RAMAKRISHNA MISSION VIDYAMANDIRA
(Residential Autonomous College affiliated to University of Calcutta)
B.A./B.Sc. THIRD SEMESTER EXAMINATION, DECEMBER 2015
SECOND YEAR [BATCH 2014-17]
Date   : 15/12/2015   **CHEMISTRY [Hons]**
Time   : 11 am – 1 pm   **Paper :** III   Full Marks : 50

[Use a separate Answer Book for each Group]

Group – A

[Answer **one** question from **each unit**]

Unit - I

1. a) Draw free energy (G) versus extent of reaction (ξ) plot for the following gas phase reaction.

$A(g) \rightleftharpoons B(g)$

Indicate the equlibrium in the plot. [2]

   b) The partition coefficient of an organic compound between CCl_4 and water is 10. 100ml of an aqueous solution of the compound is taken. Calculate the minimum volume of CCl_4 needed in a single step to extract 90% of the compound from the solution. If the same amount of solute is to extract in five consecutive separations using equal volume of CCl_4 at each time, what would be the volume of total CCl_4 needed? Comment on your answer. [4]

   c) At 100°C, Kp for the reaction $COCl_2(g) = CO(g) + Cl_2(g)$ is 8×10^9 and $\Delta S° = 249 \cdot 42\, JK^{-1}mol^{-1}$. Calculate the degree of dissociation of phosgene under a total pressure of 2 atm at 100°C and $\Delta H°$ of the reaction at the same temperature. [4]

   d) Find out the mean ionic activity of 0·1M KCl solution at 25°C using Debye-Hückel's limiting law. (Given, Dehye-Hückel's constant A = 0·51 at 25°C) [2]

2. a) Does the equilibrium constant of a chemical reaction depend on stoichiometric representation of the reaction? Explain, with suitable example. [2]

   b) A certain amount of NOCl(g) is introduced into an evacuated flask, maintained at a temperature 200°C. Nitrosyl chloride dissociates as $2NOCl(g) = 2NO(g) + Cl_2(g)$. At equilibrium, the total pressure of the reaction mixture is 1 atm and the partial pressure of NOCl(g) is 0·6 atm. Calculate K_p. Assuming K_p to increase by 2% per degree rise in temperature around 200°C, find out $\Delta H°$ and $\Delta S°$ at 200°C. [4]

   c) A solute is dissolved in a mixture of two immiscible liquid solvents A and B. If in B, the solute gets dimerised, then from thermodynamic consideration, show that the ratio $C_A / \sqrt{C_B}$ will be constant at a particular temperature.

[C_A and C_B denote concentrations of solute in respective solvent] [3]

   d) For the reaction $NH_3(g) \rightleftharpoons \frac{1}{2}N_2(g) + \frac{3}{2}H_2(g)$, show that the degree of dissociation at eqilibrium, $\alpha_e = \left[1 + \frac{3\sqrt{3}}{4}\left(\frac{P}{K_P}\right)\right]^{-\frac{1}{2}}$, where P is the total pressure of the reaction vessel. [3]

Unit - II

3. a) Lindemann proposed the following mechanism

Step 1 : $A + A \rightleftharpoons A^* + A$

Step 2 : $A^* \rightarrow B + C$

Find out the rate law predicted by the above mechanism if the 2nd step is rate determining. What condition turns the expression

$\text{Rate} = \dfrac{k_1 k_2 [A]^2}{k_2 + k_{-1}[A]}$ into this result? [3]

b) One of the reactions implicated in the destruction of the O_3 layer of the atmosphere is

$NO + O_3 \rightarrow NO_2 + O_2$.

The reaction is 2nd order and the rate constant is equal to $1\cdot3\times10^6\,L\,mol^{-1}\,sec^{-1}$ at 298 K. For initial concentration of NO and O_3, both equal to $1\cdot00\times10^{-6}\,mol\,L^{-1}$. Find the concentration of NO and O_3 at time $= 2\cdot00$ sec. [3]

c) "Any reaction having order greater or equal to one does not go to completion at finite time" — Justify. [2]

d) If the rate constant of a reaction is given by $k = aT^m e^{-E_0/RT}$ where a, m and E_0 are temperature independent constant, then find out the expression of Arrhenius pre-exponential factor. [2]

e) If $8\,\mu g$ of an enzyme having single active site and molecular mass of $30000\,g\,mol^{-1}$, catalyses the hydration of $0\cdot146\,g$ of CO_2 in 30 seconds at $37°C$, what is the value of turn over number of the enzyme (in unit of s^{-1})? [3]

