Anekant Education Society's Tuljaram Chaturchand College, Baramati 413102(Dist. Pune) (Autonomous)

Revised Syllabus for M.Sc. (Inorganic Chemistry) Part II (Semester III)

Choice based Credit System Syllabus to be implemented from Academic Year 2022-2023

M. Sc. - II Inorganic Chemistry Semester – III

PSCHI 231: Organometallic Chemistry & Homogeneous catalysis (48 L+ 12 T) (4 credit)

Learning Objective :

- To understand basic principle and applications of organometallic chemistry
- Students will be able to learn metal-metal bonds, clusters, cadges, fluxional behaviour.
- Students will be able to synthesis of carbene, carbynes, sigma and pi complexes.
- Students will be able to learn about C-C coupling reactions, applications.
- Students will be able to understand magnetic behaviour.
- To make students capable of studying chemistry in academic and industrial courses.
- To develop problem solving skills in students.

Learning Outcomes:

- Student will gets knowledge about homogeneous catalyst
- Understand the essential properties of homogeneous catalyst- zeigler Natta , c-c coupling reactions
- Student will get knowledge about synthesis, properties, metal carbon bonds, applications of OMC.

Section I- Organometallic Chemistry (24 L+ 06 T) (2 credit)

- 1. Introduction and Recapitulation Sigma complexes and π complexes: Synthesis, bonding, properties and applications.
- (3 L)
 Metal-Carbon multiple bonded compounds Carbene and Carbynes: Synthesis, bonding, properties and applications. Metal Carbonyls: Isoelectric and Isolobal Analogy, Wade Mingo's rule
 (3 L)
- nⁿCnRn: Carbocyclic Polyenes: Synthesis, bonding, properties and applications. Allyls, Pentadienyls, Cyclobutadienes, Cyclopentadienyl, Cycloheptatrienyls, Arenes, Cyclooctatetraenes.
 (6 L)
- 4. Fluxional Behaviour of organometallic compounds and study of organometallic compound by NMR, IR. (3 L)
- 5. Phosphine complexes: Synthesis, bonding, properties, and applications. (2 L)
- 6. Metal-Metal Bonds: Transition metal atom clusters and cages. (2 L)
- 7. Roll of transition metal organometallics in organic synthesis:

8. Applications Organometallic Chemistry in pharmaceutical, medical, agriculture and horticulture. (2 L)

Section II- Homogeneous Catalysis (24 L+ 06 T) (2 credit)

- 1. Introduction to catalysis: Basic principle, Definition of activity and selectivity in catalysis, Homogeneous vs. Heterogeneous catalysis, Importance of Homogeneous catalysis in synthesis of high value chemicals and its examples (4 L)
- Characteristics of central metal atom and influence of attached ligands on catalytic activity.
 Important properties of ligands: Elementary steps, important reaction types, Catalytic cycle, Catalytic intermediates and their identification. (4 L)
- Hydrogenation of Olefin: Isomerization, Dimerization, Hydrocyanation and Metathesis reaction, Carbonylation reaction: Monsanto acetic acid process and its industrial importance. (4 L)
- 4. Hydroformylation reaction in Rhodium complexes, Role of phosphine ligand in regioselective formation of ligand aldehyde. (4 L)
- Polymerization: Catalytic cycle for alkene Polymerization, Metallocene catalystsstructure and special features, advantages of Metallocene catalysis, Mechanism of polymerization and stereo control by Metallocene catalyst. (4 L)
- 6. C-C coupling : Cativa process, Heck reaction, Suzuki cross coupling reaction, Negeshi reaction, Sonogashira reaction, Kumada coupling reaction (4 L)

Reference Books:

