CE 561, Exam 2, December 15, 2006

This exam consists of 3 questions, each with multiple parts. 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 ALL 3 PROBLEMS INVOLVE THE SAME REACTION

You may use a calculator and a single letter-size sheet (2-sided) of notes to aid you on this exam. You may not exchange notes with or otherwise consult your fellow students. If you talk to your fellow students during the exam, I will assume that you are cheating, you will be asked to leave, and you will fail the exam.

You will have 2 hours and 50 minutes to complete the exam. Please use a separate blue book for each exam problem. Carefully explain any assumptions you make, label what part of what problem you are working on, and define the symbols that you use. The point value of each part is indicated – budget your effort accordingly. There are 100 points total.

Good Luck!

1. The reversible, exothermic reaction

   A + B → C + D, with rate = $k_1 C_A C_B - k_2 C_C C_D$

   is to be carried out in solution in a well-mixed **adiabatic** batch reactor. At the start of each batch, the reactor contains 100 L of a solution of A and B at a concentration of 5 mol per liter ($C_{Ao} = C_{Bo} = 5$ mol/L) and a temperature of 300 K. Emptying, cleaning, and re-filling the reactor between batches requires 15 minutes. The reactor contents have a density of 1 kg per liter and a specific heat of 4200 J/(kg K). The forward and reverse rate constants are given by

   $k_1 = 5\times10^4 \exp(-5000/T)$ L/(mol min)

   $k_2 = 10^{11} \exp(-11000/T)$ L/(mol min)

   where T is the temperature in Kelvins.

   (a) Write the species mole balance and energy balance equations for the reactor and derive relationships that allow you to write the temperature and all species concentrations in terms of a single concentration or conversion variable. (10 pts.)

   The species mole balances are

$$\frac{dC_A}{dt} = -r = -k_1 C_A C_B + k_2 C_C C_D$$

$$\frac{dC_B}{dt} = -r = -k_1 C_A C_B + k_2 C_C C_D$$

$$\frac{dC_C}{dt} = r = k_1 C_A C_B - k_2 C_C C_D$$

$$\frac{dC_D}{dt} = r = k_1 C_A C_B - k_2 C_C C_D$$

And the energy balance is

$$\frac{dT}{dt} = \frac{-\Delta H}{\rho \hat{C}_p} r = \frac{-\Delta H}{\rho \hat{C}_p}\left(k_1 C_A C_B - k_2 C_C C_D\right)$$

Adding all four species balances, we obtain

$$\frac{d}{dt}\left(C_A + C_B + C_C + C_D\right) = 0$$

From which $C_A + C_B + C_C + C_D = C_{Ao} + C_{Bo} + C_{Co} + C_{Do} = C_{Ao} + C_{Bo} = 10 \text{ mol/L}$

Likewise, subtracting the *B* mole balance from the *A* mole balance gives

$$\frac{d}{dt}\left(C_A - C_B\right) = 0$$

From which $C_A - C_B = C_{Ao} - C_{Bo} = 0$, or $C_A = C_B$.

And subtracting the *D* mole balance from the *C* mole balance gives

$$\frac{d}{dt}\left(C_C - C_D\right) = 0$$

From which $C_C - C_C = C_{Co} - C_{Do} = 0$, or $C_C = C_D$.

So, we can write:

$$C_A + C_B + C_C + C_D = 2C_A + 2C_C = 10 \text{ mol/L}$$

From which $C_C = C_D = 5 - C_A$ mol/L.

If we define the conversion *x* as

$$x = \frac{C_{Ao} - C_A}{C_{Ao}}$$

Then we have

$$C_A = C_B = C_{Ao}\left(1 - x\right) = 5\left(1 - x\right) \quad \text{mol/L}$$

And $\qquad C_C = C_D = C_{Ao} x = 5x \quad \text{mol/L}$

This is one way of writing all of the concentrations in terms of a single conversion variable. Likewise, we can combine the species A mole balance with the energy balance to obtain

$$\frac{dT}{dt} = \frac{-\Delta H}{\rho \hat{C}_p} r = \frac{-\Delta H}{\rho \hat{C}_p}\left(-\frac{dC_A}{dt}\right) = \frac{\left(-\Delta H\right) C_{Ao}}{\rho \hat{C}_p}\left(\frac{dx}{dt}\right)$$

