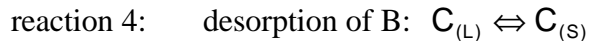
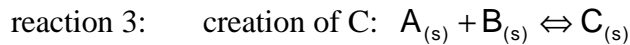


Midterm Exam  
ChE 505

Consider a batch reactor (no input or output terms) run under isothermal conditions. In this batch reactor, we have placed a liquid mixture of A and B, as well as a solid catalyst.

The following reactions take place



Thus we have 6 unknowns: the number of moles of  $N_{A(L)}$ ,  $N_{A(s)}$ ,  $N_{B(L)}$ ,  $N_{B(s)}$ ,  $N_{C(L)}$ ,  $N_{C(s)}$ .

We can write mole balances on each of these:

$$\frac{dN_{A(L)}}{dt} = -k_1 \frac{N_{A(L)}}{V_L} + k_{-1} \frac{N_{A(s)}}{A_s}$$

where  $k_1$  is the rate constant for the forward reaction in reaction 1 (given above), and  $k_{-1}$  is the rate constant for the reverse reaction in reaction 1,  $V_L$  is the volume of the liquid phase in  $m^3$ , and  $A_s$  is the surface area of the solid catalyst in  $m^2$ .

Similarly we can write the other five mole balances

$$\frac{dN_{A(s)}}{dt} = k_1 \frac{N_{A(L)}}{V_L} - k_{-1} \frac{N_{A(s)}}{A_s} - k_3 \frac{N_{A(s)}}{A_s} \frac{N_{B(s)}}{A_s} + k_{-3} \frac{N_{C(s)}}{A_s}$$

$$\frac{dN_{B(L)}}{dt} = -k_2 \frac{N_{B(L)}}{V_L} + k_{-2} \frac{N_{B(s)}}{A_s}$$

$$\frac{dN_{B(s)}}{dt} = k_2 \frac{N_{B(L)}}{V_L} - k_{-2} \frac{N_{B(s)}}{A_s} - k_3 \frac{N_{A(s)}}{A_s} \frac{N_{B(s)}}{A_s} + k_{-3} \frac{N_{C(s)}}{A_s}$$

$$\frac{dN_{C(L)}}{dt} = -k_4 \frac{N_{C(L)}}{V_L} + k_{-4} \frac{N_{C(s)}}{A_s}$$

$$\frac{dN_{C(s)}}{dt} = k_4 \frac{N_{C(L)}}{V_L} - k_{-4} \frac{N_{C(s)}}{A_s} + k_3 \frac{N_{A(s)}}{A_s} \frac{N_{B(s)}}{A_s} - k_{-3} \frac{N_{C(s)}}{A_s}$$

(This means that the units of  $k_1$ ,  $k_2$ , and  $k_4$  are  $[m^3/sec]$ . The units of  $k_{-1}$ ,  $k_{-2}$ ,  $k_{-3}$ , and  $k_{-4}$  are  $[m^2/sec]$ . The units of  $k_3$  are  $[m^4/mole/sec]$ .)

For all eight rate constants, we have the functional form

$$k_i = k_{o,i} e^{-\frac{E_{a,i}}{RT}}$$

where the exponential prefactors are (in units given above)

$$\begin{array}{ll} k_{o,1} = 1.0 \cdot 10^{-3} & k_{o,-1} = 1.0 \cdot 10^{-2} \\ k_{o,2} = 2.0 \cdot 10^{-3} & k_{o,-2} = 2.0 \cdot 10^{-2} \\ k_{o,3} = 3.0 & k_{o,-3} = 3.0 \cdot 10^{-3} \\ k_{o,4} = 4.0 \cdot 10^{-3} & k_{o,-4} = 4.0 \cdot 10^{-2} \end{array}$$

and where the activation energies are (in units of kJ/mol)

$$\begin{array}{ll} E_{a,1} = 5.0 & E_{a,-1} = 15.0 \\ E_{a,2} = 5.0 & E_{a,-2} = 2.0 \\ E_{a,3} = 30.0 & E_{a,-3} = 60.0 \\ E_{a,4} = 20.0 & E_{a,-4} = 12.0 \end{array}$$

Consider a reactor with  $V_L = 2.0 \text{ m}^3$  and with enough solid catalyst to give  $A_s = 1.5 \text{ m}^2$ . The reactor is run isothermally at  $T = 400 \text{ K}$ . The initial moles of each component are:

$$N_{A(L)} = 24.37, N_{A(s)} = 4.06, N_{B(L)} = 36.57, N_{B(s)} = 0.0, N_{C(L)} = 0.0, N_{C(s)} = 0.0.$$

(a) Find the transient and steady state behavior of the reactor. Give me plots of the six unknown number of moles as a function of time from the initial conditions to the final conditions. Give me a table of the steady state values.