- 1. Organo transition Metal Chemistry Anthony F. Hill, Royal Society of Chemistry, Tutorial Chemistry Text, 2002.Chapters1-7.
- 2. Organometallics: A concise Introduction, Ch. Elshebroicn and A. Salzer, VCH, chapters 12-16
- 3. Organotransition Metal Chemistry: Applications to Organic Synthesis, S.G. Davies, Permagaon 1982.
- 4. Inorganic Chemistry 3rd edn. D.F. Shriver and P.W. Atkins, Oxford University Press, 1999, Chapter 16.
- 5. Organometallic Chemistry -R.C. Mehrotra and A. Singh, 1992, Wiley
- 6. Principles of Organometallic Chemistry, P. Powell, Chapman & Hall
- 7. Organometallic Compounds, Morries, Sijlirn, IVY Publication House
- 8. Organometallics in Organic Synthesis Swan & Black
- 9. Organometallic Chemistry E.J. Elias and Gupta
- 10. Homogeneous Catalysis G.W.Parshall

PSCHI-232: Inorganic reaction mechanism and photochemistry (48 L+ 12 T) (4 credit)

Learning Objective :

- Student should able to understand different types of inorganic reactions.
- Student should able to differentiate between SN¹ and SN² reaction mechanism.
- Student should able to understand substitution reactions in square planer and octahedral complexes
- Student should be able to understand different types of photochemical reactions

Learning outcome:

- should be able to understand magnetic properties of compound
- Student should able to understand Student inorganic reaction mechanism.

Section I- Inorganic reaction mechanism (24 L+ 06 T) (2 credit)

1. Types of Mechanisms: Basic concepts as stability and lability, stability constants; HSAB principle, Chelate effect, Macro cyclic effect; ligand transfer and electron transfer reaction in coordination compounds, intimate and stoichiometric mechanism of ligand substitution

(8 L) 2. Substitution in square planar complexes- trans effect, trans series, applications of trans effect (2 L)

- 3. Substitution in octahedral complexes- SN¹, SN², SN¹CB mechanisms, Racemisation in coordination compounds, steric effects on substitution (6 L)
- 4. Electron transfer reactions- Potential energy diagrams as a conceptual tool, Marcus equation, types of electron transfer reactions and factors affecting on electron transfer reactions. (6 L)
- 5. Other reaction types- Oxidative addition, reductive elimination, methyl migration and CO insertion reactions (2 L)

Section II--Inorganic photochemistry, reaction types and magnetic properties (24 L+ 06 T) (2 credit)

1. **Photochemical reactions-** Prompt and Delayed reactions, Quantum yield, Recapitulation of fluorescence and Phosphorescence, Photochemical reactions by Irradiating at d-d and

charge transfer bands, Transitions in metal-metal bonded systems, photochemical reactions involving chlorophyll, Kinetics of excited state processes (8 L)

2. Reactions of coordinated ligands

i) Non-Chelate forming reactions-

Reactions of donor atoms (Halogenations of coordinated N atoms, alkylation of coordinated S and N atoms, solvolysis of coordinated P atoms), Reactions of non-donor atoms, Nuclear behaviour of ligand, Electrophilic behaviour of the ligand.

- ii) Chelate ring forming reactions- Reactions predominantly involving thermodynamic template effects, reactions predominantly involving kinetic effects
- iii) Chelate modifying reactions

(8 L)

3. Magnetic properties:

i) Magnetic moments based on crystal field ground term, perturbation theory and its applications, anomalous magnetic moments in magnetically dilute and concentrated system in various symmetrical environments of coordination complexes (6 L)
 ii).Mixed valence compounds (2 L)

Reference Books:

- 1. Inorganic Chemistry- Principles of structure and reactivity, J.E. Huheey, E.A. Keiter and R.L. Keiter 4th Edn. Harper Collins publication New York.
- 2. Mechanism of Inorganic Reactions in solution- an introduction, D. Benson, McGraw-Hill publication
- 3. Basic inorganic Chemistry by F. A. cotton and G.Wilkinson, Wiley Eastern limited new Delhi.
- 4. Inorganic Chemistry by D. F. Shriver and P.W. Atkins
- 5. Mechanisms of Inorganic reactions by C. F. Basolo and R. G. Pearson Wiley New York.
- 6. Magnetochemistry by Shamal and Dutta.

