PH 541.3

Reg. No. :

St Aloysius College (Autonomous)
Mangaluru
Semester III – P.G. Examination – M.Sc. Analytical Chemistry
November- 2019
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) Draw the structure and write IUPAC name of $[PdCl(\eta^3 - C_3H_5)]_2$

b) How does an electrophile attack a metal carbyne?

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 haemocyanin?

f) What are the roles of Co and Cu metal ions in biological system?

g) Distinguish between complementary and non-complementary reactions.

h) 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

2.a) What are Schrock carbene complexes? Give examples. Explain the bonding in them. (4)

b) What is 18-electron rule? Discuss its exceptions. (4)

c) Explain the structure and bonding in cyclopentadiene based coordination complexes. (4)

3.a) Describe the structure and bonding in Li and Be alkyls. (4)

b) Explain the bonding in metal alkene complexes. (4)

c) Write a brief account of structure and bonding in transition metal complexes with π -ligands with special reference to arenes and cyclooctadiene. (4)

UNIT – II

4.a) Discuss the mechanism involved in Monsanto acetic acid process. (4)

b) What are Ziegler-Natta catalyst systems? How do they bring about stereoregular polymerization of alkenes? Explain. (4)

c) 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^1CB 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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Mangaluru

Semester III – P.G. Examination – M.Sc. Analytical Chemistry
November- 2019

ELECTROANALYTICAL, RADIOCHEMICAL AND THERMO-ANALYTICAL TECHNIQUES

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

PART - A (5x2=10)

1. **Answer any FIVE sub divisions of the following:**

a) Define electrode potential. Why do we need a reference electrode for the measurement of electrode potential?

b) Classify the membrane electrodes with suitable examples. What are their basic properties?

c) A supporting electrolyte is essential in voltammetry. Give reasons.

d) What are the different kinds of currents observed in polarography? How are they produced?

e) Differentiate between controlled current and controlled potential electrolysis.

f) What are the characteristics of α and β rays?

g) Give two methods of temperature control in differential thermal analysis.

h) How are the thermogravimetric techniques classified? What is the basis for the classification?

PART - B

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

UNIT – I

2.a) Discuss the thermodynamics of cell potential. (3)

b) Explain the composition and working of

i) Glass electrode

ii) Hydrogen electrode (6)

c) How are the potentiometric titrations different from direct potentiometry? (3)

3.a) Explain the following.

i) Conductometric titration of a mixture of strong and weak acids with a strong base.

ii) Gas sensing probes are different from other membrane electrodes. (6)

Contd...2

b) Describe the classification of metallic indicator electrodes. What are the precautions to be taken in the use of reference electrodes? (6)

UNIT – II

4.a) Explain the following.

i) Interferences in polarographic studies and the methods to minimize them.

ii) Amperometric titrations. (8)

b) Describe the applications of polarographic estimations. (4)

5.a) Write short notes on –

i) Principle and applications of stripping analysis.

ii) Cyclic voltammetry. (8)

b) Derive on expression for Half-Wave potential. How do you determine it from the polarogram? (4)

UNIT - III

6.a) Discuss the effect of counter potential and overvoltage on electrogravimetric estimations. (4)

b) Describe – i) Activation analysis.

ii) Radiometric titrations (8)

7.a) Explain the theory and applications of coulometric titration. (6)

b) Write short notes on –

i) Decomposition potential and its significance.

ii) Chronopotentiometry (6)

UNIT - IV

8.a) Explain the principles and methods of thermogravimetric analysis. (6)

b) Describe the theory and applications of thermometric titrations. (6)

9.a) Discuss the principle and applications of differential thermal analysis. (6)

b) Write notes on – i) Dilatometry

ii) Differential scanning calorimetry (6)

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Reg. No. :

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

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

PART - A

1. **Answer any SEVEN sub divisions of the following:** **(7x2=14)**

a) What is heteronuclear coupling? Give an example.

b) Sketch and explain the ^{1}HNMR spectrum of neopentane and chloroform.

c) Even though C_2H_5OH and CH_3-O-CH_3 are having the same molecular formula, the former exhibit three peaks and later exhibit a single peak in ^{1}H-NMR of compounds. Why?

d) Why the NMR signals of ^{13}C are weaker when compared to signals of ^{1}H.

e) Distinguish between 3-methylcyclohexene and 4-methylcyclohexene on the basis of mass spectroscopy.

f) Mention the common electronic transition that occurs in aniline.

g) List the conditions for a compound to exhibit IR activity.

h) Draw the different modes of vibrations of water molecule in IR spectroscopy.

i) What are overtones? Predict the first overtone of the C-H stretching at 750cm^{-1}.

