

PH 541.3

Reg. No. : 

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**St Aloysius College (Autonomous)**

**Mangaluru**

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

**JANUARY-2021**

**ORGANOMETALLIC, BIOINORGANIC  
AND COORDINATION CHEMISTRY**

**Time: 3 Hours**

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**Max. Marks: 70**

**PART - A** MANGALORE-575 003

1. Answer any **FIVE** sub divisions of the following: (5x2=10)
- Write any four properties of coordinated alkynes in metal complexes.
  - Name the following compounds
    - $\text{Ir}(\text{CO})(\text{Cl})(\text{PPh}_3)_2$
    - $\text{C}_2\text{H}_5\text{BeH}$
  - Mention the industrial importance of Oxo-process.
  - Ferrocene is more aromatic than benzene. Justify with examples.
  - Explain the Bohr effect observed in haemoglobin.
  - Molecular nitrogen is chemically inert. Give reasons.
  - Mention the factors affecting acid hydrolysis of complexes.
  - What is an anation reaction? Give an example.

**PART - B**

Answer any **FIVE** of the following choosing at least one (5x12=60)  
full question from each unit:

**UNIT - I**

- Discuss the factors that determine the stability of transition metal alkyls. (4)
  - Discuss the bonding in Zeise's salt. Comment on the bond parameter (C=C), when ethylene is replaced by  $\text{F}_2\text{C}=\text{CF}_2$  and  $(\text{CN})_2\text{C}=\text{C}(\text{CN})_2$ . (4)
  - How is  $\text{Li}(\text{CH}_3)_2$  synthesized? How does it react with  $\text{Br}-\text{CH}=\text{CH}-\text{Et}$  and  $\alpha, \beta$ -unsaturated aldehyde? (4)
- The coordinated cyclobutadiene is aromatic in nature. Justify by explaining its bonding. (4)
  - What is 18-electron rule? Discuss its exceptions. (4)
  - Discuss the bonding in dibenzene chromium arene. (4)

**UNIT - II**

- Describe briefly the hydrocarbonylation of olefin catalysed by  $\text{HCo}(\text{CO})_4$ . What are the demerits of their catalyst? (4)
- Discuss how Zeigler-Natta catalyst is useful in bringing about stereoregular polymerization of alkenes. (4)

Contd...2

- c) Write a note on water gas shift reactions. (4)
- 5.a) What is alkene isomerisation reaction? How is it brought about by metal hydride species? (4)
- b) Write down the mechanism for the aerial oxidation of propene in the presence of  $\text{PdCl}_2$  and  $\text{CuCl}_2$  in dil.HCl. (4)
- c) Write the catalytic cycle for the manufacture of acetic acid by Monsanto process. Why  $[\text{RhI}_2(\text{CO})_2]^-$  and  $\text{CH}_3\text{I}$  are the most suitable species for this reaction? (4)

**UNIT - III**

- 6.a) Explain the role of haemoglobin in  $\text{CO}_2$  transport. (4)
- b) Explain the role of metal ions in biological system. (4)
- c) Write a note on  $\text{Na}^+ - \text{K}^+$  pump. (4)
- 7.a) Discuss the structure of transferrin and its function as metal transport protein. (4)
- b) Write a note on Iron sulphur proteins. (4)
- c) Discuss how in-vivo dinitrogen fixation occurs. (4)

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**UNIT - IV**

- 8.a) What is conjugate base mechanism? Explain the evidence in its favour. (4)
- b) Explain the outer sphere electron transfer reaction in terms of Marcus theory. (4)
- c) What is trans effect? How is it explained by polarization theory? (4)
- 9.a) Giving suitable examples, distinguish between inner sphere and outer sphere mechanism in redox reaction. (4)
- b) Write a note on substitution reaction in square planar complexes. (4)
- c) The rate constant for the electron transfer between  $[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$  and  $[\text{Fe}(\text{OH})(\text{H}_2\text{O})_5]^{2+}$  is reduced by 50% on changing the reaction medium from  $\text{H}_2\text{O}$  to  $\text{D}_2\text{O}$ . Explain. (4)

