CBE 450 Chemical Reactor Fundamentals
Fall, 2011
Homework Assignment #5 Solutions

1. CSTR Analysis via Numerical Analysis

Consider the following reactions

$$A + B \rightarrow C$$

$$A + D \rightarrow E$$

both with elementary mechanisms such that the rates are

$$r_1 = k_1 C_A C_B$$

$$r_2 = k_2 C_A C_D$$

where the rate constants are given by

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

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

The temperature is 300 K. The activation energy for reaction 1 is 5000 J/mol. The rate constant prefactor for reaction 1 is 0.001 liter/mole/s^{-1}. The activation energy for reaction 2 is 3500 J/mol. The rate constant prefactor for reaction 2 is 0.01 liter/mole/s^{-1}. The inlet flowrate is 2 liters/sec. The concentration of A in the inlet stream is 10 mol/liter. The concentration of B in the inlet stream is 10 mol/liter. The concentration of D in the inlet stream is 10 mol/liter. The reactor is initially filled with only A at 10 mol/liter.

(a) What is the steady state conversion of A for a volume of 100 liters, where conversion of A is based on the loss of A through both reactions? Show the approach to steady state of the concentrations.
(b) What volume is required to reach a 90% conversion of A at steady state, where conversion of A is based on the loss of A through both reactions?
(c) For part (b), what fraction of A was converted to C?
(d) For part (b), what fraction of A was converted to E?
(e) If you want to increase the ratio of C to E what change in operating conditions could lead to a higher yield in desired product? Use the code to illustrate this effect.

Solution:

(a) What is the steady state conversion of A for a volume of 100 liters, where conversion of A is based on the loss of A through both reactions? Show the approach to steady state of the concentrations.

This is the input file I used for sysodeinput.m

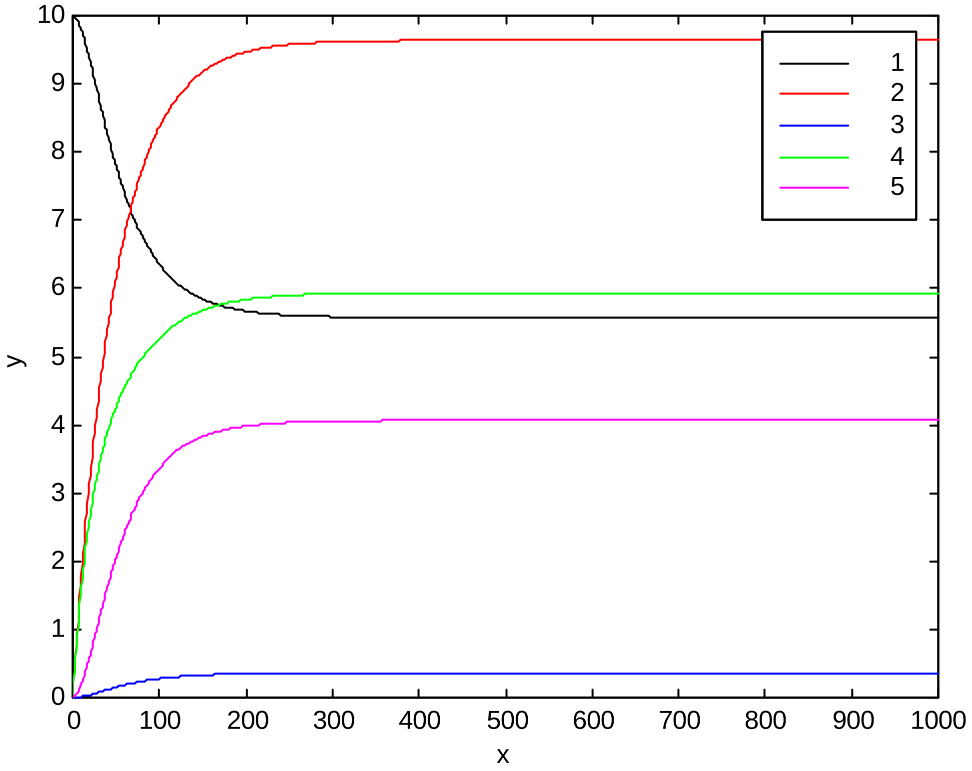
```
function dydt = sysodeinput(x,y,nvec);
%
%  two reaction
%  A + B --> C
%  A + D --> E
%
CA = y(1);
CB = y(2);
CC = y(3);
CD = y(4);
CE = y(5);
%
nuA1 = -1.0;
nuB1 = -1.0;
nuC1 = 1.0;
nuD1 = 0.0;
nuE1 = 0.0;
%
nuA2 = -1.0;
nuB2 = 0.0;
nuC2 = 0.0;
nuD2 = -1.0;
nuE2 = 1.0;
%

% constant volume;
F = 2; % liter/sec
Fin = F;
Fout = F;
CAin = 10.0; % mol/liter
CBin = 10.0; % mol/liter
CCin = 0.0; % mol/liter
CDin = 10.0; % mol/liter
CEin = 0.0; % mol/liter
%
V = 100; % liter
R = 8.314; % J/mol/K
T = 300; % K
ko1 = 1.0e-3; % liter/mol/sec
Ea1 = 5000; % J/mol
k1 = ko1*exp(-Ea1/(R*T));
rate1 = k1*CA*CB;
ko2 = 1.0e-2; % liter/mol/sec
Ea2 = 3500; % J/mol
k2 = ko2*exp(-Ea2/(R*T));
rate2 = k2*CA*CD;%
%
%  molar balances
%
```

```
dydt(1) = Fin/V*CAin - Fout/V*CA + nuA1*rate1 + nuA2*rate2;
dydt(2) = Fin/V*CBin - Fout/V*CB + nuB1*rate1 + nuB2*rate2;
dydt(3) = Fin/V*CCin - Fout/V*CC + nuC1*rate1 + nuC2*rate2;
dydt(4) = Fin/V*CDin - Fout/V*CD + nuD1*rate1 + nuD2*rate2;
dydt(5) = Fin/V*CEin - Fout/V*CE + nuE1*rate1 + nuE2*rate2;
```

