CBE 450 Chemical Reactor Fundamentals
Fall, 2009
Homework Assignment #9 Solutions

Consider the two sequential reactions

A + B → C
A + C → D

with elementary mechanism such that the rate of the first reaction is

$$r_1 = k_1 C_A C_B$$

and the reverse reaction is

$$r_2 = k_2 C_A C_C$$

where the rate constants are given by

$$k_1 = k_{o,1} \exp\left(-\frac{E_{a,1}}{RT}\right)$$

and

$$k_2 = k_{o,2} \exp\left(-\frac{E_{a,2}}{RT}\right)$$

The activation energy for the first reaction is 5500 J/mol. The rate constant prefactor for the first reaction is 0.1 liter/mole/s. The activation energy for the second reaction is 3900 J/mol. The rate constant prefactor for the first reaction is 0.1 liter/mole/s. The heat capacities of A, B, C, D and S are respectively 4.0, 3.0, 6.0, 9.0, and 4.0 J/mol/K. The heats of formation of A, B, C and D at a reference temperature of 298.15 K are respectively -1.0, -6.0, -12.0 and -18.0 kJ/mol.

1. Jacketed Batch Reactor

This reaction takes place in a jacketed batch reactor. The initial concentration is 300 K. The initial concentrations of A, B, C, D and S are 10.0, 4.0, 0.0, 0.0, and 40.0 mol/liter respectively. The volume of the reactor is 1000 liters. The surface area of the reactor is 1.5 m^2.

The jacket has a volume of 0.5 m^3. The overall heat transfer coefficient from the reactor to the jacket is 1500.0 $J/s/m^2/K$. The heat capacity of the coolant is 4.184 J/mol/K and the concentration is 55.6 mol/liter. The flowrate of coolant is 10 liters/s. The inlet temperature of the coolant is 273.15. The initial temperature of the coolant is the same as the inlet temperature.

(a) Provide a plot of the transient behavior of the concentrations of A, B, C, D and S and the temperature for a period of 1000 sec. Explain the features.
(b) What are the reactor and jacket temperatures, conversion of A and concentrations of C and D at the end of this time period?

Solution:

(a) Provide a plot of the transient behavior of the concentrations of A, B, C, D and S and the temperature for a period of 1000 sec. Explain the features.
(b) What are the reactor and jacket temperatures, conversion of A and concentrations of C and D at the end of this time period?

I used the following input file:

