CE 561, Exam 2, December 13, 2000

This exam consists of four questions, each with multiple parts, and each worth 25% of the exam score. You should be careful not to get stuck on one part. If you do not know how to do a problem, move on and return to it if you have time at the end. If you cannot find the numerical answer to a problem, explain how you would find the answer if you had more time or computational resources. Note that a table of integrals is attached at the back of the test.

Carefully explain any assumptions you make, clearly indicate what part of what problem you are working on, and define the symbols that you use. The point value of each sub-part is indicated – budget your effort accordingly. There are 100 points total.
Please use a separate blue book for each problem.
Good luck.

1. The autocatalytic reaction

   A + B → 2B, with rate = kC_AC_B

   is to be carried out in solution in a well-mixed isothermal batch reactor. The rate constant is 0.4 liter mol^{-1} hr^{-1} at the reaction temperature. At the start of each batch, the reactor is filled with a solution containing 2 moles of A per liter and 0.5 moles of B per liter. The reactor volume is 1000 liters. Emptying, cleaning, and re-filling the reactor between batches requires 1 hour.

   (a) Find the **concentrations of species A and B** in the reactor as a function of batch time. (10 pts.)

   (b) Find the **batch time** that maximizes the average production rate of species B. (10 pts.)

   (c) Find the **average production rate** of species B for this optimal batch time. (5 pts.)

(a) The species mole balance equations for the batch reactor are

$$\frac{dC_A}{dt} = -kC_AC_B$$

$$\frac{dC_B}{dt} = kC_AC_B$$

From these or from simple observation of the reaction stoichiometry, we have

$$\frac{dC_A}{dt} = -\frac{dC_B}{dt}$$

$$C_{Ao} - C_A = C_B - C_{Bo}$$

$$C_A + C_B = C_{Ao} + C_{Bo}$$

So, we can re-write the balance on species B as

$$\frac{dC_B}{dt} = k\left(C_{Ao} + C_{Bo} - C_B\right)C_B$$

This is a separable ODE, which can be re-arranged to give

$$\int_{C_{Bo}}^{C_B} \frac{dC_B}{\left(C_{Ao} + C_{Bo} - C_B\right)C_B} = kt$$

We can find the integral on the left-hand-side in the attached table of integrals. This gives

$$\frac{-1}{C_{Ao}+C_{Bo}}\left[\log\left(\frac{C_{Ao}+C_{Bo}-C_B}{C_B}\right)\right]\Bigg|_{C_{Bo}}^{C_B}=kt$$

Or

$$\log\left(\frac{(C_{Ao}+C_{Bo}-C_{Bo})C_B}{(C_{Ao}+C_{Bo}-C_B)C_{Bo}}\right)=\log\left(\frac{C_{Ao}C_B}{(C_{Ao}+C_{Bo}-C_B)C_{Bo}}\right)=(C_{Ao}+C_{Bo})kt$$

$$C_{Ao}C_B=(C_{Ao}+C_{Bo}-C_B)C_{Bo}\exp((C_{Ao}+C_{Bo})kt)$$

$$(C_{Ao}+C_{Bo}\exp((C_{Ao}+C_{Bo})kt))C_B=(C_{Ao}+C_{Bo})C_{Bo}\exp((C_{Ao}+C_{Bo})kt)$$

$$C_B=\frac{(C_{Ao}+C_{Bo})C_{Bo}\exp((C_{Ao}+C_{Bo})kt)}{C_{Ao}+C_{Bo}\exp((C_{Ao}+C_{Bo})kt)}=\frac{(C_{Ao}+C_{Bo})}{1+\left(C_{Ao}/C_{Bo}\right)\exp(-(C_{Ao}+C_{Bo})kt)}$$

$$C_A=C_{Ao}+C_{Bo}-C_B=(C_{Ao}+C_{Bo})\left(1-\frac{1}{1+\left(C_{Ao}/C_{Bo}\right)\exp(-(C_{Ao}+C_{Bo})kt)}\right)$$

$$C_A=(C_{Ao}+C_{Bo})\left(\frac{\left(C_{Ao}/C_{Bo}\right)\exp(-(C_{Ao}+C_{Bo})kt)}{1+\left(C_{Ao}/C_{Bo}\right)\exp(-(C_{Ao}+C_{Bo})kt)}\right)=\frac{C_{Ao}+C_{Bo}}{1+\left(C_{Bo}/C_{Ao}\right)\exp((C_{Ao}+C_{Bo})kt)}$$

Or, with the given values for the rate parameters and initial concentration of *A*,

$$C_B=\frac{2.5}{1+4\exp(-t)}$$

$$C_A=\frac{2.5}{1+0.25\exp(t)}=\frac{10}{4+\exp(t)}$$

with C_A and C_B in moles per liter and t in hours.

