

PH 581.3

Reg. No. :

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**St Aloysius College (Autonomous)**  
Mangaluru  
Semester III – P.G. Examination – M.Sc. Chemistry  
November- 2019

**ORGANOMETALLIC, BIOINORGANIC  
AND COORDINATION CHEMISTRY**

Time: 3 Hours

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Max. Marks: 70

- PART - A**
1. Answer any **FIVE** sub divisions of the following: (5x2=10)
- Draw the structure and write IUPAC name of  $[PdCl(\eta^3-C_3H_5)]_2$
  - How does an electrophile attack a metal carbyne?
  - What is Wilkinson's catalyst? How is it prepared?
  - What is water gas shift reaction? What is its importance?
  - What are the functions of haemocyanin?
  - What are the roles of Co and Cu metal ions in biological system?
  - Distinguish between complementary and non-complementary reactions.
  - Explain trans effect taking suitable example.

**PART - B**

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

**UNIT - I**

- What are Schrock carbene complexes? Give examples. Explain the bonding in them. (4)
  - What is 18-electron rule? Discuss its exceptions. (4)
  - Explain the structure and bonding in cyclopentadiene based coordination complexes. (4)
- Describe the structure and bonding in Li and Be alkyls. (4)
  - Explain the bonding in metal alkene complexes. (4)
  - Write a brief account of structure and bonding in transition metal complexes with  $\pi$ -ligands with special reference to arenes and cyclooctadiene. (4)

**UNIT - II**

- Discuss the mechanism involved in Monsanto acetic acid process. (4)
- What are Ziegler-Natta catalyst systems? How do they bring about stereoregular polymerization of alkenes? Explain. (4)
- Explain the mechanism of Oxo process of hydroformylation of olefin using Rhodium catalyst? (4)

Contd...2

- 5.a) Describe the mechanism of Fischer-Tropsch reaction. (4)  
b) Explain the mechanism of olefin isomerisation. (4)  
c) Discuss the steps involved in Wacker's process. (4)

**UNIT - III**

- 6.a) What role is played by globin in haemoglobin? How do myoglobin and haemoglobin differ from each other structurally and functionally? (4)  
b) What is sodium pump? How does it regulate ionic concentrations in the cell? (4)  
c) How are dinitrogen complexes useful in 'in vitro' fixation of nitrogen? (4)
- 7.a) What are cytochromes? Discuss the structure and biological functions of cytochrome C. (4)  
b) Describe briefly the structure and biological role of ferritin. (4)  
c) What are ionophores? Explain the classification and mechanism of active transport of metal ions. (4)

**UNIT - IV**

- 8.a) Distinguish between  $SN^2$  and  $SN^1$  CB mechanisms for the base hydrolysis. (4)  
b) Discuss the outer sphere mechanism of electron transfer reactions. (4)  
c) Explain pi-bonding theory of trans effect. (4)
- 9.a) Explain the mechanism of substitution reactions in square planar complexes. (4)  
b) Describe the mechanism of acid hydrolysis when the inert ligand is a pi-donor. (4)  
c) Explain the types of intermediates formed during  $SN^1$  and  $SN^2$  reactions of octahedral complexes. (4)

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St Aloysius College (Autonomous)

Mangaluru

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

November - 2019

**ELECTROCHEMISTRY AND THERMO-ANALYTICAL METHODS**

Time: 3 hrs.

Max Marks: 70

PART - A

- 1 Answer any **FIVE** sub divisions of the following. (5x2=10)
- Explain the theoretical stoichiometric weight loss (%) of calcium oxalate in the first two steps.
  - Explain Galvanic Corrosion with examples
  - Compare fuel cell with other methods of energy conversion
  - With the help of an equation, explain the electro synthesis of ozone
  - Explain the function of auxillary electrode in three electrode system.
  - Distinguish between coordination number and solvation number
  - How conductors, semiconductors and insulators are different in term of Band gap? Give examples.
  - Give Ilkovic equation and explain the terms.

