PhD Course Work – Chemistry
Paper I
RESEARCH METHODOLOGY

Unit- I – Research Methodology

Research formulation:

Motivation and objectives of the research problem – Selecting the problem. Necessity of defining the problem – Importance of literature review in defining a problem – Literature review – Primary and secondary sources – reviews, treatise and monographs – patents – web as a source - searching the web – Critical literature review – Identifying gap areas from literature review – Development of working hypothesis. Research design – Basic Principles- Need of research design – Features of good design – Important concepts relating to research design – Observation and Facts, Laws and Theories. Prediction and explanation, Induction, Deduction, Development of Models. Developing a research plan – Exploration, Description, Diagnosis, Experimentation. Methods of data collection – Sampling Methods – Data Processing and Analysis strategies.

Reporting and thesis writing:

Structure and components of scientific reports – Types of report – Technical reports and thesis – Significance - Different steps in the preparation – Layout, structure and Language of typical reports – Illustrations and tables – Bibliography, referencing and foot notes – Oral presentation – Planning – Preparation – Practice – Making presentation – Use of visual aids – Importance of effective communication – Ethical issues - Reproduction of published material – Plagiarism – Citation and acknowledgement.

Unit- II

Thermal methods of analysis: Thermogravimetry, Differential Thermal Analysis and Differential Scanning Calorimetry, instrumentation. Methodology of TG, DTA and DSC.

Atomic Absorption Spectroscopy (AAS): Principles of AAS, Instrumentation – flame AAS and furnace AAS, resonance line sources (hallow cathode lamp, electrode less discharge lamp), sample introduction system (pneumatic nebulizer), sensitivity and detection limits in AAS, interferences –chemical and spectral, evaluation methods in AAS and applications in qualitative and quantitative analysis.

Electron Probe Techniques: Scanning electron microscopy (SEM) – Principle, Instrumentation, applications. Transmission Electron Microscopy (TEM) - Principle, Instrumentation, applications. Energy Dispersive X-ray Spectroscopy (EDX) - Principle, Instrumentation, applications.

Theory and principles of fluorescence spectroscopy. Characteristic of fluorescence emission. Fluorescence life time, quantum yield, Static and dynamic/collisional quenching and comparison. Fluorescence polarization and polarization spectra of a fluorophore. Application of Fluorescence quenching.

Brunauer-Emmett-Teller (BET) : Principle, Instrumentation, Determination of surface area using BET Equation

Unit-III

^{1}H and ^{13}C NMR Spectroscopy: Introduction, Principle, Instrumentation and Applications of ^{1}H and ^{13}C NMR Spectroscopy. First order and Non-first order spectra eg: AX, AX_2, AX_3, A_2X_3, AMX, AB and ABC. Nuclear Overhauser Enhancement (NOE)

Mass spectrometry, GC-MS and LC-MS: Principle of mass spectrometry, Instrumentation and Applications of mass spectrometry, Principles of EI, CI, Fast Atom Bombardment (FAB), Secondary Ion Mass Spectrometry (SIMS), Electrospray Ionization (ESI), Matrix Assisted Laser Desorption Ionization (MALDI). High Resolution Mass Spectrometry (HRMS) Introduction, Instrumentation and applications of Gas Chromatography- Mass spectrometry (GC-MS) and Liquid Chromatography-Mass Spectrometry (LC-MS) techniques.

Chromatography: Principle and applications of TLC and Column Chromatography. Principle, Instrumentation and applications of GC and HPLC

Unit-IV

Vibrational spectroscopy:

Infrared spectroscopy- Interaction of electromagnetic radiation with matter. Selection rules. Principle and instrumentation of FTIR.

Raman spectroscopy- Raman effect. Complementary nature of IR and Raman spectra.Typical applications of Raman spectroscopy – Strucure determination of molecules from IR and Raman spectroscopic techniques.

Electronic Spectroscopy: Elementary energy levels of molecules-selection rules for electronic spectra; types of electronic transitions in molecules. Chemical analysis by electronic spectroscopy.

X-ray Spectroscopy:

X-ray fluorescence (XRF) : Experimental method, Processes in X-ray fluorescence, K-emission spectrum of tin, L-emission spectrum of gold.

X-ray absorption: Absorption techniques, Absorption edge fine structure (AEFS spectra) and extended X-ray absorption fine structure (EXAFS) spectra.