(b) There is one problematic assumption with the formulation above. There is no limit on how many moles of fluid can adsorb to the solid. In reality, there is only a finite amount of solid surface available, which limits the total amount of A, B, and C that can adsorb. If there is a maximum adsorbate density of  $\rho_{\max} = 2.71 \text{ moles/m}^2$ , then we have a maximum number of adsorbed moles of  $N_{\max} = \rho_{\max} A_s$ . We can prohibit loading more than the maximum number of

molecules on the solid catalyst by including the factor,  $\left(1 - \frac{N_{A(s)} + N_{B(s)} + N_{C(s)}}{N_{\max}}\right)$ , in the

adsorption rate constants. This factor is dimensionless. It is one when there is nothing adsorbed

to the surface and it is 0 when all sites on the solid are occupied. Therefore, the rates of adsorption will be zero, when there are no sites available. The new constants will have the form

$$k_i = \left( 1 - \frac{N_{A(s)} + N_{B(s)} + N_{C(s)}}{N_{\max}} \right) k_{o,i} e^{-\frac{E_{a,i}}{RT}}$$

for  $i = 1, 2,$  and  $4$  only. The other 5 rate constants will not be affected.

Repeat part (a) using this adsorption limit. Turn in the same plots, table, and input file. Comment on the differences in the plots and tables in terms of the physical difference between the two systems in part(a) and part(b).

Note:

The steady states can be approximated by solving the ordinary differential equations out to long times (using for example sysode.m). The steady states can be solved for much more precisely by solving the steady state mass balances (using for example syseqn.m). However, it can be shown that only four of the six mass balances are linearly independent. In order to solve for all six unknowns, we need six equations. We can, for example, strike out equations (2) and (4) above as linearly dependent. We can replace these two equations with mass balances that incorporate the initial amount of A and B in the reactor. These equations have the form.

$$N_{A(L)}(t=0) + N_{A(S)}(t=0) = N_{A(L)}(t) + N_{A(S)}(t) + N_{C(L)}(t) + N_{C(S)}(t) \quad (7)$$

$$N_{B(L)}(t=0) + N_{B(S)}(t=0) = N_{B(L)}(t) + N_{B(S)}(t) + N_{C(L)}(t) + N_{C(S)}(t) \quad (8)$$

These two equations amount to saying that the total amount of A (or B) initially is equal to the total amount of A (or B) at any time (including steady state) plus the total amount of C produced. This is true because for every mole of C produced one mole of A (or B) is consumed.

part (a) - transient behavior

```
>> sysode(2,6000,0,30000,[24.37,36.57,0.0,4.06,0.0,0.0]);
```

