Chapter 5. Chemical kinetics

5.1 Introduction

   Chemical kinetics , also known as reaction kinetics, is the branch of physical chemistry that is concerned with understanding the rates of chemical reactions. It is to be contrasted with thermodynamics, which deals with the energetics under which a process occurs but in itself tells nothing about its rate. Chemical kinetics includes investigations of how experimental conditions influence the speed of a chemical reaction and yield information about the reaction's mechanism and transition states, as well as the construction of mathematical models that also can describe the characteristics of a chemical reaction.

Time evolution of reactant and product concentration requires an appropriate model of the reactions in terms of Ordinary Differential Equations (ODE). Only simple linear equations (and in few cases also nonlinear equations) can be explicitly integrated so as to arrive at an expression relating well established thermodynamic parameters of the reactions (like activation energy, equilibrium constants) to time - varying concentrations. The alternative and generic approach is the numerical integration by means of appropriate ODE solvers. More choices are offered by Octave, so that some of them are proposed here.

5.2 First-order reactions

A simple case of reaction is a first order irreversible(5.1), in which products cannot be converted back to the original reactants. In this case, the rate of the forward reaction decreases until all the reactants have been consumed, and the reaction terminates. On the contrary, in a single-step reversible reaction, the apparent rate of the forward reaction decreases together with the accumulation of the reaction products until a condition of dynamic equilibrium is finally established (5.2). At equilibrium, forward and backward reactions proceed at equal rates.

$$(5.1) \quad A \rightarrow B \qquad (5.2) \quad A \rightarrow B \ + \ A \leftarrow B \ = \ A \Leftrightarrow B$$

The rate of a first-order reaction is proportional to the first power of the concentration of only one reactant. This means that the amount d[A] , which undergoes chemical change in the short time interval dt , depends only on the amount of A present at that instant. The rate expression which describes a first-order reaction is:

$$\frac{-dA}{dt} = k_1[A] \quad \text{irreversible reaction}$$

$$\frac{-dA}{dt} = k_1[A] - k_2[B] \qquad -\frac{dB}{dt} = k_2[B] - k_1[A] \quad \text{reversible reaction}$$

Let us start with a first degree kinetic, irreversible case, using two different ODE solver, namely *lsode* (using Hindmarsh's ODE solver LSODE) and ode45 (using Dormand-Prince method of order 4).
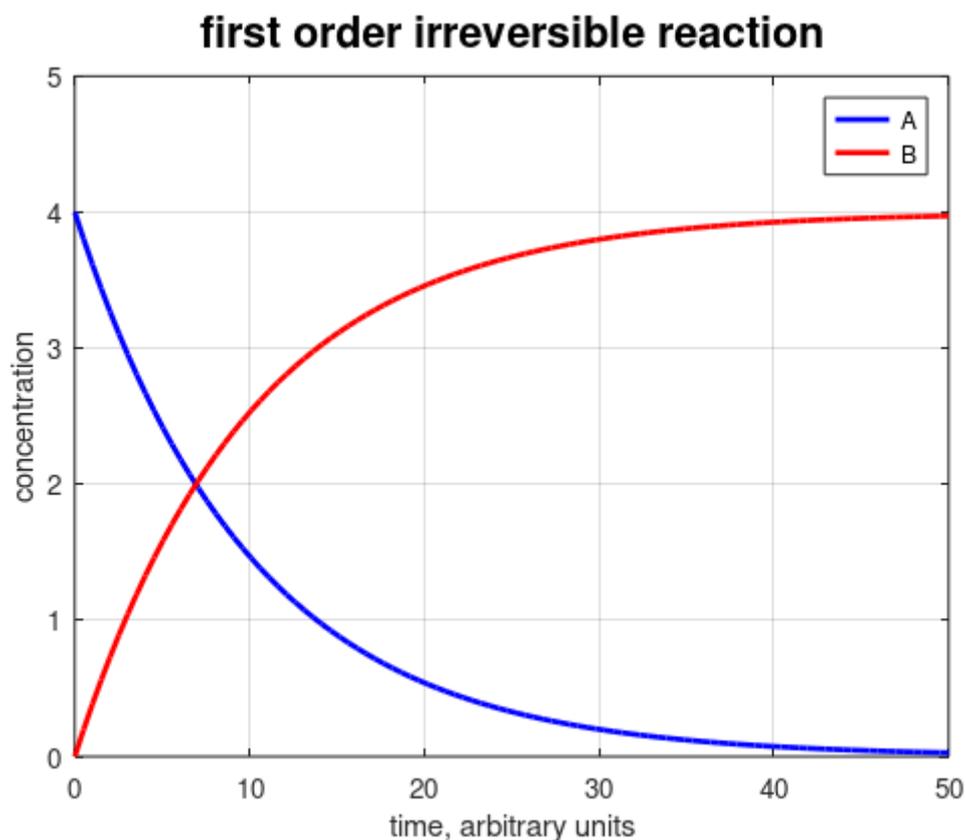
The following script uses *lsode* solver with a rate constant 0.1 , initial concentration 4 (arbitrary unit) and 100 integration steps of 0.5 time unit each.

```
clear;clc;
function xdot = f (c, tspan)
  k1 = 0.1;
  xdot(1) = - k1*c(1);
endfunction
c0 = 4;tspan = linspace (0, 50, 100);
y = lsode (@f, c0, tspan);
plot(tspan,y,'b','LineWidth',2,tspan,c0-y,'r','LineWidth',2);grid on
xlabel('time, arbitrary units');ylabel('concentration');
title('first order irreversible reaction','FontSize',16);
legend('A','B');axis([0 50 0 5]);
```

