SYLLABUS FOR ENTRANCE EXAMINATION

KANNUR UNIVERSITY

School of Chemical Sciences

Admission to M.Sc. Degree Course in Chemistry (Material Science)

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ORGANIC CHEMISTRY

UNIT 1 INTRODUCTION TO ORGANIC CHEMISTRY

Uniqueness of carbon-Classification of Organic compounds-Homologous seriesFunctional groups-IUPAC nomenclature of Organic compounds- Alkanes, , Alkenes, Alkynes, Cycloalkanes (bicycloalkanes), Mono and bifunctional compounds - Halogens, Nitro, Alcohols, Ethers, Nitriles, Amines,Aldehydes, Ketones, Carboxylic acids and their derivatives. Hybridisation in carbon atom - sp3, sp2 and sp hybridization with examples.

UNIT 2 INTRODUCTION TO REACTION MECHANISM

Representation of structural formulae –Bonding notations - Drawing electron movements with arrows- curved arrow notation- Half headed and double headed arrows. Electronegativity- Polarity in bonds- Electron displacement in organic moleculesInductive effect- Electromeric effect- Mesomeric effect/ Resonance- Hyperconjugation- Their illustrations - Homolytic and Heterolytic bond fission – Reaction intermediatesCarbocations, Carbanions, Free radicals, Carbenes and Nitrenes - Their generation , Structure and stability. Types of reagents – Electrophiles and Nucleophiles.

UNIT 3 MECHANISM OF ORGANIC REACTIONS

Substrate and reagent- Aliphatic nucleophilic substitutions-mechanism of SN1,SN2-Effect of structure on SN1 and SN2 as illustrated by Primary, Secondary and Tertiary alkyl halides - Stereo Chemistry of SN1 and SN2 reaction – Walden Inversion-Mechanism of Electrophilic addition of Hydrogen halides to Carbon – Carbon double bondMarkownikoff's rule – Kharasch effect (Free radical addition of HBr on unsymmetrical double bond)- Elimination – E1 and E2 mechanism – mechanism of dehydration of alcohol and dehydrohalogenation of alkyl halides – Saytzeff rule and Hofmann's rule.

UNIT 4 HYDROCARBONS

Alkanes – Preparation by Reduction of alkyl halides and Wurtz reaction mechanism of Kolbe's electrolytic method. Alkenes – Preparation by dehydration of alcohols, dehydrohalogenation of alkylhalides, dehalogenation of vic dihalides and by Kolbe's electrolytic method. Reactions – Hydrogenation, addition of halogens, halogen acid and water. Oxidation with KMnO4, K2Cr2O7 and Osmium tetroxide, Ozonolysis and polymerization.

Alkynes– Preparation by dehydrohalogenation of vic dihalides and gem dihalides, dehalogenation of tetrahalides and Kolbe's electrolytic method. Reactions, addition of Hydrogen, Halogen, Halogen acid and water – oxidation using alkaline KMnO4, Acidic K2Cr2O7 and Selenium dioxide. Ozonolysis and Polymerization reactions specific to 1-alkyne.

Dienes – Conjugated, cumulated and isolated dienes with example, preparation of 1, 3 butadiene-by dehydration of diols. Reactions of 1, 3 butadiene – 1,2 and 1,4 additions, polymerization.

Polynuclear Hydrocarbons- Haworth Synthesis of naphthalene, synthesis of Anthracene from benzyl chloride.

Cycloalkane – Preparation by Freunds and Wislicenus methods.

UNIT 5 HALOGEN COMPOUNDS

Alkyl halides – preparation from alcohol – Reaction of alkyl halides with metal.

Dihalides – Gem dihalides and Vic dihalides – General methods of preparation – General reaction.

Trihalogen derivative of methane – Chloroform – preparation from ethanol and acetone – Haloform reaction.

UNIT 6 HYDROXY COMPOUNDS

Alcohols – Preparation of monohydric alcohols from carbonyl compounds using Grignard reagents – Methods to distinguish 1o, 2o and 3o alcohols – Lucas method, Victor Meyer's method and oxidation method – Ascent and descent in alcohol series. Glycerol – Manufacture from fats and oils – Synthesis from propylene –Properties and uses. Phenols – Acidic character of phenol – Preparation of phenol from cumene –Preparation of cresols, nitrophenols, picric acid, dihydric phenols and naphthols. Phenolic ethers – Preparation of anisole and phenetole.Mechanism of Pinacol - Pinacolone, Fries and Claisen rearrangements.

UNIT 7 AROMATICITY

Structure of Benzene – Aromaticity and antiaromaticit y - Molecular Orbital Theory of aromaticity- Huckel's rule- Six electron systems- Mention of structures of some non benzenoid aromatic compounds-cyclopropenyl cation-cyclopentadienyl anion- ferrocenetropylium cation-azulene.