4. a) Rate of a chemical reaction is found to be decreased with increase in the temperature. Is it violating Arrhenius Theory? Explain. [2]

b) The rate of acid-base catalysed reaction has a minimum value at a particular pH. Find out the value of that pH and draw the plot showing the influence of pH on log (rate constant). [3]

c) What is the significance of Michaelis-Menten constant for enzyme catalysed reaction. [1]

d) Label the statements from following as either **true** or **false**. Explain why? (**any two**) : [2×2]
   i) A useful rule of thumb is that the rate of a chemical reaction doubles for each increase in temperature of $10°C$.
   ii) Termolecular steps are relatively rare in chemical reaction mechanism.
   iii) For the intramolecular rearrangement reaction,
 $CH_3 - CO - CH = CH - OH \rightarrow CH_3 - C(OH) = CH - CHO$
   entropy increase during formation of activated complex.
   iv) Pre exponential term is always $T^{\frac{1}{2}}$ dependent, according to bimolecular collision theory.

e) Draw qualitative plots (concentration vs. time) for A, B and C in a consecutive reaction $A \rightarrow B \rightarrow C$, for $k_1 = 0\cdot10\,sec^{-1}$ and $k_2 = 0\cdot5\,sec^{-1}$. [3]
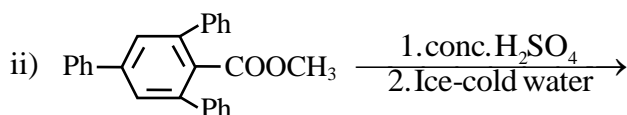
Group – B

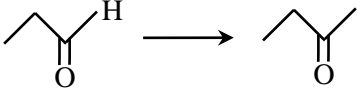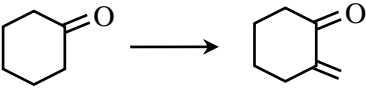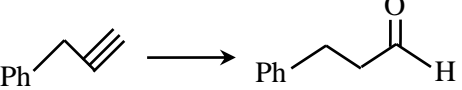[Answer **one** question from **each unit**]

Unit - I

5. a) Predict the product of the following reaction and give explanation by FMO approach : [3]
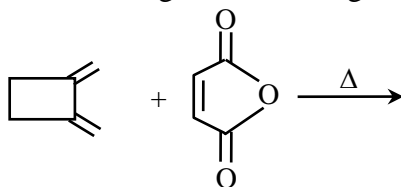

b) Predict the product (s) in the following reactions with plausible mechanism. [2×3]
   i) $(C_2H_5)_2NH \xrightarrow{HCHO,HCOOH;100°C}$

   ii)

c) What is the major product when allene is subjected to acid catalysed hydration? Give explanation. [3]

d) Alkaline hydrolysis of benzonitrile affords the salt of an acid but in presence of hydrogen peroxide, an amide is formed. Explain. [3]

6. a) Carryout the following transformations (**any three**) : [3×2]

   i)

   ii) 2-Butyne → $E-2$ - Butene

   iii)

   iv)

   b) The dithiane (*X*) is not deprotected to the corresponding carbonyl compound with acid, but $HgCl_2$ can cleave it in presence of $CdCO_3$. Explain. [3]
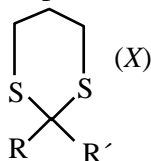
   c) Write the structures (A) to (D) in the following reaction sequence : [2]
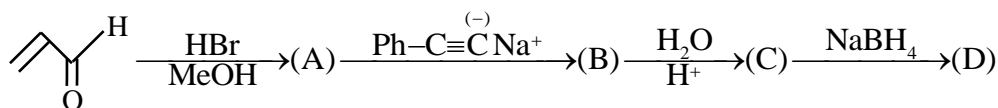
   d) Arrange the following β -ketoacids in order of their stability. Suggest explanation. [2]
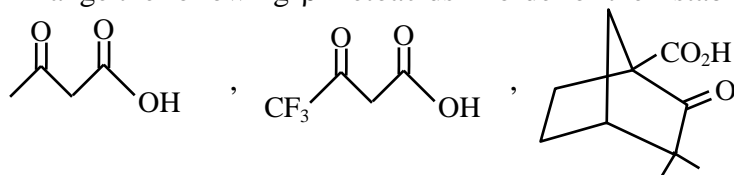
   e) Explain the role of $Li^{\oplus}$ ion in the reduction of carbonyl compounds with $LiAlH_4$ showing the mechanism. [2]

