M. Sc. II - Semester Examination, May / June 2019

Subject : Chemistry
Paper – I : Inorganic Chemistry

Time: 3 Hours

Max. Marks: 80

Note: Answer all questions from Part–A and Part–B. Each question carries 8 marks in Part–A and 12 marks in Part – B.

PART – A (4 x 8 = 32 Marks) (Short Answer Type)

13(a) What are the salient features of inner sphere mechanism?

(b) Explain SN¹ CB mechanism with an example.

 $2\gamma(a)$  Explain j-j coupling scheme.

- 4(b) Define microstate. Calculate the number of microstates possible for d<sup>2</sup> configuration.
- 3 ½ (a) Explain the total electron count theory with examples.

4(b) Write a note on Hoffman's isolable analogy.

4 \(\(\)(a) Discuss the effect of metal ion concentration on physiological effects.

(b) Write the geometric aspects of oxygen binding in Hemocyanin and Hemrythrin.

# PART – B (4 x 12 = 48 Marks) (Essay Answer Type)

5 5 (a) Discuss the factors affecting acid hydrolysis reactions.

S (b) What is Trans effect? Explain the  $\pi$ -bonding theory of Trans effect.

### OR

- (c) Explain the mechanism of nucleophilic substitution reaction without breaking metal ligand bond.
- (d) Discuss outer sphere electron transfer mechanism with suitable example.
- 6 (a) How do you arrive at the microstates of  $\rho^2$  configuration? List out all the microstales of  $\rho^2$  configuration and derive its terms.
  - (b) What is an orgel diagram? Draw the orgel diagram for d<sup>3</sup>, d<sup>7</sup> octahedral and tetrahedral complexes.

### OR

(e) Write a note on:

- (i) Inter electron repulsion parameters
- (ii) Spin orbit coupling parameters
- (d) Explain the effect of weak cubic crystal fields on S, P and D terms.
- 7 (a) Explain structural features of low nuclear  $M_3(Co)_{12}$  and  $M_4(Co)_{13}$  clusters.
  - (b) What is capping rule? Discuss the structural pattern in monocapped and bicapped metal clusters.

### OR

- (c) Discuss metal-Metal bonding features in face sharing bioctahedra with suitable examples.
  - (d) Explain structure and bonding in  $[Mo_6(CI)_8]^{4+}$  at  $[Nb_6(CI)_{12}]^{2+}$ .
- 8 (a) Write the electronic and magnetic aspects of dioxygen binding in Hemogolbin.
  - (b) Discuss the basic principles in the biological selection of elements.

### OR

(e) Explain the reaction mechanism of decarboxylation and dealdolation with vitamin B<sub>6</sub> model system.

(d) Write the Core structure of chlorophyll and explain 'Z' scheme.

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M. Sc. II - Semester Examination, May/June 2019

Subject: Chemistry

Paper - II: Organic Chemistry

Time: 3 Hours

Max. Marks: 80

Note: Answer all questions from Part-A and Part-B. Each question carries 8 marks in Part-A and 12 marks in Part - B.

# $PART - A (4 \times 8 = 32 Marks)$ (Short Answer Type)

- (a) m-Bromoanisole and o-Bromoanisole, both give some product when reacted with NH<sub>2</sub> / NH<sub>3</sub>. Explain.
- (b) Give an Account of Non-classical carbocations.
- (a) Predict the reaction condition for the following reactions and explain by PMO approach.

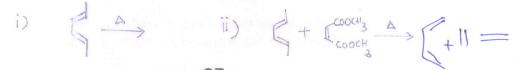
- (b) What are Frontier Molecular orbitals? Explain their use in the  $\pi^2 s + \pi^2 s$ cycloaddition.
- 3. (a) What is Di  $-\pi$ -Methane rearrangement? Explain with suitable example. (b) Explain Norish Type-II cleavage of carbonyl compounds with suitable example.
- (a) How are the carbenes and Nitrenes generated?
  (b) What is Smiles rearrangement? Suggest possible mechanism for it.

# $PART - B (4 \times 12 = 48 Marks)$ (Essay Answer Type)

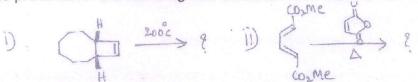
- 5. (a) Differentiate between  $S_E^1$  and  $S_E^2$  electrophilic substitutions with suitable examples.
  - (b) Suggest Mechanism for the following conversion.

(ii) Complete the following reaction and give mechanism Erythro-3-Bromo-2-butanol HBR ?

- (e) Discuss the  $S_N^2$  Ar Mechanism.
  - (d) What is Neighbouring group Participation (NGP)? Explain with examples involving oxygen and π-bonds.
  - 6. (a) Discuss the important features of Pericyclic reactions.
    - (b) Give the sterochemistry of the Product in the following and explain by FMO approach.



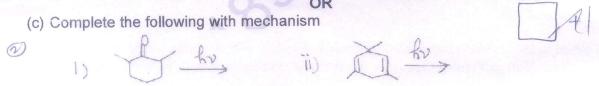
- (c) Construct the correlation diagram for disrotaory ring closure of 1,3-butadene and
  - (d) Predict the products for the following with suitable mechanism.