It produces the following figure:

The following script uses *ode45* solver with a rate constant 0.06, initial concentration 0.05 and 30 integration steps of 1 time unit each

```
clear;clc;
k = 0.06;     %rate constant of reaction
timespan = (0:30);
A0 = 0.05;    % initial concentration
first = @(t,A) - k*A;
[t,A_calc] = ode45(first,timespan,A0);
plot(t,A_calc,'LineWidth',2);grid on
xlabel('time, arbitrary units')
ylabel('[A] concentration')
title('first order irreversible reaction')
```

It also produces a figure, very similat to the above, and therefore it isn't reported in here.

If we consider a reversible reaction, two rate constants are needed, namely k1 = 0.4 and k2 = 0.2. Their ratio defines the equilibrium constant of the reaction Keq = k1/k2 = 2. As seen from the figure below after a certain time the two concentrations converge to asymptotic values 0.8 and 0.4, that satisfy Keq = 0.8/0.4. *ode45* solver is employed, with 500 integration steps, from 0 to 10 time units, as defined by the function `tspan = linspace(0,10,500);`

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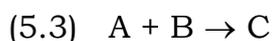
first order reversible reaction
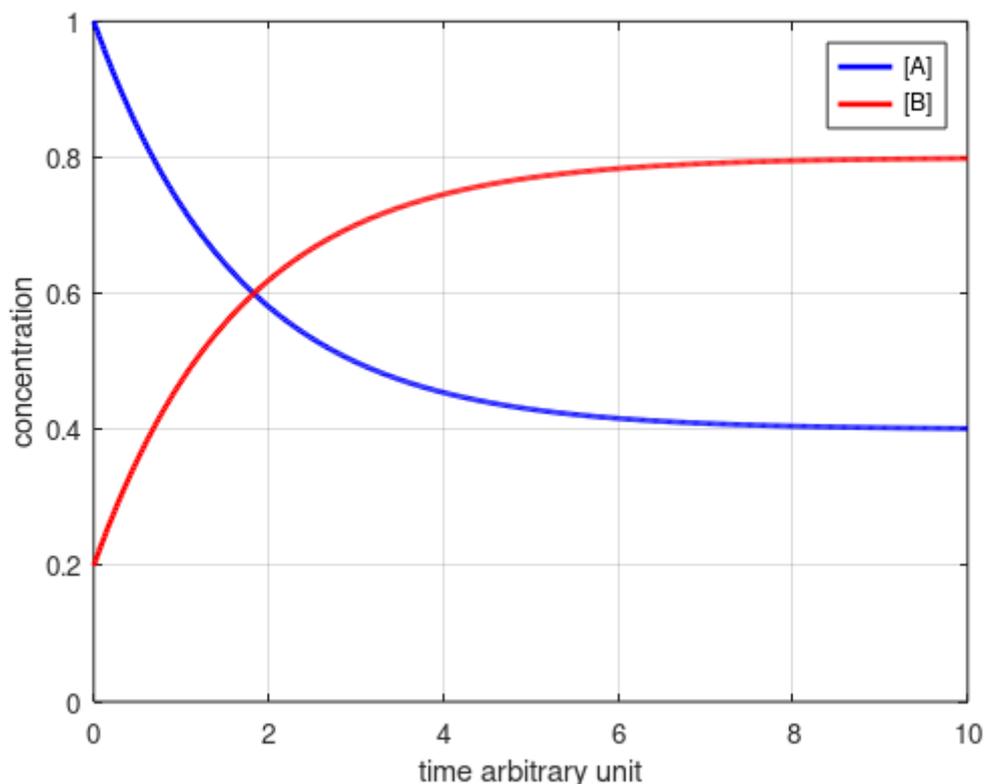

```
clear all;clc;
function dC = reversible_A_B(t, C)
  % Rate constants.
  k1 = 0.4;
  k2 = 0.2; % therefore Keq = k1/k2 = 2
  % Rate laws.
  r1 = k1*C(1); % C(1) = [A]
  r2 = k2*C(2); % C(2) = [B]
  % Mass balances.
  dCA  = -r1 + r2;
  dCB = - r2 + r1;
  % Assign output variables.
  dC(1,:) = dCA;
  dC(2,:) = dCB;
endfunction
C0 = [1,0.2];                              % Define initial concentrations.
tspan = linspace(0,10,500);               % Define time span.
[t, y] = ode45(@reversible_A_B, tspan, C0);   % Run ODE solver.
% plot
c1 = y(:,1);c2 = y(:,2);
plot(t,c1,'b','LineWidth',2,t,c2,'r','LineWidth',2);grid on;axis([0 10 0 1]);
xlabel('time arbitrary unit');ylabel('concentration');legend('[A]','[B]');
title('first order reversible reaction','fontsize',16);
```

5.3 Second- and higher order reactions

When two reactants A and B interact in such a way that the rate of reaction is proportional to the first power of the product of their respective concentrations, the compounds are said to undergo a second order reaction. The following (5.3) is the irreversible case

$$(5.3) \quad A + B \rightarrow C$$

whilst (5.4) is the reversible one

