# II Semester M.Sc. in Chemistry Examination February 2015 Inorganic Chemistry

Time: 3Hours Max. Marks: 80

**Instructions:** PART- 1 is compulsory and answers any four of the remaining questions from PART-II

## PART-1

## Answer any 8 equestions

- i) What is Lanthanide contraction?
- ii) What are the characteristics reactions of actinide +3 and +4 ions?
- iii) Calculate the EAN for  $V(CO)_6$  compound.
- iv) Write any three physical properties exhibited by metal carbonyls.
- v) Explain the formation of  $\sigma$ -complex in dihydrogen complexes.
- vi) Name the following co ordination compound according to IUPAC nomenclature.

$$\lceil Co(en)_2 Br_2 \rceil Cl, \lceil Cr(en)_5 (SCN) \rceil F_5$$

- vii) Identify the optically active compounds from the following complexes.
  - a)  $\left[ Co(en)_3 \right]^{3+}$
  - b)  $trans \left[ Co(en)_2 Cl_2 \right]^+$
  - c)  $cis \left[ Co(en)_2 Cl_2 \right]^+$
  - d)  $\left[ Cr(NH_3)_5 Cl \right]$
- viii) Octahedral complexes are always high spin complexes. Give reason.
- ix) What is Faraday Effect?
- x) Why metal  $t_{2g}$  orbitals are not overlap with ligand  $\sigma$ -orbitals?

## **PART-II**

- 1. a) Why do the electronic absorption spectra of Lanthanide ions have sharp bands unlike the broad bands in the 3d-elements?
  - b) What are the main principle involved upon separation of  $N_p$ ,  $P_u$  and  $A_m$  from U?
  - c) Explain the structure of binucleon metal carbene Fe<sub>2</sub>(CO)<sub>g</sub>.

(4+6+6)

- 2. d) What are ligands? With example discuss their classification.
  - e) What is Trans effect? Explain its mechanism.
  - f) Discuss briefly stepwise and overall stability constant of co ordination compounds

(6+4+6)

- 3. g) What is effective atomic number? How the stability of the complex is interpreting using ENA?
  - h) Which of the following complexes has more  $\Delta_0$  value? Explain why

i) 
$$\left\lceil Fe(H_2O)_6 \right\rceil^{3+}$$
 ii)  $\left\lceil Fe(CN)_6 \right\rceil^{3-}$ 

i) Discuss molecular orbital diagram of octahedral complexes.

(4+6+6)

- 4. k) Compare the CFT and MOT
  - 1) What are term symbols? Explain their significance
  - m) Explain curic temperature (T<sub>c</sub>) and Neel temperature (T<sub>N</sub>)

- 5. n) Why scandium and Yttrium are usually considered along with the Lanthanide elements?
  - o) What are Nitrosyl complexes? Discuss their structure and bonding with example.
  - p) What are di hydrogen complexes? Discuss their structure, bonding and spectroscopic characterization.

(4+6+6)

- 6. q) What is Johan Teller distortion? Illustrate with example.
  - r) Discuss the octahedral co ordination complexes with  $\pi$ -acceptor ligands
  - s) Draw the crystal field splitting diagram for  $[CoF_6]^{4-}$  and  $[Co(en)_3]^{2+}$  and explain their magnetic properties? (4 + 6 + 6)

## II Semester M.Sc. in Chemistry Examination February 2015 Organic Chemistry

Time: 3Hours Max. Marks: 80

**Instructions:** PART- 1 is compulsory and answers any four of the remaining questions from PART-II

#### PART-1

## Answer any 8 questions

2 x 8=16

- i) What is Luche reduction? Give one example.
- ii) Explain chemo selective reaction with example.
- iii) Comment on aptitude of migrating group in pinacol-pinocolone rearrangement.
- iv) Explain Benzylic acid rearrangement.
- v) What is the intermediate involved in Schemidt rearrangement.
- vi) What is menat by enantiomeric excess (ee)?
- vii) Explain Deals-Alder reaction? Give one example
- viii) What is Chichibaby reaction?
- ix) What is chiral auxylary? Give one example.
- x) Write any two acid labile protecting group used for protection of alcohol group.

### **PART-II**

1. a) Predict the structure of the product formed in the reaction below

$$H \cite{C} \cite{H} \cite{C} \cite{H} \cite{C} \cite{H} \cite{C} \cite{C} \cite{H} \cite{C} \cite{C}$$

- b) With example, explain the use of lead teraacetate in organic synthesis. And write the mechanism.
- c) With example discuss followings
  - i) Ring closing mechanism (RCM)
  - ii) Cross methathesis and
  - iii) Ring opening methathesis

(4+6+6)

- 2. d) What is Corey-Kim oxidation? Illustrate with example.
  - e) Explain the radical Mechanism of halogination of alaknes.
  - f) What is birch reduction? With example explain the stereochemistry of product in reduction of alkyne using birch reduction (4 + 6 + 6)

- 3. g) What is Fries rearrangement? Discuss with mechanism.
  - h) What is Beckman rearrangement? Discuss the mechanism and comment on aptitude of migration group.
  - i) Illustrate Rabinsion annulations reaction? Explain the mechanism with example.

$$(4+6+6)$$

- 4. j) Explain the enetioselective and diastereoselective addition to carbon-carbon double bond.
  - k) What is conjugate addition reaction? What are the factors influence regeoselectivity in conjugate addition reaction?
  - 1) With example discuss orthogonal protection strategy.

