STUDIO 1

The tank reactor: mass balance.

Important: write a readable report of your work in each studio session. You will need this at the end of the course when you prepare for the written exam; several exam questions will be based directly on the studio work which is only documented in your own notes and the instructions.

Some exercises are called homework in order to save time in the studio classroom.

1. Linear differential equations of first order

(MA2 9.2) Recall that $\frac{d}{dt}\exp(t) = \exp(t)$ and $\exp(0) = 1$. This means that the exponential function $u(t) = \exp(t)$ satisfies the initial-value problem

$$u'(t) = u(t),\ t > 0; \quad u(0) = 1. \tag{1}$$

Let a and u_0 be real numbers and consider the initial-value problem

$$u'(t) = au(t),\ t > 0; \quad u(0) = u_0. \tag{2}$$

The solution is $u(t) = u_0 \exp(at)$. Check this!

Exercise 1. Solve (2) with Matlab. Write the following *function file* `funk1.m`, which defines the right-hand side of the differential equation.

```
function y=funk1(t,u)
global a
y=a*u;
```

Then write the following *script file* `data.m`, which gives default values to the variables that are used.

```
global a
a=1; T=1; u0=1;
```

Finally write the following *script file* `solve1.m`, which solves (2) and plots the solution.

```
[t,u]=ode45('funk1', [0 T], u0);
plot(t,u);
```

Note how the value of a enters into the function via the command `global a` which is written both in the function file `funk1.m` and in the main program `data.m`. Start the computation by typing the following on the Matlab command line:

```
>> data
>> solve1
>> a=-1
>> T=2
>> solve1
```

Compute and observe the solutions for various values of a, positive, negative, and zero. If you type ≫ `hold on` then Matlab will plot several curves in the same figure.

Now let b be another real number and consider the initial-value problem

$$u'(t) = au(t) + b,\ t > 0; \quad u(0) = u_0. \tag{3}$$

Remember (MA2 10.5) that the solution is given by $u(t) = u_h(t) + u_p(t)$, where $u_h(t) = A\exp(at)$ is a solution of the homogeneous equation $u' - au = 0$ and $u_p(t) = B$ is a particular solution of the inhomogeneous equation $u' - au = b$.

Homework 1. Determine the constants A and B and show that the solution is

$$u(t) = u_0 \exp(at) + \frac{b}{a}(\exp(at) - 1) \quad (\text{if } a \neq 0). \tag{4}$$

What is the solution when $a = 0$? For which values of a does the solution approach an equilibrium $u(t) \to \bar{u}$ as $t \to \infty$? Determine $\bar{u}$.

Exercise 2. Solve (3) with Matlab. Define b in the file `data.m` and change the global command to `global a b` in both places. Observe what the solutions look like for a positive, negative, and zero. For which values of a does the solution approach an equilibrium $u(t) \to \bar{u}$ as $t \to \infty$?

Now we consider the situation when $a = a(t)$, $b = b(t)$ are not constant:

$$u'(t) = a(t)u(t) + b(t),\ t > 0; \quad u(0) = u_0. \tag{5}$$

We use the method of *integrating factor* (MA2 9.2). Write the equation as $u' - a(t)u = b(t)$ and multiply it by the integrating factor $e^{-A(t)}$, where $A(t) = \int_0^t a(s)\,ds$, so that $A'(t) = a(t)$ and A(0)=0. We get

$$\frac{d}{dt}\Big(e^{-A(t)}u(t)\Big) = e^{-A(t)}u'(t) - a(t)e^{-A(t)}u(t) = e^{-A(t)}b(t).$$

We integrate from 0 to T:

$$\Big[e^{-A(t)}u(t)\Big]_0^T = \int_0^T e^{-A(t)}b(t)\,dt$$

and hence

$$e^{-A(T)}u(T) - e^{-A(0)}u(0) = \int_0^T e^{-A(t)}b(t)\,dt.$$

Using $A(0) = 0$, $u(0) = u_0$, multiplying by $e^{A(T)}$, and replacing t by s, T by t, we finally get

$$u(t) = u_0 e^{A(t)} + \int_0^t e^{A(t)-A(s)}b(s)\,ds, \quad \text{where } A(t) = \int_0^t a(s)\,ds. \tag{6}$$

Exercise 3. Solve (5) with Matlab. Use, for example, $a = \pm 1$, $b(t) = 1 + 0.1\sin(7t)$.

Homework 2. Use constant functions $a(t) = a$, $b(t) = b$ in (6) and compute the integrals to obtain (4).

2. The tank reactor

In a sequence of studio sessions we will study the ideal mixed tank reactor, see Figure 1. The goal is to design the reactor so that it will operate in a stable way at $(c_f - c)/c_f = 0.5$ ("50 % omsättningsgrad").

Figure 1. The tank reactor.

We will use the following data:

$V = 1.2\ \mathrm{m}^3$ volume of the tank
$c_p = 4.19\ \mathrm{kJ/(kg\ K)}$ heat capacity of the fluid
$\rho = 1000\ \mathrm{kg/m}^3$ density of the fluid
$q_{\mathrm{ref}} = 3.0 \cdot 10^{-4}\ \mathrm{m}^3/\mathrm{s}$ reference flux
$c_f = 5\ \mathrm{kmol/m}^3$ concentration at inflow of the interesting substance
$T_f = 70^\circ\mathrm{C}$ temperature at inflow
$\delta H = -83.7\ \mathrm{kJ/mol}$ heat of reaction
$A_K = 1.0\mathrm{m}^2$ area of the cooler
$\kappa = 0.58\ \mathrm{kJ/(m^2\ s\ K)}$ heat transfer coefficient of the cooler

We introduce the following variables:

c $[\mathtt{mol/m^3}]$ concentration in the reactor of the interesting substance
T $[\mathtt{K}]$ temperature in the reactor
q $[\mathtt{m^3/s}]$ flux through the reactor
T_K, T_{Kf} $[\mathtt{K}]$ temperatures in the cooler and at the cooler inflow
q_K $[\mathtt{m^3/s}]$ flux through the cooler
V_K $[\mathtt{m^3}]$ volume of the cooler

