PH 541.3 Reg. No:

St Aloysius College (Autonomous)
Mangaluru
Semester III– P.G Examination – M.Sc. Analytical Chemistry
November/December -2023
Organometallic, Bioinorganic and Coordination Chemistry

Time: 3 Hrs. **Max. Marks:70**

Part A

1. **Answer any FIVE sub divisions of the following:** **(5X2=10)**

a. Describe the structural characteristics of a typical transition metal complex with pi ligands.

b. Describe the structure of a metal carbyne complex.

c. Name a catalyst used in Monsanto acetic acid synthesis.

d. Mention the advantages of water gas shift reaction.

e. How does ceruloplasmin contribute to the regulation of copper levels in the body? Provide an overview of its role.

f. How elements in the biological system are classified?

g. What is cis-platin? How it is synthesized?

h. What are non-complimentary reactions? Give example.

PART B

Answer any FIVE of the following questions choosing at least one full question from each unit. **(5X12=60)**

UNIT -I

2. a. Write a note on classification of organometallic compounds. **(4)**

b. Discuss the preparation and bonding in Fischer carbene complex. **(4)**

c. Explain the structure and bonding in ferrocene. **(4)**

3. a. How do ligands influence the reactivity and selectivity of organometallic catalysts? **(4)**

b. Discuss preparation and bonding in metal - alkene complex **(4)**

c. Explain preparation and structure of organoberyllium compounds. **(4)**

UNIT-II

4. a. Explain the role of cocatalyst such as aluminum alkyls in Ziegler-Natta polymerization reactions. How do they enhance the catalyst's activity? **(4)**

b. What is Wilkinson catalyst? Demonstrate its application with any one example. Mention the selectivity exhibited by this catalyst. **(4)**

c. Can you name some common homogeneous catalyst used in organometallic catalysis? **(4)**

5. a. Write a note on industrial applications of organometallic complexes. **(4)**

b. Describe the mechanism of Fischer – Tropsch synthesis **(4)**

c. Can you describe the key chemical reactions involved in the Wacker process including the catalysts and reactants used? **(4)**

Contd...2

UNIT -III

6. a. Write any four applications of nitrogen fixation. (4)
   b. Explain the cause and consequences of 'blue baby syndrome'. (4)
   c. Compare and contrast the structural differences between Hemocyanin and Hemerythrin, and explain how these differences relate to their oxygen-binding mechanisms. (4)

7. a. What are the structural features of cytochrome P-450? Discuss its mechanism. (4)
   b. Describe a scenario where the activity of the calcium pump (Ca^{2+}-ATPase) in muscle cells is critical for muscle contraction. How does the calcium pump function in this context? (4)
   c. Compare and contrast the roles of ion channels and ionophores in regulating ion transport across cell membranes. Highlight their similarities and differences. (4)

UNIT -IV

8. a. What is base hydrolysis? Explain its mechanism. (4)
   b. What are anation reactions? Discuss their mechanism. (4)
   c. Design two-step syntheses of cis-and trans-$[PtCl_2(NO_2)(NH_3)]^-$ starting from $[PtCl_4]^{2-}$. (4)

9. a. Explain the factors that influence lability and inertness in octahedral complexes. (4)
   b. Explain inner-sphere electron transfer reactions with an example. Point out its main characteristics. (4)
   c. Square planar complexes are generally labile. Explain. (4)

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SEMESTER III– P.G Examination – M.Sc. Analytical Chemistry

November/December -2023

ELECTROANALYTICAL, RADIOCHEMICAL AND THERMOANALYTICAL TECHNIQUES

Time: 3 Hours **Max. Marks: 70**

PART – A

1. **Answer any FIVE sub-divisions of the following:** **(5×2=10)**

a) Define Standard Electrode Potential(SRP).

b) List any four applications of Conductometric Titrations.

c) Define decomposition potential and give its significance.

d) List the advantages of biamperometric titrations over amperometric titrations.

e) Define chronoamperometry.

f) What is isotopic dilution analysis?

g) What types of temperature changes are detected by DTA?

h) What is dilatometry and what does it measure?

PART – B

Answer any FIVE of the following choosing at least one full question from each unit. **(5×12=60)**

UNIT-I

2. a) Define the term "cell potential" in electrochemistry. Explain the thermodynamics of cell potential. **(4)**

b) What is the fundamental principle behind the generation of acid and alkali errors in glass electrodes? Provide a brief explanation of the chemical processes involved. **(4)**

c) Compare and contrast the advantages of different reference electrode types, such as Ag/AgCl, saturated calomel electrode (SCE), and standard hydrogen electrode (SHE). **(4)**

3. a) Explain the principle and applications of potentiometric titrations. **(4)**

b) Analyze the advantages and limitations of glass electrodes and derive the indicator electrode equation for glass electrode. **(4)**

c) Explain why a salt bridge is essential in a galvanic cell. How does it prevent the buildup of charge and maintain electrical neutrality in the half-cells? **(4)**