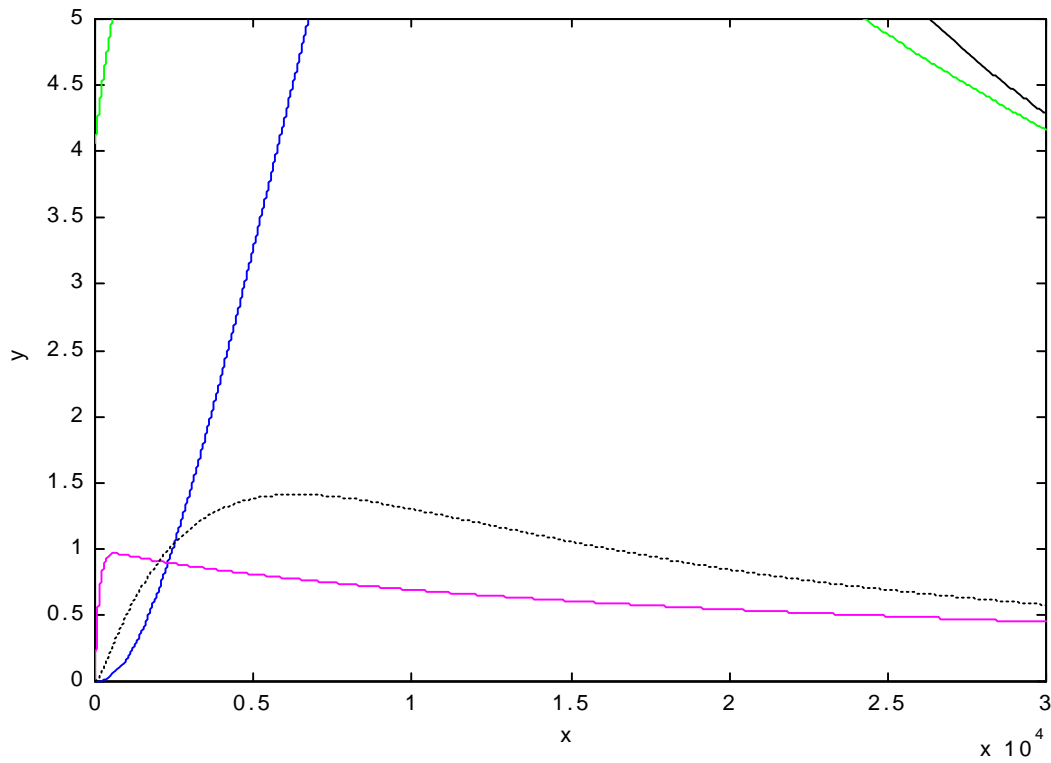
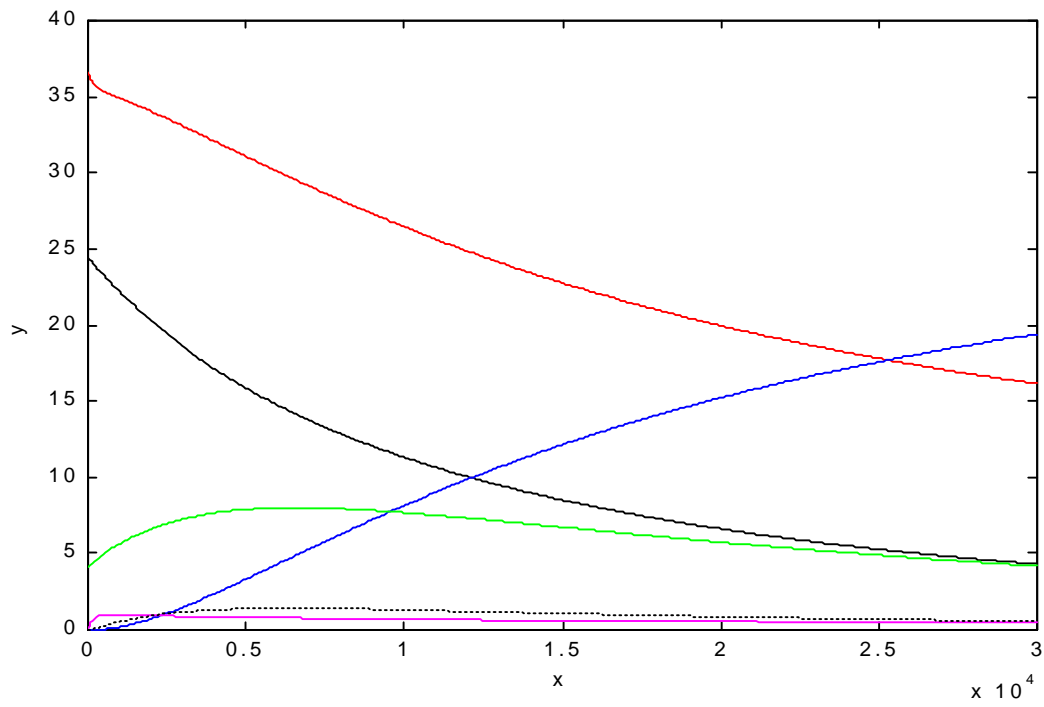
sysodeinput.m

```
function dydt = sysodeinput(t,y,nvec);

A1 = y(1);
B1 = y(2);
C1 = y(3);
As = y(4);
Bs = y(5);
Cs = y(6);

V1 = 2.0; % m^3
Area = 1.5; % m^2
R = 8.314;
T = 400; % K
% forward rate pre-exponential factors
ko(1,1) = 1.0e-3;
ko(2,1) = 2.0e-3;
ko(3,1) = 3.0e-0;
ko(4,1) = 4.0e-3;
% reverse rate pre-exponential factors
ko(1,2) = 1.0e-2;
ko(2,2) = 2.0e-2;
ko(3,2) = 3.0e-3;
ko(4,2) = 4.0e-2;
% forward reaction activation energies
Ea(1,1) = 5.0e+3;
Ea(2,1) = 5.0e+3;
Ea(3,1) = 30.0e+3;
Ea(4,1) = 20.0e+3;
% reverse reaction activation energies
Ea(1,2) = 15.0e+3;
Ea(2,2) = 2.0e+3;
Ea(3,2) = 60.0e+3;
Ea(4,2) = 12.0e+3;
%
for i = 1:1:4
    for j = 1:1:2
        k(i,j) = ko(i,j)*exp(-Ea(i,j)/(R*T));
    end
end

dydt(1) = -k(1,1)*A1/V1 + k(1,2)*As/Area;
dydt(2) = -k(2,1)*B1/V1 + k(2,2)*Bs/Area;
dydt(3) = -k(4,1)*C1/V1 + k(4,2)*Cs/Area;
dydt(4) = k(1,1)*A1/V1 - k(1,2)*As/Area - k(3,1)*As*Bs/Area^2 + k(3,2)*Cs/Area;
dydt(5) = k(2,1)*B1/V1 - k(2,2)*Bs/Area - k(3,1)*As*Bs/Area^2 + k(3,2)*Cs/Area;
dydt(6) = k(4,1)*C1/V1 - k(4,2)*Cs/Area + k(3,1)*As*Bs/Area^2 - k(3,2)*Cs/Area;
```