PSCHI-233: Physical Methods in Inorganic Chemistry (48 L+ 12 T) (4 credit)

Learning Objectives:

- Students should be able to understand principle, instrumentation of various techniques.
- Students should be able to handle various instrument and applied for characterization of various compounds.
- Student should be able to understand ESR,XRD, XPS, Mossbauer spectroscopy.
- Students will be able to identify and describe different approaches used in the treatment
- Student will learn principle of different technique.
- Student will understand basic concepts, principle and applications.

Learning Outcome:

- Student should be able to analyse ESR, XPS XRD, Mossbauer spectra.
- Student should be able to determine magnetic nature, crystalline size & structures.

Principles, Instrumentation & Applications of the following techniques,

1. Thermal techniques (DTA, DSC), DMA (dynamic mechanical analysis)	
Derivative thermogravimetric and its advantages	(10L)
2. X-Ray Diffraction Powder & Single Crystal	(8L)
3. Cyclic Voltammetry	(4L)
4. Mossbauer spectroscopy	(4L)
5. Electron Spin resonance spectroscopy	(10L)
6. X-ray Photoelectron Spectroscopy	(2L)
7. Microscopy- Electron microscopy, Laser microscopy, X-ray microscopy	(6L)
8. NQR (Nuclear Quadrupole Resonance), NMR of Inorganic Compound	(4L)

Reference Books:

- 1. Structural methods in Inorganic Chemistry E.A.V. Edsworth, D.W.H. Rankin & S. Cradock, Blackwell Scientific Publication, 1987.
- 2. Physical Methods for Chemists-R.S. Drago, (2nd edition, Saunders)
- 3. Instrumental methods of Chemical Analysis Chatwal & Anand
- 4. Laboratory Techniques in Electro analytical Chemistry edited by P.T. Kissinger and W.R.Heinman (1984) M. Dekker vinc (USA)

- 5. Dennis H. Evans, Journal of Chemical Education, vol.60, pp290 (1983).
- 6. P.T. Kissinger and W.R. Heinmann, Journal of Chemical Education, vol.60, pp702 (1983).
- 7. J.J. Van Benschoten, Journal of Chemical Education, vol.60, pp772 (1983).

PSCHI-234 : Bioinorganic and Inorganic medicinal chemistry (48 L+ 12 T) (4 credit)

Learning Objective :

- Students will able to recognise and explain the interaction of different metal ions with biological ligands
- To understand various functions and biochemistry of enzyme containing metals.
- To Understand the concept & to find out biological role
- Students will able to understand inorganic metals in biology
- Student should explain the functions of haemoglobin & myoglobin

Learning Outcome:

- Students should able to understand role of various metals in medicine
- Students should able to understand Antitumour, anti-HIV, anti-anthritic activity
- Student should able to understand the mechanism about medicinal chemistry.
- Student would be able to understand different structural forms of crystals
- To develop analytical abilities for independent thinking.

Section I- Bioinorganic chemistry (24 L + 06 T) (2 credit)

- 1. Recapitulation of biological roles of metals and ligand structure, function and biochemistry of enzymes containing
- i) Zinc: Zinc finger, carboxypeptidase, carbonic anhydrase,
- ii) **Nickel**: Ni in proteins, Nickel transport and enzyme active site assembly, coordination of biological nickel.
- iii) Molybdenum: Cofactors, antagonism between copper and molybdenum hydroxylase
- iv) Copper: Type I, Type II, Type III, Blue copper proteins and non-blue copper proteins
- v) Manganese

vi) Biochemistry of chromium and vanadium	(16 L)
2. Transition metal complexes as chemical nucleases	(4 L)
3. Radiopharmaceuticals and MRI contrast agents.	(4 L)

Section II: Inorganic medicinal chemistry (24 L + 06 T) (2 credit)

1. Overview

Introduction, metal ions in disease as chelating agents, metalloproteins as drug targets, matrix metalloproteinases, modulation of cellular responses by metal containing drugs, metal based chemotherapeutic drug, metal complexes as diagnostic agent (6 L)

2. Cis-platin based anticancer agents.

Mode of action, mechanism.

