SYLLABUS

MANONMANIAM SUNDARANAR UNIVERISTY, TIRUNELVELI-12

PG - COURSES – AFFILIATED COLLEGES

Course Structure for

M.Sc. Chemistry

(Choice Based Credit System)

(with effect from the academic year 2017- 2018 onwards)

Semester-IV				
Part	**Subject Status**	**Subject Title**	**Subject Code**	**Credit**
	Core - 20	Organic Chemistry – IV	PCHM41	4
	Core - 21	Inorganic Chemistry – IV	PCHM41	4
	Core - 22	Physical Chemistry – IV	PCHM43	4
	Core - 23 Practical - 10	Organic Chemistry Practical – IV	PCHL41	2
	Core - 24 Practical - 11	Inorganic Chemistry Practical – IV	PCHL42	2
	Core - 25 Practical - 12	Physical Chemistry Practical – IV	PCHL43	2
	Core - 26	Project	PCHP41	6

ORGANIC CHEMISTRY – IV

Objectives

- To study the intermediate reactions, conformational, synthetic analysis, important Reagents in organic synthesis and the Steroid compounds.

Unit-I :

Reaction under Intermediate chemistry

Reaction Under Carbanion Intermediate: Stobbe, Darzen, acyloin condensation Shapiro reaction and Julia olefination.

Reaction through carbene intermediate: Bamford – Stevens , Reimer- Tiemann reactions.

Reaction Under Carbocation intermediate: Oxymercuration, halolactonisation, Baeyer-villiger oxidation

Reaction following Radical intermediate: Mc Murray coupling, Gomberg-Pechmann and Pschorr reactions.

Reaction involving Ylide intermediate: Wittig reaction and Peterson olefination.

Unit-II :

Conformational analysis

Conformation and configuration-conformational free energy-conformational analysis of mono substituted (alkyl, halogens) and 1,1-disubstituted (alkyl) and 1,2-1,3-and 1,4-dimethyl substituted cyclohexanes -compounds existing in boat form-conformation of cyclohexanone, decalin and perhydrophenanthrene-Curtin-Hammett principle- conformation and reactivity of acyclic and cyclic compounds (6membered).

Unit-III :

Reterosynthetic analysis

Synthon-synthetic equivalent-Functional group interconversions -use of protecting groups for alcohols, amines, acids, carbonyl compounds- use of activating and blocking groups-Robinson annulations reaction-carbon skeletal complexity-Role of key intermediates in organic synthesis. Reterosynthetic analysis of the following compounds: Twistane, cis - Jasmone, Baclofen, Trihexyl phenydyl, S-propanediol, Isonootkatone, cascarillic acid, camphor and 2,4-dimethyl-2-hydroxy pentanoic acid.

Unit-IV :

Reagents in organic synthesis .

2,3-Dichloro-5,6-dicyano-1,4-benzoquinone (DDQ), DMSO, Super hydrides-Dess-martin-periodinane-Osmium tetra oxide.Modern Reagents: Introductory treatment of the application of silicon (Tri alkyl silyl halides, organo silanes), Boron (9 – BBN, borane, and alkyl borane), phosphorus (phosphoranes),palladium(Still coupling, Suzuki Coupling, Heck and Negishi reactions) samarium(SmI2), ruthenium(RuO2,Ru-Binap Complex), platinum(PtO2, Adam's Catalyst) reagents in organic synthesis.

Unit-V : Steroid

Classification- structural elucidation of cholesterol, irradiated products of ergosterol. Conversion of cholesterol to androsterone, progesterone, testosterone, 5α- and 5 β-cholanic acid. Conversion of Oestrone to Oestriol, Oestrodiol and vice-versa. Conformational structure of cholestane and Coprostane. General study of Bile acids and Prostoglandins.

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INORGANIC CHEMISTRY- IV

Objectives:

- To study the applications of Mossbauer, photoelectron and nuclear quadrupole resonance spectroscopic techniques in inorganic systems.
- To study the applications of ORD and CD to determine absolute configuration of chelate complexes.
- To introduce bioinorganic chemistry and to study role of metalloporphrins and metalloenzymes in various biological processes.
- To give an insight into material science.

