RAMAKRISHNA MISSION VIDYAMANDIRA

(Residential Autonomous College affiliated to University of Calcutta)

SECOND YEAR [2014-17]

B.A./B.Sc. THIRD SEMESTER (July – December) 2015

Mid-Semester Examination, September 2015

Date : 14/09/2015 **CHEMISTRY (Honours)**

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

[Use a separate Answer Book for each group]

Group – A

1. a) The reaction $A + B \rightarrow P$ obeys rate law $d[A]/dt = -k[A][B]$. In experiment1, the initial concentrations of A and B are 0·01(M) and 2(M), respectively. In experiment 2, at the same temperature, the initial concentrations are both equal to a value C_0. Derive the value of C_0, such that the time for half reaction will be same for the two experiments. [3]

   b) For the reaction, $CH_3CHO(g) \rightarrow CH_4(g) + CO(g)$, the rate is expressed in terms of partial pressure and total pressure of the system. Show that partial pressure measurement is less effective than total pressure. [2]

   c) For the decomposition of N_2O_5, one of the proposed steps are

$$N_2O_5 \rightarrow NO_2 + NO_3$$
$$NO_2 + NO_3 \rightarrow N_2O_5$$
$$NO_2 + NO_3 \rightarrow NO_2 + O_2 + NO$$
$$NO + N_2O_5 \rightarrow 3NO_2$$

   The observed rate is 1st order w.r.t N_2O_5. Using SSA, arrive at the 1st order kinetics and show that overall activation energy = $(E_1+E_2-E_{-1})$ for the given steps [3]

OR

2. a) Use the following data for the reaction

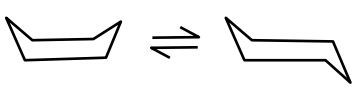
$$A + B \rightarrow C$$

[A]/(M)	[B]/(M)	Initial rate/(MS^{-1})
$2\cdot30\times10^{-4}$	$3\cdot10\times10^{-5}$	$5\cdot25\times10^{-4}$
$4\cdot60\times10^{-4}$	$6\cdot20\times10^{-5}$	$4\cdot20\times10^{-3}$
$9\cdot20\times10^{-4}$	$6\cdot20\times10^{-5}$	$1\cdot70\times10^{-2}$

   Find the orders and rate constants. [2]

   b) For a consecutive reaction, $A \rightarrow X \rightarrow P$ show that the slowest step will be the rate determining step. [2]

   c) According to Arrhenius theory, the pre-exponential factor is temperature independent, but in reality it is not the case. If the pre-exponential factor is temp. dependent, then show that activation energy is also temperature dependent. [2]

   d) Show that for an opposing reaction 

   $\ln\left(x_e / (x_e - x)\right)$ vs time plot is a straight line passing through origin, where x_e is the equilibrium concentration of 'chair' form. [2]

3. a) Deduce van't Hoff's reaction isotherm in the form $\Delta G = -RT\ln K_p + RT\ln Q_p$. [3]

   b) Discuss the effect of introduction of an inert gas on equillibrium of a gas phase reaction at constant temperature and (i) constant volume (ii) constant pressure. [3]

   c) $PCl_5(g)$ dissociates as $PCl_5(g) = PCl_3(g) + Cl_2(g)$. At 250°C the value of K_p is 1·78. Find the density of the reaction mixture at equilibrium in g/L unit at a total pressure of 1 atm. (Standard unit pressure is 1 atm and atomic weight of P is 31) [2]

OR

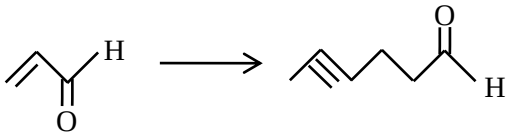
4. a) Derive, thermodynamically, the expression of Le Chatelier's principle regarding the shift of equilibrium on changing pressure on the reaction mixture. [3]

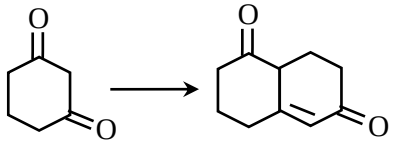
   b) For the equilibrium, C(graphite) + $CO_2(g)$ = 2CO(g), at 1123 K, mol percentage of CO gas at equilibrium is 93·77% at a total pressure of 1 atm. What is the value of mol percentage of CO(g) at equilibrium at a total pressure of 10 atm? [3]

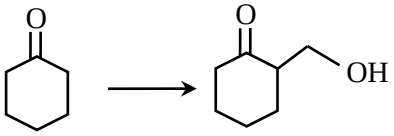
   c) Ammonium carbamate dissociates as $NH_2COONH_4(S) = 2NH_3(g) + CO_2(g)$. Find out an expression of K_p as a function of total pressure P. [2]

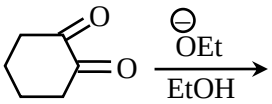
Group – B

5. a) Carry out the following conversions : [2×3]

   i) 

   ii) 

   iii) 

   b) Predict the product of the following reaction. Give mechanism.  [2]

OR

6. a) Between ethylene and acetylene which one is more reactive towards bromination and why? [2]

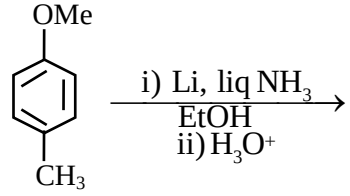
   b) Write down the product with mechanism. [3]

