RAMAKRISHNA MISSION VIDYAMANDIRA

(Residential Autonomous College affiliated to University of Calcutta)

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

FIRST YEAR [BATCH 2015-18]

Date : 18/05/2016 **CHEMISTRY (Honours)**

Time : 11 am – 1 pm **Paper :** II (Gr. A&B) Full Marks : 50

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

<u>Group – A</u>

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

<u>Unit – I</u>

1. a) Which is the more effective way to increase the thermal efficiency of a Carnot engine : to increase T_H, keeping T_L constant; or to decrease T_L, keeping T_H constant? [T_H is the temperature of the hot reservoir and T_L is the temperature of the cold reservoir] [2]

   b) The molar heat capacity of a solid metal at constant pressure is given by the following equation in the temperature interval 300K to 600K $C_P = 25\cdot94 + 5\cdot44\times10^{-3}\,TJK^{-1}mol^{-1}$.

   What is the entropy change when 1 mol of this metal is heated from 300K to 600K at constant pressure? [3]

   c) Starting from the definition of Joule-Thomson coefficient (μ_{JT}) prove that $\mu_{JT} = \dfrac{V}{C_P}(\alpha T - 1)$

   where α is the coefficient of thermal expansion. [3]

   d) Using the thermodynamic equation of state evaluate $\left(\dfrac{\partial u}{\partial v}\right)_T$ for the van-der-Waals gas. [3]

   e) Derive the condition for spontaneity of a process at constant temperature and pressure. [2]

2. a) i) Sketch the possible indistinguishable arrangements of two balls in six cells with the restriction that no two balls can be placed in a single cell.

   ii) Calculate the thermodynamic entropy for the above arrangement. [4]

   b) Draw qualitative plots of G against T at a constant pressure for three different phases of a particular substance (solid, liquid and gas). Assume entropy to be constant in the temperature range considered. [3]

   c) Justify or criticise :

   i) An adiabatic process is always isoentropic.

   ii) Any spontaneous process is always accompanied by a decrease in free energy. [3]

   d) Knowing that $C_P - C_V = \left[P + \left(\dfrac{\partial U}{\partial V}\right)_T\right]\left(\dfrac{\partial V}{\partial T}\right)_P$, show that $C_P - C_V = \dfrac{\alpha^2 VT}{\beta}$ where α is the coefficient of thermal expansion and β is the compressibility factor. [3]

<u>Unit – II</u>

3. a) Justify or criticize with arguments (**<u>any two</u>**) : [2×3]

   i) If f_1 and f_2 are eigenfunctions of any operator, $\hat{B}$, then $C_1f_1 + C_2f_2$ must be an eigenfunction of $\hat{B}$.

   ii) For the particle in a box in n = 2 stationary state, the probability of finding the particle in the left quarter of the box equals to that in the right quarter.

   iii) The wavelength of the particle in a box absorption transition from quantum no. n to n+1 decreases as the value o f n increases.

   b) Determine whether the momentum and (i) the kinetic energy and (ii) the potential energy can be known simultaneously (consider one dimension). [4]

c) Examine whether the following functions are acceptable wave function or not

i) $e^{-|x|}[-\infty \le x \le \infty]$

ii) $e^{\frac{i\varphi}{2}}[0 \le \varphi \le 2\pi]$ [2]

4. a) A particle of mass m is confined to a 1D box of length 'a'. If it makes a radiative transition from second excited state to the ground state then what will be the frequency of the emitted photon? [3]

b) Assume that a particle is confined to a box of length a, and that the system wave function is $\psi(x) = \sqrt{\frac{2}{a}} \sin\left(\frac{\pi x}{a}\right)$.

i) Is this state an eigen function of the position operator?

ii) Calculate the average value of the position (x) that would be obtained for a large number of measurements. Explain your result. [4]

c) Answer **<u>any one</u>** : [1×3]

i) Show that the 1st two eigenfunctions of the Hamiltonian operator for the particle in a hard 1D box are orthogonal to each other.

ii) Show that eigenvalues of a hermitian operator are real.

d) Comment on $[\hat{p}_x, \hat{x}]$ is related to the uncertainty relation. [2]

