

(Given: $R = 8.314 \text{ J.K}^{-1}.\text{mol}^{-1}$, $k_a = 1.3995 \times 10^{-23} \text{ J.K}^{-1}$, $h = 6.626 \times 10^{-34} \text{ J.s}$)

Name: MARKING SCHEME

Dept:

Reg. No:

1. Two reactions of the same order have identical frequency factors, and activation energies differing by 10 kJ/mol . Calculate the ratio of their rate constants at 300K .

2. Two isomers (A and B) of a given compound dimerize as follows:



Both processes are known to be second-order in the reactant, and k_1 is known to be $0.250 \text{ L mol}^{-1} \text{ s}^{-1}$ at 25°C . In a particular experiment, A and B were placed in separate containers at 25°C where the initial concentration of A was $1.0 \times 10^{-2} \text{ M}$ and the initial concentration of B was $2.5 \times 10^{-2} \text{ M}$. After each concentration had progressed for 3.00 min , $[A] = 3.00[B]$. In this case the rate laws are defined as follows:

$$\text{Rate} = -\frac{d[A]}{dt} = k_1[A]^2$$

$$\text{Rate} = -\frac{d[B]}{dt} = k_2[B]^2$$

(i) Calculate the concentration of A_2 after 3.00 min [Hint: Determine $[A]$ after 3 min]

(ii) Calculate the value of k_2

Q 1

$$k_1 = A e^{-E_{a1}/RT}$$

$$k_2 = A e^{-E_{a2}/RT}$$

$$\frac{k_1}{k_2} = \frac{A e^{-E_{a1}/RT}}{A e^{-E_{a2}/RT}} = \frac{e^{-E_{a1}/RT}}{e^{-E_{a2}/RT}} = e^{-E_{a1}/RT - (-E_{a2}/RT)}$$

$$\text{Since } \frac{k_1}{k_2} = e^{-(E_{a1}-E_{a2})/RT}$$

$$\text{and } E_{a1} - E_{a2} = 10 \text{ kJ mol}^{-1}$$

$$\frac{k_1}{k_2} = e^{-\frac{10 \times 10^3 \text{ J mol}^{-1}}{8.314 \times 300 \text{ K}}} = e^{-\frac{10 \times 10^3}{2494.2}}$$

$$\frac{k_1}{k_2} = e^{-4.009} = 0.018$$

$$\therefore \frac{k_2}{k_1} = 55.09 \quad \text{OR} \quad k_2 = 55.09 k_1$$

5 mks.

$$\text{OR } \ln\left(\frac{k_2}{k_1}\right) = \frac{E_{a1} - E_{a2}}{RT}$$

$$\ln\left(\frac{k_2}{k_1}\right) = \frac{10 \times 10^3 \text{ J mol}^{-1}}{8.314 \text{ J K}^{-1} \text{ mol}^{-1} \times 300 \text{ K}}$$

$$\ln\left(\frac{k_2}{k_1}\right) = 4.009$$

$$\frac{k_2}{k_1} = e^{4.009} = 55.09$$

$$\therefore \frac{k_2}{k_1} = 55.09 \quad \text{OR} \quad k_2 = 55.09 k_1$$

$$Q2. \quad kt = \frac{x}{a(a-x)} \quad \text{or} \quad \frac{1}{a-x} - \frac{1}{a} \quad \text{or} \quad \frac{1}{[A]_t} - \frac{1}{[A]_0} \quad \checkmark$$

Given that

$$\text{at } t=0, \quad k_1 = 0.250 \text{ L mol}^{-1} \text{ s}^{-1} \text{ at } 25^\circ\text{C}$$

$$[A]_0 \text{ or } a = 1.0 \times 10^{-2} \text{ M}$$

$$[B]_0 \text{ or } b = 2.5 \times 10^{-2} \text{ M}$$

$$\text{at } t=3 \text{ mins, } [A]_t \text{ or } (a-x) = 3.00 [B]$$

(i) To determine $[A_2]$ at ^{3.00 mins} ~~3.00 mins~~ (ii) For k_2

$$kt = \frac{1}{[A]_t} - \frac{1}{[A]_0} \quad \checkmark$$

$$0.250 \times (3 \times 60) \text{ s} = \frac{1}{[A]_t} - \frac{1}{1.0 \times 10^{-2}} \quad \checkmark$$

$$45. = \frac{1}{[A]_t} - \frac{1}{0.01}$$

$$\therefore \frac{1}{[A]_t} = 145, \quad [A]_t = 0.007 \text{ M} \quad \checkmark$$

~~$$\text{But } [A]_t = a-x$$~~

~~$$[A]_t = 0.007 \text{ M}$$~~

$$\text{Since } [A]_t = a-x \quad \checkmark$$

$$\text{When } x = [A_2] \text{ and } a = [A]_0$$

$$\therefore [A_2] \text{ after 3 mins } \Rightarrow$$

$$0.007 = 0.01 - x$$

$$x = \underline{\underline{0.003 \text{ M}}} \quad \checkmark$$

$$[A] = 3.00 [B] \text{ after 3 min}$$

$$\therefore 0.007 = 3.00 [B] \quad \checkmark$$

$$\therefore [B] = 0.0023 \text{ M} \quad \checkmark$$

Hence using the equation

$$k_2 t = \frac{1}{[B]_t} - \frac{1}{[B]_0}$$

$$k_2 \times 3 \times 60 \text{ s} = \frac{1}{0.0023} - \frac{1}{0.025} \quad \checkmark$$

$$k_2 (180) = 434.78 - 40$$

$$k_2 = \underline{\underline{2.173 \text{ L mol}^{-1} \text{ s}^{-1}}} \quad \checkmark$$

[10 marks]