From which

$$T = T_o + \frac{\left(-\Delta H\right) C_{Ao}}{\rho \hat{C}_p} x$$

The heat of reaction is given by the difference between the forward and reverse activation energies, so $\Delta H = R$*(5000 – 11000) = -49900 J/(mol K). Combining this with C_{Ao} = 5 mol/L, ρ = 1 kg/L, and C_p = 4200 J/(kg K) gives

$$\frac{\left(-\Delta H\right) C_{Ao}}{\rho \hat{C}_p} = \left(\frac{49877 * 5}{1 * 4200}\right) = 59.4 \text{ K}$$

So, $T = 300 + 59.4x$

(b) Compute the maximum conversion of the reactants that can be obtained in this adiabatic batch reactor for the conditions given. (10 pts.)

The equilibrium conversion is attained when the net reaction rate is zero. Thus, we want to set $k_1 C_A C_B - k_2 C_C C_D = 0$. Substituting into this the expressions for the rate constants in terms of T gives

$5\times10^4 \exp(-5000/T)\, C_A C_B = 10^{11} \exp(-11000/T)\, C_C C_D$

Writing the temperature and all of the concentrations in terms of the fractional conversion x gives

$$5\times10^4 \exp\left(\frac{-5000}{300+59.4x}\right)*\left(5(1-x)\right)^2 = 10^{11}\exp\left(\frac{-11000}{300+59.4x}\right)*(5x)^2$$

$$x = (1-x)\sqrt{5\times10^{-7}\exp\left(\frac{6000}{300+59.4x}\right)} = 7.07\times10^{-4}(1-x)\exp\left(\frac{3000}{300+59.4x}\right)$$

Iterating on the above form of the equation did not converge to an answer. So, it can be rearranged as

$$1-x = 1414.2x\exp\left(\frac{-3000}{300+59.4x}\right)$$

$$x = 1-1414.2x\exp\left(\frac{-3000}{300+59.4x}\right)$$

Iterating on this, starting from a guess of $x = 0.5$ rapidly converges to $x = 0.799$.

So, the maximum conversion of the reactants is about 80%. The temperature for this maximum conversion is 300 + 59.4*0.8 = 347.5 K.

(c) Compute the batch time required to convert 50% of the reactants to products. Even if you cannot evaluate this numerically, you should be able to write a single integral that, if evaluated, would give you the numerical answer.

If we start from the species mole balance on A, and then re-write everything in terms of the conversion variable x, we get

$$\frac{dC_A}{dt} = \frac{d}{dt}\left(C_{Ao}(1-x)\right) = -C_{Ao}\frac{dx}{dt} = -k_1 C_A C_B + k_2 C_C C_D$$

$$\frac{dx}{dt} = \frac{1}{C_{Ao}}\left(5\times10^4\exp\left(\frac{-5000}{T}\right)C_A C_B - 10^{11}\exp\left(\frac{-11000}{T}\right)C_C C_D\right)$$

$$\frac{dx}{dt} = \frac{1}{5}\left(5\times10^4\exp\left(\frac{-5000}{300+59.4x}\right)\left(5(1-x)\right)^2 - 10^{11}\exp\left(\frac{-11000}{300+59.4x}\right)(5x)^2\right)$$

$$\frac{dx}{dt} = 2.5\times10^5\exp\left(\frac{-5000}{300+59.4x}\right)(1-x)^2 - 5\times10^{11}\exp\left(\frac{-11000}{300+59.4x}\right)x^2$$

Rearranging this and (formally) integrating from a conversion of 0 to 0.5, we have

$$t = \int_0^{0.5}\frac{dx}{2.5\times10^5\exp\left(\frac{-5000}{300+59.4x}\right)(1-x)^2 - 5\times10^{11}\exp\left(\frac{-11000}{300+59.4x}\right)x^2}$$

If you have a calculator that does numerical integrals, you can evaluate this to obtain a batch time of 29.7 minutes.

(d) Show, *in detail*, how you would find the batch time that maximizes the average production rate of the reaction products. You do not have to find the actual numerical solution. (10 pts.)

