GANDHI INSTITUTE OF TECHNOLOGY AND MANAGEMENT (GITAM)
(Deemed to be University)
(Estd. u/s 3 of the UGC Act, 1956), NAAC Accredited with `A+' Grade
Visakhapatnam | Hyderabad | Bengaluru

GITAM Institute of Science
Department of Chemistry

Ph.D. Entrance Test - 2020-21

Part A: Research Methodology

Research Methodology: Meaning of Research, Objectives of Research, Motivation in Research, Types of Research, Research Approaches, Significance of Research, Research Methods versus Methodology.
Defining the Research Problem: What is a Research Problem? Selecting the Problem, Necessity of Defining the Problem.
Research Design: Meaning of Research Design, Need for Research Design, Features of a Good Design.
Sampling Design: Census and Sample Survey, Implications of Sample Design, Steps in Sampling Design, Criteria of Selecting a Sapling Procedure.

Part B: CHEMISTRY

SECTION A

Calibration and maintenance of Instruments / Equipment: calibration of common laboratory instrument and equipment (Analytical balances, volumetric glassware, ovens, furnaces, , pH meter, conductivity meter.
Classification of errors, accuracy-absolute and comparative method, precision, significant figures, mean and standard deviation.

Principle and instrumentation: Thermo-gravimetric analysis, X-ray Fluorescence spectroscopy, atomic emission and atomic absorption spectroscopy.

Ultraviolet spectroscopy: Introduction, Principle and instrumentation. Woodward-Fisher rules for conjugated dienes, trienes, unsaturated carbonyl compounds and aromatic compounds.

Infrared spectroscopy: Principle and Instrumentation. Molecular vibrations, functional group and fingerprint region, factors influencing vibrational frequencies, sample preparation, characteristic frequencies of organic molecules and interpretation of spectra.

Nuclear magnetic resonance spectroscopy: principle and Instrumentation. Proton and Carbon–13 NMR, the chemical shift, magnetic equivalence, coupling constant, the intensity of NMR signals and integration. Factors influencing the chemical shifts.

Mass spectroscopy: Basic Principles- instrumentation, the mass spectrometer.

Ionization techniques - EI, CI, FAB, MALDI, fragmentation processes, and fragmentation associated with functional groups, rearrangement and mass spectra of some chemical classes.

Elementary idea of Chromatography: Column Adsorption chromatography, Thin Layer Chromatography, Gas Chromatography and High Performance Liquid Chromatography.

Section B

Metal-ligand bonding: Crystal field theory - crystal field splitting patterns in octahedral, tetrahedral tetragonal, square planar, square pyramidal and trigonal bipyramidal geometries- Determination of crystal field splitting energy - calculation of crystal field stabilization energies - Factors affecting crystal field splitting energies- spectrochemical series - MLCT and LMCT transitions in coordination compounds - Jahn-Teller effect –Molecular Orbital theory - ligand field theory.

Electronic spectra: Term symbols - Russell – Saunders coupling - derivation of term symbols for various configurations - Spectroscopic ground states - selection rules -correlation diagrams; Orgel and Tanabe-Sugano diagrams for transition metal complexes (d1-d9 states) - calculations of Dq, B and β parameters - charge transfer spectra.

Metal-Ligand Equilibria in solutions: Stepwise and overall formation constants and their interaction -Trends in successive formation constants - Factors effecting the stability of metal complexes with reference to the nature of metal ion and ligand - The chelate effect - Determination of formation constants by pH metry and spectrophotometry - The Irving-Williams series.

Mechanisms of Inorganic Reactions-I: Energy profile of a reaction - reactivity of metal complexes - Inert and labile complexes - Substitution reactions in octahedral complexes: kinetics of octahedral substitution, acid hydrolysis, factors affecting acid hydrolysis, base hydrolysis, conjugate base mechanism, anation reactions, reactions without metal ligand bond cleavage - Substitution reactions in square planar complexes - The trans effect in Pt(II) complexes - Polarisation and π-bonding theories of trans effect.

Mechanisms of Inorganic Reactions-II: Oxidation-reduction reactions- classification of redox reactions - mechanism of one electron transfer reactions - Inner sphere redox reactions - outer sphere redox reactions - mixed inner and outer sphere reactions - two equivalent-one equivalent reactions of thallium(III)-thallium(I) and Hg(I)-Hg(II).