**Part B**

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

**Unit I**

- Briefly explain the Gouy-Chapman-stern Model of Electrical Double Layer (5)
  - Arrive at Lippmanns equation from fundamental equation for the thermodynamic treatment of polarizable interfaces. (3)
  - Write a note on the Diffuse-Charge Region inside an Intrinsic Semiconductor using the Garrett-Brattain Space Charge approach. (4)
- Discuss the Ion-Quadrupole Model of Ion-Solvent Interactions (5)
  - Discuss one method for the determination of solvation number (5)
  - How IR spectroscopy can be used for the study of ion-solvent interaction (2)

Contd...2

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**UNIT- II**

- 4.a) Discuss briefly the principle and working of Polarography? (6)
- b) Explain metallic and membrane indicator electrodes (4)
- c) Draw a cyclic voltammogram for a reversible process and explain the terms (2)
- 5.a) Explain the steps involved in Stripping Voltametry? What is Anodic stripping Voltametry. (4)
- b) With the help of graph explain any two amperometric titrations (4)
- c) Discuss the principle and applications of coulometry (4)

**UNIT- III**

- 6.a) Explain the principle and working of photoelectrochemical cell (5)
- b) Comment with equations on the working and construction of an alkaline battery. (5)
- c) Discuss the chemistry involved in the methanol fuel cell? (2)
- 7.a) What is the role of light at Semiconducting electrodes (3)
- b) How oxidation and reduction of hydrocarbons is achieved using electro synthesis? Discuss with examples (5)
- c) Discuss the synthesis of any two inorganic compounds by electroanalytical methods. (4)

**UNIT- IV**

- 8.a) What is corrosion? Discuss the thermodynamic and kinetic aspects of corrosion. (6)
- b) Discuss two types of Thermometric titrations with examples (6)
- 9.a) Explain passivation with an example (2)
- b) Discuss briefly the instrumentation part of thermogravimetry (4)
- c) Discuss the principles of Differential Scanning Calorimetry (DSC)? What are the applications of DSC? (6)

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**St Aloysius College (Autonomous)**  
**Mangaluru**  
**Semester III – P.G. Examination – M.Sc. Chemistry**  
**November- 2019**

**MOLECULAR SPECTROSCOPY**

Time: 3 Hours

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Max. Marks: 70

**PART - A**

1. Answer any **SEVEN** sub divisions of the following: (7x2=14)
- What is heteronuclear coupling? Give an example.
  - Sketch and explain the  $^1\text{H-NMR}$  spectrum of neopentane and chloroform.
  - Even though  $\text{C}_2\text{H}_5\text{OH}$  and  $\text{CH}_3\text{-O-CH}_3$  are having the same molecular formula, the former exhibit three peaks and later exhibit a single peak in  $^1\text{H-NMR}$  of compounds. Why?
  - Why the NMR signals of  $^{13}\text{C}$  are weaker when compared to signals of  $^1\text{H}$ .
  - Distinguish between 3-methylcyclohexene and 4-methylcyclohexene on the basis of mass spectroscopy.
  - Mention the common electronic transition that occurs in aniline.
  - List the conditions for a compound to exhibit IR activity.
  - Draw the different modes of vibrations of water molecule in IR spectroscopy.
  - What are overtones? Predict the first overtone of the C-H stretching at  $750\text{cm}^{-1}$ .

**PART - B**

Answer any **FOUR** of the following choosing at least one full question from each unit: (4x14=56)

**UNIT - I**

- What is meant by chemical shift? A compound shows  $^1\text{H-NMR}$  peak at 240Hz down field from the TMS peak in a spectrometer operating at 60MHz. Calculate the chemical shift in ppm. (3)
  - Discuss nuclear overhauser effect with suitable example. (4)
  - Illustrate the splitting of NMR signal in  $\text{A}_2\text{B}_2$  type of compounds with a suitable example. (4)
  - Briefly explain the principle and applications of COSY technique. (3)
- Describe the phenomenon of double resonance in NMR. (5)
  - Sketch and explain the splitting pattern and position of peaks for the following compounds: (5)
    - 1,1-dibromoethane and ii) 1,2-dibromoethane

