VEER NARMAD SOUTH GUJARAT UNIVERSITY

CHEMICAL SCIENCES

Inorganic Chemistry

1. Chemical periodicity
2. Structure and bonding in homo- and heteronuclear molecules, including shapes of molecules (VSEPR Theory).
3. Concepts of acids and bases, Hard-Soft acid base concept, Non-aqueous solvents.
4. Main group elements and their compounds: Allotropy, synthesis, structure and bonding, industrial importance of the compounds.
5. COORDINATION COMPOUNDS

   Classification of coordination compounds, Werner's theory of coordination,

   Electronic interpretation of coordination compounds, Factors effecting the formation of complex ions, Detection of complex ion in solution,

   Chelation, Factors influencing the stability of metal chelates, Importance of chelates, Role of metal chelates in living system

   Inner complexes and polynuclear complexes, Determination of composition of complex ions.

   Inorganic Reaction Mechanism:

   Labile ana inert complexes, factors responsible for lability and inertness of complexes.

   Reactivity of metal complexes, ligand replacement reaction: classification of mechanism and energy profile of reaction. Inert and labile complexes, interpretation of liability and inertness of transition metal complexes on the basis of reaction rate, VBT and CFT.

   Transition state or activated complex, substrate, attacking reagents electrophilic and nucleophilic, Nature of central atom. Kinetic application of CFT.

   Kinetics of octahedral substitution, acid hydrolysis, factor affecting acid hydrolysis, base hydrolysis, conjugate base mechanism, direct and indirect evidences in favor of conjugate mechanism.

6. Inner transition elements: spectral and magnetic properties, redox chemistry, analytical applications.
7. Organometallic compounds: synthesis, bonding and structure, and reactivity. Organometallics in homogeneous catalysis.
8. Metal Clusters:

   Introduction , Classification, Carbonyl clusters, Low nuclearity carbonyl clusters, High nuclearity carbonyl clusters, Electron counting scheme for HNCCS, Wade's rules.

   Halides type clusters: Dinuclear clusters, Trinuclear clusters, Tetranuclear clusters, Hexanuclear cluster.

   Chevrel phases and Zintl Ions, Carboranes, Metalloboranes, Metallocarboranes, Higher boranes (Hexaborane-10, Decaborane-14) , Number and types of bonds present in higher boranes .

9. CHROMATOGRAPHY

Thin-Layer Chromatography : Selection of stationary and mobile phase, Detection techniques –Elementary idea of HPTLC Gas Chromatography: Selection of mobile phase – Selection of stationary phase in GLC and GSC – Detectors: FID (with modifications), TCD and ECD, Their comparison, Packed column, WCOT,SCOT(advantages and disadvantages)–Temperature programming– Derivatization in GC – Quantitative Analysis.

LIQUID CHROMATOGRAPHY

Principle of Liquid – Solid chromatography, Comparison with GC, Column chromatography, Gradient elution, Displacement chromatography, Principle of HPLC, Instrument and significance of each component, Pumps, Guard column Criteria in selection of mobile phase, Stationary phases (solid, liquid), Bonded phase supports, Detectors: UV absorption, RI detectors – Normal phase and Reversed phase. Method of introducing sample.

THERMAL METHODS OF ANALYSIS

(A) THERMOGRAVIMETRY: Thermogravimetry, Instruments for TGA-thermobalance and furnace, Calibration of temperature scale, Factors affecting TGA results instrumental and experimental, Applications.

(B) THERMOMETRIC TITRATION: Thermometric Titration (TT), Advantages, Instrument, Applications of TT in Neutralization Titration, Precipitation Titration, Complexometric Titration and Redox titration.

10. Bioinorganic chemistry: photosystems, porphyrins, metalloenzymes, oxygen transport, electron- transfer reactions; nitrogen fixation, metal complexes in medicine.
11. Characterization of inorganic compounds by IR, Raman, NMR, EPR, Mossbauer, UV-vis, NQR, MS, electron spectroscopy and microscopic techniques.
12. Nuclear chemistry: nuclear reactions, fission and fusion, radio-analytical techniques and activation analysis.