Transient Behavior for part (a). Second plot is a close-up of the first plot.

part (a) -steady state behavior

Initial guess (from transient analysis)

```
» syseqn(1,[4.3 16.1 19.4 4.2 0.45 0.57]);
```

output:

Attempting solution with MATLABs fsolve function

VARIABLE	INPUT	OUTPUT
1	4.3000000e+000	9.4978154e-008
2	1.6100000e+001	7.8996228e+000
3	1.9400000e+001	2.8238936e+001
4	4.2000000e+000	1.4407978e-007
5	4.5000000e-001	2.4037742e-001
6	5.7000000e-001	1.9106408e-001

So, the steady state is

$$\begin{array}{ll}
 N_{A(L)} = 9.50e-8, & N_{A(s)} = 1.44e-7, \\
 N_{B(L)} = 7.90, & N_{B(s)} = 0.240, \\
 N_{C(L)} = 28.24, & N_{C(s)} = 0.191.
 \end{array}$$

A was the limiting reagent and it was basically used up.

B was in excess so some of it remained.

syseqninput.m

```
function [dydt] = syseqninput(y)

Al = y(1);
Bl = y(2);
Cl = y(3);
As = y(4);
Bs = y(5);
Cs = y(6);

Vl = 2.0; % m^3
Area = 1.5; % m^2
R = 8.314;
T = 400; % K
% forward rate pre-exponential factors
ko(1,1) = 1.0e-3;
ko(2,1) = 2.0e-3;
ko(3,1) = 3.0e-0;
ko(4,1) = 4.0e-3;
% reverse rate pre-exponential factors
ko(1,2) = 1.0e-2;
ko(2,2) = 2.0e-2;
ko(3,2) = 3.0e-3;
ko(4,2) = 4.0e-2;
% forward reaction activation energies
Ea(1,1) = 5.0e+3;
```

```

Ea(2,1) = 5.0e+3;
Ea(3,1) = 30.0e+3;
Ea(4,1) = 20.0e+3;
% reverse reaction activation energies
Ea(1,2) = 15.0e+3;
Ea(2,2) = 2.0e+3;
Ea(3,2) = 60.0e+3;
Ea(4,2) = 12.0e+3;
%
for i = 1:1:4
    for j = 1:1:2
        k(i,j) = ko(i,j)*exp(-Ea(i,j)/(R*T));
    end
end
%
% (b) include finite amount of surface area or (a) don't include
%
rhomax = 2.71;
part = 'a';
if (strcmp(part,'b') == 1)
    fact = 1 - (As + Bs + Cs)/(rhomax*Area); % part (b)
else
    fact = 1; %part (a)
end
k(1,1) = fact*k(1,1);
k(2,1) = fact*k(2,1);
k(4,1) = fact*k(4,1);

%
% initial amounts
%
Alo = 24.37;
Blo = 36.57;
Bso = 0.0;
Aso = 4.06;

% equations

dydt(1) = -k(1,1)*Al/Vl + k(1,2)*As/Area;
dydt(2) = -k(2,1)*Bl/Vl + k(2,2)*Bs/Area;
dydt(3) = -k(4,1)*Cl/Vl + k(4,2)*Cs/Area;
%dydt(4) = k(1,1)*Al/Vl - k(1,2)*As/Area - k(3,1)*As*Bs/Area^2 + k(3,2)*Cs/Area;
%dydt(5) = k(2,1)*Bl/Vl - k(2,2)*Bs/Area - k(3,1)*As*Bs/Area^2 + k(3,2)*Cs/Area;
dydt(6) = k(4,1)*Cl/Vl - k(4,2)*Cs/Area + k(3,1)*As*Bs/Area^2 - k(3,2)*Cs/Area;
dydt(4) = Alo + Aso - Al - As - Cl - Cs;
dydt(5) = Blo + Bso - Bl - Bs - Cl - Cs;

