RAMAKRISHNA MISSION VIDYAMANDIRA

(Residential Autonomous College affiliated to University of Calcutta)

B.A./B.Sc. FOURTH SEMESTER EXAMINATION, MAY 2017

SECOND YEAR [BATCH 2015-18]

Date : 18/05/2017 **CHEMISTRY (Honours)**

Time : 11 am – 1 pm **Paper :** IV [Gr-A&B] Full Marks : 50

[Use a separate Answer Book for <u>each group</u>]

<u>Group - A</u>

(*Attempt <u>one</u> question from <u>each Unit</u>*)

<u>Unit I</u> [13 marks]

1. a) Define ionic mobility. What is its unit in SI? Find out the relation between ionic conductance and ionic mobility. [1+3]

   b) Set up a cell without liquid junction potential for the process $HCl(a_1) \rightarrow HCl(a_2)$ where a_1 and a_2 are the activities of the electrolytes. Write the cell reactions at the electrode. [3]

   c) At 298K the potential of the cell,
   Pt(s) | H_2(g, p = 1 atm) | H_2SO_4 (aq solution) | Hg_2SO_4 (s) | Hg (l)
   is 0·61201 V in 4m H_2SO_4 solution. Given E° = 0·61515 V. Calculate the mean ionic activity coefficient in 4m H_2SO_4 solution. [3]

   d) Find out cells having the cell reactions
   (i) $NiO(s) + Fe = Ni + FeO(s)$ and (ii) $H_2(g) + \frac{1}{2}O_2(g) = H_2O(l)$ [3]

2. a) "For any cell, reversible as well as irreversible, $nFE° = RT\ln K_{eq}$ holds good." Comment. [2]

   b) Devise a cell for the reaction, $\frac{1}{2}H_2(g) + AgCl = Ag + H^+ + Cl^-$, calculate E of the cell at 25°C if ΔG for the reaction is –34·012KJ at 25°C. Would E of the cell change if we write the reaction as $H_2(g) + 2AgCl = 2Ag + 2H^+ + 2Cl^-$? [4]

   c) The equivalent conductance of LiCl at infinite dilution is $115·03 \times 10^{-4}$ S m^2/mol. The cationic transport number is 0·336. Calculate the mobility of the cation and its velocity if the applied potential difference across two electrodes, 0·4cm apart, is 6·0 volt. [3]

   d) i) At 25°C, the specific conductances of a saturated solution of $SrSO_4$ and that of water used are $1·5 \times 10^{-4}$ mho.cm^{-1} and $1·5 \times 10^{-6}$ mho.cm^{-1} respectively. Calculate solubility in gm.lit^{-1} if M.Wt of $SrSO_4$ = 182. Given, $\Lambda^o_{\frac{1}{2}SrCl_2} = 135·8$, $\Lambda^o_{\frac{1}{2}K_2SO_4} = 153·5$ and $\Lambda^o_{KCl} = 149·85$ (all are in unit of mho·cm^2·gm-eq^{-1}). [3+1]

<u>Unit II</u> [12 marks]

3. a) For any gas, given that, $\mu = \mu(T) + RT\ln P + BP$ where B is independent of temperature and pressure. Find equation of state of the gas. [2]

   b) Two grams of benzoic acid dissolved in 25 gm of benzene, K_f = 4·90 Kkg mol^{-1}, produce a freezing point depression of 1·62K. Calculate the molar mass. Comment on the difference if any of this value with the molar mass calculated from the formula for benzoic acid. [3]

   c) An aqueous solution of sucrose freezes at –0·2°C. Calculate the normal boiling point and the molality of an aqueous solution of NaCl having the same vapour pressure as that of sucrose solution. Given, K_f for H_2O = 1·86 K.kg.mol^{-1} and K_b = 0·52 K.kg.mol^{-1} . Assume NaCl to be completely ionized. [3]

d) Comment whether the osmotic pressure of a real solution is greater than, less than or same as that of the value calculated if the solution was ideal. [2]

e) Offer an explanation to the phenomena of elevation of boiling point of a solvent due to the presence of solute in terms of entropy change of vaporization. [2]

4. a) i) Prove that $\ln\gamma = \int_0^P \frac{Z-1}{P'}dP'$.

ii) Show that for a gas that obeys the equation of state P(V–b) = RT fugacity coefficient γ is given as $\gamma = \exp(bP/RT)$. [3+2]

b) How would volatile solute affect ΔT_b? Give plausible reasons. [3]

c) Shat that $\Delta T_f > \Delta T_b$ from chemical potential Vs. temperature diagram assuming that the solute is non-volatile and does not dissolve in solid solvent. [2]

