

CE 561, Exam 2, December 17, 2001

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.

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 sequential reactions



are to be carried out in dilute aqueous solution in a well-mixed, isothermal, semi-batch reactor. At the start of each batch, the reactor is empty. It is then fed with a solution containing 2 moles of A per liter and no B or C. The feed flow rate is 500 liters per hour (this is the maximum allowable feed rate at which the reactor can be maintained isothermal). The reactor volume is 1000 liters, and when it is full, the feed is shut off. That is, the feed rate is 500 liters per hour for the first two hours, and 0 after the first two hours. Emptying and cleaning the reactor between batches requires 1 hour.

- Find the **number of moles of species A and B** in the reactor as a function of time after the start of reactor filling (you should find solutions for all times, both before and after the feed is turned off). (20 pts.)
- Find the **batch time** that maximizes the average production rate of species B. (15 pts.)
- Find the **average production rate** of species B for this optimal batch time. (5 pts.)

During the first two hours, when feed is being added to the reactor, we have the following total mass and species mole balances:

$$\frac{d(\rho V)}{dt} = \rho Q$$

$$\frac{d(V C_A)}{dt} = Q C_{A0} - k_1 C_A V$$

$$\frac{d(V C_B)}{dt} = k_1 C_A V - k_2 C_B V$$

In dilute aqueous solution, we can assume that the density is constant, so it cancels out of the first equation, which can be integrated directly to give $V = Qt$ (using the initial condition that $V = 0$ at $t = 0$). In the second two equations, we could either solve for the species concentrations, or the total number of moles of the species in the reactor. It turns out that solving for the total number of moles is probably more convenient in this case, so we will solve for $N_A = VC_A$ and $N_B = VC_B$. In terms of N_A and N_B , the equations are:

$$\frac{dN_A}{dt} = QC_{Ao} - k_1 N_A$$

$$\frac{dN_B}{dt} = k_1 N_A - k_2 N_B$$

For times greater than 2 hours, we can use the same equations with $Q = 0$. But first, we will solve them for $0 < t < 2$ hours. We can guess that $N_A = f(t)\exp(-k_1 t)$, so that

$$\frac{dN_A}{dt} = f' \exp(-k_1 t) - k_1 f \exp(-k_1 t) = QC_{Ao} - k_1 f \exp(-k_1 t)$$

$$f' \exp(-k_1 t) = QC_{Ao}$$

$$f' = QC_{Ao} \exp(k_1 t)$$

$$f = \frac{QC_{Ao}}{k_1} (\exp(k_1 t) + \text{const.})$$

$$N_A = \frac{QC_{Ao}}{k_1} (1 + \text{const.} \exp(-k_1 t))$$

Using the initial condition that $N_A = 0$ at $t = 0$ shows that the constant of integration is -1, so

$$N_A = \frac{QC_{Ao}}{k_1} (1 - \exp(-k_1 t))$$

Substituting this into the equation for N_B gives

$$\frac{dN_B}{dt} = QC_{Ao} (1 - \exp(-k_1 t)) - k_2 N_B$$

Again, we guess the form of the solution as $N_B = f(t)\exp(-k_2 t)$, so that

$$\frac{dN_B}{dt} = f' \exp(-k_2 t) - k_2 f \exp(-k_2 t) = QC_{Ao} (1 - \exp(-k_1 t)) - k_2 f \exp(-k_2 t)$$

$$f' \exp(-k_2 t) = QC_{Ao} (1 - \exp(-k_1 t))$$

$$f' = QC_{Ao} (\exp(k_2 t) - \exp((k_2 - k_1)t))$$

$$f = QC_{Ao} \left(\frac{1}{k_2} \exp(k_2 t) - \frac{1}{k_2 - k_1} \exp((k_2 - k_1)t) + \text{const.} \right)$$

$$N_B = QC_{Ao} \left(\frac{1}{k_2} - \frac{1}{k_2 - k_1} \exp(-k_1 t) + \text{const.} \exp(-k_2 t) \right)$$

