

Hausaufgaben Prozessdynamik

zur Übung 4

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STK 03

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12. Dezember 2004

Aufgabe 1

Reaktionskinetik

- Matrix Stöchiometrischer Koeffizienten

$$\underline{\nu} = \begin{pmatrix} -1 \\ -1 \\ 1 \end{pmatrix}$$

- Reaktionskinetik ($c_\alpha = \frac{x_\alpha}{v^*}$)

$$r_1 = k_0 c_A c_B e^{-\frac{E_A}{RT}} = \frac{k_0}{(v^*)^2} x_A x_B e^{-\frac{E_A}{RT}}$$

Stoffbilanz

- Bilanzgleichung

$$\frac{dn}{dt} = G_{in} - G_{out} + V \sum_{\alpha} \sigma_{\alpha}$$

- Umformungen

$$G_{in} = 0 \quad G_{out} = 0 \quad \sum_{\alpha} \sigma_{\alpha} = \sum_{i,\alpha} \nu_{i,\alpha} r_i = -r_1 \quad V = v^* n$$

$$\frac{dn}{dt} = -v^* n r_1$$

Gleichung der Molenbrüche

- Partielle Stoffbilanz

$$\frac{dn_{\alpha}}{dt} = G_{in,\alpha} - G_{out,\alpha} + V \sigma_{\alpha}$$

- Umformungen

$$G_{in,\alpha} = 0 \quad G_{out,\alpha} = 0 \quad n_{\alpha} = x_{\alpha} n \quad V = v^* n \quad \sigma_{\alpha} = \sum_i \nu_{i,\alpha} r_i$$

$$n \frac{dx_{\alpha}}{dt} + x_{\alpha} \frac{dn}{dt} = v^* n \sum_i \nu_{i,\alpha} r_i$$

$$\frac{dx_{\alpha}}{dt} = \frac{v^* n \nu_{1,\alpha} r_1 + v^* n x_{\alpha} r_1}{n} = v^* r_1 (x_{\alpha} + \nu_{1,\alpha})$$

- Vektorform

$$\frac{d}{dt} \begin{pmatrix} x_A \\ x_B \\ x_C \end{pmatrix} = \begin{pmatrix} x_A - 1 \\ x_B - 1 \\ x_C + 1 \end{pmatrix} \cdot (v^* r_1)$$

Temperaturgleichung

- Enthalpiebilanz

$$\frac{dH}{dt} = G_{in}h_{in} - G_{out}h_{out} + Q + P_t + V \frac{dp}{dt}$$

– Betrachtung der linken Seite

$$\frac{dH}{dt} = \frac{d}{dt} \sum_{\alpha} h_{\alpha} x_{\alpha} n = \sum_{\alpha} x_{\alpha} n \frac{dh_{\alpha}}{dt} + \sum_{\alpha} h_{\alpha} \frac{dx_{\alpha} n}{dt} = \sum_{\alpha} x_{\alpha} n \frac{dh_{\alpha}}{dt} + v^* n \sum_i \Delta_R h_i r_i$$

Weiterhin ist:

$$\sum_{\alpha} x_{\alpha} n \frac{dh_{\alpha}}{dt} = \sum_{\alpha} x_{\alpha} n \frac{\partial h_{\alpha}}{\partial T} \frac{dT}{dt} = \left(\sum_{\alpha} x_{\alpha} n c_{p,\alpha} \right) \frac{dT}{dt}$$

– Betrachtung zur rechten Seite

$$G_{in} = 0 \quad G_{out} = 0 \quad Q = 0 \quad P_t = 0 \quad \frac{dp}{dt} = 0$$

- Dynamische Temperaturgleichung (als Ergebnis der Enthalpiebilanz)

$$\left(\sum_{\alpha} x_{\alpha} n c_{p,\alpha} \right) \frac{dT}{dt} + v^* n \sum_i \Delta_R h_i r_i = 0$$

$$\frac{dT}{dt} = \frac{-v^* \Delta_R h r_1}{c_p}$$

Modifizierte Temperaturgleichung (b)

