MAHATMA GANDHI UNIVERSITY
NALGONDA

DEPARTMENT OF CHEMISTRY
Ph.D. COURSE WORK SYLLUBUS
Effective from Academic Year 2023-24 Batch

MAHATMA GANDHI UNIVERSITY, NALGONDA
DEPARTMENT OF CHEMISTRY
SYLLABUS FOR Ph.D.
COURSE WORK--- PAPER – I
(COMMON TO ALL SPECIALIZATIONS)
(EFFECTIVE FROM ACADEMIC YEAR 2023-2024)

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.

UNIT-II: Report and Thesis Writing:

Structure and components of scientific reports – Types of report – Technical reports and thesis – Significance – Different steps in the preparations – 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. Use of software, MS-Office, PowerPoint, WORD, EXCEL and ACCESS, computer viruses.

UNIT –III: Instrumentation Techniques:

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

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.

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

Unit – IV: Spectroscopy:

Infrared spectroscopy: Introduction, Principles, Characteristic Vibrational frequencies of functional groups, Fermi resonance, Effect of hydrogen bonding on vibrational frequencies.

Electronic Spectroscopy: Introduction, Principles and Wood-Ward Fisher rules.

^{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 E.g: AX_1, AX_2, AX_3, A_2X_3, AMX, 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 Mass Spectrometry (SI-MS), Electrospray Ionization(ESI), Matrix Assisted Laser Desorption Ionization (MALDI), High Resolution Mass Spectrometry (HRMS), Principle, Instrumentation and applications of GC–MS and LC-MS techniques. Fragmentation pattern of Flavones, Aspirin, Paracetamol, Umbelliferone, Geraneol and Papavarine.

References:

1. An introduction to research methodology. Garg, B.L.karadia. R.Agarwal.F.and Agarval U.K.2002 RBSA publishers.
2. Kothari.C.R.1990 Research Methodology Methods and Techniques New Age International,418p.
3. Principles of instrumental Analysis – Skoog, Holler, Nieman, 5 th ed. Harcourt College Publishers,1998.
4. Analytical Chemistry – Gray D. Chnstan, 6th ed. John Wiley and sons Ind,New York 1994.
5. Instrumental methods of Analysis- Willard, Merit, Dean, 6th ed.CBS Publishers & distributors,1986.
6. Hand Books for instrumental Techniques for Analytical Chemistry, Ed frank settle, Prentice Hall, New Jersey, USA. 1997.5. vogel's Text book of Quantitative analysis – (J.Jeffry,J.Bassent et al.5th ed., Longmann, ELBS Puplications,2000.
7. Principles and practice of Analytical Chemistry, F.W.Fitiend & D. Kealey, 5th Ed Blackwell Science.2000.
8. Quantitative Chemical Analysis, Daniel C. Hamis, 6th Ed Will Freeman & Co.New york.2003
9. Analytical Chemistry an Introduction, Cmuch. Th ed. Saunders College Publishing,2000.
10. Spectroscopic identification of organic compounds by R.M.Silverstein and F.X.Webser.
11. Organic spectroscopy by William Kemp.
12. Mass Spectrometry for Chemists and Biochemists by m. Rose and R.A.W. Johnstone
13. Spectroscopic methods in organic chemistry by D.H.Williams and I.Herming
14. Biological mass, spectrometry by A.I.Burlingame
15. Principles and Practice of Biological mass, spectrometry by Chhabil Das
16. Spectroscopic identification of organic compounds by R.M.Silverstein, G.C.Bassler and T.E.Momill
17. NRM-A Multinuclear introduction by William Kemp.
18. Techniques and Practice of chromatography by Scott Raymond P.W.
19. Principles and Practice of modern Chromatographic methods by K.Robands, P.R.Haddad and P.E.Jackson
20. Fundamentals of Molecular Spectroscopy by Banwell & McCash
21. Introduction to molecular Spectroscopy, G,M,Barrow, McGraw Hill
22. Molecular Spectroscopy, J.D.Gmybeal, McGraw Hill
23. Basic Principles of Spectroscopy, R.Chang, McGraw Hill.
24. Physical Methods Spectroscopy, R.S.Drago, Affiliated East West Press
25. Physical Chemistry Ira N.Levine McGraw Hill
26. Atkin's Physical Chemistry by P.Atkins & Jolio de Paulo, Oxford University Press.
27. Molecular Structure and Spectroscopy, G.Aculdas, Eastern Economic Edtn.

