

Department of Chemistry

Syllabus for Ph.D. Entrance Test for Session 2023-24

Section-A

(Research Methodology)

Research Methodology and Research Publication

RPE 01: PHILOSOPHY AND ETHICS

1. Introduction to philosophy: definition, nature and scope, concept, branches
2. Ethics: definition, moral philosophy, nature of moral judgements and reactions.

RPE 02: SCIENTIFIC CONDUCT

1. Ethics with respect to science and research.
2. Intellectual honesty and research integrity.
3. Scientific misconducts: Falsification, Fabrication, and Plagiarism (FFP).
4. Redundant publications: duplicate and overlapping publications, salami slicing.
5. Selective reporting and misrepresentation of data.

RPE 03: PUBLICATION ETHICS

1. Publication ethics: definition, introduction and importance.
2. Best practices/standards setting initiatives and guidelines: COPE, WAME, etc.
3. Conflicts of interest.
4. Publication misconduct: definition, concept, problems that lead to unethical behavior and vice versa, types.
5. Violation of publication ethics, authorship and contributor ship.
6. Identification of publication misconduct, complaints and appeals.
7. Predatory publishers and journals.

RPE 04: OPEN ACCESS PUBLICSHING

1. Open access publications and initiatives.
2. SHERPA/RoMEO online resource to check publisher copyright & self-archiving polices.
3. Software tool to identify predatory publications developed by SPPU.
4. Journal finder/journal suggestion tools viz. JANE, Elsevier Journal Finder, Springer Journal Suggester, etc.

RPE 05: PUBLICATION MISCONDUCT

A Group Discussions (2 hrs.)

1. Subject specific ethical issues, FFP, authorship.
2. Conflicts of interest.
3. Complaints and appeals: ' examples and fraud from India and abroad.

B. Software tools

Use of plagiarism software like Turnitin, Urkund and other open source software tools.

RPE 06: DATABASES AND RESEARCH METRICS

A. Databases

1. Indexing databases.
2. Citation databases: Web of Science, Scopus etc.

B. Research Metrics

1. Impact Factor of journal as per Journal Citation Report, SNIP, SJR, IPP, Cite Score.
2. Metrics: h-index, g index, i10 index, altmetrics.

Molecular Luminescence Spectroscopy

Molecular Fluorescence Spectroscopy: Principles of molecular fluorescence, relaxation processes, relationship between excitation spectra and fluorescence spectra, fluorescence instrumentation, Applications of molecular fluorescence spectroscopy, molecular phosphorescence spectroscopy, Chemiluminescence methods: reactions that produce light, molecular scattering methods.

Atomic absorption spectroscopy

Elementary theory, instrumentation, flames, nebulizer burner system, graphite furnace technique. cold vapor technique and hydride generation, resonance line sources, monochromators, detectors, interferences, chemical interferences, background correction methods, atomic absorption spectrophotometers, application of atomic absorption spectroscopy, flame atomic absorption spectroscopy.

Atomic emission spectroscopy: Emission spectra, flame emission spectroscopy.

Liquid Chromatography

Introduction, Types of liquid Chromatography, Mobile Phase, Sample Injection Column design, Optimization of mobile phase, Gradient elution Column, Effect of column length. Effect of diameter. Ultraviolet and Luminescence detectors, Column efficiency. Deriyatization, Quantitative analysis.

Section-B
(Subject)
(Inorganic Chemistry)

Pi Bonding Ligand Complexes

Pi Acid Ligands CO as prototype, other pi acid ligands-isocyanide ligands, dinitrogen, the CS ligands, the NO ligands, pi acid ligands : trivalent phosphorus compound, multiple bonds from ligands to metal, pi complexes of unsaturated organic molecules : alkene & alkyne, enyl ligands, aromatic ring systems.

Theories of Bonding in Transition Metal complexes - Qualitative Approach :

Qualitative introduction to the molecular orbital theory, complexes with no pi bonding, complexes with pi-bonding, the crystal field & ligand field theories, orbital splitting and magnetic properties, the angular overlap model.

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.

Spectral Properties

Russel - Saunder's term, selection rules, break down of selection rules, band widths & shapes, energy level diagrams and dd complex spectra, Orgel diagrams - weak fields, charge - transfer spectra, photochemical reactions of chromium & ruthenium complexes.

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, other iron - porphyrin bimolecule peroxidases & catalases, cytochrome P₄₅₀ enzymes, other natural oxygen carriers - hemerythrins, iron - sulfur proteins. The biochemistry of other, metals : zinc, carboxypeptidase A, carbonic anhydrase, metallothioneins, copper, superoxide dismutase (CuZn SOD) hemocyanins, oxidases, cobalt, molybdenum & tungsten, nitrogenases, miscellaneous other elements : vanadium, chromium & nickel metal ions and chelates in chemotherapy, synthetic metal chelates as antimicrobial agents, lithium and mental health, gold and its compounds, metal complexes as antitumour agents, chelation therapy.