- Dynamische Temperaturgleichung mit $Q = {}^h k A_k (T_k - T)$

$$\left(\sum_{\alpha} x_{\alpha} n c_{p,\alpha} \right) \frac{dT}{dt} + v^* n \sum_i \Delta_R h_i r_i = {}^h k A_k (T_k - T)$$

$$\frac{dT}{dt} = \frac{{}^h k A_k (T_k - T)}{c_p n} - \frac{v^* \Delta_R h r_1}{c_p}$$

Anfangsstoffmenge (b)

$$N_0 = \frac{V}{v^*} = \frac{1000}{100} \frac{l \text{ mol}}{ml} = 10^4 \text{ mol}$$

Auswertung mittels Matlab (a)

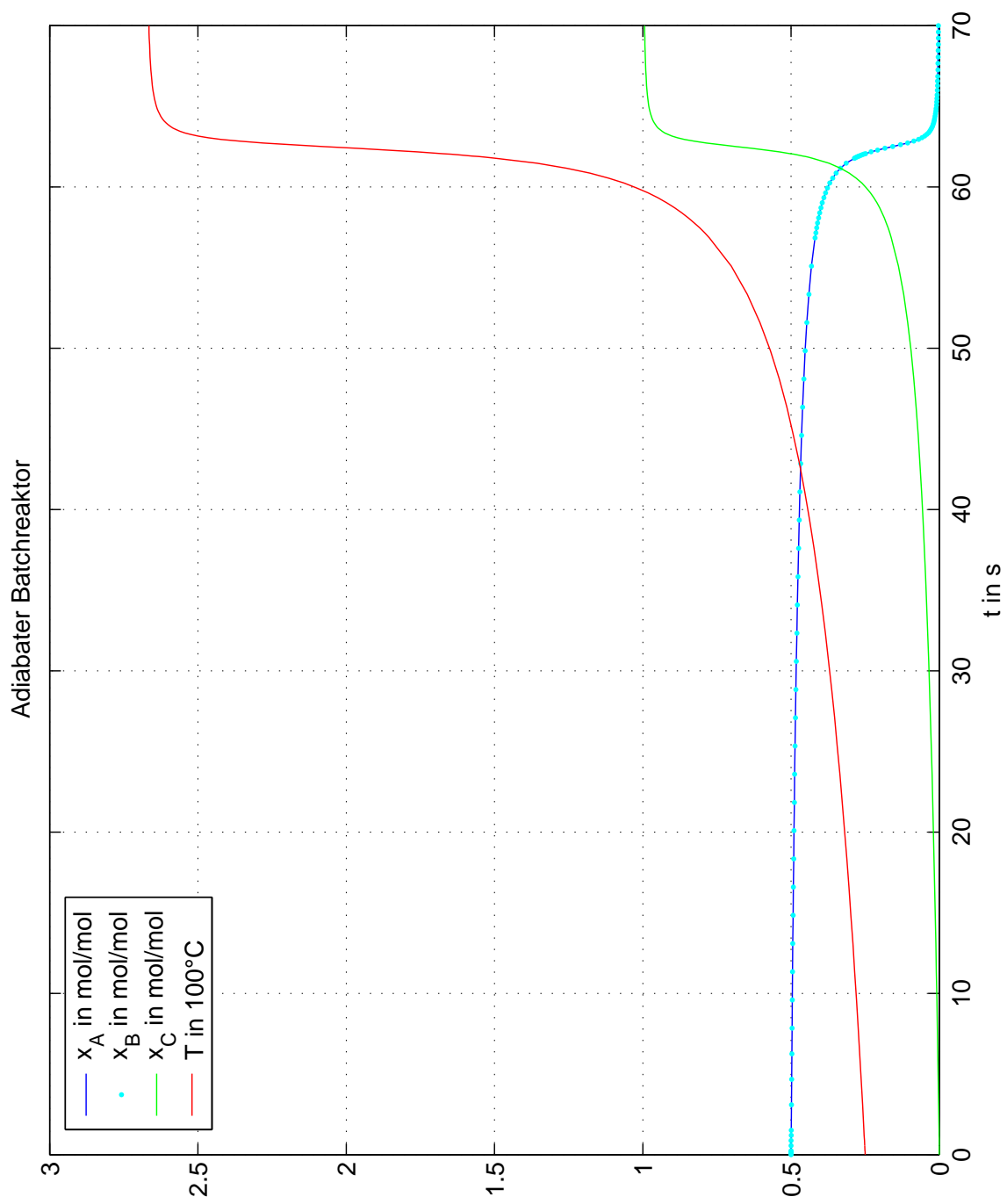
• Quellcode - Funktion

```
function f=A1(t,X);
% X ist der Vektor der Simulationsvariablen [x_A;x_B;x_C;T]
% Einheiten sind hier genormt auf: K, mol, m^3, kJ, s
%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%
%% Variablen
%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%
%Reaktionsparameter
DRh=-28;                                %[DRh]= kJ mol^-1          %Reaktionsenthalpie
nu=[-1;-1;1];                          %-                      %Matrix der Stöchiometrischen Faktoren
k0=750;                                %[k0]= m^3 mol^-1 s^-1    %Stoßfaktor
EA=53.5;                               %[EA]= kJ mol^-1         %Aktivierungsenergie
cp=80/1000;                            %[cp]= kJ mol^-1 K^-1    %Wärmekapazität (gilt für gesamtes Gemisch)
v=1E-4;                                %[v]= m^3 mol^-1         %molares Volumen (gilt für gesamtes Gemisch)
R=8314*1E-6;                           %[R]= kJ mol^-1 K^-1     %molare Gaskonstante
%Aufsplitten der Simulationsvariablen
C=[X(1);X(2);X(3)];                    %Vektor der Molenbrüche
T=X(4);                                %Temperatur
%Gleichungen der Reaktionsgeschwindigkeiten
r1=k0/v^2*C(1)*C(2)*exp(-EA/R/T);      %Reaktionskinetik
%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%
%% Funktion
%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%
c=(C+nu)*[v*r1];                        %Änderung der Molenbrüche
t=-v*DRh*r1/cp;                         %Temperaturänderung
f=[c(1);c(2);c(3);t];
```

