THIRUVALLUVAR UNIVERSITY
VELLORE – 632115
CENTRE FOR RESEARCH
SYLLABUS FOR COMMON ENTRANCE TEST OF M.PHIL AND PHD

CHEMISTRY

Unit-1

Aromaticity: Aromaticity of benzenoid - non-benzenoid and heterocyclic compounds - Huckel's rule - Aromatic systems with π electron numbers other than six - non-aromatic (cyclooctatetraeneetc,) and anti-aromatic system (cyclobutadiene etc.) - system with more than 10π electrons - Annulenes upto C18 (synthesis of all these compounds is not expected).

Stereochemistry: Optical activity and chirality, classification of chiral molecules as asymmetric and dissymmetric. A brief study of dissymmetry of allenes, biphenyls, spiro compounds. Absolute configuration - R, S notation of biphenyls and allenes. Fischer projection. Inter conversion of Sawhorse, Newman and Fischer projections. Erythro and threo nomenclature, E and Z nomenclature - Asymmetric synthesis - Cram's rule.

Conformational Analysis : Conformational analysis of disubstituted cyclohexane and their stereochemical features (geometrical and optical isomerism (if shown) by these derivatives). Conformation and reactivity of substituted cyclohexanol (oxidation and acylation), cyclohexanone (reduction) and cyclohexane carboxylic acid derivatives (esterification and hydrolysis). Conformation and stereochemistry of cis and trans-decalin and 9 -methyldecalin.

Photochemistry: Photochemical excitation - fate of the excited molecules - Jablonski diagram - study of photochemical reactions of ketone - photo reduction - photo cycloaddition -Paterno - Buchi reaction - di pi-methane rearrangement - Pericyclic analysis of electrocyclic - cyclo addition and sigmatropic reactions - correlation diagrams forbutadiene - cyclobutene system - hexatriene to cyclohexadiene systems - structure of bulvalene - fluxional molecule - Cope and Claisen rearrangement.

Unit -2

Addition Reactions

Addition to carbon - carbon and carbon – hetero multiple bonds: Electrophilic, nucleophilicand neighbouring group participation mechanisms - addition of halogen and nitrosyl chloride to olefins. Hydration of olefins and acetylenes. Hydroboration, hydroxylation, Michael addition, 1, 3 - dipolar additions, Simon - Smith reaction. Mannich, Stobbe, Darzen, Wittig, Wittig - Horner and Benzoin reactions.

Nucleophilic Substitution reactions: SN1, SN2 and SNi mechanisms - Neighboring group participation – Reactivity - structural and solvent effects - substitution in norbornyl and bridgehead systems - substitution at allylic and vinylic carbons - substitution by ambident nucleophiles - substitution at carbon doubly bonded to oxygen and nitrogen - alkylation and acylation of amines, halogen exchange, Von-Braun reaction, alkylation and acylation of active methylene carbon compounds, hydrolysis of esters, Claisen and Dieckmann condensation.

Electrophilic substitution reactions: SE1, SE2 and SEi mechanism, double bond shift - Reactivity. Migration of double bond, keto-enol interconversion, Stark- Enamine reaction, halogenation of aldehydes and ketones and decarboxylation of aliphatic acids.

Elimination Reactions: E1, E2 and E1CB mechanism - E1, E2 and E1cB spectrum - Orientation of the double bond - Hoffman and Saytzeff rules - Competition between elimination and substitution. Typical elimination reactions- dehydration, dehydrohalogenation and dehalogenation. Stereochemistry of E2 eliminations in cyclohexane systems. Mechanism of pyrolytic eliminations. Chugaev and Cope eliminations.

O**xidations and Reductions:** Mechanism - study of the following oxidation reactions - oxidation of alcohols - use of DMSO in combination with DCC and acetic anhydride in oxidising alcohols - oxidation of methylene to carbonyl, oxidation of aryl methane - allylic oxidation of olefins - ozonolysis - oxidation of olefinic double bonds and unsaturated carbonyl compounds - oxidative cleavage of C-C bond. Reduction: Selectivity in reduction of 4-t-butylcyclohexanone using select rides. Hydride reductions - reduction with $LiAlH_4$, $NaBH_4$, tritertiarybutyloxyaluminiumhydride, sodium cyanoborohydride, trialkyltin hydride and hydrazines.

Molecular Rearrangements: A detailed study with suitable examples of the mechanism of the following rearrangements: Wagner - Meerwein, Pinacol - Pinacolone, Demjanov, Dienone - phenol, Favorski, Baeyer - Villiger, Wolf, Stevens and Von Richter rearrangements.

