DEPARTMENT OF CHEMISTRY

Ph.D./M.Phil Entrance Test - 2021

Syllabus

A. Research Methodology

1. General Introduction and Principles of Analytical Techniques:

(a) Sampling in analysis, Theory of sampling importance of selecting a representative sample, criterion of a good sampling plan, Stratified sampling Vs. random sampling. Minimisation of variation in stratified sampling, sampling plan for solids, liquids and gases.

(b) Reliability of analytical data, Errors in chemical analysis, classification of errors, Minimisation of errors, accuracy and precision. Improving accuracy of analysis, correlation and Regression, linear regression.Analysis of variance.

(c) Thermogravimetric analysis, Introduction, Instrumentation, Factors affecting thermogravimetric results, applications of Thermogravimetry. Differential Thermal analysis and differential scanning calorimetry on line analysis.Thermometric titrations Introduction theory and applications.

(d) Spectrophotometry and Colorimetry, Theory of spectrophotometry and colorimetry, Beer's law, Deviation from Beer's law, absorptivity, Photometric accuracy. Spectrophotometric titrations and titration curves and applications to quantitative analysis.

(e) Chromatographic Techniques: Paper Chromatography, TLC, Column Chromatography, Gas Chromatography (Apparatus, detector and working) and HPLC (High performance liquid chromatography; Instrumentation, supports & detector).

2. General Introduction and Principles of Spectroscopic Techniques: UV-Visible, IR, NMR, Mass & ESR

(a) Ultraviolet and Visible Spectroscopy: Woodward Fieser Rules: Conjugated dienes α,β unsaturated carbonyl compounds and acyl benzenes. Numerical problems.

(b) Infrared Spectroscopy: Functional group identification: Alcolols, phenols, aldehydes, ketones, carboxylic acid, esters, amines, amides & amino acids.

(c) ^{1}H-NMR Spectroscopy : Nuclear spin resonance. Relaxation processes, Chemical shift: anisotropic effect, restricted rotation, temperature and hydrogen bonding, Spin-spin coupling, Coupling constants, simplification of complex spectra.

(d) ^{13}C-NMR spectroscopy: Carbon skelton identification-alkanes, alkenes, alkynes and aromatic rings.

(e) Mass spectrometry: Molecular ion, Base peak,metastable ion, nitrogen rule, McLafferty rearrangement, Mass fragmentations: Alcohols, phenols, ethers, aryl halides, aralkyl halides and amino acids.

(f) ESR: ESR of simple systems, McConnell's relationship, zero field splitting and Kramer's degeneracy.

B. Subject:

Inorganic Chemistry

(a) Structure and bonding: Theories of Bonding in Transition Metal complexes – Qualitative Approach , shape of molecules, Qualitative introduction to the molecular orbital theory, complexes with no pi bonding, complexes with pi-bonding, the crystal field and ligand field theories, orbital splitting and magnetic properties, the angular overlap model.

(b) Structural and Thermodynamic Consequences of Partly Filled- shells : Ionic radii, Jahn-Teller effects, thermodynamic effects of d-orbital splitting, magnetic properties of chemical compounds, origin of magnetic behavior, magnetic susceptibility and types of magnetic behavior : diamagnetism, paramagnetism, ferromagnetism : types of paramagnetic behavior : Large multiplet separation, small multiplet separations, spin only, heavy atoms, high spin-low spin cross overs.

(c) Spectral Properties: Russel - Saunder's term, selection rules, break down of selection rules, band widths and shapes, energy level diagrams and d-d complex spectra, Orgel diagrams - weak fields, charge - transfer spectra. Inner transition elements – spectral and magnetic properties.

