CBE 450 Chemical Reactor Fundamentals
Fall, 2009
Homework Assignment #8 Solutions

1. Nonisothermal CSTR – 1 irreversible reaction

Consider the irreversible reaction

$$A \rightarrow 2B$$

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

$$r = kC_A$$

where the rate constant is given by

$$k = k_o \exp\left(-\frac{E_a}{RT}\right)$$

The activation energy for the forward reaction is 4000 J/mol. The rate constant prefactor for the forward reaction is 0.1 l/s. The heat capacities of A, B and the solvent are respectively 4.0, 7.0, and 3.0 J/mol/K. The heats of formation of A and B at a reference temperature of 298.15 K are respectively -1000.0 and -10000.0 J/mol. The inlet flowrate is 10 liters/s. The inlet temperature is 500 K. The inlet concentrations of A, B and S are 10.0, 0.0, and 30.0 mol/liter respectively. The volume of the reactor is 1000 liters. The reactor is well insulated. The initial temperature and concentrations in the reactor are the same as the inlet temperature and concentrations.

(a) Provide a plot of the transient behavior of the concentrations of A, B and S and the temperature. Explain the features.
(b) What are the steady-state temperature and conversion of A?

Solution:

(a) Provide a plot of the transient behavior of the concentrations of A, B and S and the temperature. Explain the features.
(b) What are the steady-state temperature and conversion of A?

I used the following input file:

```
function dydt = sysodeinput(x,y,nvec);
%
%  one reaction in solvent S
%  A --> 2B
%
%  example usage:
%  [y,x] = sysode(2,1000,0,100,[10,0,30,500]);
%
CA = y(1); % mol/liter
```

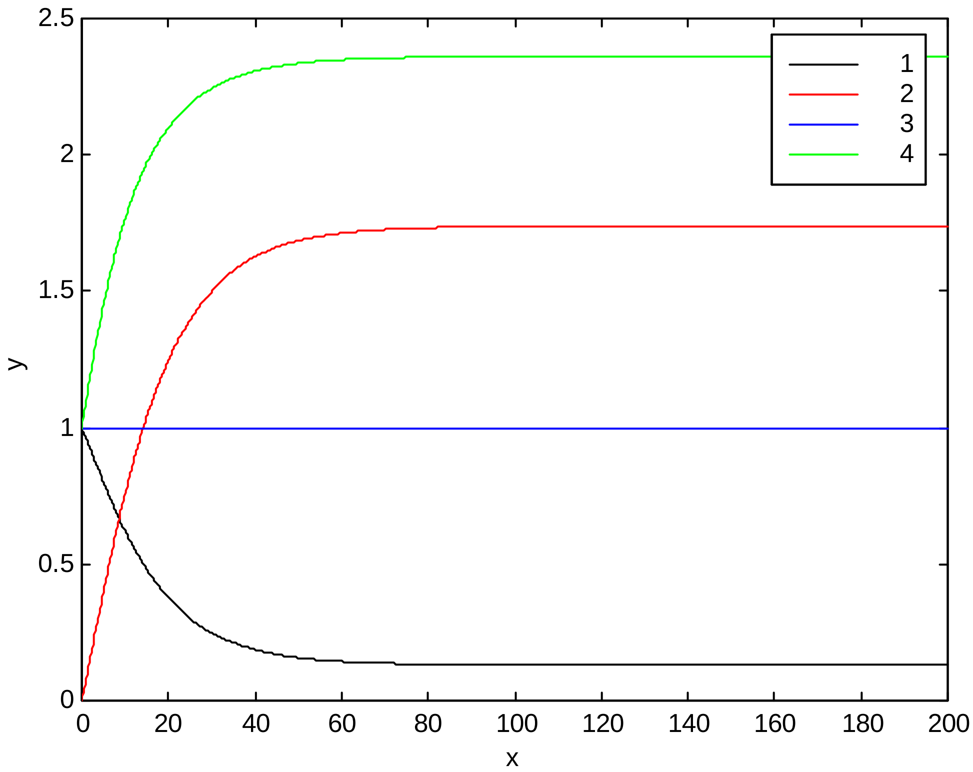
```
CB = y(2); % mol/liter
CS = y(3); % mol/liter
T = y(4); % K
%
% stoichiometry
%
nuA = -1.0;
nuB = 2.0;
nuS = 0.0;
%
% rate law
%
R = 8.314; % J/mol/K
ko = 1.0e-1; % 1/sec
Ea = 4000; % J/mol
k = ko*exp(-Ea/(R*T));
r = k*CA;
%
%  pure component heat capacities
%
CpA = 4.0; %J/mol/K
CpB = 7.0; %J/mol/K
CpS = 3.0; %J/mol/K
%
%  enthalpies of formation
%
Tref = 298.15; % K
pref = 101325; % Pa
HfrefA = -1000; %J/mol
HfrefB = -10000; % J/mol
HA = CpA*(T-Tref) + HfrefA;
HB = CpB*(T-Tref) + HfrefB;
DHR = nuA*HA + nuB*HB;
%
% constant volume
%
V = 1000.0; % liter
F = 10; % liter/sec
Fin = F;
Fout = F;
%
%  inlet concentrations
%
CAin = 10.0; % mol/liter
CBin = 0.0; % mol/liter
CSin = 30.0; % mol/liter
Tin = 500.0; % K
%
% mole fractions
%
CT = CA + CB + CS;
xA = CA/CT;
xB = CB/CT;
xS = CS/CT;
CTin = CAin + CBin + CSin;
xAin = CAin/CTin;
xBin = CBin/CTin;
xSin = CSin/CTin;
%
% mixture heat capacity
%
Cpmix = xA*CpA + xB*CpB + xS*CpS;
```

```
Cpmixin = xAin*CpA + xBin*CpB + xSin*CpS;
%
%  molar balances
%
dydt(1) = Fin/V*CAin - Fout/V*CA + nuA*r;
dydt(2) = Fin/V*CBin - Fout/V*CB + nuB*r;
dydt(3) = Fin/V*CSin - Fout/V*CS + nuS*r;
dydt(4) = ( Fin/V*CTin*Cpmixin*(Tin - T) - DHR*r )/(CT*Cpmix);
```