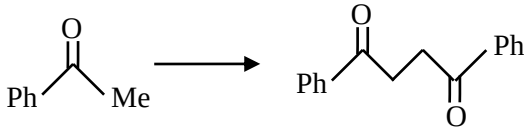
$$CH_3 - C \equiv C - CH_3 \xrightarrow{Na/liq\,NH_3}$$

   c) Write down the structure of the products of the reaction of 2-methyl-1, 3 butadiene with 1 mole of HBr. Give mechanism for their formation. Indicate with reason, which one is the major product. [3]

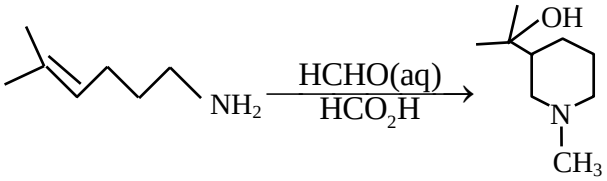
7. a) Account for the fact that in cycloaddition reaction of cyclopentadiene with maleic anhydride the less stable endo adduct predominates. [2]

   b) Write down the product of the following reaction. [2]



   c) Convert :  [2]

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

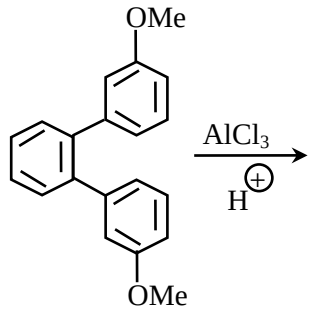


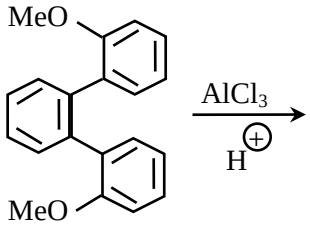
OR

8. a) Draw the structure of nitronium ion (NO_2^+). Mention the hybridization of each atom present in it. Cite an example of a linear compound which is isoelectronic with NO_2^+ and found naturally. [1]

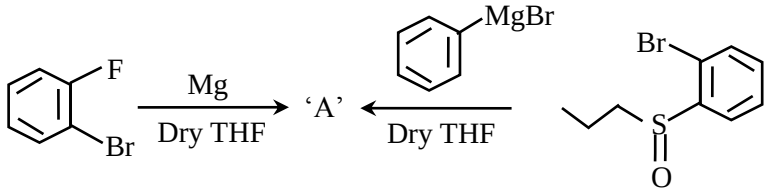
   b) How can you convert phenol into Aspirin? Give an outline of reactions. [2]

   c) Write down the product of each reaction. [1]

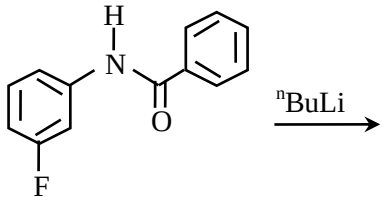
i) 

ii) 

   d) 'A' is a common reactive intermediate formed in both of these reactions. Identify 'A' and provide mechanistic approach where possible. [1]



   e) Suggest the final product of the following reaction. [1]



   f) Give an account of the reversible sulphonation of Naphthalene mentioning why the Wheland intermediate to the 1-sulphonic acid lower in energy than that to the 2-sulphonic acid where as the 2-sulphonic acid product lower in energy than the 1-sulphonic acid product? [2]

Group – C

9. a) How can you predict the geometry of EH_2 molecules ($E \rightarrow$ an element other than H) on the basis of Walsh Diagram? What are the defects of such prediction? [3+1]

   b) Draw molecular orbital diagrams for N_2 and O_2 molecules. Find HOMO in each case. [2+2+1]

OR

10. a) The photoelectron spectrum of HF shows a sharp band of approximately 16ev followed by two bands at 19ev (approximately) and at 38ev (approximately). Explain in the light of m.o. configuration of HF. [3]

    b) Draw the m.o. diagram of carbon monoxide molecule. Explain the extreme ability of the molecule to stabilise low oxidation states of metal. [2+2]

    c) "The m.o. theory provides a nice clue to explain the transition from covalent to ionic bonding in molecules." Comment on the statement. [2]

11. a) The pH of an aqueous $NaHCO_3$ solution is independent on the concentration. Comment on. [1·5]

    b) Why phenolphthalein is the most suitable indicator in the titration of a weak acid by a strong base? Explain by pH change during the titration. [3]

    c) Explain with example the Pauling Pearson paradox. [2]

    d) Cd^{+2} can be identified from a mixture of Cu^{+2} and Cd^{+2} in presence of KCN but not in absence of KCN. Explain with proper acid-base concept. [2·5]

OR

12. a) Deduce the equation for the pH of a salt solution derive from weak acids and strong bases. [2·5]

b) Calculate the pH of an aqueous solution containing 0·1 mol ammonia and 0·2 mol ammonium chloride in 0·5 dm^3. pK_b for ammonia is 4·7. [1·5]

c) Predict and justify the direction of the reaction : [3]

i) $[Fe(CN)_6]^{4-} + 6BF_3 \rightleftharpoons Fe^{2+} + 6[CN \rightarrow BF_3]^-$

ii) $2LaBr_3 + 3CdCO_3 \rightleftharpoons La_2(CO_3)_3 + 3CdBr_2$

d) Write the importance of Lux-Flood concept with a proper reaction. [2]

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