

9.7 Exercise 7

A theoretical introduction to solving numerically ODE is given in section 7.1. Here we will discuss examples of ODE of second order. Our first example is

$$\frac{d^2 y}{dt^2} = -y \quad (9.12)$$

- Translate the above differential equation of second order into a set of differential equations of first order
- Check MATLAB HELP for `ode45`. Here you will find an example very close to the above problem
- Copy the corresponding lines into a function and adapt the starting values to find $\cos(x)$ as the solution to the above problem
- Adapt the starting values to find $\sin(x)$ as the solution to the above problem
- Change the program to find $\exp(x)$ as solution
- Change the program to find $\exp(-x)$ as solution
- Change the program to find $\sinh(x)$ as solution
- Change the program to find $\cosh(x)$ as solution

```
function [T,Y] = mydglstolv

[T,Y] = ode45(@myodefun,[0 2.*pi],[1 0]);
plot(T,Y(:,1),'-',T,Y(:,2),'-.');

function dy = myodefun(t,y)
    dy = zeros(2,1);
    dy(1)=y(2);
    dy(2)=-y(1);
end

end
```

Our next example is a reaction scheme specifying three kinetic coefficients k_1 , k_2 , and k_3 for the following reaction chain



Assuming all reactions to be of first order this scheme translates into a set of differential equations

$$\frac{dI_1}{dt} = -k_1 I_1 + k_2 I_2 \quad , \quad \frac{dI_2}{dt} = +k_1 I_1 - k_2 I_2 - k_3 I_2 \quad , \quad \frac{dI_3}{dt} = +k_3 I_2 \quad (9.14)$$

As starting values we choose $I_1(0) = 1$, $I_2(0) = 0$, and $I_3(0) = 0$. As kinetic coefficients we take $k_1 = 1$, $k_2 = 0.5$, and $k_3 = 0.05$. The implementation in MATLAB is easy:

```
function [T,Y] = my_chemical_odesolv
    k1=1;
    k2=0.5;
    k3=0.05;
    [T,Y] = ode45(@myodefun,[0 100],[1 0 0]);
    plot(T,Y(:,1),'-',T,Y(:,2),'-.');

    function dy = myodefun(t,y)
        dy = zeros(3,1);
        dy(1)=-k1.*y(1)+k2.*y(2);
        dy(2)=+k1.*y(1)-k2.*y(2)-k3.*y(2);
        dy(3)=+k3.*y(2);
    end

end
```

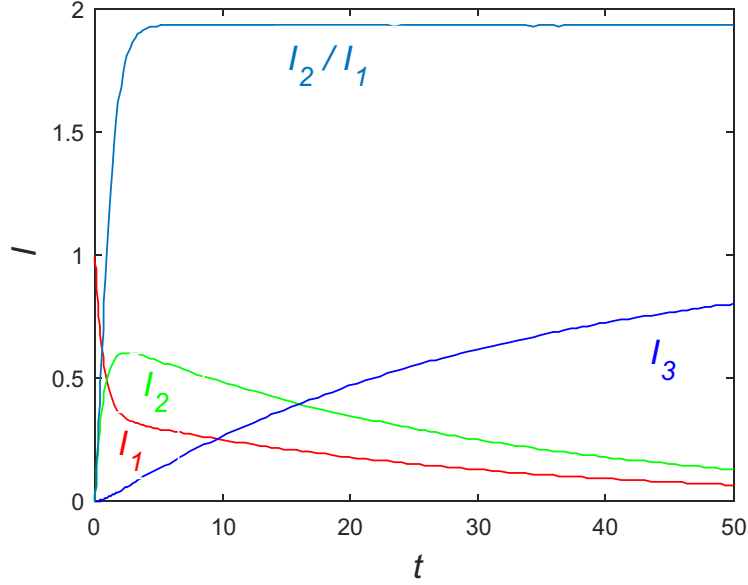


Figure 9.3: Numerical solution of the set of differential equations: $I_1(t)$, $I_2(t)$, $I_3(t)$, and the ratio $I_2(t)/I_1(t)$.