I used the following command

[y,x] = sysode(2,1000,0,200,[10,0,30,500]);

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



where the legend corresponds to A, B, S and T. The curves are normalized by the inlet values of A, A, S, and T respectively.

In this plot, A decreases as a reactant, B increases, S is constant, and T increases since the reaction is exothermic.

The final line of the unnormalized output file is

2.0000000e+002 1.3067171e+000 1.7386566e+001 3.0000000e+001 1.1805101e+003
The steady state concentration of A is 1.307 mol/liter.

The steady state temperature is 1181 K.
The steady state conversion is

$$X_A = 1 - \frac{C_A}{C_{A,in}} = 1 - \frac{1.307}{10} = 0.8693$$

2. Nonisothermal CSTR – 2 sequential reactions

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 3.0 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. The inlet flowrate is 5 liters/s. The inlet temperature is 600 K. The inlet concentrations of A, B, C, D and S are 10.0, 10.0, 0.0, 0.0, and 30.0 mol/liter respectively. The volume of the reactor is 1000 liters. The reactor is well insulated. The initial temperature and concentrations in the reactor are the same as the inlet temperature and concentrations.

(a) Provide a plot of the transient behavior of the concentrations of A, B, C, D and S and the temperature. Explain the features.
(b) What are the steady-state temperature and conversion of A?

(c) What are the steady state concentrations of C and D?

Solution:

(a) Provide a plot of the transient behavior of the concentrations of A, B, C, D and S and the temperature. Explain the features.
(b) What are the steady-state temperature and conversion of A?
(c) What are the steady state concentrations of C and D?