Bioinorganic Chemistry: Metal ions in Biology; Molecular mechanism of ion transport across membranes- ionophores; Photosynthesis; Nitrogen fixation; Oxygen uptake proteins - hemoglobin and myoglobin; Electron transfer proteins - Cytochromes and Ferrodoxins; Inorganic medicinal compounds - superoxide dismutage mimics, vanadium based diabetic drugs and platinum containing anticancer agents.

Organometallic Chemistry: Introduction, Nomenclature, the 18-electron rule. Metal carbonyls, structure and bonding, vibrational spectra of metal carbonyls for bonding and structural elucidation, important reactions of metal carbonyls; preparation, bonding, structure and important reactions of transition metal nitrosyl, dinitrogen and dioxygen complexes; tertiary phosphine as ligand; Metallocenes-ferrocene; Catalysis by organometallic compounds - hydrogenation, hydroformylation, and polymerization.

Metal Clusters: Higher boranes, carboranes, metalloboranes and metallocarboranes. Metal compounds with metal-metal multiple bonds. Preparation, properties and structures of Re2Cl82-, Mo2Cl84-, Re2(RCOO)4X2, Cr2Cl93-, W2Cl93-, Re3Cl9, Re3Cl123-, Mo6Cl84+, Nb6Cl122+.

Solid State and Structural Chemistry: Crystal structures - close packing, body centered and primitive structures; Symmetry in crystals, Crystallographic point groups; Description of structures - AB structures (NaCl, CsCl, ZnS), AB2 structures (Rutile, Fluorite), A2B3 structures (β-Al2O3), ABO3 structures (perovskite) and AB2O4Spinels.

Nature of bonding in Organic Molecules: Localised and delocalised covalent bond, concept of aromaticity annulenes and hetero annulenes, inductive and mesomeric effects. Huckel's rule for aromaticity in benzenoid and non-benzenoid compounds, anti-aromaticity and homo-aromaticity. Introduction to types of organic reactions and reactive intermediates.

Stereochemistry and Stereoisomerism: Conformational isomerism and analysis in acyclic and simple cyclic systems - substituted ethanes, cyclopentane, cyclohexane, cycloheptane, cyclo octane and decalins. Optical isomerism - optical activity -molecular dissymmetry and chirality (Chiral centre, chiral axis, chiral plane), elements of symmetry. Fisher's projection D,L. and R,S. configurations - relative and absolute configurations, optical isomerism due to asymmetric carbon atoms, optical isomerism in biphenyls, allenes and spirans. Optical isomerism of nitrogenous compounds, racemisation and resolution - geometrical isomerism and E,Z configurations, properties of geometrical isomers. Recognition of symmetry elements and chiral structures, R-S-nomenclature, diastereoisomerism in acylic and cyclic systems inter conversions of Fisher, Newman and Saw-horse projections.

Addition Mechanisms: Addition to carbon-carbon multiple bonds. Addition reactions involving electrophiles, nucleophiles and free radicals, cyclic mechanisms, orientation and stereochemistry. 12

Rearrangements: Classification and general mechanistic treatment of nucleophilic, free radical and electrophilic rearrangements, Wagner–Meerwein, Tiffeneau–Demjanov rearrangement, Neber, Hofmann, Stevens ,Wittig and Fries rearrangements.

Natural Products: Isolation, structure elucidation and synthesis of alkaloids: atropine, nicotine, papaverine, purines: caffeine. flavonoids: quercetin: genestein. terpenoids: citral ,α- terpeneol, camphor.

Aliphatic and Aromatic Substitution Reactions: Nucleophilic - The SN2, SN1, SNi and SET mechanisms, neighbouring group participation, anchimeric assistance, classical and non classical carbocations, phenonium ions, norbornyl system, allylic, aliphatic, trigonal and vinylic carbon, factors effecting substitutions.

Electrophilic: SE1, SE2 and SEi Mechanisms and related effects.

Elimination Reactions: The E2, E1 and E1cB mechanisms and their orientation of the double bond. Reactivity-effects of substrate structure, attacking base, leaving group and the medium. Stereochemistry of eliminations in acyclic and cyclic systems, orientation in eliminations – Saytzeff and Hoffman elimination, Regio and stereo selectivity reactions.

