

**FACULTY OF SCIENCE**

M.Sc. II-Semester Examination, May / June 2016

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)

- 1 a) Discuss the plane of symmetry with examples.  
b) How do you explain symmetry criteria for optical activity?
- 2 a) Derive all the possible terms for  $d^2$  configuration.  
b) Discuss j-j coupling.
- 3 a) Explain the structural and bonding aspects of  $Fe_3(CO)_{12}$  based on spectral data.  
b) What is 18e<sup>-</sup> rule and calculate valence electrons in below complexes.  
i)  $[\eta^4(C_4H_4)Fe(CO)_3]$     ii)  $[Co(NH_3)_6]^{3+}$
- 4 a) Explain the structural aspects of hemocyanin.  
b) Discuss briefly the importance of  $Na^+$ ,  $K^+$  and  $Fe^{+2}$  in biological systems.

**PART – B (4 x 12 = 48 Marks)**

(Essay Answer Type)

- 5 a) Discuss descent in symmetry with increasing substitution on  $ML_6$  of Oh point group.  
b) Assign the point group for the following molecules and identify the symmetry elements  
i)  $O-C_6H_4X_2$     ii)  $B(OH)_3$     iii) Phenol  
**OR**  
c) Discuss improper rotational axis of symmetry both in eclipsed and staggered conformations of ethane.  
d) Write briefly symmetry and dipole moment.
- 6 a) Draw the generalized Orgel diagrams for one electron and two electron systems of octahedral and tetrahedral complexes.  
b) Calculate the number of microstate for the configurations –  $d^4$ ,  $p^3$ ,  $p^1$  and  $d^{10}$ .  
**OR**  
c) Discuss the effect of weak fields on D and F terms.  
d) Write a note on spin-orbital coupling parameters.
- 7 a) Discuss electron count theory based on wades rules in metal clusters.  
b) Explain the structure and bonding patterns of  $[Mo_6(Cl)_8]^{4+}$ .  
**OR**  
c) Discuss metal-metal bonding features in face sharing biooctahedra with suitable examples.  
d) Write a note on isolobal analogy in octahedral complexes.
- 8 a) Explain the role of globin chain in hemoglobin.  
b) What is photosynthesis? Explain photosystem I and II.  
**OR**  
c) Explain the physiological effect of metal ion concentration in biological system.  
d) Explain the reaction mechanism of decarboxylation and dealdolization by Vit-B<sub>6</sub>.

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## FACULTY OF SCIENCE

M.Sc. II-Semester Examination, May / June 2016

Subject : CHEMISTRY

Paper : II  
Organic Chemistry

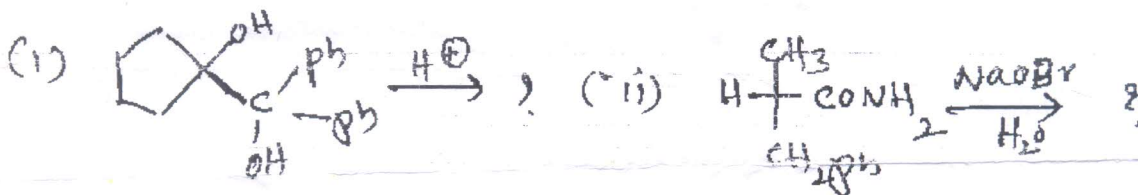
Time : 3 hours

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 x 8 = 32 Marks)  
(Short Answer Type)

- Draw the preferred conformations of butanone and 1, 2 - dichloroethane.
  - State and explain Curtin-Hammett principle.
- When o-chloro anisole is treated with potassium amide in liquid ammonia m-Anisidine is formed. Explain this rearrangement with mechanism.
  - Explain  $SE^1$  and  $SE^2$  mechanism with example.
- How free radicals are generated? Explain their detection.
  - Predict the products in the following reactions.