PART – B

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

UNIT – I

2.a) What is meant by chemical shift? A compound shows 1H-NMR peak at 240Hz down field from the TMS peak in a spectrometer operating at 60MHz. Calculate the chemical shift in ppm. **(3)**

b) Discuss nuclear overhauser effect with suitable example. **(4)**

c) Illustrate the splitting of NMR signal in A_2B_2 type of compounds with a suitable example. **(4)**

d) Briefly explain the principle and applications of COSY technique. **(3)**

3.a) Describe the phenomenon of double resonance in NMR. **(5)**

b) Sketch and explain the splitting pattern and position of peaks for the following compounds:

i) 1,1-dibromoethane and ii) 1,2-dibromoethane **(5)**

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 λ_{max} between 1,3-butadiene and 1,3,5-hexatriene?

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: $1745\ cm^{-1}$, $1225\ cm^{-1}$, $749\ cm^{-1}$, $697\ cm^{-1}$,

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)

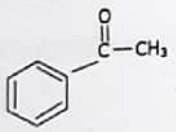
c) Predict the fragmentation modes of pent-2-ene. (3)

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

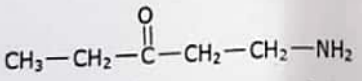
UNIT – III

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

i)



ii)



(4)

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.

ii) C-H stretch or C-C stretch (4)

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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Mangaluru
Semester III – P.G. Examination – M.Sc. Analytical Chemistry
November - 2018
ORGANOMETALLIC, BIOINORGANIC AND COORDINATION CHEMISTRY

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

PART - A

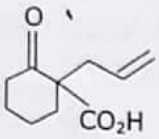
1. **Answer any FIVE sub divisions of the following:** **(5x2=10)**

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.

i) 

$\xrightarrow[CuCl_2,\ H_2O]{PdCl_2}$?

ii) $CH_2{=}\ CH\ CH_2{-}\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C}}{-}CHO \xrightarrow[H_2O,\ DMF,\ O_2]{CuCl_2\ PdCl_2}$?

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 cyclobutadine 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 π-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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St Aloysius College (Autonomous)

Mangaluru

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

November – 2018

ELECTROANALYTICAL, RADIOCHEMICAL AND THERMO-ANALYTICAL TECHNIQUES

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

PART - A

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

a) Justify that glass electrode requires frequent standardization.

b) How does a salt bridge eliminate liquid junction potential?

c) What is the concentration of cadmium in a solution if the diffusion coefficient 'D'=$0.72 \times 10^{-5} cm^2 sec^{-1}$, 'm' the mass of mercury flowing per second in milligrams is 2, 't' the drop time in seconds is 4.4 and the average diffusion current, $i_d = 10 \mu A$?

d) Distinguish between DTA and DSC.

e) What is 'decomposition potential' and what is its significance?

f) Give two reasons for using a supporting electrolyte in Voltammetry.

g) Explain how an acid-base titration can be done using Coulometry?

h) What are thermometric titrations? What is the principle underlying the titrations?

PART - B

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

UNIT - I

2. a) What are the advantages of secondary reference electrode over primary? Describe the construction and working of calomel electrode. Mention its limitation. **(6)**

b) Give reasons for the following:

i) Electrode potential of copper is positive, while that of zinc is negative.

ii) Glass electrode cannot be used accurately for measurement of pH<2 or pH>10.

iii) Justify: Gas sensing electrodes are a special type of selective electrodes. **(6)**

3. a) Sketch and explain the conductometric titration curves for the following titrations:

i) Mixture of strong and weak acids with a strong base.

ii) Precipitation reaction. **(4)**

b) Give reasons for the following:

i) In conductometric titration strength of the burette solution must be at least 10 times higher than the solution to be titrated.

ii) Direct current cannot be used in the conductivity measurements. **(4)**

Contd...2

c) What are the functions of reference and indicator electrodes used in potentiometric titrations? Explain the complexometric titration carried out by potentiometric method with a suitable example. (4)