The command I typed at the MatLab prompt was

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

The plot generated looked like



legend: black: A; red: B; blue: C; green: D; magenta: E.

From the data file,

```
time                  A                  B                  C                  D                  E
9.9600000e+002 5.5731715e+000 9.6382072e+000  3.6179277e-001 5.9349642e+000 4.0650358e+000
9.9700000e+002 5.5731715e+000 9.6382072e+000  3.6179277e-001 5.9349642e+000 4.0650358e+000
9.9800000e+002 5.5731715e+000 9.6382072e+000  3.6179277e-001 5.9349642e+000 4.0650358e+000
9.9900000e+002 5.5731715e+000 9.6382072e+000  3.6179277e-001 5.9349642e+000 4.0650358e+000
1.0000000e+003 5.5731715e+000 9.6382072e+000  3.6179278e-001 5.9349642e+000 4.0650358e+000
```

The final concentration of A is 5.57 mole/liter.

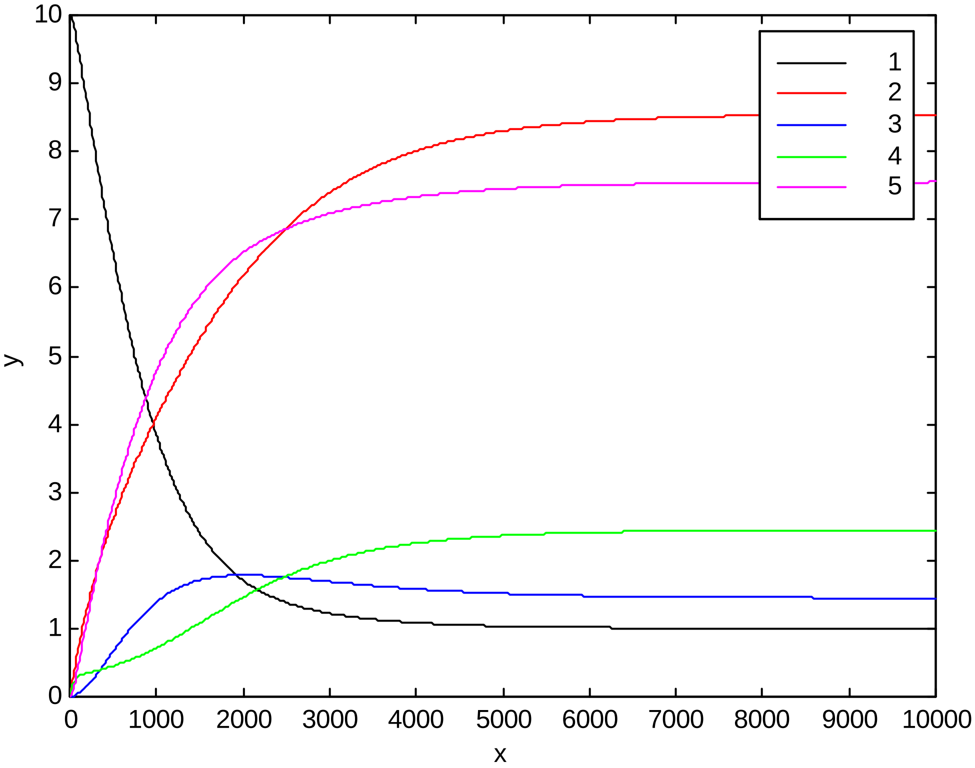
The conversion is

$$X_A = 1 - \frac{C_A}{C_{A,in}} = 1 - \frac{5.57}{10.0} = 0.443$$

(b) What volume is required to reach a 90% conversion of A at steady state, where conversion of A is based on the loss of A through both reactions?

I varied the volume in the code in part (a) until I obtained a conversion of 0.90. I had to increase the time that I solved the ODE to 10000 sec.

The plot looked like



The volume was 2514 liters.

(c) For part (b), what fraction of A was converted to C?

From the output file

```
time              A               B               C              D              E
9.9600000e+003 9.9990767e-001 8.5476673e+000  1.4487118e+000 2.4449986e+000 7.5513805e+000
9.9700000e+003 9.9990279e-001 8.5477079e+000  1.4487000e+000 2.4450106e+000 7.5513972e+000
9.9800000e+003 9.9989795e-001 8.5477481e+000  1.4486882e+000 2.4450225e+000 7.5514138e+000
9.9900000e+003 9.9989315e-001 8.5477880e+000  1.4486766e+000 2.4450343e+000 7.5514303e+000
1.0000000e+004 9.9988839e-001 8.5478275e+000  1.4486650e+000 2.4450459e+000 7.5514466e+000
```

The fraction that was converted to C was