Reactive Intermediates: Carbocations, carbanions, free radicals, radical cations, radical anions, carbenes and nitrenes, arynes – generation, stability: factors affecting stability (carbocation and carbanion), structure and their reactions in C-C bond and other multiple bond formation.

Unit- 3

Ultraviolet-Visible spectroscopy: Types of electronic transitions - chromophores and auxochromes - factors influencing the positions and intensity of absorption bands -absorption spectra of dienes, polyenes and unsaturated carbonyl compounds - Woodward - Fieser rules and its applications.

Infra-Red Spectroscopy: Vibrational frequencies and factors affecting them -identification of functional groups - intra and inter molecular hydrogen bonding – functional group region- finger print region - far IR region.

NMR spectra and its applications: Nuclear spin - magnetic moment of a nucleus - nuclear energy levels in the presence of magnetic field - basic principles of NMR experiments - CW and FT NMR - ^{1}H NMR -Chemical shift and coupling constant - factors influencing proton chemical shift and vicinal proton - proton coupling constant- 1H NMR spectra of simple organic molecules such as CH_3CH_2Cl and CH_3CHO. AX and AB spin system - nuclear overhauser effect- chemical exchange.

^{13}C NMR - proton decoupling and Off resonance decoupling spectra - factors affecting ^{13}C NMR chemical shift -^{13}C NMR spectra of simple organic molecules.

Mass spectroscopy - Principles - measurement techniques - (El, Cl, FD, FAB, SIMS) - presentation of spectral data - molecular ions - isotope ions - fragment ions of odd and even electron types - rearrangement ions - factors affecting cleavage patterns - simple and multicentre fragmentation – Mc Lafferty rearrangement - Mass spectra of hydrocarbons, alcohols, phenols, aldehydes and ketones. Problem solving (for molecules with a maximum number of C10).

Unit 4

Structure and bonding: Polyacids: Isopolyacids and heteropolyacids of vanadium, chromium, molybdenum and tungsten. Inorganic Polymers: Silicates, structure - properties - correlation and applications - molecular sieves, polysulphur - nitrogen compounds and poly – organophosphazenes Boron hydrides: Polyhedral boranes, hydroboration, carboranes and metallocarboranes. Metal clusters: Chemistry of low molecularity metal clusters (upto) trinuclear metal clusters, multiple metal-metal bonds. Cubane clusters and Zintl clusters.

Organo metallic chemistry: Carbon donors: Alkyls and aryls metallation, bonding in carbonyls and nitrosyls, chain and cyclic donors, olefins, acetylene and allyl system. Synthesis, structure and bonding of metallocenes (ferrocene only). Reactions: Association, substitution, addition and elimination reactions, ligand protonation, electrophilic and nucleophilic attack on ligands. Carbonylation, decorboxylation, oxidative addition and fluxionality.
Catalysis: Hydrogenation of olefins (Wilkinson's catalyst), hydroformylation of olefins using cobalt or rhodium catalysts (Oxo process), oxidation of olefins to aldehydes and ketones (Wacker process), polymerization (Zeigler - Natta Catalyst); cyclooligomerisation of acetylene using nickel catalyst (Reppe's catalyst); polymer-bound catalysts.

Unit 5

Coordination chemistry: Stability of complexes; thermodynamic aspects of complex formation; factors affecting stability, HSAB approach. Determination of stability constants by spectrophotometric, polarographic and potentiomteric methods.
Stereochemical aspects; stereoisomerism in inorganic complexes; isomerism arising out of ligand distribution and ligand conformation; chirality and nomenclature of chiral complexes; optical rotatory dispersion and circular dichroism. Macrocyclic ligands; types; porphyrins; corrins, Schiff bases; crown ethers and cryptates.
Evidences for metal-ligand orbital overlap, molecular orbital theory and energy level diagrams, concept of weak and strong field ligands, Jahn-Teller distortion, charge - transfer spectra. Term states for "d"- ions, energy diagrams, d-d transitions, Orgel and Tanabe - Sugano diagrams, spin orbit coupling, nephelauxetic effect, spectral and magnetic characteristics of transition metal complexes. Electron transfer reactions, outer and inner sphere processes; atom transfer reaction, formation and rearrangement of precursor complexes, the bridging ligand, precursor and successor complexes. Marcus theory. Complementary, non-complementary and two electron transfer reactions. Substitution Reactions: Substitution in square planar complexes, reactivity of platinum complexes, influences of entering, leaving and other groups, the Trans effect.
Substitution of octahedral complexes of cobalt and chromium, replacement of coordinated water, solvolytic (acids and bases) reaction applications in synthesis (platinum and cobalt

complexes only). Inorganic Photochemistry: Photo-substitution, Photoredox and isomerisation process, application of metal complexes in solar energy conversion.

