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) 2 A $\longrightarrow$ 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:

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

b)

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

Rate law:

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

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

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

Rate law:

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

Exercise 2

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

$CH_3CHO \xrightarrow{k_1} CH_3 + CHO$
$CH_3 + CH_3CHO \xrightarrow{k_2} CH_4 + CH_3CO$
$CH_3CO \xrightarrow{k_3} CH_3 + CO$
$2\,CH_3 \xrightarrow{k_4} C_2H_6$
deduce the rate law with steady-state approximation:

$$r = k_2 \left(\frac{k_1}{2k_4}\right)^{1/2} [CH_3CHO]^{3/2}$$

Solution:

$$\frac{d[CH_3]}{dt} = k_1[CH_3CHO] - k_2[CH_3][CH_3CHO] + k_3[CH_3CO] - 2k_4[CH_3]^2 = 0$$

$$\frac{d[CH_3CO]}{dt} = k_2[CH_3][CH_3CHO] - k_3[CH_3CO] = 0$$

From the second equation, we obtain

$$[CH_3CO] = \frac{k_2[CH_3][CH_3CHO]}{k_3}$$

Substitute it into the first equation:

$$k_1[CH_3CHO] - 2k_4[CH_3]^2 = 0$$

$$[CH_3] = \sqrt{\frac{k_1}{2k_4}[CH_3CHO]}$$

Therefore,

$$r = \frac{d[CH_4]}{dt} = k_2[CH_3][CH_3CHO] = k_2\sqrt{\frac{k_1}{2k_4}}[CH_3CHO]^{3/2}$$