## ANDHRA UNIVERSITY DEPARTMENT OF CHEMISTRY M.SC., CHEMISTRY (FINAL)-III-SEMESTER SYLLABUS SPECIALIZATION: INORGANIC CHEMISTRY

Paper-I: Solid State Chemistry -1 (Effective from 2021-2022 Admitted batch)

#### UNIT-I:

Description of crystal structures -close packing, Pauling's electrostatic valance rules, description of some important crystal structures of AX (NaCl, CsCl and ZnS), AX<sub>2</sub> (Cristobalite, Rutile,Fluorite), ABX<sub>3</sub> (Perovskite and Ilmenite), AB<sub>2</sub>X<sub>4</sub> (Spinel -normal and inverse). Effect of polarization, pressure and temperature, Lattice energy, basic principle and instrumentation of X-Ray diffraction technique, crystal structure determination (cubic system only) by powder X-Ray diffraction technique.

#### UNIT-II:

Crystal symmetry - screw axes, glide planes and space group notation, crystal imperfections-point defects, thermodynamics of Schottky and Frenkel defect formation, dislocations, planar defects, extended defects (Crystallographic shear and stacking faults), Non-stoichiometry, mode of incorporation, thermodynamic aspects, experimental methods of determining non-stoichiometry, Non-Crystalline solids.

#### UNIT-III:

Preparative methods: Synthesis methods for polycrystalline materials – ceramic, precursor, sol-gel, hydrothermal, chemical vapour transport, spray pyrolysis, chemie douche and self propagation methods.

#### **Unit-IV**

Techniques of single crystal growth from solution (low temperature and high temperature solution growth, gel growth), melt and vapor (Bridgman, Czochraiski, Varneuili, Floating zone and chemical vapour deposition methods), Fabrication of thin films by chemical methods, sintering – techniques and mechanism.

#### UNIT -V:

Structural transformations in solids and their classifications, Martensitic and order-disorder transformations. Reactivity of solids -Nature of solid state reactions, solid-gas, solid-liquid and solid-solid reactions, Reactions on solid surfaces -Heterogeneous catalysis. Introduction to silicates and zeolites. Applications of zeolites in petrochemical industry-isomerization, hydrocracking and hydrodesulfurization.

#### Text books:

- 1. Solid-state chemistry and its applications by A.R. West, John Wiley
- Solid-state chemistry -an introduction by Lesley Smart and Elaine Moore Viva books private limited, New Delhi. Principles of the solid-state by H.V. Keer, Wiley Eastern Ltd. 2.
- 3.
- 4.

#### Reference book:

- 1. New directions in solid state chemistry By C.N.R. Rao and J. Gopalakrishnan.
- 2. The Physics and Chemistry of NanoS olids by Frank J. Owens and Charles P. Poole Jr, Wiley-Interscience, 2008.
- 3. Chemistry of Zeolites and Related Porous Materials: Synthesis and Structure by Ruren Xu Wenqin Pang Jihong Yu QishengHuoJiesheng Chen, 2007Print ISBN:9780470823333

## MODEL QUESTION PAPER DEPARTMENT OF CHEMISTRY M.SC., CHEMISTRY (FINAL)-III-SEMESTER

SPECIALIZATION: INORGANIC CHEMISTRY Paper-I: Solid State Chemistry -1

(With effective from the 2021-2022 admitted batch)

Time: 3 hours Max. Marks: 80

#### Answer All Questions (5x16= 80 Marks)

- 1. a) Discuss principle behind powder X-ray diffraction(PXRD).
- b) Explain how PXRD can be used in the crystal structure determination of cubic systems.

OR

- a) Explain Pualing's electrostatic valance rules with examples
- b) Explain structures of normal and inverse Spinels
- 2.a) What are non-crystalline solids? Explain.
- b) Discuss the thermodynamics of Schottky and Frenkel defect formation

OR

- a) Describe the non-stoichiometry in solids. What are the various experimental methods used for the determination of non-stoichiometry in solids?
- b) Discuss screw axes, glide planes and space group notation of solid crystals.
- 3. a) Describe ceramic method used for the preparation of polycrystalline solids
- b) Describe the synthesis of zeolites using hydrothermal method.

OR

- a) What are polycrystalline solids? Explain sol-gel synthesis of polycrystalline solids with examples
- b) Describe chemical vapour transport method for the synthesis of polycrystalline solids
- 4. a) Detail out methods for the growth of single crystals from solutions.
- b) Describe Bridgman method for single crystal formation

OR

- a) What is sintering? Explain various techniques used for sintering. Also explain the mechanism of sintering.
- b) Exaplin Czochraiski method for single crystal formation

- 5. a) What are zeolites? Explain their strcture.
- b) Describe their application of zeolites in petrochemical industry.

OR

- a) Describe various structural transformations in solids and explain their classification
- b) Explain order-disorder transformations with a example

## ANDHRA UNIVERSITY DEPARTMENT OF CHEMISTRY

## M.SC., CHEMISTRY (FINAL)-III-SEMESTER SYLLABUS SPECIALIZATION: INORGANIC CHEMISTRY

Paper – II: Structure, Bonding and Reactivity of coordination compounds-I (Effective from 2021-22 admitted batch)

#### Unit I:

Theories of bonding – crystal field theory- structural and thermodynamic effects of crystal field splitting – John – Teller effect – Octahedral and tetrahedral radii – site selection in spinels - thermodynamic effects of crystal field splitting-hydration, ligation, and lattice energies.

#### Unit II:

Evidence for covalence and the adjusted crystal field or the ligand field Theory -Strong field configurations - Correlation diagrams. Molecular orbital theory applied to octahedral and tetrahedral complexes including  $\Pi$  bonding - Angular overlap model.

