DEPARTMENT OF CHEMISTRY
GITAM INSTITUTE OF SCIENCE
GITAM UNIVERSITY

Syllabus for M.Phil. & Ph.D. entrance examination

PART-A

Unit-1:

Basic principles of volumetric analysis: Expression of concentrations and Stoichiometric calculations. Neutralization Titrations: titration curves, Indicators, applications of neutralization titrations. Non-aqueous solvent: Characteristic of solvents, non-aqueous titrations- types of reactions, indicators and applications i) Determination of acids ii) Determination of bases.

Complexation Titrations: Types of titrations, EDTA titration curves, masking and de-masking agents. Detection of end point in EDTA titrations –metal ion indicators and applications of complexometric titrations. Precipitation Titrations: Law of mass action, solubility product, ionic product, principle, indicators for precipitation titrations Volhard method, Fajans method and Mohr's method. Redox Titrations: titration curves, redox indicators and applications of redox titrations.

*Solids***:** Crystal systems and lattices, miller planes, crystal packing, crystal defects; Bragg's Law, ionic crystals, band theory, metals and semiconductors, Different structures of AX, AX_2, ABX_3 compounds, spinels.

Unit-2

Nature of bonding in Organic Molecules: Localised and delocalised covalent bond, –Concept of aromaticity annulenes and hetero annulenes, inductive and mesomeric effects, Huckel's rule for aromaticity in benzenoid and non-benzenoid compounds, anti-aromaticity and homo-aromaticity –Introduction to types of organic reactions reactive intermediates.

*Stereochemistry and stereoisomerism***:** Conformational isomerism and analysis in acyclic and simple cyclic systems - substituted ethanes, cyclohexane, optical isomerism - optical activity -molecular dissymmetry and chirality. R,S. configurations - relative and absolute configurations optical isomerism due to asymmetric carbon atoms - optical isomerism , geometrical isomerism and E,Z configurations, properties of geometrical isomers. R-S-nomenclature, diastereo isomerism in acylic and cyclic systems inter conversions of Fisher, Newman and Saw-horse projections.

Spectra and structure: Introduction to application of spectroscopic methods for understanding the structure of simple organic molecules: UV, IR, NMR and Mass

Unit-3

*Electrochemistry***:** Electrochemical cells-measurement of EMF-Nernst equation-effect of complexation on electrode potential; Polarization-Decomposition potential and overvoltage- factors influencing theories of over voltage; Activity and activity coefficients-

determination of activity coefficient by EMF method; Debye-Huckel limiting law(DHLL) and its verification,Debye-Huckel-Onsagar equation(derivation not required)-verification and its limitations.

Batteries-primary and secondary cells – lechlanche cell, lead acid storage battery, Nickel-Cadmium cell; Fuel cells-Oxygen-hydrogen fuel cell; Corrosion- theories of dry and wet corrosion-different forms of corrosion- prevention and control of corrosion - cathodic protection-sacrificial anodic and impressed current methods- inhibitors-anodic and cathodic inhibitors; protective coatings-galvanising and tinning

Catalysis: Homogeneous catalysis- acid-base catalysis- mechanism of acid-base catalysis - Enzyme catalysis- Michaelis-Menten kinetics - Heterogeneous catalysis- Langmuir adsorption isotherm- unimolecular and bimolecular reactions-catalytic poisoning-active centers, surface area-determination of surface area with BET equation.

Unit-4

Vibrational and rotational Spectroscopy **:** Rotational spectra of diatomic molecules- rigid rotor-selection rules- calculation of bond length- isotopic effect- second order stark effect and its applications, infrared spectra of diatomic molecules-harmonic and anharmonic oscillators- Selection rules- overtones-combination bands-calculation of force constant-anharmonicity constant and Zero point energy . Fermi resonance, simultaneous vibration-rotation spectra of diatomic molecules

*Nuclear Magnetic Resonance Spectroscopy***:** Nuclear spin, nuclear resonance, saturation, shielding of magnetic nuclei, chemical shift and its measurements, factor influencing chemical shift, deshielding, spin-spin interaction, factor influencing coupling constant 'J'. spin decoupling.

*Electron Spin Resonance Spectroscopy***:** Basic principles, zero field splitting- factors affecting the 'g' value. Isotropic and anisotropic hyperfine coupling constants.

PART-B

Unit-1

Main group elements and their compounds: Allotropy, synthesis, structure andBonding. boranes, carboranes, silicones, silicates, boron nitride.*Transition elements and coordination compounds*: structure, bonding theories,spectral and magnetic properties, reaction mechanisms.*Inner transition elements*: spectral and magnetic properties, redox chemistry.

Organometallic compounds: synthesis, bonding and structure, and reactivity.

Bioinorganic chemistry: photosystems, porphyrins, metalloenzymes, oxygen transport,electron- transfer reactions; nitrogen fixation, metal complexes in medicine.

*Chemistry of Coordination compounds***:** Theories of bonding, Crystal field theory, Limitations of crystal field theory, Ligand field theory- orbital splitting in octahedral, tetrahedral and square planar complexes, Ligand field stabilisation energy, Π-bonding, John-Teller effect.