Mechanism of aromatic electrophilic substitution-Halogenation, Nitration and Sulphonation - Friedel –Craft's alkylation and acylation—Orientation and reactivity in monosubstituted benzene rings- Ortho/para ratio-Aromatic nucleophilic substitution- SNAr mechanism and Benzyne mechanism

UNIT 8 STEREOCHEMISTRY

Stereoisomerism - definition - classification into optical and geometrical isomerism - Projection formulae - Fischer, wedge, sawhorse and Newman projection formulae - notation of optical isomers -D-L notation- Cahn-Ingold-Prelog rules - R-S notations for optical isomers with one and two asymmetric carbon atoms - erythro and threo representations.

Optical isomerism - optical activity - optical and specific rotations - conditions for optical activity - asymmetric centre - chirality - achiral molecules - meaning of (+) and (-) - Elements of symmetry -Racemisation - Resolution - methods of resolution- Optical activity in compounds not containing asymmetric carbon atoms- Biphenyls.

Geometrical isomerism-cis-trans, syn-anti and E-Znotations- geometrical isomerism in maleic and fumaric acids.

Conformational analysis - introduction of terms - conformers, dihedral angle, torsional strain - Conformational analysis of ethane and n-butane including energy diagrams - conformers of cyclohexane (chair, boat, half chair and twist boat forms) - axial and equatorial bonds-ring flipping showing axial equatorial interconversions- conformation of methyl cyclohexane.

UNIT 9 CARBOHYDRATES

Definition- Classification and nomenclature of carbohydrates.

Monosaccharides-Configuration of Aldotrioses, Tetroses, Pentoses and HexosesStructure and configuration of glucose and fructose- Cyclic structure- Haworth projection formula-reactions of glucose and fructose- Mutarotations- ascent and descent in aldosesInterconversion of aldoses and ketoses- Anomers, Epimers and Epimerisation-Conversion of an aldose into its epimer.

Disaccharides- Configurational open chain and ring structure of sucrose, maltose and lactose (structural elucidation not expected).

Polysaccharides- Elementary study of starch and cellulose – structural difference between starch and cellulose- Industrial uses of cellulose.

UNIT 10 HETEROCYCLIC COMPOUNDS

Nomenclature of 5 and 6 membered heterocyclic compounds-Peparation, properties and structure of the following compounds- Pyrrole, Furan, Thiophene, Pyridine, Indole, Quinoline, Isoquinoline and pyrimidine- Relative basic character of Pyrrole, pyridine and piperidine- Hofmann's exhaustive methylation of piperidine.

UNIT 11 POLYMER CHEMISTRY

Classification – Natural and synthetic polymers – Thermoplastics and thermosetting plastics – Elastomers – Fibres – Liquid resins – Types of polymerization –Chain and step polymerization – Homopolymers and Co-polymers – Synthesis and application of Polyethylene, Polypropylene, PVC, Polystyrene, Polyurethanes, Phenolic and Epoxy resins – Synthetic rubber – Buna-S, Buna-Neoprene, and Butyl rubber-Biodegradability.

UNIT 12- CARBONYL COMPOUNDS

Preparation of aldehydes and ketones – Rosenmund's reduction, Stephen's reduction, Etard's reaction, Oppeanauer oxidation, Houben – Hoesh synthesis. Reactions of aldehydes and ketones. Reduction using LiA1H4 and NaBH4 MPV, Clemensen and Wolf-Kishner reduction. Reduction to pinacols – Oxidation using mild and strong oxidizing agents – SeO2 oxidation – Reaction with alcohols, KCN, sodium bisulphite and derivatives of ammonia – Distinction between acetaldehyde and benzaldehyde and acetaldehyde and acetone.

Mechanism of the following reactions – Aldol condensation , Cannizzaro's reaction, Crossed Cannizzaro's reaction, Reimer – Tiemann reaction, Perkin's reaction, Benzoin condensation and Beckmann rearrangement. Reaction of formaldehyde with aldehydes containing alpha hydrogen atoms.

Preparation of acrolein, crotonaldehyde and vanillin. Quinones – Preparation and important reactions of p-benzoquinone, 1, 4 –Naphthaquinone and 9, 10 – Anthraquinone.

UNIT 13 -CARBOXYLIC ACIDS

Carboxylic acids – Ascent and descent in aliphatic acid series, Preparation and reactions of acrylic and crotonic acids. Hydroxy acids – Effect of heat on alpha, beta, gamma and delta hydroxyl acids – Preparation and reactions of lactic acid, tartaric acid and citric acid. Dicarboxylic acids – Preparation and reactions of oxalic, malonic, succinic, maleic and fumaric acids – Blanc's rule. Aromatic acids – Preparation and reactions of Benzoic acid, anthranilic acid, salicylic acid, cinnamic acid and phthalic acid.

UNIT 14- NITROGEN COMPOUNDS

Cyanides and Isocyanides – Distinction between cyanides and isocyanides. Nitroalkanes – General methods of preparation and reactions of primary, secondary and tertiary nitroalkanes. Distinction between primary, secondary and tertiary nitroalkanes.