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DEPARTMENT OF CHEMISTRY
MAHATMA GANDHI UNIVERSITY
SYLLABUS FOR Ph.D.

COURSE WORK--- PAPER – II
INORGANIC CHEMISTRY SPECIALIZATION
(EFFECTIVE FROM ACADEMIC YEAR 2023-2024)

GROUP THEORY, BONIDNG AND ELECTRONIC SPECTROSCOPY

UNIT-I:

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, Constructions of Character Tables for C_{2v}, C_{2h} and C_{3v}.Applications 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) (ii) Sigma (σ) & Pi (π) and Square Planar Metal Complexes with (i) Sigma (σ) (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

IR and Raman: Symmetry based selection rules of Infrared and Raman-symmetry requirements for overtone, binary and ternary combination bands- Fermi resonance. Effect of coordination on ligand vibrations– aquo, suphato, 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: Pt $HCl(PEt_3)_2$, Pt $(NH_3)_3(CH_3)_3$, BH_4^- , NH_4^+, CH_3CN, [^{6}h - $C_7H_8Mo(CO)_3$], [^{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) ^{13}C-; [^{4}h C_8H_8 $Ru(CO)_3$], $Fe(CO)_5$, $Fe_2(CO)_9$, $Fe_3(CO)_{12}$, 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.

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Applications of ESR to Metal Complexes:

Principle –Selection Rules, Hyperfine splitting, Zero field splitting and Kramer's degeneracy. Factors affecting g values. Calculation of g values with simple examples. Intensities of 'g‖ and g⊥ peaks. Evidence for Metal-Ligand Bond Covalency-Cu(II)-Bis–Salicylaldimine, Cu(II)-diethyldithiophosphinate, Vanadyldithiophosphinate, 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:

Oxidative addition and Reductive Elimination: Stereochemistry and Mechanism of Oxidative Addition – Insertion Reactions – Hydrogenation of Olefins –Transfer Hydrogenation – Hydrosilation of Olefins – Isomerization 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, Negishi 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.

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

Metallo Enzymes:

Copper Enzymes: Types of Copper in Biological systems – Structural and Mechanistic Aspects of Superoxide Dismutase, Lactase 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, Mechanistic Aspects.

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 Catalyzed by i) Methyl Cobalamin ii)Deoxyadenosyl Cobalamin – 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.

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References :