- Write the synthesis of quinic acid.
  - How the structure of  $\alpha$ -terpeniol is established? Explain.

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

- Draw the staggered conformations of possible stereoisomers of 2, 3-butanediol and indicate the preferred one for each. Give reasons.
  - Explain the importance of physical and spectral methods in conformational analysis.

OR

- Explain the reactivity of (2S), (3R) - 2, 3-dibromobutane and (2R), (3S) - 2, 3-dibromobutane towards iodide induced debromination.
- What is Winstein-Holness equation? Illustrate with example.

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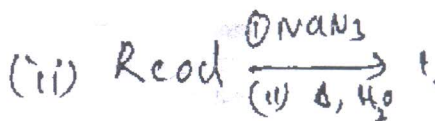
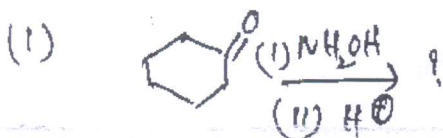
- 6 a) What is Von-Richter rearrangement? Write its mechanism and give evidences.  
 b) Illustrate neighbouring group participation reactions involving sigma ( $\sigma$ ) and Pi ( $\pi$ ) bonds.

OR

- c) Write  $SN^2Ar$  mechanism. Give evidences.  
 d) Explain with suitable examples of NGP reactions involving  
 i) Cycloalkyl group      ii) Nitrogen atom ( $NH_2$  group)
- 7 a) Discuss the generation and stability of carbocations.  
 b) Outline the mechanism of  
 i) Sommet Hauser rearrangement  
 ii) Smiles rearrangement

OR

- c) Discuss the generation and reactions of carbenes.  
 d) Predict the products formed and the mechanism of the following reactions.



- 8 a) Discuss the structure of papaverine.  
 b) Outline the synthesis of camphor.
- OR
- c) Give a brief account of the importance of the natural products as drugs.  
 d) Write the synthesis of meroquinene.

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## FACULTY OF SCIENCE

M.Sc. II-Semester Examination, May / June 2016

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) Derive Gibbs-Duhem equation.  
b) What are excess functions? Write the expressions for  $\Delta H^E$ ,  $\Delta S^E$ ,  $\Delta G^E$ .
- 2 a) Explain ferrioxalate actionometry.  
b) Give an account of isomerization reactions with examples.
- 3 a) Explain the relation between Cartesian coordinates (x, y, z) and spherical polar coordinates (r,  $\theta$ ,  $\phi$ ) of a point P in space.  
b) Compare classical and quantum mechanical particles.
- 4 a) What is photovoltaic effect?  
b) Explain in brief about the structure of defect perovskites.

## PART – B (4 x 12 = 48 Marks)

(Essay Answer Type)

- 5 a) What are Partial Molar Properties? Discuss the slope method for the determination of Partial Molar properties.  
b) Discuss the thermodynamic properties of ideally dilute solutions.  
OR  
c) Derive an expression for depression in freezing point of a solution.  
d) The vapour pressure of benzene is 74.7 atm at 20°C and vapour pressure of toluene is 22.3 atm at 20°C. A solution of benzene and toluene at 20°C has vapour pressure of 46 atm. Find the benzene mole fraction in the solution and in the above vapour phase.

- 6 a) Derive an expression for fluorescence quantum yield.  
b) Discuss the kinetics of photo physical processes.

OR

- c) What is the effect of light intensity on the rates of photochemical reactions?
- d) Benzophenone in EPA at 77K phosphoresces strongly ( $\phi_p = 0.90$  and  $\tau_p = 0.006s$ ) and is practically non-fluorescent. Calculate  $k_p$ ,  $k_{isc}$  and  $k_{isc}$  if  $\tau_f = 10^{-6} s$  and  $\phi_1 = 10^{-4}$ .

- 7 a) What are approximation methods? Discuss the variation method.  
b) Consider a small object of mass 1.00 mg which is confined to move between two rigid walls in a distance of 1 cm between them. Calculate the minimum speed of the object.

