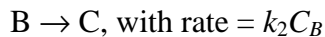
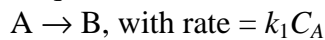


CE 561, Exam 2, December 15, 1999

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.

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. Good luck.

1. The sequential first-order reactions



are to be carried out in solution in a well-mixed isothermal batch reactor. Species B is the desired product, while species C is an undesired by-product. The values of the rate parameters are $k_1 = 0.3 \text{ hr}^{-1}$ and $k_2 = 0.6 \text{ hr}^{-1}$ at the operating temperature. At the start of each batch, the reactor is filled with a solution containing 2 moles of A per liter (and no B or C). The reactor volume is 500 liters. Emptying, cleaning, and re-filling the reactor between batches requires 15 minutes.

(a) Find the **concentration of species 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

$$\frac{dC_A}{dt} = -k_1 C_A$$

$$\frac{dC_B}{dt} = k_1 C_A - k_2 C_B$$

The first equation is our favorite ODE, whose solution is

$$C_A = C_{A0} \exp(-k_1 t)$$

Using a prime to denote differentiation and substituting in the solution for C_A , the second balance equation can be written as

$$C_B' + k_2 C_B = k_1 C_{A0} \exp(-k_1 t)$$

We guess that C_B has the form $C_B = f(t) \exp(-k_2 t)$. Substituting this into the ODE gives

$$f'(t) \exp(-k_2 t) - k_2 f(t) \exp(-k_2 t) + k_2 f(t) \exp(-k_2 t) = k_1 C_{A0} \exp(-k_1 t)$$

which simplifies to

$$f'(t) = k_1 C_{A0} \exp((k_2 - k_1)t)$$

Integrating this gives

$$f(t) = \frac{k_1 C_{A0}}{k_2 - k_1} \exp((k_2 - k_1)t) + \text{Const.}$$

So we have

$$C_B = \frac{k_1 C_{A0}}{k_2 - k_1} \exp(-k_1 t) + \text{Const.} \exp(-k_2 t)$$

Applying the initial condition $C_B = 0$ at $t = 0$ gives

$$0 = \frac{k_1 C_{A0}}{k_2 - k_1} + \text{Const.}$$

So, finally, we have

$$C_B = \frac{k_1 C_{A0}}{k_2 - k_1} (\exp(-k_1 t) - \exp(-k_2 t))$$

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

$$C_B = 2(\exp(-0.3t) - \exp(-0.6t))$$

with C_B in moles per liter and t in hours.

The concentration of C can be found from the overall stoichiometry $C_A + C_B + C_C = C_{A0}$

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

$$\text{prod. rate} = \frac{VC_B(t)}{t + t_{\text{turnaround}}}$$

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

$$\text{prod. rate} = \frac{1000(\exp(-0.3t) - \exp(-0.6t))}{t + 0.25} \text{ mol hr}^{-1}$$

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

$$\frac{d(\text{prod. rate})}{dt} = 1000 \frac{(t + 0.25)(0.6 \exp(-0.6t) - 0.3 \exp(-0.3t)) - (\exp(-0.3t) - \exp(-0.6t))}{(t + 0.25)^2} \text{ mol hr}^{-2}$$

$$\text{or } \frac{d(\text{prod. rate})}{dt} = 1000 \frac{(0.6t + 1.15) \exp(-0.6t) - (0.3t + 1.075) \exp(-0.3t)}{(t + 0.25)^2} \text{ mol hr}^{-2}$$

Setting this equal to zero, recognizing that this requires the numerator to be equal to zero, and multiplying the numerator by $\exp(-0.6t)$ gives us

$$0.6t + 1.15 - (0.3t + 1.075) \exp(0.3t) = 0$$

or

$$t = \frac{1}{0.3} \ln \left(\frac{0.6t + 1.15}{0.3t + 1.075} \right)$$

Starting with some initial guess for t , one can iterate on the above expression to get $t = 0.635$ hr.

