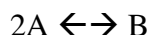


**CBE 450 Chemical Reactor Fundamentals**  
**Fall, 2009**  
**Homework Assignment #7 Solutions**

**1. Nonisothermal Batch Reactor**

Consider the reversible reaction



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

$$r_1 = k_1 C_A^2$$

and the reverse reaction is

$$r_2 = k_2 C_B$$

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 forward reaction is 5000 J/mol. The rate constant prefactor for the forward reaction is 0.001 liter/mol/s. The heat of reaction for the forward reaction is -12 kJ/mol. The rate constant prefactor for the reverse reaction is 0.001 1/s. The reaction occurs in a solvent, S. The heat capacities of A, B and the solvent are respectively 4, 7, and 3.5 J/mol/K. The initial concentration in the batch reactor for A, B and S are 10, 0 and 30 mol/liter. The initial temperature is 300 K. The reactor is well insulated.

- (a) What are the temperature and conversion of A at 1 hr?
- (b) Provide a plot of the transient behavior of the concentrations of A, B and S and the temperature. Explain the features.
- (c) Make a plot or table of conversion after 1 hr vs heat of reaction for the forward reaction with at least three points (all of which are exothermic). Explain the behavior.

**Solution:**

- (a) What are the temperature and conversion of A at 1 hr?

I used the following input file:

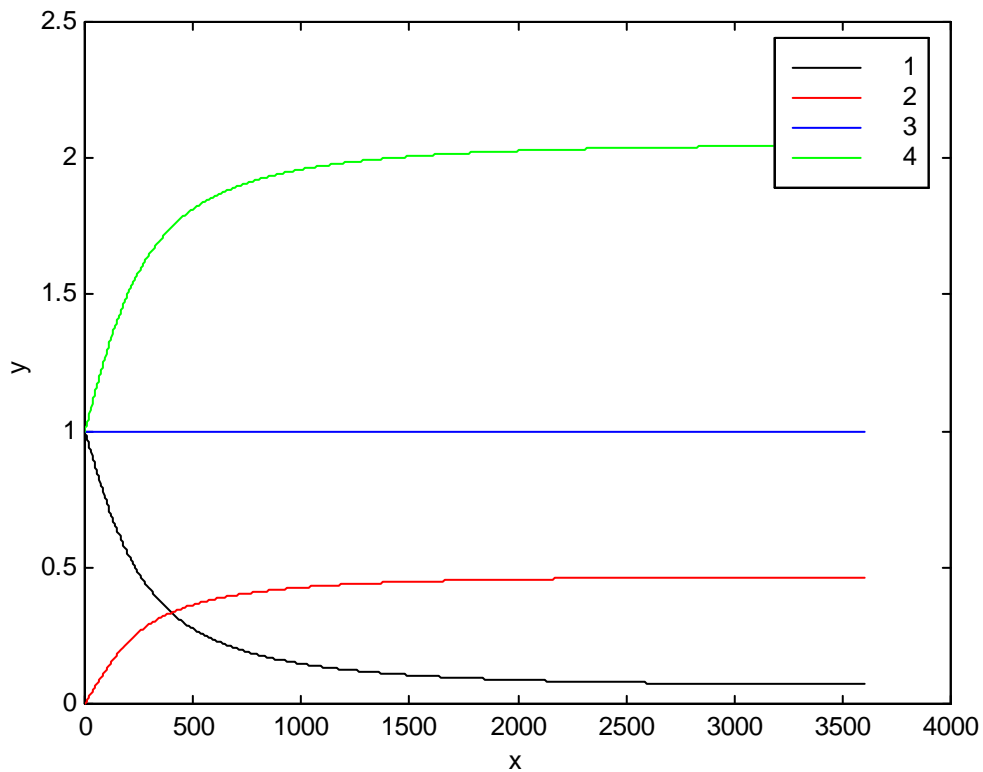
```
function dydt = sysodeinput(x,y,nvec);
%
% one reversible reaction in solvent, S
% 2A <--> B
%
% sample usage:
% [y,x]=sysode(2,1000,0,10,[10,0,40,300]);
%
CA = y(1); % mol/liter
CB = y(2);
CS = y(3);
T = y(4); % K
%
% stoichiometry
%
nuA1 = -2;
nuB1 = 1;
nuS1 = 0;
nuA2 = 2;
nuB2 = -1;
nuS2 = 0;
%
% rate law
%
ko1 = 1.0e-3; % liter/mole/sec
Ea1 = 5000; % J/mol
R = 8.314; %J/mol/K
DUR1 = -12000.0; %J/mol
k1 = ko1*exp(-Ea1/(R*T)); % liters/mole/sec
r1 = k1*CA*CA; % mole/liter/sec
%
ko2 = 1.0e-3; % 1/sec
Ea2 = Ea1 - DUR1; % J/mol
R = 8.314; %J/mol/K
DUR2 = -DUR1;
k2 = ko2*exp(-Ea2/(R*T)); % 1/sec
r2 = k2*CB; % mole/liter/sec
%
% pure component heat capacities
%
CvA = 4.0; %J/mol/K
CvB = 7.0; %J/mol/K
CvS = 3.5; %J/mol/K
%
% mole fractions
%
CT = CA + CB + CS;
xA = CA/CT;
xB = CB/CT;
xS = CS/CT;
%
% mixture heat capacity
%
Cvmix = xA*CvA + xB*CvB + xS*CvS;
%
% mole and energy balances
%
dydt(1) = nuA1*r1 + nuA2*r2;
dydt(2) = nuB1*r1 + nuB2*r2;
```

```
dydt(3) = nuS1*r1 + nuS2*r2;
dydt(4) = -(DUR1*r1 + DUR2*r2)/(CT*Cvmix);
```