#### Unit III:

Electronic Spectra -Selection rules -Mechanism of breakdown of selection rules- band Shapes- Orgel and Tanabe -Sugano diagrams .Ligand field spectra of octahedral and tetrahedral complexes of .first transition series -Calculation of crystal field splitting energy ( $\Delta$ ) and Racah Parameters (B). Charge transfer spectra of complexes -Ligand to metal and melal to ligand type.

#### Unit IV:

Optical activity of Complexes, Sterochemical notation (d- and l- system, R and S system,.  $\Lambda$  and  $\Delta$  notation,  $\lambda$  and  $\delta$  System), Optical isomerism in chelate octahedral complexes, Circular dichroism (CD), Optical rotatory dispersion (ORD) – definition, principle of measurement, -Cotton effect – determination of absolute configuration, Applications.

#### Unit V:

Magnetic properties- Magnetic properties of free ions -Spin orbit coupling  $-t_{2g}$  and  $e_g$  Orbital contribution to the Magnetic Moment, temperature independent para magnetism- Quenching of orbital momentum in complexes, Spin cross over-factors effecting spin cross over: chemical and physical.

#### Text books:

- 1. Inorganic Chemistry: Principles, Structure and .Reactivity, James E. Huheey, (4th Edition).
- 2. Advanced Inarganic Chemistry, F.A. Cotton and G. Wilkinson, Wiley Eastern Pvt., New Delhi (4th Edition).
- 3. Mechanisms of Inorganic Reactions in Solution D. Benson, McGraw Hill, London, 1968.
- 4. Inorganic Reaction Mechanisms J.O. Edwards.
- 5. Fundamentals of Photochemistry, K.K. Rohatgi Mukberjee, Wiley Eastern, New Delhi, 1978.

#### Reference books: .

- 1. Mechanisms of Inorganic Reaction: F. Basalo and R.G. Pearson.
- 2. Inorganic Chemistry, K.F. Purcell and J.C. Kotz; W.B. Saunders Company, New York, 1977.

## MODEL QUESTION PAPER M.Sc.(Final) CHEMISTRY- III-SEMESTER

**Specialization: INORGANIC CHEMISTRY** 

## Paper – II: Structure, Bonding and Reactivity of coordination compounds-I (effective from 2021-22 admitted batch)

Time: 3 hours Max. Marks: 80

#### ANSWER ALL QUESTIONS (5x16=80 Marks)

1. a) Explain theories of bonding with merit and demerits

b) Describe in detail about the evidences available in support of crystal field stabilization energies in transition metal complexes.

OR

- a) Discuss about the John Teller effect with suitable examples.
- b) Discuss site selection in spinnels
- 2.a) Explain Charge transfer spectra in co-ordination complexes
- b) Explain why KMnO<sub>4</sub> has very intense purple in colour whereas  $[Mn(OH)_6]^{2+}$  is pale pink in colour.

Or

a). Explain how MO theory is superior to CF theory in explaining the bonding in

octahedral complexes.

- b) Discuss the effect of '\[ '\]' bonding on the crystal field splitting energy of an octahedral complex according to MO theory.
- 3.a. a) Explain the d<sup>2</sup> configuration co-ordination complexes using Orgel diagrams
- b) Discuss the differences between Orgel diagrams and Tanabe-Sugano diagrams

Or

- a. Write notes on i) Racah parameters and ii) Mechanism of breakdown of selection rules.
- b) Explain why KMnO<sub>4</sub> exhibits intense color?
- 4. a) What is Optical rotatory dispersion (ORD)? Describe definition and principle of measurement
  - b) Discuss ORD application in determination of absolute configuration.

Or

- a) Write a note on optical activity of Complexes
- b) What is cotton effect? Explain its significance and give its applications.

- 5. a) Explain spin-orbit coupling in co-ordination complexes. How it effects absorption spectrum?
- b) What do you understand by quenching of orbital angular momentum? What are the consequences of such quenching? Explain with suitable examples.

Or

- a) Discuss temperature independent para magnetism in complexes
- b. Explain the magnetic properties of free transition metal ions? Discuss the anomalies of first row transition metal ions.

## ANDHRA UNIVERSITY DEPARTMENT OF CHEMISTRY M.SC., CHEMISTRY (FINAL)-III-SEMESTER SYLLABUS

### SPECIALIZATION: INORGANIC CHEMISTRY

Paper III: Bio-inorganic Chemistry (Effective from 2021-22 admitted batch)

#### UNIT I:

Structural features of prokaryotic and eukaryotic cells – Chemistry of biomolecules, general aspects, c carbohydrates, lipids, proteins, nucleic acids, structures of DNA and RNA.

Inorganic elements in biological systems – role of alkali and alkaline earth metal ions in biological systems and their transport across membrane.

#### UNIT II:

Metallo-enzymes, Structure and functions of carboxypeptidase and carbonic Anhydrase. Vitamin  $B_6$  structure, its role in transamination and oxidative deamination, Vitamin  $B_{12}$  and  $B_{12}$  Co-enzymes, Structure of Vitamin  $B_{12}$ -coordination chemistry, Oxidation states of its metal.

#### UNIT III:

Metal complexes as oxygen carriers – hemoglobin and myoglobin, Cooperativity, Bohr effect, non-porphyrin oxygen carriers – hemerythrin and hemocyanin

#### Uni IV:

Synthetic oxygen carriers – – ferredoxins, cytochromes.

Photosynthesis – light reaction, dark reaction, structural features of chlorophyll, Electron transport chain in light reaction, Z-scheme, role of manganese clusters in water splitting reaction.

#### UNIT V:

Biological nitrogen fixation – composition and structure of nitrogenase, function of different units of nitrogenase, reaction pathway of nitrogen fixation.

