RAMAKRISHNA MISSION VIDYAMANDIRA

(Residential Autonomous College under University of Calcutta)

B.A./B.SC. THIRD SEMESTER EXAMINATION, DECEMBER 2011

SECOND YEAR

Date : 15/12/2011 **CHEMISTRY (Honours)**

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

[Use separate Answer Books for each group]

Group – A

Answer **any one** from the following :

1. a) Derive thermodynamically vant Hoff's reaction isotherm for a general chemical reaction, $\sum_i \nu_i A_i = 0$ [3]

   b) Define chemical potential in the context of mixture system. Is it an extensive property? What factor(s) can influence its value? [3]

   c) A laboratory study has provided information on the reaction $FeO(\ell) + CO(g) = Fe(s) + CO_2(g)$ over the temperature range 1650 K to 1809 K.

      i) Express Gibbs free energy as a function of extent of reaction.
      [Start with 1 mol of $FeO(\ell)$ and 1 mol of CO(g)]

      ii) From the data of μ^o at 1700K of different species, calculate K_P.

      $\mu^o_{FeO} = -451{\cdot}193\,KJ\,mol^{-1}$, $\mu^o_{CO} = -494{\cdot}471\,KJ\,mol^{-1}$

      $\mu^o_{Fe} = -98{\cdot}124\,KJ\,mol^{-1}$, $\mu^o_{CO_2} = -829{\cdot}283\,KJ\,mol^{-1}$ [2+2]

   d) Show that $V = \left(\frac{\partial G}{\partial P}\right)_{Tn}$. The molar Gibbs free energy of a certain gas is given by $G_m = RT\ln\left(\frac{P}{P^o}\right) + a + bP + cP^2$, where a, b & c are numerical constants. Obtain the equation of state for 'n' mole of this gas. [4]

   e) Fugacity is considered as an effective pressure— Justify. [1]

2. a) Does the equilibrium constant of a chemical reaction depend on,
      i) Standard states chosen for the reactants and products.
      ii) The stoichiometric representation of the reaction.
      Justify your answer. [1½+1½]

   b) In the gas phase reaction : $2A(g) + B(g) \rightleftharpoons 3C(g) + 2D(g)$; it was found that, 1.0, 2.0 & 1.0 mol of A, B & D respectively were mixed and allowed to attain equilibrium at 300 K, the resulting mixture contained 0.9 mol of C at a total pressure of 1.0 bar. Assuming all gasses behave ideally, calculate K_P & ΔG^o i.e, standard Gibbs free energy change considering pressure of 1.0 bar as standard state. [4]

   c) The equilibrium constant K_P of a reaction varies with T as $\ln K_P = -1{\cdot}04 - \frac{1088}{T} + \frac{1{\cdot}51\times10^5}{T^2}$ within 300K to 600K range. Calculate ΔS^o at 400K. [3]

   d) Find the ionic strength of the medium when 25 mL 0·08 mol L^{-1} $CaCl_2$ (aq) solution is mixed with 25 mL 0·02 mol L^{-1} Na_2SO_4 (aq) solution at room temperature. Assume $CaSO_4$ is almost insoluble in water. [3]

   e) Under isobaric heating, the Gibbs free energy of a fixed mass of pure substance decreases. Justify or criticize with reason(s). [2]

Answer **any one** from the following :

3. a) Derive Laplace equation for excess pressure inside a spherical bubble suspended in air. [3]

   b) The viscosity co-efficient (η) of a liquid decreases by 2% per °C rise of temperature. Show that η (at 25°C) : η (at 75°C) = e : 1, where 'e' is the base of natural logarithm. [2]

   c) The origin of the contact angle is traced to the balance of forces at the line contact between the liquid and solid. Show that for wetting of surface

   $$2\gamma^{\ell v} > w_A^{s\ell} > \gamma^{\ell v}$$

   where the terms are carrying using significances. [3]

   d) For air at 20°C (P = 0·0013 gm cc^{-1}) and ($\eta = 1{\cdot}81\times10^{-6}$ Poise) flowing through a tube of 1 cm diameter. What is the minimum value of velocity for turbulence to occur? [2]

