

04. CHEMISTRY

DETAILS OF SYLLABUS

1 PERIODICITY AND CHEMISTRY OF MAIN GROUP ELEMENTS

Origin and abundance of elements in the universe. Periodic trends in atomic, physical and chemical properties. General discussion on main group elements. Noble gas compounds. Classification, preparation, properties application and structure of borides, carbides, nitrides, silicates, silicones, fullerenes. Inter halogen and pseudo-halogen compounds.

Nuclear Chemistry

Radioactive decay, half life -average life- equilibrium nuclear reactions, Q value, Nuclear fusion, fission. Principles of GM, proportional, Ionisation and scintillation counter. Neutron activation analysis. Applications of radioactivity.

2 CHEMISTRY OF TRANSITION AND INNER TRANSITION ELEMENTS

Transition Elements - Electronic configuration, oxidation state and general characteristics. First, second and third rows of transition elements and their important compounds.

Lanthanides and Actinides - Occurrence, electronic configuration, oxidation state, size of atoms, ions- magnetic and spectral properties. Applications of Lanthanides, actinides and their compounds.

3 COORDINATION CHEMISTRY

Nomenclature of coordination compounds. Isomerism, stability, VB theory, crystal field theory, MO theory, stereochemistry of octahedral, tetrahedral, square planar complexes, Jahn Teller effect.

Electronic spectra of transition metal complexes, selection rule, term symbols, Orgel diagram. Spectro-chemical series, nephelauxetic effect, charge transfer spectra.

Magnetic properties of transition metal complexes, spin only formula, quenching of orbital magnetic moment, measurement of magnetic moment Para-dia-ferro - ferri and antiferromagnetism.

4 ORGANOMETALLIC AND BIOINORGANIC CHEMISTRY

Types of organo metallic compounds, terminology, 18 electron rule. Metal carbonyls General properties, nature of bonding, structure and shapes of metal carbonyls of V, Cr,

Mn, Fe, Ru, Co, Rh, Ni, metal alkene complexes, metal sandwich compounds - ferrocene, dibenzene chromium.

Haemoglobin-structure and functions, myoglobin, cytochromes, ferredoxins, chlorophyll -photosynthesis, vitamin B₁₂ structure and functions, Nitrogen fixation.

5 APPLIED AND INDUSTRIAL CHEMISTRY

Metallurgy - General principles of extraction of metals from ores, refining of metals, manufacture of steel, heat treatment.

Applications of organometallic compounds Wilkinsons catalyst, hydroformylation, Wacker's process, Ziegler Natta catalysis. Importance of green chemistry

6 SOLID STATE

Crystal systems and lattice types crystal symmetry. Miller indices-BCC, FCC, HCP, voids coordination numbers. Molecular, covalent, metallic and hydrogen bonded crystals. Principles of XRD techniques. Determination of lattice type and unit cell dimension of cubic crystals.

Electronic structure of solids. Band theory, Electric, magnetic and dielectric properties of solids.

Crystal defects: point, line and plane defects. Crystal structure- Rock salt, Zinc blende, KCl, CsCl, diamond, Fluorite.

7 ANALYTICAL PRINCIPLES

Historic laws of stoichiometry, Atomic theory, chemical equation, stoichiometric calculations.

Evaluation of analytical data. Accuracy and precision, standard deviation, variance-confidence limit -'t' test. Errors -classification, distribution propagation, causes and minimisation. Significant figures and computation rules.

Titrimetric method-general principles - Theory and applications of acid-base, redox and complexometric titrations. Theory of indicators.

Gravimetric methods of analysis. Formation of precipitates. Co-precipitation, homogeneous precipitation. Drying and ignition of precipitates.

8 MECHANISM OF ORGANIC REACTIONS AND AROMATICITY

Electron displacements - inductive, electromeric, mesomeric and hyper conjugative effects. Reactive intermediates, formation and stability of carbo cation, carbanion, carbenes, nitrene, benzyne and free radicals . Type of organic reactions - substitution, addition, elimination and rearrangement

Huckel's rule. Homo, hetero and non benzenoid aromatic systems. Aromaticity of annulenes. Cyclic carbocations and carbanions. Antiaromaticity.

9 SELECTIVE ORGANIC REACTIONS

Mannich, Reimer-Tiemann, Reformatsky, Ullmann, Stork enamine, Diels-Alder, Grignard and MPV reactions. Aldol, Cannizzaro, Perkin, Dieckmann, Thorpe and acyloin condensations. Birch, Wolff-Kishner and Clemmensen reductions. Hydroboration and Oppenauer oxidation. Rearrangements -1,2, shifts 1,3, shifts, Pinacol-pinacolone, Claisen, Cope, Wagner-Meerwin, Fries, Beckmann and Curtius.