Toxicity of metals – Symptoms of metal toxicity, mechanism of metal toxicity, biomethylation, Minamata disease, chemical speciation of arsenic, mercury, Biological defence mechanism, chelating agents in metal ion detoxification.

Metal complexes as drugs and anti cancer agents – anti-arthritic gold drugs, lithium therapy in psychiatric disorders, anti-cancer activity of platinum complexes, mechanism of anti-cancer activity.

#### Books:

- 1. Biochemistry by Lehninger (1982)
- 2. Biochemistry by L. Stryer
- 3. Inorganic Chemistry of Biological processes by M.N. Hughes
- 4. Bio-inorganic Chemistry An introduction by Ei-Ichiro Ochiai, Allyn and Bacon Inc. (1977)

- 5. Inorganic Biochemistry, Vols I and II by G.L. Eichhorn.
- 6. Inorganic Chemistry by J. E. Huhey, Harper International
- 7. Bio-inorganic Chemistry by R.W. Hay, Ellis Harwood Ltd. (1984)
- 8. Bio-inorganic Chemistry by Asim K. Das, Books and Allied (P) Ltd. (2007)
- 9. Bio-inorganic Chemistry by Bertini, Gray, Lippard and Valentine, Viva Books Private Ltd. (2007)
- 10. Elements of bioinorganic Chemistry by G. N. Mukherjee and Arabinda Das, U.N. Dhur & Sons Pvt. Ltd (1993)

## MODEL QUESTION PAPER DEPARTMENT OF CHEMISTRY

## M.SC., CHEMISTRY (FINAL)-III-SEMESTER SPECIALIZATION: INORGANIC CHEMISTRY

PAPER-III: BIO-INORGANIC CHEMISTRY

(Effective from 2021-2022 admitted batch)
Time: 3 hours

Ma

me: 3 hours Max. Marks: 80
ANSWER ALL QUESTIONS (5x16=80 Marks)

- 1. a) Discuss the role of alkali and alkaline earth metals in transport across the membranes and muscle contraction.
  - b) Explain the structures of DNA and RNA

OR

a) Describe the structures of nucleic acids and explain their role in biological

systems.

- b) Discuss structural features of prokaryotic and eukaryotic cells
- 2. a) Discuss the structure and the functions Carbonic anhydrase
  - b) Explain structure and function of Carboxy peptidase.

OR

- a) Give the structure of Vitamin B<sub>12</sub> and explain its biological functions.
- b) What are co-enzymes? Discuss their role with an example
- 3. a) Discuss the structure Myoglobin
  - b) Discuss functions of Myoglobin and Hemoglobin.

OR

- b) What are non-porphyrin oxygen carriers? Give examples
- b) Discuss structure and function of hemocyanin
- 4. a) What are ferredoxins? discuss their types along with structures
  - b) Discuss the role of cytochromes in electron transfer reactions.

OR

- a) Discuss the structural features chlorophyll in photosynthesis
- b) Explain the role of manganese clusters in water splitting reaction
- 5. a) What is biological nitrogen fixation? Explain its importance
  - b) Discuss the function and structure of nitrogenase in nitrogen fixation

OR

- a) Discuss the toxicity and chemical speciation of arsenic and mercury
- b) Discuss the application of metal complexes for anti-cancer activity with examples

### ANDHRA UNIVERSITY DEPARTMENT OF CHEMISTRY

## M.SC., CHEMISTRY (FINAL)-III-SEMESTER SYLLABUS SPECIALIZATION: INORGANIC CHEMISTRY

## Paper—IV: PHYSICAL METHODS IN INORGANIC CHEMISTRY-I (Effective from 2021-22 admitted batch)

#### UNIT - I:

- **a)**Vibrational Spectroscopy: Infrared spectroscopy, Instrumentation, Quantitative Analysis, FTIR, NIR, MIR, FIR, Raman Spectroscopy Principle, Instrumentation and Applications of Raman Spectroscopy
- **b)** UV-Visible Spectroscopy: Principle Instrumentation- Single Beam, Double Beam ,Quantitative determination of  $-Fe^{3+}$ ,  $Mn^{2+}$ ,  $PO_4^{3-}$ ,  $NO_3^-$ ,  $NO_2^-$ , simultaneous determination of Cr(VI) and Mn(VII), Photometric titrations, composition of a complex ( $Fe^{2+}$  orthophenanthroline).
- **c**) Photo electron spectroscopy: Principle, UV PES spectra of HCl, Cl<sub>2</sub>, N<sub>2</sub>, O<sub>2</sub> and CO, XPES chemical analysis (ESCA), principle, chemical shift, applications of XPES for study of oxidation states, molecular structure of Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub>, N<sub>2</sub>O, N<sub>3</sub>-, Pt(NH<sub>3</sub>)<sub>3</sub>Cl<sub>3</sub>.

#### UNIT - II:

- **a)** Flame Photometry: principle nebulizer examples: Na , Alkali and Alkaline earth metals.
- **a)** Atomic absorption spectroscopy: Principle, basic instrumentation, resonance line source (Hollow cathode lamp), Interferences, evaluation methods, non-flame techniques, applications, determination of As, Pb, Hg, Al & Cd.
- **b**) Atomic Emission Spectroscopy: Principle of AES, types of flames, spark/arc and applications

#### **Unit-III:**

Inductively coupled plasma emission spectroscopy(ICP-OES): Principle of inductively coupled plasma, advantages with plasma, detectors, wavelength selection and applications

Inductively coupled plasma Mass spectrometry (ICP-MS): instrumentation, quadrupole mass spectrometers, sample introduction, Analyte atomization and ionization, analysis methods for liquids and solids, interferences, calibration curves, applications in the analysis of trace and toxic metals.