Physical Chemistry:

1. **Quantum Mechanics:**
   Discussion of solution of Schrodinger equation to same model system e.g. the one-dimensional harmonic oscillator, two particle rigid rotator. Ordinary angular momentum , generalized angular momentum, Eigen functions of angular momentum, Eigen values of angular momentum, different types of operators and their uses, addition of angular momentum, spin, Russel-Saunders terms and coupling scheme, term separation energies of the p^n and d^n configuration, magnetic effect: spin orbit coupling and Zeeman effect (splitting).

2. Approximate methods of quantum mechanics: Variational principle; perturbation theory up to second order in energy; applications.

3. Atomic structure and spectroscopy; term symbols; many-electron systems and antisymmetry principle.

4. Chemical bonding in diatomics; elementary concepts of MO and VB theories; Huckel theory for conjugated π-electron systems.

5. Symmetry and Group Theory in Chemistry and Its applications:

   Representation of Groups: Preparation of matrices and vectors matrix notations for geometrical transformations, orthogonality theorem and its consequences,

reducible and irreducible representations and their relation, preparation of character table for C_{2v} and C_{3v} point groups, Application of group theory to- Transformation properties of atomic crystals.

6. MOLECULAR SPECTROSCOPY

Molecular spectra, Microwave spectroscopy (Rotational spectroscopy): The Rotation of molecules, Linear molecule, Symmetric tops ,Spherical tops, Asymmetric tops, Rotational spectra of rigid diatomic molecule ,Intensities of spectral lines , Effect of isotopic substitution, Techniques and instrumentation of rotational spectrum, IR Spectroscopy: Classical frequency of harmonic oscillator, The classical potential energy of harmonic vibration of a diatomic molecule, Quantum expression of potential energy, energy level diagram, Relative population of energy levels ,Mechanism of interaction with radiation, selection rule, determination of force constant, Amplitude of vibration, The anharmonic vibration or oscillator , Morse potential , Vibrational energy of diatomic molecule following the Morse potential, energy level diagram, vibrational transitions. Vibrational – Rotational spectra of diatomic molecule (CO molecule) Application of Vibrational rotational spectra

7. THERMODYNAMICS

Introduction to Laws of thermodynamics, state and path functions and their applications, thermodynamic description of various types of processes, Maxwell's relations, Partial molar quantities, Calculation of partial molar quantities, determination of partial molar volume and partial molar enthalpy, Ideal and non-ideal liquid mixtures, Thermodynamics functions of mixing of non-ideal solutions (i) free energy of mixing (ii) entropy of mixing (iii) volume of mixing and (iv) enthalpy of mixing ,Excess functions(μE ,GE , SE ,HE and V E) for non-ideal solutions and expression for excess thermodynamic functions. Numerical

8. STATISTICAL THERMODYNAMICS

Basics of Statistical thermodynamics (Assembly, Canonical ensemble, occupation number statistical weight factor, probability), Thermodynamic probability, Probability and entropy, Maxwell-Boltzmann, Bose-Einstein and Fermi-Dirac statistics. Lagrange's methods of multipliers, Partition function, Thermodynamic properties in term of partition functions(i) Internal energy (ii) Heat Capacity (iii) Third law of thermodynamics(iv) Helmholtz free energy (v) Enthalpy (vi) Gibb's free energy(vii) Chemical potential (viii) Equilibrium constant Molecular partition functions for an ideal gas , Derivation for Translational, Rotational and Vibrational partition functions Numerical.

9. THEORIES OF ELECTROLYTIC CONDUCTANCE AND OVER VOLATEGE
Debye-Huckel theory of strong electrolytes, relaxation effect and electrophoretic effect, Debye Falkenhagen effect, Weineffect. Ionic strength and its determination ,Debye-Huckel limiting law. Activity and activity coefficient, determination of activity coefficient by (i) solubility (solubility product principle) (ii) EMF method (cell without transference), Determination of dissociation constant of monobasic acid by conductance method and approximate EMF method, Electrolytic polarization, Dissolution and Decomposition potential, Concentration polarization, Decomposition potential and its determination, over voltage, determination of over voltage, theories of over voltage:combination of atom as slow process (Tafel theory).

