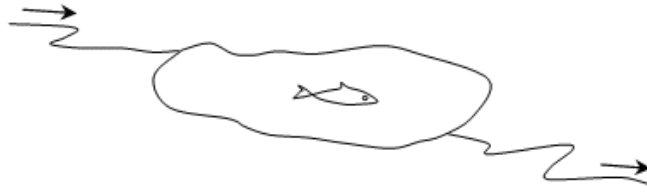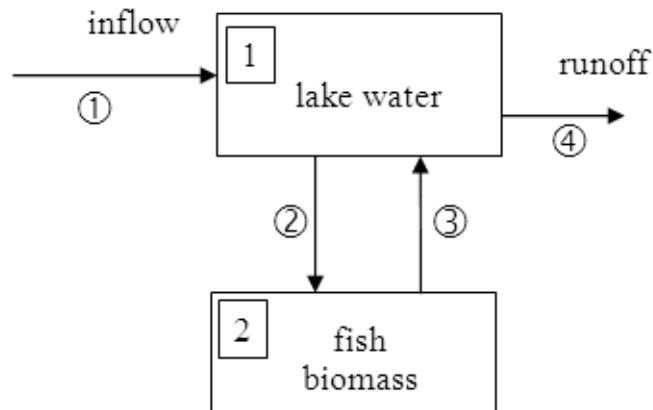## Box models

Box models are sometimes used in environmental modelling. For example, to simulate
the fate of an organic pesticide in a lake one could consider two boxes: the lake water
and the fish

The box model would be:

Such a system consists of one component (the pesticide) and two boxes. It may be described
with two equations (in general one equation for each component in each box) such as:

$$\begin{pmatrix} \text{Rate of} \\ \text{accumulation} \\ \text{of mass} \\ \text{of component} \\ \text{in the box} \end{pmatrix} = \frac{dM_i}{dt} = \begin{pmatrix} \text{Mass flow} \\ \text{of the} \\ \text{component} \\ \text{into} \\ \text{the box} \end{pmatrix} - \begin{pmatrix} \text{Mass flow} \\ \text{of the} \\ \text{component} \\ \text{out of} \\ \text{the box} \end{pmatrix} + \begin{pmatrix} \text{Rate of production} \\ \text{of the component} \\ \text{in the box} \\ \text{by reactions} \end{pmatrix}$$

This is a set of ordinary differential equations (ODE) and it may be solved given some
initial conditions. An artificial example is given below showing how box models may be
solved with SMath Studio. Many more examples of this kind of problems may be found
in the book:
J.B.Snape, I.J.Dunn, J.Ingham, J.E.Prenosil
Dynamics of Environmental Bioprocesses, VCH, Weinheim, 1995.

The example described below is a simple one-box model with two inflows and one outflow.
It could be a reactor tank in an industry, for example. The microbial reactions are
simulated according to a relatively complex model taken from the literature, to show
the capabilities of SMath. The results of the simulation are presented graphically,
and compared with some data.

Adding more compartments simply requires adding more equations to solve. Diffusion
between for example lake water and bottom sediments may also be simulated, as described
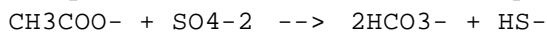in Snape et al (1995) p.429, etc.

Stirred Tank Reactor

A one-box model with five components:

1- Microbes (biomass)
2- Acetate (CH3COO-)
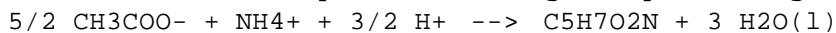3- Sulphate (SO4-2)
4- Sulphide (HS-)
5- Bicarbonate (HCO3-)

Two pipes bring two aqueous solutions into
the reactor tank: one pipe brings acetate,
and the other brings sulphate. In the tank
the two solutions are mixed and a redox
reaction takes place where microbes reduce
sulphate to sulphide, and at the same time
they oxidize acetate to bicarbonate.

