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Reg. No:

# St Aloysius College (Autonomous)

## Mangaluru

## Semester II– P.G Examination – M.Sc. Analytical Chemistry

July - 2022

## ADVANCED INORGANIC CHEMISTRY

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

### PART - A

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

a) Frost diagram is used to predict the oxidizing property of particular species. Illustrate.

b) Lanthanides exhibit sharp line like spectra. Why?

c) Calculate the CFSE of the Iron ion existing in its high spin state in $[FeCl_4]^{2-}$.

d) Justify that spectrochemical series is the limitation of CFT.

e) Give any two methods of preparation of dinitrogen complexes.

f) Mention any two evidences for M-M bonding in metal carbonyls.

g) Find out the ground state of Cobalt metal in $[Co(NH_3)_6]Cl_3$.

h) Calculate number of microstates in $d^4$ system.

### PART – B

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

#### UNIT- I

2. a) Draw and explain Ellingham diagram for the formation of CO and $CO_2$. Discuss the utility of carbon as reducing agent **(4)**

b) Explain the chemical method of reduction of oxide ores. **(4)**

c) Differentiate between 3d and 4d series of elements. **(4)**

3. a) What is Latimer diagram? How would you account for the disproportionation of $H_2O_2$ with the help of Latimer diagram? **(4)**

b) Give an account of the following i) Separation of lanthanide by ion exchange chromatography. **(4)**

c) Plot the graph depicting the variation of magnetic moments in trivalent lanthanide ions and describe the magnetic property. **(4)**

#### UNIT- II

4. a) Explain the splitting of d-orbitals in $[Co(CN)_6]^{3-}$ and write the electronic configuration. **(4)**

b) Which type of spinel structure is adopted by $Mn_3O_4$ and $Fe_3O_4$? Justify your answer. **(4)**

c) Describe ion-exchange method for the determination of composition and stability constants of complexes. **(4)**

Contd...2

5. a) Indicate the relationship between stepwise and overall formation constants. How is formation constant determined by pH metry? (4)

   b) Discuss the stereochemistry of coordination complexes exhibiting coordination number 7 (4)

   c) Explain the evidences of metal-ligand covalency based on ESR and NMR spectra. (4)

## UNIT- III

6. a) Give the structures of $Fe_3(CO)_{12}$ and $Fe_5(CO)_{15}$. Show that $Fe_3(CO)_{12}$ obeys the inert gas rule. (4)

   b) Discuss the chemistry of metal nitrosyl complexes. (4)

   c) Explain any two methods of preparation of metal carbonylates and metal carbonyl halide. (4)

7. a) Write a note on Cotton effect in metal complexes. (4)

   b) Enumerate the factors favouring M-M bond formation in metal carbonyls in metal clusters. (4)

   c) How are metal carbonyls prepared using thermal decomposition method? Describe the use of IR in the structural elucidation of metal carbonyls. (4)

## UNIT-IV

8. a) Why UV visible spectra of $[Cr(H_2O)_6]^{3+}$ shows three bands at 17000$cm^{-1}$, 24000$cm^{-1}$ and 37000$cm^{-1}$. Draw orgel diagram and assign the peaks of free metal ion has Racah parameter 1030$cm^{-1}$. Comment on the nature of metal ligand band. (4)

   b) Write a note on quenching of magnetic moment. (4)

   c) Explain the variation of magnetic susceptibility against temperature in para-, ferro- & antiferromagnetcic substances. (4)

9. a) Write a short note on charge transfer spectra. (4)

   b) State orbital selection rule and discuss relaxation of it. (4)

   c) Mention salient features of Tanabe-Sugano diagram and draw Tanabe-Sugano diagram for $d^2$ metal ion dissolved in aqueous solution in an octahedral environment. (4)

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## ADVANCED ORGANIC CHEMISTRY

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

### PART - A

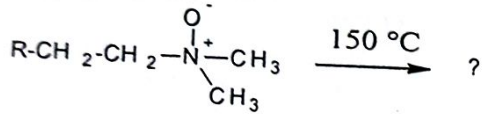
1. **Answer any FIVE sub-divisions of the following:** **(5x2=10)**

a) What is anchimeric assistance? Give example.

b) Halogen is ortho, para directing and deactivating group. Justify.

c) What is $E_{1cb}$ reaction? Give an example

d) Predict the product in the following:




e) Justify: The major product of addiotion of HBr to 2-methyl-2- butane is 2-bromo-2-methyl butane.

f) Write any two applications of Reformatsky reaction.

g) Predict the product formed on the oxidation of Thiophene.

h) Using resonance structures, explain reactive positions of pyrrole for an electrophile.

