

FACULTY OF SCIENCE

M.Sc. I – Semester Examination, Dec. 2018 / Jan. 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 (4x8 = 32 Marks)

[Short Answer Type]

- 1 a) Write a short notes on proper axis of rotation. Illustrate with example.  
b) Find out the symmetry elements present in the following point groups:  
 $C_{2v}$ ,  $C_{3v}$ ,  $D_{3h}$ ,  $O_h$ ,  $T_d$
- 2 a) Square planar complexes of Ni(II) show diamagnetic behavior while tetrahedral complexes of Ni(II) are paramagnetic. Explain.;  
b) Explain the Jahn-Teller theorem and discuss how it is helpful to deal with distortion in Cu(II) complexes.
- 3 a) Discuss briefly on the Pearsons' concept of hard and soft acids and bases.  
b) Explain how the solvation effects account for anomalous natures of acids and bases using suitable example.
- 4 a) Describe the preparation and bonding in metal dinitrogen complexes.  
b) Discuss the application of 18 electron rule in linear and bridging metal carbonyls with two examples of each type.

PART – B (4x12 = 48 Marks)

[Essay Answer Type]

- 5 a) Why do  $BF_3$  and  $ClF_3$  molecules belong to different point groups. Assign their point groups and list out the symmetry elements.  
b) Identify the symmetry elements present in the following molecules and assign the appropriate point groups:  $[CoCl_4]^{2-}$ , dichloro methane, HCN,  $XeOF_4$  and  $CH_3Cl$ .

OR

- c) Discuss the classification of molecules into different point groups and mention the point groups in each class.
- d) Discuss the concept of symmetry criteria for optical activity.

- 6 a) What is crystal field stabilization energy? Calculate CFSE for  
i)  $[\text{CoF}_6]^{3-}$       ii)  $[\text{Co}(\text{NH}_3)_6]^{3+}$       iii)  $[\text{Fe}(\text{CN})_6]^{3-}$   
b) What are high-spin low-spin complexes? Explain with suitable examples.

OR

- c) How does the d-orbital splitting change as an octahedron becoming a square planar complex. Explain.  
d) Discuss the Gouy method for the determination of magnetic susceptibility.

- 7 a) What are stepwise and overall stability constants? Explain their relationship.  
b) Describe the principle of pH metric method for the determination of stability constant of a complex.

OR

- c) What is cryptate effect? Explain with examples.  
d) Discuss the below given influencing factor of stability constants  
i) Basicity  
ii) Steric effects on ligands  
iii) Crystal field effect and  
iv) Ionization potential on metal ion.

- 8 a) Explain the carbon monoxide as a ligand and discuss the bonding modes of CO.  
b) Explain the stereochemical control of valence in metal nitrosyls  
i)  $[\text{Co}(\text{diars})_2(\text{NO})]^{2+}$  and  
ii)  $[\text{Co}(\text{diars})_2\text{NO}(\text{SCN})]^+$ .

OR

- c) Explain the bonding modes and structures of Ru(II) and Os(II) dinitrogen complexes.  
d) What is 18 electron rule? Explain the molecular orbitals of NO.

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## FACULTY OF SCIENCE

M.Sc. I – Semester Examination, Dec. 2018 / Jan. 2019

Subject: Chemistry

Paper – II  
Organic Chemistry

Time: 3 Hours

Max.Marks: 80

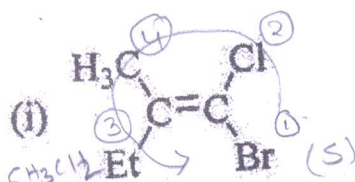
Note: Answer all questions from Part-A and Part-B.  
Each question carries 8 marks in Part-A and 12 marks in Part-B.

## PART – A (4x8 = 32 Marks)

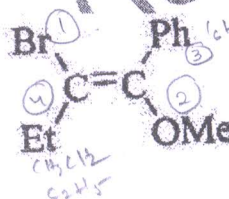
[Short Answer Type]

1 a) What is meant by desymmetrization? Explain with an example.

b) Predict E or Z configuration for the following compounds.



(ii)

2 a) Describe factors affecting E<sub>2</sub> elimination.

b) How IR and NMR is useful to investigate the reaction mechanism.

3 a) Discuss Winstein-Holness equation.

b) Write different conformations of 2,3-dibromobutane. Predict the most stable conformation.

4 a) Write any two methods of synthesis of acridine.

b) Discuss the importance of natural products as drugs.

## PART – B (4x12 = 48 Marks)

[Essay Answer Type]

5 a) Explain chirality in allenes and spiranes.

b) What is meant by racemization and discuss resolution of racemic mixture by diastereomer salt formation method.

OR

c) Describe determination of configuration of E,Z-isomers by chemical methods.

d) Discuss C<sub>2</sub> axis of symmetry and alternating axis of symmetry with appropriate examples.

6 a) Explain the mechanism of E1CB reaction.

b) Describe the stereoselectivity in addition of KMnO<sub>4</sub> across olefin.

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OR

- c) Discuss the use of isotopes in determination of reaction mechanism.
  - d) Write a note on pyrolytic syn elimination.
- 7
- a) Describe conformational diastereoisomers and conformational enantiomers with appropriate examples.
  - b) Explain Curtin-Hammett principle.

