KAKATIYA UNIVERSITY, WARANGAL, (AP)

Ph.D. ~~Eligibility~~ Test in CHEMISTRY (w.e.f ~~2010~~-11)

Entrance SYLLABUS

UNIT-1 : INORGANIC CHEMISTRY

Bonding theories of metal complexes : Crystal field theory: Salient features, Splitting of metal orbitals in regular and distorted octahedral, square planar, tetrahedral, square pyramidal and trigonal bipyramidal geometries. Measurement of crystal field splitting energy, High spin and low spin octahedral complexes. Crystal field stabilization energy. Factors affecting the magnitude of crystal field splitting. Jahn-Teller distortion. Applications and limitations of crystal field theory. Molecular orbital theory: Nephelauxetic effect. Molecular orbital diagrams of octahedral, tetrahedral and square planar complexes. Molecular orbital treatment of π *bonding* in complexes.

Magnetochemistry of metal complexes : Types of magnetism: para, dia, ferro and antiferro-magnetsm. Temperature independent paramagnetism. Behaviour of para, dia, ferro and antiferro-magnetic substances with temperature. Magnetic susceptibility measurement: Qouy method and Faraday method. Magnetic properties of metal ions spin moment and orbital moment. Orbital contribution to magnetic moment. Spin orbit coupling. Quenching of orbital angular momentum by ligand fields. Magnetic properties of complexes with A, E and T ground terms. Anomalous magnetic moments. Spin-free and spin-paired equilibria.

Reaction mechanisms of metal complexes : Reactivity of metal complexes: inert and labile complexes. Concept of lability and inertness of complexes in terms of Valence bond and crystal field theories. Nucleophilic substitution reaction of octahedral complexes: Dissociative (SN1) and associative (SN2) mechanism. Acid hydrolysis, factors affecting acid hydrolysis. Base hydrolysis, Conjugate base (CB) mechanism. Evidences in favour of conjugate base mechanism. Reaction without the breakage of metal-ligand bond. Nucleophilic substitution reactions of square planar complexes. Mechanisms of substitution in square planar metal complexes, Trans effect, theories of trans effect, polarization theory and π-bonding theory. Applications of trans-effect. Electron transfer reactions: Inner sphere and outer sphere mechanisms. Cross reactions and Marcus-Hush theory.

Metal-ligand equilibria in solution : Stability of binary metal complexes-thermodynamic stability and kinetic stability. Concentration, thermodynamic and conditional constants, Stepvvise stability constants. Trends in stepwise stability constants. Factors influencing the stability of metal complexes with reference to metal and the ligand. Chelate effect and its thermodynamic origin. Macrocyclic effect of crown ethers and cryptates. HSAB rule and its application to stability of complexes and metal-ligand interactions in the biological systems. Determination of stability constants of metal complexes. Spectra-photometric and potentiometric methods.

Organometallic Compounds : Classification and nomenclature of organometallic compounds; Principles of synthesis of organometallic compounds. Synthesis, structure and properties of organometallic compounds of **Al & Sn. 18-Electron** rule and stability of organotransition metal compounds. Synthesis, structure and bonding of olefin, allyl and cyclopentadienyl organometallic compounds of **Fe, Pd** and **Pt.** Applications of organometallic compounds of B and Si in organic synthesis. Organometallic compounds in homogeneous catalysis-Hydrogenation, Hydroformylation and Isomerization processes.

Bioinorganic Chemistry : <u>Metal ions in biological systems:</u> Brief survey of metal ions in biological systems. Basic principles underlying biological selection of elements. Effect of metal ion concentration and physiological effects. <u>Oxygen transport and storage:</u> Hemoglobin and myoglobin- Geometric, electronic and magnetic aspects of dioxygen binding, oxygen adsorption isotherms and cooperativity, physiological significance of

hemoglobin. Role of globin chain in hemoglobin. Metals in medicine: Introduction. Metals used for diagnosis Radiodiagnosis. Magnetic resonance imaging. Metals used for therapy-Lithium, gold and Platinum: Chela therapy.