10. CHEMICAL KINETICS

Theories of Unimolecular gas reactions: Lindemann theory, Kinetics of some complex reactions (i)Reversible reactions(only first order opposed by first order) (ii)Consecutive reactions(A→B→C); Steady state treatment or approximation, Enzyme catalyzed reactions, Kinetics of general Chain reaction, Kinetics of photochemical reactions(H2-Cl2and H2-Br2) , Kinetics , Mechanism ,determination of activation energy and chain length of some organic decomposition (i)

decomposition of ethane (ii) decomposition of acetaldehyde, Effect of Ionic strength on rates of ionic reactions (Primary and secondary salt effect) Numerical.

11. SURFACE CHEMISTRY

    Adsorption Multilayer Adsorption, the BET adsorption isotherms, derivation of BET equation, determination of surface area and area of cross section of molecules by BET equation. Derivation of Langmuir equation from BET equation. Explanation of different adsorption isotherms, Change in enthalpy, entropy and free energy of adsorption, Adsorption at the surface of liquid: Gibbs adsorption isotherms (derivation). Thermodynamic treatment of adsorption, Surface –Active substances, orientations of surfactants on the surface of solution, surface inactive substances, surface pressure, Insoluble surface films on liquid.

    COLLOIDS

    Types of colloidal systems, preparation of lyophobic colloidal, Properties of Colloidal systems: (i) electrical properties origin of charges on colloidal, electrical double layer, Zeta potential and its determination by electrophoresis, factor affecting zeta potential, explanation on DLVO theory of colloid stability (ii) Electro kinetic properties: Electrophoresis, electroosmosis, Surface active agents, critical micellar concentration (CMC), factors affecting the CMC of surfactants, thermodynamics of micellization: mass action and phase separation model, solubilization, emulsion, types of emulsion, methods for determination of types of emulsion, microemulsion, types of microemulsion, theories of microemulsion.

12. Solid state: Crystal structures; Bragg's law and applications; band structure of solids.

13. POLYMER CHEMISTRY

    Types of polymers, Stereochemistry of polymers, Kinetics of polymerization (Addition and Condensation),Thermodynamics of polymerization, Phase techniques of polymerization (Bulk, solution, suspension and emulsion), Number & Mass average Molecular mass, Polydispersity Index (P.D.I) Molecular mass determination by Viscometry and Osmometry, Thermal transitions in polymer: glass transition temperature and its significance, Numerical

14. Data analysis: Mean and standard deviation; absolute and relative errors; linear regression; covariance and correlation coefficient.

Organic Chemistry

1. IUPAC nomenclature of organic molecules including regio- and stereoisomers.

2. Stereochemistry

   A. Stereo chemical principles; Enantiomeric relationships; Diastereomeric relationship; R-S and E-Z nomenclature; Dynamic stereochemistry; Chiral-Prochiral relationships; Stereo selective and Stereo specific reactions; Racemates and racemic modification, Resolution of racemic modification, Optical activity in the absence of chiral carbons biphenyl, allenes, spiranes.
   B. Conformational Analysis: Interconversion of Fischer, Newman and Sawhorse projections. Newer method of asymmetric synthesis (including enzymatic and catalytic nexus), enantio and diastereo selective synthesis. Simple acyclic and cyclic (chair and boat cyclohexanes, Decalins, Perhydrophenanthrene) systems. Effects of conformation on reactivity in acyclic compounds and substituted cyclohexanes..

3. AROMATICITY

A. Aromaticity and Aromatic character; structure and stability of benzene, Frost circle diagram, concept of aromaticity; Resonance and chemical stabilization; criteria to checkaromatic character-IR, NMR, heat of hydrogenation; Huckel's rule; HMO method

B. Antiaromaticity, homoaromaticity, nonaromaticity; aromaticity in benzanoid compounds: naphthalene, pyrene, acepleialdelene.

C. Aromaticity non-benzenoid compounds: azulene, tropolones, charged rings, annulenes, fullerenes, and mesoionic compounds.

4. REACTION MECHANISM & REACTIVE INTERMEDIATES

Detailed study of organic reaction intermediates. Generation, structure, stability and reactions of –

Carbocations (Classical and non-classical):Phenonium ion, norbornyl system, common carbocation rearrangements- Demjanov, Pinacole-Pinacolone, Rupe.

Carbanions: Mechanism of condensation involving enolates - Aldol, Claisen, Mannich, Dieckmann, Michael and Shapiro reactions.

Carbenes: Mechanism of Arndt-Eistert reaction, Reimer-Tiemann reaction and Bamford Steven's rearrangement reaction.

