CHEIMSTRY

Part – 1
Research Methodology

1. **Chemistry literature work resources.**
   Name of scientific journals
   Sci-finders
   Chemical Abstract
   Research proposal, Dissertation, Ph.D. Thesis etc.
2. **Method Development and Validation.**
   Method development parameters.
   Method validation parameters.
   Sequence of method development.
3. **Reaction Synthesis :** Name reactions.
   Rearrangements
   Disconnection of molecules
   In-organic complex synthesis
   Organic chemical reagents
4. **Characterization techniques used in chemistry.** UV-Visible spectroscopy
   Single crystal X-ray techniques.
   IR Spectroscopy
   NMR Spectroscopy (^{1}H and ^{13}C)
   Mass Spectroscopy
5. **Purification techniques used in chemistry.**
   Crystallization
   Distillation
   Chromatographic tech. TLC, PC, GC, HPLC, HPTLC, UPLC, GC-MS, LC-MS. & Exclusion Chromatography
6. **Vibrational and Rotational Spectroscopy**
   NIR: Principle, instrumentation and applications.
   Raman spectroscopy: Principle, theory, instrumentation and applications.
7. **Statistical analysis of scientific data**

Part – 2
Chemistry

Inorganic Chemistry

1. Quantum Chemistry and its applications (MO-VB Theory)

Born-Oppenheimer approximation, Hydrogen molecule ion. LCAO-MO and VB treatments of hydrogen molecule, electron density, forces and their role in chemical bonding. Hybridization and valence MO's of H_2O, NH_3 and CH_4. Huckel π-electron theory and its applications to ethylene, butadiene and benzene. Idea of self-consistent field method

2. Magneto chemistry

Introduction, definition, types of magnetic bodies, Russell-Saunders and LS coupling. Derivation of Russell-Saundersterms, spin-orbit interaction, thermal energy and magnetic property. Magnetic moment for different multiple widths, multiple width large compared to kT, multiple width small compared to kT. Multiple widths comparable to kT. Stereo chemical applications of magnetic properties of the first transition series, lanthanides and actinides, determination of magnetic susceptibility by different methods. Derivation of Van- Vleck formula for susceptibility.

3. Fundaments of Mössbauer spectroscopy

Introduction of Mössbauer Spectroscopy. Principle and evaluation of Mössbauer effect. Recoil energy, Doppler Effect, Experimental techniques. Isomer shift, quadrupole splitting and applications

4. Uses of Inorganic reagents in inorganic analysis

General discussion and uses of some inorganic reagents: Potassium bromate ($KBrO_3$), potassium iodate(KIO_3), ammonium vanadate (NH_4VO_3), ceric sulphate [$Ce(SO_4)_2$], ethylenediaminetetra acetic acid (EDTA).

5. Chemistry in Nano science and technology

Introduction, definition of Nanomaterials and Nano technology, History of Nanomaterials, causes of interest in Nanomaterials, properties and types. Synthesis of Nanomaterials, their characterization techniques and applications of Nanomaterials **6. Organometallic Compounds**

Introduction, nature of bonding in organornetallic compounds of transition metals **π-bonded organometallic compounds:** Introduction, classification and synthesis of πbonded organotransition metal compounds, general characteristics, chemical reactions, bonding and structure.

π-bonded organometallic compounds: Introduction and classification of π-bonded organometallic compounds (a)π^2-alkene complexes: Preparative methods, physical and chemical properties, bonding of structure. (b) π^3allyl (or enyl) complexes: preparation, physical of chemical properties.

7. Fundaments of Bioinorganic Chemistry

Introduction to bioinorganic chemistry. Classification and role of metal ions according to their action in biological system. Essential trace elements and chemical toxicology, Introduction of trace elements. The essential ultra trace metals and non-metals. Iodine and

thyroid hormones, toxic elements, toxicity and deficiency. Transport and storage of proteins: Metalloporphyrins, oxygen carriers-hemoglobin and myoglobin, Physiology of blood.

