RAMAKRISHNA MISSION VIDYAMANDIRA

(Residential Autonomous College under University of Calcutta)

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

FIRST YEAR

Date : 21/05/2015 **CHEMISTRY (Honours)**

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

[Use a separate Answer Book for each group]

Group – A

Unit - I

[*Answer **any one** question*]

1. a) Starting with clausius inequality, prove that the following are the conditions for spontaneity
   i) $\Delta S > 0$ at constant E, V
   ii) $\Delta G < 0$ at constant T, P [2+2]
   b) Show that in a Joule-Thomson experiment $H_{initial} = H_{final}$. [3]
   c) How much work must be performed to freeze 1 kg of water at 273K in a refrigerator on a cool day (room temperature = 288 K).What will be the change in entropy of the room? Latent heat of fusion of ice = $334{\cdot}72\ Jg^{-1}$. [3]
   d) Calculate the change in Gibb's free energy when 36 g water initially at 373 K and 10 atm pressure are converted to vapour at 373 K and 0·01 atm pressure. Given, volume of 1g water at 373 K = 1 ml. [3]

2. a) For liquid water at 25°C, $\alpha = 2{\cdot}07\times10^{-4}K^{-1}$, the density may be taken as $1{\cdot}00\ gmcc^{-1}$. One mole of liquid water is compressed isothermally at 25°C, from 1atm to 1000atm. Calculate
   i) ΔS supposing water is incompressible in the range.
   ii) ΔS for the same amount of an ideal gas for the same change. [3+1]
   b) A spontaneous gas-phase polymerisation must be exothermic. Explain. [2]
   c) An ideal gas with adiabatic exponent $\gamma\left(C_P/C_V\right)$ goes through a process $P = P_0 - \alpha V$, where P_0 and α are positive constants, and V is the volume. Show that the entropy change for the process is maximum when, $V_{max} = \gamma P_0 / \alpha(\gamma+1)$. [4]
   d) Why does an isochoric curve plotted on a TS diagram have a greater slope than an isobaric curve at the same temperature? Draw the plots. [2+1]

Unit -II

[*Answer **any one** question*]

3. a) Consider a particle with quantum number 'n' moving in a one-dimensional box of length 'L'.
   i) Determine the probability of finding the particle in the left quarter of the box.
   ii) For what value of 'n' this probability is a maximum. [4]
   b) Find < x > and < y > for the ground stationary state of a particle in a 3D cubical box. [3]
   c) Prove the following (**any one**) : [3]
   i) $[A,[B,C]]+[B,[C,A]] = -[[A,B],C]$
   ii) $[H_x, p_x] = i\hbar\dfrac{\partial}{\partial x}v(x)$ for $v(x) \neq 0$
   d) Show that the first excited state and the ground state for particle in ID well are orthogonal to each other. [2]

4. a) Examine, whether the following function is well behaved or not : $\psi(x) = e^{-x}\ [-1,+1]$. [2]

b) What is a node? Determine the position(s) of node(s) for a particle in ID well of length L in the state corresponding to n = 3. [3]

c) Consider a particle in a two dimensional box. Determine $[\hat{x}, \hat{p}_y]$ and $[\hat{y}, \hat{P}_y]$. Explain the significance of the results. [3]

d) What is Compton effect? Draw a labelled diagram. Find the maximum kinetic energy of recoiled electrons when X-rays of wavelength 12·0 pm are scattered from a target. [4]

Group – B

Unit - I

[*Answer **any one** question*]

5. a) Arrange $F^{(-)}, Cl^{(-)}, Br^{(-)}, I^{(-)}$ in increasing order of their nucleophilicity in aqueous and non-aqueous solution and justify. [3]

b) Carry out the following conversions :

i) $Me_3CCH=CH_2 \rightarrow Me_3C-\underset{\underset{OH}{|}}{CH}-CH_3$. [2]

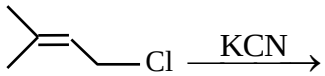
ii) Z – 2 – Butene → E – 2 - Butene [2]

c) E2 reaction of 2 – bromobutane with sodium ethoxide gives more of *trans* – 2 – butene than *cis* – 2 – butene. Why? [2]

d) What is peroxide effect? Why is this effect observed only for addition of HBr to propene and not for HCl and HI? [2]

e) Predict the product of the reactions :

