RAMAKRISHNA MISSION VIDYAMANDIRA

(Residential Autonomous College under University of Calcutta)

B.A./B.Sc. THIRD SEMESTER EXAMINATION, DECEMBER 2014

SECOND YEAR

Date : 17/12/2014 **CHEMISTRY (Honours)**

Time : 11 am – 1 pm **Paper :** III-A&B Full Marks : 50

[Use a separate Answer Book for each group]

Group – A

Unit - I

(*Answer **any one** question*)

1. a) i) Prove that $\Delta S_{mix} = -nR\sum_i X_i \ln X_i$ [assume ideal mixture]

ii) Find out the composition for which ΔS_{mix} is maximum in a two component mixture. [2+2]

b) Consider the reaction $Ag_2O(s) \rightleftharpoons 2Ag(s) + \frac{1}{2}O_2(g)$

for which $\Delta G^\circ / (J/mol) = 32385 + 17{\cdot}32 \log T - 116{\cdot}48\,T$

i) Express $\log_{10}K_P$ and ΔH° as functions of temperature.

ii) At what temperature will the equilibrium pressure of oxygen be 1 atm? [2+1]

c) If in a gas-phase closed system, all the N_2 and H_2 come from the dissociation of NH_3 according to $2NH_3 \rightleftharpoons N_2 + 3H_2$, which one of the following statements is true at any time during the reaction?

i) $x_{N_2} = 3x_{H_2}$; (ii) $3x_{N_2} = x_{H_2}$; (iii) neither (i) nor (ii) is necessarily true. [3]

d) Prove that the equilibrium vapor pressure of a liquid at a fixed temperature is proportional to latent heat of vaporization. [2]

2. a) For an ideal gas reaction evaluate $\left(\frac{\partial \ln K_x}{\partial T}\right)_p$. [2]

b) i) If ξ_e is the degree of advancement of a reaction, prove that $\left(\frac{\partial \xi_e}{\partial T}\right)_p = \frac{\Delta H}{TG''_e}$ [$\Delta H \equiv$ enthalpy of the reaction and $G''_e = \left.\frac{\partial^2 G}{\partial \xi^2}\right|_{equilibrium}$]

ii) From the above relation predict in which direction an exothermic reaction would go if T is increased. [2+1]

c) The Standard Gibbs free energy for the isomerization of borneol ($C_{10}H_{17}OH$) to isoborneol in the gas phase at 503K is 9·4 KJ mol^{-1}. Calculate the reaction Gibbs energy in a mixture consisting of 0·15 mol of borneol and 0·30 mol of isoborneol when the total pressure is 600 Torr. [3]

d) Calculate the mean ionic activity coefficient of the electrolyte in an aqueous solution of 0·001(M) $K_3[Fe(CN)_6]$ at 25°C. [Given : Debye-Hückel constant for water at 25°C = 0·509]. [2]

e) Justify / Criticize : In a solution prepared by adding 'm' moles of CH_3COOH to 1 kg of water, the H^+ molality can never exceed 'm' mol kg^{-1}. [2]

Unit - II

(*Answer **any one** question*)

3. a) The initial rate of the hydrogen-bromine reaction is given by

$$\frac{d[HBr]}{dt} = 2K_2\left(\frac{K_1}{K_5}\right)^{1/2}[H_2]_0[Br_2]_0^{1/2}$$

if we assume that no HBr is present initially. The activation energies for the reactions are :

Reaction	Rate constant	E* (KJH/mole)
$Br_2 \rightarrow Br + Br$	k_1	192
$Br + Br \rightarrow Br_2$	k_5	unknown
$Br + H_2 \rightarrow HBr + H$	k_2	74

The production rate of HBr is found to be independent of temperature. If so what is the value of E* for K_5? [3]

b) State with reason(s) whether the following statements are true or false :