#### UNIT - IV:

**a)**NMR Spectroscopy: Resonance condition, Chemical Shift, spin-spin splitting, factors affecting the appearance of NMR spectra, Classification of NMR Spectra,  $(AX, AX_2, AX_3, AMX$ and ABtypes) vicinal, geminal coupling, methods to simplify complex spectra, spin decoupling, shift reagents, Introduction to

MASNMR and 2-D NMR techniques. Applications of NMR to Inorganic <sup>1</sup>H, <sup>19</sup>F, <sup>31</sup>P, <sup>15</sup>N, <sup>11</sup>B <sup>13</sup>C (ClF<sub>3</sub>, BrF<sub>5</sub>, HPF<sub>2</sub>, PF<sub>3</sub>, SF<sub>4</sub>, NH<sub>3</sub>, NH<sup>+</sup><sub>4</sub>, B<sub>2</sub>H<sub>6</sub>).

**b)** ESR Spectroscopy: Principle, Hyperfine splitting, Krammer's degeneracy, applications of ESR of copper acetate, NH<sub>2</sub>\*,CH<sub>3</sub>\*, CH<sub>2</sub>OH\*, Naphthalene anion, copper bis (salicylaldamine), structural elucidation of copper complex through anisotropy in hyperfine coupling constants, study of free radicals, comparison of NMR and ESR techniques.

#### UNIT V: Electro analytical methods:

- a)Principle of Voltametry Polarization of electrode, over voltage, factors affecting over voltage, diffusion current, migration current. DC Polarography, AC Polarography, pulse polarography normal pulse, differential pulse and square wave polaragraphy. Applications of Polarography, Determination of Cd<sup>2+</sup>, Zn<sup>2+</sup>, Pb<sup>2+</sup>
- b) Principle of stripping analysis anode stripping voltametry.
- c) Cyclic voltametry Principle, Instrumentation, applications, diagnosis of coupled chemical reactions.
- d) Coulometry Principle, types of coulometry Potentiostatic and amperostatic, coulometric titrations, Applications.

#### **Books:**

- 1. Instrumental methods of analysis, (6<sup>th</sup> Edition) Hobart H. Willard, Lynne L Merit Jr. and John A Dean and Frank A Settle, Jr.
- 2. Vogel's Text Book of Quantitative Chemical analysis,(6<sup>th</sup> Edition) Basset Re Dnnex, G.H. Jeffery and J.Mendham.
- 3. Physical methods in Inorganic Chemistry, R.S. Drago.
- 4. Principles of Instrumental Analysis, Skoog, West and Holler.

## MODEL QUESTION PAPER DEPARTMENT OF CHEMISTRY

### M.SC., CHEMISTRY (FINAL)-III-SEMESTER

#### SPECIALIZATION: INORGANIC CHEMISTRY

#### PAPER-IV: PHYSICAL METHODS IN INORGANIC CHEMISTRY-I

(Effective from 2021-2022 Admitted batch)

Time: 3 hours Max. Marks: 80

#### ANSWER ALL QUE STIONS (5x16=80 Marks)

- 1.a) Explain the working theory and instrumentation of double beam UV-visible spectrophotometry
- b) Explain quantitative determination of Mn<sup>2+</sup>& PO<sub>4</sub><sup>3-</sup> using UV-visible spectrophotometry

OR

- b) a) Explain the principle instrumentation and application of Raman Spectroscopy
  - b) Explain IR and Raman spectrum of CO<sub>2</sub> molecule.
- 2. a)) Explain the different flame techniques involved in AAS.
  - b) Describe various interferences in AAS technique

OR

- a) Explain the principle, instrumentation and applications of flame photometry
  - b) Discuss the differences and similarities between AAS and AES
- 3. a) What is inductively coupled plasma? Describe the detectors used for ICP-OES technique
- b) Discuss the limitations of ICP-OES analysis

OR

- a) Describe atomization and ionization process of ICP-MS technique.
- b) Write the applications of ICP-MS for trace element detection.

- 4. a) Describe the NMR spectra of the following compounds for all NMR active nuclei
  - i) ClF<sub>3</sub>, ii) HPF<sub>2</sub>, iii)PF<sub>3</sub>, and iv)SF<sub>4</sub>
- b) Describe AX and AMX type NMR spectra.

Or

- a) What is hyperfine splitting in ESR spectroscopy? Explain with suitable examples.
  - b) Describe the ESR spectrum of copper bis (salicylaldamine)
- 5. a) Explain principles of DC Polarography, AC Polarography and pulse polarography techniques
- b) Describe anode stripping voltammetry principle and write its applications (or)
- a) Describe the instrumentation of dropping mercury electrode.
- b) Explain the following (i) Square wave polarography. (ii) Pulse polarography.

# ANDHRA UNIVERSITY DEPARTMENT OF CHEMISTRY M.Sc., CHEMISTRY (FINAL)-III-SEMESTER SYLLABUS SPECIALIZATION: INORGANIC CHEMISTRY INORGANIC CHEMISTRY PRACTICALS-I (CLASSICAL)

- I. Preparation of single crystal from solution and by gel growth
- II. Preparation and chemical analysis of the Complexes
  - 1. Mercury tetrathiocyanatocobaltate(III)
  - 2. Hexamminecobalt(III) chloride
  - 3. Potassium tris(oxalato)chromate(III)
  - 4. Potassium tris(oxalato)aluminate(III)
- III. Quantitative Analysis
- 1. Determination of calcium(II) by precipitation from homogeneous solution
  - 2. Determination of copper(II) and nickel(II) in a mixture
- 3. Determination of calcium and magnesium in a mixture using EDTA (Eg dolomite)
  - 4. Determination of Iron(II) and Iron(III) in a mixture (Eg Iron ore)
  - 5. Determination of Ferrocyanide and Ferricyanide in a mixture
  - 6. Determination of carbonate and bicarbonate in a mixture
  - 7. Determination of Iron(III) and Aluminium(III) in a mixture
  - 8. Determination of sodium(I) using cation exchanger
- 9. Determination of sodium(I) and potassium(I) in a mixture using cation exchanger
  - 10. Determination of chloride using anion exchanger
  - 11. Analysis of brass
  - 12. Analysis of solder
  - 13. Determination of COD and BOD of water samples
- IV. Determination crystal field splitting energy and spectrochemical series for chromium complexes.

