# RAMAKRISHNA MISSION VIDYAMANDIRA

**(Residential Autonomous College affiliated to University of Calcutta)**

**SECOND YEAR [2015-18]**

**B.A./B.Sc. THIRD SEMESTER (July – December) 2016**

**Mid-Semester Examination, September 2016**

Date : 10/09/2016 **CHEMISTRY (Honours)**

Time : 11 am – 1 pm Paper : III Full Marks : 50

**[Use a separate Answer Book for each group]**

## Group – A

[***Attempt one question from each Unit***]

### Unit - I

1. a) Show the nature of graphical plot of G vs. progress of reaction for $\left(\frac{\partial G}{\partial \xi}\right)_{T,P} < 0$ and comment on the spontaneity of the reaction. [3]

   b) For the one component pure system, chemical potential and partial molar free energy are same —Justify or Criticize. [2]

   c) For the $NH_3$ preparation, $K_P$ depends on the stoichiometry of the reaction. For 1 mole of $N_2$ and $\frac{1}{2}$ mole of $N_2$, equilibrium constants are $K_P$ and $K_P'$, find the relation between $K_P$ and $K_P'$. [3]

2. a) Show that $(\Delta G)_{T,P} = \left(\frac{\partial G}{\partial \xi}\right)_{T,P}$. [2]

   b) If 1·588 gm of nitrogen tetroxide gives a total pressure of 760 torr when partially dissociated in a 500 cc glass vessel at 25°C, what is the degree of dissociation $\alpha$? What is the value of $K_P$? [4]

   c) For the reaction $CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$ show that $K_P = \frac{p_{CO_2}}{P^o}$ from the concept of chemical potential. [2]

### Unit - II

3. a) A first order reaction is 40% complete at the end of 1 hr. What is the value of the rate constant? In how long will the reaction be 80% complete? [3]

   b) Consider the following reaction : $K + Br_2 \rightarrow KBr + Br$

   It has been observed that the steric factor (P) is greater than one for this reaction. Explain how this could be possible in the light of its plausible mechanistic pathway. [3]

   c) Prove that for the simultaneous (parallel) reactions

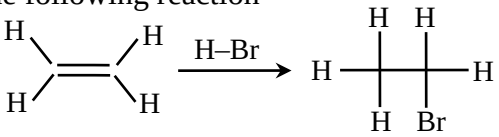
   $z \xleftarrow{K_2} A \xrightarrow{K} Y$

   $\frac{[Y]}{[Z]} = \frac{K_1}{K_2}$ for all times. [2]

4. a) Two second-order reactions have identical pre-exponential factors and activation differing by 20 KJ mole$^{-1}$. Calculate the ratio of their rate constants at (i) 0°C and (ii) 100°C. (Assuming the Arhenius Equation applies here) [3]

   b) Draw the energy diagram (H vs. Reaction Coordinate) for a one step exothermic reaction clearly depicting the activation energies of the forward and the reverse reaction. [3]

   c) Consider the following reaction

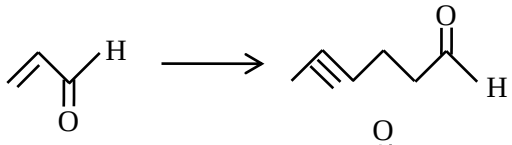
   Explain what could be a possible choice of reaction coordinate here? [2]

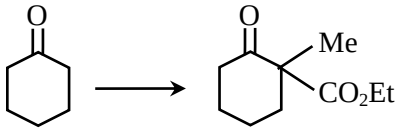
## Group – B

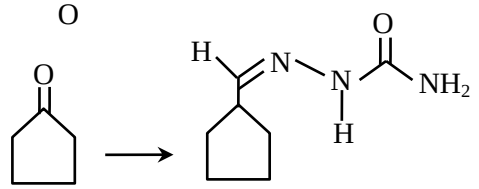
[*Attempt **one question** from **each Unit***]

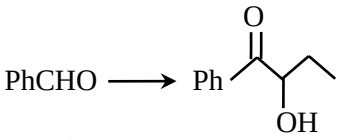
### Unit - I

5. Carryout the following conversions : [4×2]

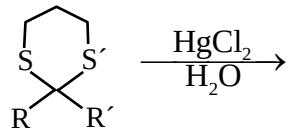
a) 

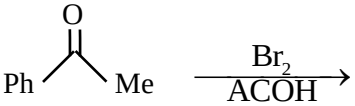
b) 

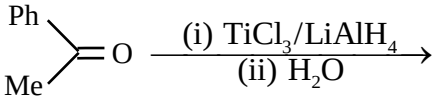
c) 

d) 

6. a) Predict the product(s) of the following reactions. Give mechanism. [3×2]

i) 

ii) 

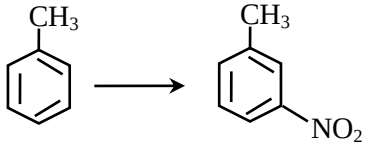
iii) 

b) In perkin reaction styrene is a side product along with Cinnamic acid. Propose a mechanism which can explain both the products. [2]