Diffraction Techniques: X-ray diffraction: experimental methods of X-ray diffraction. Primitive and nonprimitive unit cells.Indexing the reflections. Identification of unit cells from systematic absences in diffraction pattern. Structure factor and its relation to intensity and electron density. Description of the procedure for an X-ray structure analysis.Typical examples.

References:

1. An introduction to research methodology, Garg. B.L, Karadia, R. Agarwal, F. and Agarwal, U.K., 2002 RBSA publishers
2. Kothari, C.R. 1990 Research Methodologt Methods and Techniques New Age International, 418 p.
3. Principles of Instrumental Analysis - Skoog, Holler, Nieman, 5th ed., Harcourt CollegePublishers, 1998.
4. Analytical Chemistry – Gary D. Christian, 6th ed., John Wiley and sons. Inc., New York1994.
5. Instrumental methods of Analysis - Willard, Merit, Dean, 6th ed., CBS Publishers &distributors, 1986.
6. Hand Book for Instrumental Techniques for Analytical Chemistry, Ed. Frank Settle,Prentice Hall, New Jersey, USA, 1997.5. Vogel's Text book of Quantitative Analysis – GJ Jeffery, J Bassett et al, 5th ed.,Longmann, ELBS Publications, 2000.
7. Principles and practice of Analytical Chemistry, F.W.Fifield & D Kealey, 5th Ed.Blackwell Seience, 2000.
8. Quantitative Chemical Analysis, Daniel C. Harris, 6th Ed. WH Freeman & Co. NewYork,2003.8. Analytical Chemistry An Introduction, Crouch, 7th Ed. Saunders CollegePublishing,2000.
9. Spectroscopic identification of organic compounds by R.M. Silverstein and F.X. Webster.
10. Organic spectroscopy by William Kemp
11. Mass Spectrometry for Chemists and Biochemists by M. Rose and R.A. W. Johnstone
12. Spectroscopic methods in organic chemistry by D.H. Williams and I. Fleming
13. Biological Mass Spectrometry by A.L. Burlingame
14. Principles and Practice of Biological Mass Spectrometry by Chhabil Das
15. Spectrscopic identification of organic compounds by R.M.Silverstein, G.C.Bassler and T.E.Morrill
16. NMR-A multinuclear introduction by William Kemp
17. Techniques and Practice of Chromatography by Scott Raymond P.W.
18. Principles and practice of modern chromatographic methods by K. Robards, P.R. Haddad and P.E. Jackson
19. Fundamentals of Molecular Spectroscopy, Banwell&McCash
20. Introduction to Molecular Spectroscopy, G. M. Barrow, McGraw Hill
21. Molecular Spectroscopy, J. D. Graybeal, McGraw Hill
22. Basic principles of Spectroscopy, R. Chang, McGraw Hill
23. Physical Methods for Chemistry, R. S. Drago, Affiliated East West Press
24. Vibrational Spectroscopy: Theory and Applications, D. N. Sathyanarayana, New Age International
25. Introduction to Raman Spectroscopy, J. R. Ferraro & K. Nakamoto, Academic Press

26. X-ray diffraction procedures for polycrysralline and amorphous materials, H. P. Klug & L. E. Alexander, John Wiley
27. Physical Chemistry, Ira N. Levine, McGraw Hill
28. Atkin's Physical Chemistry, P. Atkins & Julio de Paula, Oxford University Press
29. Molecular structure and Spectroscopy, G.Aruldas, Eastern Economic Edn.

Proposed Syllabus of Ph.D Course Work in Chemistry
Paper II
INORGANIC CHEMISTRY

UNIT I: GROUP THEORY, BONDING AND ELECTRONIC SPECTROSCOPY 15hrs

Group Theory

Point groups, Classes of Symmetry Elements of a Group: Similarity transformation, properties of conjugate elements, salient features about Classes, Classes of C_{2v}, C_{2h} and C_{3v} Reducible and Irreducible Representations, Properties of Irreducible Representations, Construction of Character Tables for C_{2v}, C_{2h} and C_{3v}. Application of character tables to IR and Raman activity of normal modes (H_2O, NH_3, Trans N_2F_2)

Bonding in Metal Complexes

Symmetry Classification of Metal and Ligand Group Orbitals – Construction of Molecular Orbital Energy Level Diagrams -Octahedral Metal Complexes with (i) Sigma (σ), (ii) sigma(σ) &Pi (π) and (iii) sigma (σ), Pi (π) and Pi* (π*) bonding contribution from the Ligands - Tetrahedral Metal Complexes with (i) Sigma (σ) and (ii) sigma(σ) &Pi (π), and Square Planar Metal Complexes with (i) Sigma (σ) and (ii) sigma(σ) &Pi (π) bonding contribution from the ligands.