#### References

1. Vogel's Quantitative Inorganic Analysis

## ANDHRA UNIVERSITY DEPARTMENT OF CHEMISTRY M.SC., CHEMISTRY (FINAL)-IV-SEMESTER SYLLABUS SPECIALIZATION: INORGANIC CHEMISTRY

Paper-I: Solid State Chemistry -II (Effective from 2021-22 Admitted batch)

#### UNIT-1

Phase equilibria in solids: One component systems(SiO<sub>2</sub>, GeO<sub>2</sub>, TiO<sub>2</sub>, ZrO<sub>2</sub>). Two component systems with eutectic, compound and solid solution formations, general considerations of crystal chemistry, Model structures. Three component systems with binary and ternary eutectics- binary compound formation ternary compound formation.

#### **UNIT-II**

Free electron theory, Band theory of solids(Kroning Penney Model). Semiconductors, types of semiconductors, compound semiconductors, band gap, thermal excitation, photoexcitation, the Maxwell-Boltzmann distribution, Fermi level, charge carrier concentration, effective mass, Hall effect, Semiconductor devices – rectifiers, transistors and solar cells, photocatalytic applications.

#### UNIT-III

Fast ion conductors/solid electrolytes, types of solid electrolytes, applications of solid electrolytes- batteries, fuel cells, Sensors, super conductivity Meissner effect, Type-I and Type-II semiconductors, Isotope effect, specific heat, High  $T_c$  superconductors, structure of  $YBa_2Cu_3O_7$  – Application of superconductors.

#### **UNIT-IV**

Magnetic Properties: Diamagnetism, Paramagnetism, Magnetic ordering – ferro, ferri and antiferro. Hard and soft ferrites, ceramic magnets, applications of ferrites. Optical properties: Refractive index, birefringence and crystal class, phosphors and their applications, solid-state lasers and their applications, introduction to non-linear optical materials

Dielectric properties: Mechanisms of polarization, frequency dependence of polarization, dielectric loss, ferrro, piezo and pyroelectric materials – their characteristic properties, symmetry relations and applications, Introduction to liquid crystals

#### UNIT- V

Introduction to Nanomaterials concept of bulk versus nanomaterials, "Top down' vs. Bottom up' approach of synthesis with suitable examples. Growth kinetics: nucleation and growth processes. Synthesis of metal nanoparticles, metals oxides nanoparticles and semiconductor nanoparticles, preparation of nanorods (vapour-

liquid-solid growth, electro spinning), fabrication of nano thin films (atomic layer deposition, Langmuir-Blodgett methods), carbon nanotubes, properties of nanomaterials; nanocomposite.

Characterization techniques of nanomaterials(Elementary treatment only): Atomic force microscopy (AFM), Scanning electron microscopy (SEM) and Transmission Electron microscopy (TEM). Applications of nanomaterials with respect to energy, environment and biomedical.

#### Text books:

- 1) Solid-state chemistry and its applications by A.R. West John, Wiley& Sons.
- 2) Solid-state chemistry -an introduction by Lesley Smart and Elaine Moor, Viva books private limited, New Delhi.
- 3) Principles of the solid-state by H.U. Keer, Wiley Eastern Ltd.

#### Reference books

- 1. New directions in solid-state chemistry By C.N.R. Rao and J. Gopalakrishnan
- 2. Structure-property relations by R.E. Newnham Springer-Verlag Publications

## MODEL QUESTION PAPER DEPARTMENT OF CHEMISTRY M.SC., CHEMISTRY (FINAL)-IV-SEMESTER

#### SPECIALIZATION: INORGANIC CHEMISTRY

Paper-I: Solid State Chemistry -II (effective from the 2021-2022 admitted batch)

Time: 3 hours Max. Marks: 80

#### SECTION-A

#### Answer All Questions (16x5= 80 Marks)

1. a) Discuss phase diagrams of three component systems with binary eutectics b) Discuss the phase diagram of SiO<sub>2</sub>

OR

- a) What are Solid solutions? Describe the phase diagrams of two component systems with solid-solutions
- b) Discuss the phase diagram of GeO<sub>2</sub>
- 2. a) Explain electronic conductivity in semiconductors. Describe Fermi level position in various types of semiconductors.
- b) Explain hall effect with an example

OR

- a) Discuss Kronning penny model used for describing band theory of solids.
- b) Describe effective mass in semiconductors
- 3. a) What is superconductivity? Explain the mechanism behind super conductivity.
- b) Explain type-I and type-II superconductors.

OR

- a) What are fast ion conductors? Explain their applications
- b) Discuss high temperature superconductors
- 4. a) Explain hard and soft ferrites
  - b) Describe the properties of pyroelectric materials

OR

b) What are the characteristics of piezo electric materials? Explain their applications

- 5. a) Discuss in detail "Top down" and "Bottom up" approaches for the synthesis of nanomaterials
- b) Discuss vapour-liquid-solid growth method used for the synthesis of nanorods

OR

- a) Atomic layer deposition and Langmuir-Blodgett methods for the synthesis of nano thinfilms
- b) Describe transmission electron microscopy technique used for characterization of nanomaterials.