UNIT - I :

SPECTRAL METHODS TO THE STUDY OF INORGANIC COMPOUNDS – II

Mossbauer spectroscopy : Principle – isomer shift (IS) – splitting of resonance lines: quadrupole splitting and magnetic hyperfine splitting. Applications: MB spectra of iron compounds/complexes – structural elucidation, π- bonding effect, determination of high spin and low spin, spin state crossover and cis–trans isomers – nature of the complexes – mixed valence complexes. Tin compounds: MB spectra of Sn(II) and Sn(IV) compounds, oxidation states of Sn in its different compounds. Applications in bioinorganic chemistry: oxy and deoxy- hemerythrin - catalase, peroxidases, Fe-S protein systems.

ORD AND CD - Optical isomerism in octahedral complexes – absolute configuration of chelate complexes from ORD and CD.

UNIT - II:

SPECTRAL METHODS TO THE STUDY OF INORGANIC COMPOUNDS – III

Photo electron spectroscopy: Theory – types of PES –origin of fine structures – adiabatic and vertical transitions – PE spectra of homonuclear diatomic molecules (N_2, O_2) – hetero nuclear diatomic molecule (CO) – polyatomic molecules (H_2O, CO_2, CH_4, NH_3). Evaluation of vibrational constant – Koopman's theorem – application and limitation of the theorem. XPS (ESCA): structure of N_3^- ion, CCl_3CH3, N (1s) spectrum of $[Co(en)_2(NO)_2]NO_3$, C(1s) spectrum of $C_2H_5COOCF_3$. Shake-up and shake-off processes – Structural and bonding information in metal carbonyls – Auger electron spectroscopy.

NQR spectroscopy: Applications – fingerprint technique. Investigating the electronic structure of molecules – information about EFG of nuclei – ionic character and hybridization of the bonds – structure of charge transfer complexes – Phase transition – hydrogen bonding.

Unit - III:

BIOINORGANIC CHEMISTRY – I

Non-metals and metals in biological systems, essential and trace elements; classification of metallo-biomolecules, coordination environment and entatic state. Metalloporphyrins – chlorophyll and photosynthesis; cytochromes, hemoglobin, myoglobin and dioxygen binding, vitamin B_{12} and co-enzyme – in vivo and in vitro nitrogen fixation. Iron storage and transport: ferritin, transferrins and

siderophores, iron proteins: hemerythrin, cytochrome P450 enzyme, ferredoxin and rubredoxin.

Unit - IV:

BIOINORGANIC CHEMISTRY – II

Copper proteins and Enzymes : plastocyanin, azurin, hemocyanin and ascorbic oxidase – different types of Cu present in proteins and enzymes. Zinc enzymes: carboxypeptidase A, carbonic anhydrase and superoxide dismutase. Inhibition and poisoning of enzymes illustrated by xanthine oxidase and aldehyde oxidase. Toxicity of metals and the role of metallothionins – excess and deficient levels of Cu and Fe and the consequent diseases – chelate therapy – metal complexes as drugs, anticancer and antiarthritic agents. Metal complexes as probes of nucleic acids.

UNIT – V :

CHEMISTRY OF INORGANIC MATERIALS

Synthesis of inorganic materials – High temperature ceramic methods – Co-Precipitation and Precursor Methods – Combustion synthesis – High temperature reactions – precipitation, gel, solution and hydrothermal methods – Synthesis in sealed tubes and special atmospheres – Low temperature methods – Chemical Vapour Deposition (CVD) – Preparing single crystals -Epitaxy methods – Chemical Vapour Transport - Solution Methods. Insertion compounds of metal oxides – Intercalation compounds of graphite and transition metal disulphides. Zeolites: structures and properties – pillared clays – fullerenes and fullerides.

