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St Aloysius College (Autonomous)
Mangaluru
Semester III – P.G. Examination – M.Sc. Chemistry
JANUARY-2021
ORGANOMETALLIC, BIOINORGANIC
AND COORDINATION CHEMISTRY

Time: 3 Hours

Max. Marks: 70

PART - A

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.

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PART - B

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

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 ($\text{C}=\text{C}$), 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 α,β -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 catalyses 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)

- 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 PdCl_2 and 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 CH_3I are the most suitable species for this reaction? (4)

UNIT - III

- 6.a) Explain the role of haemoglobin in 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 at 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 H_2O to D_2O . Explain. (4)

PH 582.3

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

ELECTROCHEMISTRY AND THERMO-ANALYTICAL METHODS
Max.Marks:70
Time: 3 Hours

PART - A

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

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- Write a note on 'Lippmann Equation'.
 - What are the limitations of Born Model of ion solvation?
 - How do you differentiate between constant potential and constant current coulometry?
 - Why purging of Nitrogen gas is necessary in polarographic experiment?
 - What are the advantages of replacing Zinc by magnesium in Laclanche cell?
 - List out the reagents generated at the anode part of an electrolytic cell in Kolbe's synthesis by electro organic synthesis.
 - Corrosion is a 'Continuous process'. Justify the statement.
 - What is Vapour Phase Inhibitor (VPI)? Give example.

PART - B

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

UNIT - I

- What is an electrical double layer? Discuss the Helmholtz-Perrin model of electrical double layer. (4)
 - Derive Born expression for the free energy of ion solvent interactions. (4)
 - Explain the structural aspects of ion solvent interaction. (4)
- Discuss Stern theory of electrical double layer. (4)
 - Describe the method of determination of solvation number. (4)
 - Explain the effect of light at semiconductor interface. (4)

UNIT - II

- Give the characteristics of diffusion current and half wave potential. (4)
 - Draw and explain the different amperometric titration curves (current-volume and current voltage) of the reagent and the substance being titrated. Give one example to each of them. (4)
 - Define the following terms. (4)
 - Overvoltage
 - Indicator Electrode
 - Dropping mercury electrode (OME)
 - Reference electrode

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5. a) Discuss the principle and applications of classical polarography. (4)
b) Give an account of cyclic voltammetry and its applications. (4)
c) Write a note on types and analytical applications of ion selective electrodes. (4)

UNIT - III

6. a) Discuss the principle and chemical reactions involved in secondary lead acid battery. (4)
b) Describe the working of H_2 - O_2 Fuel cell. (4)
c) Explain Electroorganic synthesis of Adiponitrile. (4)
7. a) Explain the principle and working of photo-electrochemical cells (PEC) (4)
b) Discuss the design and working of a secondary alkaline battery. (4)
c) Discuss the electro organic synthesis involving reduction of Nitro compounds. (4)

UNIT - IV

8. a) Discuss thermodynamic principle of corrosion. (4)
b) Write a note on i) Pitting corrosion (4)
ii) Stress Corrosion Cracking (SCC)
c) Explain 'Cathodic Protection' method of prevention of corrosion. (4)
9. a) Explain the DSC technique of thermal characterization. (4)
b) Discuss the principle of thermometric titrations. (4)
c) Explain the kinetic of corrosion. (4)

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MOLECULAR SPECTROSCOPY

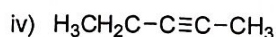
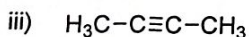
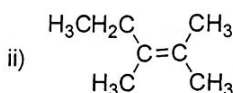
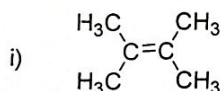
Time: 3 Hours

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?



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PART - B

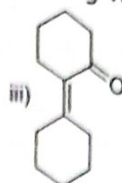
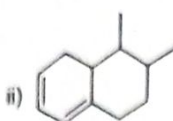
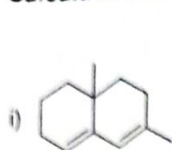
Answer any **FOUR** of the following choosing at least one full question from each unit: (4x14=56)

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)

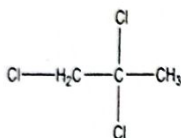
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4. a) Calculate λ_{\max} for following compounds using Woodward Fieser's rules. (6)



- b) Describe the working of mass spectrometer. (4)
 c) Explain spectrophotometric titration with suitable graphs. (4)
5. a) Write notes on (6)
 i) Effects of substituents on UV absorption
 ii) McLafferty rearrangement

- b) What is proton decoupling technique? Predict and explain the off resonance proton decoupled spectrum of (4)



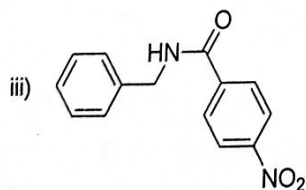
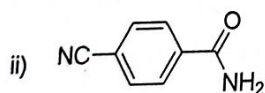
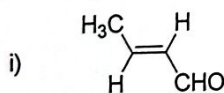
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- c) Give an account of mass spectral fragmentation of aromatic hydrocarbon and aldehydes. (4)

UNIT - III

6. a) Write notes on (6)
 i) Overtones ii) combination bands iii) Fermi resonance
 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)
