

SEMESTER V
INORGANIC & ORGANIC CHEMISTRY-II
THEORY

Program: B.Sc.
Course Code: U20/CHE/DSC/501
Course Type: DSC-5
No. of Credits: 4

Max. Hours: 60
Hours per week: 4
Max. Marks: 100

COURSE OBJECTIVES:

- To enable the students to understand the concepts of Coordination chemistry and its applications.
- To make the students understand the concepts of Metal carbonyls and mechanisms of Inorganic reactions.
- The course aims at giving an overview on principles and types of pericyclic reactions.
- Analyze and understand the stereochemistry elements, importance of retro synthesis in designing the synthesis of organic compounds.
- To understand the basic principles and to develop skills in interpretation of various spectra in elucidation of structure of simple molecules.

COURSE OUTCOMES:

- CO 1:** Understand the concepts of Coordination Chemistry in elucidating the structures of complexes and apply in isomerism.
- CO 2** Apply the theories of coordination chemistry in Isomerism. Interpret the concepts and applications of HSAB.
- CO 3:** Learn about Metal carbonyls, boranes, carboranes inorganic reaction mechanisms.
- CO 4:** Elaborate on the concepts of synthetic organic chemistry.
- CO 5:** Understand and apply the principles of spectroscopy in solving the problems related to structural analysis of simple organic molecules.

INORGANIC CHEMISTRY**MODULE 1: COORDINATION CHEMISTRY & HARD AND SOFT ACIDS AND BASES****(15 Hrs)****COORDINATION CHEMISTRY****(13 Hrs)**

Werner's theory – postulates, experimental evidences. Sidgwick's theory – Calculation of EAN, limitations. Nomenclature of inorganic complex compounds.

Valence bond theory – postulates, geometries of coordination number 4 & 6- tetrahedral $[\text{Ni}(\text{NH}_3)_4]^{2+}$, $[\text{NiCl}_4]^{2-}$ and $[\text{Ni}(\text{CO})_4]$, square planar $[\text{Ni}(\text{CN})_4]^{2-}$, $[\text{Cu}(\text{NH}_3)_4]^{2+}$, $[\text{PtCl}_4]^{2-}$ Octahedral complexes $[\text{Fe}(\text{CN})_6]^{4-}$, $[\text{Fe}(\text{CN})_6]^{3-}$, $[\text{FeF}_6]^{4-}$, $[\text{Co}(\text{NH}_3)_6]^{3+}$, $[\text{CoF}_6]^{3-}$. Limitations of VBT Crystal field theory – features, splitting of d-orbitals, in octahedral, tetrahedral and square planar complexes, Crystal field stabilization energy (calculation of CFSE for d^n configurations in octahedral complexes), Magnetic properties of transition- metal complexes: Types of magnetic behaviour, spin only formula, calculation of magnetic moments using spin only formula. Electronic spectra of metal complexes – d-d transitions, spectrochemical series, Electronic absorption spectrum of $[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$. Determination of composition of complexes - Job's method and mole ratio method, Thermodynamic and kinetic stability of transition metal complexes. Stability of metal complexes –step wise and overall stability constant and their relationship and chelate effect.

Isomerism in co-ordination compounds structural: ionization, hydrate, linkage, co- ordination, coordination- position and polymerization isomerism.

STEREOISOMERISM

Isomerism in coordination compounds, stereo isomerism – (a) geometrical isomerism in (i) square planar metal complexes of the type $[\text{MA}_2\text{B}_2]$, $[\text{MA}_2\text{BC}]$, $[\text{M}(\text{AB})_2]$, $[\text{MABCD}]$. (ii) Octahedral metal complexes of the type $[\text{MA}_4\text{B}_2]$, $[\text{M}(\text{AA})_2\text{B}_2]$, $[\text{MA}_3\text{B}_3]$ using suitable examples, (b) Optical isomerism in (i) Tetrahedral complexes $[\text{MABCD}]$, (ii) Octahedral complexes $[\text{M}(\text{AA})_2\text{B}_2]$, $[\text{M}(\text{AA})_3]$ using suitable examples.

APPLICATIONS OF COORDINATION COMPOUNDS

Applications of coordination compounds a) in quantitative and qualitative analysis with suitable examples b) in medicine for removal of toxic metal ions and cancer therapy c) in industry as catalysts polymerization – Ziegler Natta catalyst d) water softening.

HARD AND SOFT ACIDS AND BASES**(2 Hrs)**

Classification Pearson's concept of hardness and softness, application of HSAB principles, stability of complexes, predicting the feasibility of a reaction.