The reaction is exothermal and of first order with rate of reaction kc $[\mathtt{mol/(m^3s)}]$. The rate coefficient depends on the temperature according to the Arrhenius law:

$$k = k_0 \exp(-E/(RT)) \quad [\mathtt{s^{-1}}] \tag{7}$$

where R $[\mathtt{8.31\ J/(mol\ K)}]$ is the gas constant, E $[\mathtt{J/mol}]$ is the activation energy and k_0 $[\mathtt{s^{-1}}]$ is the rate constant of the reaction. The following rates have been measured:

T $[\mathtt{K}]$	343	353	363	373	383	393	403
k $[\mathtt{s^{-1}}]$	$2.8 \cdot 10^{-5}$	$5.6 \cdot 10^{-5}$	$11.2 \cdot 10^{-5}$	$22.4 \cdot 10^{-5}$	$44.8 \cdot 10^{-5}$	$89.6 \cdot 10^{-5}$	$179.2 \cdot 10^{-5}$

(Based on “Kemisk reaktionsteknik. Övningsuppgifter”, Kemisk reaktionsteknik, CTH 1993, uppgift 7.1.)

2.1. Mass balance. When we build a *mathematical model* for the tank reactor it is important not to consider all aspects at once. We therefore begin by making a big simplification: we assume that the rate coefficient k is constant, for example, $k =??$ corresponding to $T =??$ (choose a value from the table). Recall that k depends strongly on T, see (7), so this is not very realistic, but it will be a good starting point for our investigation.

The mass balance equation is

$$V\frac{dc}{dt} = q(c_f - c) - ckV. \quad [\mathtt{mol/s}]$$

This equation says that the rate of change of the total amount of the interesting substance is equal to the influx minus the outflux minus the reaction rate. In order to make the equation dimensionless we divide by $q_{\mathrm{ref}}c_f$ $[\mathtt{mol/s}]$. We get

$$\frac{V}{q_{\mathrm{ref}}}\frac{d}{dt}\Big(\frac{c}{c_f}\Big) = \frac{q}{q_{\mathrm{ref}}}\Big(1 - \frac{c}{c_f}\Big) - \frac{c}{c_f}k\frac{V}{q_{\mathrm{ref}}}. \tag{8}$$

We introduce $\tau = V/q_{\mathrm{ref}}$ `[s]` ("uppehållstid") and the dimensionless variables

$$s = t/\tau \ \text{(dimensionless time)},$$
$$X = c/c_f \ \text{(dimensionless concentration)},$$
$$U = q/q_{\mathrm{ref}} \ \text{(dimensionless flux)}.$$

Then, by the chain rule,

$$\frac{dX}{ds} = \frac{dX}{dt}\frac{dt}{ds} = \tau\frac{dX}{dt} = \frac{V}{q_{\mathrm{ref}}}\frac{d}{dt}\Big(\frac{c}{c_f}\Big),$$

and (8) becomes

$$\frac{dX}{ds} = U(1-X) - Xk\tau,$$

that is,

$$\frac{dX}{ds} = -(k\tau + U)X + U; \quad X(0) = X_0. \tag{9}$$

Note that this is of the form (5) with $a = -(k\tau + U)$ and $b = U$.

Exercise 4. Change your Matlab programs from part 1 so that they solve (9). Let first U be equal to a constant value $\bar{U}$. Does the solution $X(s)$ approach an equilibrium $\bar{X}$ as $s \to \infty$? Hint: Begin the file `data.m` by

```
global ktau Ubar
V=1.2;   qref=3.0e-4;
k=?? ;
tau=V/qref;   ktau=k*tau;
Ubar=1;  % equilibrium value of U
```

Change also the function file `funk1.m` to a file `tank.m` beginning with

```
function y=tank(s,X)
global ktau Ubar
U=Ubar;
```

Exercise 5. Recall that we want the reactor to operate at $(c_f - c)/c_f = 0.5$, i.e., at $\bar{X} = 0.5$. Determine $\bar{U}$ so that this is achieved. Hint: the equation for $\bar{X}$, $\bar{U}$ is obtained by setting $\frac{dX}{ds} = 0$ in (9), i.e.,

$$-(k\tau + \bar{U})\bar{X} + \bar{U} = 0. \tag{10}$$

Find a formula for $\bar{U}$ in terms of $k\tau$ and $\bar{X}$. Explain what happens in the extreme cases $\bar{X} = 0$, $\bar{X} = 1$. Insert the command `Xbar=.5;` in the file `data.m` and the formula for `Ubar` in the file `solve1.m`.

Exercise 6. We now investigate if the operating point $\bar{X} = 0.5$ is stable with respect to changes of the initial value X_0. Set $U = \bar{U}$ and solve (9) with Matlab with several initial values X_0. Is it stable?

Exercise 7. We next investigate if the operating point $\bar{X} = 0.5$ is stable with respect to changes of the flux U. Set $X_0 = \bar{X} = 0.5$ and solve (9) with Matlab with, for example, $U(s) = \bar{U} + 0.1\sin(7s)$. Is it stable?

Exercise 8. Finally, compute the required flux $\bar{q}$ (in dimensional units `[m`^{3}`/s]`).

Next week we will include the temperature dependence in k and we will see that the operating point $\bar{X} = 0.5$ is *not* always stable then.

STUDIO 2

The tank reactor: heat balance.

Important: write a readable report of your work in each studio session. You will need this at the end of the course when you prepare for the written exam; several exam questions will be based directly on the studio work which is only documented in your own notes and the instructions.

Some exercises are called homework in order to save time in the studio classroom.