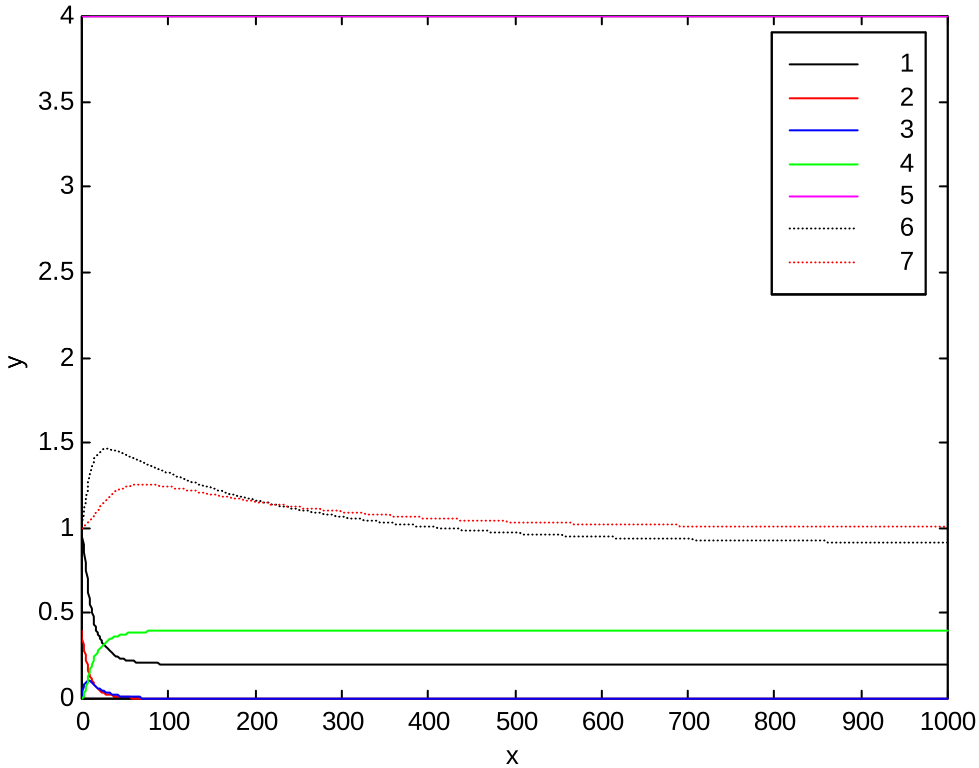
```
function dydt = sysodeinput(x,y,nvec);
%
%  two sequential reactions in solvent, S
%  A + B --> C
%  A + C --> D
%
%  sample usage:
%  [y,x]=sysode(2,1000,0,10,[10,4,0,0,40,300,273.15]);
%
CA = y(1); % mol/liter
CB = y(2);
CC = y(3);
CD = y(4);
CS = y(5);
T =  y(6); % K
Tj = y(7);
%
%  stoichiometry
%
nuA1 = -1;
nuB1 = -1;
nuC1 = 1;
nuD1 = 0;
nuS1 = 0;
%
nuA2 = -1;
nuB2 = 0;
nuC2 = -1;
nuD2 = 1;
nuS2 = 0;
%
%  rate law
%
ko1 = 0.1; % liter/mole/sec
Ea1 = 5500; % J/mol
R = 8.314; %J/mol/K
k1 = ko1*exp(-Ea1/(R*T)); % liters/mole/sec
r1 = k1*CA*CB; % mole/liter/sec
%
%  pure component heat capacities
%
CpA = 4.0; %J/mol/K
CpB = 3.0; %J/mol/K
```

```
CpC = 6.0; %J/mol/K
CpD = 9.0; %J/mol/K
CpS = 4.0; %J/mol/K
%
%  enthalpies of formation
%
Tref = 298.15; % K
pref = 101325; % Pa
HfrefA = -1000; %J/mol
HfrefB = -6000; % J/mol
HfrefC = -12000; % J/mol
HfrefD = -18000; % J/mol
HA = CpA*(T-Tref) + HfrefA;
HB = CpB*(T-Tref) + HfrefB;
HC = CpC*(T-Tref) + HfrefC;
HD = CpD*(T-Tref) + HfrefD;
DHR1 = nuA1*HA + nuB1*HB + nuC1*HC  + nuD1*HD;
DHR2 = nuA2*HA + nuB2*HB + nuC2*HC  + nuD2*HD;
%
%  rate law for reaction 2
%
ko2 = 0.1; % liter/mole/sec
Ea2 = 3900; % J/mol
R = 8.314; %J/mol/K
k2 = ko2*exp(-Ea2/(R*T)); % 1/sec
r2 = k2*CA*CC; % mole/liter/sec
%
% mole fractions
%
CT = CA + CB + CC + CD  + CS;
xA = CA/CT;
xB = CB/CT;
xC = CC/CT;
xD = CD/CT;
xS = CS/CT;
%
% mixture heat capacity
%
Cpmix = xA*CpA + xB*CpB + xC*CpC + xD*CpD  + xS*CpS;
%
%  heat loss information
%
As = 1.5; % m^2
U = 1500.0; % J/s/m^2/K
Qdot = As*U*(Tj-T);
V = 1000.0; % liters
Vj = 500; % liters
Cpj = 4.184; % J/mol/K
Cj = 55.6; % mol/liter
Fj = 10.0; % liters/sec
Tjin = 273.15; % K
%
%  mole and energy balances
%
dydt(1) = nuA1*r1 + nuA2*r2;
dydt(2) = nuB1*r1 + nuB2*r2;
dydt(3) = nuC1*r1 + nuC2*r2;
dydt(4) = nuD1*r1 + nuD2*r2;
dydt(5) = nuS1*r1 + nuS2*r2;
dydt(6) = (-V*DHR1*r1 -V*DHR2*r2 + Qdot)/(CT*Cpmix*V);
dydt(7) = Fj/Vj*(Tjin-Tj) - Qdot/(Cj*Cpj*Vj);
```

I used the following command

[y,x]=sysode(2,1000,0,1000,[10,4,0,0,40,300,273.15]);

I generated the plot of the transient behavior (the solution for part A).



where the legend corresponds to A, B, C, D S, T and Tj. The concentrations are normalized by the inlet concentration of A. The temperatures are normalized by their inlet temperatures.