(b) The average production rate is the amount produced per batch divided by the total time (including turnaround time between batches) for each batch.

$$prod.\ rate=\frac{V(C_B(t)-C_{Bo})}{t+t_{turnaround}}$$

Putting in the results from part (a) and the given values from the problem statement gives

$$prod.\ rate=\frac{1000}{t+1}\left(\frac{2.5}{1+4\exp(-t)}-0.5\right)\ \text{mol hr}^{-1}=\frac{2000(1-\exp(-t))}{(t+1)(1+4\exp(-t))}\ \text{mol hr}^{-1}$$

$$prod.\ rate=\frac{2000(1-\exp(-t))}{1+t+4\exp(-t)+4t\exp(-t)}\ \text{mol hr}^{-1}$$

We can maximize this by taking the first derivative and setting it equal to zero.

$$\frac{d(prod.\ rate)}{dt} = 2000\frac{\exp(-t)(1+t+4\exp(-t)+4t\exp(-t)) - (1-4\exp(-t)+4\exp(-t)-4t\exp(-t))(1-\exp(-t))}{(1+t+4\exp(-t)+4t\exp(-t))^2}$$

$$\frac{d(prod.\ rate)}{dt} = 2000\frac{\exp(-t)+t\exp(-t)+4\exp(-2t)+4t\exp(-2t)-1+4t\exp(-t)+\exp(-t)-4t\exp(-2t)}{(1+t+4\exp(-t)+4t\exp(-t))^2}$$

$$\frac{d(prod.\ rate)}{dt} = 2000\frac{2\exp(-t)+5t\exp(-t)+4\exp(-2t)-1}{(1+t+4\exp(-t)+4t\exp(-t))^2} = 0$$

Recognizing that this requires the numerator to be equal to zero, and multiplying the numerator by exp(t) gives

$$2+5t+4\exp(-t)-\exp(t)=0$$

This has to be solved numerically. You could plot it and see that it crosses zero between t=2.5 and t=3 to approximately get the root. To solve it by fixed-point iteration, we could make the substitution

$$x=\exp(t)$$

$$t=\log(x)$$

to get

$$2+5\log(x)+4/x-x=0$$

$$x=2+5\log(x)+4/x$$

guessing x = exp(3) = 20.1 and iterating on this leads to x = 16.16, or t = 2.78. Evaluating

$$f(x)=2+5t+4\exp(-t)-\exp(t)$$

at x = 2.75 gives f = 0.363
at x = 2.78 gives f = 0.029
at x = 2.80 gived f = -0.201

So, it appears that we have found a zero of this function near t = 2.78.

(c) Evaluating the production rate at t = 2.78 hr gives

$$prod.\ rate = \frac{2000(1-\exp(-2.78))}{1+2.78+4\exp(-2.78)+4t\exp(-2.78)} = 398 \text{ mol hr}^{-1}$$

we can verify that this is a maximum, rather than a minimum, by also evaluating the production rate at sllightly higher and lower batch times. At t = 2.7 hr, we get a production rate of 397 mol hr^{-1}, and at t = 2.9 hr, we also get a production rate of 397 mol hr^{-1}. So, t = 2.78 hr is the optimal batch time, but the production rate it quite insensitive to the exact value of t. This means that we can just select a convenient batch time near this value. Note that the total time per batch is t + 1 = 3.78 hr.

2. The irreversible, liquid phase, exothermic, first-order isomerization reaction

   A $\rightarrow$ B, with rate = kC_A

   is to be carried out in a perfectly mixed adiabatic stirred tank reactor. Pure A is fed to the reactor. The rate parameters, reactor properties, and physical properties are as follows:

   Feed temperature = 300 K
   Density of A = Density of B = 1.04 g/cm^3
   Molecular Weight of A = Molecular Weight of B = 104 g/mol
   Specific Heat of A = Specific Heat of B = 2 J g^{-1} K^{-1}
   Heat of reaction = -41.6 kJ/mol
   Rate constant = k = 1$\times$10^5 exp(-5000/T) min^{-1}
   Feed flow rate = 100 liters min^{-1}
   Reactor volume = 500 liters

   (a) Write the steady-state material and energy balances for this system and solve them to find the **steady-state temperature and composition** in the reactor. Be sure to solve for all possible steady states. (10 pts.)