(d) Group Theory and its chemical applications

Order, classes of group, representation of a group, transformation of coordinates matrices, matrix representation of symmetry operation, reducible and irreducible representations and C_{2v},C_{3v}, D_4, T_d, O_h, character tables, symmetry, the method of finding the number of irreducible representation in a reducible representation, separation of d orbitals under influence of octaheral, tetrahedral, square planar and trigonal bipyramidal symmetry, the separation of P, D, F etc. free ion terms into symmetry labelled electric field terms under the influence of octahedral field, the directed valence for T_d and $O_h$symmety, direct product for O_h, T_d, C_{3v}, D_{4h} and D_{5h} and the method of descending symmetry for d^2 configuration.

Suitable metal orbitals and ligand or orbitals combination to form molecular orbitals in coordination complexes O_h, T_d and square planar complexes, symmetry consideration regarding selection rules and spectral intensties, vibronic coupling, vibronic polarization in centrosymmetric complexes O_h and D_{4h} and non centro symmetric complexes C_{3v}, T_d polarization of electronically allowed transitions, selection rules.

(e) Bioinorganic Chemistry: Introduction, the biochemistry of Iron : iron storage and transport ferritin, transferrin, bacterial iron transport, hemoglobin and myoglobin, nature of the heme-dioxygen binding, model systems, cooperativity in hemoglobin cytochromes. The biochemistry of other metals: zinc (carboxypetidase A, carbonic anhydrase, metallothioneins), copper (superoxide dismutase (CuZn SOD), hemocyanins, oxidases), cobalt (cyanocobalamin), and molybdenum (nitrogenases). Chelates in chemotherapy, synthetic metal chelates as antimicrobial agents, lithium and mental health, gold and its compounds, metal complexes as antitumour agents, chelation therapy.

(f) Chemistry of the main group elements and their compounds:

Group I A to IV A Group Elements : Hydrogen : transition metal hydrides, the group IA elements – organometallic compounds of alkali - metals, the group II A - organo-beryllium and organo-magnesium compounds, the group III A elements - structure and bonding of polyhedral boranes, structural study by NMR, Wade's rules, carboranes and other hetro-boranes, organoboron compounds, organoalumium compounds, the group IV A element - compounds with C-N bonds, thiocarbonates, dithiocarbamates.

Group V A to VIII A Group Elements

The group V A elements - types of Covalence in nitrogen, stereochemistry, dinitrogen and nitrogen compounds as ligands, ammonia and amines, phosphorus-nitrogen compounds, group VI A elements - chemical properties of dioxygen, singlet oxygen, dioxygen superoxo and peroxo ligands peroxy compounds of boron, carbon, sulphur and sulphur - nitrogen compounds, sulphur - sulphur compounds as ligands, isoand heteropoly acids and anions of Mo and W. The group VII A elements the charge — transfer complexes of halogens, polyiodide anions, pseudohalogens, the group VIII A elements — the chemistry of xenon, krypton and radon.

(g) Organometallic compounds - synthesis, bonding and structure of metal carbonyls. Alkene complexes, Types of Alkene Complexes, Synthesis and Reactions of Alkene complexes, Alkyne and Alkyne - Derived Compounds. Allyl and Related complexes, Carbocyclic-□-Complexes, Three-membered, Four membered, Five membered Rings; Di - □5– cyclopentadienyls, Synthesis Gas and Water Gas shift Reaction, Reduction of carbon monoxide by Hydrogen. The Fischer- Tropsch Synthesis.Hydroformylation of Unsaturated Compounds.Hydrogenation of unsaturated groups.

Subject:
Organic Chemistry

1. Recall Reactive Intermadiate

- **(a)** Carbocations: Generation, Structure, Stability, Application of NMR spectroscopy in the detection of Carbocation, allylic and benzylliccarbocations. Stereochemistry and reactions.Nonclassicalcarbocations: Phenonium ion, norbornyl system, explaination based on rearrangement.
- **(b)** Carbanions : Generation, Structure, stability, stereochemistry, Tautomerism, Prototropy and general reactions.
- **(c)** Carbenes : Formation, Structure, Singlet & Triplet carbene, Stereochemsitry and reactions.
- **(d)** Nitrenes: Formation, Structure Singlet & Triplet nitrene, Stereochemsitry and reactions.
- **(e)** Arynes: Formation, Structure and reactions.
- **(f)** Free radicals: Formation, Structure, Stability, Stereo-chemistry and reactions.

