RAMAKRISHNA MISSION VIDYAMANDIRA

(Residential Autonomous College under University of Calcutta)

B.A./B.SC. THIRD SEMESTER EXAMINATION, DECEMBER 2012

SECOND YEAR

Date : 14/12/2012 **CHEMISTRY (Honours)**

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

(Use separate answer-book for each group)

Group – A

(Attempt **one** from each Unit)

UNIT-I

1. a) The standard enthalpies of formation of $KClO_3$ and $KClO_4$ are –93.50 and –103.60 Kcal mol^{-1}, respectively. And the standard free energies of formation are –69.20 and –72.70 Kcal mol^{-1}, respectively for 25ºC. Assuming that $\Delta C_P = 0$ for the reaction,

$$KClO_4 = KClO_3 + \tfrac{1}{2}O_2$$

Calculate

(i) K_P for the reaction at 25ºC

(ii) ΔG^o for the reaction at 573K

(iii)The temperature coefficient of K_P around 25ºC, i.e. dK_P/dT . [2+2+2]

b) (i) From the definition of chemical potential arrive at the equation for fugacity of a real gas following $P(v-b) = RT - \dfrac{aP}{RT^2}$. [3]

(ii) What will be the fugacity in comparison to pressure for the above gas at above Boyle temperature? [1]

c) Estimate the pH of an aqueous buffer solution that contains 0.20 $molL^{-1}$ KH_2PO_4 and 0.1 $molL^{-1}$ K_2HPO_4.
The pK_a values of H_3PO_4 are 2.16, 7.21 and 12.32 at that temperature. [3]

d) Draw a schematic diagram of Gibbs energy (G) as a function of advancement (ξ) for an endothermic chemical reaction. Mention the equilibrium position also. [2]

2. a) Show that the fugacity coefficient (ϕ) of a gas is related to its molar Gibbs energy (G_m) as

$$\ln \phi = (G_m - G_m^{id}) / RT$$

Where G_m^{id} is the molar Gibbs energy of the corresponding ideal gas at the same *T* and *P*. [3]

b) Write down the Gibbs-Duhem equation. Hence justify that in a binary mixture, if one partial molar quantity is increased then the other must be decreased. [2]

c) NOCl dissociates according to the equation

$$2\,NOCl(g) \rightleftharpoons 2\,NO(g) + Cl_2(g)$$

A certain amount of NOCl is introduced into a flask at 200ºC. At equilibrium the total pressure is 1 atm and the partial pressure of NOCl is 0.64 atm. Calculate K_p. [3]

d) (i) Give a qualitative plot of $\gamma_\pm$ vs. $C^{1/2}$ for 1:1, 1:2 and 2:2 salt, and explain the behaviour. [2]

(ii) What is primary kinetic salt effect? Explain with reference to acid catalytic reaction. [2]

e) Prove that for an ideal gas reaction

$$\left(\frac{\partial \ln K_x}{\partial P}\right)_T = -\frac{\Delta n}{P}$$

Where Δn is the change in number of moles for the reaction and other terms have their usual significance. [3]

UNIT-II

3. a) (i) Mentioning the basic assumptions for Newton's viscous flow, find out the expression of viscosity of liquid, when it is flowing through a cylindrical tube of '*l*' length and '*d*' diameter. Of course the driving force is the pressure difference at two ends. [3]
   (ii) Gas viscosity increases with temperature but for liquid, viscosity decreases with *T*. True or false? Explain. [2]
   b) Stannic oxide can have both (+) vely and (–) vely charged colloid particles. Explain. [2]
   c) Consider two liquids *A* and *B* such that *A* has half the surface tension and twice the density of *B*. If liquid *A* rises to a height of 2.0 cm in a capillary, what will be the height of which liquid *B* will rise in the same capillary? [3]