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, Maemillan Physical Science Series(1991)
7. Electronic Spectroscopy, A.B.P.Lever, Elsevier(1997)
8. Introduction to Ligand fields, B.N.Figgis
9. Infrared and Raman Spectroscopy of Inorganic and Coordination Compounds, K Nakamoto
10. Infrared spectroscopy of Inorganic Compound, Bellamy.
11. Principles of Instrumentals Analysis –Skoog, Holler, Nieman, 5th ed. Harcourt College Publishers.1998
12. Inorganic Electroscopy – A.B.P. Lever, Elsevier Publishing Company, London,1968.
13. Hand Book for Instrumental Techniques for Analytical Chemistry, Ed. Frank Settle. Prentice hall, New Jersey, USA,1997.
14. Analytical Chemistry – Gary D. Christian, 6th ed, John Wiley and Sons Inc, New York,1994.
15. Infrared and Raman Spectra of Inorganic and Coordination Compounds, Kazuo Nakamoto,5th ed, John Wiley & Sons,1995.
16. Instrumental Methods of Analysis- Willard,6th ed, CBS Publishers & distributors,1986.
17. Organometallics – A Concise Introduction, Ch. Eischeinbroich and Salzer- VCH
18. Organotransition Metal Chemistry Fundamental Concepts and Applications, John akio Yamamato, Wiley & Sons
19. Homogeneous Catalysis by Complexes, M M Taqui Khan and A E Martel
20. Organometallic Compounds, G E Coates, MCH Green, K Wade Vol II
21. Advanced Inorganic Chemistry, Cotton and Wilkinson, V & VI E
22. Basic Organometallic Chemistry – concepts and perspectives by Lean – Marie Lehn
23. Supramolecular Chemistry – Concepts and perspectives by Jean – Marie Lehn
24. Principles and method in Supramolecular chemistry, Hans-Jorg Schneider and A.Yatsimirsky, John Wiley and sons.
25. Structural Methods in Inorganic Chemistry, E.A.V.Ebsworth, D.W.Rankin and S.Chaddock, ELBS.
26. Physical Methods in Chemistry, R.S. Drago , W. B. Saunders Co.,1977,
27. Physical Methods for Chemists, Russell S.Drago Second edition, Saunders College Publishing,1992.
28. Principles of Analytical Chemistry, M.Valcareet.
29. Physical Methods Advanced Inorganic Chemistry, Hill and Day.
30. Magneto Chemistry, Dutta & Shyamal Oxford Chemistry Primers, Vol 62
31. Bio chemistry – Geoffrey L.Zubay.
32. Bioinorganic Chemistry, Berlini, Gray, Lippard and Valentine, University Science Books, California USA 1994.

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33. Principles of Bioinorganic Chemistry, S.J. Lippard and M. Berg University, Science Books, California USA 1994.
34. Metal ions in Biological Systems (Series), Ed.H.Sigel Mareel Dekkar, New York
35. Inorganic Chemistry, J. A. Cowan, VCH publishers 1993
36. Bioinorganic Chemistry, Vol-1 edited by G.L.Eichorn
37. Bioinorganic Chemistry, Inorganic elements in the Chemistry of life, Wolfgang kaim & Brigette Schwederdki.
38. Bioinorganic Chemistry Bertini, Gray, Lippard and Valentine, University Science Books, California USA 1994.
39. Bioinorganic Chemistry, ROSETTE-M, Roat Malone
40. Mechanist Bioinorganic Chemistry, edited by H, Holden Thorp and Vincent L, Pecoraro Chemical Society Washington DC 1995.

DEPARTMENT OF CHEMISTRY
MAHATMA GANDHI UNIVERSITY
SYLLABUS FOR Ph.D.
COURSE WORK--- PAPER – II
ORGANIC CHEMISTRY SPECIALIZATION
(EFFECTIVE FROM ACADEMIC YEAR 2023-2024)

Paper Title: Organic synthesis, spectroscopy and molecular modeling

Unit-I: Organic Reagents and Asymmetric Synthesis

Unit-II : Retrosynthesis

Unit-III: Spectroscopic applications of Organic compounds

Unit-IV: Molecular modeling and Biological Evaluation

Unit-I: Organic Reagents and Asymmetric Synthesis

$NiCl_2$, Corey-Kim oxidation, $ZnBH_4$, Corey-Bakshi-Shibata reduction, Prins reaction, Asymmetric transfer hydrogenation.

Asymmetric Synthesis: Introduction, Stereoselectivity

Asymmetric induction : Cram's chelate, Reetz and Cram-Reetz models; α-Alkylation of chiral enolates: William's Oxazinone, Oppolzer auxiliaries; CBS reagent, Sharpless asymmetric amino hydroxylation, Shi epoxidation, Noyori's asymmetric hydrogenation, Mukaiyama-Aldol reaction, chiral pool strategy; synthesis of R and S-Sulcatol, methyl mycaminoside from S-Lactic acid.

Unit-II: Retrosynthesis: Introduction

Selectivity: Introduction, chemoselectivity-retrosynthesis of Lipstatin; regioselectivity retrosynthesis of Gingerol; Stereoselectivity- aldol reaction-anti and syn selective aldol reactions retro synthesis of Juvabione.