   (b) Carry out a **linear stability analysis** for each set of steady-state operating conditions found in part (a) to show which are **stable** and which are **unstable**. (15 pts.)

At steady state, the species mole balances and the enthalpy balance are

In – out + production = 0

$$Q_o\left(C_{Ao}-C_A\right)+V\left(-kC_A\right)=0$$

$$Q_o\left(0-C_B\right)+V\left(k_1C_A\right)=0$$

$$\rho\hat{C}_pQ_o\left(T_o-T\right)+\left(-\Delta H\right)V\left(kC_A\right)=0$$

Let $J=\dfrac{-\Delta H}{\rho\hat{C}_p}$, and $\tau=\dfrac{V}{Q_o}$

then we have

$$C_{Ao}-C_A=\tau kC_A$$

$$C_B=\tau kC_A$$

$$T_o-T=J\tau kC_A$$

from which we have the usual relationships for a single reaction in an adiabatic reactor

$$C_B=C_{Ao}-C_A$$

$$T=T_o+J\left(C_{Ao}-C_A\right)$$

Substituting these, as well as well as the Arrhenius expression for the rate constant, into the species mole balance for A gives

$$C_{Ao}-C_A=\tau A\exp\left(\frac{-E/R}{T_o+J\left(C_{Ao}-C_A\right)}\right)C_A$$

The residence time is 500 liters/100 liters/min = 5 minutes.

J is (41600 J/mol)/(2 J g^{-1} K^{-1} * 1040 g/liter) = 20 K liter mol^{-1}.

C_{Ao} is equal to the density divided by the molecular weight = (1040 g/liter)/(130 g/mol)

C_{Ao} = 10 mol liter^{-1}

Putting in these and the rest of the numbers gives

$$10 - C_A = 5\left(10^5 \exp\left(\frac{-5000}{300 + 20(10 - C_A)}\right)C_A\right)$$

$$C_A - 10 + 5\times10^5 \exp\left(\frac{-250}{15 + 10 - C_A}\right)C_A = 0$$

$$C_A\left(1 + 5\times10^5 \exp\left(\frac{-250}{25 - C_A}\right)\right) = 10$$

$$C_A = \frac{10}{1 + 5\times10^5 \exp\left(\frac{-250}{25 - C_A}\right)}$$

The possible range of C_A is 0 to 10 mol/liter. Plotting the above expression by hand, or using your calculator, shows that this has solutions near

C_A = 0.5 mol liter^{-1}, C_A = 7.2 mol liter^{-1}, C_A = 9.6 mol liter^{-1}

We could try to get more precise values for these by iterating on

$$C_A = \frac{10}{1 + 5\times10^5 \exp\left(\frac{-250}{25 - C_A}\right)}$$

or some similar rearrangement of the equation. Iterating on this one converges nicely to

C_A = 0.516 mol liter^{-1} and C_A = 9.553 mol liter^{-1}

But does not converge to the solution near C_A = 7.2 mol liter^{-1}

However, with some trial and error, we can resolve this one to be

C_A = 7.275 mol liter^{-1}

Using this to evaluate the concentrations and temperatures shows that the three sets of steady-state operating conditions are:

(1) C_A = 0.516 mol liter^{-1}, C_B = 9.484 mol liter^{-1}, T = 490 K
(2) C_A = 7.275 mol liter^{-1}, C_B = 2.725 mol liter^{-1}, T = 355 K
(3) C_A = 9.553 mol liter^{-1}, C_B = 0.447 mol liter^{-1}, T = 309 K

(b) To analyze the stability of the steady-state operating conditions found in part (a), we will write the transient balance equations, find their Jacobian, and evaluate its eigenvalues at each set of operating conditions.

The transient balances are

$$V\frac{dC_A}{dt} = Q_o\left(C_{Ao} - C_A\right) + V\left(-kC_A\right)$$

$$V\frac{dC_B}{dt} = Q_o\left(0 - C_B\right) + V\left(kC_A\right)$$

$$\rho\hat{C}_p V\frac{dT}{dt} = \rho\hat{C}_p Q_o\left(T_o - T\right) + \left(-\Delta H\right)V\left(kC_A\right)$$

or in terms of the parameters $J = \frac{-\Delta H}{\rho\hat{C}_p}$, and $\tau = \frac{V}{Q_o}$, pre-exponential factor and activation energy

$$\frac{dC_A}{dt} = \frac{C_{Ao} - C_A}{\tau} - A\exp\left(\frac{-E/R}{T}\right)C_A$$
$$\frac{dC_B}{dt} = \frac{C_B}{\tau} + A\exp\left(\frac{-E/R}{T}\right)C_A$$
$$\frac{dT}{dt} = \frac{T_o - T}{\tau} + J\left(A\exp\left(\frac{-E/R}{T}\right)C_A\right)$$

