6.6 Parallel reactions

As a last example we will discuss parallel reactions of reactions of different order.

$$\begin{aligned} A &\xrightarrow{k_1} B \quad \text{first order} \\ A &\xrightarrow{k_2} C \quad \text{second order} \end{aligned} \tag{6.44}$$

So the set of differential equations is

$$\begin{aligned} \frac{dA}{dt} &= -k_1\,A - k_2\,A^2 = -A\,(k_1 + k_2\,A) \\ \frac{dB}{dt} &= k_1\,A \\ \frac{dC}{dt} &= k_2\,A^2 \end{aligned} \tag{6.45}$$

Having solved the differential equation for $A(t)$, the functions $B(t)$ and $C(t)$ are just found by integration. Separating the variables we get for the first differential equation

$$-t = \int_{A_0}^{A} \frac{dA}{A\,(k_1 - k_2\,A)} = \int_{A_0}^{A} \left(\frac{1}{A} - \frac{k_2}{k_1 + k_2\,A}\right)\frac{1}{k_1} dA = \frac{1}{k_1}\left(\ln\frac{A}{k_1 + k_2\,A} - \ln\frac{A_0}{k_1 + k_2\,A_0}\right) \tag{6.46}$$

Solving for $A(t)$ we get

$$\frac{1}{A(t)} = \frac{1}{A_0}\left[\exp(k_1\,t)\left(1 + \frac{k_2\,A_0}{k_1}\right) - \frac{k_2\,A_0}{k_1}\right] \tag{6.47}$$

Analyzing the limiting cases we get

- for $k_1 \gg k_2\,A_0$

  $$\frac{1}{A(t)} = \frac{1}{A_0}\exp(k_1\,t) \quad \text{i.e.} \quad A(t) = A_0\,\exp(-k_1\,t) \tag{6.48}$$

  which is the solution for a simple first order reaction.

- for $k_1 \ll k_2\,A_0$ we simplify

  $$\exp(k_1\,t) \approx 1 + k_1\,t \quad . \tag{6.49}$$

  Including this into Eq. (6.47) we find

  $$\frac{1}{A(t)} \approx \frac{1}{A_0}\left(1 + k_1\,t + \frac{k_2\,A_0}{k_1} + \frac{k_2\,A_0\,k_1\,t}{k_1} - \frac{k_2\,A_0}{k_1}\right) \approx \frac{1}{A_0}\,(1 + A_0\,k_2\,t) = \frac{1}{A_0} + k_2\,t \tag{6.50}$$

  which is the solution for a simple second order reaction as shown in the table in section 6.2.