1. Systems of differential equations

Recall that $\frac{d}{dt}\cos(t) = -\sin(t)$, $\frac{d}{dt}\sin(t) = \cos(t)$, $\cos(0) = 1$, and $\sin(0) = 0$. This means that the trigonometric functions $u_1(t) = \cos(t)$ and $u_2(t) = \sin(t)$ satisfy the initial-value problem

$$\begin{aligned} u_1'(t) &= -u_2(t),\ t > 0, \\ u_2'(t) &= u_1(t),\ t > 0, \\ u_1(0) &= 1,\ u_2(0) = 0. \end{aligned} \tag{11}$$

This is a *system* of (linear) differential equations of first order.

EXERCISE 9. Solve (11) with Matlab. Hint: Write the following *function file* `trig.m`, which defines the right-hand side of the system of differential equations.

```
function y=trig(t,u)
y = zeros(2,1); % trig(t,u) must return a column vector
y(1) = -u(2);
y(2) = u(1);
```

Then write the following *script file* `trigdata.m`, which gives default values to the variables that are used.

```
T = 2*pi;
u0 = [1; 0];
```

Finally write the following *script file* `solve2.m`, which solves (11) and plots the solution.

```
[t,u] = ode45('trig', [0 T], u0);
subplot(2,1,1) % breaks the figure into a 2-by-1 matrix; selects top half
plot(t, u(:,1)); % plots first component of u versus t
hold on
plot(t, u(:,2), '--'); % dashed line
hold off
title('Solid: u_1   Dashed: u_2'), xlabel('t')
subplot(2,1,2) % selects bottom half
plot(u(:,1), u(:,2)) % plots second versus first component of u
title('Phase portrait'), xlabel('u_1'), ylabel('u_2')
```

Start the computation by typing the following on the Matlab command line:

```
>> trigdata
>> solve2
>> T=pi
>> solve2
```

Compute and observe the solutions for various values of T. Consider in particular the *phase plot* of u_2 versus u_1, where t can be viewed as a parameter along the curve. What point on the curve corresponds to $t = 0$? $t = \frac{\pi}{2}$? $t = 2\pi$?

The *hyperbolic functions*, defined by $\cosh(t) = \frac{\exp(t)+\exp(-t)}{2}$ and $\sinh(t) = \frac{\exp(t)-\exp(-t)}{2}$, have the properties $\frac{d}{dt}\cosh(t) = \sinh(t)$, $\frac{d}{dt}\sinh(t) = \cosh(t)$, $\cosh(0) = 1$, and $\sinh(0) = 0$.

HOMEWORK 3. Verify these properties.

EXERCISE 10. Set $u_1(t) = \cosh(t)$ and $u_2(t) = \sinh(t)$. Derive an initial-value problem for $u_1(t)$ and $u_2(t)$ similar to (11). Compute the hyperbolic functions by solving this problem with Matlab. Hint: You need only slightly modify the trigonometric case above.

2. The tank reactor

Last week we considered the simplified case where we assumed that the rate coefficient k is constant, i.e., we neglected the temperature dependence of the reaction rate. Today we will include this dependence (the Arrhenius law) to improve our mathematical model of the tank reactor. Therefore, we need to consider also the temperature, T, in the reactor, and start by deriving an equation for it by considering heat balance in the tank reactor. In doing so we will need to know the temperature, T_K, in the cooler tank. Here we will once again make a simplifying assumption, namely, that T_K is constant. Physically, this can be expected to be the case when the cooler tank is large compared to the reactor tank.

2.1. Heat balance.

The heat balance equation is

$$\rho c_p V \frac{dT}{dt} = \rho c_p q (T_f - T) + (-\delta H) V c k_0 \exp(-E/(RT)) - \kappa A_K (T - T_K). \quad \texttt{[J/s]} \tag{12}$$

Recall that ρ and c_p are the *density* and the *heat capacity* of the fluid in the reactor, respectively. Since V is the *volume* of the tank reactor, the left-hand side expresses the rate of change of the internal energy of the fluid in the reactor. Three different mechanisms contribute to this:

- The first term on the right-hand side expresses the net rate of change of the energy due to the *temperature difference*, $T_f - T$, between the inflow and the outflow (q is the *flux* through the tank).
- The second term on the right-hand side expresses the increase rate of the energy due to heat released in the (exothermal) reaction. Recall that δH is the *heat of reaction*, c is the *concentration* in the reactor of the reacting substance, and $k = k_0 \exp(-E/(RT))$ is the *rate coefficient* of the reaction. Note: since the *reaction rate*, ck, depends both on the concentration and on the temperature, there is a (non-linear) *coupling* between the equation for the concentration, that we studied last week, and the equation for the temperature.
- The third term on the right-hand side expresses the decrease rate of the energy due to heat transferred from the reactor to the cooler. This rate is proportional to the *temperature difference*, $T - T_K$, between the reactor and the cooler. Recall that κ and A_K are the *heat transfer coefficient* and the *area* of the cooler, respectively.

Note that (12) is a *non-linear* differential equation for the temperature, T, in the tank reactor. In order to make the equation dimensionless we divide by $\rho c_p q_{\text{ref}} T_f$ `[J/s]`. We get

$$\frac{V}{q_{\text{ref}}} \frac{d}{dt}\Big(\frac{T}{T_f}\Big) = \frac{q}{q_{\text{ref}}}\Big(1 - \frac{T}{T_f}\Big) + \frac{(-\delta H) c_f}{\rho c_p T_f} \frac{c}{c_f} \frac{V}{q_{\text{ref}}} k_0 \exp\Big(-\frac{E}{R T_f} \frac{T_f}{T}\Big) - \frac{\kappa A_K}{\rho c_p q_{\text{ref}}}\Big(\frac{T}{T_f} - \frac{T_K}{T_f}\Big). \tag{13}$$

Recall that last week we introduced the *dimensionless time* $s = t/\tau$, where $\tau = V/q_{\text{ref}}$ `[s]`. We now also introduce

$$\begin{aligned} X_1 &= c/c_f \text{ (dimensionless concentration)}, \\ X_2 &= T/T_f \text{ (dimensionless reactor temperature)}, \\ U_1 &= q/q_{\text{ref}} \text{ (dimensionless flux)}, \\ U_2 &= T_K/T_f \text{ (dimensionless cooler temperature)}. \end{aligned}$$