4. a) Consider the cylindrical layer structure of liquid flowing through tube of radius 'r' with streamline flow. Start with Newton's law of viscosity to derive $v = \frac{1}{4\eta}(r^2 - x^2)\left(\frac{dP}{dL}\right)$ where v is the velocity of layer at x distance from the central axis of tube and $\left(\frac{dP}{dL}\right)$ is the pressure gradient. [3]

   b) The surface tension of a liquid decreases as the temperature increases. Explain qualitatively. [2]

   c) In the determination of the surface tension (γ) by 'drop count method', equal volumes of a liquid A & water gave 60 & 20 drops respectively. Calculate the γ of A. Given that 'ρ' of A & water are 0·896 & 0·964 g mL^{-1} respectively and γ of water is 72·75 mN m^{-1} at the temperature of interest. [2]

   d) i) Draw the qualitative plots of all interactions possible, in the same E vs r plot. Also mention the colloid stability curve.

   ii) When ions of opposite charge to that of colloidal particle is adsorbed aggregation occurs. Explain with zeta potential. [1½+1½]

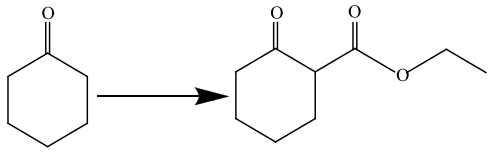
Group – B

Unit–I

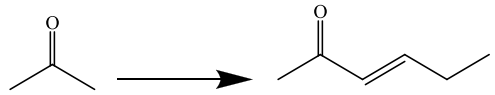
Answer **any one** question :

5. a) Carry out any three of the following conversions (mechanism is not necessary): [3x2]

(i)



(ii)



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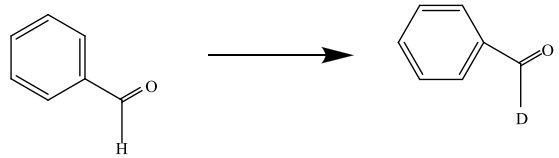
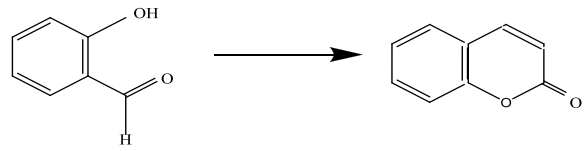
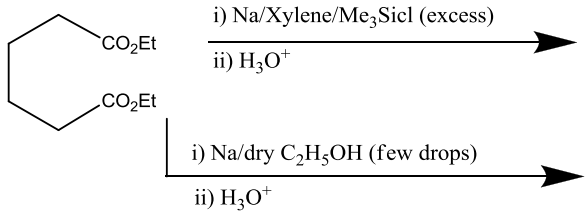


(iv)

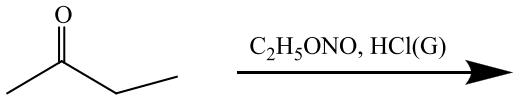


   b) Identify the products in the following reactions and explain their formation. [1½x2]



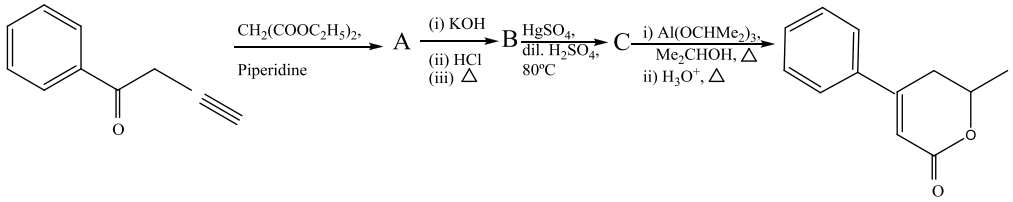
c) *p*-Dimethylanminobenzaldehyde fails to undergo benzoin condensation, but when mixed with benzaldehyde it gives a crossed condensation product — explain. [3]

d) Predict the products of the following reactions. Give mechanism. [1½x2]

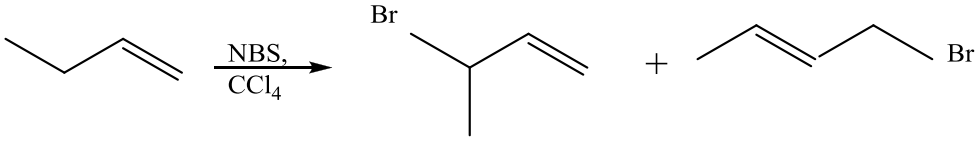
(i) 

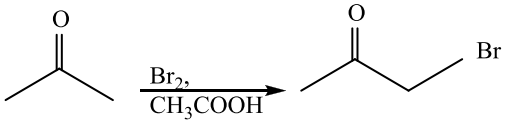
(ii) $(C_2H_5)_2NH$ $\xrightarrow[100^oC]{HCHO,\ HCOOH}$

