**Chemistry – Pre Ph.D. Syllabus**

**PAPER – I: RESEARCH METHODOLGY**

**(Common for all Specializations)**

**PART-A**

**Unit-I: Research Design & Ethics**

1. **Objectives and types of research**: Motivation in research. Approaches and significance of research. Research and scientific methods. Selecting the problem. Technique involved in defining a problem (hypothesis). Interpretation and report writing. Significance of report writing. Different steps in writing report. Stages of writing. Designing illustrations, tables, figures, general guidelines for illustrations. Oral presentation. Citation methods. Impact factor.
2. **Research Ethics**: Ethics in research. Misconduct and consequences. Forms and consequences of plagiarism. Intellectual property rights. Copy right regulations and patents.

**Unit-II: ICT in Research and Data Analysis**

1. **Use of ICT for research purposes** – Internet and web-based resources. Search engines. Advanced search techniques. Use of web as a tool for scientific literature survey.
2. **Data Analysis –** Types of errors. Accuracy and Precision. Least square analysis, average and standard deviations. Correlation and Regression analysi**s.** Methods of least squares. Regression versus correlation. Correlation versus determination. Types of correlation and their specific applications.

**PART-B**

**Unit-III: Infrared and Electronic Spectroscopy**

1. **Infrared Spectroscopy:** Vibrational energy of diatomic molecules. Anharmonic oscillator. Selection rules, Overtones, Hot bands, Zero point energy. Calculation of force constant of diatomic molecules. Rotational—Vibrational spectra, P, Q, R-branches. Instrumentation. Sampling techniques. Functional group frequencies. Factors influencing vibrational frequencies, Coupled vibrations, Fermi resonance, Combination bands. Applications of IR Spectroscopy in structure elucidation of organic molecules; cis-trans isomers, keto-enol tautomers, hydrogen bonding. IR spectra of metal coordinated NO3-, SO42- and CO32- ions
2. **Electronic Spectroscopy:** Electronic spectra: Elementary energy levels of molecules-selection rules for electronic spectra; types of electronic transitions in molecules. Chromophores: Congugated dienes, trienes and polyenes, unsaturated carbonyl compounds, Benzene, mono substituted derivative (Ph-R), di substituted derivative (R-C6H4-Rʹ) and substituted benzene derivatives (R-C6H4-CORʹ), Woodward-Fieser rules. Polynuclear aromatic compounds (Biphenyl, stilbene, naphthalene, anthracene, phenanthrene and pyrene). Heterocyclic systems. Absorption spectra of charge transfer complexes. Solvent and structural influences on absorption maxima, stereochemical factors. Cis-trans isomers, and cross conjugation. Beer’s law application to mixture analysis and dissociation constant of a weak acid.

**Unit-IV: 1H and 13C NMR spectroscopy**

**(a) 1H NMR spectroscopy:** Magnetic properties of nuclei, Principles of NMR Instrumentation, CW and pulsed FT instrumentation, equivalent and non-equivalent protons, enantiotopic and diastereotopic protons, Chemical shifts, factors affecting the chemical shifts, electronegativity and anisotropy, shielding and deshielding effects, Signal integration, Spin-spin coupling: vicinal, germinal and long range, Coupling constants and factors affecting coupling constants. Applications of 1H NMR spectroscopy: Reaction mechanisms (cyclic bromonium ion, electrophilic and nucleophilic substitutions, carbocations and carbanions), E, Z isomers, conformation of cyclohexane and decalins, keto-enol tautomerism, hydrogen bonding, proton exchange processes (alcohols, amines and carboxylic acids), C-N rotation. Types of 1H NMR First order and non-first order spectra e.g., AX, AX2, AX3, A2X3, AMX and AB, ABC. Simplification of complex spectra: increased field strength, Lanthanide shift reagents and double resonance techniques. Nuclear Overhauser enhancement (NOE) and its applications.

**(b) 13C NMR (CMR) Spectroscopy:** Equivalent and non-equivalent carbons, enantiotopic and diastereotopic carbons, Types of CMR spectra, Chemical shifts and coupling in CMR. Factors effecting on Chemical shifts and coupling constants.