The average production rate is the number of moles of C or D produced per batch, divided by the total batch time (including the time required to clean and re-fill the reactor). The concentration of C in the product is $C_C = C_{Ao}x = 5x$ mol/liter. So the number of moles of C produced per batch is $N_C = VC_C$ = 100 liters * $5x$ mol/liter = $500x$ moles per batch. The reaction time required to attain a given conversion was found in part c:

$$\theta_R = \int_0^x \frac{dx}{2.5\times10^5 \exp\left(\frac{-5000}{300+59.4x}\right)(1-x)^2 - 5\times10^{11}\exp\left(\frac{-11000}{300+59.4x}\right)x^2} \text{ minutes}$$

So, the total batch time is

$$\theta_T = \theta_R + \theta_O = \int_0^x \frac{dx}{2.5\times10^5 \exp\left(\frac{-5000}{300+59.4x}\right)(1-x)^2 - 5\times10^{11}\exp\left(\frac{-11000}{300+59.4x}\right)x^2} + 15$$

The production rate is therefore given, in terms of x, by

$$PR = \frac{500x}{\int_0^x \frac{dx}{2.5\times10^5 \exp\left(\frac{-5000}{300+59.4x}\right)(1-x)^2 - 5\times10^{11}\exp\left(\frac{-11000}{300+59.4x}\right)x^2} + 15}$$

We actually want to maximize PR with respect to the batch time θ_R. However, this is the same as maximizing it with respect to x. To see this, note that because x is a function of θ_R, we can write (using the chain rule from calculus)

$$\frac{\partial(PR)}{\partial\theta_R} = \frac{\partial(PR)}{\partial x}\frac{\partial x}{\partial\theta_R}$$

To maximize the production rate, we want to find where this is equal to zero. Since x is a monatonically increasing function of batch time, we know that $\frac{\partial x}{\partial\theta_R}$ is positive (non-zero) for all finite times. So, we will only have $\frac{\partial(PR)}{\partial\theta_R} = 0$ if we have $\frac{\partial(PR)}{\partial x} = 0$

So, we can find the batch time that maximizes the production rate by taking the derivative of the above expression for the production rate with respect to x, setting that equal to zero, and solving for x. Once we have that optimal value of x (which we can call x*), then we can evaluate the corresponding optimal reaction time from

$$\theta_R^* = \int_0^{x^*} \frac{dx}{2.5\times10^5 \exp\left(\frac{-5000}{300+59.4x}\right)(1-x)^2 - 5\times10^{11}\exp\left(\frac{-11000}{300+59.4x}\right)x^2}$$

We can formally take the derivative of the production rate with respect to x as follows:

$$\frac{\partial(PR)}{\partial x}=500\frac{\int_0^x \frac{dx}{2.5\times10^5\exp\left(\frac{-5000}{300+59.4x}\right)(1-x)^2-5\times10^{11}\exp\left(\frac{-11000}{300+59.4x}\right)x^2}+15-\frac{1}{2.5\times10^5\exp\left(\frac{-5000}{300+59.4x}\right)(1-x)^2-5\times10^{11}\exp\left(\frac{-11000}{300+59.4x}\right)x^2}}{\left(\int_0^x \frac{dx}{2.5\times10^5\exp\left(\frac{-5000}{300+59.4x}\right)(1-x)^2-5\times10^{11}\exp\left(\frac{-11000}{300+59.4x}\right)x^2}+15\right)^2}$$

Setting this equal to zero gives

$$\int_0^x \frac{dx}{2.5\times10^5\exp\left(\frac{-5000}{300+59.4x}\right)(1-x)^2-5\times10^{11}\exp\left(\frac{-11000}{300+59.4x}\right)x^2}+15-\frac{1}{2.5\times10^5\exp\left(\frac{-5000}{300+59.4x}\right)(1-x)^2-5\times10^{11}\exp\left(\frac{-11000}{300+59.4x}\right)x^2}=0$$

This could be plotted as a function of x, and the value of x that satisfied the equation could be identified. The optimal batch time and production rate would then be evaluated using the equations given above.

