Cl, $-NH_2$, –OH) and electron withdrawing groups ($-NO_2$, $-SO_3H$,-COOH-CHO) on electrophilic substitution reactions, Resonance structures of naphthalene, anthracene and phenanthrecene.

**Alkyl halides:** Classification, nucleophilic substitution reaction: $SN^1$ and $SN^2$ with mechanism (taking examples of hydro1ysis of t-butyl bromide, methyl bromide) – characteristics of $SN^1$ and $SN^2$ reactions.

**Elimination reaction:** Dehydrohalogenation, Saytzeffs' rule, Mechanism. of $E_1$ and $E_2$ reactions (taking the examples of t-butyl bromide and ethyl bromide).

**Organo metallic compounds:** Definition with examples. Grignard's reagent preparation of $C_2H_5MgI$ and synthetic applications (convertion 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 $CO_2$] and application of $CH_3$ Li.

## Unit – V

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

**Monohydric a1cohols:** Preparation of alcohols by hydroboraton method, Distinguishing tests between $1^{o}$, 2° and 3° alcohols (oxidation and Victor Meyer's method). Conversion of primary to secondary; secondary to tertiary and primary to tertiary alcohols. Dehydration of l°, 2° and 3° 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. $HNO_3$, cone. $H_2SO_4$, 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 Ko1be-Schmidt reactions. Frie's rearrangement. [no mechanism]

**Carbonyl compounds:** Nomenclature, addition reaction with HCN, $NaHSO_3$, condensation reactioins with 2, 4-DNP, $NH_2OH$, 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 □, □, □, 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 diazoniurn 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.

**Monosaccharkes:** Glucose: Reactions of glucose with $NH_2OH$, HCN, $C_6H_5NHNH_2$, $Br_2$-water, conc. $HNO_3$, complete reduction with HI/Red P, $CH_3OH$/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 $NH_2OH$, HCN, $C_5H_5NHNH_2$, $Br_2$-water, conc. $HNO_3$, complete reduction with HI/Red P. $CH_3OH$/dry HCl, Acetic anhydride, Reduction reactions).

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

**Conversion reactions:** (1) Ascending (Kiliani'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

**Streochemistry:** Introduction - definition, elements of symmetry (plane, centre, simple axes and alternative axes), asymmetry and dissymmetry. Chiral carbon atom. Designation of configaration 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 tautomeñsm in ethyl aceto acetate - 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, -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 -tcrpineol, 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 theobrornine.

**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 carbondioxide, 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).

**Liquefaction of gases:** Intermolecular forces - brief account of - dipole-dipole interactions, dipole-induced dipole, induced dipole - induced dipole. vander Waal's force of attraction - effect of force of attraction and force of interaction of liquefaction of gases- principle underlying liquefaction of gases, Joule-Thornson effect, Joule-Thomson experiment, Inversion temperature definition and its relation between vander Waal's constants a and b.

**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 phenolphthaiein 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.

**Adsorpion:** Introduction - sorption, absorption and adsorption (statement, differences and examples). Physical and Chemical adsorption - definition with example - differences between physical and chemical adsorption – Adsorption of gases on solids - factors which influence on the adsorption of gases on solids - Adsorption isotherms (definition) - mathematical expression for Freundlich's and Langmuir's adsorption isotherms. Application of adsorption (mention the applications of adsorption).

**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 l), showing positive deviation from Raoult's law (type I1 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 distilates (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).

**Semipermiable membrane:** Natura1 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 Hoffs factor. (Problenis to be worked out).

**Colloids:** Crystalloids and colloids, types (aerosol, sol, emulsion and gels). Classification of sols- lyophillic and lyophohic sols (examples and differences). Methods of preparation of sols-condesation method (colloidal gold and arseneous sulphide) - Dispersion method (Bredigs's arc method and peptisation). Methods of purification of sols-dialysis, electrodialysis and ultrafiltration.

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

**Emulsions:** Types with examples, emulsifying agents. Gels-preparation of gels double decomposition method)- elastic and non-elastic ge1s-explanation with examples, thixotropy, synerisis, imbibition of gels - explanation with examples, application of colloids - (water treatment, leather tanning cleansing action of soaps and detergents, artificial raining).

## Unit – VIII

**Ionic equilibria:** Ionic equilibria in aqueous solutions, Strong and weak electrolytes - Definition and examples, Ostwald's dilution law (to be derived) and its limitations (Numerical problems). Activity and activity coefficients- definition and their relation, mean ionic activity Coefficients – ionic strength - definition. and its calculation, Debye Huckel theory of strong electrolytes (relaxation time. effect, electrophoretic effect and viscous effect), Debye-Huckel-Onsagar equation (no derivation), Debye-Huckel limiting equation for activity coefficients (no derivation). Solvent system concept of acids and bases - Role of solvents in altering strengths of acids and bases.

**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 $H_2O$ 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 $W = -2.303\ nRT \log (V_2/V_1)$ or [$W = -2.303\ nRT \log (P_1/P_2)$] 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 11 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, Claussius-Clapeyron equation (differential form to be derived). Integrated form of Claussius-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 Hoffs 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, Claussius-Mosotti equation (no derivation) and its importance.

**Crystallography:** Elements of symmetry-plane, axis and centre, elements of symmetry in cubic crysta1s, 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 (HCI 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 argentiferrous lead).

**Electrochemistry-I:** Introduction. conductance - specific conductance, equivalent conductance and molar conductance their definitions and SI units. Conductance cel1 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 $CdCl_2$ 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 Nerast equation and EMF calculation.

**Fuel cells:** Working of $H_2$-$O_2$ fue1 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, potentionietric-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 cynanate.

**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 polyperflurovinyl 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 po1ymrs.

**Sulphur based polymers:** Polymeric sulpharnitride $(SN)_n$ 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:** thennoplastics and thermosetting resins with examples, synthesis of polystyrene, urea formaldehyde, polyurethane, pheno1-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.

**Gas chromatography:** Introduction Apparatus, Programmed temperature gas chromatography. quantitative analyis by GLC. Application of elemental analysis (C, H, N, O and S).

**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 $H_2O$ and $CO_2$ 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-spectropcopy:** Absorption frequencies for functiona1 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, [$K_2Cr_2O_7$ Vs FAS] (3) Precipitation reaction [KCI Vs Ag $NO_3$] and (4) Complexation reactions- ($ZnSO_4$ Vs $K_3$ [Fe $(CN)_6$]).

**Polaristion:** Decomposition potential, over voltage, determination of $H_2$-over voltage, factors affecting over voltage, importance.

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

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