EXERCISE # S-II

1. For the reaction,

$A + B \longrightarrow$ Product

rate law is

rate = $k [A]^2 [B]$

where $k = 5 \times 10^{-5}$ $(mol/L)^{-2}$ min^{-1}

Determine the **time (in minutes)** in which concentration of 'A' becomes half of its initial concentration. If initial concentration of A and B are 0.2 M and 2×10^3 M respectively.

2. The decomposition of a compound P, at temperature T according to the equation

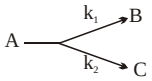
$2P_{(g)} \longrightarrow 4Q_{(g)} + R_{(g)} + S_{(l)}$

is the first order reaction. After 30 minutes from the start of decomposition in a closed vessel, the total pressure developed is found to be 317 mm Hg and after a long period of time the total pressure observed to be 617 mm Hg. Calculate the total pressure of the vessel after 75 minute, if volume of liquid S is supposed to be negligible. Also calculate the time fraction $t_{7/8}$.

Given : Vapour pressure of S (l) at temperature T = 32.5 mm Hg.

3. An optically active compound A upon acid catalyzed hydrolysis yield two optically active compound B and C by pseudo first order kinetics. The observed rotation of the mixture after 20 min was 5° while after completion of the reaction it was – 20°. If optical rotation per mole of A, B & C are 60°, 40° & – 80°. Calculate half life of the reaction.

4. A certain organic compound A decomposes by two parallel first order mechanism



If $k_1 : k_2 = 1 : 9$ and $k_1 = 1.3 \times 10{-}5\ s^{-1}$.

Calculate the concentration ratio of C to A, if an experiment is started with only A and allowed to run for one hour.

5. The reaction of formation of phosgene from CO and Cl_2 is $CO + Cl_2 \longrightarrow COCl_2$ The proposed mechanism is

(i) $Cl_2 \underset{K_{-1}}{\overset{K_1}{\rightleftharpoons}} 2Cl$ (fast equilibrium)

(ii) $Cl + CO \underset{K_{-2}}{\overset{K_2}{\rightleftharpoons}} COCl$ (fast equilibrium)

(iii) $COCl + Cl_2 \xrightarrow{K_3} COCl_2 + Cl$ (slow)

Show that the above mechanism leads to the following rate law $\frac{d[COCl_2]}{dt} = K[CO]\ [Cl_2]^{3/2}$.

Where $K = k_3 \cdot \frac{k_2}{k_{-2}} \left(\frac{k_1}{k-1}\right)^{1/2}$.

6. The rate constant for the II order ($A + B \longrightarrow X$) obeys the equation

$$\log_{10} K = \frac{3163}{T} + 12$$

T is temperature in Kelvin.

Time and concentration were in minute and mol L^{-1} respectively. At 43.3°C initial concentration of each of the reactant is 0.001 mol L^{-1}. Find half life .

7. Two reactions (i) A → products (ii) B → products, follow first order kinetics. The rate of the reaction (i) is doubled when the temperature is raised from 300 K to 310K. The half life for this reaction at 310K is 30 minutes. At the same temperature B decomposes twice as fast as A. If the energy of activation for the reaction (ii) is half that of reaction (i), calculate the rate constant of the reaction (ii) at 300K.

8. At room temperature (20°C) orange juice gets spoilt in about 64 hours. In a refrigerator at 3°C juice can be stored three times as long before it gets spoilt. Estimate (a) the activation energy of the reaction that causes the spoiling of juice. (b) How long should it take for juice to get spoilt at 40°C?

9. For the two parallel reactions $A \xrightarrow{k_1} B$ and $A \xrightarrow{k_2} C$, show that the activation energy E' for the disappearance of A is given in terms of activation energies E_1 and E_2 for the two paths by

$$E = \frac{k_1E_1 + k_2E_2}{k_1 + k_2}$$

10. An organic compound dissociates into n parallel first order reactions simultaneously and produces n different products P_1, P_2, P_3, ..., P_n having rate constants k, 2k, 3k, ..., nk and activation energies E, 2E, 3E ....., nE respectively. Calculate the overall energy of activation of the compound P.

ANSWER KEY

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1. 0050.00

2. P_t = 379.55 mm Hg, $t^{7/8}$ = 399.96 min

3. 20 min

4. 0.537

6. 10^{-19} minute

7. k = 0.0327 min^{-1}

8. (a) 43.46 $kJmol^{-1}$, (b) 20.47 hour

9. $\therefore \quad E_{a_{overall}} = \frac{k_1}{k_1 + k_2} E_{a_1} + \frac{k_2}{k_1 + k_2} E_{a_2}$

10. $E_{overall} = E/3(2n+1)$