$$(5.4) \quad A + B \rightarrow C \ + \ C \rightarrow A + B \ = \ A + B \Leftrightarrow C$$
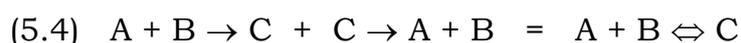
Higher order reactions are also possible, when three reactants produce one or more products, for example. Consecutive reactions like (5.5) can also be encountered

$$(5.5) \qquad\qquad A + B + C \rightarrow D$$

In every case, once reaction constants and start concentrations are assigned, is possible to write a function containing reaction rates in differential form, to be integrated by one ODE solver. The following script refers to reaction (5.5) and it is an hybrid one, as user can choose between two ODE solvers (*lsode,* `green lines` *or ode45* `red lines`).

Each solver requires an appropriate syntax, while the remaining part of the script is valid for both. Other reaction are possible, by modifying the lines inside the function xdot= f () (`grey lines`) according to the proposed mechanism.

In the following, r1,r2,r3 are the rate of the three reactions :

```
A ==> B      ,k1
B ==> C      ,k2
C ==> D      ,k3
```

which in turn are proportional to the respective concentrations c(1),c(2),c(3) multiplied by k1,k2,k3. The change in the A,B,C concentrations is expressed by xdot(1),xdot(2),xdot(3) according to the overall reaction scheme.

```
% Consecutive Irreversible Reactions
% A ==> B      ,k1
% B ==> C      ,k2
% C ==> D      ,k3
clear;clc;
function xdot = f(c,tspan)
function xdot = f(t,c)

   k1 = 0.02;
   k2 = 0.01;
   k3 = 0.006;
   r1 = k1*c(1);  % c(1) = [A]
   r2 = k2*c(2);  % c(2) = [B]
   r3 = k3*c(3);  % c(3) = [C]
   xdot(1) = -r1;
   xdot(2) = r1 - r2;
   xdot(3) = r2 - r3;
endfunction

c0 = [1,0,0];                    % Define initial concentrations.
tspan = linspace (0, 500, 100);   % Define tspan.
y = lsode (@f, c0, tspan);
[t, y] = ode45(@f, tspan, c0);
D = 1 - y(:,1) - y(:,2) - y(:,3); % [D] = 1 - [A] - [B] - [C]
% plot
plot(tspan,y(:,1),'b','LineWidth',2,tspan,y(:,2),'r','LineWidth',2,...
tspan,y(:,3),'g','LineWidth',2,tspan,D,'c','LineWidth',2);grid on;
xlabel('time, arbitrary
units','FontSize',16);ylabel('concentration','FontSize',16);
title('A => B => C => D consecutive reactions','FontSize',14);
legend('[A]','[B]','[C]','[D]');
```
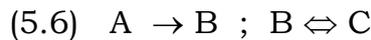
The output is identical, whichever solver is used, and is shown in figure below:

A => B => C => D consecutive reactions
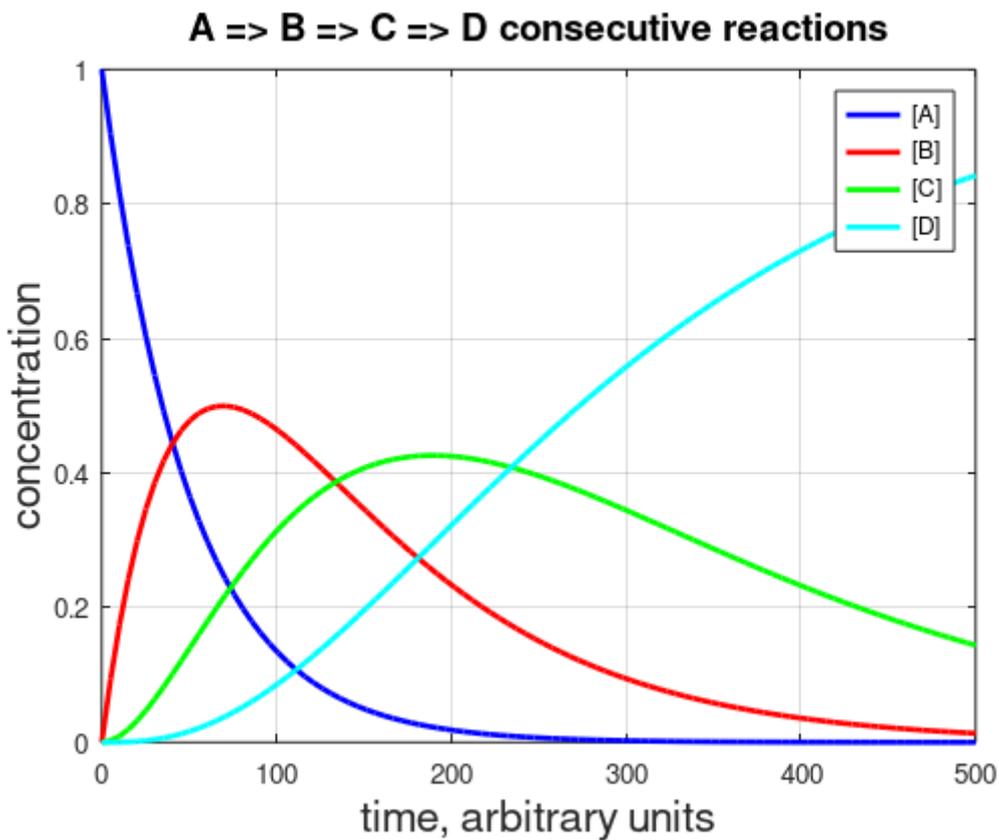
As a second example is reported the nine lines inside the function *xdot* for a coupled reactions set, the first being an irreversible one and the second a reversible (equilibrium) reaction, according to :