and substituting in the numbers

$$\frac{dC_A}{dt} = \frac{10 - C_A}{5} - 10^5\exp\left(\frac{-5000}{T}\right)C_A$$
$$\frac{dC_B}{dt} = \frac{C_B}{5} + 10^5\exp\left(\frac{-5000}{T}\right)C_A$$
$$\frac{dT}{dt} = \frac{300 - T}{5} + 2\times10^6\exp\left(\frac{-5000}{T}\right)C_A$$

taking all 9 partial derivatives, the Jacobian of this set of equations is

$$\underline{\underline{J}} = \begin{bmatrix} -\frac{1}{5} - 10^5\exp\left(\frac{-5000}{T}\right) & 0 & -\frac{5000}{T^2}\times10^5\exp\left(\frac{-5000}{T}\right)C_A \\ 10^5\exp\left(\frac{-5000}{T}\right) & -\frac{1}{5} & \frac{5000}{T^2}\times10^5\exp\left(\frac{-5000}{T}\right)C_A \\ 2\times10^6\exp\left(\frac{-5000}{T}\right) & 0 & -\frac{1}{5} + \frac{5000}{T^2}\times2\times10^6\exp\left(\frac{-5000}{T}\right)C_A \end{bmatrix}$$

Now, we must evaluate this at each steady-state solution and then find its eigenvalues.

For C_A = 0.516 mol liter^{-1}, C_B = 9.484 mol liter^{-1}, T = 490 K, k = 3.70 hr^{-1}, from which

$$\underline{\underline{J}} = \begin{bmatrix} -3.9 & 0 & -0.0398 \\ 3.7 & -0.2 & 0.0398 \\ 74 & 0 & 0.595 \end{bmatrix}$$

If you have a calculator that calculates eigenvalues, you can use it to find that the eigenvalues of this matrix are

λ_1 = -0.200, λ_2 = -3.10, λ_3 = -0.201

Each of these eigenvalues is negative, so this steady state is **stable**

For C_A = 7.275 mol liter^{-1}, C_B = 2.725 mol liter^{-1}, T = 355 K, k = 0.0764 hr^{-1}, from which

$$\underline{\underline{J}} = \begin{bmatrix} -0.2764 & 0 & -0.02205 \\ 0.0764 & -0.2 & 0.02205 \\ 1.528 & 0 & 0.2410 \end{bmatrix}$$

The eigenvalues of this matrix are

λ_1 = -0.200, λ_2 = -0.200, λ_3 = 0.1646

Since one of these is positive, this steady state is **unstable**.

For C_A = 9.553 mol liter^{-1}, C_B = 0.447 mol liter^{-1}, T = 309 K, k = 0.00939 hr^{-1}, from which

$$\underline{\underline{J}} = \begin{bmatrix} -0.2094 & 0 & -0.004696 \\ 0.00939 & -0.2 & 0.004696 \\ 0.1878 & 0 & -0.1061 \end{bmatrix}$$

The eigenvalues of this matrix are

λ_1 = -0.200, λ_2 = -0.200, λ_3 = -0.115

Since all of these are negative, this steady state is **stable**.

3. The reversible, exothermic, first-order reaction A ↔ B is to be carried out in aqueous solution at atmospheric pressure. At 300 K, the forward rate constant is 0.2 min^{-1} and the equilibrium constant is 1.0. The forward activation energy is 9.935 kcal/mol, and the heat of reaction is -10 kcal/mol. The properties of the solution can be assumed to be those of water (C_p = 1 cal g^{-1} K^{-1}, ρ = 1000 kg m^{-3}).

(a) What is the maximum conversion of A to B that can be obtained in an adiabatic reactor with a feed temperature of 300 K and feed concentrations of C_{Ao} = 2.0 mol/liter, C_{Bo} = 0.0 mol/liter? (5 points)

As we have seen in several contexts, in an adiabatic reactor with a single reaction like this, the relationship between the temperature and reactant concentration is given by

$$T - T_o = \frac{-\Delta H}{\rho C_p}\left(C_{Ao} - C_A\right)$$

Putting in the numbers for this case gives

$$T - 300\text{ K} = \frac{10000\text{ cal/mol}}{1000\text{ g/liter } 1\text{ cal/(g K)}}\left(2\text{ mol/liter} - C_A\right)$$

or, with T in K and C_A in mol/liter

$$T = 320 - 10C_A$$

The maximum conversion of A to B is attained when the reaction reaches equilibrium. If K is the equilibrium constant, then

$$K = K_o \exp\left(\frac{-\Delta H}{RT}\right) = \frac{C_{B,eq}}{C_{A,eq}} = \frac{C_{Ao} - C_{A,eq}}{C_{A,eq}}$$