In this plot, A decreases as a reactant. B is consumed as a reactant. C initially increases as a product of reaction 1 and then decreases as it is consumed in reaction 2. D increases as product. The solvent doesn't participate in the reaction and is constant. T increases since both reactions are exothermic. The jacket temperature also increases as it removes heat from the system. It appears in this normalized plot that the temperature of the jacket becomes greater than the temperature of the reactor. This is not true and is only a consequence of normalizing the two temperatures by their (different) inlet values.

The final line of the unnormalized output file is

1.0000000e+003 2.0000000e+000 1.9036804e-011 1.8814666e-011 4.0000000e+000 4.0000000e+001 2.7473424e+002 2.7403831e+002

The final concentration of A is 2.0 mol/liter.
The final concentration of B is 0.0 mol/liter.
The final concentration of C is 0.0 mol/liter.
The final concentration of D is 4.0 mol/liter.
The final temperature of the reactor is 274.7 K.
The final temperature of the jacket is 274.0 K.
The final conversion is

$$X_A = 1 - \frac{C_A}{C_{A,in}} = 1 - \frac{2}{10} = 0.8$$

2. Jacketed CSTR

This reaction takes place in a jacketed CSTR. The inlet concentration is 300 K. The inlet concentrations of A, B, C, D and S are 10.0, 4.0, 0.0, 0.0, and 40.0 mol/liter respectively. The initial conditions within the CSTR are the same as the inlet conditions. The inlet flowrate is 1 liter/s. The volume of the reactor is 1000 liters. The surface area of the reactor is 1.5 m^2.

The jacket has a volume of 0.5 m^3. The overall heat transfer coefficient from the reactor to the jacket is 1500.0 J/s/m^2/K. The heat capacity of the coolant is 4.184 J/mol/K and the concentration is 55.6 mol/liter. The flowrate of coolant is 10 liters/s. The inlet temperature of the coolant is 273.15. The initial temperature of the coolant is the same as the inlet temperature.

(a) Provide a plot of the transient behavior of the concentrations of A, B, C, D and S and the temperatures for a period of X sec. Explain the features.
(b) What are the reactor and jacket temperatures, conversion of A and concentrations of C and D at steady state?

Solution:

I used the following input file:

```
function dydt = sysodeinput(x,y,nvec);
%
%  two sequential reactions in solvent, S
%  A + B --> C
%  A + C --> D
%
%  example usage:
%  [y,x]=sysode(2,1000,0,1000,[10,4,0,0,40,300,273.15]);
%
CA = y(1); % mol/liter
CB = y(2); % mol/liter
CC = y(3); % mol/liter
CD = y(4); % mol/liter
CS = y(5); % mol/liter
T = y(6); % K
Tj = y(7); % K
%
%  stoichiometry
%
```