8. Electron spin resonance

Introduction to Electron Spin Resonance. Technique of electron spin resonance, interaction between nuclear spin and electron spin: hyper fine splitting, calculation and energies of Zeeman levels. Calculations of energies, frequency, ESR spectrum when one electron influenced by a single proton and one electron delocalized over two equivalent protons. **9. Ion-Exchangers and their applications**

General introduction, classification of ion-exchangers and their applications in the separation of 1. Zinc and Magnesium, 2. Chloride and bromide, 3. Cobalt and Nickel, 4. Cadmium and Zinc.

10. Uses of Organic reagents in Inorganic Analysis

Cupferron, DMG, dithiozone, aluminon, oxine, dithiooxamide, α-benzoinoxime, α-nitro(3-naphthol, α-nitroso-3-naphthol, diphenyl carbazone, diphenyl carbazide, anthranilic acid, tannin, pyragallol, benzidine. salicylaldoxime, o-phenanthroline.

Organic Chemistry

1. **Organic reactive intermediates and reaction mechanism**

Generation, stability and reactivity of intermediates, addition, elimination and substitution reactions. Determination of reaction pathways. Hammett equation and LFER relationship

2. Name reactionand its application in organic synthesis

Barbier–Wieland degradation , Prins, Barton, Vilsmer-Haack, *Bouveault–Blanc reduction,* Willgerodt-Kindler reaction, Biginelli reaction, Birch-reduction,Hofmann-Loffler Freytag, Hantzch, Elbs-persulphate, McMurry reaction, Noyori annulation reaction, Passerini, Reformatsky, Suzuki coupling, Stille coupling Sharplessasymetric epoxidation, Stobbecondensation, and Ugi reaction. 3. **Rearrangements**

Advances in Fries rearrangement, Beckmann rearrangement, Benzilbenzilicacid, Favorskii, Neber, Sommelet Hauser, Curtius, Schimidt, BaeyerVilliger.

4. **Important Reagents**

DCC, Gilman reagent, PTC andcrown ethers, Merrifield resin, Woodward and Prevost hydroxylation, reagent for hydroboration, TMS-I, Wilkinson's catalyst, DDQ. 5. **Photo Chemistry**

Fundamental of photochemistry**, p**rinciples of photo chemistry, singlet and triplet states, properties and nomenclature of excited states. Physical properties of excited molecules as explained by improved Jablonskii diagram, photo chemistry of carbonyl compounds. Photo chemistry of olefins. Recent reactions in photochemistry

6. **Pericyclic Reactions**

Orbitals, molecular orbital symmetry, molecular orbital of ethylene, 1,3- butadiene, 1,3,5–hexatriene and allyl systems, concerted reactions, classification of pericyclic reactions, derivation of selection rules through construction of correlation diagrams for cyclo-addition reactions and for electrocyclic reactions with 4n and 4n+2 electrons, conrotatory and disrotatory motions for electrocyclic ring opening and ring closure. FMO approach for derivation of Woodward-Hoffman selection rules for cycloaddition and electrocyclic reactions, suprafacial and antarafacial cycloadditions.

1,3-Dipolar cycloaddition reactions, classification and applications. Sigmatropic reactions, suprafacial and antarafacial rearrangements, [1,j], sigmatropic rearrangement of hydrogen, [1,j] and [i,j] Sigmatropic reactions of carbon, selection rules for [i,j]sigmatropic rearrangements using FMOs. The Cope and the Claisen rearrangements

7. **Aromaticity**

Concept of aromaticity, non-aromaticity and anti-aromaticity, Huckel's rule and its applications to simple and non-benzenoid aromatic compounds, cyclopentadiene, azulene, tropolone system, annulenes, hetero annulenes, and fullerenes (C60).