Aromatic nitrocompounds – Reduction of nitrobenzene under different conditions – Preparation of dinitrobenzene, 1, 3, 5 – trinitrobenzene, nitrotoluenes and 2, 4, 6 – trinitrotoluene –Mechanism of Benzidine rearrangement.

Amines – Separation of primary, secondary and tertiary amines – Hinsberg and Hoffmann method to distinguish primary, secondary and tertiary amines. Preparation of quaternary ammonium salts.

Aromatic amines – Preparation and reactions of aniline, toluidines, phenylene diamines, diphenyl amine, N-Methyl aniline, N, N-dimethyl aniline and naphthyl amines. Distinction between benzyl amine and toluidine.

Diazonium salts – Preparation, synthetic applications and structure of benzene diazonium chloride, Diazomethane and diazoacetic ester-Ardnt-Eistert synthesis – Wolf rearrangement – mechanism. Preparation, Properties and structure of urea- Preparation and reactions of semicarbazide and thiourea – Preparation of Urethane.

UNIT 15 PHOTOCHEMISTRY AND PERICYCLIC REACTIONS

Introduction to photochemistry- Photochemical reactions of carbonyl compounds (Acyclic only)- Norrish type I and II cleavages. Types of pericyclic reactions-Woodward –Hoffman rule-Electrocyclic reactionsAnalysis of electrocyclic reactions (Butadiene to Cyclobetene only)-CycloadditionsExamples- Diels Alder reaction- Analysis of [2+2] cycloaddition by FMO method.

UNIT 16 SYNTHETIC REAGENTS

Active methylene group- Preparation and synthetic application of Ethyl acetoacetate, Diethyl malonate and Ethyl cyano acetate- Mechanism of Claisen condensation- Preparation and synthetic applications of Grignard reagents and Frankland reagent-mechanism of Reformatsky reaction.

UNIT 17 BIOORGANIC CHEMISTRY AND NATURAL PRODUCTS

Amino acids- Classification- Structure of Glycine, Alanine, Phenyl amine, Tryptophan and Glutamic acid (Structure elucidation not expected) Synthesis of amino acids- Gabriel, Strecker and Erlemeyer synthesis- Zwitter ion property- Isoelectric pointSorenson formal titration- Peptides and poly peptides- C-terminal and N-terminal analysis. Proteins- Functions of proteins- Primary , secondary and tertiary structure of proteins Nucleic acids- Introduction- Nucleosides and Nucleotides- Structure (elucidation not expected) of DNA and RNA- Self replication- Protein synthesis- Lipids- Biological function of different types of lipids. Terpenes- Definition- Isoprene rule- Occurrence, isolation and structural elucidation of Citral- natural rubber.

Alkaloids- Introduction- Properties and structure of Coniine, Nicotine and Quinine Structural elucidation of Coniine only.

Steroids- General characteristics, structure of cholesterol, Testosterone and Oestrone.

UNIT 18 DYES AND DRUGS

Dyes- classification of dyes based on structure and application- Structures of Malachite green- Methyl orange- Eosin- Indigo- Crystal violet- Fluorescein and Alizarine (structure elucidation not expected) Chemotherapeutic agents- classification, Drug action- Antibiotics- Discovery, importance, mode of action and examples- Misuse of antibiotics- Sulpha drugs-mode of actionImportance- Examples and uses. Antipyretics & analgesic- examples-uses. Anesthetic, Antiseptic, Antihistamines and tranquillizers, narcotics- their actions and examples. Misuse of drugs.

UNIT 19 GREEN CHEMISTRY

Need for Green chemistry – Goals of green chemistry – Limitations. Twelve principles of green chemistry with their explanations and examples – Designing a green synthesis – Prevention of waste / byproducts – Atom economy (maximum incorporation of materials used in the process) – Minimization of hazardous / toxic products. Green synthesis – Microwave assisted reactions in water – Hoffann Elimination – Microwave assisted reaction in organic solvent – Diels Alder reaction, Ultrasound assisted reaction – Esterification, Saponification.Green chemistry in day to day life.

THEORETICAL AND INORGANIC CHEMISTRY

UNIT 1. EVALUATION OF ANALYTICAL DATA

Terms used in evaluation of analytical data – significant figures – Rounding of the numerical expression – Errors – Precision and accuracy – Ways of expressing precisions – Ways to reduce systematic errors - Average deviation from the mean - Standard Deviation – Relative standard deviation – Reporting of analytical data- Statistical treatment of analytical data – Population and samples – Confidence limit- Test of significance – students t-test, f-test.

UNIT 2. WAVE MECHANICAL CONCEPT OF ATOMIC STRUCTURE

Bohr model of hydrogen atom – Bohr's equation for the energy of electron in hydrogen atom – Limitations of Bohr theory- Hydrogen spectrum – Classical mechanics – concept, failure. Black body radiation- Planck's law of radiation. Photoelectric effect- Heisensberg's uncertainty principle and its significance, dual nature of electrons – Davisson and Germer's experiment. - de Broglie hypothesis - Schrodinger wave equation (derivation not ψ and ψexpected), significance of 2 - Nodal planes in atomic orbitals - Postulates of quantum mechanics. Quantum numbers - Shapes of orbitals - Aufbau, Pauli's and Hunds rule - Electronic configuration of atoms.