```

part (b)

part (b) - transient behavior

Initial guess

```
>> sysode(2,12000,0,600000,[24.37,36.57,0.0,4.06,0.0,0.0]);
```

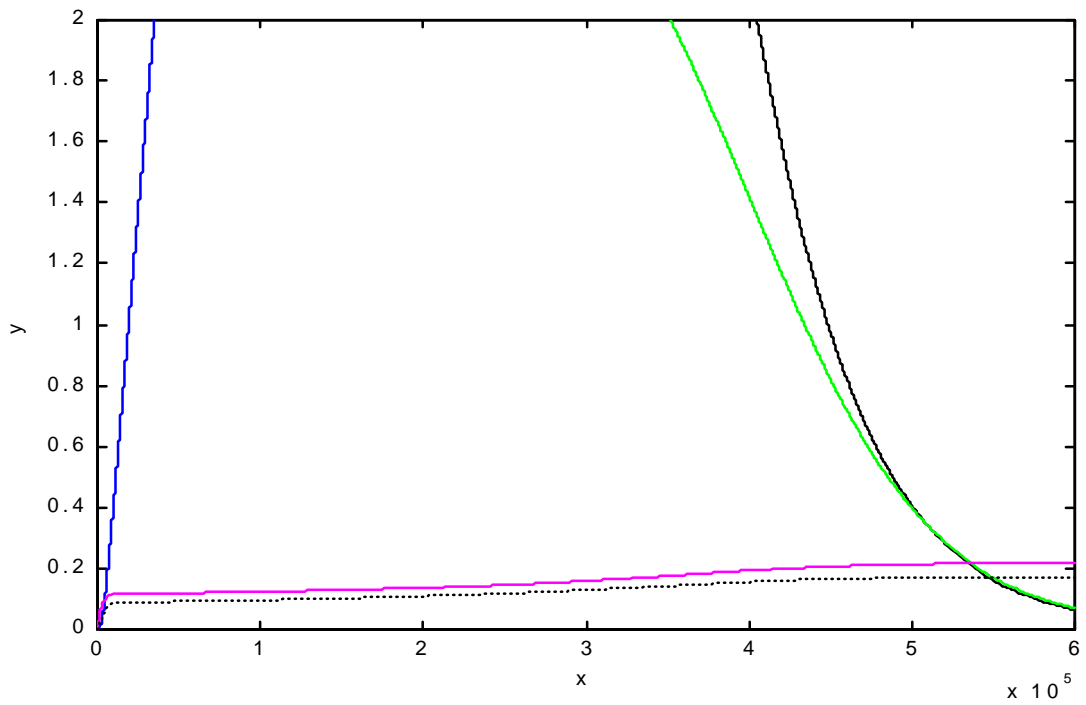
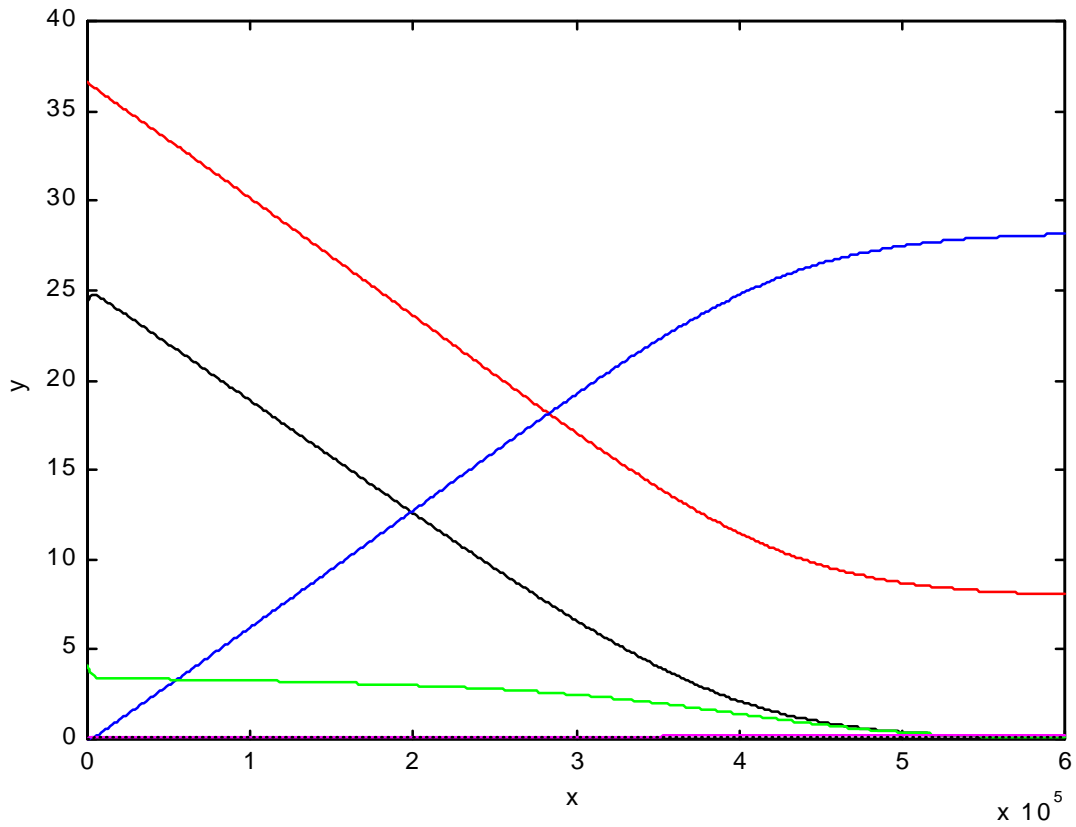
sysodeinput.m