$$\frac{C_C}{C_{A,in}} = \frac{1.449}{10.0} = 0.1449$$

(d) For part (b), what fraction of A was converted to E?

The fraction that was converted to E was

$$\frac{C_E}{C_{A,in}} = \frac{7.551}{10.0} = 0.7551$$

(e) If you want to increase the ratio of C to E what change in operating conditions could lead to a higher yield in desired product? Use the code to illustrate the effect.

The reaction that produces C has a higher activation energy. Therefore it is more sensitive to temperature. An increase in temperature, should increase the amount of C produced relative to the amount of E produced.

For example, for a reactor volume of 100 liters,

for T = 300 K

```
1.0000000e+003 5.5731715e+000 9.6382072e+000  3.6179278e-001 5.9349642e+000 4.0650358e+000
```

$$\frac{C_C}{C_E} = \frac{0.3618}{4.065} = 0.0890$$

for T = 1000 K

```
1.0000000e+004 3.6450017e+000 9.0918884e+000  9.0811156e-001 4.5531132e+000 5.4468868e+000
```

$$\frac{C_C}{C_E} = \frac{0.9081}{5.447} = 0.1667$$

2. PFR Analysis via Analytical Expressions

Consider the following isomerization reaction

$$A \rightarrow B$$

with an elementary mechanism such that the rate is

$$r = kC_A$$

where the rate constant is given by

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

The temperature is 300 K. The activation energy is 5000 J/mol. The rate constant prefactor is 10.0 s^{-1}. The initial concentration of A is 10.0 mol/liter. The volumetric flowrate is 2 liter/sec.

(a) Provide an analytical expression for the reactor volume required to achieve a specified conversion for this reaction in a PFR.
(b) What length is required to reach a conversion of 95% if your PFR is a circular pipe with diameter 0.10 m?
(c) What conversion is obtained in a PFR of length 2 m, if your PFR is a circular pipe with diameter 0.10 m?

Solution:

(a) Provide an analytical expression for the reactor volume required to achieve a specified conversion for this reaction in a PFR.