## ANDHRA UNIVERSITY DEPARTMENT OF CHEMISTRY

## M.SC., CHEMISTRY (FINAL)-IV-SEMESTER SYLLABUS SPECIALIZATION: INORGANIC CHEMISTRY

Paper –II: Structure, Bonding and Reactivity of coordination compounds-II (Effective only for 2020-21 academic year)

#### Unit I:

Mechanism of inorganic reactions -Substitution reactions of metal complexes -Mechanism of ligand replacement reactions in octahedral complexes -Acid hydrolysis, (acid dependent and independent) anation and base hydrolysis –Reactions without metal - ligand bond cleavage.

#### Unit II:

Mechanism of ligand replacement reactions in square planar complexes - Effect of nucleophiles- Effect of leaving group, effect of solvent. Effect of non-labile group; Trans effect -Mechanism of trans effect -Cis effect, Trans influence.

#### Unit III:

Electron transfer reactions of complexes -Inner and outer sphere mechanisms -Marcus theory, complementary and non-complementary reactions- Discussion of experimental data on the following redox systems. Co(III) -Ce(III); Co(III)-Fe(II); TI(III) - Fe(II); TI(III)-Hg (I) and Ce (IV) -Cr(III).

#### Unit IV:

Homogeneous catalysis, Metal ion catalyzed reactions –Redox potentials and processes- Mechanisms of redox processes 'involving ligands - Factors affecting redox potentials – other types of metal catalyzed reactions- Reactions involving Ag (I), Cu(II) and Os(VIII) –Reactions of oxyanions -factors affecting rate, (General discussion only) -Induced reactions -Free radical reactions- Thermal decomposition of peroxy disulphate -Fe(III) –  $S_2O_8$  reactions - chain reactions –H-Br reactions,  $H_2O_2$  – $S_2O_8$  reactions.

#### Unit V:

Molecular rearrangements -Four coordinated complexes - Isomerization and recemization of six coordinated complexes.

Photochemistry –Pbotophysical processes -Radioactive and non.radioactive processes -internal conversion and Inter system - Crossing Frank -Condon principle

Photochemical reactivity of transition metal complexes -photosubtitution reactions -aquation, anation and ligand exchange photo rearrangement reactions -Geometrical isomerization recemization -linkage isomerization and ligand rearrangement. photo oxidation or reduction -photo decomposition of water.

#### Text books:

- I. Inorganic Chemistry: Principles, Structure and .Reactivity, James E. Huheey.
- 2. Advanced Inarganic Chemistry, F.A. Cotton and G. Wilkinson, Wiley Eastern Pvt., New Delhi (4th Edition).
- 3. Mechanisms of Inorganic Reactions in Solution D. Benson, McGraw Hill, 1968.
- 4. Inorganic Reaction Mechanisms J.O. Edwards.
- 5. Fundamentals of Photochemistry, K.K. Rohatgi Mukberjee, Wiley Eastern, 1978.

#### Reference books: .

- I. Mechanisms of Inorganic Reaction: F. Basalo and R.G. Pearson.
- 2. Inorganic Chemistry, K.F. Purcell and J.C. Kotz; W.B. Saunders Company, 1977.

## MODEL QUESTION PAPER DEPARTMENT OF CHEMISTRY

## M.SC., CHEMISTRY (FINAL)-IV-SEMESTER SPECIALIZATION: INORGANIC CHEMISTRY

Paper- II: Structure, Bonding and Reactivity of coordination compounds- I (Effective from 2021-22 admitted batch)

Time:3 hours Max. Marks 80

#### Answer all questions (5x16 = 80 Marks)

1. a. In detail discuss the mechanism of Acid hydrolysis in octahedral complexes

b. Discuss anation reactions with examples

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Or

a. Discuss the possible mechanisms for the base hydrolysis of coordination compounds

citing evidences for the same.

- b. Discuss substitution reactions without metal ligand bond cleavage
- 2. a. Describe effect of nucleophiles and leaving group on substitution reactions in square planar complexes
  - b. Describe the role played by solvents on substitution reactions in square planar complexes.

Or

- a. Explain Cis- and trans-effects observed in square planar complex. Also detail out the mechanisms.
- b. Distinguish between the trans influence and the trans effect. Give at least two examples showing how you can detect the presence of the trans influence in a complex
- 3. a. With appropriate examples for discussing the outer sphere and inner sphere mechanisms

for electron transfer reactions.

b. Discuss Marcus theory in detail

Or

- a. What do you understand by complimentary and non-complimentary reactions.
- b. Discuss Co(III)-Ce(III) redox system

- 4. a. Describe induced reactions with examples
  - b. Discuss Ag (I) and Cu(II) catalyzed reactions.

 $O_1$ 

- a. Write the factors that affect redox potentials of metals
- b. Discuss inorganic chain reactions with two examples.
- 5. a. Explain the non.radioactive photo physical processes
  - b. Discuss Frank -Condon principle

Or

- a. Explain aquation, anation and ligand exchange photo rearrangement reactions
- b. Discuss photo decomposition of water.

## ANDHRA UNIVERSITY DEPARTMENT OF CHEMISTRY

#### M.SC., CHEMISTRY (FINAL)-IV-SEMESTER SYLLABUS

#### SPECIALIZATION: INORGANIC CHEMISTRY

Paper III: Organometallic Chemistry (Effective from 2021-22 admitted batch)

**UNIT-I:** Introduction, 16 electron rule and 18 electron rule, Nomenclature of organometallic compounds.

Synthesis, structure, bonding and reactions of metal alkyls and metal aryls, Factors affecting stability of metal alkyls and aryls.