Solving this for $C_{A,eq}$ gives

$$C_{A,eq} = \frac{C_{Ao}}{1+K} = \frac{C_{Ao}}{1 + K_o \exp\left(\frac{-\Delta H}{RT}\right)}$$

At 300 K, the equilibrium constant is 1.0, so

$$K_o \exp\left(\frac{10000}{1.987 * 300}\right) = 1.0$$

from which $K_o = 5.18\times10^{-8}$. Putting this number (and the other known numbers) and the relationship between T and C_A into the equation for the equilibrium concentration gives

$$C_{A,eq} = \frac{2}{1 + 5.18\times10^{-8} \exp\left(\frac{10000}{1.987\left(320 - 10C_{A,eq}\right)}\right)} = \frac{2}{1 + 5.18\times10^{-8} \exp\left(\frac{503}{32 - C_{A,eq}}\right)}$$

This can be solved iteratively to get $C_{A,eq}$ = 1.215 mol/liter. The amount of A converted to B is 2 - 1.215 = 0.785 mol/liter, and the fractional conversion of A to B is 0.785/2 = 0.393, or 39.3%. The temperature at equilibrium is 307.9 K, and the equilibrium constant at this temperature is about 0.65.

(b) What residence time is required to achieve 90% of the maximum conversion found in part (a) in an ideal CSTR with a feed temperature of 300 K and feed concentrations of C_{Ao} = 2.0 mol/liter, C_{Bo} = 0.0 mol/liter? (5 points)

90% of the conversion found in part (a) is attained if 0.9*(.785) = 0.7065 mol/liter of A is converted to B, so the final concentration of A is 2-0.7065 = 1.2935 mol/liter.

The species mole balance for A in an ideal CSTR is

$$C_{Ao} - C_A = \tau r = \tau\left(k_f C_A - k_r C_B\right) = \tau k_f\left(C_A - \frac{1}{K}\left(C_{Ao} - C_A\right)\right)$$

Solving for the residence time in terms of the concentration of A gives

$$C_{Ao} - C_A = \tau r = \tau\left(k_f C_A - k_r C_B\right) = \tau k_f\left(C_A - \frac{1}{K}\left(C_{Ao} - C_A\right)\right)$$

$$\tau = \frac{C_{Ao} - C_A}{k_f\left(C_A - \frac{1}{K}\left(C_{Ao} - C_A\right)\right)}$$

We already found

$$K = 5.18\times10^{-8}\exp\left(\frac{5030}{T}\right)$$

from which

$$\frac{1}{K} = 1.93\times10^{7}\exp\left(\frac{-5030}{T}\right)$$

We have k_f = 0.2 min^{-1} at 300 K, with an activation energy of 9.935 kcal/mol, so

$$k_f(300\text{ K}) = A\exp\left(\frac{-9935}{1.987*300}\right) = 0.2$$

from which $A = 3.46\times10^{6}$ min^{-1}. So we have

$$k_f = 3.46\times10^{6}\exp\left(\frac{-5000}{T}\right)$$

This then gives, for the required residence time,

$$\tau = \frac{C_{Ao} - C_A}{3.46\times10^{6}\exp\left(\frac{-5000}{T}\right)\left(C_A - 1.93\times10^{7}\exp\left(\frac{-5030}{T}\right)\left(C_{Ao} - C_A\right)\right)}$$

Now, we insert into this the expression for T in terms of C_A, and the other numbers to get

$$\tau = \frac{2 - C_A}{3.46\times10^{6}\exp\left(\frac{-500}{32 - C_A}\right)\left(C_A - 1.93\times10^{7}\exp\left(\frac{-503}{32 - C_A}\right)\left(2 - C_A\right)\right)}$$

To achieve C_A = 1.294 mol/liter, we will require a residence time of

$$\tau = \frac{2 - 1.294}{3.46\times10^{6}\exp\left(\frac{-500}{32 - 1.294}\right)\left(1.294 - 1.93\times10^{7}\exp\left(\frac{-503}{32 - 1.294}\right)\left(2 - 1.294\right)\right)} = 9.8\text{ minutes}$$