I used the following input file:

```
function dydt = sysodeinput(x,y,nvec);
%
%  two sequential irreversible reactions in solvent S
%  A + B --> C
%  A + C --> D
%
%  example usage:
%  [y,x] = sysode(2,1000,0,1000,[10,10,0,0,30,600]);
%
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
%
% stoichiometry
%
nuA1 = -1.0;
nuB1 = -1.0;
nuC1 = 1.0;
nuD1 = 0.0;
nuS1 = 0.0;
%
nuA2 = -1.0;
nuB2 = 0.0;
nuC2 = -1.0;
nuD2 = 1.0;
nuS2 = 0.0;
%
% rate law for reaction 1
%
R = 8.314; % J/mol/K
ko1 = 1.0e-1; % liter/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 = 3.0; %J/mol/K
%
%  enthalpies of formation
```

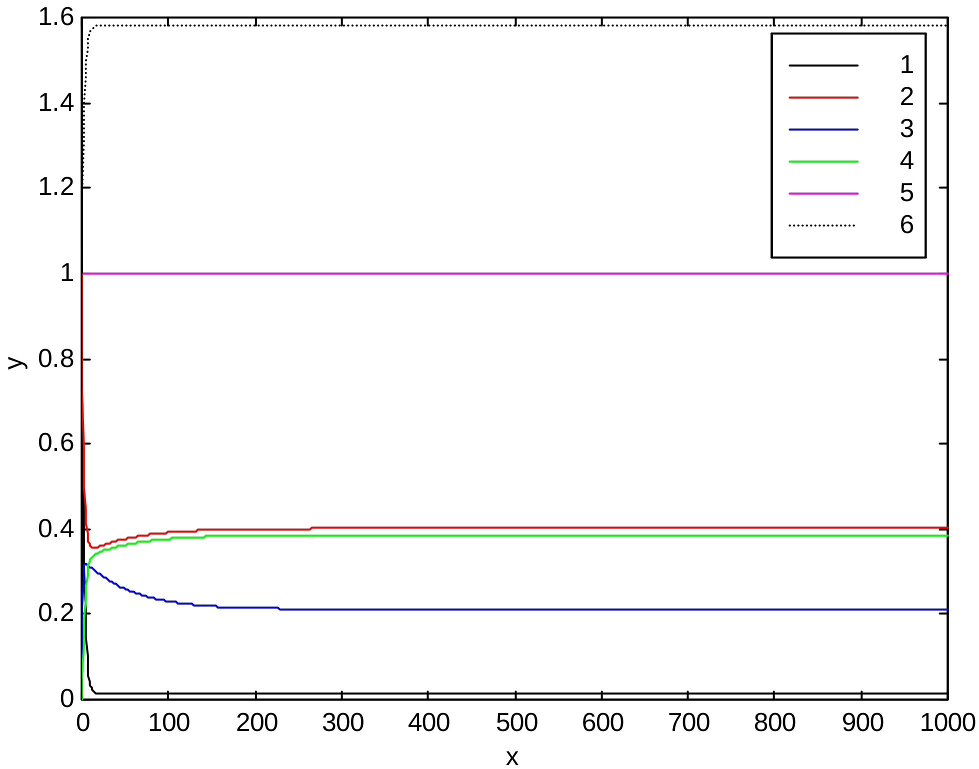
```
%
Tref = 298.15; % K
pref = 101325; % Pa
HfrefA = -1000; %J/mol
HfrefB = -6000; % J/mol
HfrefC = -12000; % J/mol
HfrefD = -18000; % J/mol
HA = CpA*(T-Tref) + HfrefA;
HB = CpB*(T-Tref) + HfrefB;
HC = CpC*(T-Tref) + HfrefC;
HD = CpD*(T-Tref) + HfrefD;
DHR1 = nuA1*HA + nuB1*HB + nuC1*HC  + nuD1*HD;
DHR2 = nuA2*HA + nuB2*HB + nuC2*HC  + nuD2*HD;
%
% rate law for reaction 2
%
ko2 = 1.0e-1; % liter/mole/sec
Ea2 = 3900; % J/mol
k2 = ko2*exp(-Ea2/(R*T));
r2 = k2*CA*CC;
%
% constant volume
%
V = 1000.0; % liter
F = 5; % liter/sec
Fin = F;
Fout = F;
%
%  inlet concentrations
%
CAin = 10.0; % mol/liter
CBin = 10.0; % mol/liter
CCin = 0.0; % mol/liter
CDin = 0.0; % mol/liter
CSin = 30.0; % mol/liter
Tin = 600.0; % 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;
%
%  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 )/(CT*Cpmix);
```

I used the following command

[y,x] = sysode(2,1000,0,1000,[10,10,0,0,30,600]);

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



where the legend corresponds to A, B, C, D S and T. The curves are normalized by the inlet values of A, A, A, A, S, and T respectively.