I used the following command

```
[y,x]=sysode(2,1000,0,3600,[10,0,40,300]);
```

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



And the final line of the output file

```
3.6000000e+003 7.0091175e-002 4.6495441e-001 1.0000000e+000 2.0468110e+000
```

This plot and output file was normalized. Since the initial concentration of A was 10 mol/liter, the final concentration of A is 0.701 mol/liter. The conversion is

$$X_A = 1 - \frac{C_A}{C_{A,in}} = 1 - \frac{0.701}{10} = 0.9299$$

The temperature is 614.0 K.

(b) Provide a plot of the transient behavior of the concentrations of A, B and S and the temperature. Explain the features.

The plot is provided above. The temperature rises because the reaction is exothermic. The concentration of the solvent is unchanged because it does not participate in the reaction and the reactor volume is constant. The concentration of A decreases since it is the reactant. The concentration of B rises half as fast as the concentration of A based on the stoichiometry of the reaction.

(c) Make a plot or table of conversion after 1 hr vs heat of reaction for the forward reaction with at least three points (all of which are exothermic). Explain the behavior.

We can repeat the process used in part (a) for two other values of the the heat of reaction.

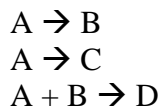
The results are below:

heat of reaction for the forward reaction (kJ/mol)	concentration of A (mol/liter)	temperature	conversion
-6	1.000	451.9	0.9000
-12	0.701	614.0	0.9299
-24	0.497	942.1	0.9503

As the heat of reaction increases the temperature naturally increases. As the temperature increases, the rates of both the forward and reverse reactions increase. However, the activation energy of the forward reaction is a constant at 5000 J/mol. The activation energy of the reverse reaction is not independent and is the  $E_{a,1} - \Delta H_{R,1}$ , and so increases with an increase in magnitude in the heat of reaction. Thus the forward reaction is favored and conversion increases.

