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St Aloysius College (Autonomous), Mangaluru

Semester III- P.G Examination – M.Sc. Analytical Chemistry

November - 2024

Organometallic, Bioinorganic and Coordination Chemistry

Time: 3 Hrs.

Max. Marks:70

**PART A**

1. Answer any FIVE sub divisions of the following: (5X2=10)
- Describe the structure of metal carbyne complex.
  - Benzene has variable hapticity 2,4 and 6. Justify.
  - What is Ziegler-Natta catalyst? Explain its applications.
  - Explain  $\beta$ -elimination reaction.
  - Which metal ion is at the centre of the haeme group in haemoglobin and myoglobin, allowing them to bind oxygen? What is its spin?
  - What are iron-sulfur proteins and what role do they play in biological systems?
  - What is a water exchange reaction? Give an example.
  - What is cis-platin? How it is synthesized?

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**PART B**

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

**UNIT -I**

- Describe hapticity in organometallic compounds with examples. (4)
  - Write a note on structure and bonding in Al and Be alkyls (4)
  - What are Schrock carbene complexes? Give examples. Explain the bonding in them (4)
- Explain the structure and bonding in metal-diene complexes (4)
  - Propose a structure for an organometallic complex that violates the 18-electron rule and discuss the implications for its stability. (4)
  - Explain bonding and synthesis of Zeise's salt (4)

**UNIT-II**

- Discuss the industrial importance of water gas shift reactions. (4)
  - Explain the Fischer-Tropsch process with its reaction, catalysts and significance. (4)
  - Describe briefly the hydrocarbonylation of olefin catalysis by  $\text{HCo}(\text{CO})_4$ . What are the demerits of this catalyst? (4)
- Alk-1-enes are hydrogenated more rapidly than alk-2-enes by homogeneous catalyst. Justify? (4)
  - Write down the mechanism of aerial oxidation of propene in the presence of  $\text{PdCl}_2$  and  $\text{CuCl}_2$  in dil.HCl. (4)
  - Explain the mechanism of olefin isomerism. (4)

Contd...2

## UNIT -III

6. a. Analyze the differences between biological nitrogen fixation and industrial nitrogen fixation. (4)
- b. How does hemerythrin differ from hemocyanin in terms of its oxygen-binding mechanism? Provide a brief overview. (4)
- c. Discuss the functioning of  $\text{Na}^+$ - $\text{K}^+$  pump. (4)
7. a. Discuss the structural features and function of transferrin. (4)
- b. Compare and contrast the roles of copper (Cu) and magnesium (Mg) ions in biological systems. (4)
- c. Describe a scenario where the activity of the calcium pump ( $\text{Ca}^{2+}$ -ATPase) in muscle cells is critical for muscle contraction. How does the calcium pump function in this context? (4)

## UNIT -IV

8. a. What type of octahedral complexes undergo acid hydrolysis by  $\text{S}_{\text{N}}2$  mechanism? What type of intermediates and products would be formed? Illustrate giving suitable examples. (4)
- b. Explain non-complimentary reactions with suitable examples. (4)
- c. What is base hydrolysis? Explain  $\text{S}_{\text{N}}1\text{CB}$  mechanism for base hydrolysis. (4)
9. a. Design two-step syntheses of cis-and trans- $[\text{PtCl}_2(\text{NO}_2)(\text{NH}_3)]$ -starting from  $[\text{PtCl}_4]^{2-}$ . (4)
- b. Explain the mechanisms of inner sphere electron transfer reactions with suitable examples. (4)
- c. Square planar complexes are generally labile. Explain. (4)

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**St Aloysius College (Autonomous)****Mangaluru****SEMESTER III- P.G Examination – M.Sc. Analytical Chemistry****November - 2024****ELECTROANALYTICAL, RADIOCHEMICAL AND THERMOANALYTICAL  
TECHNIQUES****Time: 3 Hours****Max. Marks: 70****ST.ALOYSIUS COLLEGE  
PG DEPARTMENT  
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- 1. Answer any FIVE sub-divisions of the following: (5×2=10)**
- Define standard electrode potential. Give its significance.
  - Give the composition of glass electrode.
  - Write the components of a polarographic cell. What is the role of a supporting electrolyte?
  - Give the Ilkovic equation. Explain the terms involved.
  - Differentiate between controlled current and controlled potential electrogravimetry.
  - Define natural and artificial radioactivity. Give suitable examples.
  - What are the advantages of DTA over TGA?
  - Mention the types, systems used for thermo gravimetric analysis (TGA).

**PART – B**

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

**UNIT-I**

- Discuss the thermodynamics of cell reactions. (4)
  - Explain the construction and working of calomel electrode. (4)
  - Describe the conductometric titration of a mixture of strong acid and weak acid against strong base. (4)
- Discuss the classification of metallic electrodes with suitable examples. (4)
  - Differentiate between direct potentiometry and potentiometric titrations. (4)
  - Write a short note on enzyme electrodes. (4)

**UNIT-II**

- Explain the principle and methodology of stripping analysis. (4)
  - Discuss the applications of polarographic techniques. (4)
  - Write a note on biamperometric titration. (4)
- Discuss the different currents observed in polarographic studies. (4)
  - Discuss the principle of cyclic voltammetry by valuing a suitable example. (4)
  - Give the advantages and limitations of amperometric titrations. (4)