**Unit-V : Mass Spectrometry:**

Origin of mass spectrum, principles of EI mass spectrometer. Types of fragments: odd electron and even electron containing neutral and charged species (even electron rule), Nitrogen rule, isotopic peaks, determination of molecular formula, metastable ion peaks. High resolution mass spectrometry. Salient features of fragmentation pattern of organic compounds including β-cleavage, Mclafferty rearrangement, retro Diels – Alder fragmentation and ortho effect. Principle of EI, CI, Fast Atom Bombardment (FAB), Secondary Ion Mass Spectrometry (SIMS), Electrospray (ESI) ionization method.

**References:**

1. Research Methodology: Methods and techniques - C. R. Kothari, 2nd Edn, (New Age International Publishers).
2. Research methodology and statistical tools – P. Narayana Reddy and G. V. R. K. Acharyulu. Ist Edn, (Excel books, New Delhi, 2008).
3. Statistical Methods – S. P. Gupta. (S. Chand & Sons, New Delhi, 2005).
4. R. Ganeshan. Research Methodolgy for Engineers (MJP Publications, 2011).
5. Principles of Instrumental analysis, 5th edition. Skoog (Hollar and Nieman Harcourt, Asia).
6. Vogel’s text book of quantitative chemical analysis 6th Edn. Mendham, Denney, Barnes and Thomas. Low Price edition.
7. Spectroscopy of organic compounds – P. S. Kalsi (New Age International).
8. Organic spectroscopy – Jag Mohan (Narosa Publishers)
9. Elementary Organic Spectroscopy – Y. R. Sharma (S. Chand & Company).
10. Molecular Spectroscopy – William Kemp (ELBS).
11. Applications of Spectroscopy – J. Dyer
12. Fundamentals of Molecular Spectroscopy – Banwell & M C Cash (Tata Mc Graw Hill)

**PAPER – II:ORGANIC CHEMISTRY**

**SECTION-A**

**Unit-I: Heterocycic compounds**

Synthesis and reactivity of imidazoles, isoxazoles, thiazoles, oxazoles, benzimidazoles, quinolines, acridines, Indoles, Coumarins, Quinazolines, Quinoxalines and Cinnolines.

**Unit-II: Reactive intermediates and Molecular rearrangements**

**A) Reactive Intermediates:**Generation, detection, structure, stability and reactions of carbocations, carbanions, carbenes, nitrenes and free radicals.

B) M**olecular rearrangements**: Definition and classification. Molecular rearrangements involving 1) electron deficient carbon: Wagner- Meerwein, Pinacol-Pinacolone and Wolf rearrangement. 2) electron deficient Nitrogen: Hofmann, Lossen, Curtius, Schmidt and Beckmann rearrangements 3) electron deficient Oxygen: Baeyer-Villiger oxidation. 4) Base catalysed rearrangements: Benzilic acid, Favourski, Sommlett-Hauser and Smiles rearrangement.

**SECTION-B**

**Unit-III: Synthetic Reagents**

(i) Oxidations: a) Oxidation of active C-H functions: SeO2. b) Alkenes to diols: Prevost and Woodward oxidation c) Alcohol to carbonyls: Cr(6+) oxidants (Jones reagent and PCC) and Swern oxidation d) Oxidative cleavage of 1,2-diols using Periodic acid. (ii) Reductions:a) Wilkinsons’s catalytic hydrogenation. b) Non-metallic reductions: Diimide c) Dissolving metal reductions: Birch reduction. d) Reductions by metal hydrides: LiAlH4, NaBH4, BH3 and DIBAL. (iii) Synthetic applications of Grignard reagent, Gillman reagent, LDA, Trimethyl silyl chloride, Thexyl borane and Merrifield resin.

**Unit-IV: Pericyclic Reactions**

Orbital representation of molecular orbitals. Understanding of bonding, non-bonding orbitals and anti bonding. Symmetry properties of molecules with 2, 3, 4, 5, 6 & 7 contiguous sp2 carbon systems with special reference to plane of symmetry and two–fold simple axis of symmetry. Electrocyclic reactons of (4n) and (4n+2) electron systems. OCD method: Cycloadditions, 4n and 4n+2 systems— OCD method. Endo preference to Diels-Alder reaction. (1,3), (1,5), (1,7) Sigmatropic rearrangements, Cope and Claisen rearrangements, Sommlet-Hauser rearrangement. FMO approach for Electrocyclic reactions, Cycloadditions and Sigmatropic rearrangements. Elementary treatment of PMO approach to explain Pericyclic reactions. Exercises based on Pericyclic reactions.