• Quellcode - Hauptprogramm

```
function A1_main;
clear all;
close all;
clc;
%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%
%% Variablen
%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%
%Anfangsbedingungen
T0=25+273.15;                           %[T0]= K                %Anfangstemperatur
C0=[.5;.5;0];                           %[C0]= mol l^-1         %Molenbrüche für t=0
X0=[C0(1);C0(2);C0(3);T0];              %[t_end]= s             %Ende des zu berechnenden Zeitintervalls
t_end=7E1;
%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%
%% DGL lösen
%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%
[t,C]=ode45('A1',[0 t_end],X0);
%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%
%% Ausgabe
%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%
figure(1);
plot(t,C(:,1),'b-',t,C(:,2),'c-',t,C(:,3),'g-',t,(C(:,4)-273.15)/100,'r-');
legend('x_A in mol/mol','x_B in mol/mol','x_C in mol/mol','T in 100°C',0);
title('Adiabater Batchreaktor');
xlabel('t in s');
ylabel('');
grid on;

C(end,:)
```



Auswertung mittels Matlab (b)

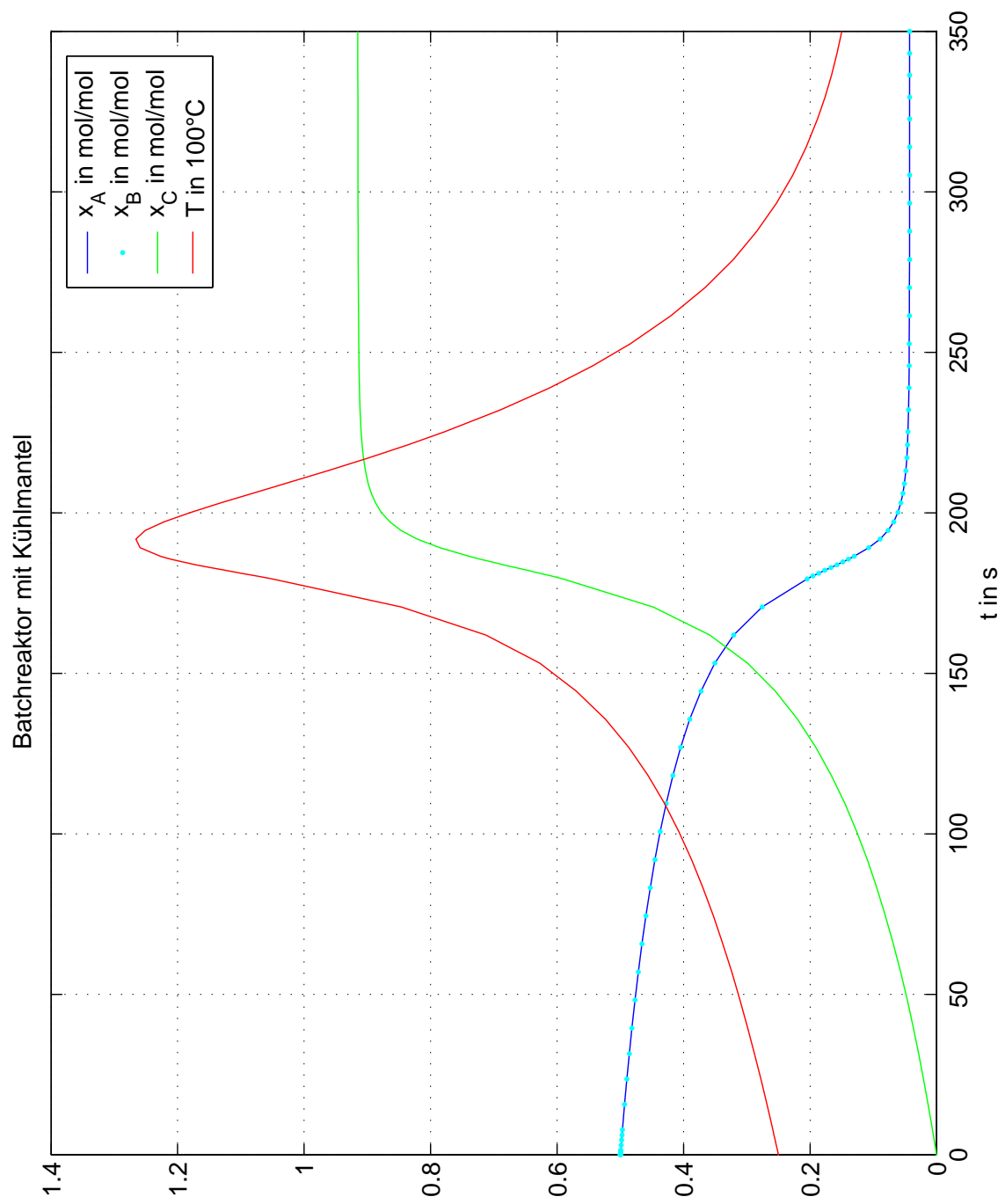
- Quellcode - Funktion

```
function f=A1(t,X);
% X ist der Vektor der Simulationsvariablen [x_A;x_B;x_C;T;N]