(c) What residence time is required to achieve 90% of the maximum conversion found in part (a) in an ideal PFTR with a feed temperature of 300 K and feed concentrations of C_{Ao} = 2.0 mol/liter, C_{Bo} = 0.0 mol/liter? (7 points)

The PFTR balance equation for species A can be written as

$$\frac{dC_A}{d\tau} = -r = -k_f\left(C_A - \frac{1}{K}(C_{Ao} - C_A)\right)$$

this is a separable ODE that can be rearranged to get

$$\tau = \int_{C_A}^{C_{Ao}} \frac{dC_A}{k_f\left(C_A - \frac{1}{K}(C_{Ao} - C_A)\right)}$$

Putting all the numbers into this, as in part (b), gives

$$\tau = \int_{1.294}^{2} \frac{dC_A}{3.46\times10^6 \exp\left(\frac{-500}{32 - C_A}\right)\left(C_A - 1.93\times10^7 \exp\left(\frac{-503}{32 - C_A}\right)(2 - C_A)\right)}$$

This can be integrated numerically to get $\tau = 3.08$ minutes.

(d) For an adiabatic reactor with a feed temperature of 300 K C_{Bo} = 0.0 mol/liter, what is the maximum feed concentration of species A (C_{Ao}) for which the reactor contents will not boil no matter how long the residence time is? (8 points)

To avoid boiling, we must keep the reactor temperature below 373 K. So, we want to find the feed concentration for which the adiabatic reaction temperature is 373 K. That is, for what value of C_{Ao} do we have T_{eq} = 373 K. In part (a), had the equilibrium relationship:

$$C_{A,eq} = \frac{C_{Ao}}{1 + K_o \exp\left(\frac{-\Delta H}{RT_{eq}}\right)}$$

Instead of writing T in terms of C_A, we can write C_A in terms of T, as

$$C_A = C_{Ao} + \frac{T - T_o}{\frac{-\Delta H}{\rho C_p}} = C_{Ao} + \frac{T - 300}{10}$$

with T in K and C_A in mol/liter. So, we have

$$C_{Ao} - \frac{T_{eq} - 300}{10} = \frac{C_{Ao}}{1 + 5.18\times10^{-8} \exp\left(\frac{-5030}{T_{eq}}\right)}$$

From here, we can solve for C_{Ao} in terms of T_{eq}. This tells us what feed concentration to start at if we want the equilibrium temperature to be some specified value.

$$C_{Ao} - \frac{T_{eq} - 300}{10} = \frac{C_{Ao}}{1 + 5.18\times10^{-8}\exp\left(\frac{5030}{T_{eq}}\right)}$$

$$C_{Ao}\left(1 - \frac{1}{1 + 5.18\times10^{-8}\exp\left(\frac{5030}{T_{eq}}\right)}\right) = C_{Ao}\left(\frac{5.18\times10^{-8}\exp\left(\frac{5030}{T_{eq}}\right)}{1 + 5.18\times10^{-8}\exp\left(\frac{5030}{T_{eq}}\right)}\right) = \frac{T_{eq} - 300}{10}$$

$$C_{Ao} = \left(\frac{T_{eq} - 300}{10}\right)\left(\frac{1 + 5.18\times10^{-8}\exp\left(\frac{5030}{T_{eq}}\right)}{5.18\times10^{-8}\exp\left(\frac{5030}{T_{eq}}\right)}\right)$$

Evaluating this for T_{eq} = 373 K gives C_{Ao} = 203 mol/liter. This is higher than any real molar concentration in solution, so we do not have to worry about the solution boiling, as long as it is dilute enough to be considered a solution of the reactant in water.

Another way to look at this is as follows: At 373 K, the equilibrium constant is

$$K = 5.18\times10^{-8}\exp\left(\frac{5030}{373}\right) = 0.0372$$

The equilibrium conversion at this temperature can be obtained from

$$K = \frac{C_B}{C_A} = \frac{C_{Ao} - C_A}{C_A} = 0.0372$$

$$1.0372 C_A = C_{Ao}$$

$$C_A = 0.964 C_{Ao}$$

$$C_B = C_{Ao} - C_A = 0.036 C_{Ao}$$

The temperature is related to the concentration by

$$T - T_o = \frac{-\Delta H}{\rho C_p}(C_{Ao} - C_A) = 10(C_{Ao} - C_A) = 0.36 C_{Ao} = 73$$

$$C_{Ao} = 73/0.36 = 203$$

This gives us the same answer of 203 mol/liter. This method is, perhaps, simpler, and makes it more clear that the reason the adiabatic temperature does not go up very fast with increasing feed concentration is because the equilibrium conversion goes down strongly with increasing temperature. So, to get more reaction (and proportionately more temperature rise) we have to add much more than proportionately more reactant.

