# RAMAKRISHNA MISSION VIDYAMANDIRA

**(Residential Autonomous College under University of Calcutta)**

**B.A./B.SC. FOURTH SEMESTER EXAMINATION, MAY-JUNE 2013**

**SECOND YEAR**

Date : 20/5/2013 **CHEMISTRY (Honours)**

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

**[Use separate Answer Books for each group]**

## Group – A

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

### Unit – I

1. a) Define 'specific conductance' of an electrolyte solution and mention its SI unit. The specific conductance of a given aqueous solution of KCl at 25°C is '**A**' units. How will '**A**' change if the solution is
   i) heated to 50°C
   ii) diluted to half its concentration
   iii) specific conductance is measured in another conductivity cell having a higher value of the cell constant.

   Explain the basis of your answers. [2+3]

   b) The equivalent conductance of an electrolyte is defined as $\Lambda = \frac{1000K}{C}$ [where K and C are the specific conductance and concentration of the solution]

   Does this imply $\Lambda$ is inversely proportional to the concentration of the solution? Explain. [2]

   c) An electrolyte MA dissociates as

   $$MA \rightleftharpoons M^+ + A^-$$

   Given, C is the initial concentration of the electrolyte $\lambda$ and $\lambda_0$ are the equivalent conductivity values of the electrolyte at concentrations C and infinite dilution respectively. $\alpha$ is the degree of dissociation of the electrolyte. Prove that $\alpha = \frac{\lambda^2 C}{\lambda_0(\lambda_0 - \lambda)}$. [3]

   d) Describe the construction and working of a glass electrode. Why is a glass electrode never used in solution whose $pH \geq 12$? [3]

2. a) The measured resistance of a conductivity cell containing 0·1(N) KCl solution is 3468·9 ohms at 25°C. An exactly 0·1(N) solution of another strong electrolyte in the same cell had a resistance of 4573·4 ohms. Calculate the equivalent conductance $(\Lambda)$ of this electrolyte at the given concentration. [Given : specific conductance of 0·1(N) KCl = 12·856 $mS.cm^{-1}$] [3]

   b) The emf of the cell :

   $$Cd \mid CdCl_2\ (1m) \mid AgCl - Ag$$

   is 0·675 volt at 25°C. The temperature coefficient of the cell e.m.f is $-6{\cdot}5\times10^{-4}$ volt/degree. Find $\Delta H$ for the cell reaction when one Faraday of electricity is drawn from it. [3]

   c) Draw the conductometric titration curves in the case of
   i) $CH_3COONa(aq)$ versus HCl as titrant
   ii) $K_2Cr_2O_7$ (aq) versus NaOH as titrant.

   Explain the nature of the curves. [2+2]

   d) i) What is the origin of liquid junction potential in a electrochemical cell when two different electrolyte solutions, directly come into contact of each other.
   ii) How does one get rid of this? [2+1]

### Unit – II

3. a) Consider the problem of a particle in an infinite well with its walls located at –a and +a.
   i) Verify that the wave functions given below would be solutions of the above problem

$$\psi_n(x) = \frac{1}{a^{1/2}}\sin\frac{n\pi x}{2a} \quad n \text{ even}$$

$$= \frac{1}{a^{1/2}}\cos\frac{n\pi x}{2a} \quad n \text{ odd}$$

ii) Give the expression for energy in terms of a 'a' and 'm' [m $\rightarrow$ mass of the particle]

iii) If the origin was placed at one end (so that the limits of length become O to L) which of the quantities : $\psi_n(X)$ or the energy, would change? Explain. [2+1+1]

b) Find out whether the variables $L_x$ (X component of angular momentum) and $L_Z$ (Z-component of angular momentum) can be measured simultaneously with unlimited accuracy in a quantum mechanical system. [2]

c) Show that if $\phi_1$ and $\phi_2$ are eigenstates of $\hat{H}_1$ and $\hat{H}_2$ with energies $E_1$ and $E_2$ respectively $(E_1 \neq E_2)$ then $\psi = \phi_1.\phi_2$ is an eigenstate of $\hat{H}(=\hat{H}_1 + \hat{H}_2)$. Find the eigenvalue. [2]

d) Examine whether $i(d/dx)$ is Hermitian. [2]

e) Estimate the de Broglie wavelength (in Å) for an electron of mass $9{\cdot}1 \times 10^{-28}$g moving with 10% of the speed of light. [2]

4. a) i) Prove that the integral $\int_{-\infty}^{+\infty} \psi^*(x,t)\psi(x,t)dx$ is independent of time

[$\psi(x,t)$ : well behaved wave function of a Schrodinger Equation]

ii) Explain why this condition is essential for the consistency of quantum formulation. [3+1]

b) Prove that an eigenfunction of a a Hamiltonian operator will be either symmetric or antisymmetric w.r.t parity operator. [2]

c) For a particle of mass '**m**' confined in a **cubical** box of edge-length L find the degree of degenaracy of the level with $n_x + n_y + n_z = 4$. [2]

d) If $\psi_1$ and $\psi_2$ are eigenfunctions for a degenerate state of energy E, prove that any linear combination of $\psi_1$ and $\psi_2$ is also an eigenfunction, of the same operator. [2]

