

Criteria for writing the Entrance Test

It was resolved that a candidate who has studied Chemistry as the Major Subject/Optional subject in B.Sc. Degree of this University or Other University and Mathematics as one of the optional subject in the two year PU or equivalent shall write the Entrance Examination. Those candidates who are appearing for final Semester Examination can also write Entrance Test.

Criteria for admission

B.Sc. with Chemistry as one of the Major/Optional subject provided the candidate has studied Mathematics as one of the optional subject in Two Year PU or equivalent

University of Mysore

Department of Studies in Chemistry, Manasagangotri, Mysore – 570 006

Syllabus for PG Entrance Examination

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 rules (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 favor 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, electronegativity, 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-} . Hybridization-directional property and geometry of sp , sp^2 , sp^3 and sp^3d^2 hybrid orbitals taking $BeCl_2$, BF_3 , $SiCl_4$, PCl_5 and SF_6 as examples respectively, VSEPR theory with NH_3 and H_2O as examples.

Polarization: Fajans rules of polarization 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 , CCl_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 and 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.

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 behaviour of beryllium in the group and its diagonal relationship to aluminum.

p-Block elements: Boron trifluoride-preparation, electron acceptor character and uses, Boron hydrides-diborane-preparation (Electric discharge and chemical reduction method), properties, uses and structure.

UNIT – II

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

Pseudohalogens-preparation, properties and structures of cyanogens 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 , $KrO_3 \cdot xH_2O$, 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, preparation, 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 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 gravimetry analysis-precipitation methods (various steps involved to be discussed), advantages of gravimetric analysis, colloidal states (particle, peptization to be discussed), super-saturation and precipitate formation (mechanism of precipitation-super-saturation, nucleation and crystal growth), purity of the precipitates, coprecipitation and postprecipitation, conditions of precipitations (mention the conditions), precipitation from homogenous solutions (hydroxides and sulphates), washing and ignition the precipitate (general discussions only).

Organic precipitants: Advantages of organic precipitants over inorganic precipitants, DMG, 8-hydroxyquinoline (oxime), Structure of Ni^{2+} -DMG and Mg^{2+} -oxime complex.

Ion exchange: Introduction, action of ion exchange resins - cationic exchange resins/anion exchange resins, exchange of inorganic ions, ion exchange capacity, separation of lanthanides by ion exchange methods.

Basic concepts of coordination chemistry: Definition of terms-molecular compounds (lattice and coordination compounds), ligands, coordination number, coordination sphere, classification of ligands, chelation, nomenclature of coordination 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 complex ion, polynuclear or bridged complexes, inner metallic complexes, isomerism in coordination compounds-(a) stereoisomerism-geometrical and optical isomerism exhibited by

coordination compounds on coordination 4 and 6. (b) Structural isomerism-ionization isomerism, hydrate isomerism, coordination isomerism, linkage isomerism, coordination position isomerism. Ligand isomerism. Role of Fe in haemoglobin and myoglobin, role of Mg in chlorophyll and Co in Vit B₁₂.

UNIT – III

Valence Bond Theory (VBT): Formation of octahedral complexes on the basis of VBT, outer and inner orbital octahedral complexes: $[\text{Fe}(\text{CN})_6]^{4-}$, $[\text{Fe}(\text{CN})_6]^{3-}$, $[\text{Co}(\text{CN})_6]^{3-}$, $[\text{CoF}_6]^{3-}$ and $[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$. Formation of tetrahedral and square complexes on the basis of VBT- $[\text{Ni}(\text{CN})_4]^{2-}$, $[\text{Cu}(\text{NH}_3)_4]^{2+}$ and $[\text{Ni}(\text{CO})_4]$. Limitations of VBT.

Crystal Field Theory (CFT): Importance features of crystal theory, crystal field splitting of d-orbitals in tetrahedral and octahedral complexes, crystal stabilization energy (CFSE), factors affecting the magnitude of Δ_0 -(nature of ligand, oxidation state of metal ion, size of the orbitals, geometry of the complex), high spin (HS) and low spin (LS) complexes, magnetic properties of the metal complexes based on CFT: $[\text{Co}(\text{NH}_3)_6]^{3+}$, $[\text{CoF}_6]^{3-}$, $[\text{Fe}(\text{CN})_6]^{4-}$, $[\text{Fe}(\text{CN})_6]^{3-}$ and $[\text{Ni}(\text{CN})_6]^{2-}$.