OR

- c) Write different conformations of ethylene glycol and halohydrin.
  - d) Write a note on factors affecting conformational stability and conformational equilibrium.
- 8
- a) Describe structural elucidation of Papaverine.
  - b) Write the synthesis of  $\beta$ -carotene.

OR

- c) Discuss any two methods of synthesis of isoquinoline.
- d) Describe the structural elucidation of  $\alpha$ -terpenoil.

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## FACULTY OF SCIENCE

M. Sc. I – Semester Examination, December 2018 / January 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) Write the Gibb's equations for non-equilibrium systems.  
(b) Describe the entropy as a function of P and T.
- 2 (a) Define chemical and concentration cells with examples.  
(b) Define the terms : (i) Decomposition potential (ii) Concentration over potential
- 3 (a) Define (i) Hermitian operator (ii) Complex functions  
(b) Explain the assumptions of quantum theory.
- 4 (a) Explain transition state theory and significance of various activation parameters.  
(b) Write a note on complex reactions.

## PART – B (4 x 12 = 48 Marks)

(Essay Answer Type)

- 5 (a) Write the thermodynamic relations and Maxwell's relations.  
(b) Discuss the measurement of partial molar volumes.

OR

- (c) Define Helmholtz and Gibbs free energies and explain the criteria for equilibrium and spontaneity in terms of A and G.
- (d) Calculate  $\Delta G$  when two moles of an ideal gas are compressed isothermally and reversibly at  $100^\circ\text{C}$  from a pressure of 10 atm to 20 atm.
- 6 (a) For the following electrode concentration cell derive the expression for the cell EMF  $\text{Pt} ; \text{H}_2 | \text{HCl} | \text{H}_2 ; \text{Pt}$   
( $P_1$ ) ( $a_2$ ) ( $P_2$ )  
(b) Explain various types of potentiometric titrations.

OR

- (c) Define and differentiate between activity, activity coefficient and mean ion activity coefficient in electrolytic solutions.
- (d) Explain Debye – Huckel – Bjerrum equation.
- 7 (a) What are commuting operators? What is their importance in quantum mechanics?  
(b) Show that the Eigen value of Hermitian operator is always real.

OR

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- (c) Write a note on  
(i) Well behaved function  
(ii) Normalized and orthogonal functions.
- (d) Write the Schrodinger wave equation for a particle in a box of dimensions  $X = 0$  to  $X = a$ . Calculate the energy of the particle in the box for  $n = 1$  when  $x = a/2$ .
- 8 (a) Write Hammett and Taft equations and explain the significance of terms and applicability of equations.  
(b) Explain reactivity selectivity principle.

OR

- (c) What are chain reactions? Write the mechanism of  $H_2 - Br_2$  reaction and derive rate law.  
(d) Write the Swain - Scott equation and Edward equation. Explain in the significance of terms in these equations.

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## FACULTY OF SCIENCE

M.Sc. I-Semester Examination, December 2018 / January 2019

Subject : CHEMISTRY

Paper : IV

Analytical Techniques and Spectroscopy

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) Briefly account the following :  
i) partition ratio      ii) selectivity factor
- b) Explain the principle of HPLC.
- 2 a) Explain enantiotopic and diastereotopic proton non equivalence in  $^1\text{H-NMR}$ .
- b) Discuss the dynamic  $^1\text{H-NMR}$  spectrum of N, N-dimethyl formamide.
- 3 a) Explain isotopic effects on rotational spectra. Give suitable example.
- b) Discuss for the complimentary nature of IR and Raman spectra.
- 4 a) Give the selection rules for electronic spectra of molecules.
- b) Sketch the UV-Vis spectrum of stilbenes and phenanthrene.

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

- 5 a) Discuss the classification of chromatographic techniques.
  - b) Explain the principle and instrumentation of Gas Chromatography.
- OR**
- b) Explain Rate theory in chromatographic separations.
  - c) Briefly describe methods of quantitation for GC and HPLC.
- 6 a) Discuss the various factors effecting the chemical shifts in  $^1\text{H-NMR}$  spectroscopy.
  - b) Explain the principle of spin-spin coupling in  $^1\text{H-NMR}$  with suitable examples.
- OR**
- c) Discuss dynamic  $^1\text{H-NMR}$  of chair conformations of cyclohexane and cis-decalin.
  - d) Calculate the resonance frequency of a proton is a magnetic field of 12.6T  
( $\gamma_{\text{H}} \approx 2.7 \times 10^8 \text{ T}^{-1} \text{ S}^{-1}$ ).

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- 7 a) Discuss the application of rotational spectra in calculation of bond length of diatomic molecules, with suitable example.  
b) Explain the quantum theory of Raman effect.

OR

- c) Discuss the types of vibrational bands and mode of vibrations in IR.  
d) How do you distinguish the following with IR group frequencies.  
i) ethyl alcohol and diethylether      ii) Acetone and propanol  
iii) methyl benzoate and phenyl acetic acid

- 8 a) Discuss the factors affecting the  $\lambda_{\max}$  in UV-Vis spectroscopy.  
b) Explain the application of Beer's law in the determination of dissociation constants of weak acid.

OR

- c) Briefly account for the absorption spectra of charge transfer complexes.  
d) Calculate the  $\lambda_{\max}$  of the following using Woodward Fieser rules.



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