RAMAKRISHNA MISSION VIDYAMANDIRA

(Residential Autonomous College affiliated to University of Calcutta)

SECOND YEAR [BATCH 2016-19]

B.A./B.Sc. FOURTH SEMESTER (January – June) 2018

Mid-Semester Examination, March 2018

Date : 14/03/2018 | **CHEMISTRY (Honours)**

Time : 2 pm – 4 pm | Paper : IV | Full Marks : 50

[Use a separate Answer Book <u>for each group</u>]

[*Attempt <u>one question</u> from each unit*]

<u>Group – A</u>

[16 marks]

<u>Unit - I</u>

1. a) Why is alternating current used in the measurement of conductivities of ions in solution? [1]

   b) Derive the relation $u_i = \frac{\lambda_1}{z_i F}$ where u_i is the ionic mobility, λ_i is molar conductivity and z_i is the magnitude of the charge number on the ith ion and F is the Faraday constant. [3]

   c) State Kohlrausch's law of independent migration of ions. How is it used to determine the equivalent conductance of acetic acid? [2]

   d) Draw and explain the conductometric titration curve for the titration of $AgNO_3$ with KCl at two different temperatures. [2]

2. a) Explain why conductivity is increased when very high electric field is applied. [2]

   b) Molar conductances at infinite dilution of HCl, NaCl and CH_3COONa are 426·2, 126·5 and 91·0 S cm^2 mol^{-1}. A conductance cell filled with 0·01M KCl has a resistance of 257·3 ohms at 25°C. The same cell filled with 0·2M acetic acid has a resistance of 508·6 ohms. Calculate the degree of dissociation of the acid. (Specific conductance of 0·01 M KCl at 25°C = $1{\cdot}41 \times 10^{-3}$ S cm^{-1}). [3]

   c) Discuss the key features of determining the transport number of an ion via moving boundary method showing the calculations involved. [3]

<u>Unit - II</u>

3. a) The S.E for Harmonic Oscillator has the form $\frac{d^2\psi}{dx^2} + \left(\frac{2mE}{\hbar^2} - b^2x^2\right)\psi = 0 \quad \left[b = \frac{2\pi\nu m}{\hbar}\right]$

   Justify that $\psi(x) = C[\exp(-\alpha x^2)]$ is a probable solution for this dynamical system, provided $E = \frac{1}{2}\omega\hbar \quad [\omega = 2\pi\nu]$. [4]

   b) State True or False. [1×4]

   i) $E_0 = \frac{1}{2}h\nu$ is the consequency of energy-time uncertainty relation.

   ii) $\langle E \rangle = 2\langle v \rangle$ for Harmonic Osc for v = 0, only.

   iii) $\psi(x) = f(x) + f(-x)$ is an odd function.

   iv) Rotation energy gives the idea of r_{eq} of a diatomic molecule.

4. a) Rotation of a mass in a ring (circular) problem can be solved like a particle in a 1D well. Consider $\psi(r,\phi) = R(r)\Phi(\phi)$ and then find out the separated variable equation in terms of ϕ and

r. Given, S.E. in the polar form be— $-\frac{\hbar^2}{2m}\left\{\frac{\partial^2\psi}{\partial r^2}+\frac{1}{r}\frac{\partial\psi}{dr}+\frac{1}{r^2}\frac{\partial^2\psi}{\partial\phi^2}\right\}=E\psi$ .What is the boundary condition applied here? [4]

b) Answer the following (**<u>any two</u>**) : [2×2]

i) For Harmonic Oscillator wavefunctions, $\langle\psi_v(x)\,|\,\psi_{v+1}(x)\rangle=0$. Explain.

ii) For $v=2$, $\psi_2=(C_0+C_2x^2)e^{\frac{-\alpha x^2}{2}}$ and the recursion relation is $C_{n+2}=\frac{2\alpha(n-v)}{(n+1)(n+2)}C_n$. show that the normalized function for v = 2 is $\psi_2=(\alpha-4\pi)^{1/4}(2\alpha x^2-1)e^{-\alpha x^2/2}$.

iii) Consider a particle of mass, m, travels on a circle of radius, r, in the 'xy' plane and PE is constant. Show that the S.E in the polar form becomes, $-\frac{\hbar^2}{2m}\left\{\frac{\partial^2\psi}{\partial r^2}+\frac{1}{r}\frac{\partial\psi}{dr}+\frac{1}{r^2}\frac{\partial^2\psi}{\partial\phi^2}\right\}=E\psi$.

<u>Group – B</u>

[18 marks]

<u>Unit - III</u>

5. a) How will you prepare superpure (impurity < 10^{-9}%) grade geemanium? (Give the outlines steps with balanced reactions) [4]

b) Explain the following : [2+3]

i) Polymeric SiO_4 and PO_4 tetrahedra are very common than SO_4 polymeric tetrahedra.

ii) the O – O bond length in O_2 (121 pm) and O_2F_2 (122 pm) is almost same but shorter than the O – O bond in H_2O_2 (148 pm).