**Contd...2**

**UNIT-III**

6. a) Describe the isotopic dilution analysis. (4)  
b) Discuss the effect of counter potential and over voltage on electrogravimetric estimations. (4)  
c) Write a note on prompt gamma neutron activation analysis. (4)
7. a) Describe the types of coulometric titrations and their applications. (4)  
b) Explain the detection and measurement of radioactivity by tracer technique. (4)  
c) Write a note on radiometric titrations. (4)

**UNIT-IV**

8. a) Explain the principle, working and instrumentation of differential thermal analysis. (4)  
b) Elaborate the factors affecting simultaneous DTA-TGA curves. What are its applications? (4)  
c) Give the applications of thermometric titrations. (4)
9. a) Explain the types of recording balances and sample holders in TGA. (4)  
b) Describe the applications of differential scanning calorimetry. (4)  
c) Write a short note on dilatometry. (4)

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**November - 2024**

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**MOLECULAR SPECTROSCOPY****Time: 3 Hours****Max. Marks: 70****PART – A**

1. Answer any **SEVEN** sub-divisions of the following: (7×2=14)
- How do you confirm the conversion of toluene to benzoic acid by  $^{13}\text{C}$  NMR analysis?
  - What are Larmour frequency and resonance phenomenon?
  - What are NMR reagents? Give examples.
  - 3-pentanone shows a peak at  $m/z$  57 in its EI-MS whereas, 2-pentanone gives a peak at  $m/z$  86. Comment on this.
  - How does the solvent effect influence in UV Spectroscopy ?
  - State nitrogen rule. Explain with an example.
  - What is metastable ion. Mention its significance.
  - How can you distinguish 1-hexene & 1-hexyne on the basis of IR spectroscopy?
  - cis*-1,2-dichloroethylene is IR active with respect to C=C double bond whereas *trans*-1,2-dichloroethylene is not. Give reasons.

**PART – B**

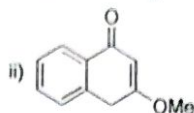
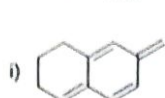
Answer any **FOUR** of the following choosing at least one (4×14=56) full question from each unit.

**UNIT-I**

- Explain the Magnetic anisotropic effect in molecules containing n-bond(s). (5)
  - Discuss the applications of NMR in medical fields. (4)
  - Why spin spin splitting occurs in PMR spectroscopy? Discuss the intensity and nature of peaks in 1,1,2-trichloroethane. (5)
- Explain the  $A_2X$  and  $AMX$  spin systems taking suitable examples and sketch their PMR spectra. (5)
  - Write the structures of all possible isomers of alcohol with the molecular formula  $C_4H_{10}O$  and predict the proton decoupled  $^{13}\text{C}$  NMR signals in each. (5)
  - What are the various methods of relaxation techniques seen in NMR experiment? Explain their significance and compare them. (4)

## UNIT-II

4. a) Predict the the  $\lambda_{\max}$  for the following.



(4)

- b) Acrolein ( $\text{CH}_2=\text{CHCHO}$ ) absorbs at 217nm ( $\epsilon_{\max} = 16000$ ). What is the weight concentration (g/ml) required to observe an absorbance of 0.8 when the cell length is 1 cm? (4)

- c) Describe the working of mass spectrometer with a neat labelled diagram. (6)

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5. a) Explain i) Mc Lafferty rearrangement (4)  
ii) Retro Diels-Alder fragmentation (4)

- b) Write a short note on factors affecting reaction pathways. (4)

- c) Discuss the fragmentation pathways for the following systems with suitable examples. (6)

- i) Alcohols ii) Amines iii) Esters (6)

## UNIT-III

6. a) Using IR spectroscopy, how would you determine whether the oxygen in an organic compound is present as a carbonyl, hydroxyl or ether linkage? (3)

- b) How would you distinguish between the following pairs by IR spectral studies?

- i) Phenol & Cyclohexanol ii) Acetaldehyde & acetone (6)  
iii) Primary amine & tertiary amine

- c) Discuss the factors which affect the band positions & intensities of peaks in IR spectroscopy. (5)

7. a) How can the following compounds be studied by using IR Spectroscopy ?

- i) Alkenes (6)  
ii) Ethers  
iii) Ketones

- b) Predict the structures of compounds whose IR data is given below and assign the IR bands. (4)

- i)  $\text{C}_3\text{H}_6\text{O}$ ,  $1620 \text{ cm}^{-1}$  ii)  $\text{C}_4\text{H}_6$ ,  $3300 \text{ cm}^{-1}$  and  $2250 \text{ cm}^{-1}$

- c) Deduce the structure of an organic compound that exhibited the following spectral data: Molecular Formula :  $\text{C}_{11}\text{H}_{12}\text{O}_2$

Mass: 176, 131(base peak), 103, 77;

IR ( $\text{cm}^{-1}$ ): 1714, 1639;

PMR ( $\delta$ ): 1.31 (t, 3H,  $J=7.1\text{Hz}$ ), 4.2 (q, 2H,  $J=7.1\text{Hz}$ ), 6.43 (d, 1H,  $J=15.8\text{Hz}$ ), 7.24-7.57 (m, 5H), 7.67 (d, 1H,  $J=15.8\text{Hz}$ );

CMR ( $\delta$ ): 14.3, 60.4, 118.4, 128.1, 128.9, 130.2, 134.5, 144.5, 166.8 (4)