

Modern Kinetics Part 2:

Complex Mechanisms, Numerical Integration

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Kinetic Models and Sets of Differential Equations

There is a surprisingly small number of reaction mechanisms that lead to a set of differential equations that can be integrated explicitly. The textbooks on chemical kinetics list the solutions for the basic first and second order reactions:

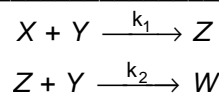
- a) $X \xrightarrow{k} Y$
- b) $2X \xrightarrow{k} Y$
- c) $X + Y \xrightarrow{k} Z$
- d) $X \xrightarrow{k_1} Y \xrightarrow{k_2} Z$

which have the solutions:

- a) $[X] = [X]_0 e^{-kt}$
- b) $[X] = \frac{[X]_0}{1+2[X]_0 kt}$
- c) $[X] = \frac{[X]_0 ([Y]_0 - [X]_0)}{[Y]_0 e^{([Y]_0 - [X]_0)kt} - [X]_0}$ ($[X]_0 \neq [Y]_0$)
- d) $[X] = [X]_0 e^{-kt}$,
 $[Y] = [X]_0 \frac{k_1}{k_2 - k_1} (e^{-k_1 t} - e^{-k_2 t})$ ($[Y]_0 = 0, k_1 \neq k_2$)

Note that the missing concentrations can be determined as the difference between initial concentrations and the above.

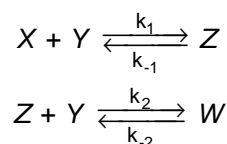
In few, also rare instances, it is possible to reduce the complexity of the mechanism by applying excess reagent and thus working under pseudo-first order conditions. E.g. the mechanism



reduces to the mechanism c) above for $[Y]_0 \gg [X]_0$. While this technique is available, it is often not advisable or possible to implement.

Numerical Integration

Fortunately, for any mechanism it is always possible to integrate the set of differential equations numerically. Without going into the details of modern algorithms for that task, it is useful to have a basic understanding of the method. Consider the mechanism:



which results in the differential equations:

$$\frac{d[X]}{dt} = -k_1[X][Y] + k_{-1}[Z]$$

$$\frac{d[Y]}{dt} = -k_1[X][Y] + k_{-1}[Z] - k_2[Y][Z] + k_{-2}[W]$$

$$\frac{d[Z]}{dt} = +k_1[X][Y] - k_{-1}[Z] - k_2[Y][Z] + k_{-2}[W]$$

$$\frac{d[W]}{dt} = +k_2[Y][Z] - k_{-2}[W]$$

This set of ordinary differential equations (ODEs) defines the derivatives of the concentrations with respect to time ($d[X]/dt, d[Y]/dt, \dots$) as a function of the concentrations ($[X], [Y], \dots$) at any time t . These differentials can be used to approximate the concentrations after a short time interval Δt , e.g.

$$[X]_{t+\Delta t} \approx [X]_t + \Delta t \frac{d[X]}{dt}$$

$$[Y]_{t+\Delta t} \approx [Y]_t + \Delta t \frac{d[Y]}{dt}$$

M

Starting from known initial conditions, usually at time zero, a long succession of such approximations will result in the concentration profiles for all reaction species. Obviously, the smaller the time intervals Δt the

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better the approximation, and the slower the progress of the computation. Here lies a fundamental dilemma of numerical integration, one has to choose between either fast or accurate computation. Modern algorithms aim at striking a satisfactory compromise by continuously optimising the step size Δt . The step size is automatically controlled, it is as large as possible to allow fast progress but still small enough to satisfy the required accuracy. During the integration, the step size can change in either direction. The workhorse in numerical integration is the Runge-Kutta method, enhanced by automatic step-size control.

Special algorithms deal with 'stiff' ODEs. In chemistry stiff systems are encountered if some of the rate constants are large (requiring small step sizes) and others are small (requiring long measuring times), a situation which is inherently difficult. 'Stiff' solvers result in acceptable computation times. Good software allows the user to choose an appropriate solver.

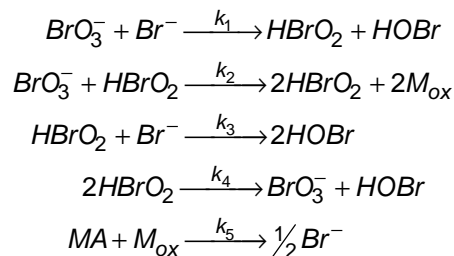
The Model Parser

The chosen kinetic model defines the set of differential equations, which in turn needs to be converted into computer code. This process is theoretically straightforward but in practise, it can be very error prone. Manual translation of the chemical model first into the set of differential equations and then into computer code can be tedious and more importantly, errors can be very difficult to detect, resulting in potentially disastrous outcomes.

It is possible to automate this process; a user-friendly model-parser has been implemented in ProKII. It allows the model to be defined by the user in a chemically sensible language. For the above example:

```
Model
X+Y<>Z
Z+Y<>W
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Imagine, having to manually translate the model

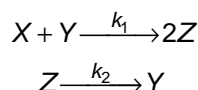


into computer code. The above model is a reduced set of 'reactions' (the Oregonator model) which display most of the essential features of the oscillating Belousov-Zhapotinsky reaction.

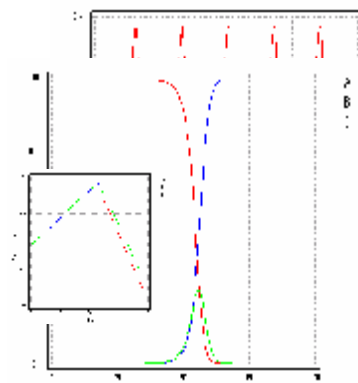
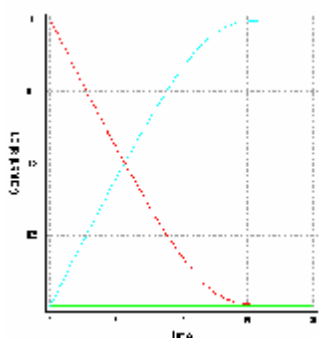
Examples

Autocatalysis

Consider the reaction mechanism below:



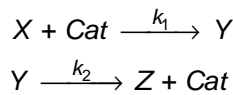
With a large excess of X and a very small amount of Y at time zero the first reaction is slow. However, the product Z is transformed back into B and thus the reaction is self-accelerating. The concentration profiles below have been modelled with initial concentrations: $[A]_0=1 \text{ M}$, $[B]_0=10^{-10} \text{ M}$ and $[C]_0=0 \text{ M}$, the rate constants are $k_1=1 \text{ M}^{-1}\text{s}^{-1}$ and $k_2=1 \text{ sec}^{-1}$. The reaction 'takes off' after some 40 sec and is essentially finished after 70 sec. Before and after these limits there is no detectable reaction. However, the insert with a logarithmic concentration scale displays small concentration changes unnoticed with a linear scale. 0th order, Catalytic Reaction



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The mechanism below models the interaction of a substrate X with a catalyst to form an intermediate complex Y that in turn releases the product Z and the catalyst.



For small concentrations of the catalyst, a pseudo-first order decay of X is observed. Up to time 10 sec the decay of X is linear which is represented by the differential equation:

$$\frac{d[X]}{dt} = -k [X]^0 = -k$$

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Model
sheep>2sheep
sheep+wolf>2wolf
wolf>
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LotkaVolterra / Population Dynamics

The third example is interesting while chemically irrelevant. It models the population dynamics on an imaginary island populated with sheep and wolves.

