RAMAKRISHNA MISSION VIDYAMANDIRA

(Residential Autonomous College under University of Calcutta)

B.A./B.SC. SECOND SEMESTER EXAMINATION, MAY 2012

FIRST YEAR

Date : 19/05/2012

CHEMISTRY (Honours)

Time : 11 am – 1 pm

Paper : II

Full Marks : 50

[Use Separate Answer Books for each group]

Group – A

UNIT-I

Answer **any one** question from the following:

1. a) Explain Clausins inequality: $Tds \geq \text{đ}q$. Therefore explain that in an isolated system entropy reaches a maximum value at equilibrium. [3]

   b) i) Represent with proper explanation, a Carnot cycle in a T–S diagram.

   ii) Explain the significance of the area under this curve. [2+1]

   c) Prove that for a van-der-waals gas C_v is independent of V. [2]

   d) A refrigerator operates between 2ºC and 27ºC. Calculate the work to freeze 1 Kg of ice (heat of fusion 335 Jg^{-1}) and the heat discharged at 27ºC. [assume the refrigerator acts reversibly] [3]

   e) Show that

   i) $\left[\frac{\partial}{\partial T}\left(\frac{\Delta G}{T}\right)\right]_P = -\frac{\Delta H}{T^2}$

   ii) $\mu_{JT} = -\frac{1}{c_p}\left(\frac{\partial H}{\partial p}\right)_T$ [4]

2. a) Prove the equivalence of Clausins' and Kelvin Planck's statement of 2nd law of thermodynamics. [3]

   b) i) A container has two chambers, they contain ideal gas of mole number and volume (N_A, V_A) and (N_B, V_B) respectively. Suddenly the wall separating the two parts is removed and the two gases allowed to mix under isothermal condition. Calculate the entropy change for the process in terms of mole numbers (N_A, N_B). [2]

   ii) From the expression of this entropy of mixing calculate the free energy of mixing. [2]

   c) Consider the following cycle using 1 mole at an ideal gas, initially at 25ºC and 1 atm pressure: [4]

   Step 1: Isothermal expansion against zero pressure to double the volume.

   Step 2: Isothermal reversible compression from 0.25 atm to 1 atm.

   i) Calculate the value $\int \frac{\text{đ}q}{T}$.

   ii) Show that $(\Delta s)_{\text{step 1}} \neq (\Delta s)_{\text{step 2}}$.

   d) i) Represent in a T–P diagram a Joule-Thermson process at a constant enthalpy.

   ii) Arrive at an expression for the inversion temperature of a van-der-Waals gas. [1+3]

UNIT-II

Answer **any one** question from the following:

3. a) Show that for the reaction $2N_2O_5(g) \rightarrow 4NO_2(g) + O_2(g)$. [3]

$$N_2O_5 \xrightarrow{K_1} NO_2 + NO_3$$

$$NO_2 + NO_3 \xrightarrow{K_2} N_2O_5$$

$$NO_2 + NO_3 \xrightarrow{K_3} NO_2 + O_2 + NO$$

$$NO + N_2O_5 \xrightarrow{K_4} NO_2 + NO_2 + NO_2$$

$$\frac{d[N_2O_5]}{dt} = -\frac{2K_1K_3[N_2O_5]}{K_2 + K_3}$$

Consider that NO and NO_3 are intermediates in this reaction.

b) i) Draw qualitatively the energy diagram of a 2-step reaction, with slower second step.

ii) In the diagram point out clearly the average energies of the reactant, product, intermediate and the two transition states.

iii) Also show in the above diagram the two activation energies.

iv) Show mathematically the rate of the above reaction depends only upon the activation energy of the slower step. [1+2+1+3]

4. a) A gas phase reaction involving a single reactant is observed to undergo the following sequence of reactions –

$$A + A \xrightarrow{K_a} A^* + A$$

$$A^* + A \xrightarrow{K_a'} A + A$$

$$A^* \xrightarrow{K_b} P$$

i) Derive the rate law for the formation of P. [2]

ii) The respective activation energies of the three reactions are 134, 165 and 291 KJ mol^{-1}. Explain how would the rate of the above reaction change if temperature is increased (assume the rate of deactivation of A^* by collision with A is much greater than the rate of unimolecular decay). [2]

b) Show that, for the enzyme – catalysed reaction

$$E + S \underset{K_{-1}}{\overset{K_1}{\rightleftharpoons}} ES$$

$$ES \xrightarrow{K_2} P$$

$\frac{d[P]}{dt}$ is independent of $[S]_0$ for a given $[E]_0$ and high value of $[S]_0$. $[\,]_0$ represents the initial concentration. [3]

c) For the reaction $R \xrightarrow{K} P$, which one of the following rate equation is true for autocatalytic reaction — Explain. [1]

i) $\frac{d[P]}{dt} = K[R]$

ii) $\frac{d[P]}{dt} = K[R][P]$

d) At a given temperature, the rate of the hydrolysis of ester catalysed by strong acid is almost double when pH is changed from 0.80 to 0.50. Justify whether this is an example of homogeneous catalysis or not. [2]

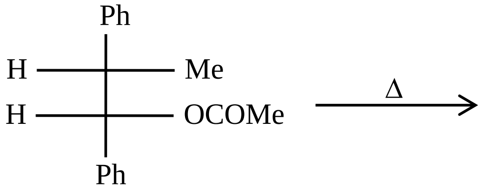
Group – B

Unit – I

(Answer **any one** question)