An equally valid approach would be to numerically integrate

$$\frac{dx}{dt}=2.5\times10^5\exp\left(\frac{-5000}{300+59.4x}\right)(1-x)^2-5\times10^{11}\exp\left(\frac{-11000}{300+59.4x}\right)x^2$$

To obtain x as a function of batch time (as a table of numbers or a graph). Then the production rate can be written as

$$PR=\frac{500x(\theta_R)}{\theta_R+15}$$

Where $x(\theta_R)$ is the numerically-evaluated conversion as a function of batch time. Then

$$\frac{\partial(PR)}{\partial\theta_R}=500\frac{(\theta_R+15)\frac{dx}{d\theta_R}-x(\theta_R)}{(\theta_R+15)^2}$$

Setting this equal to zero and substituting back the original expression for the change of x with time gives

$$(\theta_R+15)\left(2.5\times10^5\exp\left(\frac{-5000}{300+59.4x}\right)(1-x)^2-5\times10^{11}\exp\left(\frac{-11000}{300+59.4x}\right)x^2\right)=x$$

A list of numerically evaluated values of x vs θ_R could be used to identify the value of θ_R where this is most nearly satisfied.

2. The same reaction described in problem 1 is to be carried out in a continuous, adiabatic perfectly mixed flow reactor (a CSTR). The reactor volume is 100 L, the feed stream contains 15 mol/L each of A and B and contains no C or D. The feed flow rate is 85 liters per minute. Other parameters are the same as in the previous problem.

(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. (15 pts.)

The steady-state material and energy balances are

$$Q(C_{Ao} - C_A) = Vr$$
$$Q(C_{Bo} - C_B) = Vr$$
$$Q(C_C) = Vr$$
$$Q(C_D) = Vr$$
$$\rho \hat{C}_p Q(T - T_o) = (-\Delta H) Vr$$

These can be combined in the same way as in problem 1 to obtain the same relationships between the variables. So, we can again write:

$$C_A = C_B = C_{Ao}(1-x) = 15(1-x) \quad \text{mol/L}$$
$$C_C = C_D = C_{Ao}x = 15x \quad \text{mol/L}$$
$$T = T_o + \frac{(-\Delta H) C_{Ao}}{\rho \hat{C}_p} x = 300 + \frac{49900 * 15}{1 * 4200} x = 300 + 178.2x$$

Then, writing the species A mole balance in terms of x, we have

$$QC_{Ao}x = Vr = V\left(5\times10^4 \exp\left(\frac{-5000}{T}\right) C_A C_B - 10^{11} \exp\left(\frac{-11000}{T}\right) C_C C_D\right)$$
$$85 * 15x = 100\left(5\times10^4 \exp\left(\frac{-5000}{300+178.2x}\right)(15(1-x))^2 - 10^{11} \exp\left(\frac{-11000}{300+178.2x}\right)(15x)^2\right)$$
$$1275x - 1.125\times10^9 \exp\left(\frac{-5000}{300+178.2x}\right)(1-x)^2 + 2.25\times10^{15} \exp\left(\frac{-11000}{300+178.2x}\right)x^2 = 0$$

This can be solved iteratively by rearranging it in different ways, or by using a 'solve' function on your calculator. Using the 'solve' function on my calculator, I obtained solutions of x = 0.1185, x = 0.2725, and x = 0.4229. In terms of the concentrations and temperature, these correspond to

(1) $C_A = C_B$ = 13.22 mol/L, $C_C = C_D$ = 1.78 mol/L, and T = 321.1 K
(2) $C_A = C_B$ = 10.91 mol/L, $C_C = C_D$ = 4.09 mol/L, and T = 348.6 K
(3) $C_A = C_B$ = 8.66 mol/L, $C_C = C_D$ = 6.34 mol/L, and T = 375.4 K

(b) Describe, in detail, how you would 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. You do not need to actually work out the numbers, but you should write out the equations. (10 pts.)

To do the stability analysis, we want to evaluate the eigenvalues of the Jacobian of the transient balance equations at the steady state conditions we found in (a). The transient balance equations are

$$\frac{dC_A}{dt} = \frac{Q}{V}\left(C_{Ao} - C_A\right) - r = 0.85\left(15 - C_A\right) - 5\times10^4 \exp\left(\frac{-5000}{T}\right)C_A C_B + 10^{11}\exp\left(\frac{-11000}{T}\right)C_C C_D$$

$$\frac{dC_B}{dt} = \frac{Q}{V}\left(C_{Bo} - C_B\right) - r = 0.85\left(15 - C_B\right) - 5\times10^4 \exp\left(\frac{-5000}{T}\right)C_A C_B + 10^{11}\exp\left(\frac{-11000}{T}\right)C_C C_D$$