UNIT 3. CHEMICAL BONDING

Factors effecting the formation of ionic compound - Lattice energy – Born- Lande equation with derivation - Born Haber cycle and its application - Covalent bond - Valance bond theory and its limitations - Hybridization and shapes of simple molecules (BeF2, PCl3, SF6, CH4, CH3-CH3, CH2=CH2CH) - VSEPR theory – Shape of molecules and ions (NH≅, CH3, XeF6, ClF3, NH4+, H3O+) - Molecular orbital theory - LCAO method - Bond strength and bond energy - Polarisation and Fajan's rule - Metallic bonding - Free electron and band theory, explanations of metallic properties based on these theories - Weak chemical forces - Hydrogen bond and Vander Waal's forces.

UNIT 4. NUCLEAR CHEMISTRY

Radioactivity - rate of radioactive disintegration - Nature of radiation from radioactive elements – stability of nucleus-binding energy-magic numbers-packing fractions-n/p ratio.Detection and measurement of radioactivity - Gieger-Muller counter - Wilson cloud chamber. Radioactive tracers - Rock dating, Carbon dating - Artificial radio activity - Artificial transmutations of elements - cyclotrons - Induced radio activity - Q values of nuclear reactions - Nuclear reactors - Classification of reactors - Breeder reactor - India's nuclear energy programme.

Unit 5- FUNDAMENTALS OF VOLUMETRIC, GRAVIMETRIC AND QUALITATIVE ANALYSIS

Titrimetric analysis – Fundamental concepts – mole, molarity, molality, ppm, and ppb – primary standard – secondary standard, quantitative dilution – problems – acid base titrations – titration curves – pH indicators – redox titrations – titration curves - titrations involving MnO42- and Cr2O72-, redox indicators - complexometric titrations - EDTA titrations - titration

curves - metal ion indicators. Gravimetric analysis – unit operations in gravimetric analysis. Illustration using iron and barium estimation. Qualitative analysis - theoretical principles of qualitative analysis -solubility products - common ion effect - principles in the separations of cations in qualitative analysis

Unit -6 - ACIDS, BASES AND NON AQUEOUS SOLVENTS

Concepts of Lowry and Bronsted – Lux – flood concept – The solvent system concept – The Lewis concept – Relative strength of Acids and Bases – Effect of solvent – Leveling effect – Effect of polarity and substituents – Hard and soft acids and bases – Pearsons concept – Bonding in hard–hard and soft–soft combinations – HSAB principle and its applications – Basis for hard- hard and soft–soft interactions.

Classification of solvents – characteristic properties of a solvent – study of liquid ammonia, liquid HF and H_2SO_4.

Unit - 7 – SEPARATION METHODS

Solvent extraction methods – introduction – completeness of extraction – selectivity of extraction – factors favouring solvent extraction – factors affecting extraction – solvent extraction equilibria quantitative treatment – experimental methods- analytical applications Chromatographic methods – Adsorption and Partition Chromatography - Brief studies on Liquid-Liquid chromatography, TLC, gas and ion exchange chromatography.

Exclusion (Gel) Chromatography - Gel permeation chromatography – brief introduction, advantages and application of GPC.

Unit – 8- INSTRUMENTAL METHODS IN CHEMICAL ANALYSIS

Thermogravimetric analysis – introduction – instrumentation – factors affecting TGA – application of TGA. Differential thermal analysis – introduction – instrumentation – principle of working – factors affecting DTA – application. Thermometric titrations – a brief study. Radio chemical methods of analysis – introduction – activation analysis – a brief study.Neutron diffraction – theoretical aspects – thermal neutron – instrumentation – application.

UNIT 9.GENERAL PROPERTIES OF ELEMENTS

Covalent and ionic radii--Trends in the periodic table. Periodic properties-- Ionisation energy. Electron affinity and Electronegativity (Pauling and Mulliken's, approach). Metallic character.Variable valency and Oxidation states. General properties of transition elements – Electronic configurations,Oxidation states, colour, magnetic properties, tendency to form complexes and catalytic properties. Comparison of first transition series with second and third series.

UNIT 10.CHEMISTRY OF S BLOCK ELEMENTS

Hydrogen : Isotopes (separation method not needed) Ortho and para hydrogen Hydrides and their classification.

Alkali and alkaline earth metals: Occurrence and extraction (principle only). Periodic properties of hydrides, oxides, halides,hydroxides and carbonates. Flame colours and spectra. Metal solutions in liquid ammonia –characteristic properties and uses. Diagonal relationship. Macro cycles- Crowns and crypts.

UNIT 11.CHEMISTRY OF P BLOCK ELEMENTS

Comparative study based on electronic configuration and periodic properties of Hydrides,Oxides,Halides,Carbides and Oxoacids. Inert pair effect.