MODULE 2: METAL CARBONYLS, BORANES, CARBORANES AND INORGANIC REACTION MECHANISM (15 Hrs)

METAL CARBONYLS (3 Hrs)

Preparation and properties of Ni(CO)₄. Structural features of Ni(CO)₄, Fe(CO)₅, Fe₂(CO)₉, Fe₃(CO)₁₂ and Cr(CO)₆ -18 valence electron rule.

BORANES AND CARBORANES (3 Hrs)

Definition of clusters. Structures of boranes and carboranes- Wade's rules, closo, nido, arachno Boranes and carboranes

INORGANIC REACTION MECHANISM (9 Hrs)

Substitution Reactions – dissociation and association reactions, mechanism for SN¹ and SN² in octahedral and square planar complexes with one example each. Trans effect – theories and applications. Acid Hydrolysis (mechanism) and Base Hydrolysis (mechanism). Lability and inertness of complexes and factors affecting it. Electron transfer reactions – outer sphere and inner sphere mechanism (brief account only) – two electron transfer reactions.

ORGANIC CHEMISTRY

MODULE 3: PERICYCLIC REACTIONS, SYNTHETIC STRATEGIES, ASYMMETRIC SYNTHESIS & SYNTHESIS BASED ON CARBANIONS (15 Hrs)

PERICYCLIC REACTIONS (5 Hrs)

Concerted reactions, Molecular orbitals of ethene, 1,3-butadiene and allyl radical. Symmetry properties, HOMO, LUMO, Thermal and photochemical pericyclic reactions. Types of pericyclic reactions – electrocyclic, cycloaddition and sigmatropic reactions – one example each and their explanation by FMO theory.

SYNTHETIC STRATEGIES (3 Hrs)

Terminology – Target molecule (TM), Disconnection approach – Retrosynthesis, Synthons, Synthetic equivalent (SE), Functional group interconversion (FGI), Linear, Convergent synthesis. Retrosynthetic analysis of the following molecules: 1) acetophenone 2) cyclohexene and 3) phenylethylbromide.

ASYMMETRIC SYNTHESIS (4 Hrs)

Definition and classification of stereoselective reactions: substrate, product stereoselective reactions, enantio and diastereo selective reactions. Stereospecific reaction – definition – example – dehalogenation of 1,2-dibromides induced by iodide ion. Enantioselective reactions – definition – example – Reduction of Ethylacetoacetate by Yeast. Diastereoselective reaction- definition-example: Acid catalysed dehydration of 1-phenylpropanal and Grignard addition to 2-phenyl propanal. Definition and explanation of enantiomeric excess and diastereomeric excess.

SYNTHESIS BASED ON CARBANIONS**(3 Hrs)**

Acidity of Alpha - Hydrogens, Preparation of Aceto-acetic ester by Claisen condensation and synthetic applications of Acetoacetic ester. A) Acid hydrolysis and ketonic hydrolysis. Preparation of i) monocarboxylic acids ii) dicarboxylic acids (iii) ketones (iv) Reaction with urea.

Malonic Ester- synthetic applications. Preparation of i) substituted mono carboxylic acids (ii) substituted dicarboxylic acids (iii). α , β . Unsaturated acids.

MODULE 4: MOLECULAR SPECTROSCOPY II**(15 Hrs)****NMR SPECTROSCOPY****(5 Hrs)**

Principles of nuclear magnetic resonance, number of signals, equivalent & non equivalent protons, position of signals-chemical shift. NMR splitting of signals, Spin-Spin coupling, coupling constants. Application of NMR with suitable examples-Ethyl bromide, Ethanol, Acetaldehyde, 1,1,2-Tribromoethane, Ethylacetate, Toluene & Acetophenone.

MASS SPECTROMETRY**(5 Hrs)**

Basic principles – Nitrogen rule, Types of ions: Molecular ion / parent ion, fragment ions / daughter ions. Theory – formation of parent ions. Representation of mass spectrum. Identification of parent ion, (M+1), (M+2) and base peaks (relative abundance 100%). Determination of molecular formula – Mass spectra of ethyl benzene, ethyl bromide, acetophenone, n-butyl amine and 1- propanal.

SPECTRAL INTERPRETATION**(2 Hrs)**

Interpretation of IR, UV-Visible, H^1 -NMR and mass spectral data of the following compounds
1. Phenyl acetylene 2. Acetophenone 3. Cinnamic Acid 4. para-nitro aniline.

ELECTRON SPIN RESONANCE**(3 Hrs)**

Electron Spin Resonance (ESR) spectroscopy: Basic principle, hyperfine structure, ESR of simple radicals like H^\cdot , CH_3^\cdot and $CH_3CH_2^\cdot$.