$$\frac{dC_C}{dt} = -\frac{Q}{V}C_C + r = -0.85C_C + 5\times10^4 \exp\left(\frac{-5000}{T}\right)C_A C_B - 10^{11}\exp\left(\frac{-11000}{T}\right)C_C C_D$$

$$\frac{dC_D}{dt} = -\frac{Q}{V}C_C + r = -0.85C_D + 5\times10^4 \exp\left(\frac{-5000}{T}\right)C_A C_B - 10^{11}\exp\left(\frac{-11000}{T}\right)C_C C_D$$

$$\frac{dT}{dt} = \frac{Q}{V}\left(T_o - T\right) + \frac{\left(-\Delta H\right)}{\rho\hat{C}_p}r = 0.85\left(300 - T\right) + 178.2*\left(5\times10^4 \exp\left(\frac{-5000}{T}\right)C_A C_B - 10^{11}\exp\left(\frac{-11000}{T}\right)C_C C_D\right)$$

To do the full stability analysis, using all 5 equations and therefore considering all possible perturbations, we would construct the 5 by 5 Jacobian matrix containing the derivatives of each of these equations with respect to each of the 5 solution variables (C_A, C_B, C_C, C_D, and T).

Alternatively, we might consider only perturbations that are consistent with the stoichiometry of the reaction and the feed concentrations, so that we can write all of the concentrations in terms of the extent of reaction used in the previous part. In that case, we would write:

$$\frac{d}{dt}\left(15\left(1-x\right)\right) = 0.85*15x - 5\times10^4 \exp\left(\frac{-5000}{T}\right)\left(15\left(1-x\right)\right)^2 + 10^{11}\exp\left(\frac{-11000}{T}\right)\left(15x\right)^2$$

$$\frac{dT}{dt} = 0.85\left(300 - T\right) + 178.2*\left(5\times10^4 \exp\left(\frac{-5000}{T}\right)\left(15\left(1-x\right)\right)^2 - 10^{11}\exp\left(\frac{-11000}{T}\right)\left(15x\right)^2\right)$$

or

$$\frac{dx}{dt} = -0.85x + 7.5\times10^5 \exp\left(\frac{-5000}{T}\right)\left(1-x\right)^2 - 1.5\times10^{12}\exp\left(\frac{-11000}{T}\right)x^2$$

$$\frac{dT}{dt} = 0.85\left(300 - T\right) + 2.00\times10^9 \exp\left(\frac{-5000}{T}\right)\left(1-x\right)^2 - 4.01\times10^{15}\exp\left(\frac{-11000}{T}\right)x^2$$

From these, we could construct the 2 by 2 Jacobian, which is

$$\underline{\underline{J}} = \begin{bmatrix} -0.85 - 1.5\times10^6 \exp\left(-5000/T\right)\left(1-x\right) - 3.0\times10^{12}\exp\left(-11000/T\right)x & \left(\frac{5000}{T^2}\right)7.5\times10^5 \exp\left(-5000/T\right)\left(1-x\right)^2 - \left(\frac{11000}{T}\right)1.5\times10^{12}\exp\left(\frac{-11000}{T}\right)x^2 \\ -4.00\times10^9 \exp\left(-5000/T\right)\left(1-x\right) - 8.02\times10^{15}\exp\left(-11000/T\right)x & -0.85 + \left(\frac{5000}{T^2}\right)2.00\times10^9 \exp\left(-5000/T\right)\left(1-x\right)^2 - \left(\frac{11000}{T}\right)4.01\times10^{15}\exp\left(\frac{-11000}{T}\right)x^2 \end{bmatrix}$$

In either approach, evaluating the Jacobian at each steady state, then determining its eigenvalues would complete the stability analysis. If the real parts of ALL of the eigenvalues of the Jacobian are negative, then the steady state is stable with respect to infinitesimal perturbations. If any eigenvalue has a positive real part, then it is unstable. Based on our experience with such problems, we can be pretty confident that the high and low conversion steady states will be stable, while the middle one will be unstable.

If we do the analysis using all 5 equations, then the stability being tested is with independent perturbations in the temperature and all concentrations. If we only use two equations, the stability being tested is only with respect to perturbations in temperature and perturbations in concentration that are consistent with the feed concentrations and the reaction stoichiometry.