3. The second order, autocatalytic reaction A + B $\rightarrow$ 2 B to be carried out in an isothermal, partially mixed reactor. Tracer experiments show that the residence time distribution (RTD) for the reactor is well fit by the RTD for two perfectly-mixed tanks in series, with the first tank having a volume equal to twice that of the second tank. The feed to the reactor is a mixture of A and B, with C_{Ao} = 2 mol/liter and C_{Bo} = 0.5 mol/liter. The mean residence time of the reactor is 3 hours. The reaction rate is given by

   $r = 0.4\, C_A\, C_B$ mol liter^{-1} hr^{-1}, with C_A and C_B in moles per liter.

   (a) Derive the **dimensionless residence time distribution function** for two perfectly-mixed tanks in series with the first tank having a volume equal to twice that of the second tank. (5 pts.)
   (b) Compute the **concentrations** of A and B in the reactor effluent using a **segregated flow** model with the RTD derived in part (a). (8 pts.)
   (c) Compute the **concentrations** of A and B leaving the reactor by modeling the reactor as 2 perfectly-mixed **tanks in series** and solving species balance equations for the 2 tanks. (8 pts.)
   (d) **Explain any differences** between the results obtained in parts (b) and (c). (4 pts.)

   Note that the reaction kinetics and feed concentrations are the same as in problem (1), so you may be able to re-use results derived there.

(a) We can consider a tracer experiment in a series of two stirred tanks, the first having a volume 2*V*/3, and the second having a volume *V*/3, so the total volume is *V*. The volumetric flow rate through the tanks is Q_o. At $t = 0$, we put some initial pulse of tracer into the first vessel, then we measure the concentration at the outlet of the second vessel. The fraction of tracer that comes out of the second reactor in some small time interval θ to $\theta + d\theta$ is, by definition, $E(\theta)d\theta$, where $E(\theta)$ is the residence time distribution function. The total amount of tracer that comes out of the second reactor in some small time interval θ to $\theta + d\theta$ is $C(\theta)d\theta$. So, the residence time distribution function is proportional to the concentration of tracer leaving the third tank. We can compute this concentration from the tracer mole balance equations for the two tanks. These are the usual transient mass balances for a CSTR with no reaction term (since the tracer doesn't react).

$$\frac{2V}{3}\frac{dC_1}{dt} = Q_o\left(C_o - C_1\right) = -Q_o C_1$$

$$\frac{V}{3}\frac{dC_2}{dt} = Q_o\left(C_1 - C_2\right)$$

where C_o is the tracer concentration entering the 1st tank (which is zero, as shown), C_1 is the tracer concentration in the first tank and entering the second tank, C_2 is the tracer concentration in the second tank (and leaving the 2nd tank), which is proportional to the residence time distribution function. At $t = 0$, $C_1 = M/(2V/3)$, and $C_2 = C_3 = 0$, where M is the total number of moles of tracer initially put in the reactor. With this definition, $E(\theta) = Q_o C_2(\theta)/\mathrm{M}$. The residence time for the whole system is $\tau = V/Q_o$,. Writing the balances in terms of τ, we get

$$\frac{dC_1}{dt} = -\frac{3}{2\tau}C_1$$

$$\frac{dC_2}{dt} = \frac{3}{\tau}(C_1 - C_2)$$

We can integrate these sequentially, using the initial conditions:

$$C_1 = C_1(t=0)\exp\left(\frac{-3t}{2\tau}\right) = \frac{3M}{2V}\exp\left(\frac{-3t}{2\tau}\right)$$

so

$$\frac{dC_2}{dt} + \frac{3}{\tau}C_2 = \frac{9}{2\tau}\frac{M}{V}\exp\left(\frac{-3t}{2\tau}\right)$$

as usual, we guess that

$$C_2 = f(t)\exp\left(\frac{-3t}{\tau}\right)$$

substituting this into the ODE gives

$$f'(t)\exp\left(\frac{-3t}{\tau}\right) - \frac{3}{\tau}f(t)\exp\left(\frac{-3t}{\tau}\right) + \frac{3}{\tau}f(t)\exp\left(\frac{-3t}{\tau}\right) = \frac{9}{2\tau}\frac{M}{V}\exp\left(\frac{-3t}{2\tau}\right)$$

$$f'(t) = \frac{9}{2\tau}\frac{M}{V}\exp\left(\frac{-3t}{2\tau}\right)\exp\left(\frac{3t}{\tau}\right) = \frac{9}{2\tau}\frac{M}{V}\exp\left(\frac{3t}{2\tau}\right)$$