- (c) Evaluating the production rate at $t = 0.635$ hr gives

$$\text{prod. rate} = \frac{1000(\exp(-0.1904) - \exp(-0.3808))}{0.8847} \text{ mol hr}^{-1} = 162 \text{ mol hr}^{-1}$$

we can verify that this is a maximum, rather than a minimum, by also evaluating the production rate at somewhat higher and lower batch times. At $t = 0.55$ hr, we get a production rate of 161 mol hr^{-1} , and at $t = 0.75$ hr, we also get a production rate of 161 mol hr^{-1} . So, it looks like $t = 0.635 \text{ hr}^{-1}$ is a minimum, but that the production rate is quite insensitive to the exact value of t . This means that we can just select a convenient batch time in this general range.

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



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 concentration of A = 8 moles/liter

Feed temperature = 300 K

Density of A = Density of B = 1.04 g/cm³

Specific Heat of A = Specific Heat of B = 2 J g⁻¹ K⁻¹

Heat of reaction = -41.6 kJ/mol

Forward rate constant = $k_1 = 1 \times 10^8 \exp(-5000/T) \text{ hr}^{-1}$

Reverse rate constant = $k_{-1} = 1 \times 10^5 \exp(-10000/T) \text{ hr}^{-1}$

Note: Somehow, I got the pre-exponential factors here switched around from what I intended. That is, I meant to make them $k_1 = 1 \times 10^5 \exp(-5000/T) \text{ hr}^{-1}$, $k_{-1} = 1 \times 10^8 \exp(-10000/T) \text{ hr}^{-1}$. The solution given below is for those values. For the values given (which you actually used on the exam), $k_1 \gg k_{-1}$, so the reaction is effectively irreversible, and the forward rate constant is so large that there is only a single steady-state with the reaction going essentially to completion ($C_A =$ about 0.008, or 99.9% conversion). That single steady-state is then stable, and the whole problem was much easier than I had intended.

Feed flow rate = 100 liters hr⁻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

$$Q_o(C_{Ao} - C_A) + V(-k_1 C_A + k_{-1} C_B) = 0$$

$$Q_o(0 - C_B) + V(k_1 C_A - k_{-1} C_B) = 0$$

$$\rho \hat{C}_p Q_o (T_o - T) + (-\Delta H) V (k_1 C_A - k_{-1} C_B) = 0$$

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

then we have

$$C_{Ao} - C_A = \tau(k_1 C_A - k_{-1} C_B)$$

$$C_B = \tau(k_1 C_A - k_{-1} C_B)$$

$$T_o - T = \tau J(k_1 C_A - k_{-1} C_B)$$

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

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

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

Substituting these, as well as well as the Arrhenius expressions for the rate constants, into the species mole balance for A gives

$$C_{Ao} - C_A = \tau \left(A_1 \exp\left(\frac{-E_1 / R}{T_o + J(C_{Ao} - C_A)}\right) C_A - A_{-1} \exp\left(\frac{-E_2 / R}{T_o + J(C_{Ao} - C_A)}\right) (C_{Ao} - C_A) \right)$$

From the numbers in the problem statement, $\tau = 5$ hr and $J = 20$ K liter mol⁻¹. Putting in these and the rest of the numbers gives

$$8 - C_A = 5 \left(10^5 \exp\left(\frac{-5000}{300 + 20(8 - C_A)}\right) C_A - 10^8 \exp\left(\frac{-10000}{300 + 20(8 - C_A)}\right) (8 - C_A) \right)$$

We could also write this in terms of $x = C_{Ao} - C_A$ as

$$x = 5 \left(10^5 \exp\left(\frac{-5000}{300 + 20x}\right) (8 - x) - 10^8 \exp\left(\frac{-10000}{300 + 20x}\right) x \right)$$

The possible range of x is $x=0$ to $x=8$. Plotting the above expression by hand, or using your calculator, or iterating on the above expression or some combination of the above will eventually show that this has solutions at

$$x = 0.3119, x = 4.206, \text{ and } x = 6.465$$

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

- (1) $C_A = 7.69$ mol liter⁻¹, $C_B = 0.31$ mol liter⁻¹, $T = 306.2$ K
- (2) $C_A = 3.79$ mol liter⁻¹, $C_B = 4.21$ mol liter⁻¹, $T = 375.8$ K
- (3) $C_A = 1.53$ mol liter⁻¹, $C_B = 6.57$ mol liter⁻¹, $T = 429.3$ 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

$$V \frac{dC_A}{dt} = Q_o (C_{Ao} - C_A) + V(-k_1 C_A + k_{-1} C_B)$$

$$V \frac{dC_B}{dt} = Q_o (0 - C_B) + V(k_1 C_A - k_{-1} C_B)$$

$$\rho \hat{C}_p V \frac{dT}{dt} = \rho \hat{C}_p Q_o (T_o - T) + (-\Delta H) V (k_1 C_A - k_{-1} C_B)$$