This is the differential form

$$-F\frac{dC_{A,in}(1-X_A)}{dV} = -\nu_A r$$

$$r = kC_A = kC_{A,in}(1-X_A) \text{ and } \nu_A = -1$$

Substitute.

$$-F\frac{dC_{A,in}(1-X_A)}{dV} = kC_{A,in}(1-X_A)$$

Simplify

$$F\frac{dX_A}{dV} = k(1-X_A)$$

$$dV = \frac{F}{k}\frac{dX_A}{(1-X_A)}$$

Integrate

$$\int_0^V dV = \frac{F}{k}\int_0^{X_A}\frac{dX_A}{(1-X_A)}$$

$$V = -\frac{F}{k}\ln\left(1 - X_A\right)$$

(b) What length is required to reach a conversion of 95% if your PFR is a circular pipe with diameter 0.10 m?

$$k = k_o \exp\left(-\frac{E_a}{RT}\right) = 10\exp\left(-\frac{5000}{8.314 * 300}\right) = 1.347\, s^{-1}$$

$$V = -\frac{F}{k}\ln\left(1 - X_A\right) = -\frac{2}{1.347}\ln\left(1 - 0.95\right) = 4.448 \text{ liters} = 0.00448 \text{ m}^3$$

$$A_x = \frac{\pi}{4}D^2 = \frac{\pi}{4}0.1^2 = 0.007854\,\text{m}^2$$

$$L = \frac{V}{A_x} = \frac{0.00448}{0.007854} = 0.570\,\text{m}$$

(c) What conversion is obtained in a PFR of length 2 m, if your PFR is a circular pipe with diameter 0.10 m?

Rearrange the design equation.

$$X_A = 1 - \exp\left(-\frac{kV}{F}\right)$$

$$A_x = \frac{\pi}{4}D^2 = \frac{\pi}{4}0.1^2 = 0.007854\ \text{m}^2$$

$$V = LA_x = 2 \cdot 0.007854 = 0.01571\,\text{m}^3$$

$$F = 2\,\text{liter/s} = 0.002 \text{ m}^3\text{/s}$$

$$X_A = 1 - \exp\left(-\frac{kV}{F}\right) = 1 - \exp\left(-\frac{1.347 \cdot 0.01571}{0.002}\right) = 0.99997$$

3. PFR Analysis via Numerical Analysis

Consider the reactions and rate law given in problem 1. The temperature and the inlet stream composition and flowrate are all the same as that given in problem 1.

The PFR is circular with diameter 0.10 m and length 50 m.

(a) Find the conversion of A at steady state. Show the profile of each component within the PFR.
(b) Would a CSTR of a similar volume yield a higher conversion? Why?

Solution:

(a) Find the conversion of A at steady state. Show the profile of each component within the PFR.