### PART – B

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

### UNIT- I

2. a) With suitable examples, explain the stereochemical aspects in aliphatic nucleophilic substitution reactions. **(4)**

b) Write the mechanism of the following:

i) Smiles rearrangement ii) Von-Richter rearrangement **(4)**

c) Explain orientation and reactivity in monosubstituted benzenes based on charge distribution. **(4)**

3. a) Discuss the mechanism and stereochemistry of $S_E1$ reaction. **(4)**

b) In organic chemistry why Friedel-Craft acylation is preferred over Friedel-Craft alkylation? Explain. **(4)**

c) With suitable examples, discuss the Sommelet-Hauser rearrangement. What are the evidences which support this mechanism? **(4)**

### UNIT- II

4. a) Describe the Saytzeff rule. Justify the same with suitable examples. **(4)**

b) Discuss the mechanisms of pyrolysis of esters of carboxylic acid. **(4)**

c) Write a note on the following: **(4)**

i) Sandmeyer reaction ii) Hunsdiecker reaction

Contd...2

5. a) Discuss the reactivity of aliphatic and aromatic substrates towards free radical substitution reactions. (4)

b) Explain the mechanism of E1 and E2 reactions. Give example for each. (4)

c) Explain the following: i) Chugaev reaction ii) Cope elimination

## UNIT- III

6. a) Explain the mechanism of eletrophilic addition and discuss the stereochemistry of the reaction. (4)

b) Explain why 1,3-butadiene and HBr react at low temperature to give 1,2-addition product while at higher temperature I,4-addition product is the major product. (4)

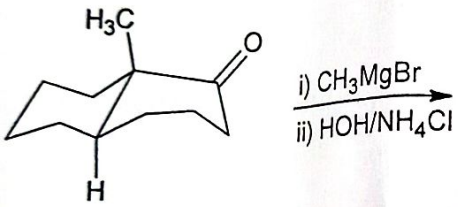
c) Discuss the mechanism of Knoevenagel condensation. (4)

7. a) State and explain Markovnikov's rule with suitable example. (4)

b) Discuss the addition of HX to unsymmetrical olefins. (4)

c) Predict the product in the following:






(4)

## UNIT-IV

8. a) Describe the Hantzsch method for the synthesis of pyridine. (4)

b) Discuss the aromaticity and their reactivity towards electrophilic substitution reaction for pyrrole, furan and thiophene. (4)

c) Explain any two general reactions of pyrazole. (4)

9. a) Give one reaction each for thiazole and imidazole. (4)

b) How will you convert indole to nitroindole? Give the mechanism. (4)

c) Discuss any two methods for synthesis of aziridine. (4)

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### Semester II– P.G Examination – M.Sc. Analytical Chemistry

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### ADVANCED PHYSICAL CHEMISTRY

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

**PART - A**

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

a) State the conditions for orthogonality and normalization of wave functions.

b) An electron is confined in a one-dimensional box of length 10A° . Calculate its ground state energy in Ev.

c) What is spin-orbit coupling?

d) State Born-Oppenheimer approximation.

e) Give the significance of coulomb integral and resonance integral in HMO theory.

f) The Huckel energies for benzene are $\alpha+2\beta$, $\alpha+\beta$, $\alpha+\beta$, $\alpha-\beta$, $\alpha-\beta$ and $\alpha-2\beta$. Calculate the delocalization energy.

g) Define electronic partition function. Give its significance.

h) Calculate the entropy change when 1 mole of argon is heated from 300 to 600K, the pressure being kept constant.

**PART – B**

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

**UNIT- I**

2. a) Describe Planck's quantum theory of radiation. State and explain Einstein's equation. **(6)**

b) Set up and solve the Schrodinger wave equation for the particle in a ring. **(6)**

3. a) Discuss the concept of degeneracy using 3-D box problem. **(7)**

b) Write a note on postulates of quantum mechanics. **(5)**

**UNIT- II**

4. a) Outline the salient features of the Hartree-Fock self-consistent field (SCF) theory for solving the Schrodinger wave equation for the ground state energy of helium atom. **(6)**

b) Discuss the application of first order perturbation theory to helium atom . **(6)**

5. a) State and explain the variation principle. Discuss its application to Helium atom. **(6)**

b) Outline the solution of the Schrodinger wave equation for $H_2^+$ ion. **(6)**