3. Bismuth in medicine

Chemistry of bismuth

Bismuth in medicine- helicobacter, pylori bacterium methods for the study of bismuth, Bismuth citrate complex

(3 L)

Bismuth complexes with biomolecules- bismuth binding to oxygen containing biomolecules, bismuth complexes with thiolate ligands, bismuth (III) complexes with metallothionine and transferring, enzyme inhibition (6 L)

4. Gold complexes with anti-arthritic, anti-tumour and anti-HIV activity

Introduction, crysotherapy, history of medicinal uses

Gold chemistry- oxidation state, Gold (I) complexes, Gold (III) complexes, oxidation-reduction potentials

Gold biochemistry and pharmacology- in vivo metabolism and ligand displacement, anti-HIV activity. (5 L)

5. Biomedical uses of lithium

Chemistry of lithium, Distribution in the body and cells, Biochemistry of lithium and lithium isotope. (4 L)

Reference books:

- 1. Bioinorganic chemistry R. J. P. Williams
- 2. Bioinorganic chemistry: An Introduction, Robert Crichton, Elsevier Science, 2007.
- 3. Metal complexes as enzyme Inhibitors A.Y. Louiwe and Thomas Meade Chem.Rev. 1999,99,2711
- 4. Bioinorganic chemistry: Inorganic elements in the chemistry of life, An introduction and guide- wolfgangKaim, BrigilleSchwedrski, John Wiley and sons 1994.
- 5. Principle of Bioinorganic chemistry- S.J. lippard and J.M. Berg, University science Books 1994.
- 6. The Biological Chemistry of the elements: The Inorganic Chemistry of life- Silva, J.J.R. Fraustoda and R.J.P. Williams second E.d. oxford university press, 2012.
- 7. Uses of inorganic chemistry in medicine Ed. Nicholas, P. Farrel

Practical course I

PSCHI-235: Analysis, Estimations and computer applications (4 Credit)

Learning objectives:

- Student should be able to select method for analysis, decide and prepare for analysis.
- Students should able to select procedure for analysis, identify sources possible errors in the result obtained.
- Students should able to introduce methods of chemical analysis.
- Perform required calculations involved in the analysis by titrametrically as well as gravimetrically.
- Students should able to know various instrumental methods of analysis.

Learning Outcomes:

- Students will gets an opportunities to handle and understand principles of different instruments.
- Exercise their critical thinking in creating new knowledge.
- Effectively communicate the knowledge of their study and research in their respective disciplines.

A. Alloy analysis (any 2)

- 1 To determine the amount and percentage of Ni, Fe, Cr from Nichrome alloy
- 2 To determine the amount and percentage of Cu, Ni, Fe from Monel metal
- 3 To determine the amount and percentage of Cu, Sn, Zn from Gun metal

B. Ore analysis (any 2)

- 1 To determine amount and percentage of Fe, Ti, Al and silica from Illemenite ore
- 2 To determine amount and percentage of Ca, Mg, Si from Dolomite ore
- 3 To determine amount and percentage of Fe, Si, Ca from cement sample

C. Instrumental analysis (any 2)

- 1 To determine Zn/Cu/Fe/Mn from soil sample by AAS method
- 2 Flame photometric estimation of each Na, K from given sample by working curve method.
- 3 Flame photometric estimation of each Na, K from given sample of binary mixture by standard addition method.

- 4 Determination of Assay of Metformin by UV
- 5 Determination of nitrogen by using nitrogen analyser from given sample.

D. Inorganic Estimations (any 4)

- 1 Estimation of Mn from tea leaves.
- 2 Estimation of Vitamin C from lemon juice.
- 3 Estimation of Cu from fungicide.
- 4 Estimation of calcium and silica from ash.
- 5 Determination of Chromium from zinc chrome.
- 6 Determination of Fe and Zn from Iron and Zinc supplementary capsule.
- 7 Determination of amount and percentage of caffeine from coffee.
- 8 Estimation of Calcium/ Magnesium by complexometric titration in Face powder
- 9 Determination of amount and percentage of titanium and silica in tooth powder.