Chromatography methods : General discussion, Adsorption and Partition chromatography, Principles a Applications of paper chromatography, Thin layer chromatography, Gas chromatography - Applications a Instrumentation: detectors used in GC - thermal conductivity detectors, flame ionization detectors, N- photoionization detectors; HPLC - Applications and Instrumentation: Refractometric, Fluorescence, Dio array detectors; GC-MS and LC-MS: techniques and applications

Thermal Analysis:Principles, Instrumentation, Comparison and interpretation of TGA and DTG curve TGA curves of mixtures, Factors affecting TGA curves. Applications of TGA.Differential Thermal Analys and Differential Scanning Calorimetry - Principles, Instrumentation, and quantitative aspects of DTA a DSC curves, Interpretation of DTA and DSC curves. Influence of atmosphere on DTA curves of a sampl Complementary nature of TGA and DTA . Applications of DTA and DSC.

Unit-II: ORGANIC CHEMISTRY

Heterocyclic Chemistry : Classification of the heterocycles based on the nature of the hetero atom and si of the ring: π-excessive and π-deficient heterocycles - Synthesis, properties and comparative study a reactivities of furan, pyrrole and thiophene: Synthesis and reactivity of indole, pyridine, quinoline, isoquinoli coumarin.pyrazoles. imidazoles, isoxazoles, pyrimidines.

Reaction Mechanisms : Investigation of reaction mechanisms: kinetics, isotopes, study of intermediates a product analyses - study of reaction intermediates: formation and stability of carbonium ions, carbanio carbenes, nitrenes, free radicals and arynes; mechanism in aromatic nucleophilic substitutions: SNAr, Benzy mechanisms-elimination reactions: various types of eliminations and their mechanistic pathways, orientati in eliminations, elimination *vs* substitution - study of nucleophilic substitutions with specific reference to t neighboring group participation(through pi- and sigma-bonds); Factors effecting the reactivity and mechanis of nucleophilic substitutions (substrate structure, nature of the leaving group and attacking nucleoph etc.)Selective organic name reactions: Mannich reaction, Michael addition, Tschitchibabin reaction, Shapi reaction, Barton reaction. Rearrangement reactions: Hoffmann, Curtius, Favorski, Bayer-Villiger, Beckmar Fries, Benzidine. Benzil-Benzilic acid and Dienone-Phenol rearrangements.Von Ritcher rearrangemen Iloffman, Loftier, Freytag reaction - Robinson's annulations - Knoevenagel condesation, The Darze condensation.

SYNTHETIC ORGANIC CHEMISTRY: Formation of -C-C- and -C=C- bonds .: C (single) bond: Alkylation - Importance of enolate anions - Alkylation of relatively acidic methylene group, Alkylation ketones - The enemine reaction lithium di-alkyl cuprates (Gilmans's reagent) - Synthetic applications carbenes and carbenoids.

C=C (double) bonds: Beta elimination reactions - Pyrolytic synthesis, eliminations - Wittig and related reactio - Peterson olefination - Stereoselective synthesis of tri and tetra substituted ethylenes - oxidative decarboxylati of carboxylic acids.

Oxidations and reductions : Oxidations: Oxidation of C=C with transition metal oxidants - $KMnO_4$ a OsO_4, stereochemistry of perhydroxylation. Epoxidation and subsequent transformation of epoxides - Reacti of alkenes with singlet oxygen - Cleavage of glycols [HIO_4 and Pb(OAc)4] - Allylic oxidation with transiti metal oxidants. Reductions: Group III - hydride transfer reagents to reduce carbonyl groups and other functio groups ($NaBH_4$ and $LiAlH_4$) - stereochemistry of hydride reductions (Cyclohexanone) - Group IV hydri donars - dissolving metal reductions - addition of hydrogen -reductive removal of functional groups -Reducti C-C (single) bond and C=C (double) bond formation.

Reagents in organic synthesis : Use of the following reagents in organic synthesis and functional group transformations: Phase transfer catalysts: tetra alkyl ammonium halides and crown ethers, Woodward-Prevost hydroxylation. 1,3-dithianes (Reactivity and umpolung effect), lithium diisopropyl amide (LDA), dicyclohexyl carbodiimide (DCC), trimethyl silyl iodide, tri-n-butyltin hydride, dichioro dicyano benzoquinone (DDQ), selenium dioxide, Wilkinson's catalyst and Baker's Yeast, Merrifield resins

Synthetic Methodology: Introduction - Target selection, retro synthesis - The disconnection approach with suitable examples (simple molecules) - Functional group inter conversions (FGI), disconnection product - Disconnection and synthon - Synthetic equivalents strategic bond approach - Chemo selectivity, regio selectivity and stereo selectivity with examples - Linear and convergent synthesis.