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**Semester III – P.G. Examination – M.Sc. Analytical Chemistry**  
**JANUARY-2021**

**ELECTROANALYTICAL RADIOCHEMICAL AND  
THERMOANALYTICAL TECHNIQUES**

Time: 3 Hours

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Max. Marks: 70

**PART - A**

1. Answer any **FIVE** sub divisions of the following: (5x2=10)
- How a salt bridge overcomes the formation of liquid junction potential?
  - Explain the sharp change of potential only near the end point in potentiometric titration of  $Fe^{+2} \leftrightarrow Cr^{+6}$ .
  - What is the main significance of supporting electrolyte in voltametry?
  - Mention any two advantage of amperometric method over the other methods.
  - Explain the principle of controlled current electrolysis of coulometry titration.
  - How radioactive labelling technique is used to study the mechanism of chemical reaction?
  - How a precipitation reaction can be studied using thermometric method?
  - Write any two advantages of DTG method over the TG method?

**PART - B**

Answer any **FIVE** of the following choosing at least one full question from each unit: (5x12=60)

**UNIT - I**

- Explain with diagram the working principle of calomel electrode. Write the electrode reactions when it acts as anode and cathode. (4)
  - A zinc rod is dipped in 0.1 M solution of  $ZnSO_4$  at  $25^\circ C$ . Assuming that salt is dissociated to the extent of 95% at this solution, calculate the potential of the electrode at this temperature. (4)  
(Given  $E^0_{(Zn^{+2}/Zn)} = -0.76 V$ )
  - Explain the principle of conductometric titration. Explain the nature of conductometric curve for titration of mixture of AcOH and HCl vs. strong base. (4)
- Give broad classification of electrodes with working principle in brief, with an example to each type. (4)
  - What are membrane electrodes? Derive an equation for a glass electrode potential. (4)
  - For a Daniel cell involving the cell reaction,  
 $Zn(s) + Cu^{2+}(aq) \dots \dots > Zn^{2+}(aq) + Cu(s)$ ,  
the standard free energies of formation of  $Zn(s)$ ,  $Cu(s)$ ,  $Cu^{2+}(aq)$  and  $Zn^{2+}(aq)$  are  $0, 0, 64.4 \text{ kJmol}^{-1}$  and  $-154.0 \text{ kJmol}^{-1}$ , respectively. Calculate the standard EMF of the cell. (4)

Contd...2

- 4.a) What is decomposition potential? Explain decomposition potential taking electrolysis of water as an example. (4)
- b) Describe the nature of a cyclic voltammogram, highlighting the significance of different terms involved. (4)
- c) Sketch the principles of amperometric titrations with its limitations. (4)
- 5.a) What is hydrogen over voltage? Discuss its any two advantages. (4)
- b) Explain with diagram the principles of dropping mercury electrode in polarography. (4)
- c) Derive the equation for half-wave potential and explain the terms involved. (4)

## UNIT - III

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- 6.a) Explain the principle of secondary coulometric titration with diagram. (4)
- b) Discuss the basic concept, methodology and application of electrogravimetry. (4)
- c) Explain the principle of Prompt Gamma Neutron Activation Analysis (PGNAA) technique and its applications. (4)
- 7.a) Explain the principle of chronopotentiometry with its applications. (4)
- b) Discuss any two applications of coulometric titrations. (4)
- c) Discuss the principle of Radioimmunoassay (RIA) technique used to measure concentrations of antigens. (4)

## UNIT - IV

- 8.a) Describe the principle of thermogravimetric analysis (TGA). What important information can be explored from the nature of TG curve? (4)
- b) Explain the principle of dilatometric technique in studying the phase transitions of materials. (4)
- c) Explain the working principle of DSC with schematic diagram. (4)
- 9.a) Referring to the instrumentation of thermogravimetry, explain the following: (4)
- i) Sample holders ii) Thermobalance (4)
- b) How thermometric titration method can be used to study the acid-base neutralization reaction? (4)
- c) Discuss any two important applications of thermogravimetry. (4)