Basic concepts of some organic reactions: Aldol, Stobbe, Cannizaro, Wittig, Grignard, Reformatsky Reactions. Openauer oxidation, Clemmensen reduction , Birch reductions, Michael addition, Mannich Reaction, Diels - Alder reaction, Ene-reaction, Bayer -Villiger Reaction, Wolf-Kishner reduction, Favorskii reaction, Chichibabin reaction. Vilsmeier, Robinson annulation.

Synthesis and Reactivity of the compounds with one heteroatom: Pyrrole, Furan, Thiophene, Pyridine, Quinoline, Isoquinoline, Indole, Benzofuran and Benzothiophene. 18

Synthesis and Reactivity of the compounds with more than one heteroatom Pyrazole, Imidazole, Oxazole, Isoxazole, Thiazole, Isothiazole, Pyridazine, Pyrimidine ,Pyrazine and Purine.

Organic Synthesis: Synthesis, reactions, mechanisms and selectivity involving the following classes of compounds – alkenes, alkynes, arenes, alcohols, phenols, aldehydes, ketones, carboxylic acids, esters, nitriles, halides, nitro compounds, amines and amides. Uses of Mg, Li, Cu, B, Zn and Si based reagents in organic synthesis.

Carboncarbon bond formation through coupling reactions: Heck, Suzuki, Stille and Sonogoshira. Selectivity in organic synthesis – chemo, region and stereoselectivity. Protection and deprotection of functional groups. Concepts of asymmetric synthesis – resolution (including enzymatic), desymmetrization and use of chiral auxilliaries. Carbon-carbon bond forming reactions through enolates (including boron enolates), enamines and silyl enol ethers. Michael addition reaction. Stereoselective addition to C=O groups (Cram and Felkin Anh models).

Pericyclic Reactions and Photochemistry: Electrocyclic, cycloaddition and sigmatropic reactions. Orbital correlations – FMO and PMO treatments. Photochemistry of alkenes, arenes and carbonyl compounds. Photooxidation and photoreduction. Diπmethane rearrangement and Barton reaction.

Theories of reaction rates: Collision theory, Arrhenious reaction; Theory of absolute reaction rates-Reaction coordinate, transition state, thermodynamic formulation of reaction rates; Unimolecular reactions- Lindemann's theory and RRKM theory; Reactions in solution- primary and secondary salt effects, effect of solvent on reaction rate; effect of substituent on reaction rate - Hamett and Taft equations with examples - Linear Free Energy relations. 13

Catalysis: Homogeneous catalysis- acid-base catalysis- mechanism of acid-base catalysis - Enzyme catalysis- Michaelis-Menten kinetics - Heterogeneous catalysis- Langmuir adsorption isotherm-unimolecular and bimolecular reactions-catalytic poisoning-active centers, surface area-determination of surface area with BET equation.

Complex reactions: Opposing, parallel and consecutive reactions (all first order type)- derivation of rate-law, Chain reactions- derivation of rate-laws for H2-Cl2 and H2-Br2 reactions; Fast reactions-study of fast reactions by flow methods and relaxation methods

Second law of thermodynamics: concept of entropy-entropy change in reversible process and irreversible process-entropy of mixing; Fugacity: concept-Determination- Variation of fugacity with pressure; concept of partial molar properties- chemical potential-significance-variation with preassure and temperature- Gibbs-Duhem equation; Van't Hoff reaction isotherm, Claussius-Claperyon equation

Third law of thermodynamics: Nernst heat theorem-determination of absolute entropy-limitations of third law of thermodynamics; Maxwell-Boltzmann, Bose-Einstein and Fermi-Dirac statistics, Partition function-rotational, translational, vibrational and electronic partition functions for diatomic molecules

Electrochemical cells: Measurement of EMF-Nernst equation-effect of complexation on electrode potential; Polarization-Decomposition potential and overvoltage- Factors affecting overvoltage-Importance of over-voltage; Activity and activity coefficients- determination of mean ionic activity coefficient by EMF method; Debye-Huckel limiting law (DHLL) and its verification, Extended Debye-Huckel law; Debye-Huckel-Onsagar equation(derivation not required)-verification and its limitations.

