RAMAKRISHNA MISSION VIDYAMANDIRA

(Residential Autonomous College under University of Calcutta)

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

FIRST YEAR

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

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

[Use separate Answer Books for each group]

Group – A

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

Unit – I

1. a) Write down the Kelvin-Planck and the Clausius statements about the second law of thermodynamics and hence show that the two statements are equivalent. [1+1+4]

   b) Define Joule-Thomson Coefficient (μ_{JT}). Although Joule-Thomson throttling process in an isenthalpic process but an isenthalpic T versus P curve is not the graph of a throttling process — explain. [1+2]

   c) Derive from 1st and 2nd law $\left(\frac{\partial E}{\partial V}\right)_T = T\frac{\alpha}{\beta} - P$ where α, β are coefficient of thermal expansion and isothermal compression, respectively. [4]

2. a) Show that, $\left[\frac{\partial\left(G/T\right)}{\partial\left(1/T\right)}\right]_P = H$ where the terms have their usual significance. [3]

   b) Prove that two reversible adiabatic paths can never cross. [2]

   c) The change in Gibbs energy of a certain constant pressure process was found to fit the expression $\Delta G/J = -73{\cdot}1 + 42{\cdot}8\left(T/K\right)$. Calculate the value of ΔS for the process. [3]

   d) Assuming all gases ideal, calculate the work invested, the heat dissipated and the change of entropy when 100 lit of air at 1 atm pressure and 298 K are separated isothermally and reversibly into 79 lit of nitrogen and 21 lit of oxygen measured at 1atm pressure and 298 K. [3]

   e) Give a process for which i) $\Delta G = 0$
   ii) $\Delta S = 0$ [1+1]
   State all necessary conditions or restrictions clearly.

Unit – II

3. a) If ψ is a normalized wave function, what is its SI unit for ID particle in a box? What do you mean by Normalization Constant? [2]

   b) Show that $\hat{p}_x$ is hermitian. [3]

   c) What is Compton effect?
   "Compton effect provides an excellent illustrations of the uncertainty principle"—explain. [1+2]

   d) The wavefunction ψ of a certain system is the linear combination $\psi = \left(\frac{1}{4}\right)^{1/2}\psi_1 + \left(\frac{3}{4}\right)^{1/2}\psi_2$ where ψ_1 and ψ_2 are energy eigenfunctions with (nondegenerate) energy eigenvalues E_1 and E_2 respectively. What is the probability that the system energy will be observed to be E_1? [3]

   e) Verify that ∇^2 is linear. [1]

4. a) Show that if two observables are to have simultaneously precise defined values, then their corresponding operators must commute. [3]

b) Suppose a particle in a 3D cubic box of length 'a' has an energy of $3h^2/2ma^2$. How many states lie in this range? Also tell the number of energy levels in this range? [3]

c) If a hexatriens molecule absorbs light of 2500Å to transfer a π electron from n = 1 to n = 2, what is the average bond length of a C – C bond? [2]

d) 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 is this probability a maximum?

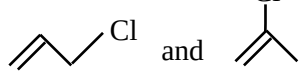
iii) What is the limit of this probability for $n \to \infty$? [2+1+1]

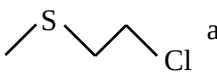
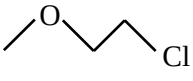
Group – B

(Answer **one** question form **each unit**)

Unit - I

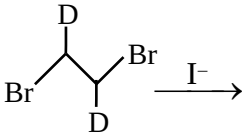
5. a) What difference in reactivity with respect to nucleophilic substitution, would you expect between the compounds in each of the following pairs : [1½+1½]

i)  and

ii)  and 

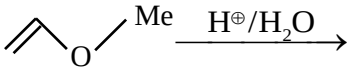
b) Convert (R)-2-chlorobutane to (S)-2-chlorobutane. [2]

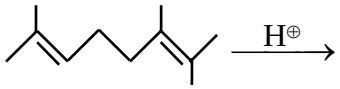
c) Predict the product with stereochemistry, if appropriate, and write mechanism in each case [2×4]

i) 