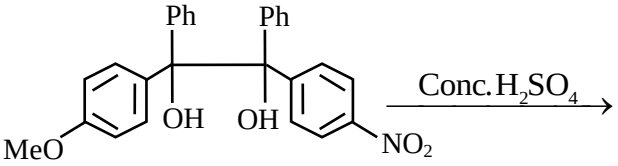
e) Prove that any two normalized wavefunctions $\psi_m$ and $\psi_n$ $(m \neq n)$ of a particle in a one-dimensional box are orthogonal to each other. [2]

## Group – B

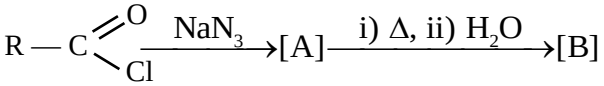
(*Answer <u>one question</u> from each unit*)

### Unit - I

5. a) i) Predict the product and offer explanation : [2½]

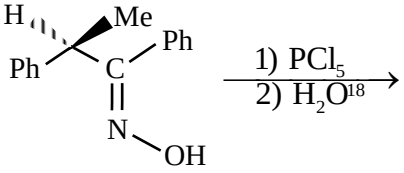


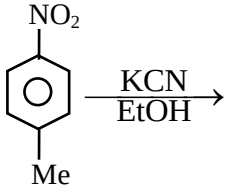

ii) Write the structures of [A] and [B] in the following reaction sequence : [2½]

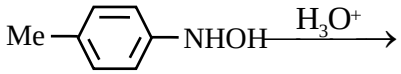



Give the mechanism of formation of [B] from [A].

b) Give the product(s) with suitable mechanism in each of the following reactions : [2×3]

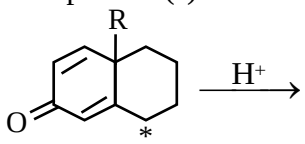
i) 

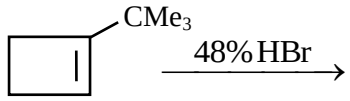

ii) 

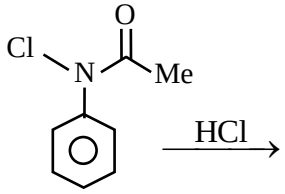
iii) 

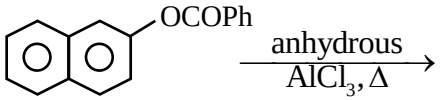

c) Describe briefly how a dry ethereal solution of diazomethane is prepared in the laboratory from N-nitrosomethylurea. Give mechanism. [2+2]
Illustrate the use of diazomethane in achieving (i) methylation of phenol (ii) synthesis of pyrazole ring.

6. a) Predict the product(s) of the following reactions. Give mechanisms (any three) : [2×3]

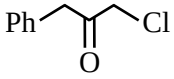
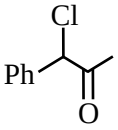
i) 


ii) 


iii) 

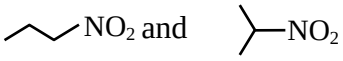

iv) 

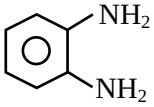
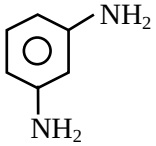

b) i) Explain mechanistically the difference in pattern of coupling of $PhN_2^{\oplus}$ with (i) aniline (ii) N,N-dimethylaniline is slightly acidic solution. [3]

ii) Both  and  [3]

furnish same product when separately treated with NaOH. Explain.

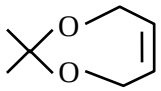
c) Suggest chemical reactions to distinguish between the members of each of the following pairs : [1½×2]

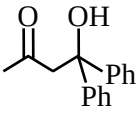
i)  and 

ii)  and 

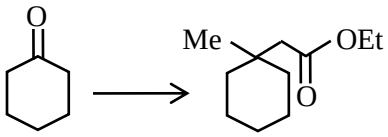
## Unit – II

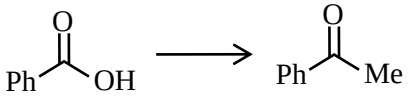
7. a) Give retrosynthetic analysis and an efficient synthesis of the following compounds : [2+2]

i) 

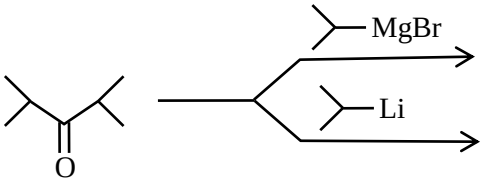
ii) 

b) Carry out the following conversions. Mechanism is not required [2+2]

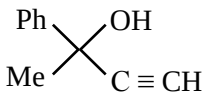
i) 

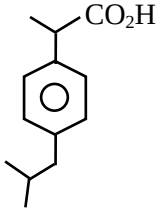

ii) 

c) Predict the product of the following reactions : [2]

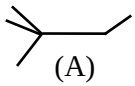



8. a) Carryout the retrosynthesis of the following to obtain easily available starting materials and also show the forward synthesis : [2+2]

i) 

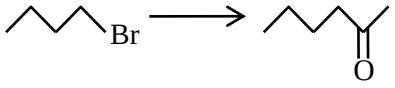
ii) 

b) Outline the synthesis of the following compound (A) using organometallic reagent. [2]



(A)

c) Carryout the following conversions. Mechanism is not required. [2+2]

i) 


ii)