Free Radicals: Allylic halogenation (NBS), coupling of alkenes and arylation of aromatic compounds by diazonium salts. Sandmeyer reactions. Free radical rearrangements, Hunsdiecker reaction.

5. SUBSTITUTION AND ELIMINATION REACTIONS

A: Aliphatic Nucleophilic Substitution: The SN1 , SN2 , SNi mechanisms. Reactions of Allylic halides, neighbouring group participation by -OH, -NH2, -COO- , -RS, - halogen, aromatic ring.

B: Aromatic Nucleophilic Substitution: The SN2 , SN1 and benzyne mechanisms, Reactivity - effect of substrate structure, leaving group and attaching nucleophile, The Von Richter rearrangement.

C: Elimination reaction: Hoffmann and Zaitsev's rule of elimination, E1, E2 and E1CB Reaction mechanism and orientation.

6. NAME REACTIONS

General nature, method, mechanism and synthetic applications of the following reactions; (1)Ugi reaction (2)Noyori reaction (3)Wittig reaction (4)Peterson olefination reaction (5)Mannich reaction (6)Stille reaction (7)Ene recation (8)Staudinger reaction (9)Corey-Fuchs reaction (10)Ritter reaction (11)Mcmurry reaction (12)Michael addition (13) Heck reaction (14) Dakin reaction (15) Darzen'sglycidic ester synthesis (16) Suzuki reaction (17) Willgerodt reaction (18) Buchwald-Hartwig reaction (19) H. V. Z. reaction (20) Mitsunobu reaction (21) Sonagashira reaction (22) Dickmann reaction

MOLECULAR REARRANGEMENTS

(A)Rearrangement involving migration to electron deficient carbon: (i) Expansion and contraction of rings/Demajnov rearrangement (ii) Benzil-benzilic acid rearrangement
(B)Rearrangement involving migration to electron rich carbon: (i) Favorskii rearrangement (ii) Sommelet-Hauser rearrangement (iii) Neber rearrangement
(C)Rearrangement involving migration to electron deficient nitrogen: (i) Schmidt rearrangement (ii) Curtius rearrangement
(D)Aromatic rearrangements: (i) Migration around the aromatic nucleus: Jacobsen rearrangement (ii) Migration of group from the side chain to the nucleus: Orton rearrangement, Hoffmann-Martius rearrangement, Rearrangement of N-nitrosoanilines (Fischer- Hepp rearrangement).
(E) Rearrangement involving migration from oxygen to ring: (i) Fries rearrangement (ii) Claisen rearrangement

7. REAGENTS FOR ORGANIC SYNTHESIS

Introduction, Preparation and Industrial Applications of the following, (1) N-Bromosuccinimide (NBS) (2) Grubbs 1st and 2nd generation catalyst (3) N,N-dicyclohexylcarbodiimide (DCC) (4) Lead tetra-acetate (LTA) (5) Baker's yeast (6) n-butyl lithium (7) K3Fe(CN)6 and DMSO (8) Grignard Reagent (9) Diazomethane (10) Polyphosphoric acid (11) Sharplessepoxidation (12) Umpolung reagent (1,3-dithiane) (13) Dess martin periodinane (14) DDQ (15) Tri-n-butyltinhydride (C4H9)3SnH (16) Diisobutyl aluminum hybride (DIDAL-H) (17) Lithium disoprpyl amide (LDA) (18) OZONE (19) Crown ethers (20) Wilkinson's Catalyst

8. PROTECTING GROUPS

Need of protecting groups – Protection of alcohols, Carbonyl, Carboxylic acid and amino groups, Synthetic equivalent groups and examples on transformations.

DISCONNECTION APPROACH

Introduction to disconnection, Concept of synthon, Synthetic equivalent, Functional group interconversion

(i) One group disconnection: Disconnection and synthesis of alcohols, olefins, simple ketones, acids and its derivatives
(ii) Two groups disconnection: Disconnections in 1,3-dioxygenated skeletons, preparation of β-hydroxy carbonyl compounds, α,β-unsaturated carbonyl compounds, 1,3-dicarbonyls, 1,5- dicarbonyls and use of Mannich reaction
(iii) Pericyclic reactions: Disconnections based on Diels-Alder reaction and

electrocyclic reaction: Its use in organic synthesis

9. Asymmetric synthesis: Chiral auxiliaries, methods of asymmetric induction – substrate, reagent and catalyst controlled reactions; determination of enantiomeric and diastereomeric excess; enantio-discrimination. Resolution – optical and kinetic.

