RAMAKRISHNA MISSION VIDYAMANDIRA

(Residential Autonomous College under University of Calcutta)

B.A./B.Sc. FOURTH SEMESTER EXAMINATION, MAY 2014

SECOND YEAR

Date : 22/05/2014 **CHEMISTRY (Honours)**

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

[Use Separate Answer Scripts for each group]

Group – A

(*Answer **one** question from each unit*)

Unit – I

1. a) Discuss how the equivalent conductance of a solution of strong electrolyte varies with dilution. How can you experimentally determine equivalent conductance of a strong electrolyte at infinite dilution? [4]

   b) Define transport number of an ion.

   Show that for a solution of a single electrolyte, $t_+ = \frac{u_+}{u_+ + u_-}$. How does the transport number of Cl^- ion, in 0·1(N) HCl, vary with increasing temperature? [3]

   c) Arrange the following electrolytes in the decreasing order of Λ_0: HCl, LiCl, NaOH, KCl [2]

   d) Discuss a method for the experimental determination of E° of Cl^-(Ag)|AgCl(s)|Ag electrode using the cell H_2(g,1bar) | HCl solution |AgCl(S) |Ag

   How can the mean ionic activity co-efficients of HCl at different molalities be calculated using this method? [4]

2. a) The specific conductances of solutions of an electrolyte at different concentrations are plotted against respective conductances, measured using the same cell. What will be the nature of the plot obtained and what information can be obtained from it? [2]

   b) A solution of $MgSO_4$ is titrated conductometrically using a solution of $Ba(OH)_2$. Draw the conductometric titration curve obtained and explain its nature. [3]

   c) The equilibrium constant for the reaction $2Cu^+ = Cu^{2+} + Cu(s)$ at 25°C is $1·646\times10^6$. [3]

      i) Construct a cell in which this reaction could occur

      ii) Calculate E° of the cell at 25°C

      iii) Evaluate $E°_{Cu^+|Cu}$ at 25°C

      (Given, $E°_{Cu^{2+}|Cu} = 0·153$ volt at 25°C)

   d) Derive the expression for e.m.f of the following electrolyte concentration cell without transference indicating the overall reaction. [5]

   H_2(g, 1 atm) | HCl(a_1), AgCl(s) | Ag-Ag | AgCl(s), HCl (a_2) | H_2(g, 1 atm)

Unit – II

3. a) Define chemical potential μ_i of a substance i in a mixture in terms of Gibbs potential. Why is μ_i often referred to as the escaping tendency of the substance i? [2]

   b) Discuss the graphical method for the determination of fugacity of a gas. [3]

   c) An exactly 1 molal aqueous solution of mannitol has a vapour pressure of 17·222 mm of Hg at 20°C, at the same temperature the vapour pressure of pure water is 17·535 mm of Hg. Calculate the activity and activity coefficient of water in the given solution. [3]

   d) For CCl_4 , K_b = 5·03 K kg/mol. If 3·00g of a substance in 100g CCl_4 raises the boiling point by 0·60K, calculate the relative vapour pressure lowering and the osmotic pressure of the solution at 300K. The density of CCl_4 is 1·59g/cm^3 and its molar mass is 154g/mol. [4]

4. a) Prove the following relations : [2+2]

i) $\left(\frac{\partial \mu_i}{\partial P}\right)_{T,N} = \bar{v}_i$

ii) $\left(\frac{\partial H}{\partial n_i}\right)_{S,P,n_{j\neq i}} = -T\left(\frac{\partial S}{\partial n_i}\right)_{u,v,n_{j\neq i}}$

b) Is the lowering of chemical potential of a solvent in ideal solution an enthalpy effect or an entropy effect? Explain. [3]

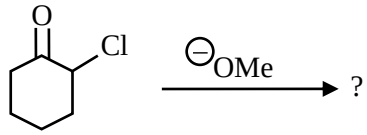
c) 1 mole of hexane is mixed with 1mole of heptane at 298 K. Calculate the values of ΔG_{mix}, ΔS_{mix}, ΔH_{mix} and ΔV_{mix}. Treat the solution as ideal. [5]

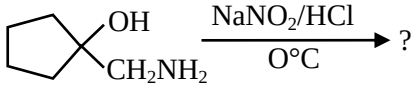
Group – B

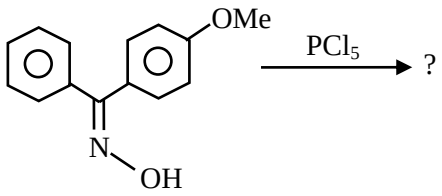
(*Answer **one** question from each unit*)