Note that X_1 is the quantity last week referred to as X, and U_1 is the quantity last week referred to as U. To express the left-hand side in (13) in the non-dimensional variables we note that, by the chain rule,

$$\frac{dX_2}{ds} = \frac{dX_2}{dt}\frac{dt}{ds} = \tau\frac{dX_2}{dt} = \frac{V}{q_{\mathrm{ref}}}\frac{d}{dt}\Big(\frac{T}{T_f}\Big). \tag{14}$$

We also express the terms on the right-hand side in (13) in the non-dimensional variables:

- The first term on the right-hand side simply becomes

$$U_1(1 - X_2). \tag{15}$$

- For the second term on the right-hand side we introduce the three dimensionless numbers

$$\alpha = \frac{(-\delta H)c_f}{\rho c_p T_f}, \quad \gamma = \frac{E}{RT_f}, \quad \delta = k_0\tau\exp(-\gamma),$$

  where γ is referred to as the *Arrhenius number*. This term then becomes

$$\alpha X_1 \tau k_0 \exp\Big(-\frac{\gamma}{X_2}\Big) = \alpha X_1 k_0 \tau \exp(-\gamma)\exp(\gamma - \frac{\gamma}{X_2}) = \alpha X_1 f(X_2), \tag{16}$$

  where

$$f(X_2) = \delta\exp(\gamma - \frac{\gamma}{X_2}).$$

  Note that we have re-written the *Arrhenius law* as $k\tau = f(X_2) = \delta\exp(\gamma - \frac{\gamma}{X_2})$. The dimensionless numbers γ and δ can be thought of as non-dimensional counterparts to the *activation energy* E and the *rate constant* k_0. Next week we will estimate γ and δ by fitting the function $k\tau = \delta\exp(\gamma - \frac{\gamma}{X_2})$ to measured reaction rates, but as for today you may use the values $\gamma = 30$ and $\delta = 0.1$. The dimensionless number α, on the other hand, can be directly computed from known data.

- Introducing the dimensionless number

$$\beta = \frac{\kappa A_K}{\rho c_p q_{\mathrm{ref}}}$$

  the third term on the right-hand side becomes

$$-\beta(X_2 - U_2). \tag{17}$$

From (14)–(17), (13) becomes

$$\frac{dX_2}{ds} = U_1(1 - X_2) + \alpha X_1 f(X_2) - \beta(X_2 - U_2), \tag{18}$$

and replacing X by X_1, U by U_1, and $k\tau$ by $f(X_2)$, in the equation for the concentration that we derived last week, we arrive at the system of differential equations,

$$\begin{aligned} \frac{dX_1}{ds} &= U_1(1 - X_1) - X_1 f(X_2), \ s > 0, \\ \frac{dX_2}{ds} &= U_1(1 - X_2) + \alpha X_1 f(X_2) - \beta(X_2 - U_2), \ s > 0, \\ X_1(0) &= X_{1,0}, \ X_2(0) = X_{2,0}. \end{aligned} \tag{19}$$

Exercise 11. Extend your Matlab programs from last week so that they solve (19). Let first U_1 and U_2 be equal to constant values $\bar{U}_1$ and $\bar{U}_2$. Does the solution $X(s) = \begin{bmatrix} X_1(s) \\ X_2(s) \end{bmatrix}$ approach an equilibrium $\bar{X} = \begin{bmatrix} \bar{X}_1 \\ \bar{X}_2 \end{bmatrix}$ as $s \to \infty$? In fact, you should be able to find two equilibrium points by choosing different initial values X_0, say, $X_0 = \begin{bmatrix} 0.5 \\ 1 \end{bmatrix}$ and $X_0 = \begin{bmatrix} 0.5 \\ 1.1 \end{bmatrix}$.

Hint: The file `data.m` could for example look like

```
global alpha beta gamma delta Ubar
dH = -83.7e3; % heat of reaction
cf = 5e3; % concentration at inflow
% here you initiate the rest of the variables needed to compute alpha
alpha = -dH*cf/(rho*cp*Tf);
% here you initiate the variables needed to compute beta
% you must choose a value for AK, for instance AK = 1
beta = ...; % insert the expression for beta
gamma = 30;
delta = 0.1;
Ubar = [1; 0.97];
S = 10; % final time
X0 = [0.5; 1]; % initial value
```

Change the function file `tank.m` to a file `tank2.m` beginning with

```
function y=tank2(s,X)
global alpha beta gamma delta Ubar
U(1) = Ubar(1);
U(2) = Ubar(2);
y = zeros(2,1);
y(1) = U(1)*(1-X(1)) - ... ; % complete the expression for dX1/ds
y(2) = ... ; % insert the expression for dX2/ds
```

(If you want, you can write a separate function file `f.m` that implements the "Arrhenius function" $f(X_2) = \delta \exp(\gamma - \frac{\gamma}{X_2})$. Then you can call `f` from `tank2`. Just don't forget to declare the variables `gamma` and `delta` as global inside `f`.)

You should finally be able to use the file `solve2.m` from Exercise 9 with obvious modifications.

In a later exercise we will look for an equilibrium at $\bar{X}_1 = 0.5$ and analyze the stability of this desired operating point.

STUDIO 3

The tank reactor: Arrhenius' law.

Important: write a readable report of your work in each studio session. You will need this at the end of the course when you prepare for the written exam; several exam questions will be based directly on the studio work which is only documented in your own notes and the instructions.

Some exercises are called homework in order to save time in the studio classroom.