10. PERICYCLIC REACTIONS

Introduction - Definition, Characteristics and Classification Molecular orbitals and symmetry properties of ethylene, 1,3- butadiene, 1,3,5- hexatriene and allyl systems.
Electrocyclic Reactions: Woodward-Hoffman Correlation diagram and derivation of selectionrules, Conrotatory and disrotatory motions, FMO and PMO approach for 4n and (4n+2) π electron system and allyl systems.
Cycloaddition Reactions: Antarafacial and suprafacial additions. FMOand PMO approach for 4n and (4n+2) π electron Systems(No correlation diagram),Diels-Alder reaction, stereoselectivity,Effect of substituents.
Sigmatropic rearrangements: Suprafacial and antarafacialshifts involving H & C moieties, retention and inversion of configurations. The Cope and Claisen rearrangements, Ene reaction, 1, 3- dipolar cydoadditions. Examples of electrocyclic, cycloaddition and sigmatropic rearrangements.

11. HETEROCYCLIC CHEMISTRY-I

(A) Nomenclature of Heterocycles: Hantzsch-Widman nomenclature systems for monocyclic and fused heterocycles and bridged heterocycles (B) Five and six membered heterocycles with two hetero atoms: Synthesis, reactivity, aromatic character and importance of following heterocyclic rings: Oxazole, Thiazole, Pyrazole, Imidazole, Pyridazine, Pyrimidine, Pyrazine (C) Condensed five membered heterocycles: Synthesis, reactivity, aromatic character and importance of following heterocyclic Rings: Benzoxazole, Benzthiazole, Benzopyrazole, Benzimidazole.

HETEROCYCLIC CHEMISTRY-II

(A)Five and six membered heterocycles with more than two hetero atoms: Synthesis, reactivity, aromatic character and importance of following heterocycles:1,2,3-triazole, 1,2,4-triazole, 1,2,4-oxadiazole, 1,3,4-oxadiazole, 1,2,5-oxadiazole
(B)Condensed six membered heterocycles: Synthesis, reactivity, aromatic character and importance of following heterocyclic Rings: Quinoline, Isoquinoline, Cinnoline, Quinoxaline, Phthalazine, Naphthyridine, Phenoxazine

12. NATURAL PIGMENTS & ALKALOIDS

(A) Natural Pigments & Porphyrins Derivatives Porphyrins: General structures, Synthesis and Spectral properties. Synthesis of cryptopyrrole, Phytopyrrole, Opsopyrrole and Haemopyrrole and their carboxylic acid derivatives. Structural elucidation of Haemoglobin and Chlorophyll (Analytical evidences only).
(B) Alkaloids: Classification of alkaloids; Structural elucidation of Morphine, Reserpine and Colchicine (Analytical evidences only)

STEROIDS & SEX HORMONES

(A) Steroids: Introduction to Sterols: Structure determination of cholesterol and ergosterol (no synthesis), Bile acids: Introduction, Structural elucidation and Synthesis of Cholanic acids (α and β both).
(B) Sex Hormones: Classification of hormones: Structure and synthesis of Androgens, Oestrogens and Gestrogens. Name and structures of Adrenocortical hormones, Partial synthesis of cortisone

VITAMINS & TERPENOIDS

(A) Vitamins: Structure determination, Synthesis and biochemical functions of Vitamin A, Vitamins B1 andB2, Vitamin H

(B) Terpenoids: Classification, nomenclature and isolation Structure determination and synthesis of Farnesol, Zingiberene, Cadinene, Gibrelic acid and Abietic acid.

Nucleic Acids & Enzymes

(A)Nucleic Acids: Purine and pyrimidine bases of nucleic acids, base pairing via H-bonding, Chemical and enzymatic hydrolysis of nucleic acids, Structure of nucleosides and nucleotides, DNA, RNA(Basics structures only), DNA replication, Transcription, Translation, Protein Biosynthesis.