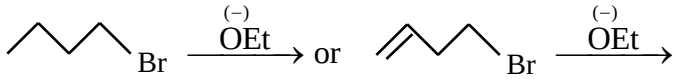
i) $H_2C-\underset{\underset{O}{\diagdown\diagup}}{CH}-CH_2Cl \xrightarrow{EtONa}$ [1]

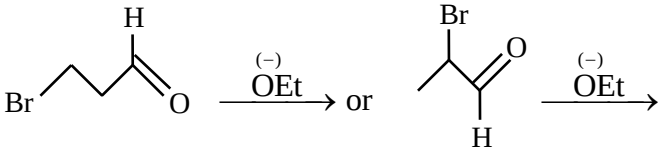
ii)  [1]

f) Predict and justify the products of the following reaction indicating major/minor product. [2]

$$PhCH_2-CH_2-\underset{\underset{Me}{|}}{\overset{Me}{\overset{|}{\overset{\oplus}{N}}}}-CH_2CH_3\ \overset{(-)}{OH} \xrightarrow{\Delta}$$

6. a) Which reaction would occur more rapidly and why?

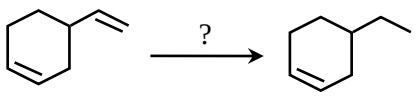
i)  [2]

ii)  [2]

b) Me_3CCH_2Br is inert to S_{N^2} reaction, though it is a primary halide. Explain. [2]

c) Each of E1CB and E2 reaction follows second order kinetics; how would you distinguish between the two mechanistic paths? [2]

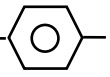
d) Provide reagent for the following conversion : [1]



e) What happens when an optically active $\alpha-$phenylethanol is allowed to react with thionyl chloride, [3]

i) in the absence of pyridine

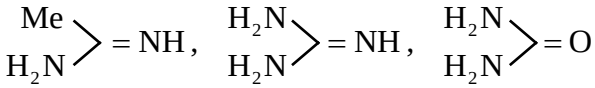
ii) in the presence of pyridine

f) Considerable amount of *threo*-isomer is obtained along with *erythro*-isomer in the bromination of *trans* . H_3CO  $CH = CH - CH_3$. Explain. [3]

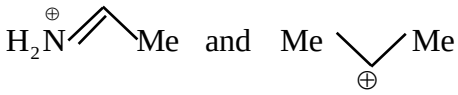
Unit - II

[*Answer **any one** question*]

7. a) Compare the base strength of the following compounds : [2]



b) Which one is more stable between the given two carbocations and why? [2]



c) Write electronic structures of trigonal (sp^2) methylene with different spin multiplicities. Comment on their bond angles. [2]

d) Identify 'A' and 'B' in the following reaction and write mechanism for their formation. [2]

$$H_3C - CH_2CH = CH_2 + NBS \xrightarrow{CCl_4/h\nu} A + B$$

e) Explain why the enol content of acetylacetone is very large in hexane medium than in acetonitrile. [2]

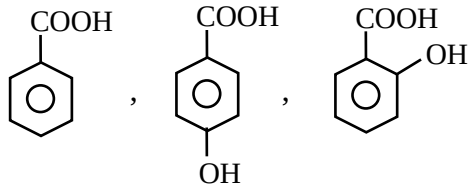
8. a) Give IUPAC names of the following compounds :

i) $H_2C = CH - CH_2 - C \equiv C - H$ [1]

ii) $H_3C - NH - CH_2 - \underset{\displaystyle CHO}{\underset{|}{CH}} - CH_2CH_3$ [1]

b) Compare the base strength of *t*-Buok in ethanol and DMSO. [2]

c) Arrange the following acids in increasing order of their pk_a values and justify. [2]



d) Account for the very high stability of triphenylmethyl radical. [2]

e) Carbene $(:CH_2)$ adds to *cis* – but – 2 – ene stereospecifically when spin state is singlet but non-stereospecifically when triplet. Explain. [2]

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