% Einheiten sind genormt auf: K, mol, m^3, kJ, s
%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%
%% Variablen
%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%
global Ak;
%Reaktionsparameter
DRh=-28; % [DRh]= kJ mol^-1 %Reaktionsenthalpie
nu=[-1;-1;1]; %- %Matrix der Stöchiometrischen Faktoren
k0=750; % [k0]= m^3 mol^-1 s^-1 %Stoßfaktor
EA=53.5; % [EA]= kJ mol^-1 %Aktivierungsenergie
cp=80/1000; % [cp]= kJ mol^-1 K^-1 %Wärmekapazität (gilt für gesamtes Gemisch)
v=1E-4; % [v]= m^3 mol^-1 %molares Volumen (gilt für gesamtes Gemisch)
R=8314*1E-6; % [R]= kJ mol^-1 K^-1 %molare Gaskonstante
kh=350/1000; % [hk]= kJ m^-2 K^-1 s^-1 %Wärmeaustauschkoeffizient
Tk=10+273.15; % [Tk]= K %Kühlwassertemperatur
%Aufsplitten der Simulationsvariablen
C=[X(1);X(2);X(3)]; %Vektor der Molenbrüche
T=X(4); %Temperatur
N=X(5); %Gesamtstoffmenge
%Gleichungen der Reaktionsgeschwindigkeiten
r1=k0/v^2*C(1)*C(2)*exp(-EA/R/T); %Reaktionskinetik
%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%
%% Funktion
%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%
n=-v*N*r1; %Stoffmengenänderung
c=(C+nu)*[v*r1]; %Änderung der Molenbrüche
t=kh*Ak*(Tk-T)/cp/N-v*DRh*r1/cp; %Temperaturänderung
f=[c(1);c(2);c(3);t;n];
```