## 2. Nonisothermal Batch Reactor

Consider the system of irreversible reactions



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

$$r_1 = k_1 C_A, \quad r_2 = k_2 C_A, \quad \text{and} \quad r_3 = k_3 C_A C_B$$

All reactions have an Arrhenius dependence on temperature

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

where the reaction properties are given in the table below

reaction	$k_o$ (1/s or liter/mol/s)	$E_a$ (J/mol)	heat of reaction (kJ/mol)
1	1.0	4000	0
2	1.0	3000	0
3	1.0	2000	-20

The reaction occurs in a solvent, S. The heat capacities of A, B, C, D and the solvent are respectively 4.0, 3.0, 5.0, 6.0, and 4.0 J/mol/K. The initial concentration in the batch reactor for A, B, C, D and S are 10, 0, 0, 0 and 40 mol/liter. The initial temperature is 300 K. The reactor is well insulated.

- (a) What are the steady state temperature and concentrations of each component?  
 (b) What operating condition could you change if you want to form a higher ratio of C to D? Demonstrate.

**Solution:**

- (a) What are the steady state temperature and concentrations of each component?

I used the following input file:

```
function dydt = sysodeinput(x,y,nvec);
%
% three reactions in solvent, S
% A --> B
% A --> C
% A + B --> D
%
% sample usage:
% [y,x]=sysode(2,1000,0,10,[10,0,0,0,40,300]);
%
CA = y(1); % mol/liter
CB = y(2);
CC = y(3);
CD = y(4);
CS = y(5);
T = y(6); % K
%
% stoichiometry
%
nuA1 = -1;
nuB1 = 1;
nuC1 = 0;
nuD1 = 0;
nuS1 = 0;
%
nuA2 = -1;
nuB2 = 0;
nuC2 = 1;
nuD2 = 0;
nuS2 = 0;
%
nuA3 = -1;
nuB3 = -1;
```

```

nuC3 = 0;
nuD3 = 1;
nuS3 = 0;
%
% rate law
%
ko1 = 1.0; % 1/sec
Ea1 = 4000; % J/mol
R = 8.314; %J/mol/K
DUR1 = 0.0; %J/mol
k1 = ko1*exp(-Ea1/(R*T)); % 1/sec
r1 = k1*CA; % mole/liter/sec
%
ko2 = 1.0; % 1/sec
Ea2 = 3000; % J/mol
R = 8.314; %J/mol/K
DUR2 = 0;
k2 = ko2*exp(-Ea2/(R*T)); % 1/sec
r2 = k2*CA; % mole/liter/sec
%
ko3 = 1.0; % liter/mole/sec
Ea3 = 2000; % J/mol
R = 8.314; %J/mol/K
DUR3 = -20000.0; %J/mol
k3 = ko3*exp(-Ea3/(R*T)); % liters/mole/sec
r3 = k3*CA*CB; % mole/liter/sec

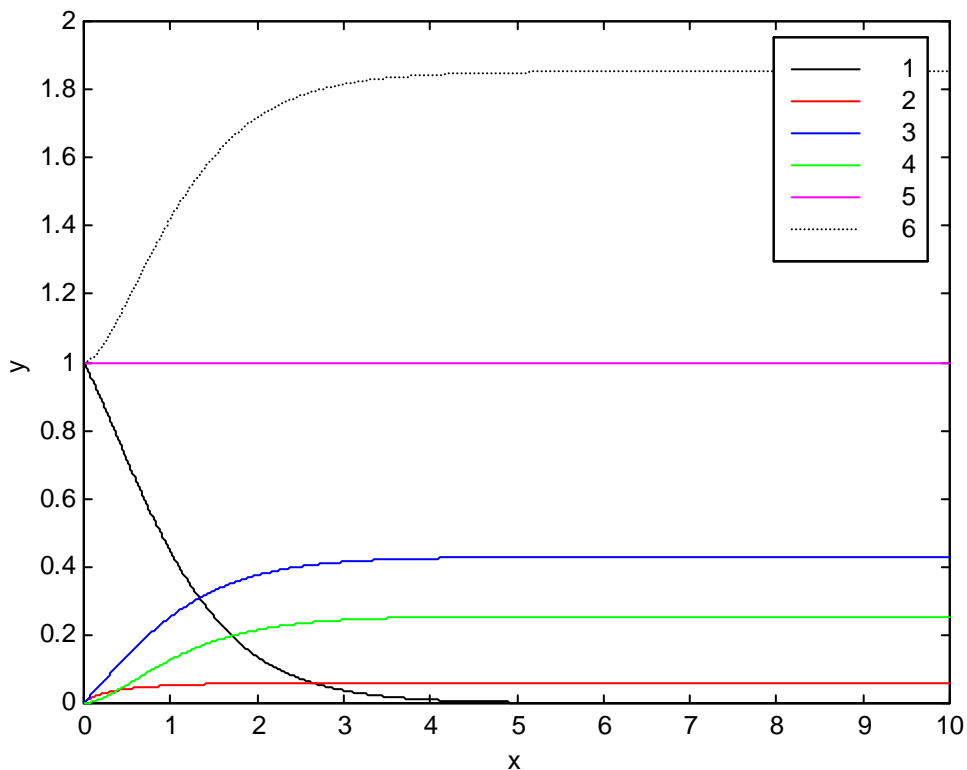
%
% pure component heat capacities
%
CvA = 4.0; %J/mol/K
CvB = 3.0; %J/mol/K
CvC = 5.0; %J/mol/K
CvD = 6.0; %J/mol/K
CvS = 4.0; %J/mol/K
%
% mole fractions
%
CT = CA + CB + CC + CD + CS;
xA = CA/CT;
xB = CB/CT;
xC = CC/CT;
xD = CD/CT;
xS = CS/CT;
%
% mixture heat capacity
%
Cvmix = xA*CvA + xB*CvB + xC*CvC + xD*CvD + xS*CvS;
%
% mole and energy balances
%
dydt(1) = nuA1*r1 + nuA2*r2 + nuA3*r3;
dydt(2) = nuB1*r1 + nuB2*r2 + nuB3*r3;
dydt(3) = nuC1*r1 + nuC2*r2 + nuC3*r3;
dydt(4) = nuD1*r1 + nuD2*r2 + nuD3*r3;
dydt(5) = nuS1*r1 + nuS2*r2 + nuS3*r3;
dydt(6) = -(DUR1*r1 + DUR2*r2 + DUR3*r3)/(CT*Cvmix);