Aromatic compounds: Orthostrategy: Introduction, ortho lithiation–anionic 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, multi stratin 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: Differentiation 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-penetene; vinyl acetate-methyl acrylate v) Mass spectra: N,N-dimethylpropanamide – N-methylbutanamide; α-ionone-β-ionine; cyclohexylpropone and 1,2,4-trimentylhexane; Pyrazole–imidazole; pyradazine-pyrimidine-pyrazine vi) All spectra: paracetamol-p-methoxybenzamide.

^{13}C-NMR spectroscopy: DEPT of Sucrose and Piperine. ^{13}C spectra of Piperine

2D-NMR spectroscopy: 2D-Inadequate techniques by taking 1-iodobutane. HOMO COSY of 2-NO_2 Propane, Thymol, Hetero-COSY of 2-NO_2 Propane, Thymol, HMQC, HMBC, 2D-Inadequate of Ipsenol, TOCSY of methoxy butane.

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 simulation. 3D pharmacophore identification, docking producers: 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 Flex X, Denovo design, Virtual screening techniques.

Biological Evaluation: In-vivo and In-vitro 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 Warrren
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 I. Patric

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DEPARTMETN OF CHEMISTRY
SYLLABUS FOR Ph.D.
COURSE WORK-- PAPER – II
PHYSICAL CHEMISTRY SPECIALIZATION
(EFFECTIVE FROM 2024 ONWARDS)

UNIT-1: Chemical Kinetics and Photochemsitry :

Chemical Kinetics: Structure reactivity relations-Linear free energy relationships. Hammett equation. The susbstitutent constant (σ) and excited signma values. The reaction constant (ρ) and the importance of rho value in arriving at the mechanism of reactions. Deviation from Hammet correlations. Taft equation and Taft four parameter equation. The reactivity-selectivity principle and Isoselectivity rule. The Intrinsic barrier and Hammond's postulate.

Photochemistry: Formation of excimers and exciplexes-quantum yields. Electronically excited states-singlet and triplet state. Unimolecular decay of the excited state-Internal conversion, inter system crossing fluoresce 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 isomerization, 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 compounds.

$Ru(bpy)_3$ as sensitizer for photoredox reactions, ex. Photochemical cleavage of water.

UNIT-2: Electrochemistry

DC Polagraphy: Dropping Mercury Electrode, Instrumentation of Polarogram, Half-Wave potential. Types of currents:Residual current, diffusion current, Migration current. Kinetics current. Illovic equation and its consequences. Applications of Polagraphy. Determination of stability constant of complex.

Cyclic Voltammetry: Principle, Instrumentation, reversible and irreversible cyclic Voltammograms.

Applications: Cyclic Voltammetric study of Insectivide – Parathion

Brief account of Pulse Polagraphy, Differential Pulse Polagraphy and AC Polagraphy.

Electro-Organic Synthesis : Electrochemical reduction o fNitro 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-3: Heterogenous 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 heterogenous catalyzed reactions. Diffusion and adsorption. Mechanism of surface-catalyzed reactions. Adsorption isotherms–Langmiur-Hinshelwood model, Rideal–Eley mechanism. Kinetics and thermodynamics of catalyzed 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 quaternary 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., quaternary ammonium salts and crown ethers.

UNIT-4: Computational Chemistry
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 Semi empirical methods and ab-initio methods.
The Hartree-Fock method: The Hartfree-Fock equation (no derivation) The Fock operator. Core Hamiltonian. Coulomb operator and exchange operator, Slator-type orbitals (STOs) as basic 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 equation. The Fock matrix. The Roothan matrix elements (no derivation required).
OTOs and different types of basis sets, Minimal basis set, Model HF calculations on H_2. Discussion of results of HF calculations on simple molecules – H_2O and NH_3. 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.