Contd...2

c) Discuss the application of NMR spectroscopy in the study of fluxional behavior of molecules. (4)

UNIT - II

4.a) i) Which has higher  $\lambda_{max}$  between 1,3-butadiene and 1,3,5-hexatriene? (4)  
ii) The  $\pi \rightarrow \pi^*$  transitions are stronger than that of  $n \rightarrow \pi^*$  transition. Why? (5)

b) Compound with a molecular formula  $C_9H_{10}O_2$  shows the following spectral data.  
NMR:  $\delta = 1.96$  (3H, S)  $\delta = 5$  (2H, S)  $\delta = 7.22$  (5H, S)  
IR:  $1745\text{ cm}^{-1}$ ,  $1225\text{ cm}^{-1}$ ,  $749\text{ cm}^{-1}$ ,  $697\text{ cm}^{-1}$ ,  
Mass :  $\frac{m}{e} = 150, 135, 91, 65$  (4)

c) What is meant by proton decoupled  $^{13}C$  spectra? Explain with two examples. (5)

5.a) Discuss the application of UV-Vis spectroscopy on the simultaneous determination Cr(Chromium) and Mn(Manganese) in a sample. (4)

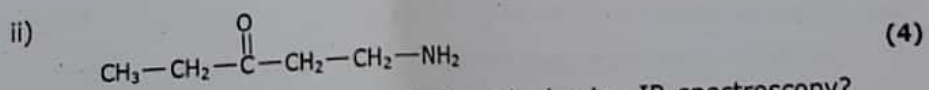
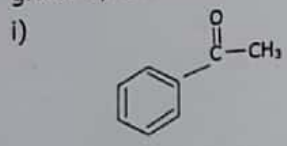
b) The mass spectrum of n-butylphenyl ketone ( $C_6H_5COCH_2CH_2CH_3$ ) shows peaks at  $m/z$ ; 148, 105, 77. Interpret the spectrum and identify the fragmented products. (3)

c) Predict the fragmentation modes of pent-2-ene. (3)

d) Explain the factors affecting chemical shift in  $^{13}C$  NMR. (4)

UNIT - III

6.a) Predict the major characteristic IR absorption bands that would be given by each of the following.



b) How are cis and trans-isomers distinguished using IR spectroscopy? Explain with suitable examples. (5)

c) Account on the principle and applications of FIR spectroscopy and NIR spectroscopy. (5)

7.a) Assuming the force constants are same, which will show a higher frequency.

i) C-O stretch or C-Cl stretch. (4)

ii) C-H stretch or C-C stretch

b) Explain the factors affecting band position and intensities in IR spectroscopy. (5)

c) With examples, explain the application of IR spectroscopy in the study of alkanes, alkenes and alkynes. (5)

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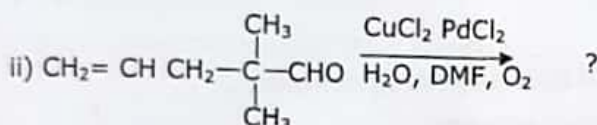
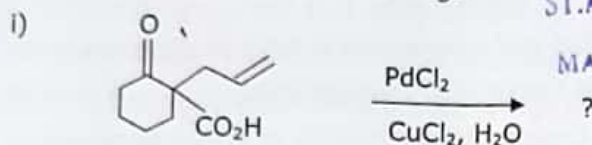
**St Aloysius College (Autonomous)**  
**Mangaluru**  
**Semester III – P.G. Examination – M.Sc. Chemistry**  
**November - 2018**  
**ORGANOMETALLIC, BIOINORGANIC**  
**AND COORDINATION CHEMISTRY**

Time: 3 Hours

Max. Marks: 70

**PART - A**1. Answer any **FIVE** sub divisions of the following: (5x2=10)

- a) What is 18-electron rule? Give an example.
- b) Give a method for the preparation of transition metal complexes with carbenes.
- c) What is the role of iodide in Monsanto acetic acid process?
- d) Write the products in the following.