3. The same reaction treated in the previous two problems is 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 equally-sized, perfectly-mixed tanks in series. The total reactor volume is 200 L, the feed stream contains 1 mol/L each of A and B and contains no C or D. The feed flow rate is 100 liters per minute. The reactor temperature is 413.5 K, and at this temperature, $k_1 = k_2 = 0.280$ L/(mol min).

   (a) Derive the dimensionless residence time distribution function for two equally-sized perfectly-mixed tanks in series. (10 pts.)

   (a) We can consider a tracer experiment in a series of two identical stirred tanks, each having a volume $V/2$, 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 second 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 of volume $V/2$ with no reaction term (since the tracer doesn't react).

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

$$\frac{V}{2}\frac{dC_2}{dt} = Q_o\left(C_1 - C_2\right)$$

   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, and C_2 is the tracer concentration in the second tank (and leaving the second tank), which is proportional to the residence time distribution function. At $t = 0$, $C_1 = M/(V/3)$, and $C_2 = 0$, 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

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

$$\frac{dC_2}{dt} = \frac{2}{\tau}\left(C_1 - C_2\right)$$

   We can integrate these sequentially, using the initial conditions:

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

   so

$$\frac{dC_2}{dt}+\frac{2}{\tau}C_2=\frac{4}{\tau}\frac{M}{V}\exp\left(\frac{-2t}{\tau}\right)$$

as usual, we guess that

$$C_2=f(t)\exp\left(\frac{-2t}{\tau}\right)$$

substituting this into the ODE gives

$$f'(t)\exp\left(\frac{-2t}{\tau}\right)-\frac{2}{\tau}f(t)\exp\left(\frac{-2t}{\tau}\right)+\frac{2}{\tau}f(t)\exp\left(\frac{-2t}{\tau}\right)=\frac{4}{\tau}\frac{M}{V}\exp\left(\frac{-2t}{\tau}\right)$$

$$f'(t)=\frac{2}{\tau}\frac{M}{V}$$

integrating this gives

$$f(t)=\frac{4t}{\tau}\frac{M}{V}+const.$$

$$C_2=\left(\frac{4t}{\tau}\frac{M}{V}+const.\right)\exp\left(\frac{-2t}{\tau}\right)$$

using the initial condition that $C_2 = 0$ at $t = 0$ shows that the constant of integration is zero, so

$$C_2=\frac{4t}{\tau}\frac{M}{V}\exp\left(\frac{-2t}{\tau}\right)$$

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

$$E(\theta)=\frac{Q_o}{M}\frac{4t}{\tau}\frac{M}{V}\exp\left(\frac{-2t}{\tau}\right)=\frac{4\theta}{\tau^2}\exp\left(\frac{-2\theta}{\tau}\right)$$

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

$$E(\theta')=\tau E(\theta)=\frac{4\theta}{\tau}\exp\left(\frac{-2\theta}{\tau}\right)=4\theta'\exp(-2\theta')$$

(b) Compute the concentrations of A and B in the reactor effluent using a segregated flow model with the RTD for 2 tanks in series. (10 pts.)

This first requires solving the batch reactor equations for the reversible second-order reaction at constant temperature and initial concentrations equal to the feed concentrations. As in problem 1, we can write (noting that the rate constants are fixed numbers for the isothermal reactor):

$$\frac{dC_A}{dt}=\frac{d}{dt}\left(C_{Ao}(1-x)\right)=-C_{Ao}\frac{dx}{dt}=-k_1C_AC_B+k_2C_CC_D$$

$$\frac{dx}{dt}=\frac{1}{C_{Ao}}\left(k_1C_AC_B-k_2C_CC_D\right)$$

$$\frac{dx}{dt}=k_1(1-x)^2-k_2x^2$$

This is a separable equation that can be written as

$$\int_0^x \frac{dx}{k_1\left(1-x\right)^2 - k_2 x^2} = t$$

For these particular conditions, where $k_1 = k_2 = 0.28$ L/(mol s), this becomes

$$\int_0^x \frac{dx}{\left(1-2x+x^2\right)-x^2} = \int_0^x \frac{dx}{1-2x} = 0.28t$$

-1/2 ln(1-2x) = 0.28t

1-2x = exp(-0.56t)

x = 0.5(1 – exp(-0.56t))