Unit - II

7. a) Compound (I) on treatment with mixed acid forms only one aromatic product of which the molecular formula is $C_8H_8N_2O_5$. Account for the reaction. [2]


   (I)
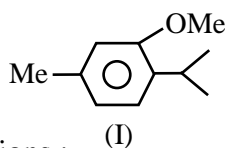
   b) Explain the following observations : [2+2]

   i) Both ortho and meta bromoanisole give the same product on treatment with sodamide in liquid ammonia.

   ii) Reaction of *p*-benzoquinone with aniline gives 2, 5-dianilino-*p*-benzoquinone while that with KCN/Conc. H_2SO_4 gives 2, 3-dicyanoquinol.

   c) Predict the product(s) of the following reactions. Give mechanism in each case (**any two**) : [2×2]

   i)

   ii)

(3)

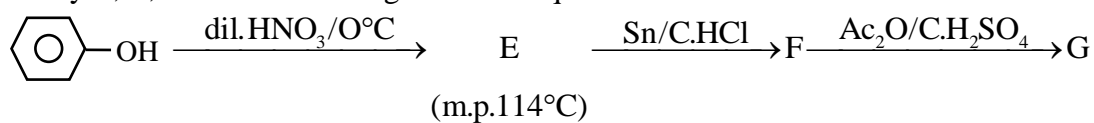iii) H_3CO—⟨O⟩ $+ (CH_3)_2N-CHO \xrightarrow{\text{POCl}_3/\Delta}$
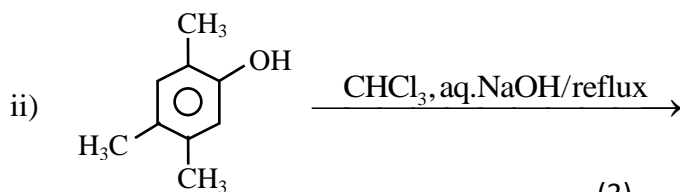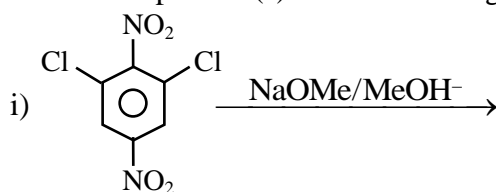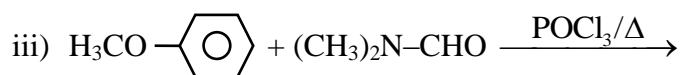
8. a) Both Phenol and Salicylic acid give identical product upon bromination —explain. [2]
   b) Predict the product(s) of the following reactions. Give mechanism. [2×2]

   i)

   $\xrightarrow[\text{NH}_3]{\text{KNH}_2}$

   ii)

   $\xrightarrow[\text{H}_2\text{SO}_4]{(\text{CH}_3\text{CO})_2\text{O}}$
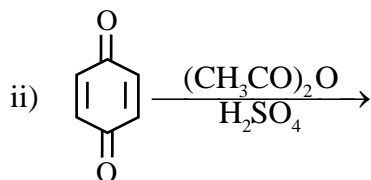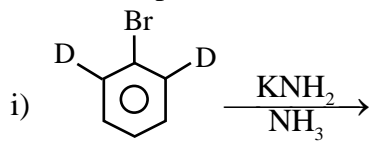
   c) Identify E, F, G in the following reaction sequence :

   ⟨O⟩—OH $\xrightarrow{\text{dil.HNO}_3/\text{O°C}}$ E $\xrightarrow{\text{Sn/C.HCl}}$ F $\xrightarrow{\text{Ac}_2\text{O/C.H}_2\text{SO}_4}$ G

   (m.p.114°C)

   Write the use of G as medicine along with its commercial name. [3+1]

   ——————— × ———————

(4)