OR

- c) Write the Schrodinger equation for a particle in a one dimensional box and obtain an expression for the wave function and energy.  
d) How do you calculate the wave functions and energies for the bonding and antibonding molecular orbitals in  $H_2^+$  ion?

- 8 a) Discuss in detail the classification of imperfections in solids.  
b) Explain the crystal of  $YBa_2Cu_3O_{7-x}$ .

OR

- c) What is superconductivity? How does it get affected by the magnetic fields?  
d) What are point defects? Explain in detail.

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## FACULTY OF SCIENCE

M.Sc. II-Semester Examination, May / June 2016

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) A cell is constructed using SCE (dipped in saturated KCl solution) and quinhydrone (Pt dipped in HCl solution containing quinhydrone) electrodes. The pH of HCl is 1.0. What is the cell emf?  
 b) In a polarographic experiment,  $10^{-3}$  M  $\text{CuCl}_2$  solution gave a diffusion current of 0.2 micro amperes. In another experiment,  $\text{CuCl}_2$  solution gave a diffusion current of 0.3 micro amperes. What is the concentration of  $\text{CuCl}_2$  solution?
- 2 a) Write a note on deuterium exchange.  
 b) Sketch the  $^1\text{H}$  nmr spectrum of  $\text{AX}_3$  and show coupling constant and chemical shift.
- 3 a) The mass spectrum of  $\text{C}_3\text{H}_6$  gave M(100%) and (M+1) peaks. What is the percentage intensity of (M+1) peak?  
 b) Write a note on ortho effect.
- 4 a) Explain how ESCA is useful in the qualitative analysis of elements.  
 b) Sketch the esr spectrum of methyl free radical and show the coupling constant and 'g'.

**PART – B (4 x 12 = 48 Marks)**

(Essay Answer Type)

- 5 a) Write short notes on i) calomel electrode and ii) quinhydrone electrode.  
 b) What is the principle involved in differential pulse polarography?

OR

- c) An amperometric titration of  $\text{Mg}^{2+}$  ions is carried out using hydroxyquinoline. Explain the type graph obtained for this titration. 8-
- d) Sketch the potentiometric titration curve of HCl versus NaOH and explain.
- 6 a) Explain the phenomenon of NOE with suitable examples.  
 b) Sketch the  $^{19}\text{F}$  and  $^{31}\text{P}$  nmr of  $\text{PF}_5$  and explain the splitting pattern.

OR

- c) What is the principle involved in MAS nmr?
- d) The nmr spectrum of AB gave peaks at 300, 290, 289 and 279 Hz away from TMS signal when recorded using 100 MHz nmr spectrometer. Calculate the chemical shifts of A and B protons.

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- 7 a) Write short notes on i) nitrogen rule and ii)  $\beta$ -cleavage.  
b) What is the principle involved in chemical ionization method?

OR

- c) An alcohol,  $C_5H_{12}O$ , gave peaks at  $m/z$  88, 70, 55, 42, and 31. Identify the compound and account the fragmentation pattern.  
d) Explain retro Diels-Alder fragmentation with an example.
- 8 a) A radical gave esr spectrum consisting of peaks at 3270, 3300 and 3330 gauss. If the frequency of radiation is 9.273 GHz, calculate the 'g' and 'A' values of the radical ( $\beta = 9.273 \times 10^{-24} \text{ JT}^{-1}$ ;  $h = 6.6 \times 10^{-34} \text{ Js}$ ).  
b) What is the principle involved in Auger electron spectroscopy?

OR

- c) Explain how the nature of molecular orbitals can be predicted from the photoelectron spectrum.  
d) Draw the spin energy level diagram for an <sup>Mn<sup>+5</sup></sup>  
i) ion showing only zero field splitting and  
ii) ion showing both zero field splitting and Kramer's degeneracy

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