$C_A = C_{Ao}(1 - x)$ = 0.5(1+exp(-0.56t))

For the segregated flow model, we integrate the product of this with the residence time distribution function:

$$\bar{C}_A = \int_0^\infty C_A\left(\theta\right)E\left(\theta\right)d\theta = \int_0^\infty 0.5\left(1+\exp\left(-0.56\theta\right)\right)\frac{4\theta}{\tau^2}\exp\left(\frac{-2\theta}{\tau}\right)d\theta$$

The mean residence time is 2 minutes, so

$$\bar{C}_A = 0.5\int_0^\infty \theta\left(1+\exp\left(-0.56\theta\right)\right)\exp\left(-\theta\right)d\theta = 0.5\int_0^\infty \theta\left(\exp\left(-\theta\right)+\exp\left(-1.56\theta\right)\right)d\theta$$

Each of the two terms can be integrated by parts to get

$$\bar{C}_A = 0.5\left(\int_0^\infty \theta\exp\left(-\theta\right)d\theta + \int_0^\infty \theta\exp\left(-1.56\theta\right)d\theta\right)$$

$$\bar{C}_A = 0.5\left(\left[-\exp\left(-\theta\right)\left(\theta+1\right)\right]_0^\infty + \left[-\frac{1}{1.56}\exp\left(-1.56\theta\right)\left(\theta+\frac{1}{1.56}\right)\right]_0^\infty\right)$$

$$\bar{C}_A = 0.5\left(1+\frac{1}{1.56^2}\right) = 0.705$$

(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. (10 pts.)

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

$$\left(C_{Ao} - C_{A1}\right) = \frac{\tau}{2}\left(k_1 C_{A1} C_{B1} - k_2 C_{C1} C_{D1}\right)$$

$$\left(C_{A1} - C_{A2}\right) = \frac{\tau}{2}\left(k_1 C_{A2} C_{B2} - k_2 C_{C2} C_{D2}\right)$$

These can be re-written in terms of the extent of reaction in each tank as

$$\left(C_{Ao} - C_{Ao}\left(1-x_1\right)\right) = C_{Ao}x_1 = \frac{\tau}{2}\left(k_1 C_{Ao}^2\left(1-x_1\right)^2 - k_2 C_{Ao}^2 x_1^2\right)$$

$$\left(C_{Ao}\left(1-x_1\right) - C_{Ao}\left(1-x_2\right)\right) = C_{Ao}\left(x_2 - x_1\right) = \frac{\tau}{2}\left(k_1 C_{Ao}^2\left(1-x_2\right)^2 - k_2 C_{Ao}^2 x_2^2\right)$$

Putting in the numbers (C_{Ao} = 1 mol/L, k_1=k_2 = 0.28 L/(mol min), and τ = 2min, we have

$$x_1 = 0.28\left(\left(1-x_1\right)^2 - x_1^2\right) = 0.28\left(1-2x_1\right)$$

$$\left(x_2 - x_1\right) = 0.28\left(\left(1-x_2\right)^2 - x_2^2\right) = 0.28\left(1-2x_2\right)$$

Solving the first equation gives

$$x_1 = \frac{0.28}{1.56} = 0.1795$$

The second equation then gives

$$\left(x_2 - \frac{0.28}{1.56}\right) = 0.28\left(1-2x_2\right)$$

$$1.56x_2 = 0.28\left(1+\frac{1}{1.56}\right)$$

$$x_2 = 0.2945$$

This corresponds to a reactant concentration of $C_A = 0.7055$

(d) Explain any differences between the results obtained in parts (b) and (c). (5 pts.)

The results in parts (b) and (c) come out exactly the same! This is, perhaps, an unexpected result, because we know in general that the segregated flow reactor model only gives the same result as solving the reactor balances when the kinetics are first order. Since this is a second-order reaction, in general we would expect to get slightly different answers from the approaches used in parts (b) and (c). The reason that the answers are exactly the same in this case is that the forward and reverse rate constants were chosen to be equal. As we saw in solving parts (b) and (c), this actually makes the quadratic (non-linear) terms in the rate expression cancel out exactly. Thus, the overall rate expression becomes linear in the conversion variable. It behaves like a first-order reaction for this very special set of conditions. At temperatures where the forward and reverse rate constants were not equal, this would not be the case, and the answers to part (b) and (c) would differ slightly.