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

energies

$$\frac{dC_A}{dt} = \frac{C_{Ao} - C_A}{\tau} - A_1 \exp\left(\frac{-E_1 / R}{T}\right) C_A + A_{-1} \exp\left(\frac{-E_2 / R}{T}\right) C_B$$

$$\frac{dC_B}{dt} = \frac{C_B}{\tau} - A_1 \exp\left(\frac{-E_1 / R}{T}\right) C_A + A_{-1} \exp\left(\frac{-E_2 / R}{T}\right) C_B$$

$$\frac{dT}{dt} = \frac{T_o - T}{\tau} + J \left(A_1 \exp\left(\frac{-E_1 / R}{T}\right) C_A - A_{-1} \exp\left(\frac{-E_2 / R}{T}\right) C_B \right)$$

and substituting in the numbers

$$\frac{dC_A}{dt} = \frac{8 - C_A}{5} - 10^5 \exp\left(\frac{-5000}{T}\right)C_A + 10^8 \exp\left(\frac{-10000}{T}\right)C_B$$

$$\frac{dC_B}{dt} = \frac{C_B}{5} - 10^5 \exp\left(\frac{-5000}{T}\right)C_A + 10^8 \exp\left(\frac{-10000}{T}\right)C_B$$

$$\frac{dT}{dt} = \frac{300 - T}{5} + 2 \times 10^6 \exp\left(\frac{-5000}{T}\right)C_A - 2 \times 10^9 \exp\left(\frac{-10000}{T}\right)C_B$$

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

$$J = \begin{bmatrix} -\frac{1}{5} - 10^5 \exp\left(\frac{-5000}{T}\right) & 10^8 \exp\left(\frac{-10000}{T}\right) & -\frac{5000}{T^2} \times 10^5 \exp\left(\frac{-5000}{T}\right)C_A + \frac{10000}{T^2} \times 10^8 \exp\left(\frac{-10000}{T}\right)C_B \\ 10^5 \exp\left(\frac{-5000}{T}\right) & -\frac{1}{5} - 10^8 \exp\left(\frac{-10000}{T}\right) & \frac{5000}{T^2} \times 10^5 \exp\left(\frac{-5000}{T}\right)C_A - \frac{10000}{T^2} \times 10^8 \exp\left(\frac{-10000}{T}\right)C_B \\ 20 \times 10^5 \exp\left(\frac{-5000}{T}\right) & -20 \times 10^8 \exp\left(\frac{-10000}{T}\right) & -\frac{1}{5} + 20 \left(\frac{5000}{T^2} \times 10^5 \exp\left(\frac{-5000}{T}\right)C_A - \frac{10000}{T^2} \times 10^8 \exp\left(\frac{-10000}{T}\right)C_B \right) \end{bmatrix}$$

or, in terms of the rate constants evaluated at a particular temperature (so we only have to evaluate them once for each set of conditions)

$$J = \begin{bmatrix} -\frac{1}{5} - k_1 & k_{-1} & -\frac{5000}{T^2} k_1 C_A + \frac{10000}{T^2} \times 10^8 \exp\left(\frac{-10000}{T}\right)C_B \\ k_1 & -\frac{1}{5} - k_{-1} & \frac{5000}{T^2} k_1 C_A - \frac{10000}{T^2} k_{-1} C_B \\ 20k_1 & -20k_{-1} & -\frac{1}{5} + 20 \left(\frac{5000}{T^2} k_1 C_A - \frac{10000}{T^2} k_{-1} C_B \right) \end{bmatrix}$$

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

For $C_A = 7.69$ mol liter⁻¹, $C_B = 0.31$ mol liter⁻¹, $T = 306.2$ K, $k_1 = 0.008097$ hr⁻¹, $k_{-1} = 6.556 \times 10^{-7}$ hr⁻¹, from which

$$J = \begin{bmatrix} -0.2081 & 6.556 \times 10^{-7} & -4.317 \times 10^{-4} \\ 8.097 \times 10^{-3} & -0.2000 & 4.317 \times 10^{-4} \\ 0.1619 & -1.311 \times 10^{-5} & -0.2086 \end{bmatrix}$$