Electronic Spectroscopy of Metal Complexes

Classification of Electronic Spectra for Metal Complexes, Selection Rules: Electric Dipole Transitions, Magnetic Dipole Transitions, Orbital Selection Rules, Spin Selection Rules, Relaxation in Selection Rules. Nature of Electronic Spectral Bands: Band Widths, Band Intensities. Factors Influencing Band Shapes: Jahn-Teller Effect, Spectrochemical Series, Nephelauxetic Effect. Calculation of 10Dq Values, Racah Parameter (B) and Nephelauxetic Ratio (β). Orgel diagrams, CT Spectra

UNIT II: IR, RAMAN AND ESR 15hrs

IR and Raman: Symmetry based selection rules of Infrared and Raman- symmetry requirements for overtone, binary and ternary combination bands- Fermi resonance. Application of IR spectroscopy in the structural elucidation of inorganic compounds and metal complexes- aquo, sulphato, carbonato, nitro and carbonyl metal complexes.

Multinuclear NMR: Characteristic Nuclear Properties of ^{1}H, ^{13}C, ^{19}F, ^{31}P and ^{15}N – Ranges of Chemical Shifts – Use of Chemical shifts and Coupling constants for the determination of simple inorganic and Coordination Compounds - 1)^{1}H-NMR: $PtHCl(PEt_3)_2$,$Pt(NH_3)_3(CH_3)_3$, BH_4^-, NH_4^+, CH_3CN, [^{6}h- C_7H_8 $Mo(CO)_3$], [^{7}h-$C_7H_7Mo(CO)_3]^+$, B_2H_6; $^{29}SiH_3SiH_3$, 2)^{19}F: BF_4^-, H_2PF_3 3)^{31}P: $Mo(CO)_3(PPh_3)_3$, [Rh $(PPh_3)_3Cl$] ,trans-$[PtCl_4(PEt_3)_2]$, $^{31}PF_2H(^{15}NH_2)_2$ 4) 13C; [^{4}h $C_8H_8Ru(CO)_3$], $Fe(CO)_5$, $Fe_2(CO)_9$, $Fe_3(CO)_{12}$, FeI $Cp(CO)_{12}$, [$^{13}C^{15}N$ $Co(DH)_2$Pyridine]. $^{13}C\{^{1}H\}$ NMR spectrum of σ-bonded C_6H_5 ligand.

Applications of ESR to Metal Complexes

Principle- Selection Rules. Hyperfine splitting, Zero field splitting and Kramers degeneracy. Factors affecting g values. Calculation of g values with simple examples. Intensities of '$g_{\|}$ and $g_{\perp}$peaks. Evidence for Metal-Ligand Bond Covalency- Cu(II)- Bis –Salicylaldimine. $[(NH_3)_5$ Co O_2 Co $(NH_3)_5]^{5+}$, Cu(II)- diethyldithiophosphinate, Vanadyldithiophsphinate, Copper(II) tetraphenylporphyrin, Co(II)- phthalocyanine, $K_2[IrCl_6]$. Interpretation of 'g' and 'A' values

from esr spectral data in- i) MnF_6^{4-}, ii) CoF_6^{4-}, and CrF_6^{3-}. ESR spectra of dinuclear Cu (II) complexes.

UNIT III: CATALYTIC ROLE OF OTMC AND SUPRAMOLECULAR CHEMISTRY

Catalytic Role of OTMC **15hrs**

Oxidative addition and Reductive Elimination : Stereochemistry and Mechanism of Oxidative Addition – Insertion Reactions – Hydrogenation of Olefins –Transfer Hydrogenation – Hydrosilation of Olefins – Isomerisation of Olefins – Ziegler –Natta Polymerization of Olefins – Oligomerization of Butadiene, Alkene Metathesis.

