

Solutions to Exercise

Exercise 1

Determine the rate constant for each of the following first-order reactions, in each case expressed for the rate of loss of A:

a) $A \longrightarrow B$, given that the concentration of A decreases to one-half its initial value in 1000.s;

b) $A \longrightarrow B$, given that the concentration of A decreases from 0.67 mol/L to 0.53 mol/L in 25s;

c) $2A \longrightarrow B + C$, given that $[A]_0 = 0.153$ mol/L and that after 115s the concentration of B rises to 0.034 mol/L.

Solution:

a) Rate constant:

$$t_{1/2} = \frac{\ln 2}{k} \Rightarrow k = \frac{\ln 2}{t_{1/2}} = 6.931 \times 10^{-4} s^{-1}$$

Rate law:

$$r = -\frac{d[A]}{dt} = 6.931 \times 10^{-4} [A] \text{ mol}/(L \cdot s)$$

b)

$$k = -\frac{\ln\left(\frac{0.53}{0.67}\right)}{25} = 9.4 \times 10^{-3} s^{-1}$$

Rate law:

$$r = -\frac{d[A]}{dt} = 9.4 \times 10^{-3} [A] \text{ mol}/(L \cdot s)$$

c) Rate constant: The process consumes $0.034 \times 2 = 0.068$ M A. The final concentration of A is therefore $0.153 - 0.068 = 0.085$ M. Similar to b),

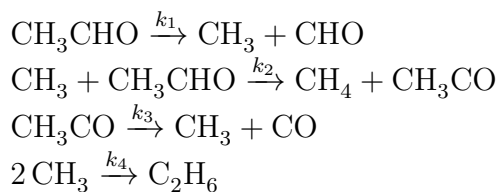
$$k = -\frac{\ln\left(\frac{0.085}{0.153}\right)}{115} = 5.1 \times 10^{-3} s^{-1}$$

Rate law:

$$r = -\frac{d[A]}{2dt} = 2.6 \times 10^{-3} [A] \text{ mol}/(L \cdot s)$$

Exercise 2

Dissociation reaction of acetaldehyde $CH_3CHO \longrightarrow CH_4 + CO$ is composed of the following steps



deduce the rate law with steady-state approximation:

$$r = k_2 \left(\frac{k_1}{2k_4} \right)^{1/2} [\text{CH}_3\text{CHO}]^{3/2}$$

Solution:

$$\frac{d[\text{CH}_3]}{dt} = k_1[\text{CH}_3\text{CHO}] - k_2[\text{CH}_3][\text{CH}_3\text{CHO}] + k_3[\text{CH}_3\text{CO}] - 2k_4[\text{CH}_3]^2 = 0$$

$$\frac{d[\text{CH}_3\text{CO}]}{dt} = k_2[\text{CH}_3][\text{CH}_3\text{CHO}] - k_3[\text{CH}_3\text{CO}] = 0$$

From the second equation, we obtain

$$[\text{CH}_3\text{CO}] = \frac{k_2[\text{CH}_3][\text{CH}_3\text{CHO}]}{k_3}$$

Substitute it into the first equation:

$$k_1[\text{CH}_3\text{CHO}] - 2k_4[\text{CH}_3]^2 = 0$$

$$[\text{CH}_3] = \sqrt{\frac{k_1}{2k_4}} [\text{CH}_3\text{CHO}]$$

Therefore,

$$r = \frac{d[\text{CH}_4]}{dt} = k_2[\text{CH}_3][\text{CH}_3\text{CHO}] = k_2 \sqrt{\frac{k_1}{2k_4}} [\text{CH}_3\text{CHO}]^{3/2}$$