Using the initial condition that $N_B = 0$ at $t = 0$ gives

$$0 = QC_{Ao} \left(\frac{1}{k_2} - \frac{1}{k_2 - k_1} + \text{const.} \right)$$

$$\text{const.} = \frac{1}{k_2 - k_1} - \frac{1}{k_2} = \frac{k_1}{k_2(k_2 - k_1)}$$

$$N_B = \frac{QC_{Ao}}{k_2(k_2 - k_1)} (k_2 - k_1 - k_2 \exp(-k_1 t) + k_1 \exp(-k_2 t))$$

$$N_B = \frac{QC_{Ao}}{k_2(k_1 - k_2)} (k_1 - k_2 + k_2 \exp(-k_1 t) - k_1 \exp(-k_2 t))$$

Putting the numbers into the solutions gives

$$N_A = 2000(1 - \exp(-0.5t))$$

$$N_B = \frac{1000}{0.25(0.25)}(0.25 + 0.25\exp(-0.5t) - 0.5\exp(-0.25t))$$

$$N_B = 4000(1 + \exp(-0.5t) - 2\exp(-0.25t))$$

For times greater than 2 hours, we have

$$\frac{dN_A}{dt} = -k_1 N_A$$

$$\frac{dN_B}{dt} = k_1 N_A - k_2 N_B$$

We can rearrange and integrate the first equation to get

$$\frac{dN_A}{N_A} = -k_1 dt$$

$$\ln(N_A) = -k_1 t + \text{const.}$$

Using the condition that at $t = 2$, $N_A = 2000(1 - \exp(-1)) = 1264$ gives

$$\ln(1264) = -1 + \text{const.}$$

From which the constant is equal to 8.142 and we have

$$\ln(N_A) = 8.142 - 0.5t$$

$$N_A = \exp(8.142 - 0.5t) = 3436\exp(-0.5t)$$

For B at times greater than 2 hours, we have

$$\frac{dN_B}{dt} = 1718\exp(-0.5t) - k_2 N_B$$

One more time, we guess that $N_B = f(t)\exp(-k_2 t)$, so that

$$\frac{dN_B}{dt} = f' \exp(-k_2 t) - k_2 f \exp(-k_2 t) = 1718\exp(-k_1 t) - k_2 f \exp(-k_2 t)$$

$$f' \exp(-k_2 t) = 1718\exp(-k_1 t)$$

$$f' = 1718\exp((k_2 - k_1)t)$$

$$f = 1718 \left(\frac{1}{k_2 - k_1} \exp((k_2 - k_1)t) + \text{const.} \right)$$

$$N_B = 1718 \left(\frac{1}{k_2 - k_1} \exp(-k_1 t) + \text{const.} \exp(-k_2 t) \right)$$

Using the condition that at $t = 2$, $N_B = 4000(1 + \exp(-1) - 2\exp(-0.5)) = 619$ gives

$$619 = 1718(-4\exp(-1) + \text{const.} \exp(-0.5))$$

From which the constant is equal to 3.02, and we have

$$N_B = 1718(3.02\exp(-0.25t) - 4\exp(-0.5t))$$

$$N_B = 5189(\exp(-0.25t) - 1.32\exp(-0.5t))$$

(b) The average production rate of B is equal to the total amount of B produced in a batch divided by the total batch time (including the hour needed to empty and clean the reactor). So, the production rate is

$$\text{Prod. Rate} = \frac{4000(1 + \exp(-0.5t) - 2 \exp(-0.25t))}{t+1} \quad \text{for } 0 \leq t \leq 2$$

$$\text{Prod. Rate} = \frac{5189(\exp(-0.25t) - 1.32 \exp(-0.5t))}{t+1} \quad \text{for } t \geq 2$$

To maximize this, we will take the derivative of each expression and set it equal to zero. We should also check to see if the derivative changes sign at $t = 2$, where the expression for N_B changes.