Reactions of Carbon monoxide and Hydrogen: Hydroformylation – Carbonylation –Syngas-Water gas shift Reaction (WGS) – Reactions of Syngas. Applications of Metal Clusters in Catalysis:Hydroformylation of Ethylene using $[HRu_3(CO)_{11}]$ – , Hydrogenation of Olefins.

Palladium catalyzed cross coupling reactions: The Heck reaction, Suzuki Miyaura coupling, Sonogashira coupling,Nagishi coupling.

SUPRAMOLECULAR CHEMISTRY

Host – Guest chemistry: Definition and different types of host and guests with examples – types of non-covalent interactions – binding constants of host guest complex and thermo dynamics involved in it – designing principles of host.

Cation guest binding – binding between metal cations and macro cycles – chelate and cryptate effects – relationship between cavity size of host and cation radius and stability of resultant complexes – binding of macro cycles having secondary binding sites.

Anion guest binding – different hosts for anionic guests capable of binding through electro static interactions, hydrogen bonds, lewis acidic hosts – enhancement of binding strength using more than non-covalent interactions.

Neutral guest binding – binding of neutral guest using hydrogen bonding, π - π stacking, hydrophobic effect and charge transfer interactions – simultaneous binding of cation and anion guests – cascade approach, individual binding sites and zwitter ions approach –present and future applications – phase transfer agents – separation of mixtures – molecular sensors – switches and molecular machinery

UNIT IV: METALLO-ENZYMES AND PLATINUM COMPLEXES IN CANCER THERAPY

Metallo-Enzymes **15hrs**

Copper Enzymes: Types of Copper in Biological Systems - Structural and Mechanistic Aspects of Superoxide Dismutase, Laccase and Galactose oxidase.

Zinc Enzymes: Structural and Mechanistic Aspects of Carbonic Anhydrase, Carboxy Peptidase,Leucin – aminopeptidase, Thermolysin, Alcohol Dehydrogenase - Role of Zinc.

Nickel Enzymes: Urease, Hydrogenase and Factor F430: Reactions Catalyzed, MechanisticAspects **Cobalt Enzymes:** Cobalt in Vitamin B12 - Structural Features of Vitamin B12 with reference to coordination of Cobalt - Different Oxidation States of Cobalt - Various forms of Vitamin B12 and Active Enzyme forms - Types of Reactions Catalysed by i) Methyl Cobalamin ii)DeoxyadenosylCobalamin - Mechanism of the Methyl Malonyl CoA conversion to Succinyl CoA - Role of the Apoenzyme - Unique features of Cobalt to suit Vitamin B12.

Iron Enzymes: Structural and Mechanistic Aspects of Cytochrome P450, Cytochrome oxidase, Catalase and Peroxidase - Role of the Metal Ion.

Platinum complexes in cancer therapy

Discovery applications and structure-effect Relationships. Cis-platin(cis$Pt(NH_3)_2Cl_2$) mode of action. Potential binding sites on nucleic acids and their bases and proteins. Drug resistance and DNA repair mechanism.

Physical effects of metal complex: DNA binding, unwinding, shortening and bending of the double helix. Biological consequences of platinum –DNA binding. Organic intercalators asdonor – acceptor pairs; Transition metal complexes as donor acceptor pairs. Non classical platinum antitumor agents.

