

RAMAKRISHNA MISSION VIDYAMANDIRA

(Residential Autonomous College affiliated to University of Calcutta)

B.A./B.Sc. FOURTH SEMESTER EXAMINATION, MAY 2016

SECOND YEAR [BATCH 2014-17]

CHEMISTRY (Honours)

Paper : IV [Gr. A&B]

Date : 18/05/2016

Time : 11 am – 1 pm

Full Marks : 50

[Use a separate Answer Book for each group]

Group – A

[Attempt one question from each Unit]

Unit – I

1. a) for an weak electrolyte HA, variation of $\frac{1}{\Lambda_{eq}}$ with $\Lambda_{eq}C$ gives a straight line with unit slope. Derive the expression of Λ_{eq} in terms of dissociation constant and degree of dissociation. [3]
- b) A conductivity cell has a resistance equal to 250 ohm with 0.02 (N) KCl solution and 10^5 ohm with 6×10^{-5} (N) NaOH solution at 25°C. If the specific conductance of 0.02 (N) KCl is 0.00277 ohm⁻¹cm⁻¹ and $\lambda_{NH_4^+}^0 = 73.4$ ohm⁻¹cm²eqv⁻¹ and $\lambda_{OH^-}^0 = 198$ ohm⁻¹cm²eqv⁻¹ at 25°C, calculate the dissociation constant of NH₄OH. [4]
- c) At 25°C, ΔG of formation of H₂O (l) is -237.244 KJ mol⁻¹ and that of its ionization into H⁺ and OH⁻ ions is 79.709 KJ mol⁻¹. What will be reversible emf of the following cell at 25°C?
Pt | H₂(g,1atm) | H⁺ || OH⁻ | O₂(g,1atm) | Pt [3]
- d) Construct a cell in which the reaction is $AgBr(s) \rightleftharpoons Ag^+ + Br^-$.
 $E_{AgBr/Br^-/Ag}^0$ (reduction) = 0.071V and $E_{Ag^+/Ag}^0 = 0.799V$ at 25°C. Calculate K_{sp} of AgBr at 25°C. [3]
2. a) Find out the expression for emf of the following concentration cell
Ag | AgCl(s) | HCl soln(a₁) : HCl soln(a₂) | AgCl(s) | Ag
where a₁ and a₂ are the mean activities of two HCl solutions. [3]
- b) The equivalent conductance of LiCl at infinite dilution is 115.03×10^{-4} Sm²mol⁻¹. The transport number of the cation is 0.336. Calculate the mobility of Li⁺ ion and its speed if 6.0 volt is applied across the electrodes 4.0 cm apart. [3]
- c) The potential of the cell Zn | ZnCl₂ soln(m = 0.01021) | AgCl(s) | Ag is 1.1566 volt at 25°C. What is the mean ionic activity co-efficient of ZnCl₂ in this solution?
($E_{Zn^{2+}/Zn}^0 = -0.7618$ volt, $E_{Cl^-|AgCl(s)|Ag}^0 = 0.2225$ volt) [3]
- d) Construct a galvanic cell where the net reaction is $H_2 + \frac{1}{2}O_2 \rightarrow H_2O$. [2]
- e) Discuss the principle of moving boundary method for determination of transport number of an ion in an electrolytic solution. [2]

Unit – II

3. a) Show that osmotic pressure, π of a dilute solution is proportional to the concentration of solute at a constant temperature. [4]
- b) An organic acid (molar mass = 60) associates in benzene to form a dimer when 1.65 g of the acid is dissolved in 100g benzene, the boiling point is raised by 0.36°C. Calculate the degree of dissociation of the acid in benzene. [$K_b = 2.6$ Kg K mol⁻¹] [3]
- c) Define an ideal solution in terms of chemical potential. [2]

d) Given that fugacity of a gas (γ) can be expressed as $\ln \gamma = \int_0^P \frac{z-1}{P} dP$ derive (and also plot) how γ varies with P at a constant temperature for a gas that obeys the law $P(\bar{V} - b) = RT$. [3]

4. a) Show that—

i) $\left(\frac{\partial \bar{V}_i}{\partial T} \right)_P = - \left(\frac{\partial \bar{S}_i}{\partial P} \right)_T$.

ii) $\left(\frac{\partial A}{\partial n_i} \right)_{P,T,n_j(j \neq i)} = \left(\frac{\partial H}{\partial n_i} \right)_{P,S,n_j(j \neq i)}$ (The used terms have their usual significance). [2+2]

b) Starting with the van't Hoff isochore corresponding to the equilibrium constant for the equilibrium between a solution and frozen solvent, show that the freezing point (T_f) of the solvent in solution decreases linearly with solute molality (m) for very dilute solutions. [3]

c) Justify or criticize : Lowering of freezing point is an entropy effect. [2]

d) At 25°C a solution containing 2.50 gm of a substance in 250.0 cc of solution exerts an osmotic pressure of 400 pascal. What is the molar mass of the substance? [3]