- e) What are the roles of Zinc and Manganese in biological system?
- f) What are ferritins? Mention their importance in biological system.
- g) Give an account each for the substitution reaction of square planar and octahedral complexes.
- h) Differentiate between complimentary and non-complimentary electron transfer reactions.

**PART - B**

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

**UNIT - I**

- 2.a) Illustrate the exceptions of 18-electron rule. (4)
- b) Explain the bonding in cyclobutadiene based coordination complexes. (4)
- c) What are Fischer and Shrock carbenes? Give an account of these synthesis and reactivity. (4)
- 3.a) Explain structure and bonding in Mg and Al alkyls. (4)
- b) Discuss synthesis, structure and bonding in transition metal complexes of following  $\pi$ -ligands, with suitable examples.
  - i) Alkenes (4)
  - ii) Arenes (4)

Contd...2

## UNIT - II

- 4.a) What is Wilkinson's catalyst? Illustrate its application in the hydrogenation of olefins. (4)
- b) Explain the mechanism of Oxo process. (4)
- c) Write a note on Fischer-Tropsch reaction. (4)
- 5.a) Explain the mechanism of Wacker's reaction. (4)
- b) What is Monsanto acetic acid process? Write the catalytic cycle involved in the process. (4)
- c) Explain the mechanism of polymerization of propene using Ziegler-Natta catalyst. The catalyst generally gives stereo regular polymer. Why? (4)

## UNIT - III

- 6.a) Explain the roles of calcium and magnesium in biological system. (4)
- b) Discuss the structure and functions of haemoglobin. (4)
- c) What is an ionophore? Explain the mechanism of active transport of cations through ionophores. (4)
- 7.a) Explain the mechanism of biological nitrogen fixation. (4)
- b) Write a note on iron-sulphur proteins. (4)
- c) Write a note on hemerythrin. (4)

## UNIT - IV

- 8.a) Differentiate between association and dissociation mechanisms. Mention the factors that favours these mechanisms. (4)
- b) Explain the significance of trans effect in substitution reactions of square planar complexes. (4)
- c) Discuss the inner sphere mechanism of electron-transfer reaction. (4)
- 9.a) Explain acid hydrolysis of octahedral complexes. Mention the factors affecting the reaction. (4)
- b) Discuss the mechanism of substitution reaction of square planar complexes. (4)
- c) Write a note on electron-transfer reactions. (4)

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November - 2018

**ELECTROCHEMISTRY AND THERMO-ANALYTICAL METHODS**

Time: 3 Hours

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Max. Marks: 70

- PART - A** (5x2=10)
1. Answer any **FIVE** sub divisions of the following:
- Define solvation number with an example.
  - What is ion-dipole interaction?
  - Differentiate between reference electrode and indicator electrode.
  - Define limiting current and residual current.
  - What are Reserve batteries? Give example.
  - What is the importance of alternate energy systems over conventional energy systems?
  - What is passivation? Explain.
  - What is microbial corrosion? Comment.

**PART - B**

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

**UNIT - I**

- Discuss Born model and its limitations. (4)
  - Explain the structural aspects of ion solvent interaction. (4)
  - Discuss any one method for the determination of solvation number. (4)
- Write a note on Helmholtz-Perrin electrified interface. (4)
  - Briefly explain the effect of light at semiconductor interface. (4)
  - Explain thermo chemical approach to ion solvent interaction. (4)

**UNIT - II**

- Explain in detail the working principle of amperometric titrations. (4)
  - List out the important application of polarography. (4)
  - Define the following terms:
    - Potentiostat
    - Working electrode
    - Reference electrode
    - Auxiliary electrode(4)
- Explain the working principle of pulse polarography technique. (4)
  - Write a note on i) Ilkovic equation & ii) Half wave potential (4)
  - Compare the constant and controlled potential coulometry. (4)

Contd...2

**UNIT - III**

- 6.a) Explain the principle and working of photo electrochemical cells. (4)
- b) Discuss the principle and chemical reactions involved in Leclanche dry cell. (4)
- c) Explain the mechanism of electro-organic synthesis of adiponitrile. (4)
- 7.a) Describe the experimental setup and electro-inorganic synthesis of ozone. (4)
- b) Compare primary and secondary batteries. (4)
- c) Write a note on  $H_2-O_2$  fuel cell. (4)