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

Fluorocarbons: Definition-examples-preparation, properties and uses of Freon 12, Freon 22, PTFE and polyperfluorovinyl chloride.

Phosphorous based polymers: Phosphazenes-Definition-types and structures, crystalline polymetaphosphates-Maddrell's salts, Kuroll's salts-properties and uses, applications of phosphorous based polymers.

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

Gaseous fuels: Definition of fuels-classification with eg.-Characteristics, calorific values 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 sulphide ore-general metallurgy followed by Mond's process (purification), Manganese from oxide ores-reduction by the aluminothermite process-refining by electrolytic process.

Hydrometallurgy: Extraction of gold from native ore by cyanide process and refining by quaternary 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 blende-production of U_3O_8 by carbonate method, U_3O_8 to UO_2 by fluoride method and (3) Plutonium by 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 hardening, case hardening-carbiding and nitriding, temperature and annealing.

ISO 9000: Historical 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, fuel, 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, hydroxyl acids and amines.

Principles of purification of organic compounds.

Crystallization, fractional crystallization, 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

Heterocyclic 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 –CH₃ as an example

Influence of these on the properties of molecules.

Aliphatic Hydrocarbons

Alkanes: 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 KMnO₄ (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 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 (Lassaigenes' method), Estimation of sulphur and halogen by Carius method and nitrogen by Kjeldhal's method (Problems to be worked out)

Organic Reagents: One method of preparation and applications of the reagents – acetic anhydride, benzyl chloride, dimethyl sulphate, Raney nickel and sodium ethoxide.

Cycloalkanes – Definition and examples. Reactions – hydrogenation and halogenations, 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, -SO₃H, -COOH, -CHO) on electrophilic substitution reactions, Resonance structures of naphthalene, anthracene and phenanthracene.

Alkyl halides: Classification, nucleophilic substitution reaction: S_N¹ and S_N² with mechanism (taking examples of hydrolysis of *t*-butyl bromide, methyl bromide) – characteristics of S_N¹ and S_N² reactions.

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

Organometallic 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).

Organolithium compounds: Preparation, properties (reaction with water, ethylene oxide, aldehydes including HCHO, ketones and CO₂) and applications of CH₃Li.

Alcohols: Definition-Classification with examples.

Monohydric alcohols: Preparation of alcohols by hydroboration method, Distinguishing tests between 1°, 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 1°, 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 conc. HNO₃, conc. H₂SO₄, oxalic acid and HI, Uses of glycerol.

UNIT – V

Phenols: Definition-Classification with examples. Acidity of phenols-effect of substituents on acidity. Mechanism of Reimer-Tiemann's and Kolbe-Schmitt reactions. Frie's rearrangement (no mechanism).

Carbonyl compounds: Nomenclature, addition reaction with HCN, NaHSO₃, condensation reactions with 2,4-DNP, NH₂OH, Knoevenagel reaction with mechanism, Aldol condensation, Perkin's reaction, Cannizzaro's reaction, Claisen condensation, conversion of HCHO to sugar during photo synthesis (mechanism 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 -hydroxy 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 HI/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 HI/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 (Killiani'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.

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-superimpossibility), enantiomers, diastereomers, Optical isomerism in tartaric acid and biphenyls, Racemization, 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 and 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.

UNIT – VI

Dyes: Colour an 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 chiral and its synthesis, Structural formulae of α -terpineol, camphor and menthol.

Chromatography:

Paper chromatography: Definition, Introduction to ascending, descending and circular chromatograph, R_f 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 analysis by GLC. Applications to elemental analysis (C, H, N, O and S).

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

Electrocyclic 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 guanine, 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, anesthetics, sedatives, narcotics, antiseptics, antibacterials, antibiotics, antimalarials, sulphadruugs with examples, Synthesis of paracetamol, sulphanilamide, sulphaguanidine.

Polymers: Definition, Polymerization, types.

Synthetic rubbers: Synthesis of butyl rubber, neoprene, Buna-S.

Synthetic fibres: 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.

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.

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 shifts, (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).

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 of 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 & Mathias method-van der Wall's equation-relation with van der Wall'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, van der Wall's force of attraction and force of interaction of liquefaction of gasses-principle underlying liquefaction of gases, Joule-Thomson effect, Joule-Thomson experiment, inverse temperature (definition) and its relation between van der Wall's constants a & 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 phenolphthalein and methyl orange in acid base solutions – pH titration curves for: - strong acid vs strong base – weak acid vs strong base – weak base vs strong acid – choice of indicators in these type of titrations – colour change and pH range – universal indicator – definition.