UNIT - II

4. a) Justify that Cyclic Voltammetry is a potentiodynamic electrochemical measurement technique. With relevant plot explain the principle involved in cyclic Voltammetry measurements. (4)

b) Draw and explain a polarogram. How are quantitative and qualitative information obtained from it. (4)

c) Derive an expression for half-wave potential. List any two application of polarography in inorganic analysis. (4)

5. a) Mention any two advantages of using a dropping mercury electrode? With a suitable example explain how amperometric titrations are carried out. (4)

b) Write short notes on

i) Bioamperometry ii) Overvoltage and factors affecting. (4)

c) Discuss the factors influencing the diffusion current. (4)

UNIT - III

6. a) How does the constant current electrolysis differ from that of a controlled potential electrolysis in coulometry? (3)

b) Discuss the Radiometric titration. Give its applications. (5)

c) Write short notes on chronopotentiometry. (4)

7. a) What is activation analysis? List any 4 of its applications. (4)

b) What is isotopic dilution method? How is it different from neutron activation analysis? (5)

c) Write a note on the characteristics of alpha, beta and gamma rays. (3)

UNIT - IV

8. a) Explain the instrumentation and working of Thermo gravimetric analysis. (6)

b) What are the criteria for a good thermobalance. Give reason: The decomposition temperature of a compact sample is higher than a loose sample. (3)

c) Discuss the applications of DSC. (3)

9. a) Explain the instrumentation and working of Differential thermal analysis apparatus. (6)

b) Give reason: Physical changes can be studied by DTA but not by TG. Write short note on Dilatometry. (6)

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St Aloysius College (Autonomous)

Mangaluru

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

November - 2018

MOLECULAR SPECTROSCOPY

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

PART – A

1 Answer any SEVEN sub divisions of the following. **(7x2=14)**

a) Differentiate between spin lattice and spin-spin interaction.

b) Define coupling constant.

c) Calculate the chemical shift of benzene when proton chemical shift of TMS and benzene is 505 Hz at magnetic field of 1.5 T.

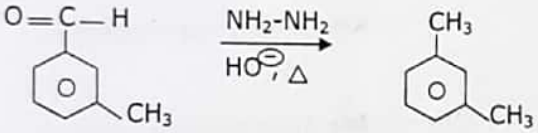
d) Explain solvent effects on absorption band in UV spectroscopy.

e) How mass spectrometry helps in knowing isotopic abundances?

f) For some organic compounds, either the M^+ ion peak is absent or weak. Explain.

g) What are overtones and hot bands?

h) How could you determine by IR spectroscopy that following reaction had occurred?



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

1651 cm^{-1}, 1690 cm^{-1}, 1750 cm^{-1}, 1657 cm^{-1}

PART B

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

UNIT I

2.a) Explain the working of FT-NMR spectrometer and list its advantages **(4)**

b) Discuss the nature of reference (TMS) compounds used in NMR. **(3)**

c) Explain factors affecting chemical shift in NMR spectroscopy. **(3)**

d) Briefly discuss the following coupling patterns **(4)**

i)AX ii)AX_3 iii)AX_5 and iv) draw Pascal triangle

Contd...2

PS 543.3

3.a) Predict and explain the splitting pattern and position of peaks for the following compounds (6)

i) 1,1 – dibromoethane ii)1,2 - dibromoethane

b) Write a note on (6)

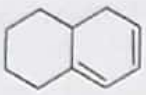
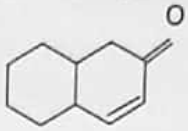
i)NMR shift reagent ii) Double resonance technique

c) Discuss Karplus relationships in NMR spectroscopy. (2)

UNIT- II

4.a) Predict ^{1}H decoupled and off resonance decoupled ^{13}C NMR spectra of 1,2,2 – trichloropropane. (3)

b) Using Woodward Fischer rules, calculate λ_{max} for the following compounds: (6)

i)  ii)  iii) 

c.i) Describe with an example, the simultaneous determination of metal ions by spectrophotometric method. (5)

ii) Explain spectrophotometric titration of metal ions.

