

RAMAKRISHNA MISSION VIDYAMANDIRA

(Residential Autonomous College under University of Calcutta)

B.A./B.Sc. FOURTH SEMESTER EXAMINATION, MAY 2015

SECOND YEAR

CHEMISTRY (Honours)

Paper : IV

Date : 21/05/2015

Time : 11 am – 1 pm

Full Marks : 50

[Use a separate Answer Book for each group]

Group – A

Unit - I

[Answer any one question]

1. a) At 25°C, resistance of a cell filled with 0.01N KCl solution is 525 ohm. The resistance of the same cell filled with saturated solution of SrSO₄ is 4990 ohm. The specific conductance of water used is $1.5 \times 10^{-6} \text{ Scm}^{-1}$ and that of 0.01 N KCl solution is $1.4087 \times 10^{-4} \text{ Scm}^{-1}$ at 25°C. Determine the solubility of SrSO₄ in g/L unit at 25°C. (Atomic weight of Sr = 87.62) [3]
- b) A cell comprising a glass electrode and a saturated calomel electrode is used to measure pH of buffer solutions. Using a buffer of pH 4.0, emf of this cell is found to be 0.1120 volt. When a buffer of unknown pH is used, the potential of the cell is found to be 0.3865 volt. What is the pH of this buffer solution? [2]
- c) Standard potential of Ag⁺/Ag electrode is 0.7991 volt. For AgI, the value of solubility product is 8.7×10^{-17} . What will be the potential of the Ag⁺/Ag electrode in a saturated solution of AgI? Calculate the standard potential of the I⁻ | AgI(s) | Ag electrode. Assume the temperature to be 25°C. [3]
- d) Using Debye-Hückel limiting law calculate the mean ionic activity coefficient of 0.001(M) aqueous solution of K₃[Fe(CN)₆] at 25°C. [Debye-Hückel constant = 0.51 at 25°C] [2]
- e) The emf (E) of galvanic cell changes with temperature accordingly $E = a + bT + cT^2$, where a, b, c are the constants. If n be the number of electrons exchanged for the cell reaction, evaluate ΔS , ΔH and ΔC_p in terms of a, b, c and T. [3]
2. a) The solubility of a sparingly soluble salt increases in presence of added electrolytes without a common ion—explain. [2]
- b) Depict a cell which may be used to determine the solubility product (K_{sp}) of AgBr. If $E^\circ_{\text{Br}^-/\text{AgBr}/\text{Ag}} = 0.071 \text{ V}$ and $E^\circ_{\text{Ag}^+/\text{Ag}} = 0.799 \text{ V}$ at 25°C, find out the value of K_{sp} at 25°C. [3]
- c) The emf of the cell Zn(S) | ZnCl₂ (m = 0.01021 mol/kg) | AgCl(s) | Ag(s) was found to be 1.1566V. What is the mean ionic activity coefficient of ZnCl₂ in the solution? [3]
[$E^\circ_{\text{Cl}^-/\text{AgCl}/\text{Ag}} = +0.222 \text{ V}$, $E^\circ_{\text{Zn}^{2+}/\text{Zn}} = -0.762 \text{ V}$]
- d) Consider the following concentration cell with transport,
 $\text{Ag} | \text{AgCl(s)} | \text{KCl solution } (a_1) : \text{KCl solution } (a_2) | \text{AgCl(s)} | \text{Ag}$ where a_1 , a_2 are mean ionic activities of two solutions. [3]
- e) What will be the expected values of equivalent and specific conductances of 0.1 N NH₄OH solution at 25°C? Given, $\Lambda_0 = 271.4 \text{ Scm}^2 \text{ mol}^{-1}$ and $K_b = 1.81 \times 10^{-5}$ for NH₄OH. [2]

Unit - II

[Answer any one question]

3. a) Derive the expression for osmotic pressure of an ideal solution of a nonvolatile solute in terms of its molar concentration. [4]

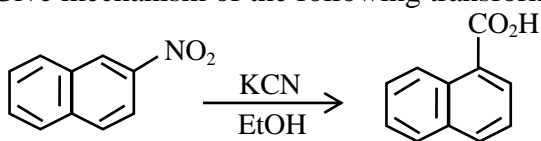
- b) 1 mol of hydrogen gas at 0°C and 1 atm pressure is mixed adiabatically with another mol of the same gas at 100°C and 1 atm pressure to yield a mixture whose pressure is also 1 atm. Assuming hydrogen to behave ideally, calculate the value of ΔS for this mixing process. [2]
- c) Freezing point of a solution may be increased in presence of a solute —justify or criticise. You may use a graphical plot to illustrate your answer. [3]
- d) If α be the departure of volume from ideal behaviour and $\ln f = \ln P - \frac{1}{RT} \int_0^P \alpha dP$, then show that at low pressure, $f = zP$, where f and z are fugacity and compressibility factor, respectively. [3]
4. a) Derive an expression for Gibbs potential of isothermal mixing for a number of ideal gases. [2]
- b) Find out an expression for the chemical potential of the solvent of an ideal solution as a function of mol fraction of the solvent in solution. [3]
- c) Benzoic acid dimerises when dissolved in benzene. The osmotic pressure of a solution of 5g of benzoic acid in 100ml of benzene is 5.73 atm at 10°C. Find out the van't Hoff factor and degree of dissociation. [3]
- d) Show that
- i) $\left(\frac{\partial \mu_i}{\partial T}\right)_{P, n_i, n_j} = -\left(\frac{\partial S}{\partial n_i}\right)_{P, T, n_j (j \neq i)} = -\frac{\mu_i}{T}$
- ii) $\mu_i = \left(\frac{\partial E}{\partial n_i}\right)_{S, V, n_j (j \neq i)}$ (the terms have their usual significance) [2+2]

