Example 2.10 (Autocatalysis) \[ A + B \xrightleftharpoons[k_1]{k_i} 2A \]

As long as enough chemical B is present, chemical A stimulates its own production, a process called \textit{autocatalysis}\footnote{Or more generally, \textit{positive feedback}}.

Let \( a = [A], \ b = [B] \). Suppose \( b = \text{constant} > 0 \), i.e., there is so much B present that its concentration hardly changes, or B is fed in at a fixed rate; it is "used up" going forward, there is a net gain of one molecule of A per reaction.

\[ \text{Rate} = \frac{da}{dt} \]

\text{Law of mass action:} \[ \text{Rate} = k_1 [A][B] - k_i [A]^2 \]

So now \[ \frac{da}{dt} = k_1 b - k_i a^2 \] where \( b > 0 \) is a constant, a non-negative parameter.

\text{Equilibrium:} \[ 0 = k_1 a - k_i a^2 \]

\[ a^* = 0 \text{ or } a^* = \frac{k_1 b}{k_i} \]

\text{Stability:} \[ f(a) = k_1 a - k_i a^2, \quad f'(a) = k_1 - 2k_i a \]

At \( a^* = 0 \): \[ \lambda = f'(0) = k_1 b > 0 \]; \( a^* = 0 \) is unstable.

At \( a^* = \frac{k_1 b}{k_i} \): \[ \lambda = f'\left(\frac{k_1 b}{k_i}\right) = -k_1 b < 0 \]; \( a^* = \frac{k_1 b}{k_i} \) is stable.

\text{Vector field:} \[ \frac{da}{dt} = \frac{k_1 b}{k_i} a - k_i a^2 \]

\text{Phase plot:} \[ \frac{da}{dt} = k_1 b - k_i a^2 \]

\text{Integral curve:} \[ a(t) \]

\text{Exercise:} Solve explicitly \[ \frac{da}{dt} = k_1 b - k_i a^2 \], \( a(0) = a_0 \).

After some time we expect to see the concentration of A to be very near \( \frac{k_1 b}{k_i} \) (equilibrium: toward and backward reactions in balance).

\[ \text{Non-elementary reactions, reaction mechanisms} \]

\[ \text{NO}_2 + CO \xrightarrow{k_1} \text{NO} + \text{CO}_2 \] (assume negligible back reaction).

\text{Expect from law of mass action:} \[ \text{Rate} = k[\text{NO}_2] \]

\text{but measure:} \[ \text{Rate} = k[\text{NO}_2]^2 \] \text{, Law of mass action not working!}.

\text{Explanation: reaction is not elementary; it is actually the result of a sequence of elementary reactions called a reaction mechanism:} \[ 2\text{NO}_2 \xrightarrow{k_1} \text{NO}_3 + \text{NO}, \quad \text{NO}_3 + \text{CO} \xrightarrow{k_i} \text{NO}_2 + \text{CO}_2 \]

\text{Chemist: proposes a reaction mechanism, work out predicted Rate, measure Rate} \[ \text{accept/reject proposed reaction mechanism} \]
Example 2.11 (Michaelis-Menten kinetics)

Consider an enzyme reaction

\[ S + E + R \rightarrow P + E \]

(E = enzyme, S = substrate, R = reactant, P = product, C = complex)

What is an enzyme? <catalyst>

Proposed mechanism \( S + E \xrightarrow{k_1} C \), \( R + C \xrightarrow{k_2} P + E \)

Typically \( P \) is continuously removed so can assume \( k_2 = 0 \)

Also, assume \([R] = \text{constant} > 0\) (there is so much it's concentration hardly changes, \( s \approx [S], e \approx [E], c \approx [C], r \approx [R] \text{ constant} \), \( p \approx [P] \) or it is continuously added)

Using law of mass action get system of ODEs

\[
\begin{align*}
\frac{ds}{dt} &= -k_1se + k_1c \\
\frac{de}{dt} &= -k_1se + k_1c + k_2rc \\
\frac{dc}{dt} &= k_1se - k_1c - k_2rc \\
\frac{dp}{dt} &= k_2rc
\end{align*}
\]

Eliminate some eqns: last eqn \( p(t) = \int_0^s \frac{ds}{k_2rc} = k_2r \int_0^s c(s) \, ds \)

Also notice \( \frac{de}{dt} + \frac{dc}{dt} = 0 \)

\[
\Rightarrow e(t) + c(t) = \text{constant} = e_0 + c_0 = e_0 + c_0 = e_0 \quad \text{so} \quad e(t) = e_0 - c(t) \text{ for all } t
\]

We are left with

\[
\begin{align*}
\frac{ds}{dt} &= -k_1(s - e_0)c + k_1c = -k_1e_0s + (k_1 + k_1s)c \\
\frac{dc}{dt} &= k_1(s - e_0)c - k_1c - k_2rc = k_1e_0s - (k_1 + k_2r + k_1s)c
\end{align*}
\]

In some situations (to be justified later) \( \frac{|\frac{dc}{dt}|}{|\frac{ds}{dt}|} \ll 1 \)

In this case we take a quasi-station (or adiabatic) approximation \( \frac{dc}{dt} = 0 \)

\[
0 = k_1(s - e_0)c - k_1c - k_2rc
\]

This allows us to solve for \( c \) in terms of \( s \) (then sub into 1st eqn)

\[
0 = k_1e_0s - k_1c - k_2rc
\]

Thus \( c = \frac{k_1e_0s}{k_1 + k_2r + k_1s} \)

Sub into 1st eqn, get 1st order eqn for \( s \) alone. Entire problem reduces to