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15. Lesley E.Smart Elaine A.Moore, Solid St

PHYSICAL CHEMISTRY- IV

Objective

- To understand the Principles and applications of Vibrational and Raman spectroscopy
- To obtain Knowledge Fast reaction study
- To learn the Theories and applications of Kinetics
- To Know the Principles of Surface Chemistry and Catalysis

UNIT - I:

Vibrational Spectroscopy

Vibrating diatomic molecule: Energy of diatomic molecules as simple harmonic oscillator- energy levels, vibrational transitions, selection rules; anharmonic oscillator-energy levels, selection rules, vibrational transitions. Diatomic vibrating rotator: Born-Oppenheimer approximation, vibration-rotation spectra, selection rules, P, Q, R branches. Vibrations of polyatomic molecules: symmetry and fundamental vibrations, normal modes of vibration, overtones, combination, difference bands; influence of rotations on the spectra of polyatomic molecules-parallel and perpendicular vibrations in linear and symmetric top molecules.

UNIT-II: Raman Spectroscopy

Lasers: Nature of stimulated emission-coherence and monochromaticity, population inversion, cavity and mode characteristics, Q-switching, mode locking; types of lasers-solid-state, gas, chemical, and dye lasers.

Raman Effect: Quantum theory of Raman effect, Classical theory of Raman effect, Pure rotational Raman spectra- linear molecules, symmetric top and spherical top molecules, Vibrational Raman spectra-symmetry and Raman active vibrations, rule of mutual exclusion; Overtone and combination vibrations, Vibrational Raman spectra, Rotational Fine structure. Polarisation of light and Raman effect-The nature of Polarized effect, Vibrations of spherical top molecules and other types of molecules. Structure determination from Raman and Infra-red spectroscopy, Applications of IR and Raman spectroscopy: skeletal and group vibrations, finger printing and absorption frequencies of functional groups for inorganic and organic compounds. Techniques and instrumentation, Near-Infra-red FT-Raman spectroscopy.

UNIT-III:

Chemical Kinetics I

Reactions in Flow systems-Techniques for very fast reactions-Stopped-Flow method, Relaxation methods, Shock-Tube methods, Temperature, Pressure, electric field and magnetic field jump methods, Flash photolysis and pulse radiolysis. NMR and ESR methods of studying fast reactions.

Collision theory. Potential Energy surfaces-energy of activation. Statistical mechanics and chemical equilibrium- Derivations of rate equations Symmetry numbers and statistical factors. Application of ARRT to Reaction between atoms and reaction between molecules. Thermodynamic Formulation of conventional transition

state theory, Limitations of transition state theory. Vibrational transition state theory, Quantum mechanical transition state theory , Microscopic reversibility. Unimolecular reactions- Lindemann-Christiansen hypothesis, Hinshelwood, RRK, RRKM and Slater theories.

UNIT-IV: Chemical Kinetics II

Elementary reactions in solution-Solvent effects on reaction rates, Factors determining reaction rates in solution- collisions in solution, Transition State Theory, Influence of internal pressure, influence of salvation. Reaction between ions-Influence of solvent dielectric constant, Pre-exponential Factors, Single-Sphere Activated Complex, Influence of ionic strength. Influence of Hydrostatic Pressure-Van't Hoff's equation and volumes of activation. Substituent and correlation effects-Hammett equation, Compensation effect.

Composite reactions-Types of composite mechanism, Rate equations for composite mechanisms, Simultaneous and consecutive reactions, Steady –State Treatment, Kinetics of H_2-Cl_2 and H_2-Br_2 reactions, Formation of Phosgene-decomposition of O_3 and N_2O_5. Rice-Herzfeld mechanism, Explosive reactions: H_2-O_2 reaction.

UNIT-V:

Surface Chemistry & Catalysis

Introduction: Adsorption- Physisorption and chemisorptions. Adsorption isotherms: Freundlich, Langmuir, BET and Gibbs adsorption isotherms. Surface area dertermination. ARRT to surface reactions. Micelles: Micelles and reverse micelles-microemulsion-solubilisation.