In this plot, A decreases as a reactant. B decreases as reactant in the first reaction. 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 final line of the unnormalized output file is

```
1.0000000e+003 1.4972623e-001 4.0159360e+000 2.1178542e+000 3.8662098e+000 3.0000000e+001 9.4781729e+002
```

The steady state concentration of A is 0.150 mol/liter.
The steady state concentration of B is 4.016 mol/liter.
The steady state concentration of C is 2.118 mol/liter.
The steady state concentration of D is 3.866 mol/liter.
The steady state temperature is 948 K.
The steady state conversion is

$$X_A = 1 - \frac{C_A}{C_{A,in}} = 1 - \frac{0.150}{10} = 0.985$$

3. Nonisothermal PFR – 1 irreversible reaction

Consider the irreversible reaction

$$A \rightarrow 2B$$

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

$$r = kC_A$$

where the rate constant is given by

$$k = k_o \exp\left(-\frac{E_a}{RT}\right)$$

The activation energy for the forward reaction is 4000 J/mol. The rate constant prefactor for the forward reaction is 0.1 l/s. The heat capacities of A, B and the solvent are respectively 4.0, 7.0, and 3.0 J/mol/K. The heats of formation of A and B at a reference temperature of 298.15 K are respectively -1000.0 and -10000.0 J/mol. The inlet flowrate is 10 liters/s. The inlet temperature is 500 K. The inlet concentrations of A, B and S are 10.0, 0.0, and 30.0 mol/liter respectively. The volume of the reactor is 1000 liters. The reactor is well insulated. The initial temperature and concentrations in the reactor are the same as the inlet temperature and concentrations.

(a) Provide a plot of the transient behavior of the concentrations of A, B and S and the temperature. Explain the features.
(b) What are the steady-state temperature and conversion of A?
(c) Compare this result with problem 1, in which the same reaction was carried out in a CSTR of the same volume. Explain the result.

Solution:

(a) Provide a plot of the transient behavior of the concentrations of A, B and S and the temperature. Explain the features.
(b) What are the steady-state temperature and conversion of A?

I used the following input file:

```
function dydt = sysodeinput(x,y,nvec);
%
%  one reaction in solvent S
%  A --> 2B
%
%  example usage:
%  [y,x] = sysode(2,1000,0,5.0930,[10000,0,30000,500]);
%
CA = y(1); % mol/m^3
CB = y(2); % mol/m^3
CS = y(3); % mol/m^3
T = y(4); % K
%
% stoichiometry
%
nuA = -1.0;
nuB = 2.0;
nuS = 0.0;
%
% rate law
%
R = 8.314; % J/mol/K
ko = 1.0e-1; % 1/sec
%ko = ko/1000; % m^3/mol/sec
Ea = 4000; % J/mol
k = ko*exp(-Ea/(R*T));
r = k*CA;
%
%  pure component heat capacities
%
CpA = 4.0; %J/mol/K
CpB = 7.0; %J/mol/K
CpS = 3.0; %J/mol/K
%
%  enthalpies of formation
%
Tref = 298.15; % K
pref = 101325; % Pa
HfrefA = -1000; %J/mol
HfrefB = -10000; % J/mol
HA = CpA*(T-Tref) + HfrefA;
HB = CpB*(T-Tref) + HfrefB;
DHR = nuA*HA + nuB*HB;
%
%  inlet concentrations and temperature
%
CAin = 10000.0; % mol/m^3
CBin = 0.0; % mol/m^3
CSin = 30000.0; % mol/m^3
Tin = 300.0; % K
%
% mole fractions
%
CT = CA + CB + CS;
xA = CA/CT;
xB = CB/CT;
xS = CS/CT;
CTin = CAin + CBin + CSin;
```