Applications: Batteries-primary and secondary cells – lechlanche cell, lead acid storage battery, Nickel-Cadmium cell; Fuel cells-Oxygen-hydrogen fuel cell; Corrosion- theories of dry and wet corrosion-different forms of corrosion- prevention and control of corrosion - cathodic protection-

sacrificial anodic and impressed current methods- inhibitors-anodic and cathodic inhibitors; protective coatings-galvanising and tinning 19

Adsorption: Gibbs adsorption isotherm, types of adsorption isotherms, physisorption and chemisorption, , Langmuir and Freundlich isotherms. BET equation (derivation not required) and surface area determination. Kinetics of surface reactions involving adsorbed species, Langmuir-Hinshelwood mechanism

Micelles: Surface active agents- classification- critical micellar concentration (CMC)- factors affecting the CMC of surfactants- determination of cmc. Solubilisation-factors influencing the solubilisation. Micellization-thermodynamics of micellization. Micro emulsions- comparision of microemulsions with conventional emulsions-applications. Reverse micelles.

Polymer chemistry: Basic concepts- monomers, repeat units, degree of polymerization, linear, branched and network polymers, classification of polymers. Polymerization-Free radical, ionic and co-ordination polymerization. Kinetics of condensation (step-growth), free-radical and ionic polymerizations. Physical characterization: Number and mass average molecular weights (Mn, Mw), Determination of molecular masses – Osmometry, viscometry and light scattering methods

Wave equation-interpretation of wave function-properties of wave function-normalization and orthogonalisation, operators-linear and non linear commutators of operators. Postulates of quantum mechanics, setting up of operators observables- Hermitian operator-Eigen values of Hermitian operator Particle in one dimensional box. 20

Particle in a three dimensional box, rigid rotor, wave mechanics of systems with variable potential energy- simple harmonic oscillator- solution of wave equation-selection rules.

Approximation methods: Perturbation theory- application to ground state energy of Helium atom; Variation principle-applications- calculation of zero point energy of harmonic oscillator. Many electron atom-Hartee-Fock Self consistent field method (qualitative treatment only).

Bonding in molecules: Born-Oppenheimer approximation- Hydrogen molecule ion, LCAO-MO and VB treatments of the hydrogen molecule (fundamental concepts only); electron density, forces and their role in chemical bonding. Hybridization and valence MOs of H_2O, NH_3 and CH_4. Huckel pi-electron theory and its applications to Ethylene, Butadiene and Benzene.

Symmetry and Group Theory in Chemistry: Symmetry elements and symmetry operations and point groups, Schoenflles symbols, classification of molecules into point groups, Axioms of group theory, group multiplication tables for C_{2v} and C_{3v} point groups, representations-reducible and irreducible representations, Mulliken symbols, orthogonality theorem (without proof) and its implications, Character table and its anatomy.

Spectroscopy-Unifying Principles: Electromagnetic radiation- interaction of electromagnetic radiation with matter- absorption, emission, transmission, reflection, refraction, dispersion and scattering Polarization: polarization of light; plane of vibration,plane of polarization, optical activity, factors effecting the angle of rotation, specific rotation, optical rotator dispersion and circular dichroism, cotton effect .

Vibrational and rotational Spectroscopy : Rotational spectra of diatomic molecules- rigid rotor-selection rules- calculation of bond length- isotopic effect- second order stark effect and its applications, infrared spectra of diatomic molecules-harmonic and anharmonic oscillators-Selection rules- overtones-combination bands-calculation of force constant-anharmonicity

constant and Zero point energy . Fermi resonance, simultaneous vibration-rotation spectra of diatomic molecules .

Raman Spectroscopy: Raman effect-Classical and quantum mechanical explanations- pure rotational, vibrational and vibrational-rotational Raman spectra- selection rules, mutual exclusion principle.

Electronic Spectroscopy: Electronic spectra of diatomic molecules- vibrational course structure-intensity of spectral lines- Franck-Condon principle –applications- rotational fine structure –band head and band shading- charge transfer spectra.

Electron Spin Resonance Spectroscopy: Basic principles, zero field splitting- factors affecting the 'g' value. Isotropic and anisotropic hyperfine coupling constants- experimental technique - applications of ESR studies:deuterium, methyl free radical, benzene free radical, parabenzo semi quinine, copper phthalo cyanine, chloroform, haemoglobin, glycene and alanine.