Metallic and non-metallic character. Acid-base properties of oxides. Hydrolysis of halides. Exceptional behavior of second period element in the following groups of elements-Group13 (B,Al,Ga,In andTl). Group14 (C,Si,Ge,Sn and Pb) Group15 (N,P,As,Sb and Bi). Group16 (O,S,Se,Te and Po) and Group17 (F,Cl,Br and I).

UNIT 12. NOBLE GASES

History of discovery of noble gases. Electronic configuration and position in the periodic table. General physical properties, uses of noble gases. Compounds of noble gases– Clathrates, compounds of Xenon—XeF2, XeF4, XeF6, XeO2F2 , XeOF2, XeOF4 and XeO3. Preparation, hybridization and geometry of these compounds.Fluorides of Krypton and Radon.

UNIT 13 PREPARATION, PROPERTIES, STRUCTURE AND USES OF SOME INORGANIC COMPOUNDS

Hydrides of boron – B2H6 and B4H10. Borazine, Boric acid, oxoacids of halogens, Interhalogen compounds, Pseudo halogens, Fluorocarbons. **Inorganic polymers -** Phosphorous based, sulphur based and silicon based - silicones and silicates - polymers. **Refractories -** Introduction- classification- super refractories - silicon carbide. Pure oxide refractories.

UNIT 14. ORGANOMETALLIC COMPOUNDS

Introduction. Classification based on the nature of metal-carbon bond. preparation,properties, structure - valence bond theory - and uses of mononuclear (Ni,Fe), binuclear (Fe,Mn,Co) and trinuclear (Fe) metal carbonyls - Application of 18 electron rule to predict M-M bond. Preparation, properties, structure and bonding of Ferrocene.

UNIT 15. COORDINATION CHEMISTRY- I

Introduction-Double salts and Coordination compounds. Nomenclature. Effective Atomic Number (EAN). Shapes of d orbitals.-Types of ligands. Chelates. Stereo chemistry of coordination compounds with coordination numbers 2 to 6. Isomerism. Stability of complex ions-stability constant. Factors affecting the stabilityof complexes. Application of complex formation in qualitative and quantitative analysis.

UNIT 16. COORDINATION CHEMISTRY- II

Theories of bonding in transition metal complexes– Valence bond theory . Application to some complexes-Hybridization in tetrahedral, square planar and octahedral complexes – explanation of magnetic properties based on VBT. Limitations of VBT. Crystal field theoryCrystal field splitting in octahedral, tetrahedral and square planar geometries. Factors affecting the magnitude of crystal field splitting. Crystal field stabilization energy(CFSE). Explanation of colour, spectral and magnetic properties .Spectrochemical series.

UNIT 17. BIOINORGANIC CHEMISTRY

Myoglobin and Haemoglobin - Structure and functions of haemoglobin and myoglobin. Cooperativity effect.Explanation of cooperativity effect in haemoglobin.Metallo enzymes of iron and zinc (structural details not needed).Role of metal ions in biological systems. Metal ion transport across cell membrane – sodium/potassium pump. Biochemistry of Mg and CaBiological functions and toxicity of some elements - Cr, Mn,Co,Ni,Cu,As,Cd,Pb,Hg, I, Fe, and Zn.Biological fixation of nitrogen.

UNIT 18. INNER TRANSITION ELEMENTS

Lanthanides -Occurrence and separation by ion - exchange chromatography. Electronic configurations,oxidation states,magnetic properties and spectra of lanthanides. Lanthanide contraction causes and consequences.**Actinides :** Electronic configurations, oxidation states, spectra and magnetic properties. Transactinide elements Preparation, IUPAC nomenclature. Comparison of transition and inner transition elements

UNIT 19. METALS AND ALLOYS

Occurrence of metals.Various steps involved in metallurgical processes. Electrometallurgy, Hydrometallurgy. Coinage metals-Occurrence and extraction of copper, silver and gold. Powder metallurgy(brief discussion).Alloy steels-application of alloy steels.Heat treatment of steel.Nonferrous alloys and their uses.

UNIT 20. CORROSION AND CORROSION CONTROL

Introduction. Types of corrosion. Causes of corrosion. Theories of corrosion- Direct chemical attack or dry corrosion. Electrochemical theory or wet corrosion. Differential Aeration or concentration cell corrosion. Factors influencing corrosion- nature of the metal- nature of the environment. Corrosion control.

PHYSICAL CHEMISTRY

UNIT 1 THE PROPERTIES OF GASES

Gas laws – The general gas equation– The Kinetic model of gases – gas laws from the kinetic theory of gases ---Molecular Speeds – Maxwell's distribution of molecular speeds – Most probable velocity, average velocity and root mean square velocity — Collision diameter – Mean free path, Collision number and collision frequency – Degrees of freedom of a gaseous molecule – Principle of equipartition of energy and contribution towards heat capacity of an ideal gas. Real gases – Molecular attractions – The compressibility factor – virial equation of state – Van der waals equation expressed in virial form –

calculation of Boyle's temperature – Isotherm of real gases and their comparison with Van der waals isotherms – continuity of states – critical phenomenon – critical constants of a gas and its determination – Determination of molecular mass by limiting density method – Principle of corresponding states .Liquefaction of gases by Joule Thomson effect.