References:

1. Chemical Kinetics, K.L.Laidler, McGraw Hill.
2. Kinetics and Mechanism, A.A. Frost & R.G. Pearson, John Wiley & Sons
3. Kinetics and Mechanism of Chemical Transformation J.Rajaraman & J.Kuriacose
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 Photochemistry, Rohatgi-Mukherjee, Wiley Eastern
9. Essentials of Molecular Photochemistry ,A.Gilbert & J.Baggott, Blackwell science
10. Introduction of Molecular Photochemistry H J Wells, Chapman and Hall
11. Modern electrochemistry by Bockri, and Reddy, Plenum .
12. Introduction to Electrochemistry by S.Glasstone, East west press Pvt.Ltd.
13. Engineering Chemistry by Jain and Jain.
14. Principles of Heterogeneous Catalysis, in practice, G.C.Bond ,Oxford Publishing
15. J.M.Thomas and W.I.Thomas, Principles and Practice of Heterogeneous Catalysis, Wiley VCH,1997
16. B.C.Gates Catalytic Chemistry, Wiley, New York 1992.
17. Heterogeneous Catalysis by D.K. Chakrabarthy and B. Viswanatham, New Age International Publishers 2008.
18. Catalysis, J.C.Kuriacose, Macmillan
19. Phase Transfer Catalysis, Fundamentals, Applications and Industrial prespective, C.M.Stark.C.Liotta & M.Halpern, Academic Press.
20. Phase Transfer Catalysis,E.V.Dehmlow & S.S.Dehmlow, Verlag Chemie, Weinheim
21. F.Jensen, Introduction to Computational Chemistry,(Wiley, New York,1999).
22. A.Szabo and N.S.Ostlund. Modern Quantum Chemistry, Introduction to Advanced Electronic Structure Theory,1st ed., revised (Dover,1989). More mathematical detail for many of the ab initio electronic structure methods.
23. D.A. Mc Quarrie, Quantum Chemistry (University Science Books, Mill Valley, CA,1983).Very readable introductory text for undergraduate-level quantum chemistry,
24. N.Levine,Quantum Chemistry,4th ed.(Prentice Hall, Englewood Cliffs,NJ,1991).Covers some of the topics in this course.

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DEPARTMETN OF CHEMISTRY
SYLLABUS FOR Ph.D.
COURSE WORK-- PAPER – II
GENERAL CHEMISTRY
SPECIALIZATION

(EFFECTIVE FROM ACADEMIC YEAR 2023-2024 ONWARDS)

Unit-I: SYMMETRY OF MOLECULES & REACTION MECHANISMS OF TRANSITION METAL COMPLEXES

15 hrs

i) Symmetry of Molecules: Concept of Symmetry in Molecules – Symmetry Operations & Symmetry,Elements: Rotational Axis of Symmetry and Types of Rotational Axes, Plane of Symmetry and types of Planes, Improper Rotational Axis of Symmetry, Inversion Center and Identity Element – More about Symmetry Elements – Molecular Point Groups: Definition and Notation of Point Groups, Classification of Molecules in to C1, Cs , Ci, Cn, Cnv, Cnh, Cv, Dn, Dnh, Dnd, Sn (n = even), , Td, , Oh and Ih Groups. Properties of a group-sub group.

ii) Reaction mechanisms of transition metal complexes:
Ligand substitution reactions: Energy profile of a reaction- Transition state of Activated complex. Types of substitution reactions (SE,SN, SN1, SN2).

Ligand substitution reactions in octahedral complexes: Acid hydrolysis reactions, Factors effecting Acid Hydrolysis, Base Hydrolysis, Conjugate Base Mechanism, Evidences in favour of SN1CB Mechanism. Substitution reactions without Breaking Metal-Ligand bond.

Ligand Substitution reactions in Square-Planar complexes: Mechanism of Substitution in Square-Planar complexes- Trans-effect, Grienberg's Polarization theory and π - bonding theory – Applications of Trans-effect in synthesis of Pt (II) complexes.