5.a) Discuss the factors influencing fragmentation in mass spectrometry (3)

b) Write briefly about the following: (4)

i) Meta stable ions ii) McLafferty rearrangement

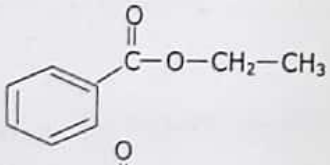
c) Write notes on (3)

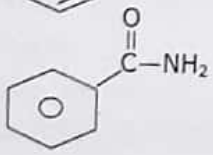
i) nitrogen rule ii)retro Diels-Alder fragmentation

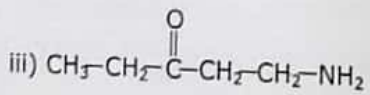
d) Describe the working of mass spectrometer. (4)

UNIT- III

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

i) 

ii) 

iii) 

b) Discuss any two factors influencing vibrational frequencies. (4)

c) Describe the application of IR spectroscopy in the study of alkanes, alkenes and alkynes aromatic hydrocarbons with suitable examples. (4)

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

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) 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 (4)

ii) Reductive elimination

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)

Contd...2

c) Explain the mechanism for the aerial oxidation of propene in the presence of $PdCl_2$ and $CuCl_2$ 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 $[RhI_2(CO)_2]^-$ and CH_3I 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 Na^+-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 SN_1 (CB) mechanism of base hydrolysis. (4)

b) Explain the mechanism of acid hydrolysis when the inert ligand is a 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 SN_2 and rather than SN_1. (4)

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Reg. No. :

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Mangaluru
Semester III – P.G. Examination – M.Sc. Analytical Chemistry
November- 2017
ELECTROANALYTICAL RADIOCHEMICAL AND THERMOANALYTICAL TECHNIQUES

Time: 3 Hours

Max. Marks: 70

PART - A

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

a) Define specific conductance and equivalent conductance.

b) What is liquid junction potential? How can it be minimized?

c) It is desirable to remove oxygen from the test solution prior to polarographic analysis. Justify.

d) Stripping methods are more sensitive over other voltammetric procedures. Give reason.

e) What are radioactive tracers? Mention one of their advantages.

f) What is radio immune assay?

g) Differentiate between isothermal and dynamic thermogravimetric analysis.

h) Draw the thermogram for CuSO4.5H2O decomposition. Give reactions.

PART - B

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

UNIT – I

2.a) What are conductometric titrations? Discuss the applications of conductometric titrations of i) strong acid with weak base ii) weak acid with weak base (4)

b) Discuss the mechanism of operation of gas sensing probes. (4)

c) Explain briefly –
i) acid errors of glass electrodes
ii) hygroscopy of glass membranes (4)

3.a) Give the principle involved in the functioning of the ion selective electrode. (4)

b) Explain the principle of potentiometric titrations and methods of detecting end points. (4)

c) Write the differences between indicator electrode of first kind and second kind with one example each. (4)

UNIT – II

4.a) Discuss the principle of cyclic voltammetry with an example. (4)

b) Explain the principle of stripping analysis. (4)

c) What is over voltage? Explain the various mechanisms of mass transport from electrolyte to electrode. (4)

Contd...2

5.a) What is diffusion current? Explain the factors affecting diffusion current in polarography. (4)

b) Differentiate between differential pulse and square wave polarography. (4)

c) Discuss briefly the principle and applications of biamperometric titrations. (4)

UNIT - III

6.a) Explain the principle of different type of coulometric methods. (4)

b) Discuss briefly the method of detection and measurement of radioactivity using scintillating counter. (4)

c) Write briefly on –

i) chronopotentiometry

ii) radioactive tracers (4)

7.a) Describe the procedure for the estimation of copper-nickel alloy by electrogravimetry. (4)

b) Briefly explain prompt gamma ray neutron activation analysis (PGNAA). (4)

c) Explain the similarity and differences between radiometric titrations and coulometric titrations. (4)

UNIT - IV

8.a) Explain how TGA can be used to explain the thermal stability and degradation temperature of a material. (4)

b) With a schematic diagram explain the working of DSC. (4)

c) Explain the types of thermometric titrations with suitable examples. (4)

9.a) Discuss the effect of heating and furnace atmosphere on TGA curves. (4)

b) Discuss the decomposition of calcium oxalate monohydrate and its thermal behaviour in DTA technique. (4)

c) Describe the differences between heat flux and power compensated DSC techniques. (4)

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PS 543.3

Reg. No. :

St Aloysius College (Autonomous)
Mangaluru

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

November- 2017

MOLECULAR SPECTROSCOPY

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

PART - A

1. **Answer any SEVEN sub divisions of the following:** **(7x2=14)**

a) Define the term chemical shift and coupling constant with examples.

b) 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.

c) Why is it more difficult to record ^{13}C NMR spectra than ^{1}H NMR spectra?

d) State Beer-Lambert's law.

e) Why trans-stilbene shows higher λ max compared to cis-stilbene?

f) Why Parention or molecular ion peak is not seen in mass spectrum of tertiary - butanol?

g) How do you predict a compound as aromatic based on its IR spectrum? Explain with example.

h) List the factors influencing vibrational stretching frequencies of carbonyl compounds.

i) What is the frequency range of fingerprint region? Mention its significance.