The solution are shown in Fig. 9.3. In what follows we will briefly discuss three concepts often used for discussing transport and kinetics:

1. rate limiting step
2. pre- steady state condition
3. steady state

The rate limiting step is always the slowest process, i.e. that with the smallest kinetic coefficient, in our case k_3 . Somehow counter intuitively not the large kinetic coefficients dominate the time dependencies, but the slowest process needs the longest time to reach steady state.

Steady state means that no changes in time exist, i.e. all derivatives on the left hand side of the set of differential equations are zero. From the third equation we find $I_3(t \rightarrow \infty) = 0$. Therefore from the first equation we find $I_1(t \rightarrow \infty) = 0$. From particle conservation we find $I_3(t \rightarrow \infty) = 1$. This are the relations visualized in Fig. 9.3; additionally the ration of I_2/I_1 is shown. Obviously this ratio reaches a constant value long before steady state is reached. This effect is called pre-steady state condition and is implied by the large kinetic coefficients k_1 and k_2 . Taking for the moment $k_3 = 0$ the (pre-) steady state condition is reached for $dI_1/dt = dI_2/dt = 0$, i.e. $k_1/I_1 = k_2/I_2$ or $I_2/I_1 = k_1/k_2$. This value is very close to the ration found from Fig. 9.3. The deviation can easily be understood from an analysis in linear order in k_3 . We will write

$$I_2 = \frac{k_1 - \Delta}{k_2} I_1 \quad \text{i.e.} \quad \frac{dI_2}{dt} = \frac{k_1 - \Delta}{k_2} \frac{dI_1}{dt} - \frac{1}{k_2} \frac{d\Delta}{dt} I_2 \approx \frac{k_1 - \Delta}{k_2} \frac{dI_1}{dt} \quad (9.15)$$

The last equation holds for pre-steady state since in this regime the ration between I_2 and I_1 is constant, i.e. Δ is constant.

Including this into the set of differential equations we get

$$\begin{aligned} \frac{dI_1}{dt} &= -\Delta I_1 \\ \frac{dI_2}{dt} &= +\Delta I_1 - k_3 \frac{k_1 - \Delta}{k_2} I_1 \\ \frac{dI_3}{dt} &= +k_3 \frac{k_1 - \Delta}{k_2} I_1 \end{aligned} \quad (9.16)$$

So for pre-steady state we find

$$\frac{k_1 - \Delta}{k_2} = \frac{I_2}{I_1} \approx \frac{dI_2/dt}{dI_1/dt} = -\frac{\Delta - k_3 \frac{k_1 - \Delta}{k_2}}{\Delta} \quad (9.17)$$

i.e.

$$k_1 \Delta - \Delta^2 = -k_2 \Delta + k_3(k_1 - \Delta) \quad (9.18)$$

Since we discuss the problem in linear order in k_3 , i.e. $\Delta \propto k_3$, we ignore Δ^2 (it is tiny!) and find

$$\Delta = k_3 \frac{k_1}{k_1 + k_2 + k_3} \quad (9.19)$$

So at pre-steady state

$$I_2 = \frac{k_1}{k_2} \frac{k_1 + k_2}{k_1 + k_2 + k_3} I_1 \quad , \quad (9.20)$$

somewhat smaller than for $k_3 = 0$.

For the set of differential equations we find

$$\begin{aligned} \frac{dI_1}{dt} &= -k_3 \frac{k_1}{k_1 + k_2 + k_3} I_1 \\ \frac{dI_2}{dt} &= -k_3 \frac{k_1}{k_2} \frac{k_1}{k_1 + k_2 + k_3} I_1 \\ \frac{dI_3}{dt} &= +k_3 \frac{k_1}{k_2} \frac{k_1 + k_2}{k_1 + k_2 + k_3} I_1 \end{aligned} \quad (9.21)$$

which in a very good approximation reflect the numerical solutions in Fig. 9.3. So as typical we can use the exact numerical results to identify possible simplifications to find good/reasonable analytic approximation of the numerical results. Here we learned most from the constant ratio of I_2/I_1 for nearly the whole time of the simulation.

Your next jobs:

- Use your program to check for the accuracy of the Eqs. (9.21).
- Change your program so that the rate determining step is of second order.
- Why does it take much longer before steady state is reached?
- Discuss your results in terms of half life time.
- Use log plots and log-log plots of your numerical results to identify if the solutions reflect an exponential law (linear order reaction) or a power law (second order reaction).