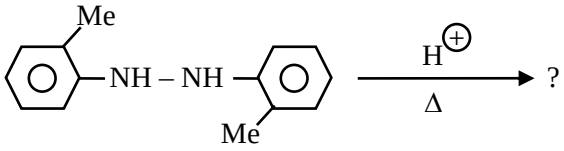
Unit – I

5. a) Predict the product(s) of the following reactions and Give mechanism for each case (**any three**) [3×2]

i) 

ii) 

iii) 

iv) 

b) Why is excess diazomethane used in the Arndt-Eistert Synthesis? [2]

c) Alkaline hydrolysis of benzonitrile affords a salt of benzoic acid but that of 2,6-dimethyl benzonitrile gives the corresponding amide. Explain. [3]

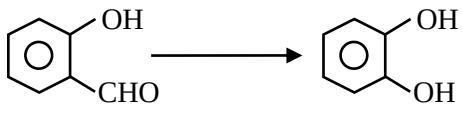
d) Carryout the following conversions (**any two**) : [2×2]

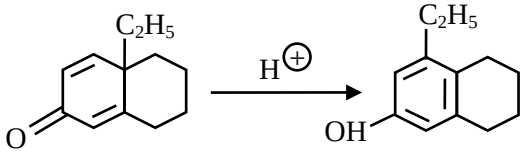
i) Piperidine ⟶ 1,4-Pentadiene.

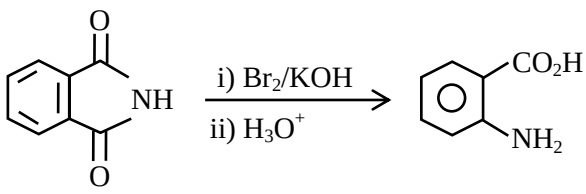
ii) *p*-Nitrotoluene ⟶ *m*-Nitrotoluene

iii) Nitrobenzene ⟶ *p*-Hydroxyaniline

6. a) Carryout the following conversions and explain the mechanism involved (**any two**) [2×2]

i) 

ii) 

iii) 

b) Two isomeric pinacols $Ph_2C(OH)C(OH)Me_2$ and PhMeC(OH)C(OH)PhMe undergo acid catalysed rearrangement to give a common product. Explain [2]

c) Identify the product(s) of the following reaction with plausible mechanism : [2×2]

i) $R-COCl \xrightarrow{NaN_3} ? \xrightarrow[ii)\,Water]{i)\,\Delta} ?$ ii)  $+ N_2CHCO_2Et \xrightarrow{h\gamma}$

d) Explain why *t*-butyl amine cannot be prepared by Gabriel synthesis. Propose a syntheis of *t*-butylamine. [2+1]

e) What happens when (**<u>any one</u>**) : [2]

i) *m*-phenylene diamine is treated with nitrous acid in cold condition.

ii) *o*-phenylene diamine is treated with Glyoxal.

<u>Unit – II</u>

7. a) Give synthetic equivalents corresponding to the following synthons : [2]

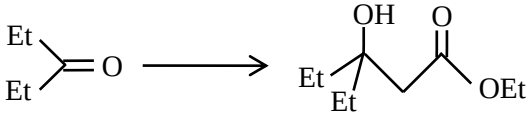
i) $^{\oplus}CH_2-CH_2OH$ ii) $^{\ominus}CH_2CO_2H$

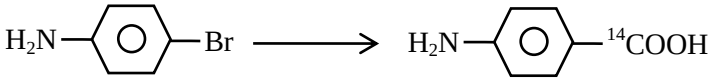
b) Write the structure of the product(s) of the following reactions and explain. [2+3]

i) $(Me_2CH)_2C=O \xrightarrow[ii)\,H_3O^+]{i)\,Me_2CHMgBr} ?$

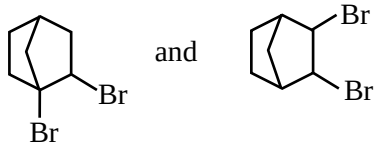
ii) $PhCH=CH-\overset{O}{\overset{\|}{C}}-Ph$ → (MeLi) ?; (Me_2CuLi) ?

c) Carryout the following conversions using organometallic compounds. [1½×2]

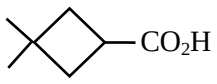
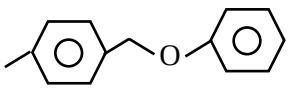
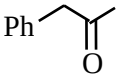
i) 

ii) 

8. a) Explain which of the following compounds can form a suitable Grignard reagent and which can not. [2]



b) Give a retrosynthetic analysis and efficient synthesis of **<u>any two</u>** of the following compounds : [2×3]

i)  ii)  iii) 

c) Synthesize the following compound with reasonable route. [2]