Text Books:

1. Wahid.U.Malik, Tuli G.D and Madan R.D (1976) *Selected topics in Inorganic Chemistry*: S.Chand Publishers
2. Puri B.R, Sharma L.Rand Khalia K.C (2014) *Principles of Inorganic Chemistry*: Milestone publishers and Distributers.
3. Tuli G.D, Madan R.D, Basu S.K, Sathyaprakash. *Advanced Inorganic Chemistry Volume II* : S.Chand and company ltd (New Delhi ,India)
4. Sharma, Y.R. *Text Book of Complete Organic Chemistry*, 2nd Edn. Kalyani, 2007.
5. Jain, M.K. & Sharma, S.C. *Modern Organic Chemistry*, 4th Edn. Vishal, 2009.

6. Sharma Y.R (2005) *Elementary Organic Spectroscopy; Principles and Chemical applications* : S.Chand & Company Ltd *Spectroscopy: MacMilan* Colin Banwell, Elaine McCash (1994) *Fundamentals of Molecular Spectroscopy (West lake village U.S.A): Mcgraw Hill*
7. Sharma B.K, *Instrumental Methods of Chemical Analysis: Krishna Prakashan media Ltd*

Reference Books:

1. Cotton, F.A. & Wilkinson, G, *Basic Inorganic Chemistry,(London): John Wiley and sons Ltd.*
2. Lee, J.D. *Concise Inorganic Chemistry* ELBS, 1991.
3. Huheey, J.E., Keiter, E.A., Keiter, R.L. & Medhi, O.K. *Inorganic Chemistry: Pearsons education , South Asia*
4. L. Pavia and Lampman Kriz Vyal, *Spectroscopy* : Singh Age Publications
5. Morrison, R.T. & Boyd, R.N. *Organic chemistry*, 6th edition Prentice Hall, 1992. Ferguson,
6. L.N. *Textbook of organic chemistry*, 2nd edn. V. Nostrand, 1965.

INORGANIC & ORGANIC CHEMISTRY-II**MODEL QUESTION PAPER****THEORY****Course Code: U20/CHE/DSC/501****Credits: 4****Max. Marks: 60****Max Time: 2 Hrs****SECTION - A****I. Answer the following:****4X10=40 M**

1. a) What is CFT? How does it account for the fact that $[\text{CoF}_6]^{3-}$ is paramagnetic but $[\text{Co}(\text{NH}_3)_6]^{3+}$ is diamagnetic though both are octahedral? (CO 1) 5M
- b) What is optical isomerism? Draw and explain the optical isomerism in octahedral complexes. (CO 1) 5M
- OR**
2. a) Discuss Werner's theory with example. (CO 1) 5 M
- b) Explain the Crystal field splitting in octahedral complexes. (CO 1) 5 M
3. Write the mechanism of SN_1 in the octahedral and SN_2 in square planar complexes with one example each. (CO 3) 10 M
- OR**
4. a) What is trans effect? Discuss the theories and applications of trans effect. (CO 3) 6M
- b) What are labile and inert complexes? Explain with examples. (CO 3) 4 M
5. a) Write a brief note on electrocyclic reactions. (CO 4) 5 M
- b) Explain stereoselective reactions by taking acid catalysed dehydration of 1-Phenylpropanol as an example. (CO 4) 5 M
- OR**
6. a) What is Claisen condensation? Give the mechanism. (CO 4) 6 M
- b) Using Malonic Ester, how are α , β -unsaturated acids synthesized? (CO 4) 4M
7. a) What is chemical shift? Explain the change in position of signals with example. (CO5) 5 M
- b) Discuss about (M+1), (M+2) and base peaks with two examples in Mass spectrometry. (CO 5) 5M
- OR**
8. a) Write the number of signals possible for $\text{CH}_3\text{-CH}_2\text{-CH}_2\text{-OH}$ and explain about spin-spin splitting. (CO 5) 5 M
- b) Explain the basic principles of ESR spectroscopy. (CO 5) 5 M

SECTION - B**II. Answer any FOUR****4x5=20 M**

9. Explain the Job's method of determination of composition of a complex. (CO 1)
10. Discuss the applications of HSAB principle. (CO 2)
11. What is 18 electron rule? Discuss the structure of $\text{Ni}(\text{CO})_4$. (CO 3)
12. How is molecular formula of a compound determined based on its Mass spectrum? (CO 5)
13. How many types of NMR signals are expected for 1,1,2-tribromoethane? What is the intensity ratio of the peaks? (CO 5)
14. Outline retro synthesis of phenyl ethyl bromide. (CO 4)