**Contd...2**

## UNIT- III

6. a) Construct the wavefunctions for $sp^3$ hybrid orbitals and calculate the bond angle. (5)

   b) Set up and solve Huckel secular equation for 1,3-butadiene and show the result on a M.O. diagram. (7)

7. a) Explain the theory of directed valence (5)

   b) Set up and solve HMO determinants for allyl system. Calculate bond order, charge density and free valence for allyl radical system. (7)

## UNIT - IV

8. a) Derive the expression of equilibrium constant for an ideal mixture in terms of partition function. (6)

   b) Explain thermodynamic probability using Maxwell-Boltzmann statistics. Deduce its distribution law. (6)

9. a) Discuss the Einstein theory of heat capacity of solids. (6)

   b) Obtain the expression of vibrational partition function. (6)

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### Semester II– P.G Examination – M.Sc. Analytical Chemistry

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## MOLECULAR SYMMETRY AND MOLECULAR SPECTROSCOPY

Time: 3 Hours Max. Marks: 70

### PART - A

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

a) What is a dihedral plane? How many dihedral planes are present in allene molecule?

b) Write the three dimensional matrix representation for $C_2$ operation along z axis.

c) Show that $S_2 = i$ by taking trans 1,2 dichloro ethylene as an example.

d) How does the population of states affect the intensity of spectral lines?

e) Predict the degeneracy of rotational and vibrational energy levels of a diatomic molecule treated as a rigid rotor and harmonic oscillator.

f) Define symmetric top and spherical top in terms of moment of inertia.

g) State the selection rules for vibration of a diatomic molecule treated as a simple harmonic oscillator and an anharmonic oscillator.

h) With schematic, explain occurrence of Stokes and anti-Stokes lines.

i) Comment on the polarization of Raman lines.

### PART – B

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

#### UNIT- I

2. a) Describe the procedure for the classification of molecules into point groups. (6)

b) Deduce the matrix representation for

(i) rotational $C_n$ axis of symmetry along z-axis

(ii) plane of symmetry along xy plane. (8)

3. a) Explain the Great Orthogonality Theorem (GOT) and its consequences. How property (iii) and (iv) of irreducible representations (IRs) will be useful in construction of character table? Explain with respect to $C_{2v}$ point group. (8)

b) Using symmetry and group theory construct the hybrid orbitals for tetrahedral geometry involving sigma bonding. (6)

#### UNIT- II

4. a) Obtain an expression for moment of inertia of a linear triatomic OCS molecule. (5)

b) Discuss in detail the vibrational spectrum of a simple harmonic oscillator. (4)

c) Three consecutive lines in the rotational spectrum of $H^{79}Br$ are observed at 84.544, 101.355 and 118.112 $cm^{-1}$. Assign the lines to their appropriate J' and J'' transitions. Then deduce the values of rotational constant, centrifugal distortion constant and evaluate the bond length & approximate vibrational frequency of the molecule. Given, masses of $^1H = 1.673 \times 10^{-24}$g; $^{79}Br = 131.03 \times 10^{-24}$g. (5)

Contd...2

5. a) Write a comparative note on the rotational energy levels, selection rules and the rotational spectra of a diatomic molecule treated as a rigid and non-rigid rotator. (5)

b) Which transitions are responsible for fundamental, overtones and hot bands in vibrational spectroscopy? Predict their occurrence in a spectrum if a molecule is treated as anharmonic oscillator. (5)

c) The fundamental and first overtone transitions of $^{14}N^{16}O$ are centered at 1876.06 $cm^{-1}$ and 3724.20 $cm^{-1}$ respectively. Evaluate the equilibrium vibrational frequency, the anharmonicity constant, exact zero point energy and the force constant of the molecule. Give reduced mass of $^{14}N^{16}O$ = $12.397 \times 10^{-24}$g. (4)

## UNIT- III

6. a) Sketch the changes in polarizability ellipsoid of $CO_2$ during symmetric stretching. Also, plot variation of polarizability vs. displacement coordinate during this mode of vibration. (5)

b) Outline various components of an IR spectrometer. (4)

c) Discuss the rotational-vibrational spectroscopy of symmetric top molecules treated as a rigid rotor and an anharmonic oscillator. (5)

7. a) Draw the schematic of a Raman spectrometer. What are the advantages of Raman technique over IR during vibrational measurements? (5)

b) Discuss the pure rotational Raman spectroscopy of linear molecules. (5)

c) Describe any two applications and two advantages of Raman spectroscopy. (4)

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