10 STEREO CHEMISTRY OF ORGANIC COMPOUNDS

Molecular chirality-enantiomers, diastereomers, stereo chemical nomenclature, optical activity. Racemisation, resolution, conformational analysis of cycloalkanes, Conformational analysis of disubstituted cyclohexane derivatives, stereo selective and stereospecific reactions. Assigning-configuration and conformation.

11 ORGANIC PHOTOCHEMISTRY AND PERICYCLIC REACTIONS

Photo chemistry: Laws of photochemistry Radiative and non radiative transitions. Fluorescence and quenching. Photosensitisation. Chemiluminescence.

Cis-trans isomerization, Paterno-Buchi reaction, Norrish Type I and II reactions, dipimethane rearrangement, photochemistry of arenes.

Selection rules and stereochemistry of electrocyclic reactions, cycloaddition and sigmatropic shifts. Cope and Claisen rearrangements.

12 ORGANIC SPECTROSCOPY

U.V. Electronic transition in enes, enones and arenes. Woodward-Fieser rules. Group frequencies in IR-Identification of functional groups with IR. Mass spectrometry-NMR spectroscopy ^1H NMR ^{13}C NMR-chemical shifts, spin-spin-interactions, spectral interpretation.

13 CHEMISTRY OF NATURAL PRODUCTS

Terpenoids - classification, structure of alpha pinene and Camphor Alkaloids-classification - structure of papavarine and quinine, structure of synthesis of flavones and isoflavons, Lipids - classification and structure.

14 CHEMISTRY OF BIOMOLECULES

Stereochemistry of steroids-cholesterol. Structure and synthesis Vitamin A, C, B, K and biotin. Proteins-Structure organisation of proteins, sequence determination in peptides and proteins. Edman degradation. Chemistry of -nucleic acid, structure of DNA. Starch, Cellulose, Glycogen.

15 CHEMISTRY OF POLYMERS

Types and mechanism of polymerisation reaction Stereo chemistry and kinetics of polymerisation, Measurement of molecular mass and size, Synthesis of stereo regular polymers, Ziegler-Natta catalysts. Manufacture and application of polyolefins, thermoplastics, polyamide, polyester, polyurethane, epoxides and industrial polymers.

16 SEPARATION AND CHARACTERISATION TECHNIQUES

Chromatographic methods, classification, column, TLC, PC, HPLC, GC. Detectors, theory of chromatography. Affinity and chiral columns, solvent extraction, liquid-liquid extraction. Distribution law- successive extraction Craig method. Normal and ultracentrifugation, Electrophoresis.

Qualitative and quantitative analysis of elements in organic compounds, determination of molecular mass of compounds.

17 QUANTUM CHEMISTRY

Black body radiation, photoelectric effect, Compton effect and atomic spectra. de Broglie hypothesis, Heisenberg uncertainty principle. Postulates of quantum mechanics. Operators, wave function, Eigen function and eigenvalue. Orthogonality, normalisation, probability and expectation value.

Schrodinger wave equation for a free particle, particle in a one dimensional box degeneracy.

Application of quantum mechanics to simple systems. Simple harmonic oscillator. Hydrogen like atom, Schrodinger wave equation in spherical polar coordinate. Separation of variables. Atomic orbitals, space quantisation, Perturbation theory and variation principle. Self consistent field method. Term symbols, Slater's rule.

18 CHEMICAL BONDING AND MOLECULAR SYMMETRY

MO theory of hydrogen molecule ion. VB theory of H_2 . Resonance. MO theory of homonuclear diatomic molecules and simple heteronuclear diatomic molecules bond order and stability. Concept of hybridisation - types, shapes of polyatomic molecules, VSEPR theory,

Symmetry elements and symmetry operations. Point groups. Multiplication of operations. Conditions for a set of elements to form a group. Group multiplication table .

Similarity transformation and classification of symmetry operations. Reducible and irreducible representations. Orthogonality theorem and rules derived from it. Setting up of character tables of simple groups such as C_{2v} and C_{3v} . The four areas of the character table.

19 SPECTROSCOPY

Energy levels in molecules principle and selection rules. Born-Oppenheimer approximation. Microwave spectroscopy. Intensity of spectral lines. Calculation of internuclear distance. Rotational spectrum of polyatomic molecules. Instrumentation.