Adsorption: 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 isotherm (definition) – mathematical expression for Freundlich's & Langmuir's adsorption isotherms. Application of adsorption (mention the application 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 v/s 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, 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 molecular 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 boiling point (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-Hartley's 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)

Colloids: Crystalloids and colloids, types (aerosol, sol, emulsion and gels) Classification of sols – lyophilic and lyophobic sols (examples and differences). Methods of preparation of sols-condensation method (colloidal gold and arseneous

sulphide) – Dispersion method (Bredigs's arc method and peptisation). Methods of purification of sols - dialysis, electro dialysis and ultrafiltration.

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.

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

Ionic equilibria: Ionic equilibria in aqueous solutions, strong and weak electrolytes – definition & examples, Ostwald's dilution law (to be derived) and its limitations (Numerical problems). Activity and activity co-efficients – definition & their relation, mean ionic activity co-efficients – ionic strength – definition and its calculation, Debye-Huckel-Onsagar equation (no derivation), Debye-Huckel limiting equation for activity coefficients (no derivation). Solvent system concept of acid and bases – Role of solvents in altering strength of acids and bases.

Buffer solutions: Introduction – Definition, Types with examples, Henderson's & 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.

UNIT – VIII

Distribution law: Nernst distribution law in liquid –liquid systems, Distribution co-efficient, statement of Nernst distribution law – verification of distribution law taking distribution of I_2 in H_2O & 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 - definitions 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 conversion of heat and work, maximum work, maximum work done during an isothermal reversible expansion of an ideal gas. $[W = -2.303 nRT \log (P_1/P_2)]$ 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 & heat capacity at constant volume C_v and their definitions, relation between C_p and C_v (derivation using thermodynamic concept), C_p/C_v 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 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 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-Clapeyron 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 co-efficient 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 stalagmometer.

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 & parachor applications.

Polarisation: Induced, orientation and molar polarization – 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.

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

Photophysical processes: Definition with examples – photosensitization (e.g. Photosynthesis in plants), photo inhibition, fluorescence, phosphorescence, chemiluminescence and bioluminescence with examples. Determination of absorbed intensity- schematic diagram of apparatus used. Detectors- thermophile, photo electric cell & 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, 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, (desilveration of argentiferrous lead).

UNIT – IX

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).

Electrochemistry-I: Introduction, conductance – specific conductance, equivalent conductance and molar conductance – their definitions & SI units. Conductance cell 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 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 application of a, b, & c to be worked out.

Conductometric titration: Strong acid v/s strong base, weak acid v/s strong base, strong acid v/s weak base, weak acid v/s weak base, with suitable examples for each.

Hydrolysis of salts: Derivation of hydrolysis constant and degree of hydrolysis of 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 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 of 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 Nernst equation and EMF calculation.

Fuel cells: Working of H_2-O_2 fuel cell and its importance.

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 & procedure. (b) Potentiometric titration- principle, location of end points in - 1) Neutralization reactions; [NaOH v/s HCl], 2) Oxidation reduction reactions; [$K_2Cr_2O_7$ v/s FAS], 3) Precipitation reaction; [KCl v/s $AgNO_3$] and 4) complexation reactions ($ZnSO_4$ v/s [$Fe(CN)_6$]).

Polarisation: Decomposition potential, over voltage, determination of H_2 -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.

Chemical kinetics: Introduction-differential and integrated rate equations for second order kinetics. Derivation of second order rate equation when $a=b$ and $a \neq b$, 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-differential and time for half-change method, Experimental methods of chemical kinetics, conductometric-example saponification of esters, potentiometric-example – kinetics of bromination of *N,N*-dimethyl 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

Theory and principles involved in the following practicals:

Volumetric estimation, gravimetric estimation including ore and alloy estimations, semi-micro qualitative analysis of inorganic salt mixtures, organic preparations, systematic qualitative organic analysis of different class of organic compounds, quantitative estimation of glucose, Vit-C and phenol; iodine value of oil.

Determination of density, viscosity, surface tension, molecular weight by elevation in boiling point, rate constant, transition temperature of hydrated salt, energy of activation, critical solution temperature of water-phenol system, equivalent conductance, dissociation constant, hydrolysis constant, conductometric, potentiometric and colorimetric estimations.

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