Stereochemistry: Molecular symmetry in organic molecules: Symmetry elements (C_n, C, & S_n) and symmetry operations - Configuration — R, S nomenclature; E. Z nomenclature for unsaturated systems, Re and Si faces, prochirality — Racemization and racemic modifications — Resolution of racemic modifications — Principles of chemical reactivity: Kinetic control and thermo dynamic control — Partial and absolute asymmetric syntheses — Introduction to stereo-selective syntheses — Stereochemistry of nitrogen compounds with a tetra co-ordinate chiral centre — Stereochemistry of the compounds containing — C=N- and —N=N- ; Concept of dynamic enantiomerism and Atrop-isomerism — Conformational analyses of mono and di substituted cyclohexanes.

Unit-III: PHYSICAL CHEMISTRY

Thermodynamics :Concept of standard states - standard entropy - entropy changes in chemical reactions-entropy of mixing, standard entropies of ions. Third law of thermodynamics - calculation of absolute entropies of solids, liquids and gases - tests and exceptions - Gibb's and Helmhoitz free energy, standard free energy of formation- Variation of free energy with temperature and pressure - free energy change in phase transformations Clapeyron and Clausius-Clapeyron equation - Maxwell's relationships and thermodynamic equation of state. - Non-ideal systems: Fugacity of a gas, determination (general and graphieal methods). Aetivity and aetivity coefficients of electrolyte solutions - Determination using Debye-Huckel equation and emf method - vant Hoffs reaction isotherm. Non-ideal mixtures: Concept of partial molar properties-partial - molar free energy-chemical potential. Gibbs-Durhem equation-variation of chemical potential with temperature and pressure- determination of partial molar properties (direct method, method of intercepts and general method). Mixing properties - excess functions and their significance.

Electrochemistry : <u>Conductance:</u> Conductance of strong electrolytes - interionic attraction theory -Thickness of ionic atmosphere (no derivation). Debye Huckel Onsager treatment and derivation of conductance equation - tests and deviations - ion association - ion pair formation-association constant - conductance minima and triple ions.

Electrochemical cells: Reversible and irreversible cells - Nernst equation of cell emf (thermodynamic formulation) - relation to equilibrium constant of cell reaction and other thermodynamic parameters. Chemical cells and Concentration cells with and without transference; Liquid junction potential and its determination; Applications of emf measurements. Determination of pH, pKa and Ksp-potentiometric titrations (acid-base, redox and precipitation). Polarization: Electrode polarization and concentration polarization-Decomposition potential and over voltage-theories of over voltage-factors influencing over voltage.

Kinetics : Simultaneous reactions: Derivation of first order rate expression for parallel, opposing and consecutive reactions. Theory of absolute reaction rates-application to reactions between atoms and molecules-Thermodynamic formulation of reaction rates-Calculation of activation parameters. Lindemann's theory of unimolecular reactions and Hinshelwood modification-Effect of Solvent and Ionic strength on rates of ion-

ion and ion dipole reactions-Isotopic effect on reaction rates-substrate and solvent isotopic effect-Termolecular reactions: Reactions of nitric oxide with hydrogen, oxygen and halogens.

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. Effect of substituent on the rate of reaction - Hammett's and Taft's equations- use of σ and ρ constants and extended Hammett equation. Yukawa-Tsuno equation-Nonlinear Hammett plots- Isokinetic temperature and its determination. Homogeneous acid-base catalysis-mechanism of acid-base catalysis-protolytic and prototropic mechanism.

Quantum Chemistry : Planck's quantum theory and derivation of Planck's temperature radiation law-Derivation of time independent Schrodinger wave equation-wave function and significance of 'P and 'F2-Normalization and orthogonality of wave function-well behaved functions-Operators like momentum (p), angular momentum (L), Energy (E), Hamiltonian (H) and Hermitian- Properties of Hermitian operator-Operator algebra-Postulates of quantum mechanics. **Applications:** Application of Schrodinger wave equation to particle in a one dimensional box and three dimensional box-degenerate states-quantum mechanical tunnelling (qualitative treatment). Rigid rotator: Application of Schrodinger equation to rigid rotator- derivation of energy expression and wave function of a rigid rotator-solution of (φ) and (θ) parts of wave functions-total wave function of rigid rotator.