1. The method of least squares

(TLA 4.9) Consider the linear system of equations

$$Ax = b, \tag{20}$$

where $A \in \mathbf{R}^{m\times n}$, $x \in \mathbf{R}^n$, $b \in \mathbf{R}^m$. If $m > n$ (more equations than unknowns), then the system is "overdetermined" and such a system has no solution in general. Geometrically, the reason for this is that (in general) the vector b lies outside the *range* ("värderummet") of A,

$$R(A) = \big\{ y \in \mathbf{R}^m : y = Ax \text{ for some } x \in \mathbf{R}^n \big\}.$$

Since the dimension of $R(A)$ is $\le n$ and $m > n$, we realize that the space $R(A)$ does not "fill out" the whole space $\mathbf{R}^m$. Therefore it is likely that a given vector $b \in \mathbf{R}^m$ will lie outside $R(A)$, see Figure 1, and then Ax cannot be equal to b and (20) has no solution.

FIGURE 1. Orthogonal projection onto the range of A.

In this situation we seek an approximate solution which makes the *residual*

$$b - Ax$$

as small as possible. More precisely, we seek a vector $\hat{x} \in \mathbf{R}^n$, which minimizes the square of the norm (length) of the residual:

$$f(\hat{x}) = \min f(x), \quad f(x) = \|b - Ax\|^2. \tag{21}$$

Recall the scalar product $\langle x, y\rangle = y^t x$ and the norm $\|x\| = \sqrt{\langle x, x\rangle} = \sqrt{x^t x}$ of column vectors. From (TLA 6.9) we know that there is a unique vector $\hat{y} = A\hat{x} \in R(A)$ such that the distance $\|b - Ax\|$ is minimal, i.e., $\|b - A\hat{x}\| \le \|b - Ax\|$ for all x. The vector $\hat{y} = A\hat{x}$ is the *orthogonal projection* of b onto $R(A)$, see Figure 1. It is characterized by the condition that $b - \hat{y} = b - A\hat{x}$ is orthogonal to all vectors $Av \in R(A)$. This means that

$$0 = \langle b - A\hat{x}, Av\rangle = (Av)^t(b - A\hat{x}) = v^t A^t (b - A\hat{x}) = v^t(A^t b - A^t A\hat{x}).$$

Since this holds for all $v \in \mathbf{R}^n$, we may take $v = A^t b - A^t A\hat{x}$ to get

$$A^t A\hat{x} - A^t b = 0. \tag{22}$$

Thus, we can compute $\hat{x}$ by solving the linear system

$$A^t A x = A^t b. \tag{23}$$

Note that the coefficient matrix $A^t A$ is $n \times n$ and symmetric. The system (23) has at least one solution (namely $\hat{x}$).

In order to see that the minimization problem (21) is equivalent to solving the linear system (23), we write $x = \hat{x} + v$, $v = x - \hat{x}$, and compute

$$\begin{aligned} f(x) &= f(\hat{x}+v) = \|(b - A\hat{x}) - Av\|^2 = \langle (b - A\hat{x}) - Av, (b - A\hat{x}) - Av\rangle \\ &= \langle b - A\hat{x}, b - A\hat{x}\rangle - 2\langle b - A\hat{x}, Av\rangle + \langle Av, Av\rangle \\ &= \|b - A\hat{x}\|^2 + 2(Av)^t(A\hat{x} - b) + \|Av\|^2 \\ &= f(\hat{x}) + 2v^tA^t(A\hat{x} - b) + \|Av\|^2 \\ &= f(\hat{x}) + 2v^t(A^tA\hat{x} - A^tb) + \|Av\|^2. \end{aligned} \tag{24}$$

Taking (22) into account we get

$$f(x) = f(\hat{x}) + \|Av\|^2 \geq f(\hat{x}).$$

This shows that x minimizes $f(x)$, if and only if $\|Av\| = 0$, in which case $Ax = A\hat{x} + Av = A\hat{x}$ and $A^tAx = A^tA\hat{x} = A^tb$. Therefore, x minimizes $f(x)$ if and only if x is a solution of (23).

We can also interpret this in terms of the general minimization problem in (MA3 2.9–10). Recall Taylor's formula:

$$f(x) = f(\hat{x}+v) = f(\hat{x}) + v^tf'(\hat{x}) + \tfrac{1}{2}v^tf''(\hat{x})v + R(x). \tag{25}$$

Noting that $\|Av\|^2 = \langle Av, Av\rangle = (Av)^t(Av) = v^t(A^tA)v$, we re-write (24) as

$$f(x) = f(\hat{x}+v) = f(\hat{x}) + 2v^t(A^tA\hat{x} - A^tb) + v^t(A^tA)v. \tag{26}$$

Comparing (25) with (26), we identify the Jacobi matrix (gradient vector) $f'(\hat{x}) = 2(A^tA\hat{x} - A^tb)$, the Hesse matrix $f''(\hat{x}) = 2A^tA$, and the remainder $R(x) = 0$. Recall that stationary points are given by the system of equations $f'(x) = 2(A^tAx - A^tb) = 0$, which is the same as (23). Note also that the Hesse matrix is constant (with respect to x) and positive semidefinite: $v^tf''(x)v = 2v^t(A^tA)v = 2\|Av\|^2 \geq 0$.

Exercise 12. Suppose that the variables y and x are related by $y = kx + m$. In order to determine the coefficients k and m we make measurements of y and x:

x	5	6	7	8	9	10
y	19.5888	23.4043	25.5754	29.1231	31.9575	35.8116

This leads to an overdetermined system of the form

$$\begin{gathered} kx_1 + m = y_1 \\ \vdots \\ kx_6 + m = y_6 \end{gathered}$$

or, in matrix form $Av = y$,

$$\begin{bmatrix} x_1 & 1 \\ \vdots & \vdots \\ x_6 & 1 \end{bmatrix} \begin{bmatrix} k \\ m \end{bmatrix} = \begin{bmatrix} y_1 \\ \vdots \\ y_6 \end{bmatrix}.$$

Solve this system by the least squares method in Matlab. Hint: set up the column vectors `x`, `y` and the matrix `A=[x ones(size(x))]`, then form the matrices `B=A'*A` and `g=A'*y`. Solve the system $Bv = g$ by the command `v=B\g`.