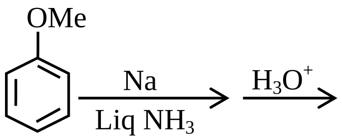
5. a) Predict the product with stereochemistry of the following reactions : [2×2]

i) Erythro – 3 – bromo – 2 – butanol $\xrightarrow{\text{HBr}}$

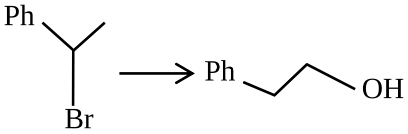
ii) 

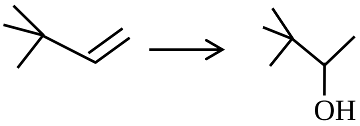
b) Predict the product of the following reactions : [2×2]

i) 

ii) 

c) Carry out the following conversions (**any one**) : [2]

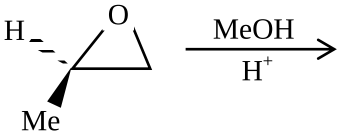
i) 

ii) 

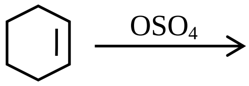
d) Account for the observation that alkyl halides give mainly cyanides with aqueous ethanolic KCN, but with AgCN isocyanides are the main products. [2]

e) Write down the structure of ozonides formed when 2, 3-dimethyl-2-butene was subjected to ozonolysis in the presence of HCHO. Give mechanism of the ozonide formation. [3]

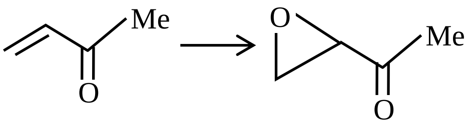
6. a) Predict the product with stereochemistry of the following reactions (**any two**) : [2×2]

i) 

ii) (R) – α – phenylethanol $\xrightarrow[\text{ether}]{SOCl_2}$

iii) 

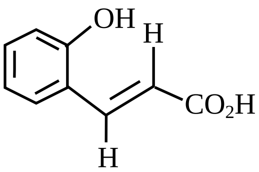
b) Transform : [2×2]

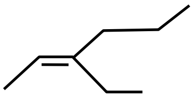
i) 

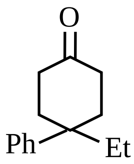
ii) (E) – 2– butene $\longrightarrow$ (Z) – 2 – butene

c) When $Cl_2C = CHCl$ is treated with NaOD in D_2O then at the end of the reaction $Cl-C\equiv C-Cl$ is formed. If the reaction is stopped at the half complete stage, the recovered alkene is found to contain deuterium. —Explain mechanistically. [3]

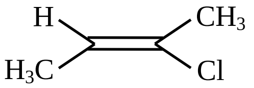
d) Give IUPAC names of the following compounds (**any two**) : [2]

i) 

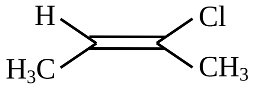
ii) 

iii) 

e) Account for the following observations with mechanism in each case. [2]

i) 

$\xrightarrow{NaNH_2} H_3C-C\equiv C-CH_3$

ii) 

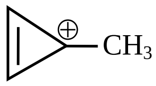
$\xrightarrow{NaNH_2} \underset{\text{(major)}}{H_3C-CH=C=CH_2} + \underset{\text{(minor)}}{H_3C-C\equiv C-CH_3}$

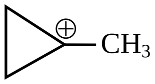
Unit – II

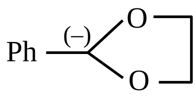
(Answer **any one** question)

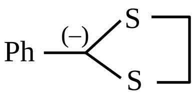
7. a) Addition of HBr to 1,3-butadiene yields two products and the product composition depends on the reaction temperature. Write the structure of the products and account for the observations with suitable energy profile diagram. [3]

b) Arrange the following ions in order of increasing stability. Give reasons. [2+1]

i) $CH_3-\overset{\oplus}{CH}-CH_3$, 

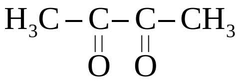
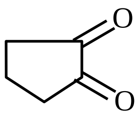
, 

ii) 

and 

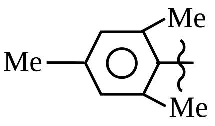
c) i) Make a comparative discussion on the basicity of acetamidine and propanamine.

ii) Which one of the following diketones has higher enol content? Explain. [2×2]


$H_3C-\underset{\underset{O}{\|}}{C}-\underset{\underset{O}{\|}}{C}-CH_3$; 

8. a) What do you mean by primary kinetic isotope effect? Indicate the pertinent one in connection with establishing the rate-determining step in the chromic acid oxidation of isopropyl alcohol. [3]

b) The following compound exist mainly in enol form. Explain. [1·5]

Ar_2CHCHO (where Ar = 

)

c) i) Cite one pathway for generation of carbene.

ii) Draw the orbital picture of diphenylcarbene and explain its triplet character. [1+1½]

d) Arrange the following compounds in order of increasing acidity. Explain briefly. [3]

i) Benzoic acid, ii) 2-hydroxybenzoic acid,
iii) 4-hydroxybenzoic acid, v) 2,6-didydroxybenzoic acid

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