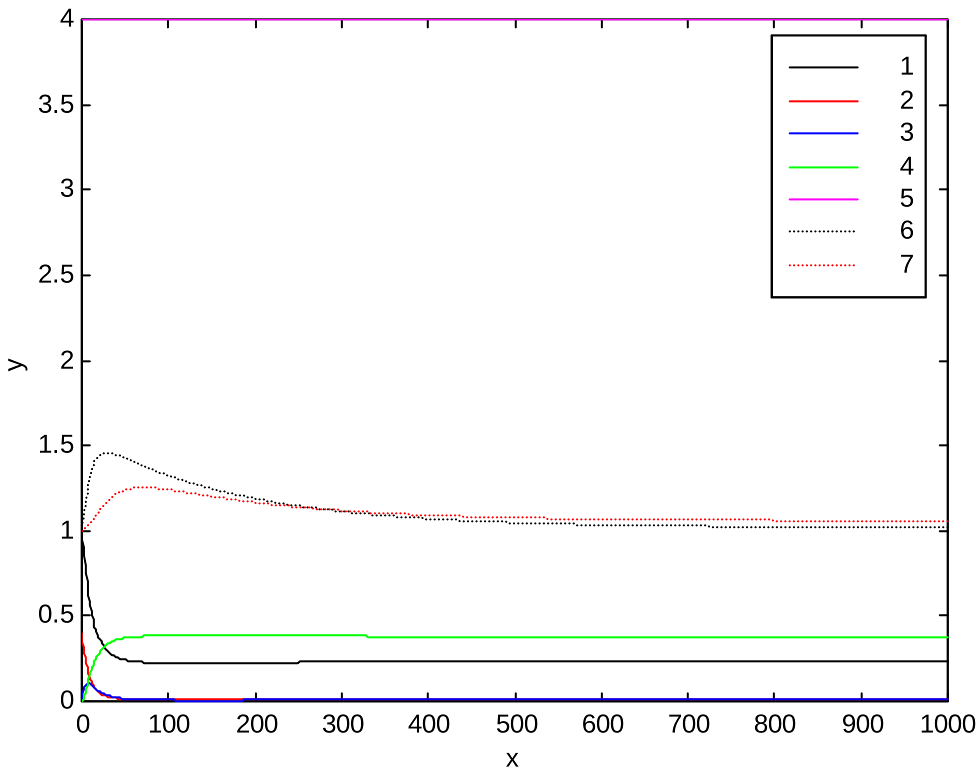
```
nuA1 = -1;
nuB1 = -1;
nuC1 = 1;
nuD1 = 0;
nuS1 = 0;
%
nuA2 = -1;
nuB2 = 0;
nuC2 = -1;
nuD2 = 1;
nuS2 = 0;
%
% rate law for reaction 1
%
ko1 = 0.1; % liter/mole/sec
Ea1 = 5500; % J/mol
R = 8.314; %J/mol/K
k1 = ko1*exp(-Ea1/(R*T)); % liters/mole/sec
r1 = k1*CA*CB; % mole/liter/sec
%
%  pure component heat capacities
%
CpA = 4.0; %J/mol/K
CpB = 3.0; %J/mol/K
CpC = 6.0; %J/mol/K
CpD = 9.0; %J/mol/K
CpS = 4.0; %J/mol/K
%
%  enthalpies of formation
%
Tref = 298.15; % K
pref = 101325; % Pa
HfrefA = -1000; %J/mol
HfrefB = -6000; % J/mol
HfrefC = -12000; % J/mol
HfrefD = -18000; % J/mol
HA = CpA*(T-Tref) + HfrefA;
HB = CpB*(T-Tref) + HfrefB;
HC = CpC*(T-Tref) + HfrefC;
HD = CpD*(T-Tref) + HfrefD;
DHR1 = nuA1*HA + nuB1*HB + nuC1*HC  + nuD1*HD;
DHR2 = nuA2*HA + nuB2*HB + nuC2*HC  + nuD2*HD;
%
% rate law for reaction 2
%
ko2 = 0.1; % liter/mole/sec
Ea2 = 3900; % J/mol
R = 8.314; %J/mol/K
k2 = ko2*exp(-Ea2/(R*T)); % 1/sec
r2 = k2*CA*CC; % mole/liter/sec
%
% constant volume
%
V = 1000.0; % liter
F = 1; % liter/sec
Fin = F;
Fout = F;
%
%  inlet concentrations
%
CAin = 10.0; % mol/liter
CBin = 4.0; % mol/liter
```

```
CCin = 0.0; % mol/liter
CDin = 0.0; % mol/liter
CSin = 40.0; % mol/liter
Tin = 300.0; % K
%
% mole fractions
%
CT = CA + CB + CC + CD + CS;
xA = CA/CT;
xB = CB/CT;
xC = CC/CT;
xD = CD/CT;
xS = CS/CT;
CTin = CAin + CBin + CCin + CDin + CSin;
xAin = CAin/CTin;
xBin = CBin/CTin;
xCin = CCin/CTin;
xDin = CDin/CTin;
xSin = CSin/CTin;
%
% mixture heat capacity
%
Cpmix = xA*CpA + xB*CpB + xC*CpC + xD*CpD + xS*CpS;
Cpmixin = xAin*CpA + xBin*CpB + xCin*CpC + xDin*CpD + xSin*CpS;
%
%  heat loss information
%
As = 1.5; % m^2
U = 1500.0; % J/s/m^2/K
Qdot = As*U*(Tj-T);
Vj = 500; % liters
Cpj = 4.184; % J/mol/K
Cj = 55.6; % mol/liter
Fj = 10.0; % liters/sec
Tjin = 273.15; % K
%
%  molar balances
%
dydt(1) = Fin/V*CAin - Fout/V*CA + nuA1*r1 + nuA2*r2;
dydt(2) = Fin/V*CBin - Fout/V*CB + nuB1*r1 + nuB2*r2;
dydt(3) = Fin/V*CCin - Fout/V*CC + nuC1*r1 + nuC2*r2;
dydt(4) = Fin/V*CDin - Fout/V*CD + nuD1*r1 + nuD2*r2;
dydt(5) = Fin/V*CSin - Fout/V*CS + nuS1*r1 + nuS2*r2;
dydt(6) = ( Fin/V*CTin*Cpmixin*(Tin - T) - DHR1*r1 - DHR2*r2 + Qdot/V )/(CT*Cpmix);
dydt(7) = Fj/Vj*(Tjin-Tj) - Qdot/(Cj*Cpj*Vj);
```