```

I used the following commands

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

I generated the following plot



From the output file

```

9.9500000e+000 3.4365569e-006 6.1307264e-002 4.2862813e-001 2.5503059e-001 1.0000000e+000 1.8525516e+000
9.9600000e+000 3.3907845e-006 6.1307264e-002 4.2862815e-001 2.5503060e-001 1.0000000e+000 1.8525517e+000
9.9700000e+000 3.3456219e-006 6.1307265e-002 4.2862816e-001 2.5503061e-001 1.0000000e+000 1.8525517e+000
9.9800000e+000 3.3010607e-006 6.1307266e-002 4.2862818e-001 2.5503063e-001 1.0000000e+000 1.8525517e+000
9.9900000e+000 3.2570931e-006 6.1307267e-002 4.2862820e-001 2.5503064e-001 1.0000000e+000 1.8525518e+000
1.0000000e+001 3.2137111e-006 6.1307268e-002 4.2862821e-001 2.5503065e-001 1.0000000e+000 1.8525518e+000
    
```

These values are normalized by the inlet concentration of A for A, B, C, and D, by the inlet concentration of S for S and by the inlet temperature for T. Unscaling them yields

```

CA = 3.2e-005 mol.liter
CB = 0.61 mol.liter
CC = 4.29 mol.liter
CD = 2.55 mol.liter
CS = 40 mol.liter
T = 555.8 K
    
```

(b) What operating condition could you change if you want to form a higher ratio of C to D? Demonstrate.

You could change the initial temperature of the reactor. If the initial temperature is 300 K as in the problem above, then the final ratio of C to D is 1.68. If the initial temperature is 100 K, the ratio of C to D is 2.4. Lowering the temperature works because D is kinetically favored. Lowering the temperature reduces the kinetic advantage.