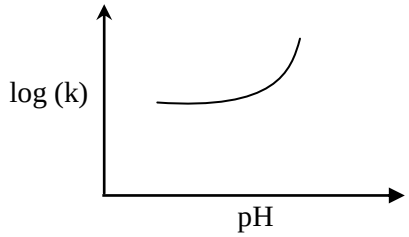
i) The larger the activation energy, the lesser is the effect of temperature on the rate constant.

ii) Collision theory justifies non-linear Arrhenius plots. [2+2]

c) The following homogeneous catalyzed reaction takes place in aqueous solution

$$\text{Reactant} \rightarrow \text{Product}$$

The rate constant for the reaction when plotted against pH gives the following curve



Argue whether the reaction is catalysed by acid or base.

d) The half life at 25°C is 30 minutes for an elementary reaction $A + B \rightarrow P$, where $[A] = [B] = 0{\cdot}01(M)$. Calculate the half-life when [A] = 0·01(M) and [B] = 0·1(M). [2]

e) For the mechanism

$$2NO_2 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} N_2O_4 ; \; NO_2 + SO_2 \xrightarrow{k_2} NO + SO_3$$

write down the expression for the rate of disappearance of NO_2. [2]

4. a) A reaction (single step) given as : $A^{++} + B^{-} \rightarrow P$

The rate constant is given as K_0 mole^{-1} litre sec^{-1}, when occurs in pure aqueous solvent. If the reaction takes place in 0·01mole/L^{-1} NaCl solution.

i) What will be the value of the new rate constant?

ii) Explain the change in rate constant in terms of stability of the initial and the transition states. [2+2]

b) The reaction $A \rightarrow P$ is catalysed by the product.

If at time 't' ,'x' is the amount of 'A' consumed up from an initial amount of a_0 per volume, prove that: $\ln \dfrac{a_0(p_0 + x)}{p_0(a_0 - x)} = k(a_0 + p_0)t$.

[p_0 is the amount per volume of P initially present.] [3]

c) State the values of the slope and intercept of the following plots :

i) log(rate) versus log (reactant concentration) for an n^{th} order reaction,

ii) log (initial rate) versus log (substrate concentration) at low substrate concentrations for an enzyme catalysed reaction, and

iii) log(rate constant) versus pH for a specific acid catalyzed reaction. [3]

d) The decomposition of acetaldehyde was studied in the gas phase at 791 K. The results of two measurements are :

Initial conc. (mole/L)	9·72 (10^{-3})	4·56 (10^{-3})
Half-life/S	328	572

i) What is the order of the reaction?

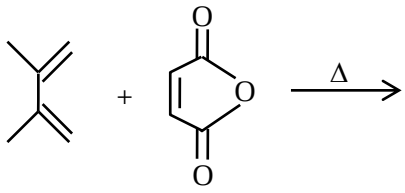
ii) Calculate the rate constant for the reaction with proper unit. [3]

Group – B

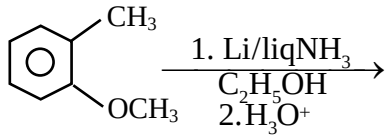
Unit - I

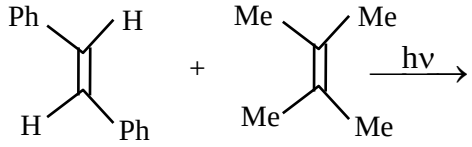
(*Answer **any one** question*)

5. a) Predict the product of the following reaction and give explanation by FMO approach : [3]



b) Identify the product(s) of the following reactions with plausible mechanism (**any two**) : [2×3]

i) 

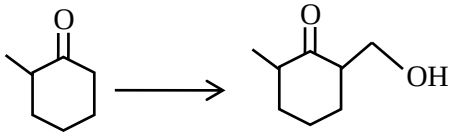
ii) 

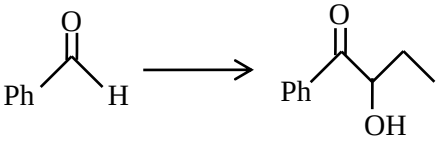
iii) $n-C_5H_{11}C\equiv CH \xrightarrow[2.H_2O_2/^-OH]{1.Si\alpha_2BH}$