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

$$\lambda_1 = -0.2084 + 8.357 \times 10^{-3}i, \lambda_2 = -0.2084 - 8.357 \times 10^{-3}i, \lambda_3 = -0.2000$$

The real part of each of these eigenvalues is negative, so this steady state is **stable**

For $C_A = 3.79$ mol liter⁻¹, $C_B = 4.21$ mol liter⁻¹, $T = 375.8$ K, $k_1 = 0.1666$ hr⁻¹, $k_{-1} = 2.776 \times 10^{-4}$ hr⁻¹, from which

$$J = \begin{bmatrix} -0.3666 & 2.776 \times 10^{-4} & -0.02227 \\ 0.1666 & -0.2003 & 0.02227 \\ 3.332 & -5.552 \times 10^{-3} & 0.2454 \end{bmatrix}$$

The eigenvalues of this matrix are

$$\lambda_1 = 0.07852, \lambda_2 = -0.20002, \lambda_3 = -0.2000$$

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

For $C_A = 1.53 \text{ mol liter}^{-1}$, $C_B = 6.57 \text{ mol liter}^{-1}$, $T = 429.3 \text{ K}$, $k_1 = 0.8746 \text{ hr}^{-1}$, $k_{-1} = 7.650 \times 10^{-3} \text{ hr}^{-1}$, from which

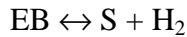
$$\underline{\underline{J}} = \begin{bmatrix} -1.075 & 7.650 \times 10^{-3} & -0.03386 \\ 0.8746 & -0.2077 & 0.03386 \\ 17.49 & -0.1530 & 0.4772 \end{bmatrix}$$

The eigenvalues of this matrix are

$$\lambda_1 = -0.4071, \lambda_2 = -0.1984, \lambda_3 = -0.2000$$

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

3. Consider the dehydrogenation of ethylbenzene (EB) to styrene (S) in an adiabatic packed bed catalytic reactor



Data for the reaction are as follows:

Feed temperature = 925 K

Feed pressure = 2.4 bar

Molar flow of EB in the feed = 85 mol s⁻¹

Molar flow of S in the feed = 0 mol s⁻¹

Molar flow of H₂ in the feed = 0 mol s⁻¹

Molar flow of H₂O in the feed = 1020 mol s⁻¹ (H₂O does not react)

Reaction rate = $k (p_{\text{EB}} - p_{\text{S}}p_{\text{H}_2}/K)$ mol (kg catalyst)⁻¹ s⁻¹

with $k = 3.46 \times 10^3 \exp(-10980/T)$ mol (kg catalyst)⁻¹ s⁻¹ bar⁻¹

and $K = 8.2 \times 10^6 \exp(-15200/T)$ bar

(in the absence of any pore diffusion limitations)

heat of reaction = -120 kJ mol⁻¹

specific heat of feed mixture = 2.4 J g⁻¹ K⁻¹

molecular weight of EB = 106 g mol⁻¹

Note: the heat of reaction should have been +120 kJ/mol, but the solution shown here uses the given (wrong) value of -120 kJ/mol. Note that this heat of reaction is inconsistent with the expression given for the equilibrium constant.

- (a) If the molar flow rate of styrene (S) at the reactor exit is 40 mol s⁻¹, what is the **temperature at the reactor exit**? (5 pts.)
- (b) Calculate the **mass of catalyst** required to achieve a styrene (S) molar flow rate of 40 mol s⁻¹ at the reactor exit. (15 pts.)
- (c) Assuming the kinetics given above were measured in the absence of pore diffusion limitations, estimate the **maximum catalyst pellet diameter** for which pore diffusion limitations within the spherical catalyst pellets will be negligible throughout the reactor. Be sure to explain your reasoning. The catalyst density is 2.0 g cm⁻³. The effective diffusion coefficient for EB in the catalyst pores is about 0.5 cm² s⁻¹ in the temperature range in which the reactor is operated. (5 pts.)