I used the following command

```
[y,x]=sysode(2,1000,0,1000,[10,4,0,0,40,300,273.15]);
```

I generated the plot of the transient behavior (the solution for part A).



where the legend corresponds to A, B, C, D S, T and Tj. The concentrations are normalized by the inlet concentration of A. The temperatures are normalized by their inlet temperatures.

In this plot, A decreases as a reactant. B is consumed as a reactant. C initially increases as a product of reaction 1 and then decreases as it is consumed in reaction 2. D increases as product. The solvent doesn't participate in the reaction and is constant. T increases since both reactions are exothermic. The jacket temperature also increases as it removes heat from the system. It appears in this normalized plot that the temperature of the jacket becomes greater than the temperature of the reactor. This is not true and is only a consequence of normalizing the two temperatures by their (different) inlet values.

The final line of the unnormalized output file is

1.0000000e+003 2.3582167e+000 1.4199325e-001 7.4230191e-002 3.7837766e+000 4.0000000e+001 3.0602761e+002 2.8935481e+002

The final concentration of A is 2.36 mol/liter.
The final concentration of B is 0.14 mol/liter.
The final concentration of C is 0.07 mol/liter.
The final concentration of D is 3.78 mol/liter.
The final temperature of the reactor is 306.0 K.
The final temperature of the jacket is 289.3 K.
The steady state conversion is

$$X_A = 1 - \frac{C_A}{C_{A,in}} = 1 - \frac{2.36}{10} = 0.764$$

3. Jacketed PFR

This reaction takes place in a jacketed CSTR. The inlet concentration is 300 K. The inlet concentrations of A, B, C, D and S are 10.0, 4.0, 0.0, 0.0, and 30.0 mol/liter respectively. The initial conditions within the CSTR are the same as the inlet conditions. The inlet flowrate is 1 liter/s. The volume of the reactor is 1000 liters. The reactor is circular with diameter 0.1 m.

The jacket is a cylindrical shell of diameter 0.2 m around the reactor. It is of the same length as the reactor. The overall heat transfer coefficient from the reactor to the jacket is 1500.0 $J/s/m^2/K$. The heat capacity of the coolant is 4.184 J/mol/K and the concentration is 55.6 mol/liter. The flowrate of coolant is 10 liters/s and is co-current. The inlet temperature of the coolant is 273.15. The initial temperature of the coolant is the same as the inlet temperature.

(a) Provide a plot of the steady state profiles of the concentrations of A, B, C, D and S and the temperatures. Explain the features.
(b) What are the reactor and jacket temperatures, conversion of A and concentrations of C and D at the exit of the reactor?