F_{in} (acetate)

F_{in} (sulphate)

F_{out}

Stirred Tank
Reactor
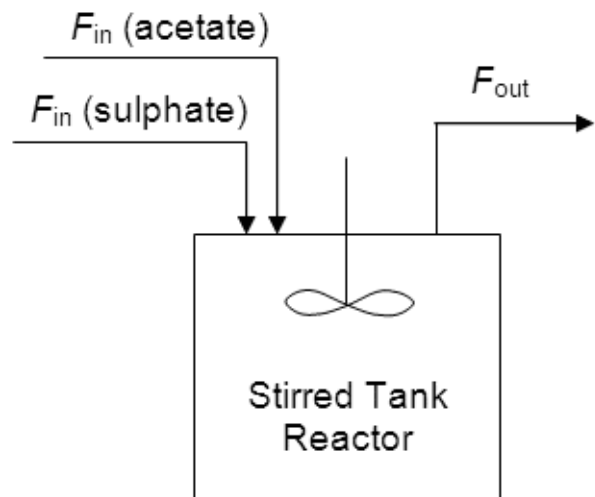
The sulphate reduction reaction may be written as:
    CH3COO- + SO4-2 --> 2HCO3- + HS-
Acetate is also used by microbes to grow by creating biomass (C5H7O2N):
    5/2 CH3COO- + NH4+ + 3/2 H+ --> C5H7O2N + 3 H2O(l)
Many simplifications are made here: enough ammonium is added through the aqueous
solutions going into the reactor tank. Also acid-base reactions are not considered
in this example: H2S(aq), H2S(g) and CO3-2 are excluded.

The system may be described with some initial conditions and five ordinary differential
equations (ODE), one for each component in the single box.

Definition of the tank reator: $Vol := 1\ \text{м}^3$

$$F_{in\_acetate} := 0.002\ \text{м}^3\ \text{ч}^{-1} \qquad F_{in\_SO4} := 0.002\ \text{м}^3\ \text{ч}^{-1}$$

$$F_{out} := F_{in\_acetate} + F_{in\_SO4}$$ (the volume of the tank is fixed)

Residence time: $Vol \cdot F_{out}^{-1} = 250\ \text{ч}$

The concentrations of the influents: $Ac_{in} := 0.001\ \dfrac{\text{моль}}{\text{л}} \qquad SO4_{in} := 0.010\ \dfrac{\text{моль}}{\text{л}}$
(acetate and sulphate)
Note that sulfate is in excess.

The "microbial" model developped by Jin and Bethke will be used, see:
- Jin, Q., & Bethke, C. M. (2005). Predicting the rate of microbial respiration in geochemical environments. Geochimica et Cosmochimica Acta, Vol.69, p.1133-1143.
- Jin, Q., & Bethke, C. M. (2007). The thermodynamics and kinetics of microbial metabolism. American Journal of Science, Vol.307, p.643-677.

Define the thermodynamic potential factor (F_T)

$$\Delta G0 := \left(2 \cdot (-586.845) + (12.243) - ((-744.004) + (-369.41))\right) \frac{\text{кДж}}{\text{моль}} \qquad \Delta G0 = -48 \frac{\text{кДж}}{\text{моль}}$$

$$\Delta G_C := 1 \cdot 45 \text{ кДж моль}^{-1} \qquad \chi := 6 \qquad$$ Note, these two values taken from: Jin, Roden and Giska, Geomicrobiology Journal 30 (2013) 173-185

function used below to avoid "log" of zero or negative numbers:
$$mn(x) := \left(10^{-50} \cdot \left(x \le 10^{-50}\right)\right) + \left(x \cdot \left(x > 10^{-50}\right)\right)$$

In the integration of the ODEs, a vector "y" will contain the variables (concentrations) of the components: X (biomass, mg/L), acetate, sulphate, sulphide, and bicarbonate; y = (X, ac, so4, hs, hco3)

$$T := 298.15 \text{ K}$$

$$\Delta G_A(y) := -\Delta G0 - R_m \cdot T \cdot \left(\ln\left(mn\left(Y_4\right)\right) + 2 \cdot \ln\left(mn\left(Y_5\right)\right) - \ln\left(mn\left(Y_3\right)\right) - \ln\left(mn\left(Y_2\right)\right)\right)$$

$$F_T(y) := 1 - \exp\left(\frac{-\Delta G_A(y) + \Delta G_C}{\chi R_m \cdot T}\right)$$

