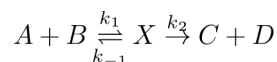


Dynamics and Kinetics. Exercises 3: Solutions

Problem 1

(a)



Note step 2 is irreversible $\Rightarrow$ goes to completion (limited only by initial concentration).

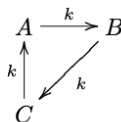
Final extent $x_\infty = [B]_0 = 1$ since $[B]_0 < [A]_0$.

I.e., all of B reacts to X to $C + D$.

An equivalent amount of A is consumed, so:

$$[A]_\infty = 1, [B]_\infty = [X]_\infty = 0, [C]_\infty = [D]_\infty = 1.$$

(b) Not reversible, but cyclic:



In equilibrium, $\frac{d[A]}{dt} = \frac{d[B]}{dt} = \frac{d[C]}{dt} = 0$.

$$\frac{d[A]}{dt} = -k[A] + k[C] = 0 \Rightarrow k[A] = k[C] \Rightarrow [A] = [C]$$

$$\frac{d[B]}{dt} = -k[B] + k[A] = 0 \Rightarrow k[B] = k[A] \Rightarrow [A] = [B]$$

$$\frac{d[C]}{dt} = -k[C] + k[B] = 0 \Rightarrow k[C] = k[B] \Rightarrow [B] = [C]$$

Note that

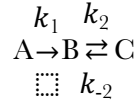
$$\frac{d[A]}{dt} + \frac{d[B]}{dt} + \frac{d[C]}{dt} = 0.$$

Therefore, $[A] + [B] + [C]$ is constant (cons. of mass).

Finally, since $[A] = [B] = [C]$ and $[A] + [B] + [C] = \text{const.} = [A]_0 = 1$, we get $[A]_\infty = [B]_\infty = [C]_\infty = 1/3$, as you might have expected intuitively.

Problem 2

Given is the following consecutive reaction with a reversible second step.



a) Derive expressions for the concentrations of A and B for the initial conditions $[B]_0 = [C]_0 = 0$.

For A, we find a first-order decay,

$$[A] = [A]_0 e^{-k_1 t}$$

For B,

$$\frac{d[B]}{dt} = k_1[A] + k_{-2}[C] - k_2[B]$$

With $[C] = [A]_0 - [A] - [B]$ and $[A] = [A]_0 e^{-k_1 t}$

$$\frac{d[B]}{dt} = [A]_0 (k_{-2} + (k_1 - k_{-2})e^{-k_1 t}) - (k_{-2} + k_2)[B]$$

For this inhomogeneous linear ODE, we obtain a general solution (variation of constants)

$$[B] = c(t)e^{-(k_2+k_{-2})t}$$

$$\dot{c}(t)e^{-(k_2+k_{-2})t} = [A]_0 (k_{-2} + (k_1 - k_{-2})e^{-k_1 t})$$

$$\dot{c}(t) = [A]_0 k_{-2} e^{(k_2+k_{-2})t} + [A]_0 (k_1 - k_{-2}) e^{(k_2+k_{-2}-k_1)t}$$

After integration ($c(t) = 0$ because of the boundary conditions), we find

$$c(t) = \frac{[A]_0 k_{-2}}{k_2 + k_{-2}} (e^{(k_2+k_{-2})t} - 1) + \frac{[A]_0 (k_1 - k_{-2})}{k_2 + k_{-2} - k_1} (e^{(k_2+k_{-2}-k_1)t} - 1)$$

so that

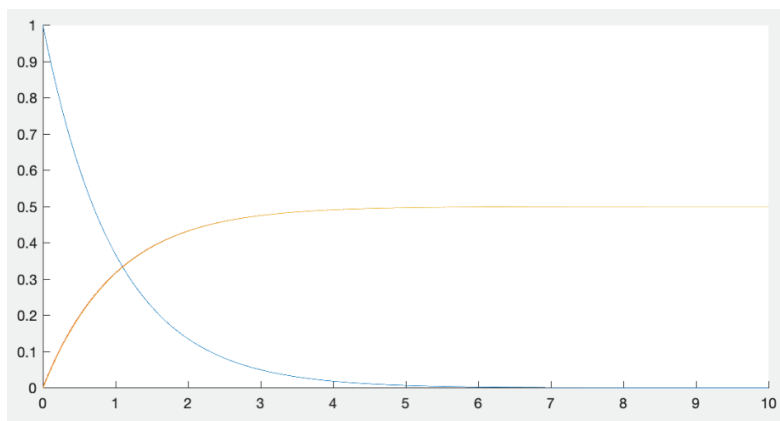
$$[B] = [A]_0 \left\{ \frac{k_{-2}}{k_2 + k_{-2}} (1 - e^{-(k_2+k_{-2})t}) + \frac{k_1 - k_{-2}}{k_2 + k_{-2} - k_1} (e^{-k_1 t} - e^{-(k_2+k_{-2})t}) \right\}$$

b) How can you obtain an expression for the concentration of C? (No need to write the expression down, just give the ansatz).

$$[C] = [A]_0 - [A] - [B]$$

c) Draw a sketch of the concentrations of A, B, and C if $k_2 = k_{-2} \gg k_1$. Describe the most important features of your sketch and the reasons why the system behaves as you sketched it. Which other complex reaction has the same time dependence for the concentrations of A, B, and C ?

For $k_2 = k_{-2} \gg k_1$, B and C are in a pseudo-equilibrium with equal concentrations. The concentration of A decays exponentially, while the concentrations of B and C rise simultaneously, reaching both half the initial concentration of A at long times. The concentrations evolve as for a parallel reaction of A to B and of A to C, with both rate constants equal.



d) Draw a sketch of the concentrations of A, B, and C if $k_2 = k_{-2} \ll k_1$. Describe the most important features of your sketch and the reasons why the system behaves as you sketched it.

Compound A decays exponentially. Since the reaction from B to C is slow, B initially accumulates as in a first-order reaction $A \xrightarrow{k_1} B$. In a second step, B and C then equilibrate as in a reversible reaction $B \xrightleftharpoons[k_{-2}]{k_2} C$, reaching the same concentration at long times.