Solution:

I used the following input file:

```
function dydt = sysodeinput(x,y,nvec);
%
%  two sequential reactions in solvent, S
%  A + B --> C
%  A + C --> D
%
%  example usage:
%  [y,x] = sysode(2,1000,0,127.324,[10000,4000,0,0,40000,300,273.15]);
%
CA = y(1); % mol/m^3
CB = y(2); % mol/m^3
CC = y(3); % mol/m^3
CD = y(4); % mol/m^3
CS = y(5); % mol/m^3
T = y(6); % K
Tj = y(7); % K
%
% stoichiometry
%
nuA1 = -1;
nuB1 = -1;
nuC1 = 1;
nuD1 = 0;
nuS1 = 0;
%
nuA2 = -1;
nuB2 = 0;
```

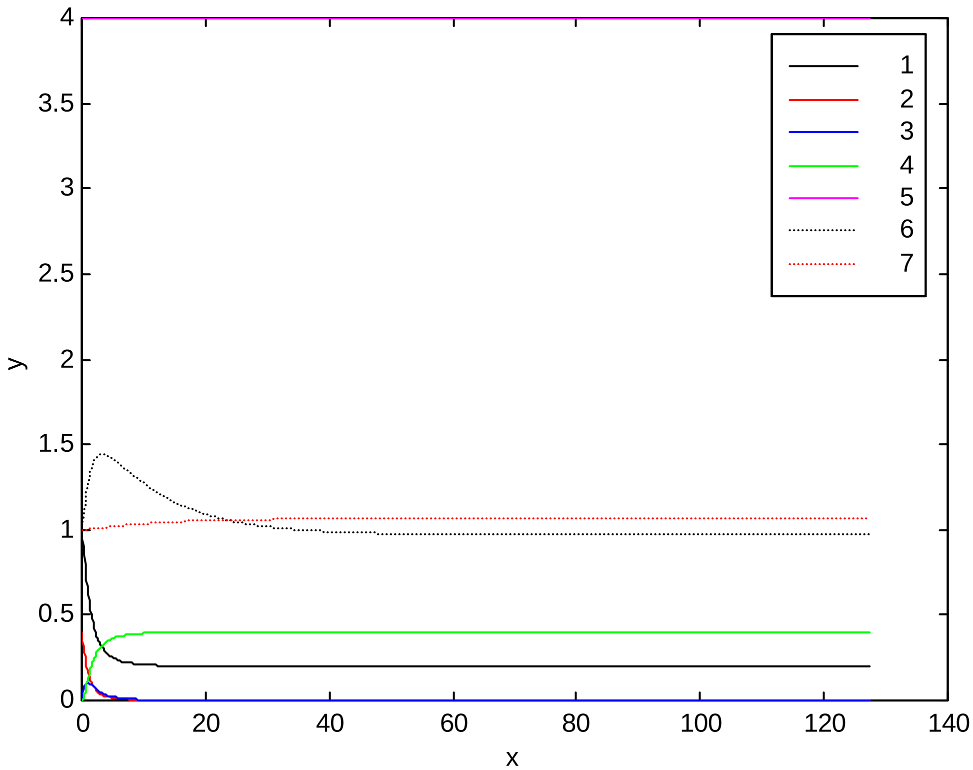
```
nuC2 = -1;
nuD2 = 1;
nuS2 = 0;
%
% rate law for reaction 1
%
R = 8.314; % J/mol/K
ko1 = 0.1; % liter/mol/sec
ko1 = ko1/1000; % m^3/mol/sec
Ea1 = 5500; % J/mol
k1 = ko1*exp(-Ea1/(R*T));
r1 = k1*CA*CB;
%
%  pure component heat capacities
%
CpA = 4.0; %J/mol/K
CpB = 3.0; %J/mol/K
CpC = 6.0; %J/mol/K
CpD = 9.0; %J/mol/K
CpS = 4.0; %J/mol/K
%
%  enthalpies of formation
%
Tref = 298.15; % K
pref = 101325; % Pa
HfrefA = -1000; %J/mol
HfrefB = -6000; % J/mol
HfrefC = -12000; % J/mol
HfrefD = -18000; % J/mol
HA = CpA*(T-Tref) + HfrefA;
HB = CpB*(T-Tref) + HfrefB;
HC = CpC*(T-Tref) + HfrefC;
HD = CpD*(T-Tref) + HfrefD;
DHR1 = nuA1*HA + nuB1*HB + nuC1*HC  + nuD1*HD;
DHR2 = nuA2*HA + nuB2*HB + nuC2*HC  + nuD2*HD;
%
% rate law for reaction 2
%
ko2 = 0.1; % liter/mol/sec
ko2 = ko2/1000; % m^3/mol/sec
Ea2 = 3900; % J/mol
k2 = ko2*exp(-Ea2/(R*T));
r2 = k2*CA*CC;
%
%  inlet concentrations and temperature
%
CAin = 10000.0; % mol/m^3
CBin = 4000.0; % mol/m^3
CCin = 0.0; % mol/m^3
CDin = 0000.0; % mol/m^3
CSin = 40000.0; % mol/m^3
Tin = 300.0; % K
%
% mole fractions
%
CT = CA + CB + CC + CD + CS;
xA = CA/CT;
xB = CB/CT;
xC = CC/CT;
xD = CD/CT;
xS = CS/CT;
CTin = CAin + CBin + CCin + CDin + CSin;
```

```
xAin = CAin/CTin;
xBin = CBin/CTin;
xCin = CCin/CTin;
xDin = CDin/CTin;
xSin = CSin/CTin;
%
% mixture heat capacity
%
Cpmix = xA*CpA + xB*CpB + xC*CpC + xD*CpD + xS*CpS;
Cpmixin = xAin*CpA + xBin*CpB + xCin*CpC + xDin*CpD + xSin*CpS;
%
% volumetric flowrate
%
F = 1; % liter/sec
F = F/1000; % cubic meters/sec
%
%  circular pipe
%
V = 1.0; % m^3
Dp = 0.10; % m
Across = 0.25*pi*Dp*Dp; % m^2
l = V/Across; % m
V = Across*l; % m^3
%
% axial velocity
%
vz = F/Across; % m/s
%
% residence time
%
tr = l/vz; % sec
%
%  heat loss information
%
As = 1.5; % m^2
U = 1500.0; % J/s/m^2/K
Qdot = As*U*(Tj-T);
Cpj = 4.184; % J/mol/K
Cj = 55.6; % mol/liter
Cj = Cj*1000; % mol/cubic meter
Fj = 10.0; % liters/sec
Fj = Fj/1000; % cubic meters/sec
Tjin = 273.15; % K
Dpj = 0.20; % m
Acrossj = 0.25*pi*Dpj*Dpj; % m^2
Vj = Acrossj*l; % m^3
vzj = Fj/Acrossj; % m/s
%
%  molar balances
%
% dCAdz = nuA*r/v
dydt(1) = (nuA1*r1 + nuA2*r2)/vz;
dydt(2) = (nuB1*r1 + nuB2*r2)/vz;
dydt(3) = (nuC1*r1 + nuC2*r2)/vz;
dydt(4) = (nuD1*r1 + nuD2*r2)/vz;
dydt(5) = (nuS1*r1 + nuS2*r2)/vz;
dydt(6) = (-DHR1*r1 - DHR2*r2 + Qdot/V)/(vz*CT*Cpmix);
dydt(7) = -Qdot/(vzj*Vj*Cj*Cpj);
```