UNIT 2 LIQUID STATE

Properties of liquids– Surface tension and its determination – Interfacial tension – surface active agents - effect of temperature on surface tension- Parachor and its applications – Viscosity -determination of coefficient of viscosity and its variation with temperature – refractive index – specific and molar refraction – Measurement of refractive index – Abbe's refractometer – optical activity and its measurement using Polarimeter.

UNIT 3 SOLID STATE

Amorphous and crystalline solids – Laws of crystallography – Law of constancy of interfacial angles – Law of constancy of symmetry – Law of rationality of indices – space lattice and unit cell – Miller indices –seven crystallographic systems – Bravais lattices – Spacing of lattice planes in simple cubic, body centred and face centred cubic systems –Number of particles per unit cell in each of these - Calculation of Avogadro number, density and molecular mass from crystallographic data. Determination of internal structure of crystals by X-ray diffraction methods – derivation of Bragg's equation – Bragg's rotating crystal method and De bye Scherrer Powder diffraction method – Crystal structure of NaCl –anomalous nature of diffraction pattern of KCl. Co-ordination Number – Efficiency of packing – Cubic and Hexagonal packing – Radius ratio rule – Tetrahedral and Octahedral voids. Liquid crystals – types – Examples – applications Classification based on cohesive forces in crystals-ionic, covalent, molecular and metallic crystals - Properties of solids – Electrical conductivity – Conductor, semiconductors– extrinsic, intrinsic-n-type and p-type – Hall effect – super conductors – magnetic properties of solids.

UNIT 4 SOLUTIONS

Types of solutions and methods for expressing concentration — Gas Liquid system — Henry's Law – Liquid systems — Completely miscible- Ideal and non- ideal solutions – Raoult's Law – Vapour pressure – composition diagrams-Azeotropic mixtures– Temperature – composition curves – Partially miscible liquids –Upper and Lower Critical solution temperature –Immiscible liquids – Steam distillation – Molar mass from steam distillation –**Dilute Solutions** Colligative properties – Lowering of vapour pressure and Raoult's law – Calculation of molar mass. Elevation of boiling point – relation to lowering of vapour pressure – Thermodynamic derivation – Calculation of molar mass –Depression of freezing point – Thermodynamic derivation – Calculation of molar mass – Measurement by Beckmann's method – Osmotic pressure – Measurement by Berkely and Hartley's method – Laws of Osmotic pressure – Van't Hoff equation – Calculation of molar mass – Abnormal molar mass – Van't Hoff factor – Degree of dissociation and association and their calculation from colligative properties

UNIT 5 THERMODYNAMICS

The first Law – the basic concepts – System – surrounding– open, closed and isolated system — intensive and extensive properties -Isothermal, Isochoric and Isobaric process – work – Heat – Energy — state and path functions – exact and inexact differentials– The statement of first law – – the conservation of energy– Internal energy – Expansion work – general expression of work – free expansion – Expansion against constant pressure – reversible expansion– Heat capacity at constant volume (Cv) and at constant pressure (Cp) – relation between Cp and Cv – Thermodynamic derivation– Adiabatic change –Relation between P,V &T in reversible adiabatic change - work of adiabatic change. The internal pressure Changes in enthalpy at constant volume – isothermal compressibility – Joule – Thomson effect –inversion temperature -Zeroth Law of Thermodynamics. Thermo chemistry – Standard enthalpy changes – Enthalpies of physical change – Enthalpy of vapourisation, enthalpy of transition and enthalpy of fusion – enthalpy chemical changes – Thermo chemical equation – Standard enthalpy of reaction, combustion and formation – Change in internal energy(ΔU) and enthalpy (ΔH) of chemical reactions, relation between ΔU and ΔH,variation of enthalpy of reaction with temperature-Kirchhoff's equation.

UNIT 6 THERMODYNAMICS II

The Second Law – the concepts – Spontaneous and non-spontaneous process – statement of second law – Entropy –Entropy as a state function – Carnot cycle – efficiency of a heat engine– Entropy changes in isothermal expansion of an ideal gas –Calculation of entropy change of an ideal gas with change in P, V and T –Entropy changes accompanying phase transitions.Helmholtz and Gibbs free energies – their significance – Maxwell's relations – Criteria of spontaneity – Gibbs–Helmholtz equation – Partial molar free energy – Concept of chemical potential – Gibbs - Duhem equation– Clausius – Clapyeyron equation applicable to solid –liquid, solid-vapour and liquid-vapour equilibria.