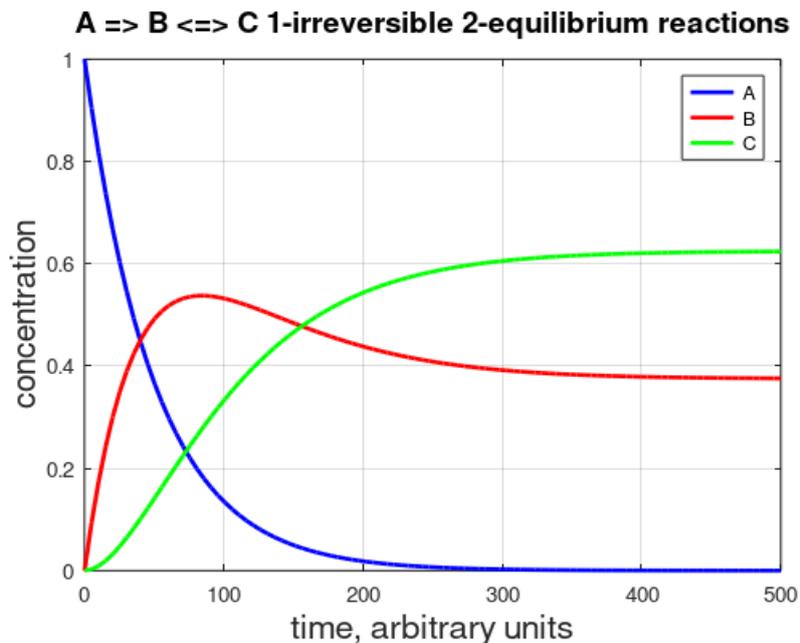$$(5.6) \quad A \rightarrow B \;\; ; \;\; B \Leftrightarrow C$$

```
k1 = 0.02;
k2 = 0.01;
k3 = 0.006;
r1 = k1*c(1); % c(1) = [A]
r2 = k2*c(2); % c(2) = [B]
r3 = k3*c(3); % c(3) = [C]
xdot(1) = - r1;
xdot(2) = r1 - r2 + r3;
xdot(3) = r2 - r3;
```

starting from initial concentrations c0 = [1,0,0] the output is in figure below:

A => B <=> C 1-irreversible 2-equilibrium reactions

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5.3 More complex and oscillating reactions

The iodine oscillating reaction, discovered by Briggs-Rauscher in 1973, also known as the oscillating clock, is one of the most common demonstrations of a chemical oscillating reaction.

Reactants are :

1) KIO3 (*potassium iodate*) + H2SO4 (*sulfuric acid*), aqueous solutions.

2) CH2(COOH)2 (*malonic acid*), aqueous solution.

3) H2O2 (*hydrogen peroxide*), aqueous solutions

When the three colorless solutions are mixed together, the color of the resulting mixture oscillates between clear, amber, and deep blue for about three to five minutes. The solution ends up into a blue and black mixture.

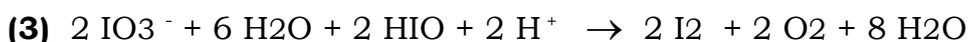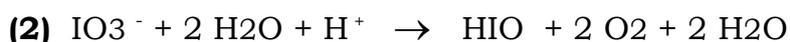Smaller amounts of auxiliary reactants are needed, they are:

1) MnSO4 (*manganese sulfate*), in water solution where Mn^{++} ions act as a catalyst for the reactions.

2) Starch as color enhancer for I2 (*molecular iodine*) in solution.

The reaction encompasses different steps, its overall scheme can be simplified as follows (in ionic form):

$$(1) \quad IO_3^- + 2\,H_2O_2 + H^+ + CH_2(COOH)_2 \rightarrow CHI(COOH)_2 + 2\,O_2 + 3\,H_2O$$

This first stage is the reduction of iodine in iodate ions from +5 to +1 oxidation state to HIO (*hypoiodous acid*) with a contemporary oxidation of 4 oxygen atoms in water peroxide from -1 to 0 and evolution of molecular oxygen gas.

Before reaction (1) is complete, newly produced HIO reacts with still present IO_3^- to produce molecular iodine and oxygen, the latter evolving again as a gas from solution.

$$(2) \quad IO_3^- + 2\,H_2O + H^+ \rightarrow HIO + 2\,O_2 + 2\,H_2O$$

$$(3) \quad 2\,IO_3^- + 6\,H_2O + 2\,HIO + 2\,H^+ \rightarrow 2\,I_2 + 2\,O_2 + 8\,H_2O$$