Hydrogen atom: Separation of (r), (φ) and (θ) equations - Solution of radial equation-Total wave function for hydrogen atom-radial and angular plots-probability functions and radial probability density plots for Is and 2s orbitals.

Photochemistry :Photophysical processes - Radiationless processes (Vibrational relaxation, internal conversion, intersystem crossing) and their rate constants- Radiative processes - fluorescence emission, phosphorescence emission. Kinetics of photophysical unimolecular processes. Delayed fluorescence. Quantum yield and its determination, fluorimetry, phosphorimetry. Bimolecular processes - quenching - Stern -Volmer relationship derivation and deviations. Photochemical processes- Unimolecular processes. Isomerisations and rearrangements (Photochromism), Photoreduction # (hydrogen abstraction by carbonyl group) Norrish Type I and II processes.

Unit IV- SPECTROSCOPY

Microwave Spectroscopy: Classification of molecules based on moment of inertia. Diatomic molecule as rigid rotator and its rotational energy levels. Selection rules (derivation not required). Calculation of bondlengths from rotational spectra of diatomic molecules. Isotope effect on rotational spectra. Calculation of atomic mass from rotational spectra.

Vibrational Spectroscopy : Vibrational energy levels of diatomic molecules, selection rules. Calculation of force constant from vibrational frequency. Anharmonic nature of vibrations. Fundamental bands, overtones and hot bands, Fermi Resonance. Vibration-rotation spectra of diatomic molecules. Vibrations of poly atomic molecules. Normal modes of vibration, concept of group frequencies. Characteristics of vibrational frequencies of functional groups; Stereochemical effects on the absorption pattern in carbonyl group, cis-trans isomerism and hydrogen bonding.

Raman Spectroscopy - Quantum theory of Raman effect, Vibrational Raman spectra, Stokes and anti- Stokes lines. Complementary nature of IR and Raman spectra.

Electronic Spectroscopy: 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 and its derivatives, Woodward-Fieser rules. Polynuclear aromatic hydrocarbons

and diketones. Solvent and structural influences on absorption maxima, Stereochemical factors. Cis-trans isomers, and cross conjugation. Application of electronic spectra of metal complexes-"3d' and 3d" hexa aquo metal complexes. Quantitative applications of electronic Spectroscopy, Beer's law application to mixture analysis and dissociation constant of a weak acid, Charge transfer spectra.

NMR Spectroscopy : Theory of NMR-Nuclear energy levels- Instrumentation-Relaxation phenomenon-spin-spin and spin-lattice relaxations. Shielding and de-shielding mechanism-chemical shift. Factors affecting the chemical shift. Isotropic and anisotropic effects-alkanes, olefins, acetylenes and aromatic systems. Low and High resolution of NMR spectrum of ethyl alcohol. Spin-spin coupling of strongly and weakly coupled systems-coupling mechanism-Types of coupling constants. Factor affecting coupling constants-hybridization-dihedral angle and steric effects. Applications of spin-spin coupling to structure and stereochemistry of organic molecules - NOE and its applications, Lanthanide shift reagents.

ESR Spectroscopy : Introduction-Principles involved in ESR Spectroscopy. Instrumentation-Presentation of ESR speetra-Hperfine coupling constant. ESR spectrum of hydrogen atom. Lande's splitting factor and its significance. ESR spectra of organic radicals like methyl, ethyl, isopropyl, benzene (anion & cation redicals) 1 ,4-benzosemiquinone and naphthalene anion and Cu(II)- salicylaldimine complex.

Mass Spectroscopy : Ionization of molecules - Instrumentation - Determination of molecular formula - General patterns of fragmentation - Preliminary account of chemical ionization - Applications of mass Spectroscopy in the structural determinations: Fragmentation patterns in different functional group systems.

Combined Applications of UV, IR, ^{1}H NMR and Mass Spectroscopy.

Model Question Paper

Time: 3 Hours

Max. Marks : 100

Section-A

a) There shall be 14 short type questions and 10 questions should be answered for 50 marks (10 x 5 = 50), and

Section - B

b) There shall be 7 essay type questions and 5 questions should be answered for 50 marks (5 x 10 = 50)

The medium of eligibility test is English except for language subjects.

100 Multiple choice questions

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