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St Aloysius College (Autonomous)

Mangaluru

Semester III- P.G Examination – M.Sc. Analytical 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)
- Justify the complex $[\text{RhCl}(\text{PPh}_3)_3]$ follows 16 electron rule.
 - Outline a method for the synthesis of η^4 alkyne complexes.
 - What properties of AlCl_3 and TiCl_4 in Ziegler Natta compound make it a polymerisation catalyst?
 - Mention the advantages of water gas shift reaction.
 - Identify the significant role of Mg and Ca in biological process.
 - What is Bohr effect?
 - What are inert and labile complexes? Give an example.
 - 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

- Discuss the structure and bonding in transition metal alkyl compounds with suitable example. (4)
 - Explain the structure and synthesis of cyclopentadiene complexes and mention its properties. (4)
 - How are organic ligands classified based on hapticity (4)
- Compare and contrast Fischer carbene from Schrock carbene. Comment on their reactivity. (4)
 - Explain how $\text{Pd}(\text{II})$ complexes with $16e^-$ are stable. (4)
 - How metal carbynes are prepared? Give their applications. (4)

UNIT-II

- Explain the mechanism of Monsanto acetic acid process. (4)
 - Explain the Wacker process. How do regeneration of the original catalyst be done? (4)
 - Discuss Fischer Tropsch reaction. (4)
- Write the differences between homogeneous and heterogeneous catalysis. (4)
 - Explain water gas shift reaction. (4)
 - 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)

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St Aloysius College (Autonomous), Mangaluru

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

December - 2022

**ELECTROANALYTICAL, RADIOCHEMICAL AND THERMOANALYTICAL
TECHNIQUES**

Time: 3 Hours

Max. Marks: 70

PART – A

1. Answer any **FIVE** sub-divisions of the following: (5×2=10)
- Define an electrochemical cell. Give its classification.
 - What is meant by liquid junction potential? How does it vary with current?
 - Define half wave potential. Give its significance.
 - Define over voltage. What are the factors affecting it?
 - Define decomposition potential and give its significance.
 - Write the principle of chronopotentiometry.
 - What is the effect of temperature on hydrated organic and inorganic compounds?
 - What are the criteria for a good thermobalance?

PART – B

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

UNIT-I

- Discuss the principle, methodology and applications of conductometric titrations taking suitable examples. (5)
 - Describe the construction and working of glass electrode. Give its significance. (4)
 - Discuss the effect of Ohmic potential on electrochemical measurements? (3)
- Define reference electrodes. Give a comparison between silver/silver chloride and hydrogen electrodes. (5)
 - Write a note on potentiometric titrations and their applications. (4)
 - Give the theory of ion selective electrodes. (3)

UNIT-II

- Explain the theory of polarography. Discuss the various currents observed in polarographic measurements. (5)
 - Explain the principle and applications of amperometry. (4)
 - Write a short note on oxygen interference in polarographic estimations. (3)
- Explain the principle and applications of cyclic voltammetry. How is it different from simple voltammetric technique? (5)
 - Describe biamperometric titrations. Compare it with amperometric titrations. (4)
 - Write a short note on organic polarography. (3)

Contd...2

UNIT-III

6. a) Differentiate between activation analysis and radiometric analysis. (5)
 - b) Discuss the effect of experimental variables on electrogravimetry. (4)
 - c) Write a note on characteristics of alpha, beta and gamma rays. (3)
7. a) Explain the methodology and applications of coulometry. (6)
 - b) Discuss the application of radioactivity measurement in radioimmuno assay. (3)
 - c) Write the Faraday's laws of electrolysis. (3)

UNIT-IV

8. a) Describe the instrumentation of thermogravimetric analysis apparatus. What are the types of TGA? (6)
 - b) Explain the simultaneous DTA-TGA curves. What are the factors affecting it? (3)
 - c) Write a short note on thermometric titrations. (3)
9. a) Explain the principle and applications of differential scanning calorimetry. (5)
 - b) Discuss the factors affecting TGA results. (4)
 - c) Describe the dilatometric analysis. (3)

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Mangaluru

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

December - 2022

MOLECULAR SPECTROSCOPY

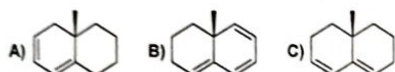
Time: 3 Hours

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.



- 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 (4×14=56) full question from each unit.

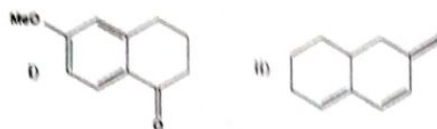
UNIT-I

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 λ_{max} 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. (4)
 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 (6)
 i) Alkynes
 ii) Aldehydes
 iii) Alcohols
 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. (4)
 UV (nm): 250 (very intense) Molecular Formula : $C_8H_8O_2$
 IR (cm^{-1}): 820, 1230, 1670, 2740, 2850, 3050
 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.