Catalysis: Homogeneous catalysis- acid-base catalysis- Van't Hoff and Arrehenius complexes for Protropic and Protolytic mechanisms. Bronsted catalysis law- Hammett acidity function. Heterogeneous catalysis. Chemical reactions on solid surfaces. Enzyme catalysis: Michaelis-Menton Kinetics- Rate of enzyme catalyzed reaction- effect of substrate concentration, pH and temperature on enzyme catalyzed reactions.

REFERENCE BOOKS

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Organic Chemistry Practical – IV

Estimation, two stage preparations and chromatographic techniques have been included as the practical components.

Microscale preparations are recommended for the simple reason, they are both economic-friendly and eco-friendly

A.List of Estimation

1. Glucose-Lane Eynon and method
2. Glucose-Bertrand's method
3. Iodine value of an oil
4. Estimation of acetyl group
5. Purity of Glucose.

B. List of Two stage preparations

1. Benzophenone Benzpinacol Benzpinacolone
2. Phthalic acid Phthalic anhydride Phthalimide
3. Thiourea s-benzyl isothiuronium chloride s- Benzyl-isothiuronium benzoate
4. Aniline Tri bromoaniline Sym-Tribromobenzene
5. Phthalic anhydride Phthalimide Anthranilic acid

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INORGANIC CHEMISTRY – IV

I. Preparation of inorganic complexes and quantitative estimation by volumetric or Instrumental methods.

1. Preparation, and analysis of potassium trisoxalatochromate(III) trihydrate K3[Cr(C2O4)3].3H2O
2. Preparation and analysis of potassium hexathiocyanatochromate(III) tetrahydrate K3[Cr(SCN)6].4H2O
3. Preparation and analysispotassium trisoxalatomanganate(III) trihydrate K3[Mn(C2O4)3].3H2O
4. Preparationand analysis of potassium trisoxalatoferrate(III) trihydrate K3[Fe(C2O4)3].3H2O
5. Preparation and analysis of potassium trisoxalatocobaltate(III) trihydrate, K3[Co(C2O4)3].3H2O
6. Preparation and analysis of Durrant's salt, K4[C2O4) 2Co(OH)2Co(C2O4)2].3H2O
7. Preparation and analysishexamminecobalt(III) Chloride, [Co(NH3)6]Cl3
8. Preparation and analysis of chloropentaamminecobalt(III) chloride, [Co(NH3)5Cl]Cl2
9. Preparation and analysis of trinitrotriamminecobalt(III), [Co(NH3)3(NO2)3]
10. Preparation and analysis of trans-dichlorobis(diaminoethane)cobalt(III) chloride, trans-[Co(en)2Cl2]Cl
11. Preparation and analysis of (NH4)2[VO(C2O4)2].2H2O
12. Preparation and analysis of tris(thiourea)copper(I) sulphate dihydrate, [Cu(tu)3]2SO4.2H2O

II. Characterisation of metal complexes prepared during the practicals by UV and IR spectral techniques (Course work).

III. Study of linkage isomerism in pentaamminenitritocobalt(III) chloride, and pentaamminenitrocobalt(III) chloride using IR (Course work).

REFERENCES

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5. Geoffrey Pass, Haydn Sutcliffe, Practical Inorganic Chemistry - Preparations, reactions and instrumental methods, Springer 1974.

PHYSICAL CHEMISTRY PRACTICAL-IV

Objective:

- To obtain and improve the Knowledge of Potentiometric Titrations.
- To understand the Principles and applications of Adsorption

POTENTIOMETRIC TITRATIONS

I. **Precipitation titrations**

Mixture of Cl-and I-vs Ag+

II . Redox titrations

(i) Fe^{2+} vs Ce^{4+}

(ii) I- vs $KMnO_4$

III. Solubility Product Determination of solubility product of sparingly soluble silver salts.

ADSORPTION

Freundlich Adsorption isotherm:

Adsorption of acetic acid on charcoal.

REFERENCE BOOKS (Practical I to IV)

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Project