RAMAKRISHNA MISSION VIDYAMANDIRA

(Residential Autonomous College under University of Calcutta)

SECOND YEAR

B.A./B.Sc. FOURTH SEMESTER (January – June) 2015

Mid-Semester Examination, March 2015

Date : 18/03/2015 **CHEMISTRY (Honours)**

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

[Use a separate answer book for each group]

Group – A

Attempt <u>any one</u> question :

1. a) Define 'ionic mobility' of an ion. At 18°C, ionic mobilities of NH_4^+ and ClO_3^- ions are $6{\cdot}6\times10^{-4}$ and $5{\cdot}7\times10^{-4}$ $cm^2volt^{-1}s^{-1}$ respectively. Calculate Λ° of the salt and transport number of chlorate ion. [1+2]

   b) Find out the value of ionic product of water at 25°C from the given data. At 25°C, Λ° of water is $548{\cdot}1\times10^{-4}Sm^2mol^{-1}$ and κ is $5{\cdot}5\times10^{-6}Sm^{-1}$. Use unit standard concentration as 1 $moldm^{-3}$. [3]

   c) Form an electrochemical cell having the cell reaction $H_2O = H^+ + OH^-$. The value of E° of the right hand electrode of this cell is –0·828 volt at 25°C. What useful information can you get about the system besides the cell emf? [2]

2. a) Discuss the moving boundary method of determination of ionic transport number. [2]

   b) Equivalent conductances at infinite dilution of HCl, NaCl and CH_3CO_2Na are 426·2, 126·5 and 91 Scm^2equiv^{-1}. A cell filled with 0·01 M KCl solution has a resistance of 257·3 ohm at 25°C. The same cell filled with 0·2 M acetic acid solution has a resistance of 508·6 ohm at 25°C. Specific conductance of 0·01 M KCl solution is $1{\cdot}41\times10^{-3}$ Scm^{-1}. Calculate the dissociation constant of the acid. [3]

   c) The emf of the cell $Zn|ZnCl_2$ (m = 0·01021) $|AgCl(s)|Ag$ is found to be 1·1566 volt at 25°C. Find out the mean activity and the mean activity coefficient of $ZnCl_2$ in this solution at 25°C. Given, E° of Zn^{+2} | Zn electrode is –0·763 volt at 25°C. [3]

Attempt <u>any one</u> question :

3. a) Starting with the condition for solid-liquid equilibrium, deduce the condition under which a solvent's freezing point might be elevated due to the dissolution of solute in it. [3]

   b) Justify or criticize —phenomena like freezing point depression or boiling point elevation are consequences of solute-solvent interaction. [2]

   c) Offer a qualitative explanation to the phenomena of boiling point elevation of a solvent due to solute dissolved in it in the light of entropy change of the process. [3]

4. a) Draw and explain the nature of a μ vs T curve for the three states of a pure substance. [3]

   b) Point out the boiling and the freezing points in the above diagram. [1]

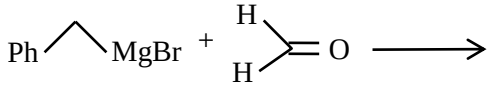
   c) Draw and explain how the above diagram changes when a solute is added to the liquid state of the substance. (Assume that this solute does not go to the solid or vapor phase). [2+1]

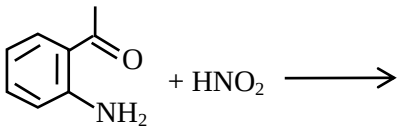
   d) Show in the diagram how the boiling and the freezing points of the solvent changes due to the solute. [1]

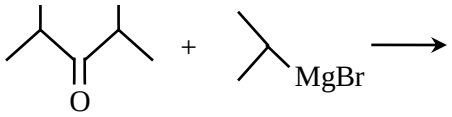
Group – B

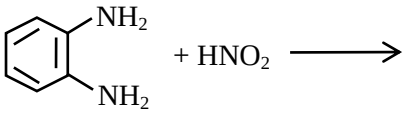
Attempt <u>any one</u> question :

5. a) Predict the major product of the following reactions : [1×4]

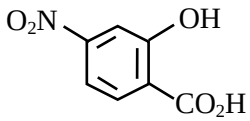
i) 

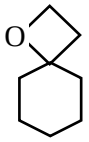
ii) 

iii) 

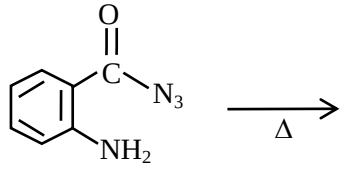
iv) 

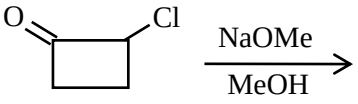
b) Give retrosynthetic analysis and an efficient synthesis of the following starting from RASM. [2×2]