(B) Enzymes: Classification, nomenclature and inhibition, factors affecting catalytic activity and specificity in action, regulation of enzyme activity

13. NMR SPECTROSCOPY

Theory and principles of NMR spectroscopy, Theory of Fourier Transform

(i) 1H NMR Spectroscopy Proton resonance condition, Aspects of PMR spectra – number of signals, chemical shift, factors influencing chemical shift, deshielding, chemical shift values and correlation for protons bonded to carbons (aliphatic, olefinic, aldehydic, aromatic) and other nuclei (alcohols, phenols, enols, acids, amides and mercaptans), effect of deuteration, spin-spin coupling, (n+1) rule, factors effecting coupling constant "J"

(ii) 13C NMR spectroscopy Types of 13C NMR Spectra: proton coupled and decoupled 13C spectra, chemical shift, calculations of chemical shifts of aliphatic, olefinic, alkyne, aromatic, hetero aromatic and carbonyl carbons, factors affecting chemical shifts

(iii) 2D NMR Techniques Preliminary idea of 2D NMR

MASS SPECTROMETRY

Theory and principles of mass spectroscopy; Instrumentation; low and high resolution mass spectra; Ionization techniques – Electron Impact (EI) ionization, Chemical Ionization (CI), Field Desorption (FD), Fast Atom Bombardment (FAB), Electronspray Ionization (ESI); Determination of molecular weight and molecular formula, nitrogen rule, detection of molecular ion peak, metastable ion peak; Fragmentations – rules governing the fragmentations, McLafferty rearrangement; Interpretation of mass spectra of different class of compounds – saturated and unsaturated hydrocarbons, aromatic hydrocarbons, alcohols, ethers, ketones, aldehydes, carboxylic acids, amines, amides, compounds containing halogens; To write possible fragmentation for given compound; To identify structure from mass spectral data; To identify structure from combined spectral data.

UV-Visible Spectrophotometry

Types of electronic transition, autochrome, chromophore, Bathochromic effect, Hypso chromic effect, Hyper chromic effect, Hypo chromic effect, Factor affecting λmax like resonance, hyper conjugation, hydrogen bonding, steric effect , Woodward's rules for α,β-unsaturated ketones, Diene systems, aromatic system, Effect of solvent on absorption bands, law of absorption with derivation, Elementary idea of double beam automatic recording, Spectrophotometer, Application.

IR SPECTROPHOTOMETRY

IR Spectroscopy: Introduction: Theory, Instrumentation: single beam, double beam spectrophotometers, radiation sources, sample cells, monochromators, detectors, sample handling, Resolution, wave number measurement, Useful terms: IR region, types of vibrations: fundamental and overtones, linear and nonlinear molecule, equation for vibrational frequency, selection rule, coupling interactions, hydrogen bonding information, Fermi resonance. IR spectra: group frequency, group

frequency region, finger print region, spectra interpretations (Amino, carboxyl, hydroxyl, ethers groups containing compounds) and structure elucidation. FTIR: principle, instrument design, and function of beam splitter, Advantages of FTIR vs. IR.

Interdisciplinary topics

1. Chemistry in nanoscience and technology.
2. Catalysis and green chemistry.
3. Medicinal chemistry.
   Introduction, Classifications: On the basis of their chemical structure and therapeutic action, Nomenclature: Proprietary and Non-proprietary name, Nomenclature of new drugs by WHO, Names of drugs: Generic and brand names
   Theories of drug action: Occupancy theory, Rate theory and induced fit theory
   Biological defence, chemical defences, Furguson principle
   Absorption of drugs: Routes of administration, factors that affect on absorption
   Physico chemical properties: Solubility, Partition coefficients, Ionization constant, Electronic effect, Steric effect, Stereochemical consideration
4. Supramolecular chemistry.
5. Environmental chemistry.
   (i)Water Pollution: Basic Concepts of Eutrophication, Water Quality, Water contaminants, Heavy minerals, Organic contaminants, PCBs and other Halogens materials, PAH, Pesticides, Waterborne Pathogens, Aquatic toxicology, Water Purification Methods, Sewage treatment.
   (ii)Air Pollution: Air pollution sources and emissions- Particulates, Aerosols, Photochemical smog, Determination of SOx, NOx, COx and hydrocarbons, Air pollution control technologies of particulate and gaseous pollutants
   (iii)Effluent treatment: Industrial pollution of sugar, distillery, drug, pulp & paper and their analysis. Effluent treatment plants of above industries.