- Quellcode - Hauptprogramm

```
function A1_main;
clear all;
close all;
clc;
%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%
%% Variablen
%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%
global Ak;
Ak=25.3; % [Ak]= m^2 %Wärmeaustauschfläche
%Anfangsbedingungen
T0=25+273.15; % [T0]= K %Anfangstemperatur
C0=[.5;.5;0]; % [C0]= mol l^-1 %Molenbrüche für t=0
N0=1E4; % [N0]= mol %Anfangsstoffmenge
X0=[C0(1);C0(2);C0(3);T0;N0];
t_end=3.5E2; % [t_end]=s %Ende des Zeitintervalls
%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%
%% DGL lösen
%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%
[t,C]=ode45('A1b',[0 t_end],X0);
%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%
%% Ausgabe
%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%
figure(1);
plot(t,C(:,1),'b-',t,C(:,2),'c.',t,C(:,3),'g-',t,(C(:,4)-273.15)/100,'r-');
legend('x_A in mol/mol','x_B in mol/mol','x_C in mol/mol','T in 100°C',0);
title('Batchreaktor mit Kühlmantel');
xlabel('t in s');
ylabel('');
grid on;

[C(end,1) C(end,2) C(end,3)]
C(end,4)
```



Diskussion der Ergebnisse

- Die Reaktion läuft im *adiabaten Batchreaktor* mit dem Ergebnis $\underline{x} = \begin{pmatrix} 0,0029 \\ 0,0029 \\ 0,9941 \end{pmatrix}$ bei $t_{end} = 70 \text{ s}$ vollständig ab, die Temperatur im Reaktor beträgt dann $T = 540 \text{ K}$ bzw. $T = 267 \text{ }^\circ\text{C}$.
- Die Ermittlung der Wärmeaustauschfläche beim *Batchreaktor mit Kühlung* wurde näherungsweise durch Ausprobieren und Schätzen bestimmt und auf eine Kommastelle in m^2 angenähert, sie beträgt $A_k = 25,3 \text{ m}^2$.
- Aufgrund der Kühlung nimmt die Temperatur im Reaktor wieder ab und sinkt sogar unter die Anfangstemperatur (Bei $t_{end} = 350 \text{ s}$ ist $T = 288 \text{ K}$ bzw. $T = 15 \text{ }^\circ\text{C}$). Die Folge ist ein starkes Absinken der Reaktionsgeschwindigkeit, auch auf Grund der sinkenden Konzentration der Ausgangsstoffe, damit stockt die Reaktion und läuft nicht, wie im adiabaten Reaktor, annähernd vollständig ab. Die Molenbrüche bei $t_{end} = 350 \text{ s}$ betragen $\underline{x} = \begin{pmatrix} 0.0424 \\ 0.0424 \\ 0.9152 \end{pmatrix}$.