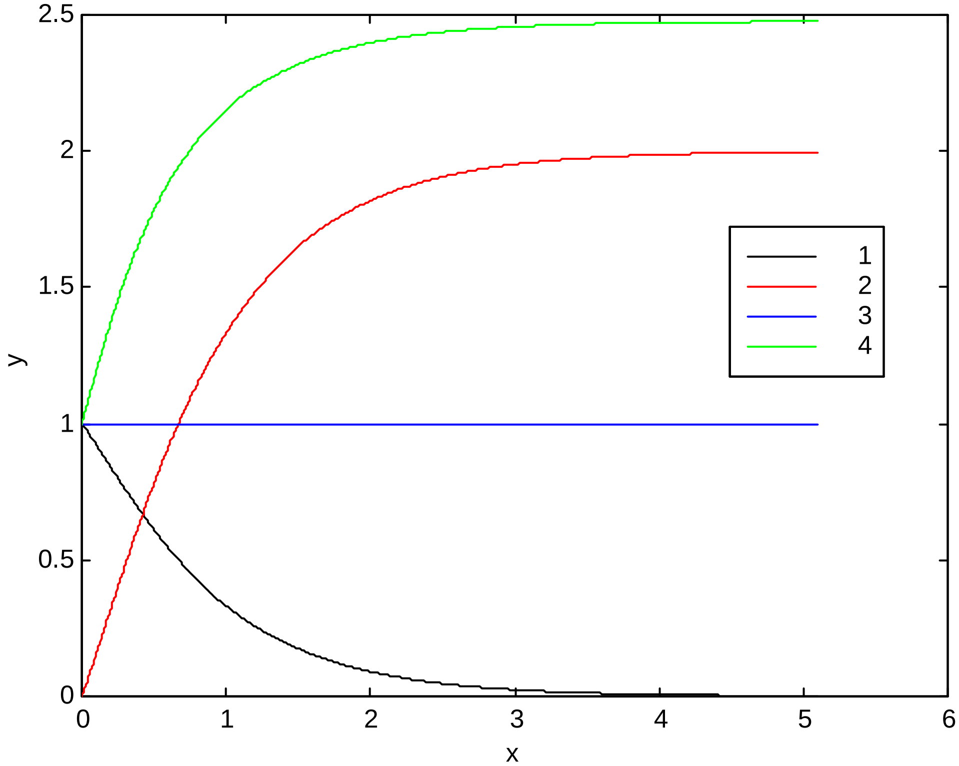
```
xAin = CAin/CTin;
xBin = CBin/CTin;
xSin = CSin/CTin;
%
% mixture heat capacity
%
Cpmix = xA*CpA + xB*CpB + xS*CpS;
Cpmixin = xAin*CpA + xBin*CpB + xSin*CpS;
%
% volumetric flowrate
%
F = 10; % liter/sec
F = F/1000; % cubic meters/sec
%
%  circular pipe
%
volume = 1000; % liters
volume = volume/1000; % m^3
Dp = 0.50; % m
Across = 0.25*pi*Dp*Dp; % m^2
l = volume/Across;
%
% velocity
%
v = F/Across; % m/s
%
% residence time
%
tr = l/v; % sec
%
%  molar balances
%
% dCAdz = nuA*r/v
dydt(1) = (nuA*r)/v;
dydt(2) = (nuB*r)/v;
dydt(3) = (nuS*r)/v;
dydt(4) = -DHR*r/v/(CT*Cpmix);

%
```

I used the following command

```
[y,x] = sysode(2,1000,0,5.0930,[10000,0,30000,500]);
```

I generated the plot of the transient behavior



where the legend corresponds to A, B, S and T. The curves are normalized by the inlet values of A, A, S, and T respectively.

In this plot, A decreases as a reactant, B increases, S is constant, and T increases since the reaction is exothermic.

The final line of the unnormalized output file is

5.0930000e+000 1.5044283e+001 1.9969911e+004 3.0000000e+004 1.2376979e+003

The steady state concentration of A is 150 mol/m^3.
The steady state temperature is 1232 K.
The steady state conversion is

$$X_A = 1 - \frac{C_A}{C_{A,in}} = 1 - \frac{150}{10000} = 0.985$$

(c) Compare this result with problem 1, in which the same reaction was carried out in a CSTR of the same volume. Explain the result.

The conversion was greater in the PFR. In this case, the conversion was much greater, because as the reaction went further in the PFR, the temperature increased, causing the rate to increase and the reaction to go even further.