RAMAKRISHNA MISSION VIDYAMANDIRA

(Residential Autonomous College affiliated to University of Calcutta)

B.A./B.Sc. SECOND SEMESTER EXAMINATION, MAY 2019

FIRST YEAR (BATCH 2018-21)

Date : 16/05/2019 **CHEMISTRY (Honours)**

Time : 11.00 am – 1.00 pm **Paper : II [Gr-A]** Full Marks : 40

[Use one Answer Book for Unit I and another Answer Book for Unit II & III]

(Attempt one question from each Unit)

Unit I [15 marks]

1. a) Predict whether the reaction rate would increase or decrease with increase of solvent polarity in the following reaction: [2]

$$Et_3N + EtI \xrightarrow[ROH/C_6H_6]{S_N2} Et_4N^+I^-$$

b) What are the characteristic difference between E_2 and E_1CB reactions? How would you establish that the following reaction follows E_2 and not E_1CB mechanism ? [4]

$$Ph\ CH_2CH_2Br \xrightarrow{\ominus OEt} Ph\ CH{=}CH_2$$

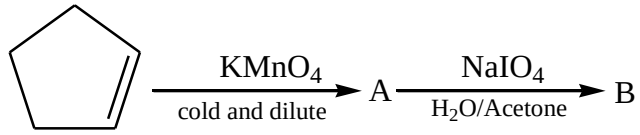
c) Complete the following reactions with mechanism. Also mention the sterochemistry of products, if possible. [2×2]

i) Cis-2- Butene $\xrightarrow{(BD_3)_2,\ THF}$ $\xrightarrow{AcOD}$

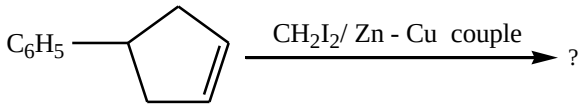
ii) Cis-2- Butene + Br_2 $\xrightarrow{CCl_4}$

d) 'Alkyl halides give mainly cyanides with ethanolic KCN but with AgCN isocyanides are the main product' — Explain. [2]

e) Identify the products for the following reactions. Also give mechanism for formation of B from A. [3]

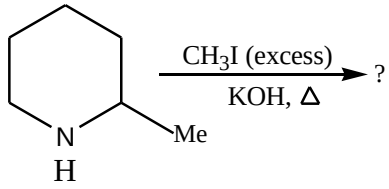


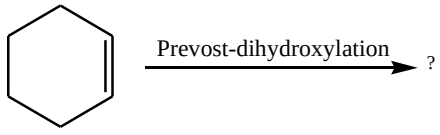
2. a) Explain the following reactions with mechanism. [2×2]

(i) 

(ii) Trans-2-butene $\xrightarrow[ii)\ PPh_3]{i)\ RCO_3H}$?

b) Explain the following reactions with mechanism. [2.5×2]





c) Starting from PhCH = CH_2 how will you synthesize; [3]
i) α- phenylethyl alcohol and ii) β- phenylethyl alcohol.

d) Under appropriate condition, (S)-1-bromo-1-fluoroethane reacts with sodium methoxide to give pure(S)- 1-fluoro-1-methoxyethane. [3]

$(S)-CH_3CHBrF + NaOCH_3 \rightarrow (S)-CH_3CHFOCH_3 + NaBr$

i) Why is bromide rather than fluoride replaced?
ii) Draw perspective structures for the starting material, the transition state, and the product.
iii) Does the product show retention or inversion of configuration?
iv) Is this result consistent with reaction by the S_N2 mechanism?

Unit II [13 marks]

(Take T = 298 K and P = 1 atm, if not mentioned)

3. a) A fixed amount of pure ideal gas is confined in a chamber that has two sub-units (A and B) separated by a closed, immovable boundary. All outside boundaries are non-adiabatic, immovable and closed so that the temperature, number of gas molecules and total volume are constant. The pressure of the gas in the two subunits are different (P_A and P_B respectively in sub-units A and B). The separating boundary is now made 'open' with respect to the gas.
i) Show that as a consequence there will be a net spontaneous flow of gas from A to B (if $P_A > P_B$) .
ii) Under what condition equilibrium would be reached?
iii) Purely on a thermodynamic basis can you predict how much time the process will take to reach equilibrium?
iv) Now imagine we radioactively mark a particular molecule in the chamber A before opening up the separating wall. Does the spontaneous flow of gas from A to B necessarily mean that once equilibrium is reached the marked molecule will be found in the chamber B? [4+1+1+1]

b) Show that for an irreversible process $(dU)_{T,S} < 0$, stating the conditions applicable. [2]

c) How would a Carnot cycle look in a T-S diagram? Label the states and various processes involved. What does the closed area signify? [4]

4. a) An Air conditioner is used to cool a room to a temperature T_L when the outside temperature is T_H. Show that the efficiency of the air-conditioner is inversely proportional to the difference between the outside temperature (T_H) and that of the room (T_L), provided we cool the room to a fixed temperature (i.e. T_L is constant). (Assume the air-conditioner works reversibly) [3]

b) Water has $V_m = 18\ cm^3/mol$, $C_{p,m} = 75.3\ J/K.mol$ *and* $\alpha = 2.07\times10^{-4} K^{-1}$. Compute the (i) change of entropy and (ii) decrease in temperature that occurs, if water at 298 K and 1000 atm pressure is brought reversibly and adiabatically to 1 atm pressure. Assume $\kappa = 0$. [hint : what is the entropy of a reversible, adiabatic process?] [3]

c) In what proportions should n-hexane and n-heptane be mixed to achieve the greatest ΔS mix assuming ideal mixing. [3]

d) Find the Joule-Thomson coefficient $\mu_{J.T}$. of a gas obeying the equation $P(V-b) = RT$. Comment on the result. [4]

Unit III [12 marks]

5. a) Consider a consecutive reaction $A \xrightarrow{k_1} B \xrightarrow{k_2} C$. Assume that only A is present initially, find the expression for [B] and [C] as function of time. [3]

b) A gas decomposes according to second order kinetics. When the initial pressure is 500 torr, 40 % decomposition occurs in 30 minutes. Find out the time required for 75% decomposition of the gas and the value of rate constant. [3]

c) The reaction in aqueous solution involves the following two elementary steps:

Step 1: $Hg_2^{2+} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} Hg^{2+} + Hg$ (rapid equilibrium)

Step 2: $Hg + Tl^{3+} \xrightarrow{k_2} Hg^{2+} + Tl^{+1}$ (slow)

Applying appropriate approximation method show that the reaction is of negative order with respect to Hg^{2+}? [3]

d) Graphically represent the plot of log k versus pH for a reaction that is catalyzed homogenously both by acid and base. Justify the plot from appropriate mathematical expression. [3]

6. a) How can the following two mechanisms for production of B and C from A be distinguished experimentally? When would they appear indistinguishable? [3]

(i) $A \xrightarrow{k_1} B + C$ (ii) $A \begin{cases} \xrightarrow{k_2} B \\ \xrightarrow{k_3} C \end{cases}$

b) The data of a chemical reaction is plotted as 1/[reactant] vs time and the plot is a straight line with intercept 4.0×10^2 mol^{-1} dm^3 and slope 4.0 mol^{-1} dm^3 s^{-1} as shown in the figure. Calculate the half-life of the reaction. [3]

c) "unimolecular reactions are not always first order"— Justify the statement using Lindemann's mechanism. [3]

d) A certain first order reaction is 20% complete in 15 minutes at 27°C but for the same extent of reaction it takes 5 minutes at 37°C. What is the activation energy of the reaction? [3]

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