Chemistry of Main Group Elements

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, organoaluminium compounds, the group IV A element - compounds with C-N bonds, thiocarbonates, dithiocarbamates, zeolites, clays.

Chemistry of Main Group Elements

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 peroxy ligands peroxy compounds of boron, carbon, sulphur and sulphur - nitrogen compounds, sulphur - sulphur compounds as ligands, iso & heteropoly acids & 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.

Electronic Structure of Atom

Electronic states of complex atoms, anti-symmetry and Pauli's exclusion principle, Hartree method, Russel Saunder's terms and coupling schemes, term separation energies for p² and d² configurations.

Molecular Orbital Theory

Huckel Theory of conjugated systems, bond order and charge density calculation, applications of Huckel molecular orbital theory to ethylene, butadiene, cyclopropenyl radical, cyclobutadiene systems. Introduction to extended Huckel theory.

(Organic Chemistry)

Nature of Bonding in Organic Molecules

- (i) Introduction to fullerenes
- (ii) Aromaticity in benzenoid and non-benzenoid compounds, alternant and non-alternant hydrocarbons, Huckel's Rule, anti-aromaticity, homo-aromaticity, PMO - approach.
- (iii) Bonding weaker than Covalent :
Addition compounds, Crown ether complexes and Cryptands, inclusion compounds, Cyclodextrins, Catenanes and rotaxane.

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 etc. use of isotopes in reaction mechanism studies in case of Favorskii, Claisen's and Benzyne reactions.

Elimination Reactions

- (a) E_2 , E_1 and E_1 CB mechanism, Stereochemistry Product ratio, Orientation of double bond, Hofman Rule, Saytzeff Rule. Factors Governing E_2 & E_1 Mechanism.
- (b) Cyclic Elimination : Amine Oxide, Esters, Xanthate, and Free radical elimination. Dehalogenation by zinc. Triple bond by elimination. Elimination versus substitution. Effect of solvent, temperature, Nature of Base, Structure of the reactants.
- (c) Aromatic Elimination : Benzyne, Nucleophilic aromatic substitution, addition elimination.

Stereochemistry

Stereoisomerism : Introduction and different types of stereoisomers.

Fischer, Newman and saw horse representations for organic Molecules.

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.

Disastereoisomerism

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

Conformation Isomerism

Meaning of conformation, Conformation and reactivity in alicyclic compounds. Conformation and Physical properties, dipole moment, NMR, IR and X-rays, conformational effects on stability and reactivity. Ionic elimination. Intra molecular rearrangement, Neighbouring group participation. Elimination. Pyrolysis of acetate, Xanthates and amine oxide. Relation of conformation to reactivity. Optical Isomerism due to restricted rotation in biphenyls allenes, Alkylidenes and spiranes.

Systems

Conformational studies in Cycloalkanes; mono and disubstituted Cycloalkanes. Its stability and reactivity. Energy determination in chair and boat form. Studies in fused systems. Decalins and Perhydrophenanthrenes.

Geometrical Isomerism

Nomenclature (E & Z) Nature of geometrical isomerism and determination of Configuration Curtin – Hammet Principle Study of Physical properties of the isomers, Relative stability and interconversion of Geometrical isomers.

(Physical Chemistry)

Thermodynamics

- (i) Recall : Concepts involved in first and second law of thermodynamics, Entropy, free energy and chemical equilibrium. Thermodynamic equation of state. Maxwell relations.
- (ii) 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.
- (iii) Third law of the thermodynamics : Identification of statistical and thermodynamic entropy. Nernst postulate, Planck's contribution. Alternate formulation of third law. Cooling by adiabatic and demagnetisation. Evaluation of absolute entropy.
- (iv) Thermodynamic and living systems : Simultaneous or coupled reactions. Coupled reactions and metabolism. Free energy utilisation in metabolism. Terminal oxidation chain. Overall metabolic plan. General thermodynamic consideration of living systems.

Electrochemistry

- (i) Ion-solvent interactions : Born model of ion-solvent interactions, Structural models of ion - solvent interactions. 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.
- (ii) 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.
- (iii) Conductance and Ionic mobilities : Conductance of electrolytic solution. Variation of equivalent conductance with concentration. Debye - Huckel - Onsager theory. Modification of Debye - Huckel - Onsager equation. Ionic conductances. Ion-association and ion-pair formation. Ion-triplets in electrolyte solutions. Ion-triplets and conductance.

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.

Chemical Kinetics

1. Introduction : Rate of reaction, empirical rate-equation, order and molecularity of a reaction, effect of temperature on reaction rates.
2. 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, comparison of collision and transition state theories.
3. Fast reactions : Study of fast reactions by stopped flow technique, relaxation methods, magnetic resonance technique.