**UNIT - IV**

- 8.a) Explain the various factors affecting the TGA curves. (4)
- b) What are thermometric titrations? Discuss its principle. (4)
- c) Write a note on electrochemical phenomenon of rusting. (4)
- 9.a) Discuss in general the various factors affecting corrosion rate. (4)
- b) Briefly discuss the principle and applications of DSC. (4)
- c) write a note on i) Methods of prevention of corrosion  
ii) Galvanic series (4)

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

November - 2018

MOLECULAR SPECTROSCOPY

Max Marks: 70

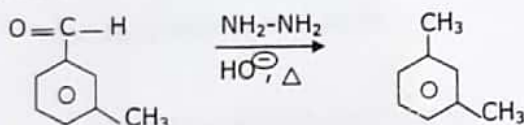
Time: 3 hrs.

PART - A

(7x2=14)

1 Answer any **SEVEN** sub divisions of the following.

- Differentiate between spin lattice and spin-spin interaction.
- Define coupling constant.
- Calculate the chemical shift of benzene when proton chemical shift of TMS and benzene is 505 Hz at magnetic field of 1.5 T.
- Explain solvent effects on absorption band in UV spectroscopy.
- How mass spectrometry helps in knowing isotopic abundances?
- For some organic compounds, either the  $M^+$  ion peak is absent or weak. Explain.
- What are overtones and hot bands?
- How could you determine by IR spectroscopy that following reaction had occurred?



- Assign the C=C stretching wave numbers given to the compounds shown below.

1651  $\text{cm}^{-1}$ , 1690  $\text{cm}^{-1}$ , 1750  $\text{cm}^{-1}$ , 1657  $\text{cm}^{-1}$



PART B

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

(4x14=56)

UNIT I

- Explain the working of FT-NMR spectrometer and list its advantages (4)
- Discuss the nature of reference (TMS) compounds used in NMR. (3)
- Explain factors affecting chemical shift in NMR spectroscopy. (3)
- Briefly discuss the following coupling patterns (4)
  - AX
  - AX<sub>3</sub>
  - AX<sub>5</sub>
  - and iv) draw Pascal triangle

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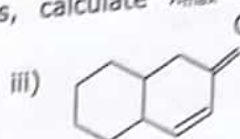
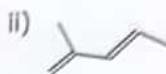
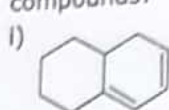
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- 3.a) Predict and explain the splitting pattern and position of peaks for the following compounds
- i) 1,1 - dibromoethane      ii) 1,2 - dibromoethane
- b) Write a note on
- i) NMR shift reagent      ii) Double resonance technique
- c) Discuss Karplus relationships in NMR spectroscopy.

### UNIT- II

- 4.a) Predict  $^1\text{H}$  decoupled and off resonance decoupled  $^{13}\text{C}$  NMR spectra of 1,2,2 - trichloropropane.

- b) Using Woodward Fischer rules, calculate  $\lambda_{\text{max}}$  for the following compounds:



- c.i) Describe with an example, the simultaneous determination of metal ions by spectrophotometric method.
- ii) Explain spectrophotometric titration of metal ions.

- 5.a) Discuss the factors influencing fragmentation in mass spectrometry

- b) Write briefly about the following:

i) Meta stable ions

ii) McLafferty rearrangement

- c) Write notes on

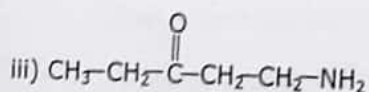
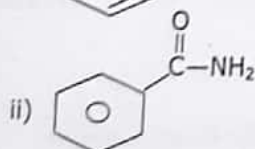
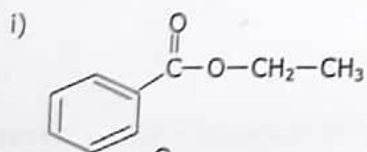
i) nitrogen rule

ii) retro Diels-Alder fragmentation

- d) Describe the working of mass spectrometer.