E. Ion exchange chromatography (any 1)

- 1 Separation and estimation of mixture of Zn(II) and Mg(II)
- 2 Separation and estimation of mixture of Al(III) and Mg(II)

(Note: Minimum 10 experiments should be completed in this course.)

Reference:

- 1. A textbook of qualitative inorganic analysis: A. I. Vogel
- 2. Inorganic synthesis King
- 3. Synthetic inorganic chemistry: W.L.Jolly
- 4. Experimental Inorganic chemistry by W.G.Palmer
- 5. The analysis of minerals and ores of rare elements: W.R.Schoeller, A.R.Powell, Charles, Griffin and company limited.

Practical course II

PSCHI 236: Inorganic preparations and Instrumental analysis (4 Credit)

Learning Objectives:

- Students should able to know various instrumental methods of analysis.
- Students should be able to introduce methods of chemical analysis.
- Student should be able to knowledge about magnetic susceptibility, TGA, CV aquation etc.
- Student should able to know the various instrumental methods of analysis.

Learning Outcomes:

- should be able to understand magnetic properties of compound.
- student will get knowledge about instrumental methods and analysis of compound.

A. Inorganic preparations (any 4)

- 1 Preparation of dichloro(triphenylphosphine)nickel(II) sulphate
- 2 Preparation of potassium hexathiocyanato chromate (III)
- 3 Preparation of trans-dichloro bis-ethylenediamine cobalt(III)chloride
- 4 Preparation of tris (acetyl acetonato) Aluminum (III) Sulphate.
- 5 Preparation of chloroaquotetrammine cobalt sulphate
- 6 Preparation of chrome alum
- 7 Preparation of Cu(o-phen)₂
- 8 Preparation of potassium dihydroxodioxalato titanate(IV) and estimation of titania

B. Preparation of solid-state material (any 3)

- 1 Nickel ferrite
- 2 zinc ferrite
- 3 BaZrO₃
- 4 MnO₂
- 5 Nickel oxide
- 6 TiO₂

C. Instrumentation (any 3)

- 1. Magnetic susceptibility of Co-ordination complexes by Gauy's method to determine number of unpaired electrons from given complex.
- Thermo gravimetric analysis
 TGA for analysis of CuSO₄ and NaCl find out the percentage of each constituent in mixture.

To determine the number of water molecules in each hydrated complex using thermo gravimetric analysis

- 3 Photocatalytic degradation of dye using ZnO/TiO₂ nanoparticles (synthesis by Sol-gel method)
- 4 To determine amount of chloride/ Sulphate / Phosphate from given sample solution by turbidometric titration
- 5 Cyclic Voltametric study of Fe (II)/Fe (III) system. Basic principle and calculation of basic parameters from CV.

E. Chemical Kinetics (Any 2)

- 1 To study rate of aquation of tris 1-10 phenanthrolein Fe (II) in acid solution by spectrophotometer.
- 2 To study rate of aquation of trans dichlorobisethylenediammine cobalt (III) chloride
- 3 To determine corrosion rate of metal strips (mild steel or aluminum) in different concentration of acidic or alkali medium
- 4 To study the effect of 1, 10 phenanthroline on corrosion inhibition of mild steel in H_2SO_4
- **F.** Table Work: Spectral interpretation of some solid crystalline substances by XRD, NMR, FTIR (2 spectra each)

(Note: Minimum 10 experiments should be completed in this course.)

Reference:

- 1. A textbook of qualitative inorganic analysis: A. I. Vogel
- 2. Inorganic synthesis King
- 3. Synthetic inorganic chemistry: W.L.Jolly
- 4. Experimental Inorganic chemistry by W.G.Palmer
- 5. The analysis of minerals and ores of rare elements: W.R.Schoeller, A.R.Powell, Charles, Griffin and company limited