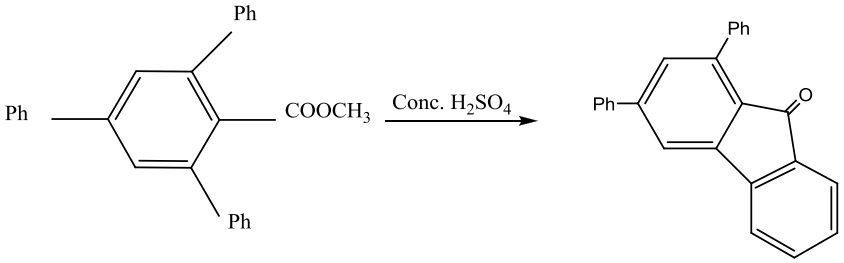
6. a) Identify *A, B,* & *C* in following reaction sequence: [3]



b) Outline the mechanism of the following transformations: [3x2]

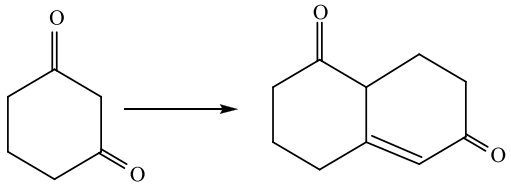
(i) 

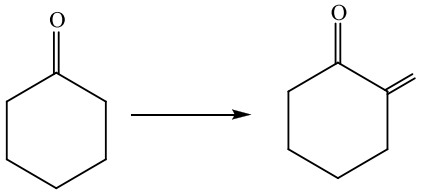
(ii) 

(iii) 

c) Carry out the following conversions: [3x2]

(i) $CH_3C \equiv CH \longrightarrow CH_3CH_2CHO$

(ii) 

(iii) 

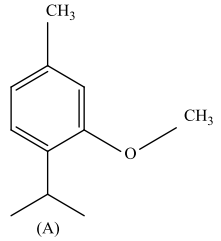
Unit–II

Answer **any one** question

7. a) Arrange the following compounds in order of increasing rates of nitration. Give reasons. [3]

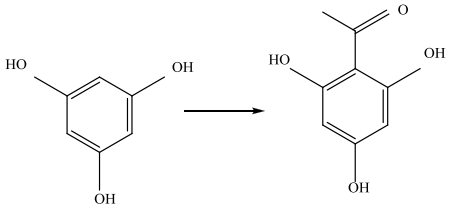
C_6H_6, C_6H_5F, C_6H_5Cl, $C_6H_5NO_2$, $C_6H_5CH_3$

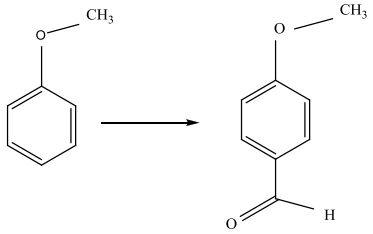
b) When the following compound (A) is treated with mixed acid, a single product having the molecular formula, $C_8H_8N_2O_5$ is produced. Explain the observation. [2]



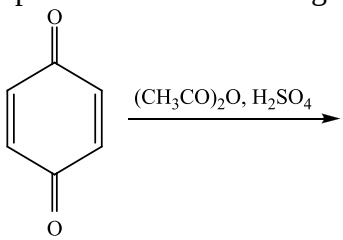
(A)

c) Carry out the following transformations (Mechanism is not necessary). [1½x2]

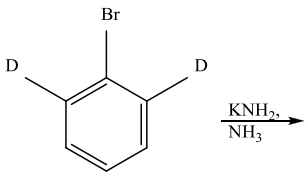
(i) 

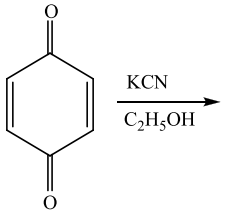
(ii) 

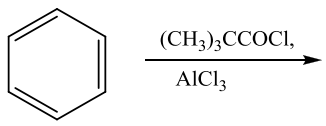
d) Predict the product of the following reaction showing the mechanism. [2]



8. a) Predict the product(s) of the following reactions. Give mechanism. [3x2]

(i) 

(ii) 

(iii) 

b) Write down the main product of nitration of Cinnamic acid. Give explanation behind its formation. [2]

c) Both Phenol and salicylic acid give identical product upon bromination — explain. [2]