SUGGESTED BOOKS

1. Symmetry and Spectroscopy of Molecules, K. Veera Reddy, Second Edition, New Age International (P) Limited Publishers (2009)
2. Chemical Applications of Group Theory, F. A. Cotton, 3rd edition, Wiley NY (1990)
3. Symmetry and Group Theory in Chemistry, Mark Ladd, Harwood Publishers, London (2000)
4. Symmetry through the Eyes of a Chemist, I. Hargittai and M. Hargittai, 2nd Edition, Plenum Press, NY (1995)
5. Molecular Symmetry and Group Theory, Robert L. Carter, John Wiley & Sons (1998)
6. Group Theory for Chemists, G. Davidson, Macmillan Physical Science Series (1991)
7. Molecular Symmetry, Schoenland
8. Electronic Spectroscopy, A. B. P. Leve, Elsevier (1997)
9. Introduction to Ligand fields, B. N. Figgis
10. Infrared and Raman Spectroscopy of Inorganic and Coordination Compounds, K. Nakamoto
11. Infrared spectroscopy of Inorganic Compound, Bellamy.
12. Principles of Instrumental Analysis– Skoog, Holler, Nieman, 5th ed., Harcourt College Publishers, 1998.
13. Introduction to Ligand Fields – Figgis, Wiley Eastern Ltd, 1966.
14. Inorganic Electronic Spectroscopy – A.B.P. Lever, Elsevier Publishing Company, London, 1968.
15. Hand Book for Instrumental Techniques for Analytical Chemistry, Ed. Frank Settle. Prentice hall, New Jersey, USA, 1997.
16. Analytical Chemistry – Gary D. Christian, 6th ed, John Wiley and sons. Inc., NewYork, 1994.
17. Infrared and Raman Spectra of Inorganic and Coordination Compounds, KazuoNakamoto, 5th ed., John Wiley & Sons, 1995.
18. Instrumental methods of Analysis - Willard, 6th ed., CBS Publishers &distributors, 1986.
19. Organometallics-A Concise Introduction, Ch.Eischeinbroich and Salzer-VCH
20. Organotransition Metal Chemistry Fundamental Concepts and Applications, John AkioYamamato, Wiley & Sons.
21. Homogeneous Catalysis by Metal Complexes, M MTaqui Khan and A E Martel
22. Applied Homogenous Catalysis with Organo Metallic Compounds Vol I & II, Boy Cornillsand W A, Herrmann – VCH
23. Organometallic Compounds, G E Coates, M C H Green, K Wade vol II
24. Advanced Inorganic Chemistry, Cotton and Wilkinson, V & VI Ed
25. Symmetry and spectroscopy, K Veera Reddy

26. Homogenous catalysis, G W Parshall, John Wiley & Sons, New York
27. Basic organometallic Chemistry, B.D. Gupta / A. J. Elias
28. Supramolecular Chemistry – concepts and perspectives by Jean-Marie Lehn
29. Principles and methods in Supramolecular chemistry, Hans-Jorg Schneider and A.Yatsimirsky, John Wiley and Sons
30. Analytical Chemistry of Macrocyclic and Supramolecular Compounds, S.M.Khopkar, Narosa Publishing House.
31. Structural Methods in Inorganic Chemistry, E. A. V. Ebsworth, D. W. H. Rankin and S. Craddock, ELBS.
32. Physical Methods in Chemistry, R. S. Drago, W.B. Saunders Co., 1977.
33. Physical Methods for Chemists, Russell S. Drago Second edition, Saunders College Publishing, 1992.
34. Principles of Instrumental Analysis, Skoog, Holler and Nieman.
35. Instrumental Techniques for Analytical Chemistry, Frank Settle.
36. Principles of Analytical Chemistry, M. Valcarcel.
37. Physical Methods in Advanced Inorganic Chemistry, Hill and Day
38. Magneto Chemistry, Dutta &Shyamal Oxford Chemistry Primers, Vol 62
39. Biochemistry - Geoffrey L. Zubay.
40. Biochemistry - Mary K. Campbell. (added these books)
41. Bioinorganic Chemistry, Bertini, Gray, Lippard and Valentine, University ScienceBooks, California USA 1994.
42. Principles of Bioinorganic Chemistry, S.J. Lippard and M.Berg University ScienceBooks, California 1994.
43. Biological Chemistry of Elements, J.J.R. Franstodasilva and R.J.P. Williams OxfordUniversity Press 1991.
44. Metal Ions in Biological Systems (Series), Ed. H. Sigel Marcel Dekkar, New York
45. Inorganic Biochemistry, J.A. Cowan, VCH publishers 1993.
46. Advances in Inorganic Biochemistry, edited by G.L.Eichorn&Marzilli
47. Bioinorganic Chemistry, Vol-I edited by G.L.Eichorn.
48. Interactions of metal ions with nucleotides and nucleic acids and their constituents Helmut Sigel Chem. Soc. Rev., 1993,22, 255-267.
49. Bioinorganic Chemistry. Inorganic elements in the Chemistry of life, Wolfgang Kaim & Brigette Schwederdki.
50. Bioinorganic Chemistry, Bertini, Gray, Lippard and Valentine, University ScienceBooks, California USA 1994.
51. Handbook of Metal-Ligand interactions in Biological fluid Bioinorganic medicine, Vol – Edt. Guy Berthon.
52. Bioinorganic Chemistry, Rosette M. RoatMalone.
53. Mechanistic Bioinorganic Chemistry Edited by byH.Holden Thorp and Vincent L. Pecoraro, Chemical Society, Washington DC 1995.
54. Metal Complex -DNA Interactions, Editor(s): Nick Hadjiliadis, EinarSletten, Copyright @ Blackwell Publishing Ltd.

