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

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

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

Exercise 1. Solve (1) 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 (1) 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 1. Verify these properties.

Date: May 7, 2001, Niklas Ericsson, Stig Larsson, Mathematics, Chalmers University of Technology.

Exercise 2. 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 (1). 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

$$\rho c_p V \frac{dT}{dt} = \rho c_p q(T_f - T) + (-\delta H) V c k_0 \exp(-E/(RT)) - \kappa A_K (T - T_K). \quad \texttt{[J/s]} \tag{2}$$

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

$$\frac{V}{q_{\mathrm{ref}}} \frac{d}{dt}\Big(\frac{T}{T_f}\Big) = \frac{q}{q_{\mathrm{ref}}}\Big(1 - \frac{T}{T_f}\Big) + \frac{(-\delta H) c_f}{\rho c_p T_f} \frac{c}{c_f} \frac{V}{q_{\mathrm{ref}}} k_0 \exp\Big(-\frac{E}{R T_f} \frac{T_f}{T}\Big) - \frac{\kappa A_K}{\rho c_p q_{\mathrm{ref}}}\Big(\frac{T}{T_f} - \frac{T_K}{T_f}\Big). \tag{3}$$

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

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

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 (3) in the non-dimensional variables we note that, by the chain rule,

$$\frac{dX_2}{ds} = \frac{dX_2}{dt}\frac{dt}{ds} = \tau \frac{dX_2}{dt} = \frac{V}{q_{\mathrm{ref}}} \frac{d}{dt}\Big(\frac{T}{T_f}\Big). \tag{4}$$

We also express the terms on the right-hand side in (3) in the non-dimensional variables:

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

$$U_1(1 - X_2). \tag{5}$$

- 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

$$\alpha X_1 \tau k_0 \exp\left(-\frac{\gamma}{X_2}\right) = \alpha X_1 k_0 \tau \exp(-\gamma) \exp(\gamma - \frac{\gamma}{X_2}) = \alpha X_1 f(X_2), \tag{6}$$

  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

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

  the third term on the right-hand side becomes

$$-\beta(X_2 - U_2). \tag{7}$$

From (4)–(7), (3) becomes

$$\frac{dX_2}{ds} = U_1(1 - X_2) + \alpha X_1 f(X_2) - \beta(X_2 - U_2), \tag{8}$$

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,

$$\begin{aligned} \frac{dX_1}{ds} &= U_1(1 - X_1) - X_1 f(X_2), \ s > 0, \\ \frac{dX_2}{ds} &= U_1(1 - X_2) + \alpha X_1 f(X_2) - \beta(X_2 - U_2), \ s > 0, \\ X_1(0) &= X_{1,0}, \ X_2(0) = X_{2,0}. \end{aligned} \tag{9}$$

Exercise 3. Extend your Matlab programs from last week so that they solve (9). 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 1 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.

Finally we give a some reasons for writing the mathematical model in dimensionless form:

- the dimensionless equations (9) contain fewer constants and variables than the original equations and they are therefore more convenient to work with;
- it gives a possibility of scaling the variables so that they are not very big or very small;
- it is useful for scaling an apparatus from laboratory size to factory size; this should be done so that the dimensionless constants are the same.