UNIT-II

4. a) Write a short note on organic polarography **(4)**

b) Describe the nature of cyclic voltammogram, highlighting the significance of different terms involved **(4)**

c) Compare biamperometric titrations with amperometric titrations. **(4)**

5. a) Explain pulse polarography. **(4)**

b) Explain the principle of cyclic voltammetry. **(4)**

c) Analyze the nature of solvents and the base electrolytes used for organic polarography. **(4)**

Contd...2

UNIT-III

6. a) Explain the principle of coulometric titrations. (4)
   b) How does Proportional Counters act as the detector in radiochemical analysis? (4)
   c) Explain isotopic dilution analysis with reference to direct method. (4)

7. a) Discuss the applications of coulometric titrations. (4)
   b) How does ionization chamber acts as the detector in radiochemical analysis? (4)
   c) Write the principle of chronopotentiometry with its applications. (4)

UNIT-IV

8. a) Discuss how DSC can be used to study the nature of materials and provide practical examples. (4)
   b) Explain the working principle of a thermometric titration for acid-base titrations. (4)
   c) How can TGA be used to determine the purity, composition, and moisture content of a sample? (4)

9. a) Compare the working principles and application of dilatometry and thermometric titrations. (4)
   b) Illustrate the thermogram for the degradation of $CaCO_3$ and explain the various steps involved (4)
   c) Compare and contrast DSC with other thermal analysis techniques like TGA and DTA, highlighting their unique capabilities. (4)

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SEMESTER III– P.G Examination – M.Sc. Analytical Chemistry

November/December -2023

MOLECULAR SPECTROSCOPY

Time: 3 Hours **Max. Marks: 70**

PART – A

1. **Answer any SEVEN sub-divisions of the following:** **(7×2=14)**

a) How does NMR spectroscopy assist in determining the relative stereochemistry of stereoisomeric compounds?

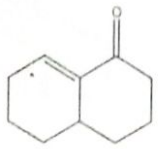
b) How does the choice of solvent influence chemical shift?

c) Describe the differences between an AX and an AB system in NMR spectroscopy. What molecular characteristics lead to these distinct patterns?

d) Explain why chlorobenzene has no nitrogen based on nitrogen rule.

e) How does the presence of double bonds affect the mass spectrometry fragmentation pattern compared to alkanes?

f) Determine the λ_{max} of the following organic compound:



g) Discuss the relationship between the strength of a chemical bond and its contribution to the vibrational frequency in an IR spectrum.

h) How do alkene compounds differ from alkanes in terms of the absorption bands observed in the IR spectrum?

i) List the electronic factors affecting the Vibrational frequencies of an organic compound

PART – B

Answer any FOUR of the following choosing at least one full question from each unit. **(4×14=56)**

UNIT-I

2. a) What is the difference between continuous wave (CW) NMR and pulsed (FT) NMR? **(4)**

b) An organic compound with molecular formala:$C_8H_8O_2$ has a mass of 136 and exhibited the following data: IR (nm): 820, 1230,1670, 2740, 2850, 3050 PMR: 3.9 s (3H), 6.9 d (2H), 7.8 d (2H), 9.8 s (1H) MS (m/z): 29, 51, 77, 92, 135, 136 . Elucidate the structure with proper explanation **(5)**

c) Compare and contrast T_1 and T_2 techniques in NMR spectroscopy. When is each method preferred, and why? **(5)**

Contd...2

3. a) Explain how the sensitivity of ^{13}C NMR spectroscopy differs from ^{1}H NMR spectroscopy. What strategies are employed to enhance the sensitivity of ^{13}C NMR experiments? **(4)**

   b) Explain shielding effect in NMR spectroscopy. How is chemical shift value affected by shielding effect? Elaborate with examples. **(5)**

   c) Discuss how the J-coupling constant (scalar coupling constant) between two nuclei can provide information about the dihedral angle (torsion angle) between their respective chemical bonds in a molecule, and how this information is applied in the study of conformational isomerism using NMR spectroscopy. **(5)**

UNIT-II

4. a) Meta-stable ions are often observed in mass spectra. Discuss the formation of meta-stable ions during the ionization process and their importance in mass spectrometry. **(5)**

   b) Explain the Retro Diels Alder Reaction. **(5)**

   c) Briefly discuss the effect of substituents on the absorption maximum. **(4)**

5. a) Benzaldehyde shows prominent peaks at 114, 105, 77, 51 respectively. Explain. **(4)**

   b) Explain the concept of steric hindrance and its influence on reaction pathways and fragmentation. Provide examples of molecules where steric hindrance plays a crucial role **(5)**

   c) Explain mode I , mode II and mode III of homolytic cleavage. **(5)**

UNIT-III

6. a) Explain the IR spectrum of

   (i)Acetophenone (ii)Benzaldehyde **(5)**

   b) Give the characteristic vibrational frequencies of alcohol with any two examples. **(4)**

   c) Identify the significance of Fermi resonance in IR spectroscopy **(5)**

7. a) Explain the IR spectrum of 1- Hexene and Toluene **(4)**

   b) Explain the characteristic vibrational frequencies of Ketones with any two examples. **(5)**

   d) Write a note on FIR spectroscopy & NIR spectroscopy. **(5)**

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