Contents

Find conservation laws, if possible. i.e. combination of variables that are constant in time. One method: Combine ODE's so

$$\begin{aligned} \frac{d}{dt}(+\cdots+) &= 0 \\ +\cdots+ &= \text{constant} \end{aligned}$$

$$\begin{cases} \frac{dA}{dt} = -k_1 Ax, & A(0) = A_0 \\ \frac{dx}{dt} = -k_1 Ax - k_2 zx & x(0) = x_0 \\ \frac{dz}{dt} = k_1 Ax - k_2 xz & z(0) = 0 \\ \frac{dp}{dt} = k_2 xz & p(0) = 0 \end{cases} \tag{1}$$

$$\begin{aligned} \frac{dA}{dt} + \frac{dp}{dt} + \frac{dz}{dt} &= \frac{d}{dt}(A + P + Z) \\ &= 0 A(t) + P(t) + Z(t) \quad = \text{constant for all time} \end{aligned}$$

What is the constant? Set $t = 0$, $A(0) = A_0$, $z(0) = 0$, $p(0) = 0$:

$$\begin{aligned} A(t) + P(t) + Z(t) &= A_0 \\ P(t) &= A_0 - A(t) - Z(t) \end{aligned}$$

Eliminate P from (**??**)

$$\begin{cases} \frac{dA}{dt} = -k_1 Ax, & A(0) = A_0 \\ \frac{dx}{dt} = -k_1 Ax - k_2 zx & x(0) = x_0 \\ \frac{dz}{dt} = k_1 Ax - k_2 xz & z(0) = 0 \end{cases} \tag{2}$$

Look for other conservation laws

$$\begin{aligned} \frac{d}{dt}(2A - x + z) &= 0 \\ 2A(t) - x(t) + z(t) &= \text{constant for all time} \\ 2A(t) - x(t) + z(t) &= 2A_0 - x_0 \\ x(t) &= 2A(t) + z(t) - 2A_0 + x_0 \end{aligned}$$

2 equations and 2 unknowns

Example 1 Simple reaction modeling

Reversible conformational change 1st order

$$\begin{cases} \frac{dA}{dt} = -k_1 A + k_{-1} B, & A(0) = A_0 \\ \frac{dB}{dt} = k_1 B - k_{-1} B, & B(0) = B_0 \end{cases} \tag{3}$$

What to do? By luck, first order reactions have linear systems with constant coefficients:

$$\frac{d}{dt}\left(\begin{bmatrix} A \\ B \end{bmatrix}\right) = M \begin{bmatrix} A \\ B \end{bmatrix}$$

Assume: $\begin{bmatrix} A \\ B \end{bmatrix} = \begin{bmatrix} v_1 \\ v_2 \end{bmatrix} e^{\lambda t}$ which leads to the eigenvalue problem

$$\begin{aligned} 0 &= \begin{vmatrix} -k_1 - \lambda & k_{-1} \\ k_1 & -k_{-1} - \lambda \end{vmatrix} \\ &= (-k_1 - \lambda)(-k_{-1} - \lambda) - (k_{-1})(k_1) \end{aligned}$$

$$\lambda_1 = 0 \qquad \lambda_2 = -(k_1 + k_{-1})$$

If reactions are more complicated (nonlinear systems): find conservative laws

Example 2 Dimerization of 2 monomers

Kinetic equations:

$$\begin{aligned} \frac{dA}{dt} &= -2k_1 A^2 + 2k_{-1} C \qquad & A(0) = A_0 \\ \frac{dC}{dt} &= -k_{-1} C + k_1 A^2 \qquad & C(0) = 0 \end{aligned} \tag{4}$$

Given $[A] = \frac{M}{L^3}$, $[C] = \frac{M}{L^3}$, $[A_0] = \frac{M}{L^3}$, $[t] = T$: find k:

$$\begin{aligned} \left[\frac{dA}{dt}\right] &= \left[-2k_1 A^2\right] + [2k_{-1} C] \\ \frac{ML^{-3}}{T} &= [k_1]\left[A^2\right] + [k_{-1}]\,[C] \\ \frac{ML}{L^3 T} &= [k_1]\left(\frac{M}{L^3}\right)^2 + [k_{-1}]\left(\frac{M}{L^3}\right)^2 \\ \frac{ML}{L^3 T} &= [k_1]\frac{M^2}{L^6} + [k_{-1}]\frac{M^2}{L^6} \end{aligned}$$

$$\frac{ML}{L^3 T} = [k_1]\frac{M^2}{L^6} \qquad \frac{ML}{L^3 T} = [k_{-1}]\frac{M^2}{L^6}$$

$$A = f(t, k_1, k_{-1}, A_0) \qquad C = g(t, k_1, k_{-1}, A_0)$$

$$
\begin{aligned}
[A] &= [t]^a [k_1]^b [k_{-1}]^c [A_0]^d \\
\frac{M}{L^3} &= T^a \left(L^3 M^{-1} T^{-1}\right)^b T^{-1c} \left(M L^{-3}\right)^d \\
M L^{-3} &= T^a L^{3b} M^{-b} T^{-b} T^{-c} M^d L^{-3d} \\
M^1 L^{-3} T^0 &= M^{-b+d} L^{3b-3d} T^{a-b-c}
\end{aligned}
$$

$$
\begin{bmatrix} 1 & -1 & -1 & 0 \\ 0 & 3 & 0 & -3 \\ 0 & -1 & 0 & 1 \end{bmatrix}
$$

$$
\begin{aligned}
\frac{dA}{dt} + 2\frac{dC}{dt} &= 0 \\
A(t) + 2C(t) &= A_0 + 0
\end{aligned}
$$

Leonor Michaelis - Maud Menton Kinetics

MM Kinetics – rate is used frequently instead of 1st order kx terms. Where does it come from?
Prototype in biological setting. How do bacteria consume organic substances (e.g. glucose)?

$$
\begin{aligned}
c + x_0 &\leftrightarrows^{k_{-1}}_{k_1} x_1 \\
x_1 &\rightarrow^{k_2} p + x_0
\end{aligned}
$$