I used the following command

[y,x] = sysode(2,1000,0,127.324,[10000,4000,0,0,40000,300,273.15]);

I generated the plot of the transient behavior (the solution for part A).



where the legend corresponds to A, B, C, D S, T and Tj. The concentrations are normalized by the inlet concentration of A. The temperatures are normalized by their inlet temperatures.

In this plot, A decreases as a reactant. B is consumed as a reactant.   C initially increases as a product of reaction 1 and then decreases as it is consumed in reaction 2. D increases as product. The solvent doesn't participate in the reaction and is constant. T increases since both reactions are exothermic. The jacket temperature also increases as it removes heat from the system. It appears in this normalized plot that the temperature of the jacket becomes greater than the temperature of the reactor. This is not true and is only a consequence of normalizing the two temperatures by their (different) inlet values.

The final line of the unnormalized output file is

1.2732400e+002 2.0000000e+003 4.0767164e-008 4.3518457e-008 4.0000000e+003 4.0000000e+004 2.9113046e+002 2.9112881e+002

The final concentration of A is 2.00 mol/liter.
The final concentration of B is 0.00 mol/liter.
The final concentration of C is 0.00 mol/liter.
The final concentration of D is 4.0 mol/liter.

The final temperature of the reactor is 291.1130 K.
The final temperature of the jacket is 291.1128 K.
The final conversion is

$$X_A = 1 - \frac{C_A}{C_{A,in}} = 1 - \frac{2.}{10} = 0.8$$