- (a) For this problem, I think it is most convenient to write the species mole balances in terms of the total molar flow rate of each species. Of course it could also be done in terms of concentration. In this form, the mole balances can be written as

$$\frac{dF_{\text{EB}}}{dz} = -\Omega r$$

$$\frac{dF_{\text{S}}}{dz} = \Omega r$$

$$\frac{dF_{\text{H}_2}}{dz} = \Omega r$$

where F_{EB} , F_{S} , and F_{H_2} are the molar flow rates of ethylbenzene, styrene, and hydrogen, Ω is the reactor cross-sectional area, and r is the rate of reaction in moles per volume per time,

$$r = \rho_B k (p_{\text{EB}} - p_{\text{S}}p_{\text{H}_2}/K) \text{ mol m}^{-3} \text{ s}^{-1}$$

where ρ_B is the density of the packed bed (kg catalyst per m^3 of reactor volume). Similarly to the mole balances, the enthalpy balance can be written as

$$\rho \hat{C}_p u_s \frac{dT}{dz} = -(\Delta H)r$$

From the species mole balances, we see that

$$\frac{dF_{EB}}{dz} = -\frac{dF_S}{dz} = -\frac{dF_{H_2}}{dz}$$

which reflects the stoichiometric constraint that $(F_{EB,o} - F_{EB}) = F_S = F_{H_2}$.

Similarly, for the temperature, we have the usual sort of relationship for an adiabatic reactor:

$$\frac{dT}{dz} = \frac{\Delta H}{\rho u_s \hat{C}_p \Omega} \frac{dF_{EB}}{dz}$$

since the temperature and total number of moles are changing with position in the reactor, the density and velocity can both change with position. However, the overall continuity equation requires that

$$\frac{d(\rho u_s)}{dz} = 0, \text{ or } \rho u_s = \rho_o u_{s,o}$$

So the product of density and superficial velocity is constant, and we have

$$\frac{dT}{dz} = \frac{\Delta H}{\rho_o u_{s,o} \hat{C}_p \Omega} \frac{dF_{EB}}{dz}$$

This can now be integrated to get the relationship for which we are looking:

$$T - T_o = \frac{-\Delta H}{\rho_o u_{s,o} \hat{C}_p \Omega} (F_{EB,o} - F_{EB})$$

Now, we just need to plug in the numbers to find the temperature for $F_S = 40 \text{ mol s}^{-1}$, or $F_{EB} = 45 \text{ mol s}^{-1}$. To do this, we need to recognize that the group appearing in the denominator of the expression above, $\rho_o u_{s,o} \Omega$ is the total mass flow rate into the reactor. This is

$$\begin{aligned} \text{Total mass flow rate} &= 1020 \text{ mol H}_2\text{O s}^{-1} * 18 \text{ g mol}^{-1} + 85 \text{ mol EB s}^{-1} * 106 \text{ g mol}^{-1} \\ \text{Total mass flow rate} &= 27370 \text{ g s}^{-1} \end{aligned}$$

Putting all this together gives, for the reactor outlet temperature,

$$T = 925 \text{ K} + \frac{120000 \text{ J mol}^{-1}}{27370 \text{ g s}^{-1} \times 2.4 \text{ J g}^{-1} \text{ K}^{-1}} (85 - 45) \text{ mol s}^{-1} = 998 \text{ K}$$

(b) From part (a), we have the relationship between the molar flow rate of ethylbenzene and the temperature

$$T = T_o + \frac{-\Delta H}{\rho_o u_{s,o} \hat{C}_p \Omega} (F_{EB,o} - F_{EB}) = 925 + 1.83(85 - F_{EB})$$

From stoichiometry, we have

$$F_S = F_{EB,o} - F_{EB} = 85 - F_{EB} \text{ mol s}^{-1}$$

$$F_{H_2} = F_{EB,o} - F_{EB} = 85 - F_{EB} \text{ mol s}^{-1}$$

$$F_{H_2O} = F_{H_2O,o} = 1020 \text{ mol s}^{-1}$$

$$F_{total} = F_{EB} + F_S + F_{H_2} + F_{H_2O} = 1190 - F_{EB} \text{ mol s}^{-1}$$