Unit-2

*Named Reactions***:**Basic concepts of some named and unnamed reactions: Aldol, Perkin, Benzoin, Stobbe, Cannizaro, Wittig, Grignard, Openauer oxidation, Clemmensen reduction - Meerwein - Pondorf Verley and Birch reductions**;** Michael addition, Mannich Reaction, Diels - Alder reaction, Wolf-Kishner,reduction, Friedel – Crafts reactions, Robinson annulation.
*Rearrangements***:** Classification and general mechanistic treatment of nucleophilic, free radical and electrophilic rearrangements, Wagner – Meerwein and related reactions, Hofmann, Stevens and Wittig rearrangements

*Natural Products***:**Isolation, structure elucidation and synthesis of alkaloids; atropine, caffeine, terpenoids: α-terpeneol, camphor.

*Aliphatic and Aromatic Substitution Reactions***:** *Nucleophilic* **:** The S_N2, S_N1, S_Ni and SET mechanisms, neighbouring group participation, anchimeric assistance, classical and non-classical carbocations, phenonium ions, norbornyl system allylic, aliphatic trigonal and a vinylic carbon, factors effecting substitutions.*Electrophilic***:** SE^1, SE^2 and SE^i Mechanisms and related effects.*Elimination Reactions***:** The E2, E1and E1cB mechanisms and their orientation of the double bond. Reactivity-effects of substrate structure, attacking base, leaving group and the medium. Stereochemistry of eliminations in acyclic and cyclic systems, orientation in eliminations – Saytzeff and Hoffman elimination.*Addition Mechanisms*:Addition to carbon multiple bonds- Addition reactions involving electrophiles, nucleophiles and free radicals, cyclic mechanisms, orientation and stereochemistry.

Chemistry of Heterocyclic compounds: Synthesis and Reactivity of the following system, Pyrrole, Furan, Thiophene, Pyridine, Quinoline, Indole, Benzofuran, Pyrazole, Imidazole, Oxazole, Thiazole, Pyridazine, Pyrimidine.

Unit-3

*Chemical Kinetics***:** Theories of reaction rates- Collision theory of reaction rates, steric factor; Theory of absolute reaction rates, comparison of results with Eyring and Arrhenius equations; unimolecular reactions and RRKM theory; Reactions in solution- primary and secondary salt effects, effect of dielectric constant. Homogeneous catalysis-acid-base catalysis- protolytic and prototropic mechanism; Enzyme catalysis- Michaelis-Menten kinetics. Heterogeneous catalysis- Langmuir adsorption isotherm.

*Thermodynamics***:**Second law of thermodynamics-Entropy-entropy changes accompanying specific process-entropy of mixing of ideal gases-Entropy and disorder; Helmoltz and Gibb's energies, real gases-fugacity-definition, standard states of real gases- relation between fugacity and pressure; Van't Hoff equation, Claussius-Claperyon equation, Gibbs-Duhem equation. Third law of thermodynamics-determination of absolute entropy-limitations of third law of thermodynamics;
*Photochemistry***:**Photophysical and photochemical processes- Jablonski diagram—radiative and radiationless transitions-internal conversion and inter system crossing- fluorescence and phosphorescence- Quantum yield and determination-photochemical reactions with

high and low quantum yields with examples;sensitization and quenching-derivation of Stern-Volmer equation

Unit-4

Quantum Chemistry:Wave equation-interpretation of wave function-properties of wave function-normalization and orthogonalisation, operators-linear and nonlinear commutators of operators. Postulates of quantum mechanics, setting up of operators observables-Hermitian operator-Eigen values of Hermitian operator Particle in one dimensional box, particle in a three dimensional box, rigid rotor,

Bonding in molecules: Born-Oppenheimer approximation- Hydrogen molecule ion, LCAO-MO and VB treatments of the hydrogen molecule (fundamental concepts only); electron density, forces and their role in chemical bonding. Hybridization and valence MOs of H2O, NH3 and CH4.

Symmetry and Group Theory in Chemistry: Symmetry elements and symmetry operations and point groups, Schoenflles symbols, classification of molecules into point groups, Axioms of group theory, group multiplication tables for C_{2v} and C_{3v} point groups.

Text Books

1. Advanced Inorganic Chemistry by F.A.Cotton and R.Wilkinson, IV Edition, Johnwilly and sons, New York, 1980.
2. Inorganic Chemistry by J.E.Huheey, III Edition, Harper International Edition, 1983.
3. Inorganic Chemistry by D. Shriver and Peter Atkins, 4th Edition, OUP Oxford, 2006.
4. Organic Chemistry Vol. I and Vol. II by IL Finar ELBS, 1964.
5. Organic Chemistry by Morrison and Boyd, PHI, India, V Edition, 1987
6. Physical Chemistry by P. W. Atkins, Oxford University press, VII Edition,2002.
7. Text book of Physical Chemistry by S. Glasstone,D. Van Nostrand company, inc, 2ndEdition, 1946
8. Thermodynamics A Core Course- R. C. Srivastava, S. K. Saha and A. K. Jain, Prentice-Hall of India, II Edition, 2004.
9. Introduction to Quantum Chemistry, A.K. Chandra, Tata McGraw Hill, IV Edition, 1994
10. Symmetry and Spectroscopy of Molecules by K.Veera Reddy, New Age, 1988.
11. Fundamentals of Molecular Spectroscopy by C.N. Banwell and E.M. Mc Cash, IV Edition, Tata McGraw Hill, New Delhi,1994.