added to sysodeinput.m from part (a) the following lines, after calculation of rate constants.

```
rhomax = 2.71;  
part = 'b';  
if (strcmp(part,'b') == 1)  
    fact = 1 - (As + Bs + Cs)/(rhomax*Area); % part (b)  
else  
    fact = 1; %part (a)  
end  
k(1,1) = fact*k(1,1);  
k(2,1) = fact*k(2,1);  
k(4,1) = fact*k(4,1);
```

plots on the next page:





Transient Behavior for part (b). Second plot is a close-up of the first plot.

part (b) - steady state behavior

```
» syseqn(1,[0.0, 10.0, 27.0, 0.0,0.1,0.1])
```

output:

Attempting solution with MATLABs fsolve function

VARIABLE	INPUT	OUTPUT
1	0.0000000e+000	1.0373111e-007
2	1.0000000e+001	7.9221081e+000
3	2.7000000e+001	2.8257188e+001
4	0.0000000e+000	1.4386675e-007
5	1.0000000e-001	2.1789219e-001
6	1.0000000e-001	1.7281174e-001

So, the steady state is

$$\begin{aligned} N_{A(L)} &= 1.04e-7, & N_{A(s)} &= 1.44e-7, \\ N_{B(L)} &= 7.92, & N_{B(s)} &= 0.218, \\ N_{C(L)} &= 28.26, & N_{C(s)} &= 0.173. \end{aligned}$$

syseqninput.m

added to syseqninput.m from part (a) the following lines, after calculation of rate constants.

```
rhomax = 2.71;
part = 'b';
if (strcmp(part,'b') == 1)
    fact = 1 - (As + Bs + Cs)/(rhomax*Area); % part (b)
else
    fact = 1; %part (a)
end
k(1,1) = fact*k(1,1);
k(2,1) = fact*k(2,1);
k(4,1) = fact*k(4,1);
```

Model (b) causes different and slower approach to steady state, because amount adsorbed is limited. The steady states in both parts are similar but vary slightly due to the differences in the rate constants. (The ratio of the rate constants will give the equilibrium constant.)