Department of Chemistry
Paper_II, Ph.D course work syllabus-2018

Paper Title: Organic synthesis, spectroscopy and molecular modeling

Unit-I: Organic Reagents and Reactions
Unit-II: Asymmetric and retro synthesis
Unit-III: Spectroscopic applications of organic compounds
Unit-IV: Molecular modelingand Biological Evaluation

Unit-I: Organic Reagents and Reactions

$NiCl_2$, Corey-kim oxidation, $ZnBH_4$, Corey-bakshi-shibata reduction, Prins reaction, Asymmetric transfer hydrogenation

Unit-2-Asymmetric andRetrosynthesis

AsymmetricSynthesis : Introduction, stereoselectivity
Asymmetric induction: Cram's chelate, Reetz and Cram-Reetz models; α-Alkylation of chiral enolates: William's Oxazinone, Oppolzerauxiliaries; CBS reagent, Sharpless asymmetric aminohydroxylation, Shi epoxidation, Noyori's asymmetric hydrogenation, Mukaiyamaaldol reaction, chiral pool strategy; synthesis of R and S-Sulcatol, methyl mycaminoside from S-Lactic acid.
Retrosynthesis: Introduction,
Selectivity: Introduction, chemoselectivity- retrosynthesis of Lipstatin; regioselectivity-retrosynthesis of Gingerol; Stereoselectivity- aldol reaction-anti and syn selective aldol reactions retrosynthesis ofJuvabione.
Aromatic compounds-orthostrategy : introduction, ortholithiation-aninonic Fries rearrangement retrosynthesis of Pancratistatin
One and two group C-C, C-X disconnections: Introduction ,retrosynthesis of Rogeltimide, Linalol, Doxpicomine.
Reconnections: Introduction, Polarity reversal, Synthesis of 1,2 and 1,4-dicarbonyl compounds.
Retrosynthetic analysis: Application of disconnection approach to synthesis of α-Bisaboline, multistriatin and α& β- Sinensals

Unit-III Spectroscopic applications of organic compounds

Differentiation of possible isomers: i) $C_9H_{10}O_2$ - Number of possible isomers and their detection by ^{1}H-NMR spectra. ii) Hydroxycinnamic acid – number of possible isomers and their detection.

Differentiation of pair of isomers: Differenciation of isomers using different spectra:

i) IR spectra: 3-Phenylpropanaldehyde -Propiophenone: 4-ethylaniline, 4-methyl-N-methylaniline, N,N-dimethylaniline. ii) UV spectra: Propiophenone – Phenylacetone; levopimaric acid and abietic acid. iii) ^{1}H-NMR Spectra: Vinyl acetate - Methyl acrylate; α-pinene - β-pinene. iv) ^{13}C-NMR spectra: 1-pentene – 2-pentene; vinyl acetate - methyl acrylate. v) Mass spectra: N,N-dimethylpropanamide – N-methylbutanamide; α-ionone – β-ionone; cyclohexylpropane and 1,2,4-trimentylcyclohexane; Pyrazole – imidazole; pyradazine – pyrimidine - pyrazine. vi) All spectra: paracetamol – p-methoxybenzamide.

^{13}C-NMR spectroscopy: Sucrose (DEPT), Piperine and Morphine.

Quantitative estimation: Quantitative estimation of APC tablets by ^{1}H-NMR spectroscopy.

Determination of absolute configuration of enantiomers by Mosher's method.

2D-NMR spectroscopy: principle – Homo-2D-J-resolved and hetero-2D-J-resolved spectroscopy, Homo-COSY, TOCSY, Hetero-COSY, HMQC, HMBC, NOESY and 2D-Inadequate techniques by taking 1-iodobutane as an example. HOMO COSY of Sucrose, Hetero-COSY, HMQC, HMBC, 2D-Inadequate of Ipsenol, TOCSY of methoxybutane. Homo-COSY and Hetero-COSY of Thymol.

Interpretation of the structure of natural products using spectral data (IR, UV, NMR & Mass): Camphor, β-carotene, caffeine, penicillin-G, adenosine and cis-jasmone.