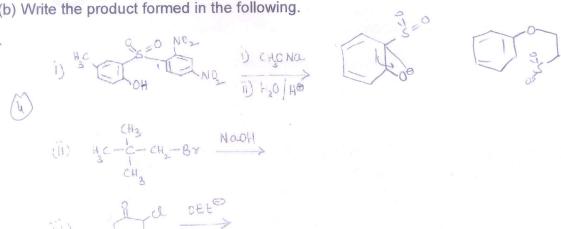
7. (a) What is the Pterno-Biuchi reaction? Predict the product in the following.



(b) Account the Photochemistry of  $\alpha \beta$  – unsaturated carbonyl compounds.



- (d) Explain in detail about photochemical cis/trans isomerisation.
- 8. (a) Give any two methods of generation of Benzyne. Illustrate its reactions in anomatic nucleophilic substitution.
  - (b) Write the product formed in the following.



$$R-\overset{\circ}{c}-cl. \rightarrow R-\overset{\circ}{clo}$$

## OR

(c) Predict the products for the following? Suggest suitable mechanism.



- (d) (i) What are Transannular rearrangement? Suggest mechanism with suitable example.
  - (ii) Discuss the Plausible mechanism for the following.

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M. Sc. II - Semester Examination, May / June 2019

Subject : Chemistry
Paper – III : Physical Chemistry

Time: 3 Hours

Max. Marks: 80

Note: Answer all questions from Part–A and Part–B. Each question carries 8 marks in Part–A and 12 marks in Part – B.

PART – A (4 x 8 = 32 Marks) (Short Answer Type)

1 (a) Explain Raoult's law of vapour pressure.

(b) Write about fugacity and fugacity coefficient.

2 (a) Explain the Radiative lifetimes of excited states.

(b) Discuss the light intensity on the rates of photochemical reactions.

3 (a) Explain the Radial and angular functions.

(b) Write the Varaiational integral for  $H_2^+$  ion.

4 (a) Illustrate the effect of temperature on conductivity of extrinsic semi-conductors.

(b) Explain the optical properties of nanoparticles.

# PART – B (4 x 12 = 48 Marks) (Essay Answer Type)

5 (a) Define (i) Fugacity and (ii) fugacity coefficient. Explain one method for the determination of fugacity.

(b) Explain various thermodynamic properties of dilute solutions.

OR

(c) Explain:

(i) Vapour pressure lowering

(ii) Freezing point depression

(d) Write the expressions for translational and rotational partition functions.

6 (a) What is Quantum yield and derive the quantum yield of fluorescence.

(b) What is delayed fluorescence and explain about E-type delayed fluorescence?

## OR

(c) Write the Kinetics of photophysical Unimolecular reactions.

(d) Define Quenching and derive Stern-Volmer equations.

7 (a) Write about contour plots and boundary diagrams.

(b) Explain the Variation theorem and its proof.

### OR

(c) Illustrate the secular equations and secular determinant with example.

(d) Explain the MO of H<sub>2</sub> molecule by LCAO method.

8 (a) Explain the photoconductivity and photovoltaic effect.

(b) Write the following:

(i) Meissner effect (ii) Types of super conductors

### OR

(e) Describe the phase diagram of Y-Ba-Cu-O systems.

(d) Explain the sol gel method of preparation of nanoparticles.

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M. Sc. II - Semester Examination, May / June 2019

Subject : Chemistry

Paper - IV: Analytical Techniques and Spectroscopy - II

Time: 3 Hours Max. Marks: 80

Note: Answer all questions from Part–A and Part–B. Each question carries 8 marks in Part–A and 12 marks in Part – B.

## PART – A (4 x 8 = 32 Marks) (Short Answer Type)

- 1 (a) What is the principle involved in Thermogravimetry?
  - (b) Write the applications of amperometric titrations.
- 2 (a) Give an account on magic angle spinning.
  - (b) Write short notes on Nuclear overhauser Enhancement.
- 3 (a) Explain the significance of ortho effect.
  - (b) Write a brief note on isotopic peaks.
- 4 (a) Discuss the principles of Auger Electron spectroscopy.
  - (b) Give an account on Kramer's degeneracy.

# PART – B (4 x 12 = 48 Marks) (Essay Answer Type)

- 5 (a) Write the consequences of Ilkovic equation.
  - (b) Describe pulse polarography and give its advantages.

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- (c) Explain the cyclic voltammetric study of insecticide parathion.
- (d) Explain how Zn<sup>2+</sup> ion can be estimated by amperometric titrations.
- 6 (a) Explain how enantiomers can be differentiated by chiral lanthanide shift reagents.
  - (b) Discuss the applications of <sup>19</sup>F NMR involving coupling with <sup>31</sup>P.

### OR

- (c) Sketch the <sup>31</sup>P NMR spectra for
  - (i) H<sub>3</sub>PO<sub>3</sub> (ii) PH<sub>3</sub> (iii) Ph<sub>3</sub>PSe
- (d) Discuss the applications of solid state NMR.
- 7 (a) What is the principle involved in Electrospray Ionization?
  - (b) Discuss the applications of Gas chromatography-mass spectroscopy.

### OR

- (c) What is the principle involved in liquid chromatography mass spectrometry?
- (d) Write short notes on Retro Diels Alder Fragmentation.
- 8 (a) Write short notes on:
  - (i) Koopman's theorem (ii) Instrumetnation of XPS
  - (b) Explain PES of N<sub>2</sub> molecule.

## OR

- (c) Give an account on selection rules in e.s.r. spectroscopy.
- (d) Write short notes on hyperfine coupling constants.

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