### UNIT- III

- 6.a) Predict the major characteristics IR absorption bands that would be given by each of the following compounds



- b) Discuss any two factors influencing vibrational frequencies.

- c) Describe the application of IR spectroscopy in the study of alkanes, alkenes and alkynes aromatic hydrocarbons with suitable examples.

Contd..3

- 7.a) What is meant by fingerprint region? Discuss its importance in the interpretation of IR spectra with example. (3)
- b) Discuss the application of IR spectroscopy in the identification and study of amines, amides, Ketones and aldehydes with suitable example. (6)
- c) Write note on NIR and FIR spectroscopy (5)

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November- 2017**

**ORGANOMETALLIC, BIOINORGANIC  
AND COORDINATION CHEMISTRY**

Time: 3 Hours

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PART - A

Max. Marks: 70

1. Answer any **FIVE** sub divisions of the following: (5x2=10)
- a) Mention the industrial importance of Oxo-process.
  - b) Ferrocene is more aromatic than benzene. Justify the answer.
  - c) What is Wilkinson’s catalyst? How is it prepared?
  - d) What is water gas shift reaction? What is its importance?
  - e) What are the functions of myoglobin?
  - f) What are the roles of copper and magnesium in biological system?
  - g) How does the crystal field activation energy affect the liability of a complex?
  - h) What are noncomplimentary two electron transfer reactions? Give examples.

**PART - B**

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

**UNIT – I**

- 2.a) The coordinated cyclobutadiene is aromatic in nature. Justify by explaining its bonding. (4)
- b) What is 18-electron rule? Discuss its exceptions. (4)
- c) Discuss the bonding in dibenzene chromium arene. (4)
- 3.a) What are Fischer’s carbene complexes? Give examples and explain their characteristic features. (4)
- b) Explain the structure and bonding of ferrocene. (4)
- c) Explain the bonding in metal-alkene complexes. Justify that alkene bonded to metal is susceptible for nucleophilic effect. (4)

**UNIT – II**

- 4.a) Illustrate the following with examples.
  - i) Oxidative addition reaction
  - ii) Reductive elimination (4)
- b) Explain the mechanism of the oxo process of hydroformylation of olefin using rhodium catalyst. What are the advantages of rhodium catalyst over cobalt catalyst? (4)

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- c) Explain the mechanism for the aerial oxidation of propene in the presence of  $\text{PdCl}_2$  and  $\text{CuCl}_2$  in dil.HCl. (4)
- 5.a) What is alkene isomerisation reaction? How is it brought about by metal hydride species? (4)
- b) 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)
- c) What is Zeigler Natta catalyst? Explain the mechanism of Zeigler Natta catalysis. (4)

**UNIT - III**

- 6.a) Explain the function of  $\text{Na}^+ - \text{K}^+$  pump. (4)
- b) Explain the mechanism of biological nitrogen fixation. (4)
- c) What is co-operative effect in haemoglobin? How is it explained? (4)
- 7.a) Explain the structural features of hemerythrin. (4)
- b) What is an ionophore? Explain the mechanism of active transport of cations through ionophores? (4)
- c) Write a note on iron-sulphur proteins. (4)

**UNIT - IV**

- 8.a) Explain  $\text{SN}_1$  (CB) mechanism of base hydrolysis. (4)
- b) Explain the mechanism of acid hydrolysis when the inert ligand is a  $\text{Pi}$  donor. (4)
- c) Discuss the inner sphere mechanism of electron-transfer reaction with suitable examples. (4)
- 9.a) Explain the mechanism of substitution reactions in square planar complexes. (4)
- b) How does trans effect account for the observed reactivity towards substitution in square-planar complexes? (4)
- c) Explain two supporting evidences to show that substitution reactions of square planar complexes are  $\text{SN}_2$  and rather than  $\text{SN}_1$ . (4)

