PH 581.3 Reg. No:.

St Aloysius College (Autonomous)

Mangaluru

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

December -2022

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. Justify the complex $[RhCl(PPh_3)_3]$ follows 16 electron rule.

b. Outline a method for the synthesis of η^4 alkyne complexes.

c. What properties of $AlCl_3$ and $TiCl_4$ in Ziegler Natta compound make it a polymerisation catalyst?

d. Mention the advantages of water gas shift reaction.

e. Identify the significant role of Mg and Ca in biological process.

f. What is Bohr effect?

g. What are inert and labile complexes? Give an example.

h. Define energy profile of a reaction.

Part B

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

UNIT -I

2. a. Discuss the structure and bonding in transition metal alkyl compounds with suitable example. (4)

b, Explain the structure and synthesis of cyclopentadiene complexes and mention its properties. (4)

c. How are organic ligands classified based on hapticity (4)

3. a. Compare and contrast Fischer carbene from Schrock carbene. Comment on their reactivity. (4)

b. Explain how Pd(II) complexes with $16e^-$ are stable. (4)

c. How metal carbynes are prepared? Give their applications. (4)

UNIT-II

4. a. Explain the mechanism of Monsanto acetic acid process. (4)

b. Explain the Wacker process. How do regeneration of the original catalyst be done? (4)

c. Discuss Fischer Tropsch reaction. (4)

5. a. Write the differences between homogeneous and heterogeneous catalysis. (4)

b. Explain water gas shift reaction. (4)

c. How stereoregular polymers are synthesized by using Ziegler Natta catalyst? (4)

Contd...2

UNIT -III

6. a. Classify the ionophores in terms of mechanism of ion transport. How do you distinguish them? (4)
   b. Discuss the importance of trace metals in biological system. (4)
   c. Explain nitrogen fixation process. (4)

7. a. Discuss the structure and function of haemoglobin. (4)
   b. Give the structural representation of active sites of 2Fe-2S and 4Fe-4S ferredoxin. Comment on their biological activities. (4)
   c. Differentiate between hemerythrin and hemocyanin. (4)

UNIT -IV

8. a. Explain substitution reactions in square planar complexes. (4)
   b. Explain kinetic aspects of base hydrolysis and its conjugated base mechanism. (4)
   c. Explain the inner and outer sphere mechanism (4)

9. a. Discuss on complimentary and non-complimentary reactions. (4)
   b. Write a note on kinetics and mechanism of octahedral substitution reactions in which inert ligands are present .Give any 3 factors justifying the mechanism. (4)
   c. Explain association and dissociation mechanism. Give the intermediates in these mechanisms. (4)

****

PH 582.3 Reg. No:.:

St Aloysius College (Autonomous)
Mangaluru
SEMESTER III– P.G Examination – M.Sc. Chemistry
December - 2022
ELECTROCHEMISTRY AND THERMO-ANALYTICAL METHODS

Time : 3 hours **Max marks : 70**

PART-A

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

a. Explain the theory of electrode and electrolyte interface and explain the origin of electrode potential.

b. Define Solvation number.

c. Explain how to identify the endpoint in the potentiometric titrations of the acid-base titration.

d. Differentiate between primary and secondary battery.

e. Differentiate between classical organic reaction and electro organic reaction and write the advantages of electro organic reaction.

f. Write the need of galvanic series over electrochemical series.

g. Write the different factors affecting TGA curves.

h. Differentiate between energy storage devices and energy conversion devices and give example of each cases.

PART-B

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

UNIT-I

2. a. Explain the term
   (i) Lipmann equation
   (ii)Double layer capacitance (4)
   b. Explain the Gouy-Chapmann theory of diffuse double layer. (4)
   c. Write in detail Ion-solvent interaction and ion-quadruple models. (4)
3. a. Give an account of the Helmoholtz-Perrin model of an electrified interface. (4)
   b. Discuss the salient features of the Stern model of electrified interface. (4)
   c. Write a note on solvation number and its determination. (4)

UNIT-II

4. a. Explain the construction and working of a glass electrode. Mention the advantages and disadvantages. (4)
   b. Sketch the basic circuit for the polarographic method of analysis. How is it used for obtaining the polarogram of an electroactive species. (4)
   c. Write short notes on the following:
   (a) Biamperometry (b) Rotating microelectrode (4)

Contd...2

5. a. Describe the experimental set-up required for the potentiometric titration of Fe^{2+} with $Cr_2O_7^{2-}$? (4)

   b. Discuss the following:-

   (i)Half wave potential

   (ii)Current Maxima and Maximum suppressors in polarography. (4)

   c. Write short notes on controlled current electrolysis and controlled electrode potential electrolysis (4)

UNIT-III

6. a. Draw a neat diagram of photogalvanic cells and explain the working function. (4)

   b. Explain the construction of lead storage battery. Write the discharging and charging reactions. (4)

   c. Write the advantages of electro-organic and electro-inorganic synthesis. Explain the kolbes synthesis and synthesis of fluorine in electrochemical methods. (4)

7. a. Explain the construction and working of the following fuel cells:

   (i) $H_2 - O_2$ fuel cell (ii) Methanol fuel cell (4)

   b. Mention the cell performance of a primary cell. Explain why dry cell cannot be recharged. (4)

   c. Explain oxidation and reduction of hydrocarbons by electrochemical methods. (4)

UNIT-IV

8. a. Explain the sacrificial anode and impressed current techniques for prevention of corrosion. (4)

   b. Describe instrumentation for thermogravimetry. (4)

   c. What are thermometric titrations? What is the principle underlying the titrations. (4)

9. a. What are anodic and cathodic inhibitors? Explain how corrosion control can be achieved? (4)

   b. TGA studies reveal that MgC_2O_4 exists as MgO above 480^0C, CaC_2O_4 changes to $CaCO_3$ between 398^0 and 420^0 C and $CaCO_3$ changes to CaO between 660^0 and 840^0 C. A mixture of CaC_2O_4 and MgC_2O_4 obtained from 0.35 g dolomite ($CaCO_3$ + $MgCO_3$) weighed 0.24 g at 500^0C and 0.1696 g at 900^0C respectively. Calculate the % $CaCO_3$ and % $MgCO_3$ in the original sample of dolomite.
   (At.wts of Ca and Mg are 40 and 24 respectively). (4)

   c. Draw a schematic diagram of DTA apparatus and give the function of its different components. (4)

****

PS 583.3

Reg. No: | | | | | | |

St Aloysius College (Autonomous)

Mangaluru

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

December - 2022

MOLECULAR SPECTROSCOPY

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

PART – A

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

a) A proton is coupled to two non-equivalent neighbouring protons. What will be the multiplicity and the relative intensity of lines in the signal?

b) Why TMS is considered as reference standard for recording PMR and CMR analysis?

c) The proton decoupled spectrum of a trichlorobenzene consists of two signals only. What trichlorobenzene is it?

d) Arrange the following in the order of their λ_{max} in the UV-Vis spectra and give reasons.

A)  B)  C) 

e) What are auxochromes and chromophores ?

f) Distinguish between 'molecular ion peak' and 'basepeak' with suitable examples.

g) What are the conditions for a molecule to exhibit vibrational spectra?

h) What is Fermi resonance? Explain by taking suitable example.

i) What is finger print region. Give its significance.

PART – B

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

UNIT-I

2. a) How will you distinguish among the carbonyl isomers pertaining to the molecular formula C_4H_8O on the basis of proton coupled ^{13}C NMR spectroscopy? (4)

b) Write a note on the following. (6)

i) NOE ii) Shift reagents

c) Discuss the factors influencing chemical shift values in NMR spectroscopy. (4)

3. a) Discuss the AX_2 and A_2X spin systems taking suitable examples. (5)

b) Why and how spin-spin coupling occurs? Discuss the spin-spin coupling in ethylacetate. (5)

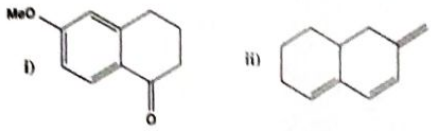
c) Differentiate decoupled and Off resonance coupled ^{13}C NMR with suitable examples. (4)

Contd...2

UNIT-II

4. a) Discuss the effect of substituents and solvents on UV absorption of aromatic compounds. (4)

b) Discuss the Woodward Fieser's rules and predict the λmax for the following.



(6)

c) Write a short note on factors affecting reaction pathways in mass spectroscopy. (4)

5. a) Discuss the fragmentation pathways for the following systems with suitable examples (6)
i)Halides ii)Aldehydes iii) Alkanes

b) Write a short note on spectrophotometric titrations (4)

c) Discuss any 2 basic fragmentation types in Mass spectrometry with suitable examples. (4)

UNIT-III

6. a) How does the vibrational coupling and hydrogen bonding affect vibrational frequencies in IR spectroscopy. (4)

b) How would you distinguish between the following compounds in each pair by IR spectral studies? Name the vibrations and appropriate positions of absorption in each case.

i) Propyne & Acetonitrile

ii) 1-Hexene & 1-Hexyne

iii) Dimethylamine & Ethylamine (6)

c) Write note on NIR and FIR Spectroscopy. (4)

7. a) How can the following be identified & studied by IR spectroscopy

i) Alkynes

ii) Aldehydes

iii) Alcohols (6)

b) Deduce the structure of an organic compound that exhibited the following spectral data: Molecular Formula : $C_9H_{10}O_2$

IR (cm^{-1}): 1690;

PMR (δ): 2.5 (s, 3H), 3.8 (s, 3H), 6.9 (d, 2H, J=8Hz), 7.8 (d, 2H, J=8Hz);

CMR (δ): 26, 56, 114, 129, 130, 165, 197 (4)

d) An organic compound containing two oxygen atoms has a mass 136 and exhibited the following data. Deduce its structure.

UV (nm): 250 (very intense) Molecular Formula :$C_8H_8O_2$

IR (cm^{-1}): 820, 1230, 1670, 2740, 2850, 3050 (4)

PMR (δ): 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.

****