Plot the data points (x_i, y_i) and the fitted function $y = kx + m$ in the same figure. The following commands are useful: `plot(x,y,'or')`, `fplot('ykxm',[x(1) x(6)])`. Here `ykxm.m` is a function file that implements the function $y = kx+m$. Don't forget to declare `global k m` both inside the function file and in the main program.

Actually, Matlab's backslash command `v=A\y` automatically uses the least squares method when the system $Av = y$ is overdetermined. Try this also!

2. The tank reactor

The rate coefficient depends on the temperature according to the Arrhenius law:

$$k = k_0 \exp(-E/(RT)) \quad \texttt{[s}^{-1}\texttt{]} \tag{27}$$

where R `[8.31 J/(mol K)]` is the gas constant, E `[J/mol]` is the activation energy and k_0 $\texttt{[s}^{-1}\texttt{]}$ is the rate constant of the reaction. The following rates have been measured:

T `[K]`	343	353	363	373	383	393	403
k $\texttt{[s}^{-1}\texttt{]}$	$2.8 \cdot 10^{-5}$	$5.6 \cdot 10^{-5}$	$11.2 \cdot 10^{-5}$	$22.4 \cdot 10^{-5}$	$44.8 \cdot 10^{-5}$	$89.6 \cdot 10^{-5}$	$179.2 \cdot 10^{-5}$

The task is now to determine the coefficients k_0 and E by fitting the rate law (27) to these data. Last week we wrote (27) in dimensionless form

$$k\tau = \delta e^{\gamma(1-1/X)}, \quad \text{where } \gamma = \frac{E}{RT_f}, \quad \delta = k_0 \tau e^{-\gamma}, \quad X = \frac{T}{T_f}, \quad \tau = \frac{V}{q_{\text{ref}}}. \tag{28}$$

Introducing new variables $r = k\tau$ and $\xi = 1 - 1/X$ we get

$$r = \delta e^{\gamma\xi}. \tag{29}$$

The task is now to fit this function to the given data points (ξ_i, r_i).

Exercise 13. (Linear least squares method.) Form the logarithm of (29) so that you get a linear relation of the form $y = kx + m$, namely, (see also (TLA 5.2))

$$\log(r) = \gamma\xi + \log(\delta). \tag{30}$$

(Note that the natural logarithm is denoted $\log(x)$ in English and in Matlab, but $\ln(x)$ in Swedish.) Solve for γ and δ by using the least squares method as in Exercise 12. Begin by forming column vectors `X`, `r`, `xi` and so on. Plot the data points (X_i, r_i) and the fitted function $r = \delta e^{\gamma(1-1/X)}$ in the same figure. Finally, determine k_0 and E.

Homework 4. (A nonlinear least squares method.) Alternatively, we can form the residual $r - \delta e^{\gamma\xi}$ from the nonlinear relation (29) and minimize the square of its norm

$$g(\delta, \gamma) = \sum_i \left(r_i - \delta e^{\gamma \xi_i} \right)^2. \tag{31}$$

Write a Matlab function that implements this function and use Matlab's program `fminsearch` to minimize it. Why does this method give a slightly different result? Hint: the Matlab function `norm` may be useful for computing the right side of (31).

Exercise 14. Insert the new values for δ and γ in your Matlab programs from Studio 2. Repeat all the computations. Let U_1 and U_2 be equal to constant values $\bar{U}_1$ and $\bar{U}_2$. Does the solution $X(s) = \begin{bmatrix} X_1(s) \\ X_2(s) \end{bmatrix}$ approach an equilibrium $\bar{X} = \begin{bmatrix} \bar{X}_1 \\ \bar{X}_2 \end{bmatrix}$ as $s \to \infty$? In fact, you should be able to find two equilibrium points by choosing different initial values X_0, say, $X_0 = \begin{bmatrix} 0.5 \\ 1 \end{bmatrix}$ and $X_0 = \begin{bmatrix} 0.5 \\ 1.1 \end{bmatrix}$.

Next week we will look for an equilibrium at $\bar{X}_1 = 0.5$ and analyze the stability of this desired operating point.

STUDIO 4

The tank reactor: Stability.

Theory: S. Larsson, “Kompletterande föreläsningsanteckningar och övningar” (K).

1. Introduction

(K 1.1) Recall from Studio 2 the system of differential equations,

$$\begin{aligned}
&\frac{dX_1}{ds} = U_1(1 - X_1) - X_1 f(X_2) = F_1(X, U), \; s > 0,\\
&\frac{dX_2}{ds} = U_1(1 - X_2) + \alpha X_1 f(X_2) - \beta(X_2 - U_2) = F_2(X, U), \; s > 0,\\
&X_1(0) = X_{1,0}, \; X_2(0) = X_{2,0},
\end{aligned} \tag{32}$$

which is our mathematical model for the dynamics of the tank reactor. Recall, also, the *state variables* $X_1 = X_1(s)$ (dimensionless concentration) and $X_2 = X_2(s)$ (dimensionless reactor temperature), depending on s (dimensionless time). These two variables, that describe the *state* of the tank reactor, are the ones that we compute by solving (32), i.e., X_1 and X_2 are *output data.*

There are two kinds of *input data*. First we have the *initial data*, $X_0 = \begin{bmatrix} X_{1,0} \\ X_{2,0} \end{bmatrix}$, then the *control variables* $U_1 = U_1(s)$ (dimensionless flux) and $U_2 = U_2(s)$ (dimensionless cooler temperature).

Recall, finally, that $k\tau = f(X_2) = \delta e^{\gamma(1-1/X_2)}$ is the dimensionless rate coefficient given by the Arrhenius law. In Studio 3 you determined the dimensionless numbers γ and δ, which can be thought of as non-dimensional counterparts to the activation energy and the rate constant of the reaction, by fitting the rate law to data. As for the other two dimensionless numbers appearing in (32), α is also reaction dependent since it is proportional to the heat of reaction, whereas β is proportional to the area and the heat transfer coefficient of the cooler.