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**St Aloysius College (Autonomous)****Mangaluru****Semester III – P.G. Examination – M.Sc. Chemistry****November - 2017****ELECTROCHEMISTRY AND THERMO-ANALYTICAL METHODS**

Time: 3 Hours

Max. Marks: 70

**PART - A**

1. Answer any **FIVE** sub divisions of the following: (5x2=10)
- What is solvation number? Give an example.
  - Define ion-dipole forces?
  - Distinguish between reference electrode and working electrode.
  - Differentiate between migration current and limiting current.
  - Give an example for electro organic synthesis.
  - What is the importance of alternate energy systems over conventional energy systems?
  - Explain passivation with an example.
  - What is microbial corrosion? Give an example.

**PART - B**

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

**UNIT - I**

- Write a note on Born model and its limitations. (4)
  - Briefly discuss the structural aspects of ion solvent interaction. (4)
  - Explain a method for the determination of solvation number. (4)
- Explain the Helmholtz-Perrin electrified interface. (4)
  - What is semiconductor interface? Explain the effect of light at semiconductor interfaces. (4)
  - Discuss the spectroscopic and thermo chemical approach to ion solvent interaction. (4)

**UNIT - II**

- Explain in detail the working principle of biomperometric titrations. (4)
  - Explain the mass transport theory of classical polarography. (4)
  - Define the following terms. Give example. (4)
 

i) Counter electrode	ii) Working electrode
iii) Reference electrode	iv) Auxillary electrode
- Explain the working principle of pulse polarography techniques. (4)
  - Write a note on i) Ilkovic equation & ii) Half wave potential (4)
  - What are coulometric titrations? Write applications of coulometric titration. (4)

Contd...2



**UNIT - III**

- 6.a) Explain with a neat diagram the working principle of photo electrochemical cells. (6)
- b) Discuss the principle and chemical reactions involved in Laclanche dry cell. (6)
- 7.a) Describe the experimental setup and electro-inorganic synthesis of ozone. (4)
- b) What are primary and secondary batteries? Explain. (4)
- c) What is fuel cell? What are the main benefits of hydrogen fuel cells? (4)

**UNIT - IV**

- 8.a) Briefly discuss the various factors affecting the TGA curves. (4)
- b) Discuss in detail the use of indicators in acid-base titrations? (4)
- c) Write a note on electrochemical phenomenon of rusting. (4)
- 9.a) Discuss factors influencing the corrosion rate of metal objects. (4)
- b) Briefly discuss the principle and applications of DSC. (4)
- c) Define galvanic corrosion? What are the factors affecting on galvanic corrosion? (4)

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**St Aloysius College (Autonomous)**  
**Mangaluru**

**Semester III – P.G. Examination – M.Sc. Chemistry**  
**November- 2017**

**MOLECULAR SPECTROSCOPY**

Time: 3 Hours

Max. Marks: 70

**PART - A**

1. Answer any **SEVEN** sub divisions of the following: (7x2=14)
- Define the term chemical shift and coupling constant with examples.
  - Calculate the chemical shift for a proton which has a resonance at 140 Hz down field from TMS on a spectrometer that operates at 60 MHz.
  - Why is it more difficult to record  $^{13}\text{C}$  NMR spectra than  $^1\text{H}$  NMR spectra?
  - State Beer-Lambert's law.
  - Why trans-stilbene shows higher  $\lambda$  max compared to cis-stilbene?
  - Why Parention or molecular ion peak is not seen in mass spectrum of tertiary - butanol?
  - How do you predict a compound as aromatic based on its IR spectrum? Explain with example.
  - List the factors influencing vibrational stretching frequencies of carbonyl compounds.
  - What is the frequency range of fingerprint region? Mention its significance.