This is the input file I used for sysodeinput.m

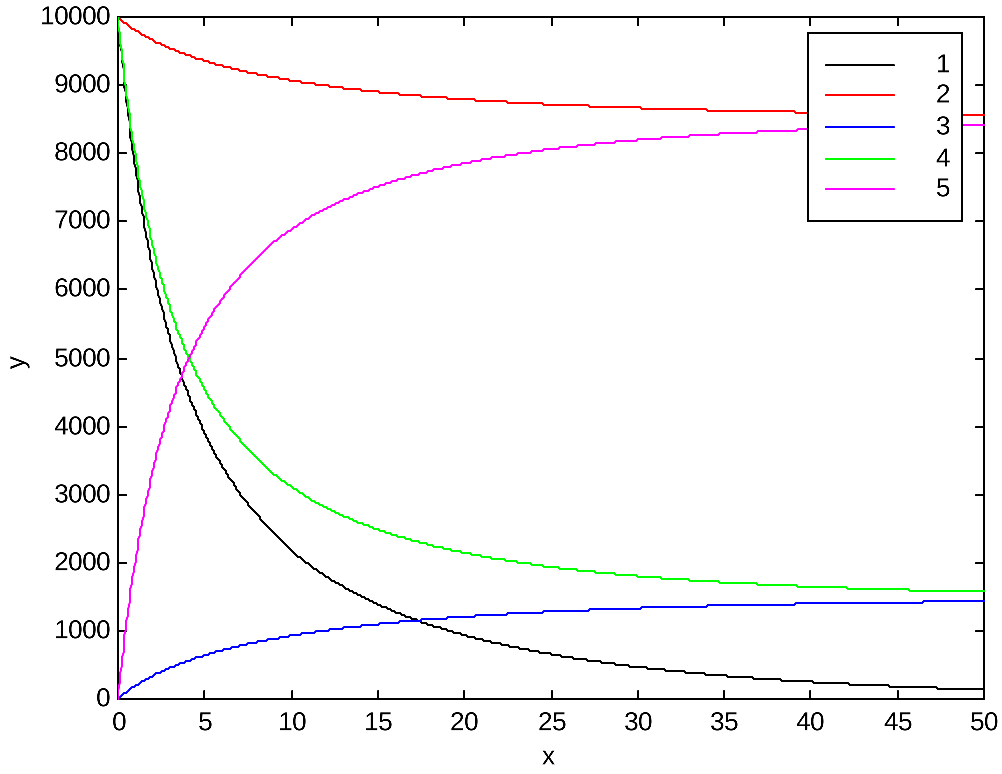
```
function dydt = sysodeinput(x,y,nvec);
%
%  two reaction
%  A + B --> C
%  A + D --> E
%
%  sample input:
% [y,x] = sysode(2,1000,0,20,[10000,10000,0,10000,0]);
%
CA = y(1);
CB = y(2);
CC = y(3);
CD = y(4);
CE = y(5);
%
nuA1 = -1.0;
nuB1 = -1.0;
nuC1 = 1.0;
nuD1 = 0.0;
nuE1 = 0.0;
%
nuA2 = -1.0;
nuB2 = 0.0;
nuC2 = 0.0;
nuD2 = -1.0;
nuE2 = 1.0;
%
% constant volume;
F = 2; % liter/sec
F = F/1000; % cubic meters/sec
%
%
V = 100; % liter
R = 8.314; % J/mol/K
T = 1000; % K
ko1 = 1.0e-3; % liter/mol/sec
ko1 = ko1/1000.0; % m^3/mol/sec
Ea1 = 5000; % J/mol
k1 = ko1*exp(-Ea1/(R*T));
rate1 = k1*CA*CB;
ko2 = 1.0e-2; % liter/mol/sec
ko2 = ko2/1000.0; % m^3/mol/sec
Ea2 = 3500; % J/mol
```

```
k2 = ko2*exp(-Ea2/(R*T));
rate2 = k2*CA*CD;%
%
Dp = 0.10; % m
Across = 0.25*pi*Dp*Dp; % m^2
%
% velocity
%
v = F/Across; % m/s
%
% residence time
%
l = 20; % m
tr = l/v; % sec
%
%  molar balances
%
dydt(1) = (nuA1*rate1+nuA2*rate2)/v;
dydt(2) = (nuB1*rate1+nuB2*rate2)/v;
dydt(3) = (nuC1*rate1+nuC2*rate2)/v;
dydt(4) = (nuD1*rate1+nuD2*rate2)/v;
dydt(5) = (nuE1*rate1+nuE2*rate2)/v;
```

The command I typed at the MatLab prompt was

```
[y,x] = sysode(2,1000,0,50,[10000,10000,0,10000,0]);
```

The plot generated looked like



legend: black: A; red: B; blue: C; green: D; magenta: E.

From the data file,

position	A	B	C	D	E
4.9800000e+001	1.3982102e+002	8.5683603e+003	1.4316397e+003	1.5714607e+003	8.4285393e+003
4.9850000e+001	1.3940954e+002	8.5682316e+003	1.4317684e+003	1.5711780e+003	8.4288220e+003
4.9900000e+001	1.3899933e+002	8.5681032e+003	1.4318968e+003	1.5708961e+003	8.4291039e+003
4.9950000e+001	1.3859038e+002	8.5679753e+003	1.4320247e+003	1.5706151e+003	8.4293849e+003
5.0000000e+001	1.3818268e+002	8.5678477e+003	1.4321523e+003	1.5703350e+003	8.4296650e+003

The exit concentration of A is 13.82 mole/m^3. or 0.01382 mole/liter.

The conversion is

$$X_A = 1 - \frac{C_A}{C_{A,in}} = 1 - \frac{0.01382}{10.0} = 0.9862$$

(b) Would a CSTR of a similar volume yield a higher conversion? Why?

No. A CSTR of the same volume as a PFR will yield a lower conversion because the reaction in a CSTR is carried out at the exit concentration, whereas the reaction in a PFR is carried out at the local concentration as shown in the concentration profile above.