PART – B

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

UNIT – I

2.a) Predict and explain the splitting pattern and position of peaks for the following.
i) 1, 1 – dibromoethane and ii) 1, 2 - dibromoethane **(3)**

b) Discuss the chemical shift assignment and solving of the ABC pattern of NMR spectrum. **(3)**

c) Explain the application of NMR in medical diagnostics. **(4)**

d) An organic compound with molecular formula $C_8H_8O_2$ exhibits the following spectral data:
IR (cm^{-1}): 1710, 3540; Mass: m/z 136 (M+), 91, 65
^{1}HNMR (δ, ppm): 7.2 (5H, s), 3.5 (2H,s), 10.2 (1H, bs).
Deduce the structure of the compound A. **(4)**

3.a) Sketch a neat schematics of NMR spectrometer and explain its functioning. **(3)**

b) Describe the application of double resonance technique in conversion of complex spectra into simple spectra. **(3)**

Contd...2

c) Explain how hybridization and H-bonding affect the chemical shift in NMR spectra. (4)

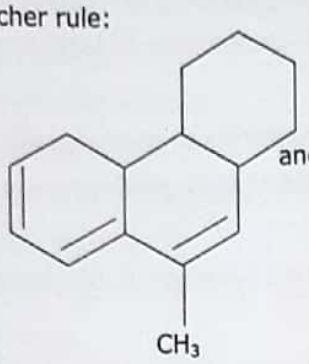
d) Write short notes on:
i) NMR shift Reagents and ii) Karplus curves (4)

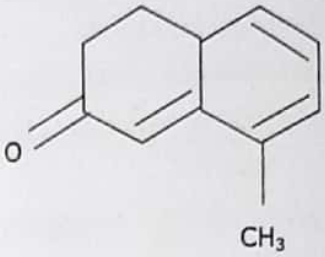
UNIT – II

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 λ max for the following compounds using Woodward and Fischer rule:

i) 

and ii) 

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d) What is meant by proton decoupled ^{13}C spectra? Explain with an example. (4)

5.a) Deduce the expression $m/e=H^2r^2/2v$ or $\frac{m}{e}=\frac{B^2r^2}{2V}$ 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)

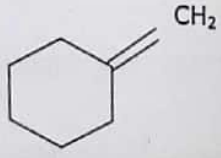
d) Briefly describe the application of UV-Vis spectroscopy. (4)

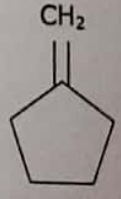
UNIT – III

6.a) The force constant 'k' for HF is $9.7x10^5$ dyne cm^{-1}. Calculate the frequency of vibration of H-F bond.
(Given atomic mass H=1.008 and F=19) (3)

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?

i) 

and 

ii) $C_6H_5CH_2NH_2$ and $CH_3\text{-}CO\text{-}N(CH_3)_2$ (4)

Contd...3

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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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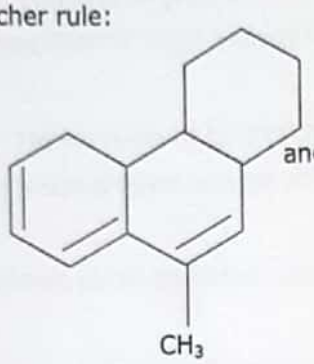
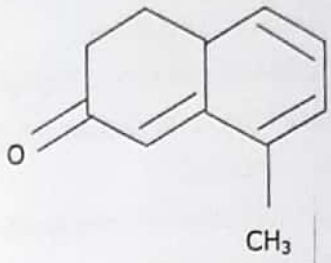
i) 

and ii) 

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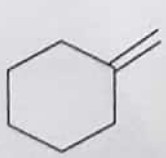
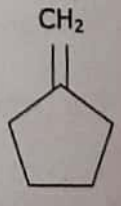
i) 

and 

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