2. Techniques used.for determination of reaction mechanism

(Non-kinetic method):

Use of optical, Stereochemical and isotopic techniques. Reaction studies from identification of products. Trapping of intermediate, crossover experiments, use of Catalyst, use of isotopes in reaction mechanism studies in case of Favorskii, Claisen's and Benzyne reactions.

3.Pericyclic Reactions

Molecular Orbital symmetry, Frontier Orbitals of ethylene, 1,3 - butadiene, 1, 3, 5-hexatrience and allylsystem. Classification of Pericyclic reactions. Woodward-Hoffman rule, correlation diagrams. FMO and PMO approach.

(a) Electrocyclic reactions - conrotatory and disrotatorymotions 4n, 4n+2 and allylsystems.

(b) Cycloadditions - antarafacial and suprafacial additions 4S+2S Systems and 2S+2S additions of alkene.

(c) Sigmatropic rearrangement - suprafacial and antarafacial shift involving carbon moieties. 3, 3-and 5, 5-sigmatropic rearrangement Claisen, Cope-rearrangement reactions.

4. Stereochemistry:

(a) Optical Isomerism:

Requirement for a compound to be optically active, compounds with one asymmetric centre. Dissymmetry as a cause of optical activity.Compounds with two asymmetric centres. Racemic Modification Racemisation: Thermal, anionic, cationic, free radical, epimerisation, Mutarotation Racemic compounds, mixtures and solid solutions.

(b) Disastereoisomerism:

Resolution of acids, bases, aminoacids, alcohols, aldehydes and ketones, Absolute and Relative configuation, Different systems of rotation.Assymetric induction, methods of determining the configuration.Cram's Rule and Prelog's Rule.

Subject:
Physical Chemistry

1. Thermodynamics

(a) Recall : Concepts involved in first and second law of thermodynamics, Entropy, free energy and chemical equilibrium. Thermodynamic equation of state.Maxwell relations.

(b) Non-ideal systems: Excess functions for non-ideal systems. Activity and activity coefficients and their determination.Concept of fugacity and its experimental determination.Partial molal properties and their determination.

(c) Third law of the thermodynamics: Indentification of statistical and thermodynamic entropy. Nernst postulate, Plank's contribution. Alternate formulation of third law.Cooling by adiabatic and demagnetisation.Evaluation of absolute entropy.

2. Electrochemistry

(a) Ion-solvent interactions: Born model of ion-solvent interactions, Structural models of ion-solvent interations. Experimental determination of salt-solvent interactions. Relative heats of solvation of ions in the hydrogen scale. Evaluation of ion-solvent interactions from experimental data of salt-solvent interactions.

(b) Ion-ion interactions: Debye-Huckel theory of ion-ion interactions. Verification of Debye-Huckel limiting law. Activity, coefficients at moderate concentrations and higher concentrations.Activity coefficients as a function of ion-ion and ion-solvent interactions. Mean activity coefficients and their experimental determination.

3. Angular Momentum

Ordinary angular momentum, the quantum mechanical operators for angular momentum. Eigen function and eigen values of angular momentum using ladder operators, addition of angular momentum.

4. Chemical Kinetics

(a) Introduction: Rate of reaction, empirical rate-equation, order and molecularity of a reaction, effect of temperature on reaction rates.

(b) Theories of reaction rates: Number of bimolecular collisions and derivation of rate constant from it, steric factor & its calculation, factors determining effectiveness of collisions, Lindemann mechanism, statistical derivation of rate equation (Eyring equation), transmission co-efficient, tunnelling effect, partition functions for translation, rotation & vibration, comparision of collision and transition state theories.