Third Law of thermodynamics – The Nernst heat theorem – Absolute entropy – Calculation of absolute entropies of solids, liquids and gases

UNIT 7 CHEMICAL EQUILIBRIUM

Law of mass action-equilibrium constant – Relation between Kp, Kc and Kx – Thermodynamic treatment of the law of mass action – Vant Hoff reaction isotherm – Temperature dependence of the equilibrium constant – The Van't Hoffs isochore– Pressure dependence of the equilibrium constant Kp– Study of heterogeneous equilibria – Factors that change the state of equilibrium – Le –chatelier's principle and its application to chemical and physical equilibria. Mention homogeneous gaseous equilibria having zero, positive and negative values of Δn. Calculation of degree of dissociation and Kp. Heterogeneous equilibria –Dissociation of solid calcium carbonate and decomposition of solid NH_4HS.

UNIT 8 PHASE RULE

Statement – Explanation of terms involved – Thermodynamic derivation of phase rule –Application to water system and sulphur system – Solid – liquid equilibria involving simple eutectic system – Ag-Pb system – De silverisation of lead – Freezing mixtures – Solid – liquid equilibria involving compound formation with congruent and incongruent melting points– FeCl3–H2O system and Na2SO4 water system–Solid – gas system – Dehydration of CuSO4.5H2O-Deliquescence and efflorescence (mention only). Nernst distribution Law – Thermodynamic derivation– Limitations of the law – Application of the

law to study association and dissociation – Solvent extraction – Hydrolysis of salts – The equilibrium of $KI + I2 \rightarrow KI3$.

UNIT 9 COLLOIDS, SURFACE CHEMISTRY

Colloids, Classification – preparation – structure and stability – The electrical double layer –Zeta potential (no derivation)– Properties of Colloids – Tyndall effect – Brownian movement – Coagulation of colloidal solution – Hardy – Schulze rule – Flocculation value – Electrokinetic properties – Electrophoresis – Electro-osmosis – Protective colloids – Gold number –Emulsion – Oil in water emulsion and water in oil emulsion – Emulsifying agents – Gels –Micelles.Physical and chemical adsorption – Adsorption isotherms – Freundlich adsorption isotherm – effect of temperature on adsorption– Langmuir adsorption isotherm – derivation – use and limitation.B.E.T. equations (B.E.T. no derivation) – Gibbs adsorption equation(no derivation)—– Surface films - Determination of surface area using Langmuir equations.

UNIT 10 ELECTRICAL CONDUCTANCE

Ohm's Law – Electrical energy – volt – coulomb – Mechanism of electrical conduction – Arrhenius theory – The laws of electrolysis – Faraday's law and its significance – Transference Number – Determination by Hittorf's method and moving boundary method. Equivalent conductance and Molar conductance Effect of Dilution on conductance – Effect of dielectric constants of solvents – Ionic mobilities – Kohlrausch's Law – applications – Mobilities of Hydrogen and Hydroxyl ions – Diffusion and ionic mobility. Activity and activity coefficient – standard state ionic activities and activity coefficient – ionic strength – Debye – Huckel Theory – Ionic atmosphere – Debye – Huckel limiting law –determination of solubilities by conductance measurements – conductometric titrations –conductance in non-aqueous solvents – Temperature dependence of ionic conductance.

UNIT 11 IONIC EQUILIBRIA

Acids and bases –Arrhenius Concept- Lowry – Bronsted concept – Dissociation of acids and bases – Lewis concept of acids and bases – hard and soft acids and bases and its applications– Ionic product of water – Dissociation constants of acids and bases – pH and its determination – Heat of neutralization – Incomplete neutralization – Hydrolysis of different types of salts – Degree of hydrolysis and hydrolytic constant – and its relation with pH and pOH – Buffer solution – pH of Buffer solution – Henderson's equation – Buffer capacity – Application of buffer – Acid – base indicators –Theory of acid–base indicators.

UNIT 12 ELECTROMOTIVE FORCE

Electrochemical cell-Daniell cell – Reversible and Irreversible cell – Single electrode potential – EMF of cells – Standard potential and standard emf – Standard Hydrogen electrode and calomel electrode – Types of electrodes – electrode reaction – cell reaction. Nernst equation for electrode potential and emf of the cell – Electrochemical series – IUPAC sign convention – Application of Gibb's Helmholtz equation to galvanic cells – Calculation of ΔG, ΔH, ΔS and equilibrium constant from emf data – The standard cells – Weston Cadmium cell and its emf. Concentration cells – Electrode and electrolytic concentration cells with and without transference and their emfs – Liquid junction potential – Elimination

of liquid junction potential – salt bridge – application of potential measurements – Determination of solubility product, ionic product of water, transport number and the pH value – Hydrogen, Quinhydrone electrode and glass electrode – potentiometric titration – redox indicators — Fuel cells. (hydogen-oxygen, hydrocarbon-oxygen)