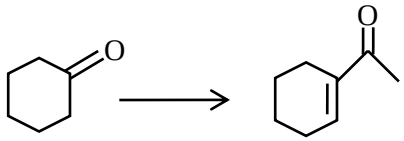
c) When the benzoin $Ar^1CHOHCOAr^2$ is heated with an aldehyde Ar^2CHO in presence of alcoholic KCN, a mixed benzoin $Ar^2CHOHCOAr^1$ is obtained —Explain. [3]

d) What happens when a solution of methyl mesitoate in conc. H_2SO_4 is poured into large volume of ice-cold water. [3]

6. a) Carry out the following conversions (mechanism not necessary) (**any three**) : [3×2]

i) 

ii) 

iii) 

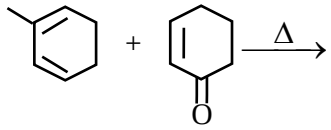
iv) acetone $\rightarrow CH_2=CHCOCH_3$

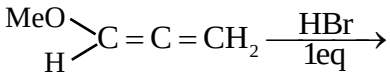
b) Explain why— [2×2½]

i) Ethyl 2-methylpropanoate fails to undergo Claisen condensation in presence of NaOEt, but can do so in presence of NaH.

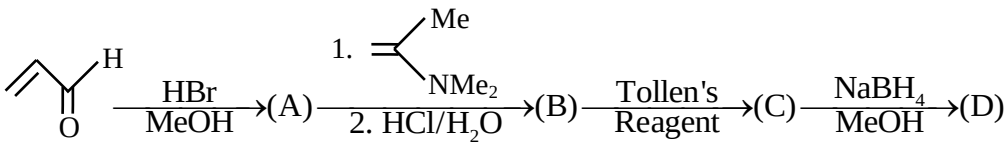
ii) In Knoevenagel condensation use of excess active methylene compound is not recommended.

c) Predict the major product of the following reactions : [2]

i) 

ii) 

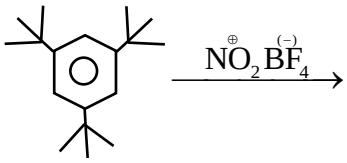
d) Write the structure (A) to (D) in the following reaction sequence : [2]

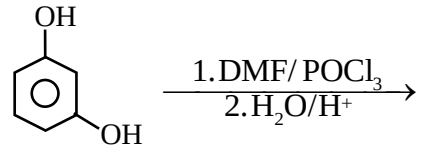


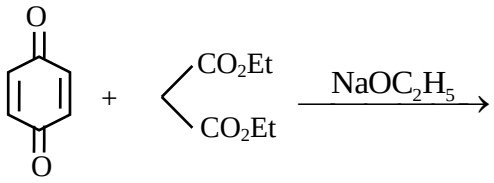
Unit - II

(*Answer **any one** question*)

7. a) Predict the product of the following reactions. Give mechanism. [3×2]

i) 

ii) 

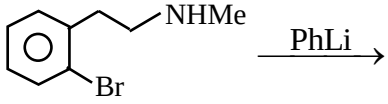
iii) 

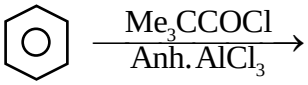
b) Account for the following observations :

i) 1, 3-Dichloro-2, 5-dinitorobenzene on treatment with methanolic NaOMe produces only 1,3-dichloro-2-methoxy-5-nitrobenzene.

ii) Phenol reacts with Br_2 water to form 2,4,6-tribromophenol, but forms a mixture of 2-and 4-bromophenol when it is treated with Br_2 in CCl_4 solution. [2×2]

8. a) Predict the product(s) with plausible mechanism : [2×2]

i) 

ii) 

b) Carry out the following conversions : [3×2]

i) Phenol → Paracetamol

ii) *p*-Cresol → *p*-Hydoxybenzoic acid

iii) *p*-Benzoquinone → Dichlorodicyanoquinone

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