6. a) Compare and contrast the chemistry of trimethylamine and trisilayl amine with respect to their (i) structure and (ii) reaction with an acid (HCl). [4]

b) Tetravalent lead is unstable while tetravalent tin is stable.. Explain with evidence. [3]

c) What is hydrosilation reaction? [2]

<u>Unit - IV</u>

7. a) Discuss the structure of borazine. Give two chemical reactions to show its greater reactivity than benzene. [2+2]

b) Comment on the non existence of nitrogen (v) chloride and bismuth (v) chloride. [3]

c) Tetracoordinated boron compounds are always tetrahedral and never square planar —Explain. [2]

8. a) PCl_5 is well known but PH_5 cannot be prepared —Explain. [2]

b) Compare the hydrolytic behaviour of the trichlorides of nitrogen, phosphorous and bismuth. [3]

c) Discribe the reaction of diborane with (i) ammonia and (ii) dimethy amine [2]

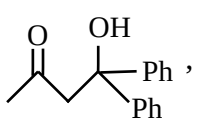
d) AlF_3 has a very much higher melting point than $AlCl_3$ —Explain. [2]

<u>Group – C</u>

[16 marks]

<u>Unit - V</u>

9. a) Identify suitable synthons for the following molecules and also show the retro synthesis. [2×2]



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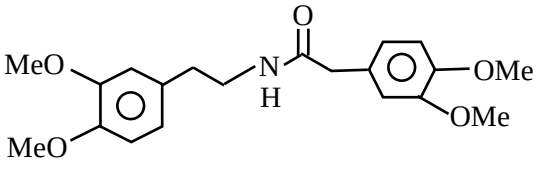
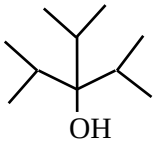
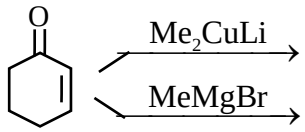


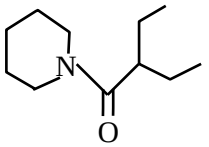
b) Draw the outline for the synthesis of following 3°alcohol; with proper reagents. [2]



c) Identify the products in the following reactions with proper reason. [2]



10. a) Identify the suitable synthons for the following molecules and also show the retro synthesis. [2×2]



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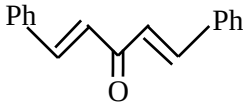
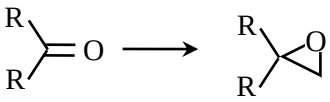


b) Complete the following conversion via sulphur ylide. [2]

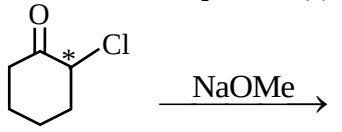


c) For the following reaction, sequence of addition of reagents is very important to get ketone as major product. —Explain. [2]

Unit - VI

11. a) When optically active (s) – 2 – methyl – 1, 2 – butanediol is subjected to pinacol rearrangement. a racemic product obtained. —Explain. [2]

b) Write down the product(s) for the following reaction with proper mechanism. [2×2]



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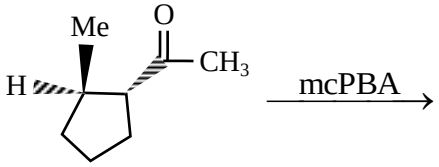
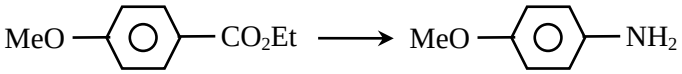
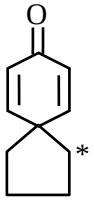


* = ^{14}C, .

c) Convert ester group to amine group for the following compound using Curtius rearrangement (mechanism for Curtins rearrangement only). [2]



12. a) Write down the products for the following reaction with proper mechanism. [2×2]



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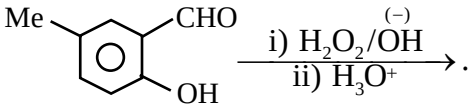

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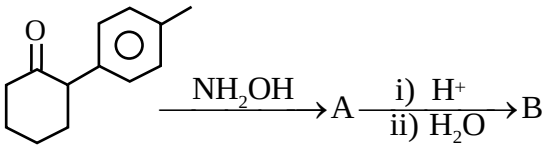
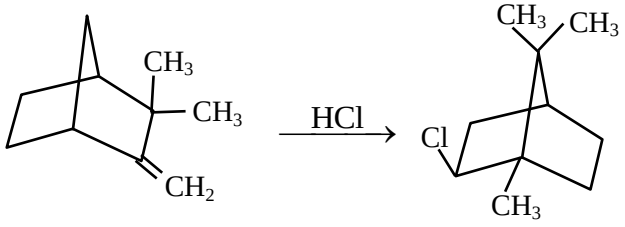
b) Write down the product for the following reactions (no mechanism require). [2]



c) Justify the formation of the product. [2]



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