The partial pressures of the species (which we need in the rate expression) are then related to the total pressure and molar flow rates by

$$p_{EB} = p_{total} \left(\frac{F_{EB}}{F_{total}} \right) = 2.4 \left(\frac{F_{EB}}{1190 - F_{EB}} \right) \text{ bar}$$

$$p_S = p_{total} \left(\frac{F_S}{F_{total}} \right) = 2.4 \left(\frac{85 - F_{EB}}{1190 - F_{EB}} \right) \text{ bar}$$

$$p_{H_2} = p_{total} \left(\frac{F_{H_2}}{F_{total}} \right) = 2.4 \left(\frac{85 - F_{EB}}{1190 - F_{EB}} \right) \text{ bar}$$

Note that the total pressure is assumed to be equal to the feed pressure (that is, we are neglecting pressure drop through the reactor at this point).

The species mole balance for ethylbenzene can then be written as

$$\frac{dF_{EB}}{dz} = -\Omega \rho_B k (p_{EB} - p_S p_{H_2} / K)$$

and the expressions for the partial pressures in terms of the molar flow rates can be substituted in. Before doing this we will re-write the ODE in terms of catalyst mass instead of distance z . Note that $\rho_c \Omega dz$ is the mass of catalyst in a 'slice' of the reactor of thickness dz . We can call it dW , where W is the mass of catalyst. Then we have

$$\frac{dF_{EB}}{dW} = -k (p_{EB} - p_S p_{H_2} / K)$$

Substituting into this the expressions for the partial pressures gives

$$\frac{dF_{EB}}{dW} = -k \left(2.4 \left(\frac{F_{EB}}{1190 - F_{EB}} \right) - \left(2.4 \left(\frac{85 - F_{EB}}{1190 - F_{EB}} \right) \right)^2 / K \right)$$

Next, substituting the expressions for the rate constant and equilibrium constant into this gives

$$\frac{dF_{EB}}{dW} = -3.46 \times 10^3 \exp\left(\frac{-10980}{925 + 1.83(85 - F_{EB})}\right) \left(2.4 \left(\frac{F_{EB}}{1190 - F_{EB}} \right) - \frac{\left(2.4 \left(\frac{85 - F_{EB}}{1190 - F_{EB}} \right) \right)^2}{8.2 \times 10^6 \exp\left(\frac{-15200}{925 + 1.83(85 - F_{EB})}\right)} \right)$$

This can be rearranged to give

$$dW = \frac{-(1190 - F_{EB})^2}{8304 \exp\left(\frac{-10980}{925 + 1.83(85 - F_{EB})}\right) \left(F_{EB}(1190 - F_{EB}) - 2.93 \times 10^{-7} \exp\left(\frac{15200}{925 + 1.83(85 - F_{EB})}\right) (85 - F_{EB})^2 \right)}$$

The catalyst mass required is obtained by integrating this from $F_{EB} = 85$ to $F_{EB} = 45$ (or integrating the negative of it from 45 to 85).

$$W = \int_{45}^{85} \frac{(1190 - F_{EB})^2 dF_{EB}}{8304 \exp\left(\frac{-10980}{925 + 1.83(85 - F_{EB})}\right) \left(F_{EB}(1190 - F_{EB}) - 2.93 \times 10^{-7} \exp\left(\frac{15200}{925 + 1.83(85 - F_{EB})}\right) (85 - F_{EB})^2 \right)}$$

You can probably evaluate this integral using a function on your calculator. My calculator says $W = 7873$ kg catalyst.

- (c) Pore diffusion becomes important when the Thiele modulus is about 1. If k is intrinsic first-order rate constant per catalyst mass, ρ_s is the catalyst pellet density, and D_{eA} is the effective diffusion coefficient of the reactant in the catalyst pores, then the Thiele modulus is

$$\phi = \frac{V}{S} \sqrt{\frac{k\rho_s}{D_{eA}}}$$

Note that this is for an irreversible 1st order reaction. For a reversible reaction, diffusion effects will be somewhat smaller, since the net reaction rate will be smaller. We can therefore use the estimate from the irreversible reaction to get a conservative value for the reversible reaction.