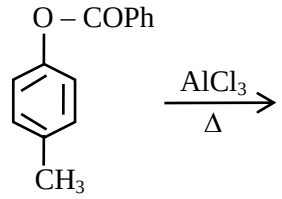
i) 

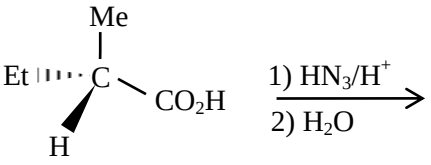
ii) 

c) Predict the products with mechanism : [4×2]

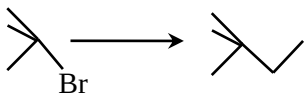
i) 

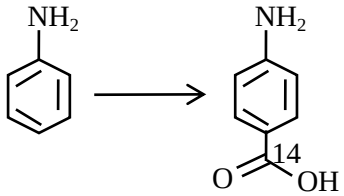
ii) 

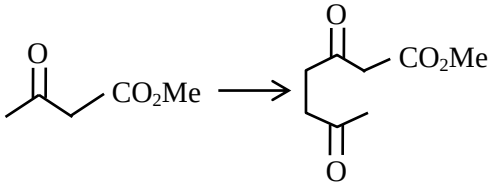
iii) 

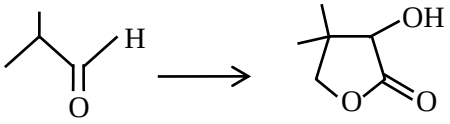
iv) 

6. a) Carryout the following conversions : [4×2]

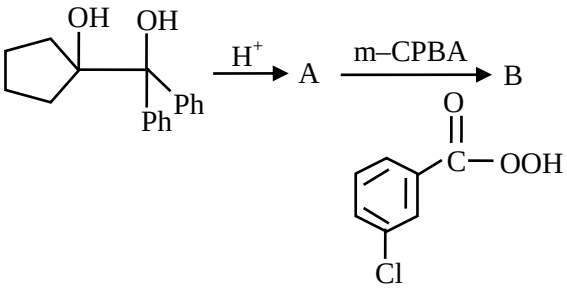
i) 

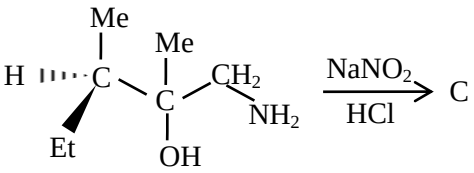
ii) 

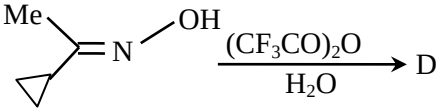
iii) 

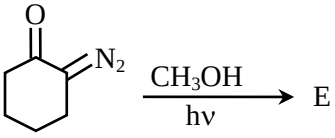
iv) 

b) Predict the products of the following reactions with mechanism. [4×2]

i) 

ii) 

iii) 

iv) 

Group – C

Attempt <u>any one</u> question :

7. a) Why is $N(SiH_3)_3$ and $N(CH_3)_3$ on reaction with HCl give different products? Explain with equations. [2·5]

   b) Why the molecular formula of nitrogen and phosphorous is different? Explain chemically and thermodynamically (Given bond energy in KJ mol^{-1}] $P \equiv P - 490, N \equiv N - 946, P - P = 209$ and $N - N = 160$. [2·5]

8. a) Briefly explain the proton affinity of NH_3, PH_3 and AsH_3 and the stability of their ium salts at water. [3]

   b) Comment about the Ligand properties of NF_3 and PF_3 with example(s). [2]

Attempt <u>any one</u> question :

9. a) Melting points of tin halides are given below. SnF_4 [705°C], $SnCl_4$ [–33°C], $SnBr_4$ [31ºC], SnI_4 [144·5°C]. Explain the order. [3]

   b) Silanes have good thermal stability and water repellant property. Explain. [2]

   c) Catenation in silanes are found to be much less than that in alkanes. Explain. [2]

10. a) When SnF_2 is added to an aqueous solution containing fluride ions, a set of anions are produced. Write down the structure of these anions [upto trimers] stating their mode of hybridisation. [3]

    b) Explain the action of conc. HNO_3 on red lead. [2]

    c) Explain the electrical conductivity of graphite. The conductivity increases after intercalation with alkali metals. Justify. [2]

Attempt <u>any three</u> questions : [3×2]

11. a) Explain why a solution of borax is a good buffer solution.

    b) AlF_3 dissolves appreciably in anhydrous HF, only when KF is also present. But AlF_3 is reprecipitated when BF_3 is passed into the solution.

    c) What happens when B_2H_6 is separately treated with NH_3 and PH_3?

    d) All synthesis of BH_3, result formation of B_2H_6, explain.

    e) What happens when chlorine water is added to an aqueous solution of KBr and the mixture is shaken with CCl_4?

    f) Neither BrF_3 nor ClF_3 are good conductors of electricity but a mixture of the two makes a good conductor, explain.

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