Synthesis, structure, bonding and reactions of metal carbonyls, carbonylate anions, carbonyl hydrides and carbonyl halides. Role of IR and Mossbauer in structure elucidation of metal carbonyls, structures of polynuclear metal carbonyls.

Dinitrogen, cyanide, isocyanide and nitric oxide complexes.

**UNIT-II:** Carbon  $\pi$  donors: Synthesis, structure, bonding and reactions of complexes of olefin, alkyne, allyl and diene complexes, Double  $\sigma$  bonding model, Dewar-Chatt-Duncanson Model.

Cyclic  $\pi$  donors: Synthesis, structure, bonding and reactions of cyclobutadiene, cyclopentadienyl (metallocenes) and benzenoid (dibenzene) complexes.

#### **UNIT III:** Reaction pathways of organometallic compounds

Associative reactions-Lewis acidity, Lewis basicity and ligand protonation.

Substitution reactions-Nucleophilic ligand substitution, electrophlic and nucleophilic attack on coordinated ligands.

Addition reactions -1,1-addition,1,2-adition, and oxidative addition.

Elimination reactions – 1,2-elimination, binuclear elimination and reductive elimination.

Rearrangement reactions - Redistribution reaction and fluxional isomerism.

#### **UNIT IV:** Applications of organometallic compounds

Catalytic application - Fischer-Tropsch Synthesis, olefin hydrogenation (Wilkinson catalyst), olefin oxygenation (Wacker process or Smidt reaction), olefin hydroformylation (Oxo process), carbonylation reactions, olefin polymerization (Ziegler-Natta catalysis)

#### Unit -V

Synthetic applications of organo-lithium,-magnesium, and-aluminum compounds

Biological applications of organometallic compounds in medicine, agriculture and horticulture.

#### Books:

- 1. Advanced Inorganic Chemistry by F.A. Cotton and R.G.Wilkinson, Wiley Publications.
- Inorganic Chemistry by J.E. Huhey, Harper International.
   Organometallic Chemistry-A unified approach by A.Singh and R.C.Mehrotra, Wiley Eastern Ltd.

## MODEL QUESTION PAPER DEPARTMENT OF CHEMISTRY

#### M.SC., CHEMISTRY (FINAL)-IV-SEMESTER

#### SPECIALIZATION: INORGANIC CHEMISTRY

Paper—III: ORGANOMETALLIC CHEMISTRY

(Effective from 2021—2022 admitted batch)

Time: 3 Hours Maximum marks: 80

#### Answer ALL questions (5x16 = 80 marks)

- 1. a) Discuss the synthesis, structure and bonding features of carbonyl complexes
  - b) Write a note on dinitrogen complexes

OR

a) Explain the application of IR and Mossbauer spectroscopy techniques in the

structural elucidation of metal carbonyls.

- b) Discuss 18 electron rule with examples
- 2. a) Discuss synthesis, structure, bonding and reactions of complexes of olefin.
  - b) Discuss Dewar-Chatt-Duncanson model with an example.

OR

- a) How is ferrocene synthesized? Explain the molecular orbital treatment of bonding in ferrocene
- b) Discuss structure and bonding in benzenoid complexes
- 3. a) Write a detailed account of oxidative addition reactions
  - b) Write a detailed account of elimination reactions

OR

- a) Explain the concept of Lewis acidity and Lewis basiscity with respect to organometalics.
- b) Discuss fluxional isomerism observed in organometallic complexes
- 4. a) Discuss olefin hydrogenation using Wilkinson catalyst.
  - b) Discuss the catalytic cycle involved in Wacker process

OR

- a) Explain olefin polymerization reaction over Ziegler-Natta catalyst
- b) Write an account on Fischer-Tropsch Synthesis
- 5. a) Describe synthetic applications of organo-lithium compounds
  - b) Discuss synthetic applications of aluminum compounds

OR

- a) Discuss biological applications of organometallic compounds in agriculture
  - b) Discuss use of organometallic compound in the area of medicine.

### ANDHRA UNIVERSITY DEPARTMENT OF CHEMISTRY

## M.SC., CHEMISTRY (FINAL)-IV-SEMESTER SYLLABUS SPECIALIZATION: INORGANIC CHEMISTRY

Paper—IV: PHYSICAL METHODS IN INORGANIC CHEMISTRY-II (Effective only for 2020-21 academic year)

#### UNIT I

- a) Mossbauer Spectroscopy: Mossbauer effect, isomer shift, Quadrupole splitting, differentiation of cis- and trans-  $MA_4B_2$  type complexes, structural elucidation of Fe compounds Fe(CO)<sub>5</sub>, Fe<sub>2</sub>(CO)<sub>9</sub>, Fe<sub>3</sub>(CO)<sub>12</sub>.
- b) Mass Spectrometry: Principle, basic instrumentation, Ionization methods (electron impact, photo ionization, chemical ionization, fast atom bombardment, MALDI), mass analyzers (magnetic, electrostatic, quadrupole and time of flight), energetic of ion formation, types of peaks, resolution, fingerprint applications.
- C) Magnetic susceptibility: Experimental methods for the determination of the magnetic susceptibility and magnetic moments- importance to inorganic compounds- VSM, SQID.

#### Unit II

a) Thermal methods of analysis: Thermogravimetry, factors affecting TG, applications of thermogravimetry, Differential thermal analysis (DTA), applications of DTA, TG and DTA of CaC<sub>2</sub>O<sub>4</sub>.H<sub>2</sub>O, Cu<sub>2</sub>S, CuSO<sub>4</sub>.5H<sub>2</sub>O, Differential scanning calorimetry – Principle and applications.