Electron Transfer Reactions (or Oxidation-Reduction Reactions) in Coordination compounds: Mechanism of One-electron Transfer Reactions: Atom (or group) Transfer or Inner Sphere Mechanism, Direct electron Transfer or Outer Sphere Mechanism.

Unit- II: STRATEGIES IN ORGANIC SYNTHESIS **15 hrs**

i) Oxidations: Swern, Prevost and Woodward oxidations.
ii) Reductions: Birch reduction, Reduction with LiAlH4 , NaBH4 , BH3, AlH3, and tri-n-butyl tin hydride.

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Organo- metallic reagents: Use of Organo lithium, Silicon and boron reagents in Organic synthesis.

iii) Modern Organic Synthetic Reactions: Aza-Cope and Aza-Wittig reactions, Baylis-Hillman reaction, BINAL and BINAP assisted reactions, Buchwald-Hartwig coupling, Click reaction, Grubb's catalyst and RCM olefin metathesis, Heck reaction, Julia- Lythgoe olefination, Mukayama aldol reaction, Mitsunobu reaction, McMurray reaction, Peterson's stereoselective olefination, Suziki coupling.

Unit - III: CHEMICAL KINETICS & PHOTO CHEMISTRY **15 hrs**

Chemical Kinetics: Structure-Reactivity relationships- Linear free energy relationships. Hammett equation – The substituent constant (σ) and exalted sigma values. The Reaction constant (ρ) and the importance of rho value in arriving at the mechanism of reactions. Deviations 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 isoselectivity rule. The intrinsic barrier and Hammond's postulate.

Photo Chemistry: Formation of excimers and exciplexes –Quantum yields. Electronically excited states- singlet and triplet states. Uni molecular decay of the excited state- internal conversion, inter system crossing, fluorescence and phosphorescence. Principles of energy transfer- photosensitization. Flash photolysis and it's applications. Organic photochemistry. Properties of (n,π^*) and (π,π^*) states. Photochemistry of alkenes: Cis-trans isomerization, di-π - methane rearrangement. Photochemistry of carbonyl compounds: i) Norrish type-I reactions. Photoreduction and photooxidation. ii) Norrish type-II reactions. Addition of carbonyl to carbon- carbon multiple bonds (Paterno-Buchi) reaction. Barton reaction. Singlet oxygen – photo oxidation and reactions with C=C compounds. $Ru(bpy)_3^{+2}$ as sensitizer for photo redox reactions. Photochemical cleavage of water.

Unit-IV: PRINCIPLES OF SPECTROSCOPY **15 hrs**

i) IR Spectroscopy: Introduction, Principles, Characteristic vibrational frequencies of functional groups, Fermi resonance, Effect of hydrogen bonding on vibrational frequencies.

ii) Electronic spectroscopy: Introduction, Principles and Wood -Ward Fisher rules.

iii) NMR Spectroscopy (1H NMR): Introduction, Principles, factors effecting the chemical shifts, spin-spin coupling, first order spectra.

iv) Mass Spectrometry: Introduction, Principles, use of isotopic peaks, salient feature of fragmentation of organic compounds, McLafferty rearrangements, retro Diels-Alder fragmentation and ortho effects. Simple problems on structure determination based on the above spectral methods.

Atomic Absorption Spectroscopy (AAS): Principles of AAS– flame AAS and furnace AAS, sensitivity and detection limits in AAS, interferences – chemical and spectral, evaluation methods in AAS and applications in qualitative and quantitative analysis.

Atomic Emission Spectroscopy (AES): Principles of AES, Instrumentation, evaluation methods and application in quantitative analysis.