(Threo –)

ii) (E) – MeCD = CDMe $\xrightarrow{\text{cyclohexene, Pd,100°C}}$

iii) 

iv) 

d) Threo-1, 2-diphenyl-1-bromopropane reacts with base, ten times faster than erythro isomer. — Explain. [2]

6. a) Benzyl chloride reacts with $I^{(-)}$ ion almost at the same rate as methyl chloride, though the former substrate has a large α-substituent —Explain. [2]

b) In addition of HBr to 3,3-dimethyl but-1-ene, the following results ae observed :

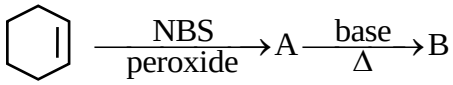
$$Me_3CCH=CH_2 + HBr \rightarrow Me_2C(Br)CHMe_2(A) + Me_3CCH(Br)Me(B) + Me_3CCH_2CH_2Br(C)$$

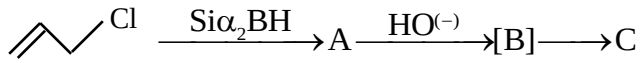
	A	B	C
No peroxide	71%	29%	none
With peroxide	trace	trace	100%

i) Explain why there is a different product distribution under the different sets of conditions.

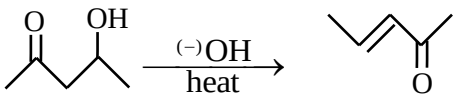
ii) Write a detailed mechanism for each reaction that explains the origin of all products. [4]

c) Identify the products in each case :

i) 

ii)  [2+2]

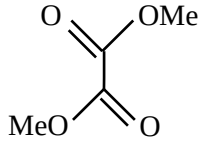
d) What kind of elimination does the following reaction follow? Write mechanism. [2]

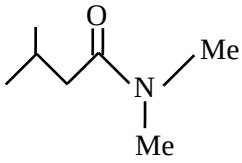


e) Solvolysis of (+) – $C_6H_5CHMeCl$ in acetone water (4:1) leads to 98% racemisation while (+) – $C_6H_{13}CHMeCl$ leads to only 34% racemisation —explain. [3]

Unit - II

7. a) Write IUPAC name of each of the following compounds :

i) 

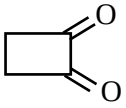
ii)  [2]

b) Arrange the following carbanions in order of increasing stability with proper justification. [2]

$\bar{C}H_2NO_2$, $\bar{C}H_2COCH_3$, $\bar{C}H_2CO_2Et$

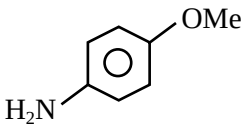
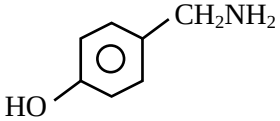
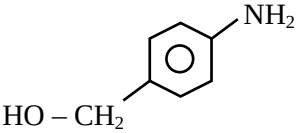
c) The azo-compound dibenzyldiazene ($PhCH_2N{=}N{-}CH_2Ph$) decomposes thermally to give nitrogen at a faster rate than di-t-butyldiazene ($Me_3C{-}N{=}N{-}CMe_3$). Explain. [2]

d) Which compound of following pair has greater enol content? Explain. [2]

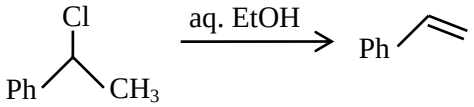
$CH_3COCOCH_3$, 

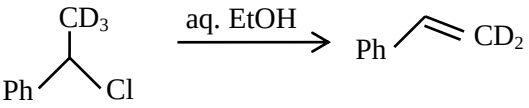
e) Cis–2–butene when photolysed with CH_2N_2 in C_3F_8 solvent, reaction becomes stereoselective — explain the reaction with products. [2]

8. a) Arrange, with reason, the following isomeric amines in increasing order of basicity [2]

 ;  ; 

b) Propose a mechanism of the following reaction on the basis of the given experimental evidence. [2]





[Given $K_H/K_D \approx 1{\cdot}2$]

c) Draw orbital picture of triplet carbene. [1]

d) Why cyclopropylmethyl cations are more stable than benzyl cation? [2]

e) Triplet carbene adds to E– and z– alkene with loss of stereochemical integrity. Explain with suitable example. [3]