Unit 6

The chemistry of solid state: Structure of solids; Comparison of X-ray and Neutron Diffraction; structure of pyrovoskite, cadmium iodide and nickel arsenide; spinels and antispinels, defects in solids, non-stoichometeric compounds. Electrical, magnetic and optical properties of solids, band theory. Semiconductors, superconductors, solid state electrolytes. Types of magnetic behaviour, dia, para, ferro, antiferro and ferrimagnetism, hysterisis. Solid state lasers, inorganic phosphors and ferrites.

Nuclear chemistry: Nuclear properties: Nuclear spin and moments, origin of nuclear forces, Nuclear models: liquid drop model and nuclear shell model. Modes of radioactive decay: Orbital electron capture, nuclear isomerism, internal conversion. Detection and determination of activity by cloud chamber, nuclear emulsion, bubble chamber, Geiger-Muller, scintillation andCherenkov counters.

Nuclear reactions: Types, cross section, compound nucleus theory, high energy nuclear, direct nuclear, photonuclear and thermonuclear reactions.

Stellar energy: synthesis of elements, hydrogen burning, carbon burning. Nuclear reactors: fast breeder reactors, particle accelerators, linear accelerators, cyclotron and synchrotron. Radio analytical methods: Isotope dilution analysis, radiometric titrations, radioimmuno assay. Neutron activation analysis.

Lanthanides, actinides and nanotechnology: The chemistry of solid state, lanthanides and actinides, oxidation state, spectral, magnetic characteristics, coordination numbers, stereochemistry, nuclear and non-nuclear applications.

Nanotechnology: Introduction - preparatory methods, characterization, application as sensors, biomedical applications, application in optics and electronics.

Bioinorganic chemistry

Transport proteins: Oxygen carriers, metalloenzymes, carboxy peptidase, carbonic anhydrase, redox process, iron-sulphur proteins, chlorophyll, salient features of the photo synthetic process, vitamin-B_{12}, role of sodium, potassium, calcium, zinc and copper; fixation of nitrogen, nitrogen cycle.

Inorganic spectroscopy

Applications to inorganic systems of the following: ultra violet, visible, infra-red and Raman spectra of metal complexes, organometallic and simple inorganic compounds with special reference to coordination sites and isomerism.

Application to Inorganic systems of the followings NMR, NQR and Mossebauer spectra - NMR of ^{31}P, ^{19}F, NMR shift reagents. NQR - Nitrosyl compounds. Mossebauer spectra of Fe and Sn systems.

ESR Introduction - Zeeman equation, g-value, nuclear hyperfine splitting, interpretation of the spectrum, simple carbon centered free radicals. Anisotropy - g-value and hyperfine splitting constant. McConnell's equation, Kramer's theorem.ESR of transition metal complexes of copper, manganese and vanadyl complexes. Photoelectron spectroscopy (UV and X-ray) - photo

electron spectra - Koopman's theorem, fine structure in PES, chemical shift and correlation with electronic charges.

Instrumental analysis: AAS, AES and AFS – Principle, instrumentation and applications, advantages of AAS, interferences; GLC and HPLC – Principle, instrumentation and working, types of detectors; Inductively coupled plasma spectroscopy (ICP)- introduction, instrumentation, interferences and applications.

Laser Raman spectroscopy - principle, interfaces, advantages and applications.

Magnetic susceptibility and its determination - Guoy method, Faraday method and applications. Polarography and Amperometry - Principle, instrumentation and applications.

Unit 7

Thermodynamics: Partial molar properties -Partial molar free energy (chemical potential), Partial molar volume and Partial molar heat content - Their significance and determination of these quantities. Variation of chemical potential with temperature and pressure. Definition of fugacity - determination of fugacity by graphical method - variation of fugacity with temperature and pressure - the concept of activity and activity coefficients – determination of activity and activity coefficient by emf method - determination of activity and activity coefficients for non-electrolytes - determination of standard free energies - choice of standard states.

Statistical thermodynamics: Objectives of statistical thermodynamics - concept of thermodynamic and mathematical probabilities - permutations and combinations, distribution of distinguishable and non-distinguishable particles. Stirling approximation, Maxwell - Boltzmann distribution law - Fermi - Dirac and Bose - Einstein statistics - comparison with Maxwell - Boltzmann distribution law and their applications - radiation law - electron gas in metals. Partition function - evolution of translational, vibrational and rotational partition functions for mono and diatomic ideal gases.