**Unit-V: Green synthesis and new synthetic reactions:**

**A) Green Synthesis:i**) Microwave Assisted Organic Synthesis: Introduction, benefits and limitations. a) Microwave assisted reactions in organic solvents: Esterification and Diels- Alder reaction. b) Microwave assisted Solvent-free reactions: Saponification of esters and synthesis of nitriles from aldehydes. ii) Ultrasound Assisted Organic Synthesis: introduction and applications of ultrasound-Cannizaro reaction and Strecker synthesis. iii) Organic Synthesis in Green Solvents: introduction. a) Aqueous Phase Reactions: Diels-Alder and Hoffmann elimination reaction. b) Organic Synthesis using Ionic liquids: Introduction, applications-Beckmann rearrangement.

**B) New synthetic reactions:** Suzuki, Heck, Sonogishira, Shapiro, McMurrey, Ugi, Mannich, Nazerov, Baylis-Hilman, Mitsunobu, Stork-enamine and Michael reactions with mechanisms.

**References:**

1. Heterocyclic Compounds – R. K. Bansal.
2. Heterocyclic Chemistry – Jack & Smith.
3. Organic Synthesis – O. House.
4. Organic Synthesis – Michael Smith.
5. Pericyclic reaction – Mukherjee & Singh..
6. Photochemistry & Pericyclic reactions – Jagadamba Singh & Maya Singh..
7. Organic Chemistry Vol.II – I. L. Finar.
8. Reagents – Fieser & Fieser.
9. Green chemistry, Theory and Practical, Paul T.Anastas and John C.Warner.
10. New trends in green chemistry By V.K.Ahulwalia and M.Kidwai.
11. Some modern methods of organic synthesis by W. Carruthers
12. Organic Reactions and their mechanisms by P.S.Kalsi
13. Organic reaction mechanisms by V.K.Ahulwalia and Rakesh Kumar Parashar
14. Reactions, rearrangemtns and reagents by S. N. Sanyal

**PAPER – II:INORGANIC CHEMISTRY**

**SECTION-A**

**Unit – I: Coordination Chemistry – I: Bonding and electronic Spectra of Metal Complexes**:

1. Crystal Field Theory and its Limitations; Molecular Orbital Theory & Ligand Field Theory – Symmetry classification of metal and ligand orbitals in cubic and non-cubic environments; octahedral, square planar and tetrahedral geometries; Concept of ligand group orbitals; Molecular Orbital Energy level Diagrams for Oh, D4h and Td metal complexes with - and -bonding contribution.
2. Electronic Spectra: Ligand field terms, Orgel diagrams for d1 – d9 configurations; Tanabe & Sugano diagrams for d2 and d6 configurations; Jahn-Teller Effect – Crystal Field Spectra of Oh and Td metal complexes of 3d metals; Calculation of 10Dq values, Racah and Nephelauxetic parameters; Charge Transfer Spectra.

**Unit – II: Coordination Chemistry – II: Stabilities of Metal Complexes and Host-Guest Chemistry:**

1. Stabilities metal complexes in solution; Stepwise and overall stability constants; Determination of stability constants by spectrophotometric and pH-metric methods; Factors affecting the stability of metal complexes (Metal and Ligand factors); chelate effect, macrocyclic effect and cryptate effect.
2. Host-Guest Chemistry: Ligands for binding cations, anions and neutral molecules; Macrocyclic ligands and Cryptands; Types of interactions in Host-Guest complexes, Importance of supramolecular interactions in biology and chemistry; Molecular self-assembly; Molecular sensors.

**SECTION-B**

**Unit – III: Instrumental Methods of Analysis:**

1. Electrometric Methods: polarography and cyclic voltametry:
2. Thermal methods of Analysis: Principle and instrumentation techniques of Thermogravimetry (TG), Differential Thermal Analysis (DTA) and Differential Scanning Calorimetry (DSC). Interpretation of TG curves; factors affecting TG curves. Complimentary applications of TGA, DTA and DSC.
3. Atomic Absorption Spectrometry (AAS): Principles of AAS, Instrumentation – Flame and Furnace Atomic Absorption Spectrometers; Sensitivity and detection limits in AAS; Interferences – chemical and spectral. Applications of AAS in qualitative and quantitative analysis.