We will evaluate the rate constant at the maximum temperature in the reactor (998 K, from part (a)). At this temperature, $k = 0.0577 \text{ mol (kg catalyst)}^{-1} \text{ s}^{-1} \text{ bar}^{-1}$. If we try to substitute this into the expression for the Thiele modulus, we realize that the units don't work out right. That is because the rate constant is expressed in a mixture of pressure and concentration units. That is, the reactant concentrations are expressed as pressures, but the rate is given in concentration units (moles per volume). A 'pure' 1st order rate constant for the rate per catalyst mass would have units of $(\text{volume (kg catalyst)}^{-1} \text{ s}^{-1})$. So, we need to convert the units, using the concentration (moles per volume) of an ideal gas at a pressure of 1 bar and the reaction conditions. Using the ideal gas law, we find that at 998 K, a pressure of 1 bar corresponds to a concentration of $1.21 \times 10^{-4} \text{ moles m}^{-3}$. Dividing the rate constant by this conversion factor gives $k = 479 \text{ m}^3 (\text{kg catalyst})^{-1} \text{ s}^{-1}$.

The volume to surface ratio for the spherical catalyst pellet is $d/6$. So, we have

$$\phi = \frac{d}{6} \sqrt{\frac{479 \text{ m}^3 (\text{kg catalyst})^{-1} \text{ s}^{-1} \times 2000 (\text{kg catalyst}) \text{ m}^{-3}}{0.5 \text{ cm}^2 \text{ s}^{-1} \times 10^{-4} \text{ m}^2 \text{ cm}^{-2}}}$$

$$\phi = \frac{d}{6} (138420 \text{ m}^{-1})$$

Setting this equal to 1 and solving for d gives $d = 4.3 \times 10^{-5} \text{ m} = 43 \text{ microns}$. Thus, pore diffusion limitations will actually *always* be present for any practical catalyst size at this temperature.

4. The second order, irreversible reaction $A + B \rightarrow C + D$ 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 three equally-sized, perfectly-mixed tanks in series. The feed to the reactor is an equimolar mixture of A and B, with $C_{Ao} = C_{Bo} = 5$ moles/liter. The mean residence time of the reactor is 10 minutes. The reaction rate is given by
- $$r = 2 C_A C_B \text{ mol liter}^{-1} \text{ hr}^{-1}, \text{ with } C_A \text{ and } C_B \text{ in moles per liter.}$$
- (a) Derive the **dimensionless residence time distribution function** for three equally-sized perfectly-mixed tanks in series. (5 pts.)
- (b) Compute the **concentrations** of A and B in the reactor effluent using a **segregated flow** model with the RTD for 3 tanks in series. (8 pts.)
- (c) Compute the **concentrations** of A and B leaving the reactor by modeling the reactor as 3 perfectly-mixed **tanks in series** and solving species balance equations for the 3 tanks. (8 pts.)
- (d) **Explain any differences** between the results obtained in parts (b) and (c). (4 pts.)

- (a) We can consider a tracer experiment in a series of three identical stirred tanks, each 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 third vessel. The fraction of tracer that comes out of the third reactor in some small time interval θ to $\theta + d\theta$, 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 third 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 three tanks. These are the usual transient mass balances for a CSTR of volume $V/3$ with no reaction term (since the tracer doesn't react).

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

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

$$\frac{V}{3} \frac{dC_3}{dt} = Q_o(C_2 - C_3)$$

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 entering the third tank, and C_3 is the tracer concentration in the 3rd tank (and leaving the 3rd tank), which is proportional to the residence time distribution function. At $t = 0$, $C_1 = M/(V/3)$, and $C_2 = C_3 = 0$, where M is the total number of moles of tracer initially put in the reactor. With this definition, $E(\theta) = Q_o C_3(\theta)/M$. The residence time for the whole system is $\tau = V/Q_o$. Writing the balances in terms of τ , we get

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

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

$$\frac{dC_3}{dt} = \frac{3}{\tau} (C_2 - C_3)$$

We can integrate these sequentially, using the initial conditions:

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

so

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

as usual, we guess that

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

substituting this into the ODE gives

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

$$f'(t) = \frac{3M}{\tau V}$$

integrating this gives

$$f(t) = \frac{9tM}{\tau V} + \text{const.}$$

$$C_2 = \left(\frac{9tM}{\tau V} + \text{const.}\right) \exp\left(\frac{-3t}{\tau}\right)$$