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

JANUARY-2021

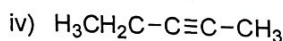
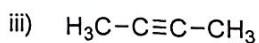
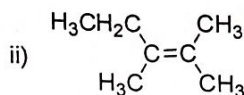
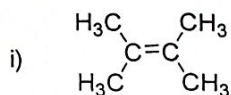
### MOLECULAR SPECTROSCOPY

Time: 3 Hours

Max. Marks: 70

#### PART - A

1. Answer any **SEVEN** sub divisions of the following: (7x2=14)
- NMR spectrum of dimethyl formamide shows two peaks at room temperature and at high temperature only one signal is obtained. Give reason.
  - Define coupling constant.
  - Why are deuterated solvents used in NMR spectroscopy?
  - How will you distinguish between cis and trans butenes on the basis of C 13-NMR spectroscopy?
  - Amines absorb UV light at higher wavelength than alcohols. Why?
  - Predict the relative intensities of molecular ion & isotope peaks for the following compounds
    - p-dibromobenzene
    - p-dichloro benzene
  - Define combination band and Fermi resonance.
  - Arrange the following compounds in the decreasing order of Carbonyl stretching frequency of IR spectrum.
    - Acetic acid
    - Acetamide
    - ethyl acetate
    - acetyl chloride.
  - Which among the following is IR Active?



#### PART - B

Answer any **FOUR** of the following choosing at least one full question from each unit:

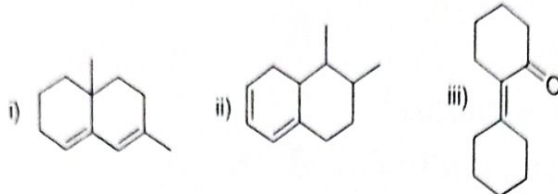
(4x14=56)

#### UNIT - I

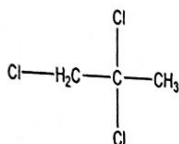
- Predict and explain the splitting pattern and position of peaks for the following compounds. (6)
    - 1,3 -Dichloropropane
    - 1,1,2 -Trichloroethane
  - Explain the effect of hybridisation, inductive and resonance effects on chemical shift. (4)
  - Write a note on solvents used in recording of NMR spectra. (4)
- Write a note on
    - COSY
    - TMS
 (6)
  - Give an account for NMR Shift reagent. (5)
  - Discuss the Karplus relationship in NMR spectroscopy. (3)

## UNIT - II

4. a) Calculate  $\lambda_{max}$  for following compounds using Woodward Fieser's rules. (6)



- b) Describe the working of mass spectrometer. (4)  
 c) Explain spectrophotometric titration with suitable graphs. (4)
5. a) Write notes on  
 i) Effects of substituents on UV absorption (6)  
 ii) McLafferty rearrangement
- b) What is proton decoupling technique? Predict and explain the off resonance proton decoupled spectrum of

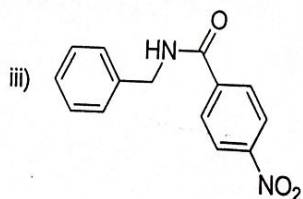
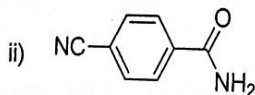
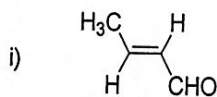


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- c) Give an account of mass spectral fragmentation of aromatic hydrocarbon and aldehydes. (4)

## UNIT - III

6. a) Write notes on  
 i) Overtones ii) combination bands iii) Fermi resonance (6)  
 b) Discuss the application of IR spectroscopy in the identification and study of alkenes, alcohols and ethers with suitable example. (6)  
 c) The carboxylic acids show broad stretching frequencies for the OH stretch. Explain why? (2)
7. a) Predict the important stretching frequencies in the IR spectrum of the following compounds. (6)



- b) Discuss the factors that affect carbonyl stretching frequencies in acid, ester and anhydrides. (5)  
 c) What is meant by fingerprint region? Discuss its importance in the interpretation of IR spectra with example. (3)

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