**Unit – IV: Bioinorganic Chemistry:**

1. Metalloenzymes: Zinc enzymes – Structural and mechanistic aspects of Carbonic anhydrase, Carboxy peptidase; Role of Zinc; Iron enzymes – Structural and mechanistic aspects of Cytochrome P450, Cytochrome oxidase and peroxidise; Role of Iron. Metalloporphyrins: Hemoglobin – structure, dioxygen binding and transport; physiology of haemoglobin; Synthetic oxygen carriers,
2. Metal ions in protein folding: Selection and insertion of metals for protein sites; Metal ion folding and cross linking of biomolecules; Calcium and Zinc binding domains in nucleic acids; Protein binding to metallated DNA.

**Unit – V: Organometallic Chemistry:**

1. Organometallic compounds of transition metals: metal carbon bond and hapticity; 18 electron rule – Importance in stabilizing structures and reactivities of organotransition metal complexes; General methods of preparation of organotransition metal complexes. Applications of organotransition metal complexes in organic synthesis.
2. Organometallic compounds in homogenous catalysis: Catalytic reactions and the valence electron (16 vs 18) rule; Oxidative addition, reductive elimination and - and -elimination reactions; detailed study of – hydrogenation; olefin oxidation (Wacker’s process); Oligomerization and Polymerization reactions (Ziegler-Natta Catalysis).

**Reference Books**:

1. Advanced inorganic chemistry; F. A. Cotton, G. Wilkinson, C. A. Murillo and M. Bochmann, 6th edn. (Wiley Interscience, NY 1999).
2. Inorganic Chemistry, J. E. Huhey, K. A. Keiter and R. L. Keiter, 4th edn. (Harper Cottens College Publications, 1993).
3. Inorganic Chemistry; K. F. Purcell and J .C. Kotz, Holt-Saunders. (International Edn, London 1977).
4. Symmetry and spectroscopy of molecules; K. Veera Reddy, 2nd edn. (New Age International Ltd.)
5. Electronic spectroscopy; A. B. P. Lever.
6. Infrared and Raman spectroscopy of inorganic and coordination compounds, K. Nakamoto
7. Structural methods in Inorganic Chemistry; E. A. V. Ebsworth, D. W. H. Rankin and S. Craddock, ELBS
8. Physical methods in Chemistry; R. S. Drago, (Saunders College Publishing, 1977).
9. Principles of instrumental analysis; Skoog, Holler and Wieman, (Harcount Asia Pvt Ltd.)
10. Instrumental methods of analysis; Willard, Dean and Settle
11. Principles and Practice of Analytical Chemistry; F. W. Fifield & D. Kealy (Backwell Science Ltd.)
12. Principles of Bioinorganic Chemistry; S. J. Leppard and J. M. Berg.
13. Bioinorganic Chemistry; Bertini, Gray, Lippard and Valentine.
14. Inorganic biochemistry; J. A. Cowan, (VCH Publications).
15. Supramolecular Chemistry; J. M. Lehn.
16. Core concepts in Supramolecular Chemistry and Nanochemistry; J. W. Steed, D. R. Turner and K. Wallace, Wiley 2007.
17. Principles and applications of organotransition metal chemistry; Collman.
18. The Organometallic chemistry of transition metals; Crabtree.
19. Metalloorganic chemistry; Pearson.
20. Homogenous catalysis by metal complexes; M. M. Taqui Khan and A. E. Martel, Vol. I & II.
21. Homogenous catalysis; G. W. Parshall, John Wiley & Sons, New York.

**PAPER – II:PHYSCIAL CHEMISTRY**

**SECTION-A**

**Unit-1: Thermodynamics**

Second law of thermodynamics: Different statements of the law. Concept of entropy, standard entropy, entropy of mixing. Third law of Thermodynamics, calculation of absolute entropies of solids, liquids and gases, tests and exceptions. Clausius-clapeyron equation.

Non-ideal systems: Fugacity of a gas, determination (general and graphical method).Activity and activity coefficients of electrolyte solutions. Determination of activity coefficients by using Debye-Huckel equation and EMF method.

Non-ideal mixtures: Concept of partial molar properties, partial molar free energy, chemical potential-Gibbs-Duhem equation. Thermodynamics probability, Maxwell-Boltzmann distribution law, partition functions. Molar and molecular partition functions. Translational, rotational, vibrational and electronic functions. Relation between Thermodynamic functions (E, H, S and G) and partition functions.