Physical Chemistry

1. Statistical Thermodynamics

Basic terms: probability, cell, phase, space, micro and macro states, thermodynamic probability, statistical weight factor, assembly, ensemble and its classification and statistical equilibrium. Derivation of Boltzmann-Maxwell, Bose-Einstein and Fermi-Dirac statistics, Partition function and derivations of translational, rotational, vibrational and electronic partition functions and thermodynamic functions such as internal energy, heat capacity, entropy, work function, pressure, heat content, etc. Partition function and third law of thermodynamics. Applications of partition function to monoatomic gases, diatomic molecules, equilibrium constant and equilibrium constants of metathetic reactions.
Problems.

2. Fugacity and Activity

Definition, determination of fugacity by graphical, equation of state, approximate and generalized methods. Variation of fugacity with temperature and pressure. Mixture of ideal gases and real gases. Activities and Activity coefficients in liquid solution, Problems **3. The Debye-Huckel Theory**

Ionic interactions in solutions. Mean ionic activity coefficients (D-H limiting law).Applications of D-H theory: quantitative and qualitative, solubility and D-H theory, solubility of sparingly soluble salt in presence of inert electrolyte. The D-H theory in more concentrated solutions. D-H theory and equilibrium constant, Problems **4. The properties of solutions**

Ideal solutions: Properties, the Duhem-Ma rgules equation, vapor pressure curves. Composition of liquid and vapor in equilibrium influence of temperature on gas solubility and solid-liquid equilibria.

Non ideal solutions: Deviation from ideal behavior, liquid and vapor compositions. **Dilute solutions:** Determination of molecular weight by freezing and boiling point methods, Problems.

5. Electrochemical cells

Classification, chemical cells with and without transference, concentration cells with and without transference, liquid junction potential.

Commercial cells: Dry cell, lead accumulator, nickel iron accumulator, zinc silver accumulator.

6. Basic Concept of Polymer Chemistry

Classification of polymers, Types of polymer chains. Stereo regular polymers. Polymer nomenclature. Functionality and polymerization concept **7. Chain Polymerization**

Free Radical Polymerization: Methods of initiating free radical polymerization. Chain transfer reactions. Kinetics of free radical polymerization and chain transfer reactions.Factors affecting radical polymerization and properties of the resulting polymers.
Ionic (Catalytic) Polymerization: Kinetics of cationic and anionic polymerization. Coordination, polymerization. Copolymerization and its kinetics. Evaluation of reactivity ratios.
Methods of Free Radical Polymerization: Bulk polymerization, solution polymerization, emulsion polymerization and solid phase polymerization, Problems

8. Polycondensation

Reaction route of poly functional compounds.Kinetics of polycondensation reaction. Molecular weight control in polycondensation. Nonlinear polycondensation. Statistics of linear polycondensation.Effect of monomer concentration and temperature on direction of polycondensation reaction.Polycondensation equilibrium and molecular weight of polymer.Factors affecting the rate of polycondensation and molecular weight of the polymer.

Methods of Polycondensation

Melt, interfacial, solution and solid phase polycondensation. Problems.

9. Stepwise Polymerization and Ring scission Polymerization

Thermodynamics of ring transformation to a linear polymer.Effect of temperature and monomer concentration on ring-polymer equilibrium.Kinetics and mechanism of ring scission polymerization.Effect of activator concentration and temperature on ring scission polymerization and molecular weight of the polymer.

10. Physico-chemical Transformation Reactions

Types of reactions in polymer chemistry.Degradation and its classification.Cross-linking, addition and substitution reactionsReactions of functional groups. **11. Fractionation of Polymers**

Isolation and purification of polymers.fractionation ofpolymers. Methodspolymer fractionation: Fractional precipitation, partial dissolution or extraction method, Gradient elution method and gel permeation chromatography method.