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

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

Likewise, guessing that

$$C_3 = f(t) \exp\left(\frac{-3t}{\tau}\right)$$

and substituting into the 3rd ODE gives

$$\frac{dC_3}{dt} + \frac{3}{\tau}C_3 = \frac{9}{\tau} \left(\frac{3t}{\tau} \frac{M}{V} \exp\left(\frac{-3t}{\tau}\right) \right)$$

$$f'(t) \exp\left(\frac{-3t}{\tau}\right) - \frac{3}{\tau} f(t) \exp\left(\frac{-3t}{\tau}\right) + \frac{3}{\tau} f(t) \exp\left(\frac{-3t}{\tau}\right) = \frac{27t}{\tau^2} \frac{M}{V} \exp\left(\frac{-3t}{\tau}\right)$$

$$f'(t) = \frac{27t}{\tau^2} \frac{M}{V}$$

$$f(t) = \frac{27t^2}{2\tau^2} \frac{M}{V} + \text{const.}$$

$$C_3 = \left(\frac{27t^2}{2\tau^2} \frac{M}{V} + \text{const.} \right) \exp\left(\frac{-3t}{\tau}\right)$$

$$C_3(t=0) = \text{const.} = 0$$

$$C_3 = \frac{27t^2}{2\tau^2} \frac{M}{V} \exp\left(\frac{-3t}{\tau}\right)$$

The residence time distribution function is $E(\theta) = Q_o C_3(\theta) / M$

$$E(\theta) = \frac{Q_o}{M} \frac{27\theta^2}{2\tau^2} \frac{M}{V} \exp\left(\frac{-3\theta}{\tau}\right) = \frac{27\theta^2}{2\tau^3} \exp\left(\frac{-3\theta}{\tau}\right)$$

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

$$E(\theta') = \tau E(\theta) = \frac{27\theta^2}{2\tau^2} \exp\left(\frac{-3\theta}{\tau}\right)$$

- (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

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

for the second order reaction with the stoichiometric feed, $C_A = C_B$, and the material balance on A gives

$$\frac{dC_A}{dt} = -kC_A C_B = -kC_A^2 = -2C_A^2$$

$$\frac{dC_A}{C_A^2} = -2dt$$

$$\frac{1}{C_A} - \frac{1}{C_{A0}} = 2t$$

$$C_A = \frac{C_{A0}}{1 + 2tC_{A0}} = \frac{5}{1 + 10t}$$

So, the segregated flow model gives

$$\bar{C} = \int_0^{\infty} \left(\frac{5}{1 + 10\theta} \right) \left(\frac{27\theta^2}{2\tau^3} \exp\left(\frac{-3\theta}{\tau}\right) \right) d\theta$$

$$\bar{C} = \int_0^{\infty} \left(\frac{5}{1 + 10\theta} \right) (2916\theta^2 \exp(-18\theta)) d\theta$$

Integrating this numerically using a calculator gives

$$\bar{C} = 2.11 \text{ moles / liter}$$

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

$$(C_{A0} - C_{A1}) = \frac{\tau}{3} k C_{A1}^2$$

$$(C_{A1} - C_{A2}) = \frac{\tau}{3} k C_{A2}^2$$

$$(C_{A2} - C_{A3}) = \frac{\tau}{3} k C_{A3}^2$$

plugging in the numbers gives

$$\frac{1}{9} C_{A1}^2 + C_{A1} - 5 = 0$$

$$C_{A1} = \frac{-1 + \sqrt{1 + 20/9}}{2/9} = 3.578 \text{ moles / liter}$$

$$\frac{1}{9} C_{A2}^2 + C_{A2} - 3.578 = 0$$

$$C_{A2} = \frac{-1 + \sqrt{1 + 1.5901}}{2/9} = 2.742 \text{ moles / liter}$$

$$\frac{1}{9} C_{A3}^2 + C_{A3} - 2.742 = 0$$

$$C_{A3} = \frac{-1 + \sqrt{1 + 1.2188}}{2/9} = 2.203 \text{ moles / liter}$$

(d) The segregated flow model predicts slightly lower reactant concentration, or slightly higher extent of reaction, because it neglects micromixing. In the segregated flow model, the reaction, on average, takes place at a higher reactant concentration than in the reactor model, where in each reactor the reaction takes place at the concentration in that tank.