The rate equations: the microbial process is calculated with a dual Monod-equation.
Parameters taken from:
Jin, Roden and Giska, Geomicrobiology Journal, Vol.30 (2013) p.173-185

$$K_{max} := 1.3 \cdot 10^{-6} \frac{\text{моль}}{\text{г с}} \qquad K_{ac} := 5 \cdot 10^{-6} \frac{\text{моль}}{\text{л}} \qquad K_{SO4} := 68 \cdot 10^{-6} \frac{\text{моль}}{\text{л}} \qquad D := 10^{-8} \text{ с}^{-1}$$

$$Y := 3.8 \cdot 10^{3} \frac{\text{мг}}{\text{моль}}$$ biomass generated per mol SO4 reduced

mol biomass carbon generated per mol SO4 reduced: $$5 \cdot Y \cdot \left(113.115 \frac{\text{г}}{\text{моль}}\right)^{-1} = 0.17$$

functions used to avoid negative concentrations which might be generated by numerical oscillations, etc:
$$c(x) := x \cdot (x > 0) \text{ моль л}^{-1}$$
$$cx(x) := x \cdot (x > 0) \text{ мг л}^{-1}$$

The dual Monod-equation with the thermodynamic potential factor:

Note: y=(X,ac,so4,hs,hco3)

$$r_{redox}(y) := K_{max} \cdot cx\left(Y_1\right) \cdot \frac{c\left(Y_2\right)}{K_{ac} + c\left(Y_2\right)} \cdot \frac{c\left(Y_3\right)}{K_{SO4} + c\left(Y_3\right)} \cdot F_T(y) \cdot \left(F_T(y) > 0\right)$$

for sulphate (flow in - flow out + reactions):

$$dSdt(y) := \frac{\left(F_{in\_SO4} \cdot SO4_{in}\right) - \left(F_{out} \cdot c\left(Y_3\right)\right)}{Vol} - \left(r_{redox}(Y)\right)$$

biomass: production minus outflow minus decrease:

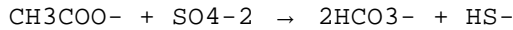$$dXdt(y) := \left(Y \cdot r_{redox}(Y)\right) - \left(\frac{F_{out} \cdot cx\left(Y_1\right)}{Vol}\right) - \left(D \cdot cx\left(Y_1\right)\right)$$

sulphide and bicarbonate: production minus outflow:

Note: y=(X,ac,so4,hs,hco3)

$$dHSdt(y) := \left(r_{redox}(Y)\right) - \left(\frac{F_{out} \cdot c\left(Y_4\right)}{Vol}\right)$$
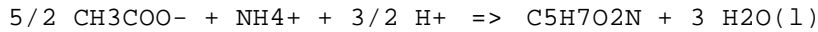
$$dHCO3dt(y) := 2 \cdot \left(r_{redox}(Y)\right) - \left(\frac{F_{out} \cdot c\left(Y_5\right)}{Vol}\right)$$

For acetate: flow in - flow out - consumption.
The rate of acetate consumption is the sum of the sulphate reduction process
    CH3COO- + SO4-2 → 2HCO3- + HS-
and the biomass growth with the reaction:
    5/2 CH3COO- + NH4+ + 3/2 H+ => C5H7O2N + 3 H2O(l)
The molecular mass of C5H7O2N is 113.115 g/mol.

$$dAcdt\,(y) := \frac{\left(F_{in\_acetate} \cdot Ac_{in}\right) - \left(F_{out} \cdot c\,(Y_2)\right)}{Vol} - \left(\left(2 + Y \cdot \left(\frac{5}{2}\right) \cdot \left(113.115\,\frac{\text{г}}{\text{моль}}\right)^{-1}\right) \cdot r_{redox}\,(y)\right)$$

Initial conditions:

At the start there are 5x10^5 cells/mL in the reactor tank $Cell\_dry\_mass := 10^{-12}$

$$biomass := 5 \cdot 10^4 \cdot \frac{1}{\text{мл}} \cdot Cell\_dry\_mass \ \text{г} \qquad\qquad biomass = 0.05\,\frac{\text{мг}}{\text{л}}$$

Using C5H7O2N
for biomass: $carbon := biomass \cdot 5 \cdot \left(113.115\,\frac{\text{г}}{\text{моль}}\right)^{-1}$ $carbon = 2.21 \cdot 10^{-6}\,\frac{\text{моль}}{\text{л}}$

Initially the tank contains only water, except for some microbes:
Note: y=(X,ac,so4,hs,hco3)

$$Y_{initial} := \begin{bmatrix} 0.05 \\ 10^{-6} \\ 10^{-6} \\ 10^{-6} \\ 10^{-6} \end{bmatrix}$$

check for possible mistakes in the equations above
by controlling that the units are correct:

$\Delta G_A\,(Y_{initial}) = 82.3\ \text{кДж моль}^{-1}$

$F_T\,(Y_{initial}) = 0.9184$

$dSdt\,(Y_{initial}) = 5.55 \cdot 10^{-9}\ \text{моль л}^{-1}\,\text{с}^{-1}$

$dXdt\,(Y_{initial}) = -5.55 \cdot 10^{-8}\ \text{мг л}^{-1}\,\text{с}^{-1}$

$dAcdt\,(Y_{initial}) = 5.54 \cdot 10^{-10}\ \text{моль л}^{-1}\,\text{с}^{-1}$

$dHSdt\,(Y_{initial}) = -9.6691 \cdot 10^{-13}\ \text{моль л}^{-1}\,\text{с}^{-1}$

Note that the units for biomass
concentration are "mg/L" (mass
concentration) while for the other
components the concentration is
expressed as "mol/L" (amount
concentration).

Finally the system of ODEs may be solved to calculate the concentrations in the reaction tank. A "plugin" is used that requires a Jacobian matrix (the rates for each component) and the initial conditions. The "plugin" can not work with units, so the units must be removed:

$$dydt\,(t\,,y) := \begin{bmatrix} dXdt\,(y)\,\frac{\text{ч л}}{\text{мг}} \\ dAcdt\,(y)\,\frac{\text{ч л}}{\text{моль}} \\ dSdt\,(y)\,\frac{\text{ч л}}{\text{моль}} \\ dHSdt\,(y)\,\frac{\text{ч л}}{\text{моль}} \\ dHCO3dt\,(y)\,\frac{\text{ч л}}{\text{моль}} \end{bmatrix}$$

The time here must be units-less,
corresponding to the values in the Jacobian,
in this example "hours"

$t_{start} := 0 \qquad t_{end} := 1000$

$n_{steps} := 50$

Note: the "plugins" solving the ODEs require that the variables "t" (a scalar) and "y" (a vector) in the Jacobian may not be defined above: they must be symbolic.

The calculations are performed here with the "plugin" which implements an algorithm called Gear's BDF (Backward Differentiation Formulae).
The results are stored in the matrix "res".

$$res := \text{dn\_GearsBDF}\left(Y_{initial}\,,\,t_{start}\,,\,t_{end}\,,\,n_{steps}\,,\,dydt\,(t\,,y)\right)$$

The matrix "res" contains the time as the first column, and the other columns contain the component concentrations (X,ac,so4,hs,hco3) at the time given in the first column. The concentrations are in the same order as in the vectors "y.initial" and "dydt".
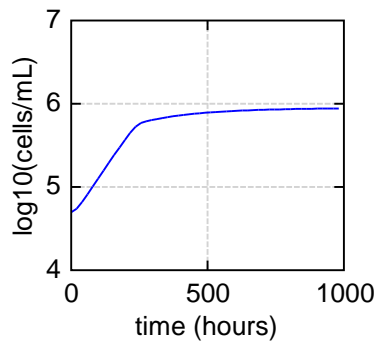
$time := \text{col}(res, 1)$ (the time in hours, as defined in "dydt" above) $end := n_{steps} + 1$

$X := \text{col}(res, 2)$ $Cells := \dfrac{X \cdot 10^{-6}}{Cell\_dry\_mass}$ $Carb := \dfrac{X \cdot 5}{113115}$ for $j \in [1..end]$
$logCells_j := \lg(Cells_j)$