Group – B

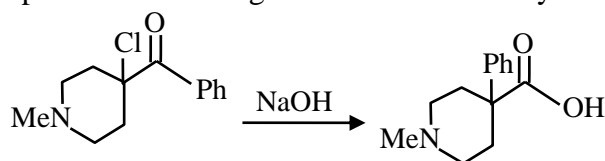
Unit - I

[Answer any one question]

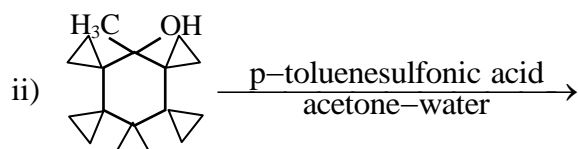
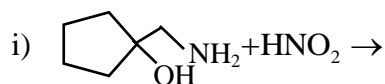
5. a) Give mechanism of the following transformation [3]



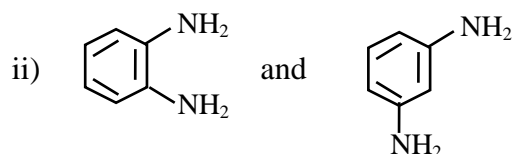
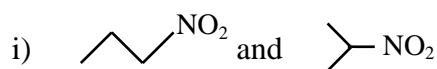
- b) “The mechanism of Dakin reaction may be similar to that of the Baeyer-Villiger reaction.” Justify (with possible mechanism). [3]
- c) Explain the following result mechanistically : [4]



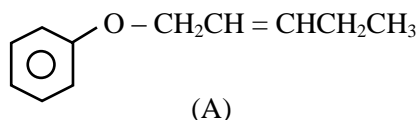
- d) Predict the product of the following reactions. Give mechanism. [2×2.5]



6. a) Suggest chemical reactions to distinguish between the members of each of the following pairs : [2×2]



- b) *p*-Toluidine reacts with benzenediazonium chloride to form a compound which, on boiling with dil H_2SO_4 , gives four products (excluding nitrogen) Write the products with appropriate mechanism. [3]
- c) Give the structure of the products when the following compound (A) is heated. Explain the result with plausible mechanism. [4]

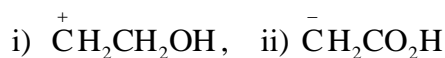


- d) The nitration of phenylboronic acid, $\text{PhB}(\text{OH})_2$, with mixed acid -20°C gives predominantly the *m*-derivative. With $\text{HNO}_3\text{-Ac}_2\text{O}$, the predominant product is the *O*-derivative. Suggest an explanation. [2]
- e) What is the product of the reaction of styrene with diazomethane? Explain. [2]

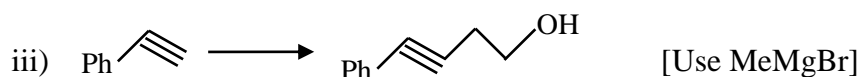
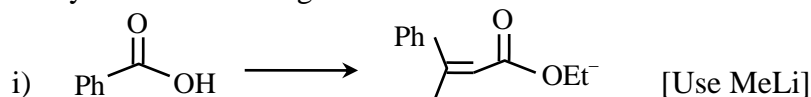
Unit - II

[Answer any one question]

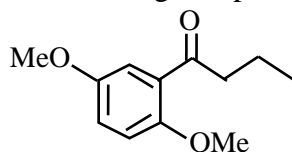
7. a) Give the synthetic equivalents corresponding to the following synthons : [1]



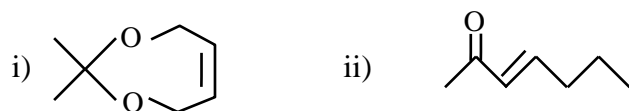
- b) Carry out the following conversions. Mechanism is not necessary. [2×2]



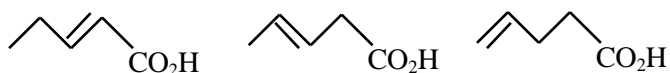
- c) Explain why the synthesis of $\text{Me}_3\text{-C}(\text{H})=\text{C}(\text{H})\text{-CMe}_3$ can not be accomplished by the Wittig reaction? [2]
- d) How could you prepare the following compound using *ortho*-lithiation procedures? [3]



8. a) Give retrosynthetic analysis and efficient synthesis of the following : [2×2]



- b) Show how the relationship between the alkene and the carboxylic acid influences your suggestions for a synthesis of these unsaturated acids. [6]



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