**PART - B**

Answer any **FOUR** of the following choosing at least one (4x14=56) full question from each unit:

**UNIT - I**

- Predict and explain the splitting pattern and position of peaks for the following.
  - 1, 1 - dibromoethane and
  - 1, 2 - dibromoethane

(3)
- Discuss the chemical shift assignment and solving of the ABC pattern of NMR spectrum. (3)
- Explain the application of NMR in medical diagnostics. (4)
- An organic compound with molecular formula  $\text{C}_8\text{H}_8\text{O}_2$  exhibits the following spectral data:
 

IR ( $\text{cm}^{-1}$ ): 1710, 3540;      Mass: m/z 136 ( $\text{M}^+$ ), 91, 65

$^1\text{H}$ NMR ( $\delta$ , ppm): 7.2 (5H, s), 3.5 (2H, s), 10.2 (1H, bs).

Deduce the structure of the compound A. (4)
- Sketch a neat schematics of NMR spectrometer and explain its functioning. (3)
- Describe the application of double resonance technique in conversion of complex spectra into simple spectra. (3)

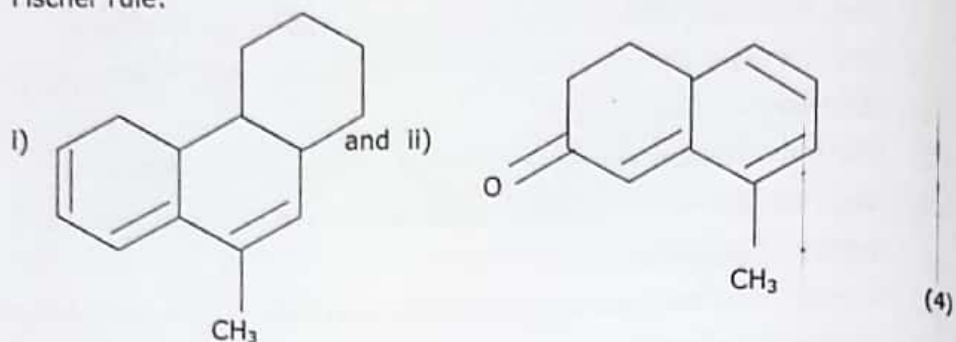
Contd...2

## PS 583.3

- c) Explain how hybridization and H-bonding affect the chemical shift in NMR spectra. (4)
- d) Write short notes on:  
 i) NMR shift Reagents and ii) Karplus curves (4)

## UNIT - II

- 4.a) What are molecular ion peak and base peak in mass spectrum and how these are recognized in mass spectrum. Explain with example. (3)
- b) Explain the various fragmentation patterns of 2 pentanone. (3)
- c) Predict the  $\lambda_{max}$  for the following compounds using Woodward and Fischer rule:



- d) What is meant by proton decoupled  $^{13}\text{C}$  spectra? Explain with an example. (4)
- 5.a) Deduce the expression  $m/e = H^2 r^2 / 2v$  or  $\frac{m}{e} = \frac{B^2 r^2}{2V}$  and explain the terms. (3)
- b) Briefly discuss the criteria required for the spectrophotometric determination of Fe(II). (3)
- c) What is McLafferty arrangement? Explain with example. (4)
- d) Briefly describe the application of UV-Vis spectroscopy. (4)

## UNIT - III

- 6.a) The force constant 'k' for HF is  $9.7 \times 10^5$  dyne  $\text{cm}^{-1}$ . Calculate the frequency of vibration of H-F bond. (3)  
 (Given atomic mass H=1.008 and F=19)
- b) Explain NIR (Near) spectroscopy and FIR (Far IR) in the characterization of organic compounds. (3)
- c) How will you differentiate the following compounds by IR - spectroscopy?



Contd...3

- d) Assuming the force constants are same, which will accurate a higher frequency.
  - i) C-O stretch or C-Cl stretch
  - ii) C-O stretch or C-C stretch? Explain. (4)
  
- 7.a) With the help of suitable examples, explain the application of IR spectroscopy in differentiating the intra and intermolecular hydrogen bonding. (3)
  
- b) Discuss the affect of the following on band-position and intensity in IR spectroscopy.
  - 1) Vibrational coupling
  - 2) Field effect (3)
  
- c) How can you distinguish between n-hexane, 1-hexene, 1-hexyne using IR spectroscopy. (4)
  
- d) Write short notes on: i) Fermi resonance and ii) solvent effect on vibrational frequencies. (4)

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