$$\frac{d}{dt}(\text{Prod. Rate}) = \frac{4000((t+1)(-0.5 \exp(-0.5t) + 0.5 \exp(-0.25t)) - (1 + \exp(-0.5t) - 2 \exp(-0.25t)))}{(t+1)^2} \quad \text{for } 0 \leq t \leq 2$$

$$\frac{d}{dt}(\text{Prod. Rate}) = \frac{5189((t+1)(-0.25 \exp(-0.25t) + 0.66 \exp(-0.5t)) - (\exp(-0.25t) - 1.32 \exp(-0.5t)))}{(t+1)^2} \quad \text{for } t \geq 2$$

Evaluating the first expression at $t = 0$ gives 0, and evaluating it at 1 and at 2 gives positive values, so probably it is positive over the whole region from zero to 2. Evaluating the second expression at 2 also gives a positive number, so we should probably search for solutions for values of t greater than 2. Setting the second expression equal to zero gives:

$$(t+1)(-0.25 \exp(-0.25t) + 0.66 \exp(-0.5t)) - (\exp(-0.25t) - 1.32 \exp(-0.5t)) = 0$$

We may recognize that we can divide through by $\exp(-0.25t)$ to leave

$$(t+1)(-0.25 + 0.66 \exp(-0.25t)) - (1 - 1.32 \exp(-0.25t)) = 0$$

Then we might let $x = \exp(-0.25 t)$ or $t = -4 \ln(x)$ to get

$$(1 - 4 \ln(x))(-0.25 + 0.66x) - (1 - 1.32x) = 0$$

$$(\ln(x) - 1.25) + (1.98 - 2.64 \ln(x))x = 0$$

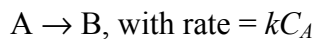
$$x = \frac{1.25 - \ln(x)}{1.98 - 2.64 \ln(x)}$$

We might take as an initial guess $t = 3$, for which $x = 0.472$

Iterating on the above expression from this guess converges to $x = 0.5123$, or $t = 2.68$ hr.

(c) Evaluating the production rate for $t = 2.68$ gives 234.17 moles/hour. Evaluating it for $t = 2.65$ gives 234.15 moles/hour, and evaluating it for $t = 2.7$ gives 234.15, so indeed $t = 2.68$ hours does give a maximum in the production rate.

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



is to be carried out in aqueous solution in a perfectly mixed adiabatic stirred tank reactor.

Properties of the reaction and reactor are as follows:

Feed temperature = $T_o = 300$ K

Feed Concentration of A = $C_{Ao} = 2$ mol/liter

Heat of reaction = $\Delta H = -41800$ J/mol

Density = $\rho = 1000$ g/liter

Specific Heat = $C_p = 4.18$ J/(g K)

Feed flow rate = $Q = 100$ liters min^{-1}

Reactor volume = $V = 500$ liters

The reaction rate constant can be expressed as

$$k = k_o + A \left(\frac{T - T_o}{T_o} \right) + B \left(\frac{T - T_o}{T_o} \right)^2$$

where T_o is the feed temperature and

$$k_o = 0.002 \text{ min}^{-1}$$

$$A = 0.04 \text{ min}^{-1}$$

$$B = 0.4 \text{ min}^{-1}$$

- (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. (20 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.)

The steady-state material and energy balances are just

$$Q(C_{Ao} - C_A) - VkC_A = 0$$

$$\rho C_p Q(T_o - T) + (-\Delta H)VkC_A = 0$$

where I have not explicitly written out the temperature dependence of k . Defining the residence time as $\tau = V/Q$ and defining $J = -\Delta H/(\rho C_p)$ these can be written as:

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

$$T - T_o = J \tau k C_A$$

From which we see that we have the usual relationship for an adiabatic reactor

$$C_{Ao} - C_A = \frac{1}{J}(T - T_o)$$

Substituting this relationship into the energy balance, and explicitly writing out the temperature dependence of k gives

$$T - T_o - J \tau \left(k_o + A \left(\frac{T - T_o}{T_o} \right) + B \left(\frac{T - T_o}{T_o} \right)^2 \right) \left(C_{Ao} - \frac{1}{J}(T - T_o) \right) = 0$$

$$T - T_o - \tau \left(k_o + A \left(\frac{T - T_o}{T_o} \right) + B \left(\frac{T - T_o}{T_o} \right)^2 \right) (J C_{Ao} - (T - T_o)) = 0$$