<u>Group - B</u>

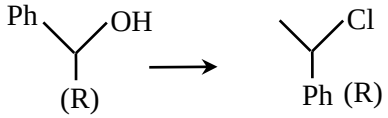
[***Attempt <u>one question</u> from <u>each Unit</u>***]

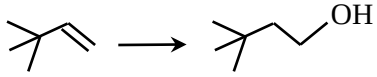
<u>Unit – III</u>

5. a) What reactivity difference would you expect when KI reacts separately with CH_3CH_2Br and $(CH_3)_3CCH_2Br$ in acetone? [2]

b) Show the mechanism of addition of bromine to *cis*- and *trans*-2-butene and write down the products indicating their stereochemistry. [3]

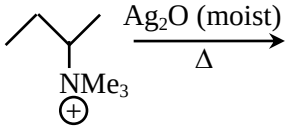
c) Carryout the transformations with mechanisms : [2·5+2·5]

i) 

ii) 

d) Arrange the following anions in order of increasing nucleophilicity. Give reasons for your answer. R_2N^-, RO^-, F^-, R_3C^- [3]

e) Give the products of the following reaction, indicate the major one with explanation. [2]



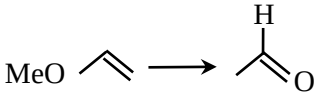
6. a) Give product(s) in the following reactions with plausible mechanism. [2+2]

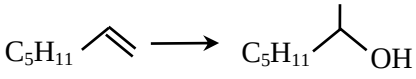
i) $PH-\underset{\diagdown O \diagup}{CH}-CHMe \xrightarrow[H_2SO_4(cat.)]{MeOH}$

ii) $PhCH=CHEt \xrightarrow{h\nu, HBr/(PhCO_2)_2}$

b) How can you convert (show the steps) : [2+2+2]

i) (R) – 2 – octanol → (S) – 2 – octanol

ii) 

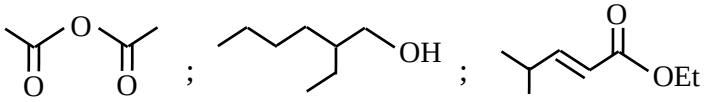
iii) 

c) Scrambling of ^{14}C label occurs when $PhCH_2\overset{14}{C}H_2Br$ is treated with $AlBr_3$ at low temperature — Explain with mechanism. [3]

d) 'Alkyl halides gives mainly cyanides with ethanolic KCN but with AgCN isocyanides are the main product' —Explain. [2]

Unit – IV

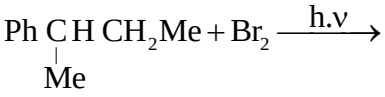
7. a) Give IUPAC name to **any two** of the following : [2]



b) Arrange the following compounds in order of increasing pka values and give reasons. [3]
Aniline, 4 – nitroaniline, 2, 6 – dimethyl – 4 – nitroaniline, 3, 5 – dimethyl – 4 – nitroaniline

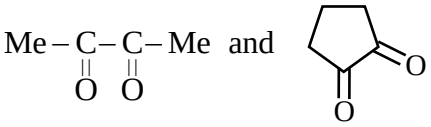
c) State the principle of microscopic reversibility with an example. [2]

d) Write down the major product with reason. [3]



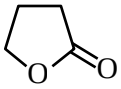
8. a) Arrange the following in increasing order of acid strength : 4-nitrophenol; 3,5 – dimethyl – 4 – nitrophenol and 2, 6 – dimethyl – 4 – nitrophenol. Give reason. [3]

b) Which of the two α-diketones has higher enol content? [2]

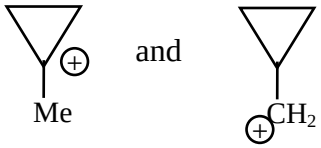


c) Which of the following two reactions conducted at the same temperature is expected to have larger value of equilibrium constant and why? [3]

i) $CH_3CO_2H + CH_3CH_2OH \rightleftharpoons CH_3CO_2CH_2CH_3 + H_2O$

ii) $HO-CH_2CH_2CH_2CO_2H \rightleftharpoons$  $+ H_2O$

d) Compare stability of the ions in each case : [2]

i) 

ii) 

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