Vibrational spectroscopy-Harmonic and anharmonic diatomic molecules. Mass function Determination of force constant. Different branches of spectrum. Vibrational spectra of polyatomic molecules classification of vibrations. Overtones, combination and Fermi resonance. Finger print and group frequencies. Instrumentation.

Raman Spectra. Polarizability and classical theory of Raman spectrum. Mutual exclusion principle complementarity of Raman and IR spectra Instrumentation.

Electronic Spectra Frank-Condon principle. Types of electronic transitions. Franck-Condon diagram. Predissociation. Effect of conjugation on electronic absorption frequencies. Instrumentation.

Resonance spectroscopy. NMR spectrum. Nuclear spin. Proton NMR chemical shift Relaxation methods. Spin-Spin coupling. Instrumentation.

ESR spectrum. The 'g' factor. Fine structure and hyperfine structure.

20 GASES, LIQUIDS, LIQUID CRYSTALS

The distribution of molecular velocities. Maxwell's equation. Average, RMS and most probable velocities. Influence of temperature on molecular velocities. Mean free path, effusion. Transport properties: Viscosity, thermal conductivity and diffusion. Influence of temperature and pressure on transport properties.

Liquid state - properties, Lennard-Jones theory of melting, specific heat of liquids.

Liquid crystals - types - theories - applications.

21 THERMODYNAMICS AND STATISTICAL MECHANICS

Laws of thermodynamics. Thermodynamic properties-Intrinsic energy, enthalpy, entropy, free energy- their relation and significances. Maxwell relation. Joule-Thomson effect. Joule-Thomson coefficient. Properties of solutions - Raoult's law, Colligative properties. Thermodynamics of ideal solution. Partial molar quantities. Chemical potentials. Duhem-Margules equation. Excess thermodynamic properties. Fugacity and activity.

Chemical Equilibrium - Le Chatelier principle, homogeneous and heterogeneous system. Spontaneity of reactions. Free energy functions.

Phase Equilibria. Derivation of phase rule. Two component and three component systems. Isothermal evaporation.

Microstates and ensembles, Maxwell Boltzman distribution. The partition functions- translational, vibrational and rotational. Partition functions and thermodynamics properties.

Quantum Statistics: Bose- Einstein statistics Fermi- Dirac statistics. Relations between Maxwell Boltzman, Bose- Einstein and Fermi-Dirac statistics.

22 CHEMICAL KINETICS

Types of reactions - simple & complex, order and molecularity.

Branching reactions - steady state treatment. Unimolecular reactions Lindemann treatment . Kinetics of fast reactions. Reaction like $H_2 - Cl_2$, $H_2 - Br_2$ and decomposition of ethane, acetaldehyde Influence of temperature on reaction rate- energy of activation. Collision theory and absolute reaction rate theory. Free energy of activation and volume of activation Thermodynamic formulation of reaction rate.

Reactions in solution: Comparison between reaction in gas phase and in solutions. Factors determining reaction rates in solution- primary and secondary kinetic salt effects. Influence of solvent on reaction rate. Hammett equation.

23 SURFACE CHEMISTRY, COLLOIDS AND CATALYSIS

Types of surfaces. Examination of surfaces using ESCA, Auger, SEM and STM.. Thermodynamics of surface. Surface tension. Surfactants and micelles. Surface film. Surface pressure and surface potential. Freundlich, Langmuir and BET adsorption isotherms. Physisorption and Chemisorption. Measurement of surface area.

The colloidal state: Types of colloids. Stability and zeta potential. Properties of colloids. Kinetic, optical and electro kinetic. Donnan membrane equilibrium.

Catalysis: Homogeneous and Heterogeneous catalysis. Acid-base and enzyme catalysis. Langmuir Hinshelwood mechanism.

24 ELECTRO CHEMISTRY AND ELECTRO ANALYTICAL METHODS

Ions in solution, ionic equilibrium and Electrolysis. Deviation from ideal behaviour, ionic activity ion solvent interaction. Born equation. Ion Ion interaction. Activity coefficient and its determination. Debye Huckel limiting law. Debye Huckel treatment . Onsager equation. Conductance of high frequencies and high potentials.

Different types of electrodes. Electrochemical cells. Concentration cell and activity coefficient determination. Liquid junction potential. Evaluation of thermodynamic properties. Electrokinetic-phenomenon. Electrolysis current potential curves. Dissolution, deposition and decomposition potentials. Different types of over potentials. Hydrogen and Oxygen over voltage. Theories of over voltage.

Conductometric titrations. Potentiometric methods: reference and indicator electrodes. Hydrogen calomel, Ag-AgCl electrodes. The glass electrode. Measurement of pH. Potentiometric titrations. Electrogravimetry principle and method.