Our final goal is to *design* the tank reactor in such a way that it runs in a stable manner at a specified, desired, operating point $\bar{X} = \begin{bmatrix} \bar{X}_1 \\ \bar{X}_2 \end{bmatrix}$. In order to achieve this goal, we first determine corresponding values of the control variables $\bar{U} = \begin{bmatrix} \bar{U}_1 \\ \bar{U}_2 \end{bmatrix}$, for which $\bar{X}$ *is* a stationary point. Then, we analyze the stability of $\bar{X}$ with respect to perturbations of input data and, if necessary, change the value of one or more *design parameters*. This could, for instance, physically mean varying the area of the cooler, i.e., varying the value of β in our mathematical model (32).

2. Stationary points

(K 1.2) Our first task is, *given* a desired operating (stationary) point $\bar{X} = \begin{bmatrix} \bar{X}_1 \\ \bar{X}_2 \end{bmatrix}$, to *determine* corresponding values of the control variables $\bar{U} = \begin{bmatrix} \bar{U}_1 \\ \bar{U}_2 \end{bmatrix}$ by solving the system of equations,

$$\begin{aligned}
0 &= \bar{U}_1(1 - \bar{X}_1) - \bar{X}_1 f(\bar{X}_2),\\
0 &= \bar{U}_1(1 - \bar{X}_2) + \alpha \bar{X}_1 f(\bar{X}_2) - \beta(\bar{X}_2 - \bar{U}_2).
\end{aligned} \tag{33}$$

EXERCISE 15. Show that the solution to (33) is given by,

$$\begin{aligned} \bar{U}_1 &= \frac{\bar{X}_1}{1-\bar{X}_1} f(\bar{X}_2), \\ \bar{U}_2 &= \bar{X}_2 - \frac{1}{\beta}\Big(\frac{\bar{X}_1}{1-\bar{X}_1}(1-\bar{X}_2)f(\bar{X}_2) + \alpha \bar{X}_1 f(\bar{X}_2)\Big). \end{aligned} \tag{34}$$

We here stress a subtle point. *Given* $\bar{X}$, clearly, $\bar{U}$ is *uniquely* defined by (34). On the other hand, if we instead consider $\bar{U}$ as fixed, we know that $\bar{X}$ is *one* solution to (33), however, it might not be the *only* solution, i.e., there may exist more than one stationary point corresponding to $\bar{U}$. We will return to this later.

To concretize, let us now specify the values of the state variables at the desired operating point: our objective is to design the tank reactor to operate in a stable manner at $(c_f - \bar{c})/c_f = 0.5$ ("50% omsättningsgrad") and at reactor temperature $\bar{T} = 99°C$, i.e., at $\bar{X} = \begin{bmatrix}\bar{X}_1\\ \bar{X}_2\end{bmatrix} = \begin{bmatrix}0.5\\ (99+273.15)/T_f\end{bmatrix}$.

EXERCISE 16. Modify the file `data.m` from Studio 2, so that, given $\bar{X}$ (as above), $\bar{U}$ is computed from (34). At the same time, check that you have changed the old values of γ $(=30)$ and δ $(=0.1)$ that we used in Studio 2 to the new ones that you determined in Studio 3. Also, check that you have set $A_K = 1$ m^2. Hint: You need to change the line

```
Ubar = [1; 0.97];
```

into

```
Xbar = [0.5; (99 + 273.15)/Tf]; % Tf = 70 + 273.15
Ubar = zeros(2,1); % initialize (column vector) Ubar
Ubar(1) = ...; % insert the expression for Ubar(1)
Ubar(2) = ...; % insert the expression for Ubar(2)
```

EXERCISE 17. Check `data.m` by calling `tank2.m` that you wrote in Studio 2:

```
>> data
>> Xprime = tank2(0, Xbar)
```

What should the result be? (Note that the value of the first argument may be given arbitrarily, since there is no explicit time dependence in the right-hand side of (32).)

3. Instability of the operating point

We now perform a first stability check of the operating point $\bar{X}$. We do this by introducing small initial perturbations, i.e., small initial deviations from $\bar{X}$, in X. In this test, we do not consider perturbations in the control variables, i .e., we take $U = \bar{U}$ in `tank2.m`.

EXERCISE 18. Assuming that `solve2.m` is the name of your script file from Studio 2, from which the call to `ode45` is made and the solution is plotted, solve (32) by giving the following Matlab commands:

```
>> data
>> S = 20;
>> X0 = Xbar + [0; 0.05];
>> solve2
>> X0 = Xbar - [0; 0.05];
>> solve2
```

Is $\bar{X}$ stable with respect to these perturbations? Also try some other initial perturbations.

As you have just seen, a small deviation from $X = \bar{X}$ causes the tank reactor to depart from the desired operating point. Since these kinds of perturbations are inevitable in practice, the reactor will not remain in the desired state, which is therefore *not* stable. Rather, it will (depending on the initial perturbation) reach one of two *other* equilibrium points, which seem to be stable ones. These two are also stationary points, corresponding to $\bar{U}$, i.e., they are also solutions to (33). This is the non-uniqueness mentioned in Section 33.

4. Linear stability analysis

(K 1.3) In order to learn how to "adjust" the tank reactor so that it will operate in a stable way at $\bar{X}$, we need to systematically study the stability of solutions to (32). We will perform a *linear stability analysis* based on the assumption of *small perturbations*.

Let $X(s)$ with input data X_0, $U(s)$ be a solution to (32) that is close to $\bar{X}$. With

$$X(s) = \bar{X} + \Delta X(s), \quad X_0 = \bar{X} + \Delta X_0, \quad U(s) = \bar{U} + \Delta U(s), \tag{35}$$

we may consider $\Delta X(s)$ as a *perturbation* in $X(s)$ caused by the perturbations ΔX_0 and $\Delta U(s)$ in input data.