Analytical Chemistry

1. Basic concept of Analytical Chemistry

Introduction, scope and objectives, Classification of analytical methods. Basics of classical and instrumental methods of analysis.Method of selection, sample processing, steps of total quantitative analysis, the tools of analytical chemistry and good laboratory practices.
Basic of volumetric methods of analysis: General principle, concentration units, standard solution and standardization, detection of end point, indirect and back titration techniques. Minimization of titration errors, types of reactions in titrimetric analysis.
Non-aqueous titrations: Role of solvents, properties of solvents, autoprotolysis and dielectric constant. Titration of acids-bases, solvent system, titrants, standard titration curves, effect of water, end point detection, application to determination of carboxylic acid, phenols and amines.

2. Spectroanalytical Techniques

Fundamental of spectroscopy, electromagnetic radiations and their properties. Introduction to absorption and emission spectroscopy. Lambert-Beer law.
Atomic absorption spectroscopy: Basic principle, theory, instrumentation and applications. Advantages over flame photometry.

Fluorometry and Phosphorimetry: Introduction, principle, theory, instrumentation and applications.

UV-Visible spectrophotometric titrations.

3. Edible oil Analysis

Basic terminology, analytical importance and quantitative determination of oil, fat, wax, iodine value, saponification value, RMPK value, hydroxyl value, moisture, etc.

Detection of oil adulterants: (1) Argemone oil, (2) Rice bran oil, (3) Sesame oil, and Palm oil.

4. Environmental Chemistry

Concept and scope of Environmental Chemistry. Terminology and classification of environmental segments, particles, ions and radicals in the atmosphere

Air pollution: Introduction, major sources of air pollution, air pollutants.Sources of pollutants: gaseous NOx, SOx, CO, hydrocarbons, particulates (Inorganic and Organic particulate matters).Effect of pollutants on humans, animals, materials, and vegetation.

Greenhouse effect and global warming: El Nino and La Nina phenomenon, Asian brown cloud.

Ozone layer: Creation, mechanism of depletion and its effect.

Smog: Sulphurous and photochemical smog, formation mechanism, and its control.

Analysis of air pollutants: Sampling techniques of gases and particulate, analysis of NOx, SOx, CO, H_2S, oxidants and ozone by chromatography and spectrophotometric methods. Analysis of particulates by HVAS techniques.

Water pollution: Introduction, sources of pollutants, water pollutants, classification of inorganic, organic, thermal and radioactive pollutants.

Analysis of water pollution: Determination of pH, conductivity, TDS, acidity, alkalinity, chloride, iron, sulphate, sulphide, fluoride, ammonia, nitrate, nitrite, calcium, magnesium, DO,BOD, COD, etc.

Soil pollution: Origin and nature of soil, sources of soil pollution, purpose of analysis. Methods of soil analysis:pH, moisture, total nitrogen, lime potential, total sulphur, manganese, iron, Na, K, Ca, Mg, etc. **5. Green Chemistry**

Introduction, importance andtwelve principles of Green Chemistry. Designing a green synthesis using these principles. Green Chemistry in day to day life. Green solvents (alternatives of organic solvents)

Ionic liquids, supercritical fluids, CO_2 and H_2O and aqueous phase organic synthesis.

Non-traditional greener alternative approaches: Green reagents, catalysis, bio-catalysis.

Applications of non-conventional energy sources: Microwave, ultrasonic assisted synthesis, electro-synthesis and sunlight (UV) radiation assisted synthesis. **6. Analytical Chemometrics**

Propagation of measurement of uncertainties, useful statistical tests: Test of significance, F-test, t-test, chisquare-test, correlation coefficient, confidence limist of mean, comparison of mean with true values. Regression analysis (least square method for linear and nonlinear plots). Statistics of sampling and detection limit evaluation. Specific study for analytical method radiation by using validation parameters: (1) accuracy, (2) precision (repeatability and reproducibility), (3) linearity and range, (4) Limit of Detection (LOD) and Limit of quantification (LOQ),(5) selectivity/specificity, and (6) Robustness and Ruggedness.

ADVANCE CHROMATOGRAPHIC TECHNIQUES