integrating this gives

$$f(t) = \frac{3M}{V}\exp\left(\frac{3t}{2\tau}\right) + const.$$

$$C_2(t) = \left(\frac{3M}{V}\exp\left(\frac{3t}{2\tau}\right) + const.\right)\exp\left(\frac{-3t}{\tau}\right)$$

using the initial condition that $C_2 = 0$ at $t = 0$ gives

$$C_2(t=0) = 3\frac{M}{V} + const. = 0$$

$$const. = -3\frac{M}{V}$$

$$C_2(t=0) = 3\frac{M}{V} + const. = 0$$

$$C_2(t) = \frac{3M}{V}\left(\exp\left(\frac{3t}{2\tau}\right) - 1\right)\exp\left(\frac{-3t}{\tau}\right) = \frac{3M}{V}\left(\exp\left(\frac{-3t}{2\tau}\right) - \exp\left(\frac{-3t}{\tau}\right)\right)$$

The residence time distribution function is $E(\theta) = Q_o C_2(\theta)/M$

$$E(\theta) = \frac{Q_o}{M}\frac{3M}{V}\left(\exp\left(\frac{-3\theta}{2\tau}\right) - \exp\left(\frac{-3\theta}{\tau}\right)\right) = \frac{3}{\tau}\left(\exp\left(\frac{-3\theta}{2\tau}\right) - \exp\left(\frac{-3\theta}{\tau}\right)\right)$$

If we transform this to the dimensionless residence time distribution, in terms of $\theta' = \theta/\tau$, we have

$$E(\theta') = \tau E(\theta) = 3\left(\exp\left(\frac{-3\theta'}{2}\right) - \exp(-3\theta')\right)$$

(b) For the segregated flow model, we integrate the concentration that would be obtained in a batch reactor after time θ over the residence time distribution

$$\bar{C} = \int_0^\infty C(\theta)E(\theta)d\theta$$

Conveniently, we already solved the batch reactor problem for these exact kinetics and feed composition in problem 1. As shown there, we get

$$C_B = \frac{2.5}{1+4\exp(-t)}$$

$$C_A = \frac{2.5}{1+0.25\exp(t)} = \frac{10}{4+\exp(t)}$$

So, the segregated flow model gives

$$\bar{C} = \int_0^\infty \left(\frac{10}{4+\exp(\theta)}\right)\left(\frac{3}{\tau}\left(\exp\left(\frac{-3\theta}{2\tau}\right) - \exp\left(\frac{-3\theta}{\tau}\right)\right)\right)d\theta$$

For a mean residence time of 3 hours, this gives

$$\bar{C} = \int_0^\infty \left(\frac{10}{4+\exp(\theta)}\right)\left(\exp\left(\frac{-\theta}{2}\right) - \exp(-\theta)\right)d\theta$$

Integrating this numerically using a calculator gives

$$\bar{C} = 0.738 \text{ moles/liter}$$

(c) For this part, we write the steady-state mole balances for A as

$$(C_{Ao} - C_{A1}) = \frac{2\tau}{3}kC_{A1}C_{B1} = \frac{2\tau}{3}kC_{A1}(C_{Ao} + C_{Bo} - C_{A1})$$

$$(C_{A1} - C_{A2}) = \frac{\tau}{3}kC_{A2}(C_{Ao} + C_{Bo} - C_{A2})$$

plugging in the numbers gives

$$(2 - C_{A1}) = 0.8C_{A1}(2.5 - C_{A1})$$

$$0.8C_{A1}^2 - 3C_{A1} + 2 = 0$$

$$C_{A1} = 0.867 \text{ moles/liter}$$

$$(0.867 - C_{A2}) = 0.4C_{A2}(2.5 - C_{A2})$$

$$0.4C_{A2}^2 - 2C_{A2} + 0.867 = 0$$

$$C_{A2} = 0.479 \text{ moles/liter}$$

(d) The segregated flow model predicts substantially higher reactant concentration, or substantially lower extent of reaction, because it neglects micromixing. In the segregated flow model, the reaction, on average, takes place at lower reactant conversion than in the reactor model, where in each reactor the reaction takes place at the concentration in that tank. Usually, this causes the segregated flow model to predict higher extent of reaction than models that include micromixing. However, because this reaction is autocatalytic, the reaction rate actually increases with increasing extent of reaction (up to a point). It happens that in the CSTR, the reaction takes place at concentrations where the rate is relatively high.