If $\Delta X(s)$ and $\Delta U(s)$ are *small*, we obtain the *linear system*

$$\begin{aligned} x'(s) &= Ax(s) + Bu(s), \quad s > 0, \\ x(0) &= x_0, \end{aligned} \tag{36}$$

for the *approximate perturbation* $x(s) \approx \Delta X(s)$ caused by the perturbations in input data $x_0 = \Delta X_0$ and $u(s) = \Delta U(s)$. In (36),

$$A = \begin{bmatrix} \dfrac{\partial F_1}{\partial X_1}(\bar{X},\bar{U}) & \dfrac{\partial F_1}{\partial X_2}(\bar{X},\bar{U}) \\ \\ \dfrac{\partial F_2}{\partial X_1}(\bar{X},\bar{U}) & \dfrac{\partial F_2}{\partial X_2}(\bar{X},\bar{U}) \end{bmatrix} = \begin{bmatrix} -\bar{U}_1 - f(\bar{X}_2) & -\bar{X}_1 f'(\bar{X}_2) \\ \\ \alpha f(\bar{X}_2) & -\bar{U}_1 + \alpha \bar{X}_1 f'(\bar{X}_2) - \beta \end{bmatrix}, \tag{37}$$

where $f'(\bar{X}_2) = \dfrac{\gamma}{\bar{X}_2^2} f(\bar{X}_2)$, and

$$B = \begin{bmatrix} \dfrac{\partial F_1}{\partial U_1}(\bar{X},\bar{U}) & \dfrac{\partial F_1}{\partial U_2}(\bar{X},\bar{U}) \\ \\ \dfrac{\partial F_2}{\partial U_1}(\bar{X},\bar{U}) & \dfrac{\partial F_2}{\partial U_2}(\bar{X},\bar{U}) \end{bmatrix} = \begin{bmatrix} 1 - \bar{X}_1 & 0 \\ \\ 1 - \bar{X}_2 & \beta \end{bmatrix}, \tag{38}$$

are called *Jacobi matrices* of $F(X,U) = \begin{bmatrix} F_1(X,U) \\ F_2(X,U) \end{bmatrix}$ at $\bar{X}$, $\bar{U}$.

HOMEWORK 5. Verify (37) and (38).

5. Stability with respect to perturbations of initial data

(K 1.4) In this section we consider the case $u(s) = 0$, i.e., we only consider perturbations in initial data. In this case, (36) simplifies to

$$\begin{aligned} x'(s) &= Ax(s), \quad s > 0, \\ x(0) &= x_0, \end{aligned} \tag{39}$$

with solution (we assume that A is diagonalisable)

$$x(s) = c_1 e^{\lambda_1 s} g_1 + c_2 e^{\lambda_2 s} g_2, \tag{40}$$

where λ_i, g_i are eigen-values and eigen-vectors of A, and the c_i are constants depending on x_0. Clearly, the growth of $x(s)$ (and accordingly the stability of $\bar{X}$) depends on the eigen-values of A.

EXERCISE 19. Compute the eigen-values of A using Matlab. Hint: First write the function file `jacobianA.m` that computes A:

```
function A = jacobianA(Xbar)
global alpha beta gamma delta Ubar
A = zeros(2,2); % initialize (2x2 matrix) A
A(1,1) = ...; % insert the expression for A(1,1)
```

```
  A(1,2) = ...; % insert the expression for A(1,2)
  A(2,1) = ...; % insert the expression for A(2,1)
  A(2,2) = ...; % insert the expression for A(2,2)
```

Then you can compute the eigen-values of A by typing:

```
>> data
>> global A % we declare A as global because we will need this later
>> A = jacobianA(Xbar)
>> eig(A)
```

As you (hopefully!) noticed, A has two real eigen-values, one positive and one negative. Because of the positive eigen-value one of the terms in (40) will grow exponentially with time, and this explains the instability of $\bar{X}$.

EXERCISE 20. Solve (39) with the same initial perturbations as in Exercise 18. Hint: First write the function file `lineartank.m` that computes the right-hand side of (39):

```
  function y = lineartank(s,x)
  global A % this is the reason we declared A as global
  y = A*x;
```

Then modify `solve2.m` into `linearsolve.m`. (Just replace `tank2` by `lineartank` in the call to `ode45`, and `X` by `x` everywhere.) Now you can solve (39) by typing:

```
>> figure % opens a new figure
>> data
>> S = 1;
>> x0 = [0; 0.05];
>> linearsolve
>> x0 = [0; -0.05];
>> linearsolve
```

One clearly sees the perturbation growth. Note that (39) was derived on the basis of the assumption of *small* perturbations and that it is not valid if $x(s)$ becomes “too” large. So there is no point in computing much further than to $S = 1$.

It is instructive to compare $X(s)$, computed as in Exercise 18, to $\bar{X}+x(s)$, with $x(s)$ computed as in Exercise 20:

EXERCISE 21.

First solve (32), as in Exercise 18, with `S = 1` and `X0 = Xbar + [0; 0.05]`. Then solve (39), as in Exercise 20, with `S = 1` and `x0 = [0; 0.05]`. Now compare the first solution, `X`, to `Xbar + x`, where `x` is the second solution. You can do the comparison by writing and running the following script:

```
  clf % clear current figure
  plot(X(:,1), X(:,2)) % plots second versus first component of X
  hold on
  plot(Xbar(1) + x(:,1), Xbar(2) + x(:,2), '--')
  title('Phase portraits:   Solid: X   Dashed: Xbar + x')
  xlabel('X_1, Xbar_1 + x_1')
  ylabel('X_2, Xbar_2 + x_2')
  hold off
```

Note how the two curves successively diverge, and how the linear approximation fails to find the stable equilibrium point.

Next week we will conclude the exercise on the tank reactor by “adjusting” it in such a way that the operating point $\bar{X}$ becomes stable. The idea is to try to “move” the eigen-values of A so that their real parts get the right (negative!) sign. We will also briefly consider stability with respect to perturbations in the control variables.