Iodine undergoes in water to a dismutation reaction :

$$(4)\; I_2 + H_2O \Leftrightarrow HIO + I^- + H^+$$
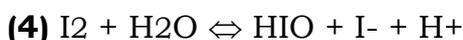
In acidic medium this equilibrium reaction is shifted to the left, therefore only small traces of I- ions are produce, which are however enough to trigger reaction (5),

$$(5)\; CH_2(COOH)_2 + I_2 + I^- \rightarrow CHI(COOH)_2 + 2\,I^-$$
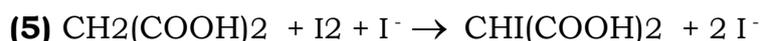
Reaction (5) is the so called breeding reaction, indeed two iodide ions are produced from one. At the end hypoiodous acid and iodine are consumed to give as end product iodomalonic acid:
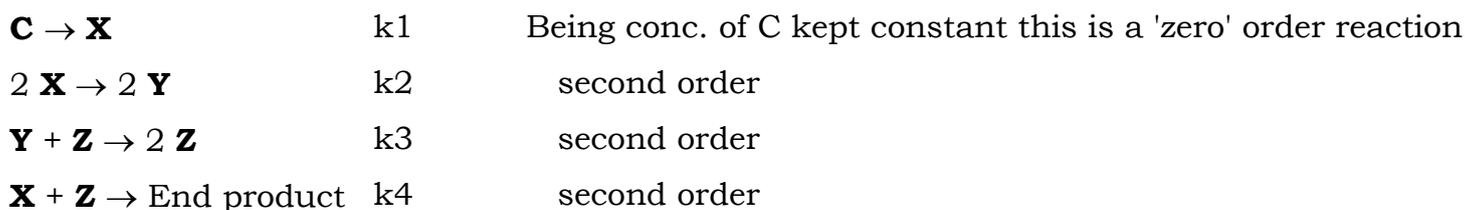
$$(6)\quad HIO + I^- + H^+ + 2CH_2(COOH)_2 \rightarrow 2\,CHI(COOH)_2 + 2\,H_2O$$

Reaction (6) is the so called moderating reaction, as it controls reaction (5) by capturing I^- ions.

The complex reactions can be simplified by assuming that the starting reagent, *potassium iodate, malonic acid* and *sulfuric acid* all keep their concentration constant. This value is

indicated as **C**. Water is considered to have constant concentration, as usual in diluted aqueous reactions.

By further indicating HIO = **X** ; I2 = **Y** and I⁻ = **Z**, the reactions (2),(3),(5),(6) can be resumed as:

C → **X**	k1	Being conc. of C kept constant this is a 'zero' order reaction
2 **X** → 2 **Y**	k2	second order
Y + **Z** → 2 **Z**	k3	second order
X + **Z** → End product	k4	second order

The four kinetic constants and initial concentration C are assigned in the first script lines of the function xdot(), evidenced in gray), to be integrated by the chosen ODE solver (in the example below *lsode*). The reaction rates (r1 to r4) are assigned according to the above mechanism and eventually mass balance of X,Y,Z is imposed.

```
clear;clc;
function xdot = f(c, tspan)
 % Rate constants.
 k1 = 0.02;k2 = 0.008;
 k3 = 0.04;k4 = 0.06;
 c_Init = 1;
 % Rate laws.
 r1 = k1*c_Init;              % c(1) = [X]
 r2 = k2*c(1)^2;             % c(2) = [Y]
 r3 = k3*c(2)*c(3);          % c(3) = [Z]
 r4 = k4*c(1)*c(3);
 % Mass balances and output assignement.
 xdot(1) = r1 - 2*r2 - r4;
 xdot(2) = 2*r2 - r3;
 xdot(3) = r3 - r4;
end
% Define initial concentrations.
c0 = [1,0.1,0.1];
tspan = linspace(0,2000,500);
y = lsode ("f", c0, tspan);

plot(tspan,y(':',1),'b','LineWidth',2,tspan,y(':',2),'r','LineWidth',2,tspan,y(':'
,3),'g','LineWidth',2);grid on;
xlabel('time,arbitrary  unit','FontSize',16);ylabel('concentration','FontSize',16);
legend('[X]','[Y]','[Z]');
title('Briggs-Rauscher oscillating reaction','FontSize',16);
```

The figure resulting from the orange part of the above script is shown here below.

A deeper discussion about modelling of chemical kinetics is contained in (Mazza 2022) and a wider choice of Matlab scripts are to be found here

Briggs-Rauscher oscillating reaction