Midterm Exam (Take home Exam)
ChE 505
Due Monday, November 20, 2000

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 reversible reactions take place

reaction 1: adsorption of A from liquid to solid surface: $A_{(L)} \Leftrightarrow A_{(s)}$
reaction 2: adsorption of B from liquid to solid surface: $B_{(L)} \Leftrightarrow B_{(s)}$
reaction 3: creation of C on surface: $A_{(s)} + B_{(s)} \Leftrightarrow C_{(s)}$
reaction 4: desorption of C from liquid to solid surface: $C_{(L)} \Leftrightarrow C_{(S)}$

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:

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

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

$$\frac{dN_{A_{(s)}}}{dt} = k_1 \frac{N_{A_{(L)}}}{V_L} - k_{-1} \frac{N_{A_{(s)}}}{A_s} - k_3 \frac{N_{A_{(s)}}}{A_s} \frac{N_{B_{(s)}}}{A_s} + k_{-3} \frac{N_{C_{(s)}}}{A_s} \tag{2}$$

$$\frac{dN_{B_{(L)}}}{dt} = -k_2 \frac{N_{B_{(L)}}}{V_L} + k_{-2} \frac{N_{B_{(s)}}}{A_s} \tag{3}$$

$$\frac{dN_{B_{(s)}}}{dt} = k_2 \frac{N_{B_{(L)}}}{V_L} - k_{-2} \frac{N_{B_{(s)}}}{A_s} - k_3 \frac{N_{A_{(s)}}}{A_s} \frac{N_{B_{(s)}}}{A_s} + k_{-3} \frac{N_{C_{(s)}}}{A_s} \tag{4}$$

$$\frac{dN_{C_{(L)}}}{dt} = -k_4 \frac{N_{C_{(L)}}}{V_L} + k_{-4} \frac{N_{C_{(s)}}}{A_s} \tag{5}$$

$$\frac{dN_{C(s)}}{dt} = k_4 \frac{N_{C(L)}}{V_L} - k_{-4} \frac{N_{C(s)}}{A_s} + k_3 \frac{N_{A(s)}}{A_s} \frac{N_{B(s)}}{A_s} - k_{-3} \frac{N_{C(s)}}{A_s} \qquad (6)$$

(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 m^3 and with enough solid catalyst to give A_S = 1.5 m^2. The reactor is run isothermally at T = 400 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. Turn in only plots of these variables (put them on the same plot if their magnitudes are the same), a table with steady state values, and a copy of sysodeinput.m. In the plots and tables, clearly indicate which lines and values correspond to which of the six variables.

(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 $\rho_{max} = 2.71$ 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 their 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 limitation. 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). Is the transient behavior the same? Is the steady state the same? Why or why not?

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.

$$N_{A_{(L)}}(t=0) + N_{A_{(S)}}(t=0) = N_{A_{(L)}}(t) + N_{A_{(S)}}(t) + N_{C_{(L)}}(t) + N_{C_{(S)}}(t) \tag{7}$$

$$N_{B_{(L)}}(t=0) + N_{B_{(S)}}(t=0) = N_{B_{(L)}}(t) + N_{B_{(S)}}(t) + N_{C_{(L)}}(t) + N_{C_{(S)}}(t) \tag{8}$$

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 produce one mole of A (or B) is consumed.