$Ac := \text{col}(res, 3)$ $SO4 := \text{col}(res, 4)$ $HS := \text{col}(res, 5)$ $HCO3 := \text{col}(res, 6)$
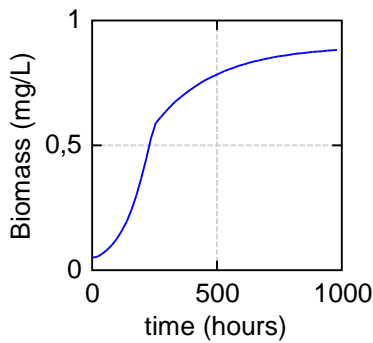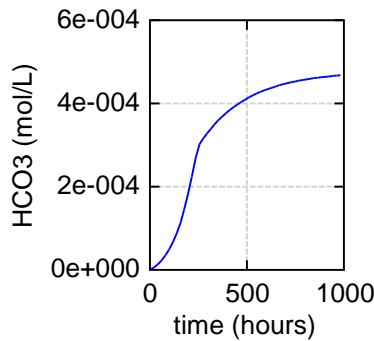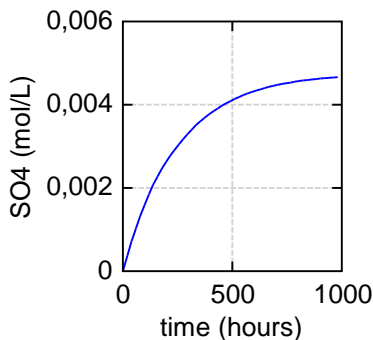

augment(time, X)
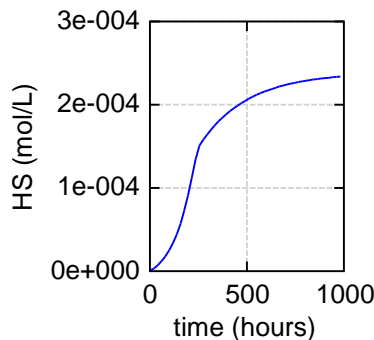

augment(time, logCells)
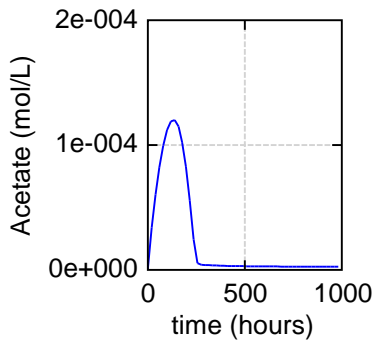
augment(time, Ac)

augment(time, HCO3)

Example of comparing a simulation with some experimental data
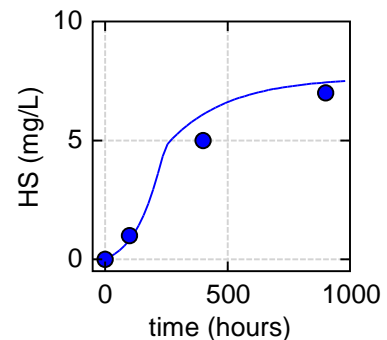
$$data := \begin{bmatrix} 0 & 0 \\ 100 & 1 \\ 400 & 5 \\ 900 & 7 \end{bmatrix}$$
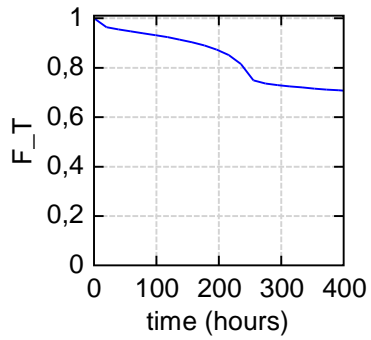

augment(time, SO4)

augment(time, HS)

$\begin{cases} \text{augment(time, HS} \cdot 32070) \\ \text{data} \end{cases}$

Note that sulphate is in excess and reaches a steady state value, while the steady state concentration of acetate is close to zero. The biomass stabilises to a value correspondir to the substrate amounts entering the reactor tank.
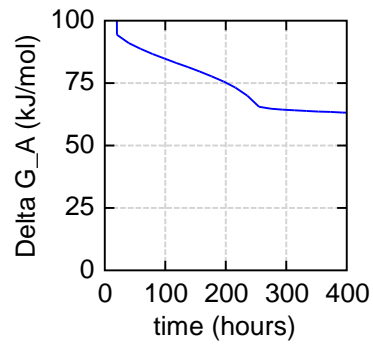
Plot the thermodynamic potential factor in the reactor tank

for $j \in [1..end]$

$$F_{Tcalc_j} := F_T\left(\text{submatrix}(res, j, j, 2, 6)^{\text{T}}\right)$$

$$\Delta G_{Acalc_j} := \Delta G_A\left(\text{submatrix}(res, j, j, 2, 6)^{\text{T}}\right) \frac{\text{моль}}{\text{кДж}}$$

$\text{augment}\left(\text{time}, F_{Tcalc}\right)$

$\text{augment}\left(\text{time}, \Delta G_{Acalc}\right)$