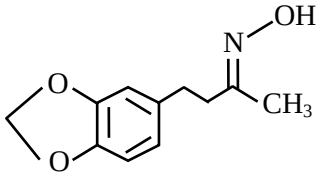
d) What are the values of ΔV_{mix} and ΔH_{mix} for ideal binary solution? Give molecular interpretation to justify your answer. [2]

Group - B

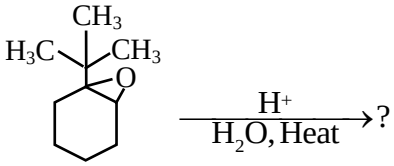
(*Attempt one question from each Unit*)

Unit III [15 marks]

5. a) What happens when the following compound is treated with PCl_5? [3]



b) Predict the product of the following reaction with possible mechanism : [3]



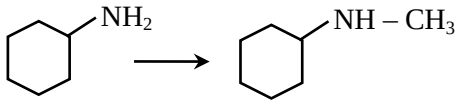
c) Comment on the following : [2]

i) Excess diazomethane is recommended for Arndt-Eistert synthesis.

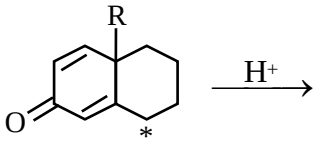
ii) Choice of phthalimide in the Gabriel's method for the synthesis of pure primary amine.

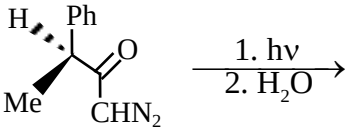
d) Carry out the following conversions : [1·5×2]

i) $Me_3CCl \rightarrow Me_3CNH_2$

ii) 

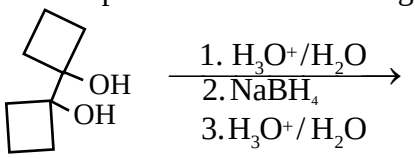
e) Predict the product(s) of the following reactions. Give mechanism. (**any two**) : [2×2]

i) 

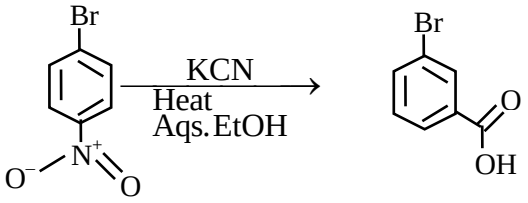
ii) 

iii) 

6. a) Predict the product of the following reaction with possible mechanism : [4]



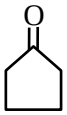
b) Provide the stepwise mechanism for the following reaction :



What will happen if ^{15}N-labeled is used in this transformation? [4+1]

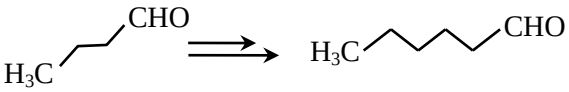
c) Outline the preparation of a dry ethereal solution of diazomethane from N-nitrosomethylurea in the laboratory. Give mechanism. What happens when diazomethane is treated with the following compounds. [6]

i) 

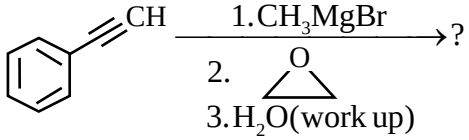
ii) 

Unit IV [10 marks]

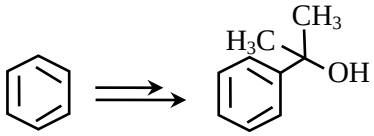
7. a) Outline the following synthesis with retrosynthetic approach : [3]



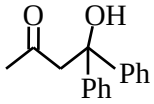
b) Give the major product of the following reaction : [4]

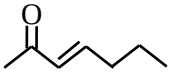


c) Propose a synthesis with retrosynthesis approach : [3]

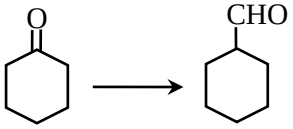


8. a) Give retrosynthetic analysis and outline an efficient synthesis of the following compounds : [2·5×2]

i) 

ii) 

b) Carry out the following conversions. [1·5×2]

i) 

[Use Wittig reaction]

ii) $Me-C\equiv C-H \rightarrow Me-C\equiv C-CH_2CH_2OH$ [Use MeMgBr]

c) Predict the major product of the following reactions. [2×1]

i) $PhCH_2Cl \xrightarrow[n-pentane]{Li}$

ii) $Ph-CH_2MgBr + HCHO \rightarrow$

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