Group - B

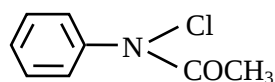
[Attempt one question from each Unit]

Unit – III



Predict the products of the above reactions, with plausible mechanism in each case.

iii) Delineate the mechanism of Orton rearrangement of [2]

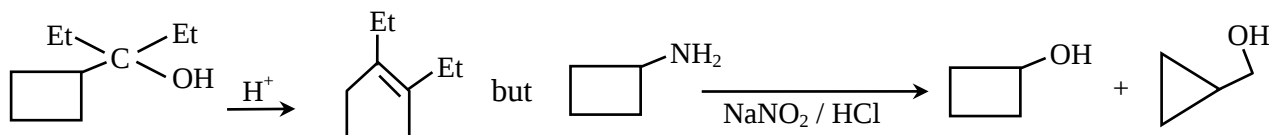


b) Alkaline hydrolysis of C_6H_5CN affords the salt of an acid but in the presence of H_2O_2 an amide is formed; explain. [2]

c) Explain the feature of higher stability of a diazoacetic ester compared to that of diazomethane. [2]

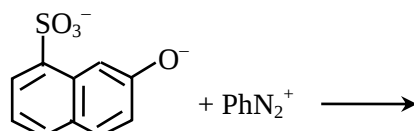
d) Write the product and reaction mechanism of C_6H_6 with ethyl diazoacetate in the presence of an appropriate radiation. [2]

e) Explain the following sets of reaction, give proper explanation. [3]



6. a) Two isomeric α -chloroketones having the molecular formula C_9H_9ClO , when treated separately with aqueous NaOH, give the sodium salt of β -phenylpropionic acid. Explain with mechanism. [3]

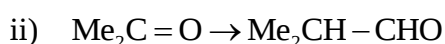
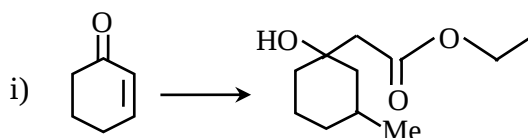
b) Predict the product of following reaction and write the mechanism. Comment on the rate-determining step and pH of the reaction medium. [3]



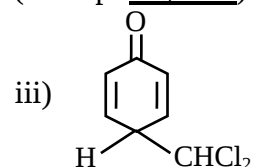
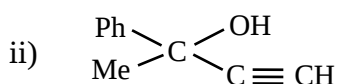
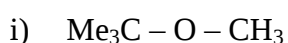
- c) Arndt-Eistert reaction of an acyl chloride requires two molar quantities of diazomethane. What is the role of the second molecule of diazomethane? Show the mechanism of the reaction involving a migration process, induced generally by moist Ag_2O . The reaction can be used for homologation of a carboxylic acid (RCO_2H) to $\text{RCH}_2\text{CO}_2\text{H}$; explain. [4]
- d) $\text{ClCH}_2\text{COO}^-\text{Na}^+$ can be converted to CH_3NO_2 with the help of an aqueous solution of sodium nitrite. Explain the transformation. [2]
- e) N, N, N- trimethylanilinium chloride undergoes reaction on strong heating (300°C) to produce a primary amine hydrochloride. What is the role of high temperature? Show the development in a stepwise manner. [3]
- Phenylhydrazine hydrochloride is heated at 250°C to afford two products of which one is produced in major. Explain the reaction.

Unit – IV

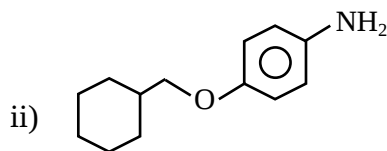
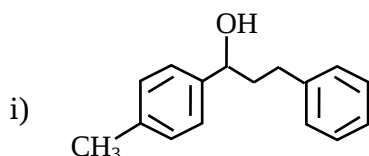
7. a) Ethyl acetoacetate reacts with one molar proportion of methyl magnesium bromide; explain the reaction. [1]
- b) Show the steps occurring in the reaction of $\text{R}_2\text{C}=\text{O}$ with RMgX (OEt_2). [2]
- c) Show steps for reaction of alkyl Lithium (RLi) with an appropriate starting material for generating $\text{R}_2\text{C}=\text{O}$. [1]
- d) Reaction of isopropyl magnesium bromide with diisopropyl ketone produces diisopropyl carbinol; explain. [2]
- e) Use appropriate organometallic reagents to carryout the following conversions. [2×2]



8. a) Explain with examples
 i) Synthone and synthetic equivalent
 ii) Functional group interconversion and functional group addition. [2×1.5]
- b) Synthesize the following compounds showing proper disconnections (attempt any two) : [2×1.5]



- c) Carry out the retrosynthesis of the following compounds to obtain easily available starting materials, show the forward synthesis also. [2×2]



_____ × _____