#### **Unit-III**

**Radiochemical methods**: Measurement of Radioactivity, Ionization detectorsgas ionization(Ionization chamber, Proportional counter, Geiger –Muller counter) and solid ionization, scintillation detectors, Activation analysis, Isotope dilution analysis. Tracer techniques in analytical chemistry, carbon dating, preservation of food materials and surgical items using radioactive radiations.

#### **Unit IV**

a)Ion Selectometry: Basic principle, types of ion selective electrodes - solid membrane, glass, liquid membrane and enzyme based electrodes, gas sensing electrodes, applications – determination of fluoride in water.

b)Separation methods: Solvent extraction- ion exchange, molecular sieving-chromatography.

#### IInit V

Chromatography: Classification of chromatographic techniques, methods of development, paper chromatography (1D, 2D and multi dimensional), Thin layer chromatography, variation in development techniques, advantages of TLC

over paper chromatography, Gas chromatography – Principle, basic instrumentation, types of detectors, applications, Hyphenated technique GC-MS. High performance liquid chromatography (HPLC) – Instrumentation, preconcentration procedures for HPLC, Van Demeter equation, comparison of HPLC and GC, applications of HPLC.

#### **Books:**

- 1. Instrumental methods of analysis, (6th Edition) Hobart H. Willard, Lynne L Merit Jr. and
  - John A Dean and Frank A Settle, Jr.
- 2. Vogel's Text Book of Quantitative Chemical analysis,(6<sup>th</sup> Edition) Basset Re Dnnex,
  - G.H. Jeffery and J.Mendham.
- 3. Physical methods in Inorganic Chemistry, R.S. Drago.
- 4. Principles of Instrumental Analysis, Skoog, West and Holler.

## MODEL QUESTION PAPER DEPARTMENT OF CHEMISTRY

## M.SC., CHEMISTRY (FINAL)-IV-SEMESTER SPECIALIZATION: INORGANIC CHEMISTRY

#### PAPER-IV: PHYSICAL METHODS IN INORGANIC CHEMISTRY-II

(Effective from 2021-2022 Admitted batch)

Time: 3 h Total Marks = 80 M

#### Answer all questions (5 x 16M = 80 M)

1. a) describe the principle of Mossbauer spectroscopy and explain isomer shift b) Discuss the structural elucidation of iron carbonyls using Mossbauer spectroscopy

OR

- a) Explain various ionization techniques used in massspectrometry including merits and demerits.
- b) Describe finger print applications of massspectrometry
- 2. a) State the principle and explain the instrumentation of DTA and its applications
- b) Discuss various factors that effect TGA curves.

OR

- a) Discuss the aplications of DSC
- b) Discuss the differences between DTA and DSC
- 3) a) Describe the principle and working of Geiger-Muller counter used for the detection of radioactive radiation
- b) Discuss Solid ionization detectors used for the detection of radioactive radiation

OR

- a) Explain preservation of food materials and surgical items using radioactive radiations.
- b) Discuss carbon-dating technique and its applications
- 4) a) What are the ion selective electrodes. Explain the working of solid membrane electrode.
- b) Discuss principle and applications of gas sensing electrode.

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- a) What are ion exchangers? Discuss working principle of ion exchange chromatography
- b) What are molecular sieves? Discuss working principle of exclusion chromatography.

- 5.a) Explain the principle and Instrumentation of Gas Chromatography. Discuss about various types of detectors.
  b) Discuss the applications of gas chromatography

- a) Explain the principle and instrumentation of HPLC
- b) Discuss the principle and applications of TLC chromatography.

# ANDHRA UNIVERSITY DEPARTMENT OF CHEMISTRY M.SC., CHEMISTRY (FINAL)-IV-SEMESTER SPECIALIZATION: INORGANIC CHEMISTRY INORGANIC CHEMISTRY PRACTICALS-II (INSTRUMENTATION)

#### I. pH metry

- 1. Determination of concentration of strong acid using strong base
- 2. Determination of concentration of weak acid using strong base
- 3. Determination of concentration of weak base using strong acid
- 4. Determination of concentration of polybasic acid using strong base
- 5. Determination of stability constant of copper glycinate
- 6. Determination of dissociation constant of an indicator

#### II. Conductometry

- 1. Determination of concentration of strong acid using strong base
- 2. Determination of concentration of sodium carbonate using strong acid
- 3. Determination of concentration of weak acid using strong base
- 4. Determination of concentrations of weak and strong acids in a mixture using strong base
  - 5. Determination of barium
  - 6. Determination of lead
  - 7. Determination of sulfate

#### III. Potentiometry

- 1. Determination of Iron(II) using potassium permanganate
- 2. Determination of Iron(II) using sodium vanadate
- 3. Determination of Iron(II) using Ceric sulphate
- 4. Determination of Iron(II) and vanadate in a mixture using potassium permanganate
- 5. Determination of potassium permanganate and vanadate in a mixture using Iron(II)
- 6. Determination of ceric sulfate and sodium vanadate in a mixture using Iron(II)

#### IV. Colorimetry

- 1. Determination of concentration of Iron(III) using potassium thiocyanate
- 2. Determination of concentration of Manganese(II) using potassium periodate
  - 3. Determination of Phosphate using molybdate
  - 4. Determination of nitrite by using diazotization method
  - 5. Photometric titration of Copper(II) using EDTA
- 6. Determination of composition of Iron(II) and 1,10-phenanthroline using Job's method and

mole-ratio method

6. Simultaneous determination of chromium(VI) and manganese(VII) in a mixture

#### V. Electrogravimetry

1. Determination of Copper(II) in a solution VI. Flame photometry

1. Determination of sodium, potassium and calcium

VII. Thermogravimetry

1. TGA and DTA of calcium oxalate of alkaline earth metals

#### References:

1. Vogel's Quantitative Inorganic Analysis