4. a) What is 'zeta-potential'? Explain the stability of lyophobic colloids in the context of zeta-potential. [4]
   b) A brass sphere of diameter 5.5 mm and density 8.55 g cm^{-3} falls through a distance of 22.8 cm in a liquid having density 1.17 g cm^{-3} in 12.3 seconds. Calculate the coefficient of viscosity of the liquid. [3]
   c) For hydrogen gas at a certain temperature and pressure, it turns out that the mean free path is $5x10^{-9}$ m and the bimolecular frequency, Z_{AA} is $1.6x10^{14}$ moles collision $m^{-3}s^{-1}$. Calculate from above data the viscosity of gas. [3]

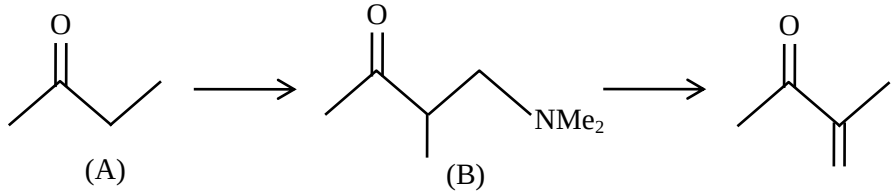
Group-B

Unit – I

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

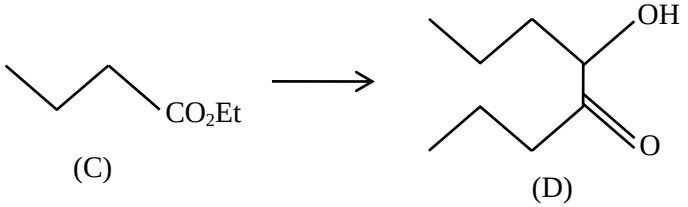
5. a) Give the reagents and the reaction conditions for the following transformations. Also provide mechanisms for the conversion of (A) to (B) or (C) to (D). [4]

i)



(A) (B)

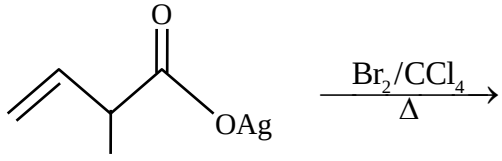
ii)



(C) (D)

   b) Prdict the products(s) of the following reactions and give plausible mechanisms in each case : (**any two**) [6]

i)

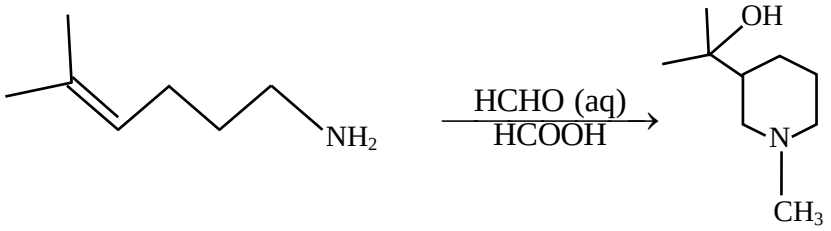


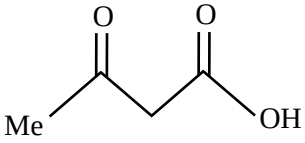
ii)

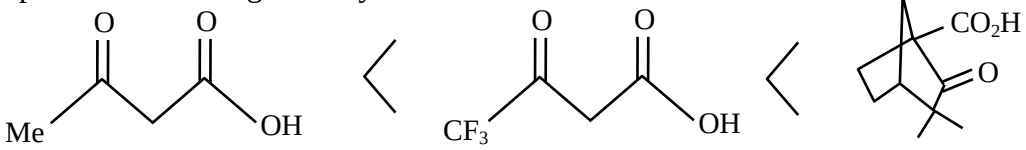
iii) $H_2C=C=CH_2 \xrightarrow{CH_2N_2/h\gamma}$

   c) p-N, N-dimethylaminobenzaldehyde fails to undergo benzoin condensation with KCN/EtOH, but the condensation takes place when mixed with benzaldehyde. Explain. [3]

d) Suggest a mechanism for the following transformation : [2]