Unit-IV: Molecular Modeling and Biological Evaluation

Introduction, Computational chemistry approaches, Molecular behaviors: Computing the energy of a model system, Quantum Mechanic; Molecular Mechanics. Energy minimization: Steepest Descent, Conjugate gradient, Newton Rapson procedure. Molecular Dynamic Simulations. 3D pharmacophore identification, Docking procedures: Manual docking, Automated docking, Defining the molecular surface of a binding site, Rigid docking by shape complementarity, use of grid in docking program, rigid docking by matching hydrogen bonding groups, Rigid docking of flexible ligands, docking of flexible ligands, Anchor and grow program FlexX, Denovo design, Virtual screening techniques.

Biological Evaluation: Invivo and Invitro studies. Cell line assay, Enzyme inhibition, Toxicity testing, cell viability assay, High through put screening.Explanation for IC_{50}, EC_{50}, EC_{90}, LD_{50} ED_{50}, Ki, MIC, Zone of inhibition studies.Ethical issues and regulatory affairs.

References :

1.Organic chemistry Jonathan Clayden, Nick Greeves and Stuart Warren
2. Organic Synthesis-The disconnection approach by S Warren
3. Organic Synthesis: Strategy and Control by Paul Wyatt and Stuart Warren
4. Fundamentals of Asymmetric synthesis by G, L, David Krupadanam
5. Organic synthesis by Michael B Smith
6. Principles of Medicinal chemistry – Foye
7. An Introduction to Medicinal chemistry Graham L Patric

DEPARTMENT OF CHEMISTRY, OSMANIA UNIVERSITY
SYLLABUS FOR PhD COURSE WORK
PHYSICAL CHEMISTRY SPECIALISATION
(EFFECTIVE FROM 2018 – ONWARDS)
(TO BE APPROVED IN THE PG BOARD OF STUDIES)

UNIT 01 Chemical Kinetics and Photochemistry

Chemical kinetics: Structure reactivity relationships- Linear free energy relationships. Hammett equation- The substituent constant (σ) and excited sigma values. The Reaction constant (ρ) and the importance of rho value in arriving at the mechanism of reactions. Deviation from Hammett correlations. Taft equation and Taft four parameter equation. The Swain – Scott equation-correlations for nucleophilic reactions. The Edward equation. The reactivity-selectivity principle and the Isoselectivty rule. The Intrinsic barrier and Hammond's postulate.

Photochemistry: Formation of excimers and exciplexes –quantum yields. Electronically excited states – singlet and triplet states. Unimolecular decay of the excited state- internal conversion, inter system crossing, fluorescence and phosphorescence. Principles of Energy transfer-photosensitization. Flash photolysis and applications.

Organic Photochemistry: properties of (n-π^*) and (π-π^*) states. Photochemistry of alkenes: cis-trans isomerisation, di-π methane rearrangement. Photochemistry of carbonyl compounds:
i) Norrish type I reactions. Photoreduction and photo oxidation.
ii) Norrish type II reactions. Addition of carbonyl group to carbon-carbon multiple bonds (Paterno-Buchi) reaction, Barton reaction. Singlet oxygen-photo oxidation and reactions with C=C compunds.

$Ru(bpy)_3^{2+}$ as sensitizer for photoredox reactions, ex. Photochemical cleavage of water.

UNIT 02 Electrochemistry

DC Polarography: Dropping Mercury Electrode, Instrumentation-Polarogram, Half-Wave potential. Types of currents: Residual current, diffusion current, Migration current. Kinetic current. Ilkovic equation and its consequences. Applications of Polarography, Determination of stability constant of complex.
Cyclic Voltammetry: Principle, Instrumentation, reversible and irreversible cyclic Voltammograms, Applications: Cyclic Voltammetric study of Insecticide- Parathion.
Breif account of Pulse Polarography, Differential Pulse Polarography and AC Polarography.
Electro-Organic Synthesis: Electrochemical reduction of Nitro compounds and carboxylic acids.
Anodic Oxidation of Metals, Instrumentation. Characteristics and Industrial applications of anodic oxide films.
Electrode double layer. The Helmholtz- Perrin parallel model, The Gouy- Chapman diffuse model and Stern Model.
Corrosion: Chemical corrosion: Different metal oxide layers, Electrochemical corrosion and its mechanism. Galvanic corrosion. Waterline corrosion.