UNIT 13 CHEMICAL KINETICS

The rates of chemical reactions – Experimental techniques – rate laws and rate constant –Order and molecularity of reactions – Methods of determining the order of reaction – Integrated rate laws of zero order, first order and second order reactions — General integrated rate equation for nth order reaction - Zero and fractional order reactions - Half life –Examples of consecutive parallel and opposing reactions (first order only). Temperature dependence of reaction rates – Arrhenius equation – Interpretation of parameters – steady state approximation – Kinetics of unimolecular reactions –Lindemann's theory. Theories of reaction rates – collision theory – Derivation of rate equation for second order reaction from collision theory – thermodynamic approach of transition state theory – Entropy activation. Catalysis – Homogeneous and Heterogeneous catalysis – examples – Features of homogeneous catalysis – Enzymes– Michalis – menten mechanism. Heterogenous catalysis– Langmuir – Hinshelwood mechanism – Kinetics of unimolecular surface reactions.

UNIT 14 PHOTO CHEMISTRY

Photochemistry – consequences of light absorption – The Jablonski diagrams – Radiative and non radiative transition – Light absorption by solutions – Lambert – Beer Law – Laws of photochemistry – The Grotthus – Draper law – Stark – Einstein law – Quantum efficiency / Quantum yield – Experimental determination of quantum yield – High and low quantum yield -Photochemical rate law – Energy transfer in photochemical reactions – Photo sensitisation and quenching – Chemiluminescence – Lasers – uses.

UNIT 15 SPECTROSCOPY

Introduction: electromagnetic radiation, regions of the spectrum, interaction of electromagnetic radiation with molecules, Born-Oppenheimer approximation.

Microwave Spectroscopy – Rotation spectra-Instrumentation- Moment of inertia, Rotational Quantum numbers, Rotational Constant, Intensities of rotational spectral lines, Rotational – Vibrational Spectrum of diatomic molecules – Selection rules for rotational spectra.

Infrared Spectroscopy – Instrumentation -Theory of infrared spectra, Sampling techniques, Selection rule, Molecular vibration – Stretching and Bending modes, Calculation of stretching frequencies Fundamental Bands and Overtones, Factors influencing vibrational frequency – Electronic effects, hydrogen bonding, solvent effect . Applications of IR Spectroscopy .

UV Spectroscopy –Absorption laws, Selection Rules – Types, Electronic transitions – Position and Intensity of absorption, Molar extinction coefficient, Chromophore – Auxochrome Concept, Absorption and Intensity Shifts, Types of Absorption Bands, Interpretations of spectra of simple conjugated dienes and enons, Woodward-Fieser Rule, Application to dienes and enons.

Raman Spectroscopy – Instrumentation, quantum theory of Raman scattering- Stokes and anti stokes lines-classical theory of Raman scattering-concept of polarizability-selection rules, rule of mutual exclusion.

NMR Spectroscopy – Instrumentation- Introduction, Theory of NMR, Phenomena of resonance, Modes of nuclear spin-Relaxation Process, Chemical Shift – Internal standard, δ and τ scale, Shielding Effects, Factors affecting Chemical Shift, Spin-Spin interaction, Interpretations of spectra of ethylbromide,ethanol,acetaldehyde,acetone,toluene,and acetophenone.

Mass Spectrometry – Basic principles, Instrumentation, Fragmentation pathway, Molecular ion peak, base peak, Meta stable ion, General rules for predicting the prominent peaks, Mc Lafferty Rearrangement, Mass spectra of alkanes, cyclo alkanes, saturated alcohols and aliphatic ketones.

UNIT 16 INSTRUMENTAL METHODS POLAROGRAPHY

Dropping Mercury Electrode, Polarization – Concentration polarization, Half wave Potential and Diffusion current (Significance), Ilkovic equation, Advantages of polarographic analysis – Applications.**Amperometry :** Amperometric Titrations, Instrumentation-Procedure, Biamperometric Titrations – Advantages and disadvantages, Applications. **Atomic Absorption Spectroscopy :** Flame Atomization and Flame Structure – Hollow Cathode lamp, Interference. **Colorimetry and Spectrophotometry :** Instrumentation of photocolorimeter and spectrophotometer-block diagrams with description of components-Beer- Lambert law – Application- and its limitations-Colorimetric Methods – general procedure for colorimetric determination.

UNIT 17 MOLECULAR SYMMETRY AND GROUP THEORY

Symmetry of molecules-symmetry elements and symmetry operations – centre of symmetry, plane of symmetry, Identity – proper axis of rotation, improper axis of rotation – Schonflies notation – Point groups of simple molecules – Cnv, Cnh,H_2O,NH_3,N_2O_4,N_2F_2.

UNIT 18 CONCEPTS AND APPLICATIONS OF NANO SCIENCE

Introduction - Nanomaterials – synthesis – chemical precipitation, mechano-chemical method, micro emulsion method, reduction technique, chemical vapour deposition and solgel method (brief study)- Important methods for the characterization of nanomaterials – electron microscopy (SEM), transmission electron microscopy (TEM). Properties and applications of fullerenes - electrical and optical properties of carbon nanotubes(brief study).