Thermodynamic functions in terms of partition functions - application of partition function to heat capacity of ideal gases - nuclear partition function - contribution to heat capacity of ortho and para hydrogen. Heat capacity of solids - Einstein and Debye models, Negative Kelvin temperature. Entropy of monoatomic gases -Sackur-Tetrode equation. Irreversible thermodynamics - forces and fluxes - linear force - flux relation - phenomenological equations.

Chemical kinetics: Absolute Reaction Rate Theory (ARRT) - Potential energy surfaces - partition function and activated complex- Eyring equation - estimation of free energy, enthalpy and entropy of activation and their significance. Reactions in solutions - effect of pressure, dielectric constant and ionic strength on reactions in solutions - kinetic isotope effects - linear free energy relationships. Hammett and Taft equation.

Kinetics of complex reactions, reversible reactions, consecutive reactions, parallel reactions, chain reactions, general treatment of chain reactions - chain length - Rice Herzfeld mechanism - explosion limits.

Study of fast reactions - relaxation methods - temperature and pressure jump methodsstopped flow and flash photolysis methods.

Unit 8

Electrochemistry: Mean ionic activity and mean ionic activity coefficient - activity coefficient of strong electrolytes - determination of activity coefficient byelectrochemical method. Debye Huckel limiting law - qualitative and quantitative verification - limitation - Debye Huckel limiting law at appreciable concentrations of electrolytes - Debye - Huckel - Bronsted equation. Electrode - electrolyte interface - adsorption at electrified interface - electrical double layer - electro capillary phenomenon - Lippmann equation - Structure of double layers - Helmholtz - Perrin, Guoy - Chapman and Stern model of electrical double layers. Diffusion - Fick's law of diffusion - Effect of ionic association on conductance-electro kinetic phenomena -membrane potential.

Mechanism of electrode reactions - polarization and over potential - the Butler-Volmer equation for one step and multistep electron transfer reactions - significance of electron exchange current density and symmetry factors - transfer coefficient and its significance - mechanism of the hydrogen and oxygen evolution reactions. Corrosion and passivation of metals - Pourbaix diagram - Evan's diagram - fuel cells - electrodeposition - principle and applications.

SPECTROSCOPY:

Microwave spectroscopy – Rotational spectroscopy of rigid rotator - non-rigid rotator - diatomic and polyatomic molecules.
Vibrational spectroscopy - Harmonic oscillator - anharmonicity - vibrational spectra of polyatomic molecules - vibrational frequencies - group frequencies - vibrational coupling-overtones - Fermi resonance.
Raman Spectroscopy- Raman effect, Stoke's and Anti-stoke's lines, rotational and vibrational Raman spectra.
Electronic spectroscopy - Progressions and sequences, selection rules, Franck - Condon principle, types of electronic transitions - solvent effects.

Resonance spectroscopy - Zeeman effect - equation of motion of spin in magnetic fields - chemical shift - spin-spin coupling - NMR of simple AX and AMX type molecules - calculation of coupling constants - ^{13}C, ^{19}F, ^{31}P NMR spectra - applications - a brief discussion of Fourier Transformation Resonance Spectroscopy.

Phase equilibria: Physical equilibria involving phase transition: Two component system - Congruent **system** (phenol-aniline) and Incongruent system (sodium chloride- water) - Peritectic reactions. Three component system: Solid - Liquid equilibria - hydrate formation (sodium chloride - sodium sulphate - water); Liquid - Liquid equilibria - one pair of partially miscible liquids (acetic acid - chloroform - water and alcohol - benzene - water); two pairs of partially miscible liquids (water - ethyl alcohol - succinic nitrile).

Colloids: Surface phenomena - surfactants, micellization, critical micelle concentration (CMC), factors affecting CMC of surfactants, micro emulsions, reverse micelles and surface films (electro kinetic phenomena). Structure and stability of colloids - Zeta potential (derivation),

electro osmosis, protective colloids, gold number, sedimentation potential, streaming potential and Donnanmembrane equilibrium.

Catalysis: Acid - Base catalysis - mechanism of acid - base catalyzed reactions - Bronsted catalysis law. Catalysis by enzymes - Kinetics of enzyme catalyzed reaction -Michaelis - Menten equation and its interpretation. Effect of substrate concentration, pH and temperature on enzyme catalyzed reactions - inhibition of enzyme catalyzed reactions - Competitive, Non-competitive and Uncompetitive inhibition.