$$(4+6+6)$$

- 5. m) How phosphorus and sulphur ylids reacts with carbonyl compounds? Write the reaction mechanism in both reactions.
  - n) Write the any two major reactions of N-halo succinamides in organic synthesis.
  - o) Write the structure of products in the following reaction.

$$(4+6+6)$$

6. Write the structure of products in the following reactions.

$$(4+6+6)$$

$$p) \qquad \qquad \underbrace{ \begin{array}{c} \mathbf{i_{)} \, NaBH_{4}/EtOH} \\ \mathbf{ii_{)} \, H_{2}O/H^{+}} \end{array}} \begin{array}{c} \mathbf{0} \quad \mathbf{0} \\ \mathbf{0} \\ \hline \\ \mathbf{ii_{)} \, H_{2}O/H^{+}} \end{array}$$

q) 
$$\begin{array}{c} \text{i}_{\text{j}} \text{ DIBHAL}^{\text{-}}\text{H/THF} \\ \hline \phantom{}^{\text{780}^{\text{c}}} \end{array} \begin{array}{c} \text{Ph}^{3}\text{Ph}^{\text{-}^{\text{-}}}\text{CH}^{\text{2}^{\text{-}}}\text{CH}_{3}/\text{LDA} \\ \text{Benzene/50}^{0}\text{C} \end{array} \\ \text{B} \begin{array}{c} \text{MCPBA/DCM} \\ \text{Benzene/50}^{0}\text{C} \end{array}$$

r) 
$$\begin{array}{c|c} & & & & \\$$

# II Semester M.Sc. in Chemistry Examination February 2015 Physical Chemistry

Time: 3Hours Max. Marks: 80

**Instructions:** PART- 1 is compulsory and answers any four of the remaining questions from PART-II

## **PART-1**

# Answer any eight questions

- i) What is meant by freezing point depression?
- ii) What is activity and activity coefficients?
- iii) With example define degree of freedom.
- iv) Explain the Faraday law of electrolysis?
- v) State the limitation of Debye- Hukel theory?
- vi) What are concentration cells? Give two examples.
- vii) Define the term liquid junction potential?
- viii) Write the statement of variation theorem.
- ix) How adsorption is different from absorption phenomenon?
- x) What is de- emulsification? Name two de emulsifications.

### PART-2

- 2. a) What are colligative properties? What are the different colligative properties exits?
  - b) Discuss the thermodynamics of non ideal solution.
  - c) Derive the phase diagram of the water system and explain the term triple point.

(4+6+6)

- 3. d) Derive expression of Arrhenius theory of electrolytic dissociation
  - e) Explain the HelmHoltz perrir model of electrical double layer.
  - f) How trans port numbers are determined by Hittot's method.

(4+6+6)

- 4. g) Derive mathematical expression for application of schrodinger equation for a free particle.
  - h) Setup the S equation to polar co ordinates.
  - i) Derive the general theory of perturbation method.

(4+6+6)

- 5. j) Derive the equation for uni molecular surface reactions.
  - k) Derive the Brunauer Emmet Teller-Adsorption isotherm.
  - 1) Explain electro osmosis phenomenon.

(4+6+6)

- 6. m) Explain variation of activity with temperature.
  - n) Discuss the phase diagram of the silver lead system.
  - o) Derive the expression for Debye-Huckel on sager conductance equation.

(4+6+6)

7. p) Derive the mathematical expression for particle in a three dimensional Box.

- q) Derive the expression for inhibition of unimolecualr surface reaction.
- r) How are the colloidal solution are classified on the basis of physical states of the dispersed phase and dispersion medium?

(4+ 6+ 6)

# II Semester M.Sc. in Chemistry Examination February 2015 Analytical Chemistry

Time: 3Hours Max. Marks: 80

**Instructions:** PART- 1 is compulsory and answers any four of the remaining questions from PART-II

# PART-I

## Answer any eight questions

- i) What is error? Mention the difference types of error.
- ii) How accuracy can be improved in analysis?
- iii) What is gravimetric analysis?
- iv) What is redox reaction? Give one example.
- v) What are the difference between equivalence point and end point?
- vi) What are masking agents? Give two examples.
- vii) What is leaving effect or solvent leveling?
- viii) What is distribution ratio(D) in solvent extraction?
- ix) What is column efficiency?
- x) What is diffusion current?

### **PART-II**

- 1. a) Explain Gaussian distribution and standard deviation(s)?
  - b) What is accuracy and precision? Discuss any two methods of expressing accuracy?
  - c) Explain the principle of precipitation? What are the difference between post-precipitation and co-precipitation?

(4+6+6)

- 2. d) Discuss the isotopic exchange methods?
  - e) With example explain visual and adsorption indicator used in precipitation titration.
  - f) Explain the inorganic and organic analysis using redox titration.

(4+6+6)

- 3. g) Write a note on complexometric titration with EDTA?
  - h) Explain the process of determination of Hardness of water?
  - i)With example explain direct and back titration methods.

(4+6+6)

- 4. j) Explain the basic concept of non-aqueous titrations.
  - k) What is separation factor (r)? How it will be calculated?
  - 1) Discuss column selectivity and column efficiency?

(4+6+6)

- 5. m) Discuss methods of minimizing error.
  - n) What is meant by seeding? Explain its advantages in precipitation.
  - o) Write a note on Quantitative estimation of oxalic acid.

(4+6+6)

7. p) Write a note on direct and reverse isotopic dilution analysis?

- q) Explain the titration of halogen acid salts of bases with perchloric acid. s) Explain the general theory of column chromatography.

(4+ 6+ 6)