**Unit-II: Electrochemistry**

Conductance, specific conductance, equivalent conductance (⅄c and *⅄*∞) and molar conductance. Effect of dilution on specific, equivalent and molar conductance. Conductance of strong electrolytes, Debye-Huckel theory of strong electrolytes. Ion association, ion-pair formation, triples ions and conductance minima.

Electrochemical cells: Types of electrodes, thermodynamic formulation of Nernest equation of cell emf. Relation to the thermodynamic parameters.

Polarization: Electrode polarization and concentration polarization. Decomposition potential and over-voltage.

Polarography: Principle involved in polarography, current-voltage curves, diffusion current, IIkovic equation, polarographic maxima, half-wave potential and its applications.

**SECTION-B**

**UNIT-III: Kinetics**

Rate, order, molecularity of a reaction, determination of order of a reaction. Theory of absolute reaction rates. Applications of reactions between atoms and molecules. Thermodynamic formulation of reaction rates. Calculation of activation parameters. Simultaneous reactions: Derivation of first – order rate expression for parallel, opposing and consecutive reactions, explosive reactions and oscillatory reactions.

Kinetics of fast reactions: Flow methods. Stopped flow and Continuous flow methods. Relaxation methods. Relaxation time and its relation to rate constant .Temperature jump and pressure jump methods. Flash photolysis.

Substituent effect: Effect of substitution on the reaction rates –Hammett’s equation, Modification of Hammett’s equation constants. Yukawa-Tsuno equation. Non-linear Hamett’s plots, concept of isokinetic temperature and its determination.

**UNIT-IV: Quantum Chemistry**

Schrodinger wave equation, properties of wave equation. Postulates of Quantum mechanics- Applications to a particle in one dimensional box and three dimensional box.

Approximation methods: variation methods- principle and application to hydrogen atom. Perturbation method , first order correction terms of energy. Application to particle in one dimensional box under an electric field. Labeling of molecular orbitals. Molecular orbital diagram of homo and hetero nuclear diatomic molecules like H2, N2, O2, Cl2 , HF, CO and NO.

Concept of hybridization-sp, sp2 and sp3 hybrid wave functions. HMO theory of ∏- electron systems. Application to ethylene, butadiene and allyl systems. Calculation of resonance energy , free valency index, bond order, electron density, charge density and HMO coefficients.

**UNIT-V: Catalysis**

Homogeneous catalysis: Acid-base catalysis-protolytic and prototropic mechanism. Acidity functions determination. Zucker- Hammett’s hypothesis, Bunnet-Olson’s criteria of acid-base catalysis.

Heterogeneous catalysis: B.E.T. equation (derivation) and its limitations. Mechanism of heterogeneous catalysis. Langmuir-Hinshelwood mechanism and Langmuir-Reidel mechanism.

Phase Transfer Catalysis: Classification , characteristics and criterion for P.T.C catalysts. Mechanism and types of phase transfer catalysed reactions. Application to hydrolysis, oxidation, esterification and formation of ethers.

Enzyme catalysis: Kinetics and mechanism of single substrate reaction. Michaelis-Menten law- Brigg’s Haldane modification. Lineweaver-Burk plots. Influence of temperature and pH on the enzyme reaction.

Metal-ion catalysis: Molecular activation, proximity interaction and catalytic cycle. Application to hydrogenation , isomerisation, oxidation and hydroformylation. Zieglar-Natta polymerization. Mono metallic mechanism versus Bi-metallic mechanism.

**References:**

1. Chemical kinetics- K.J.Laidler

2. Enzyme castalysis- K.J.Laidler

3. Principles of Physical Chemistry- S.H. maron & C.F. Prutton

4. Thermodynamics-Samuel Glasstone

5. A Textbook of Physical Chemistry- Gurdeep Raj, Goel publishers.

6. A Textbook of Physical Chemistry- Puri and Sharma

**MODEL FOR BOTH PAPER-I AND PAPER-II**

**Time : 3 hours Max. Marks: 100**

**[Two questions from each Unit]**

**[Each question carries 14 ]**

**[The candidate has to answer any five questions]**

1. (a) [10 Marks]

(b) [10 Marks]

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