Photochemistry: Absorption and emission of radiation - Franck - Condon Principle - decay of electronically excited states - Jablonski diagram - radiative and non-radiative processes - fluorescence and phosphorescence - spin forbidden radiative transition - Internal conversion and intersystem crossing - energy transfer process - kinetics of unimolecular and bimolecular photophysical processes - excimers and exciplexes - static and dynamic quenching - Stern-Volmer analysis.

Experimental methods - quantum yield and life time measurements - steady state
principle - quantum yield and chemical actinometry. Kinetics of photochemical reactions: hydrogen and halogen reactions, Brief study about photoredox, photosubstitution, photoisomerization and photosensitized reactions - photovoltaic and photogalvanic cells, photo electrochemical cells, photo.

Unit 9

SOLID STATE: Classification of solids - Imperfection in solids - point, line and plane defect - Electrons and holes - Non-stoichiometry - Imperfection and physical properties of solids (brief study). **Electrical properties** - electrical conductivity - Hall effect - dielectric properties - piezo electricity, Ferro electricity and conductivity; **Optical properties** - Photo conductivity - luminescence - color center - lasers - refraction - birefringence; **Magnetic properties** - diamagnetism - paramagnetism - ferro - antiferro and ferrimagnetisms. Calculation of magnetic moments. Mechanical and thermal properties.

GROUP THEORY: Definition of basic terms in group theory – Group – Abelian group, cyclic group, subgroup, group multiplication table - similarity transformation and class, symmetry elements and symmetry operations -Point groups (any examples limited to n = 4 of Cnv, Cnh, Dnh, Dnd, & T, Td, O, Oh), Reducible and Irreducible representations - direct product representation. Character Table - explanation of various column and Mullliken Symbol.

Orthogonality theorem and its consequences - construction of character table for
C_2V, C_3V, C_2h, and D_2d point groups - hybrid orbitals in nonlinear molecules (CH_4, BF_3, and NH_3). Determination of representations of vibrational modes in nonlinear molecules (H_2O, NH_3, BF_3 and $[PtCl_4]^{2-}$). Symmetry selection rules of Infra-red and Raman spectra.

Quantum chemistry: Failure of classical mechanics - Compton effect - wave particle duality - uncertainty principle - waves - wave equation for electrons - quantum mechanical postulates - The concept of operators - Hermitian property. Schrodinger wave equation - application of Schrodinger's equation - the particle in a box (one, and three-dimensional cases) - particle in a

ring, solution to rigid rotor and harmonic oscillator. Schrodinger equation for hydrogen atom (no derivation is required) and the solutions.

Approximation methods - Perturbation and Variation methods - application to hydrogen molecule and helium atoms. Born - Oppenheimer approximation - valence bond theory for hydrogen molecule - LCAO - MO theory for diatomic molecules. Concept of hybridization - Huckel theory for conjugated molecules (Ethylene, butadiene and benzene).

Unit 10

Terpenes and Alkaloids: Introduction - classification - isoprene rule - structural determination of terpenoids'-Citral, geraniol - linalool - farnesol - α-pinene and camphor. Introduction - isolation of alkaloids - total synthesis of quinine - morphine and reserpine.

Proteins and Nucleic acids: Proteins - peptides and their synthesis - synthesis of tripeptide - merrifield synthesis - determination of tertiary structure of protein - biosynthesis of proteins - nucleic acids - types - DNA & RNA polynucleotide chain - components - biological functions - structure and role of (genetic Code) DNA and RNA (nucleotides only) - Biosynthesis of cholesterol. \

Dyes: Introduction - classification and various methods of dyeing - preparations and applications of dyes - Nitroso dyes - Azodyes - Fast green - Methyl Orange - Methyl Red - Fast Red - Tripheylmethane dyes - Malachite green - Rosaniline - Aniline blue - Crystal violet - Xanthene dyes - Fluorescein - Rhodamine-B - Anthroquinone dyes - Alizarin.

Heterocycles, Vitamins and Steroids: Synthesis of imidazole, oxazole, thiazole, flavones, isoflavones, anthocyanins, pyrimidines (cytocine, uaracil only) and purines (adenine, guanine only). Synthesis of vitamin-A1 using Wittig method. Conversion of cholesterol to progesterone, estrone and testosterone.

Modern synthetic methods, reactions and reagents: Synthesis of simple organic molecules using acetylation and alkylation of enamines, Grignard reactions, Diels - Alder reaction, phosphorus and sulphur ylides, Robinson annulations. Retrosynthetic Analysis: Basic principles and terminology of retrosynthesis, one group and two group C-X disconnections, one group C-C and two group C-C disconnections, amine and alkene synthesis. Protection and deprotection of functional groups (R-OH, R-CHO, RCO-R, R-NH2 and R-COOH).