6. a) Write the mechanism of decarboxylation of the β-ketoacid  and hence explain the following stability order. [3]

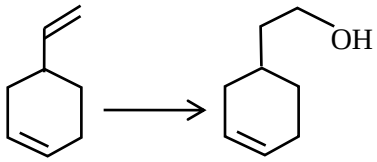


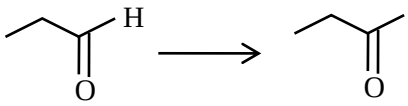
b) Write only the structures of the final products in the following cases :

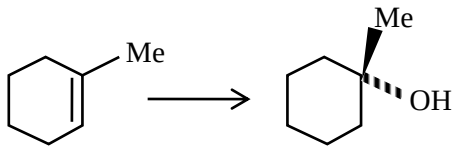
i) CH_3CHO (1 eq) + HCHO (4 eq) $\xrightarrow{HO^-}$

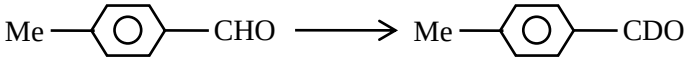
ii) PhCOMe (1 eq) + EtO_2C CO_2Et (2 eq) $\xrightarrow{\text{Piperidine}}$ [2]

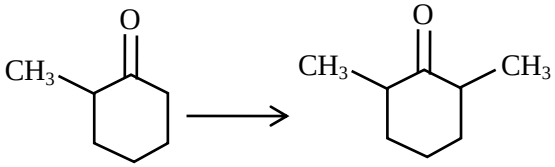
c) Carryout the following conversions with mechanism (**<u>any three</u>**) [3×2½]

i) 

ii) 

iii) 

iv) 

v) 

d) Predict the product with plausible mechanism when a solution of methyl mesitoate in conc. H_2SO_4 is poured into large volume of ice-cold water. [2½]

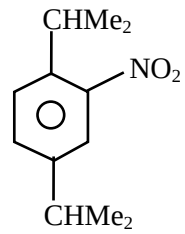
Unit – II

(*Answer **<u>any one</u>** question*)

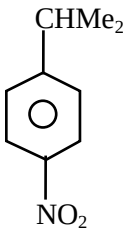
7. a) Give the mechanism of nitration reaction of chlorobenzene with mixed acid. Explain the directive influence of chlorine in this reaction. Draw the energy profile diagram of the reaction. [4]

b) Account for the formation of <u>m</u>-$MeOC_6H_4NH_2$ from either <u>o</u> or <u>m</u>-$MeoC_6H_4Br$ by treatment with $NaNH_2$ in liq NH_3. [3]

c) Nitration for p-diisopropylbenzene gives two products (A) and (B), the latter being formed in major amount — explain the observation. [3]



(A)



(B)

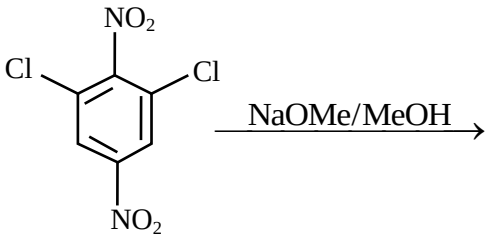
8. a) Explain the following observations : [4]

i) The products obtained from the treatment of sodium phenoxide and potassium phenoxide separately with carbondi-oxide under pressure differ widely.

ii) Reaction of p-benzoquinone with aniline gives 2,5-diamilino – p-benzoquinone while that with KCN/Conc. H_2SO_4 gives 2,3-dicyanoquinol.

b) Write down the course of each of the following reactions giving appropriate mechanism : [4]

i) 

ii) 

c) Nitration of cinnamic acid affords 4-nitrocinnamic acid. Explain. [2]