### Unit - II

7. a) Carry out the following transformations. [2×2]

i) $HC \equiv C - H \rightarrow CH_2 = CH - \underset{\displaystyle CH_3}{\underset{|}{CH}} = CH_2$

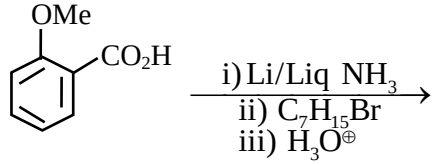
ii) 

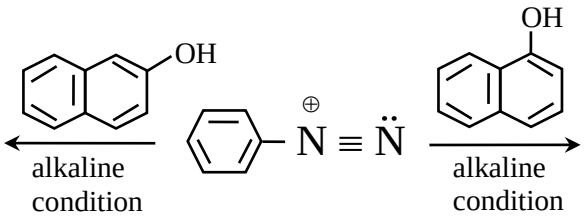
b) Between alkene and alkyne which one will react with $Br_2/CCl_4$ at faster rate and why? [2]

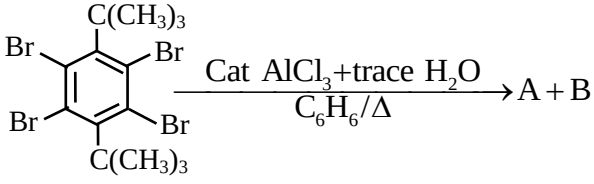
c) Write an equation for the formation of each of the following sulfonating electrophile from concentrated $H_2SO_4$. [2]

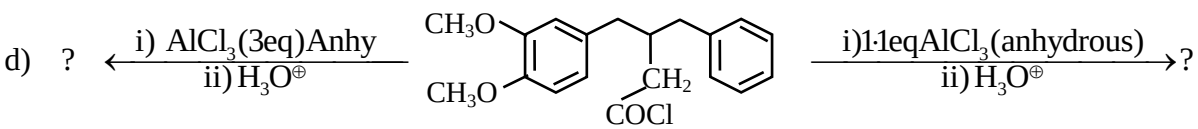
i) $H_3SO_4^{\oplus}$ ii) $HSO_3^{\oplus}$ iii) $H_2S_2O_7$

8. Write down the product of the following reactions ; [4×2]

a) 

b) ? 

c) 

d) ? 

## Group – C

[*Attempt <u>one question</u> from <u>each Unit</u>*]

### Unit - I

9. a) One red coloured coordination compound A slowly transforms into another coordination compound B. Elemental analysis of both A and B given the same composition, $Co:NH_3:Cl:NO_2 = 1:5:2:1$ 1 m.mol of each of A and B on treatment with an excess of $AgNO_3$ solution in dil $HNO_3$ medium give 2m.mol of AgCl.
Write the possible coordination formulae of A and B, explaining the facts. Rationalize the transformation, $A \rightarrow B$. [2+1]

b) Write IUPAC names of $[Ni(NH_3)_6][Co(NO_2)_6]$ and $\left[(NH_3)_4Co\begin{matrix}OH\\NH_2\end{matrix}Co(NH_3)_4\right]Br_4$. [2]

c) $He_2$ in non-existent in the light of —
(i) bond order (ii) energy of molecular orbitals [2+2]

10. a) Define a ligand. Give an example of a hexadentate ligand showing their donor sites towards the central in a complex of your choice. How many chelate rings are formed if the ligand forms an octahedral complex. [3]

b) Give two examples of coordination isomers of $[Pt(NH_3)_4[PtCl_6]$. [1]

c) Same symmetric molecular orbitals with electrons can never be concentrated in the same regional space between two atomic nuclei. Explain with suitable example. [3]

d) Point out the differences between atomic orbitals and molecular orbitals. [2]

### Unit - II

11. a) Predict the binding moles of $SCN^-$ with reasons in the following ions $[Co(NH_3)_5(SCN)]^{+2}$ and $[Co(CN)_5(SCN)]^{-3}$. [3]

b) A, B and C are three complexes of chromium (III) with the empirical formula $H_{12}O_6Cl_3Cr$. Complex A does not lose any weight when kept over concentrated $H_2SO_4$, whereas complexes B and C lose 6·75% and 13·5% of their original weight, respectively on keeping over conc. $H_2SO_4$. Identify A, B and C (at wt of Cr = 52] [3]

c) State the rules of LCAO for atomic orbital combinations for molecular orbitals. [3]

12. a) A solution containing 0·319 gm of a hydrate isomer with molecular formula $CrCl_3 \cdot 6H_2O$ was passed through a cation exchange resin in acidic form and the acid liberated was neutralised with 19ml of 0·125(N) sodium hydroxide. Identify the isomer. (Molecular weight of $CrCl_3 \cdot 6H_2O$ = 266·35) Give its IUPAC nomenclature. [3]

b) In addition to the two geometrical isomers of $[Pt(NH_3)_2Cl_2]$. There is a third isomer. It has the same empirical formula. But it is electrically conducting in solution. Write the structure of the complex. [1]

c) Discuss the formation of different molecular orbitals of AB type molecule with energy level diagram (Both A and B are second period element and E.N of A < B). [3]

d) Explain the bond order, polarity and ligating ability of CO. [2]

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