UNIT 03 Heterogeneous Catalysis

Definition of catalytic activity, selectivity, TOF and active site concentration, volcano plots.
Concepts in heterogeneous catalysis:
Broad categories of catalysts – metals, bimetals, semiconductors, insulators, zeolites, oxides, nano materials.
Preparation of metal catalysts, supported metal catalysts and non- metallic catalysts; Co-precipitation, Impregnation, sol-gel method, deposition-precipitation, hydrothermal synthesis
Steps in heterogeneous catalyzed reactions. Diffusion and adsorption. Mechanism of surface-catalyzed reactions. Adsorption isotherms - Langmiur Hinshelwood model, Rideal - Eley mechanism, Kinetics and thermodynamics of catalysed reactions. Catalytic activity – the determining factors. Structure sensitive and structure insensitive catalysts.
Instrumental methods of catalyst characterization: Adsorption techniques - BET isotherm - surface area measurements; pore size distribution and pore volume by BJH method; Diffraction (XRD, LEED) and thermal methods (TPR, TPD); spectroscopic (IR, XPS, AFM, AES) and microscopic techniques (SEM, TEM).
Model catalysts: Ammonia synthesis; Fischer-Tropsch synthesis of methanol; Cracking and reforming; Auto exhaust emissions- catalytic converters.

Phase-transfer catalysis (PTC): Principles of phase-transfer catalysis. PTC classification. Factors influencing the rate of PTC reactions. PTC reactions: nucleophilic substitution reaction by quarternary ammonium salts, Crown ethers as phase transfer catalysts (PTC) in the reaction of alkyl halides with super oxide. Permanganate oxidation of alkenes and phenols in presence of PTC's viz., quarternary ammonium salts and crown ethers.

UNIT 04 Computational Chemistry **(15hrs)**

Introduction, scope of computational chemistry. Various types of computational methods.
Molecular mechanics methods: Introduction to molecular mechanics; comparison of popular force fields; performance of molecular mechanics; Introduction to molecular dynamics.
Quantum mechanical methods: Postulates of quantum mechanics.
Approximate methods. The variation method- Trial variation function and variation integral. Construction of trial function by the method of linear combinations. Variation parameters. Secular equations and secular determinant.
Types of Semiempirical methods and ab-initio methods.
The Hartree-Fock method: The Hartree-Fock equations.(no derivation). The Fock operator. Core hamiltonian. Coulomb operator and exchange operator. Slater-type orbitals (STOs) as basis functions. Orbital energies and total energy. Helium atom example. Electron correlation energy.
The Hartree-Fock method for molecules: Restricted and unrestricted HF calculations. The Roothan equations. The Fock matrix. The Roothan matrix elements. (no derivation required)
GTOs and different types of basis sets. Minimal basis set. Model HF calculations on H2. Discussion of results of HF calculations on simple molecules – H2O and NH3. Introduction to configuration interaction.
Density functional theory (DFT). Hohenberg-Kohn theorem. Kohn-Sham (KS) formulation of DFT. KS equations and KS orbitals. Brief explanation of exchange-correlation energy and exchange-correlation potential.

Reference Books:

1 Chemical Kinetics, K.J.Laidler, McGraw Hill.
2 Kinetics and Mechanism, A.A. Frost & R.G.Pearson, John Wiley & Sons
3 Kinetics and Mechanism of Chemical Transformations, J. Rajaraman & J. Kuriacose, McMillan
4 Chemical Kinetics and Reaction Mechanisms, J.H. Espenson, McGraw Hill
5 Physical Organic Chemistry, N.S. Isaccs, ELBS
6 The Physical basis of Organic Chemistry, Howard Maskill, Oxford University Press
7 Molecular Photochemistry, N.J.Turro, W.A. Benzamin
8 Fundamentals of Photochemistry, Rohatgi-Mukherjee, Wiley Eastern
9 Essentials of Molecular Photochemistry, A. Gilbert & J.Baggott, Blackwell Science
10 Introduction to Molecular Photochemistry, C H J Wells, Chapman and Hall
11 Modern Electrochemistry by Bockris, and Reddy, Plenum
12 Introduction to Electrochemistry by S. Glasstone, East west press Pvt. Ltd.
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