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REFERENCE 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. Reaction mechanism in transition metal complexes .K.Veera Reddy New Age International (P) Limited Publishers.
6. Some modern methods of organic synthesis by W Carruthers
7. Guidebook to organic synthesis, by R K Meckie, D M Smith & R A Atken
8. Organic synthesis by O House
9. Organic synthesis by Michael B Smith
10. Reagents for organic synthesis, by Fieser & Fieser, Vol 1-11(1984)
11. Organic synthesis by Robert E Ireland
12. Organic Synthesis - The disconnection approach by S Warren
13. Organic Synthesis by C Willis and M Willis
14. Handbook of reagents for organic synthesis by Reich and Rigby, Vo I, IV
15. Problems on organic synthesis by Stuart Warren
16. Total synthesis of natural products: the Chiron approach by S.Hanessian
17. Organic chemistry Claydon and others 2005
18. Name Reactions by Jie Jack Li
19. Reagents in Organic synthesis by B.P.Mundy and others.
20. Tandem Organic Reactions by Tse-Lok Ho.
21. Chemical Kinetics, K. J. Laidler, McGraw Hill
22. Kinetics and Mechanism, A. A. Frost & R. G. Pearson, John Wiley & sons
23. Kinetics and Mechanism of Chemical Transformations, J. Rajaraman & J. Kuriacose, McMillan
24. Chemical Kinetics and Reaction Mechanisms, J. H. Espenson, McGraw Hill
25. Physical Organic Chemistry, N. S. Isaacs, ELBS
26. The Physical basis of Organic Chemistry, Howard Maskill, Oxford University Press
27. Molecular Photochemistry, N. J. Turro, W. A. Benzamin
28. Fundamentals of Photochemistry, Rohatgi-Mukherjee, Wiley Eastern
29. Essentials of Molecular Photochemistry, A. Gilbert & J. Baggott, Blackwell Science
30. Introduction to Molecular Photochemistry, C. H. J. Wells, Chapman and Hall
31. Molecular Reactions and Photo chemistry by Depuy and Chapman
32. Fundamentals of Molecular Spectroscopy, Banwell and McCash.
33. Introduction to Molecular Spectroscopy, G.M. Barrow
34. Absorption Spectroscopy of Organic Compounds, J.R. Dyer
35. Biochemistry: Hames and Hooper.
36. Spectroscopic identification of organic compounds by R.M.Silverstein. G.C.Bassler and T.E.Morrill

37. NMR-A multinuclear introduction by William Kemp
38. Organic Spectroscopy by William Kemp
39. Spectroscopic methods in Organic chemistry by DH Williams and I Fleming .
    Modern NMR techniques for chemistry research by Andrew B Derome
40. NMR in chemistry - A multinuclear introduction by William Kemp
41. Spectroscopic identification of organic compounds by P S Kalsi
42. Introduction to organic spectroscopy by Pavia
43. Carbon-13 NMR for organic chemists by GC Levy and O L Nelson
44. Principles of Instrumental Analysis. Skoog. Holler and Nieman.
45. Instrumental Techniques for Analytical Chemistry. Frank Settle.
46. Principles of Analytical Chemistry. M. Valcarcel

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MODEL PAPER

FACULTY OF SCIENCE

Pre. Ph.D Examination

Subject : RESEARCH METHODOLOGY

PAPER- 1

(Common to All Branches)

Code No.:

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

I. Answer any Five questions

PART –A (5 x 8 = 40 Marks)

(Short Answer Type)

1.
2.
3.
4.
5.
6.
7.
8.

PART –B (4 x 15 = 60 Marks)

(Essay Answer Type)

9.a.
b.

Or

c.
d.

10.a.
b.

Or

c.
d.

11.a.
b.

Or

c.
d.

12.a.
b.

Or

c
d

MAHATMA GANDHI UNIVERSITY, NALGONDA

MODEL PAPER **Code No.:**

FACULTY OF SCIENCE

Pre. Ph.D Examination

Subject : CHEMISTRY

PAPER- II

(SPECIALIZATION)

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

I. Answer any Five questions

PART –A (5 x 8 = 40 Marks)
(Short Answer Type)

1.
2.
3.
4.
5.
6.
7.
8.

PART –B (4 x 15 = 60 Marks)
(Essay Answer Type)

II. Answer all questions

9.a.
b.

Or

c.
d.

10.a.
b.

Or

c.
d.

11.a.
b.

Or

c.
d.

12.a.
b.

Or

c
d