To make the equation more compact, we can let $x = (T - T_o)/T_o$, to get

$$T_o x - \tau (k_o + Ax + Bx^2) (J C_{Ao} - T_o x) = 0$$

Putting in the numbers from the problem statement gives

$$300x - 5(0.002 + 0.04x + 0.4x^2)(20 - 300x) = 0$$

$$300x - (0.01 + 0.2x + 2x^2)(20 - 300x) = 0$$

$$300x - (.2 - 3x + 4x - 60x^2 + 40x^2 - 600x^3) = 0$$

$$600x^3 + 20x^2 + 299x - 0.2 = 0$$

This is a cubic equation for x , so we expect it to have either 1 or 3 real solutions. The concentration of A is limited to the range C_{Ao} to zero, so in the adiabatic reactor, the temperature

range is limited to T_o to $T_o + JC_{Ao}$, and therefore x is limited to the range from 0 to $JC_{Ao}/T_o = 0.06667$ for this problem. Looking at the values of the terms in this range, we see that the linear term is completely dominant. At $x = 0.06667$, we have $600x^3 = 0.178$, $20x^2 = 0.0889$, and $299x = 19.93$. So, in this range, the equation will basically look like a straight line, with slope 299 and intercept -0.2. There will be only one solution, and it will be approximately $0.2/299 = 0.00067$. We could refine this by iterating on

$$x = \frac{0.2 - 600x^3 - 20x^2}{299}$$

Iterating on this gives a final value of 0.000669. For this value of x , we have $T = 300.2$, and $C_A = 2 - 0.1 \cdot 0.2 = 1.980$ moles/liter. There is only about 1% conversion of A. We probably want to try heating the reactor.

(b) This is almost unnecessary, since when we have only 1 steady state, we certainly expect it to be stable. However, we should check to make sure (and because I asked you to). The transient CSTR equations are

$$\frac{dC_A}{dt} = \frac{C_{Ao} - C_A}{\tau} - \left(k_o + A \left(\frac{T - T_o}{T_o} \right) + B \left(\frac{T - T_o}{T_o} \right)^2 \right) C_A$$

$$\frac{dT}{dt} = \frac{T_o - T}{\tau} + J \left(k_o + A \left(\frac{T - T_o}{T_o} \right) + B \left(\frac{T - T_o}{T_o} \right)^2 \right) C_A$$

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

$$J = \begin{bmatrix} -\frac{1}{\tau} - \left(k_o + A \left(\frac{T - T_o}{T_o} \right) + B \left(\frac{T - T_o}{T_o} \right)^2 \right) & - \left(\frac{A}{T_o} + \frac{2B}{T_o} \left(\frac{T - T_o}{T_o} \right) \right) C_A \\ J \left(k_o + A \left(\frac{T - T_o}{T_o} \right) + B \left(\frac{T - T_o}{T_o} \right)^2 \right) & -\frac{1}{\tau} + J \left(\frac{A}{T_o} + \frac{2B}{T_o} \left(\frac{T - T_o}{T_o} \right) \right) C_A \end{bmatrix}$$

Putting in $\tau = 5$, $(T - T_o)/T_o = 0.000669$, $k_o = 0.002$, $A = 0.04$, $B = 0.4 \text{ min}^{-1}$, $T_o = 300$, $J = 10$, and $C_A = 1.980$ gives

$$J = \begin{bmatrix} -0.2 - \left(0.002 + 0.04(0.000669) + 0.4(0.000669)^2 \right) & - \left(\frac{0.04}{300} + \frac{0.8}{300}(0.000669) \right) 1.98 \\ 10 \left(0.002 + 0.04(0.000669) + 0.4(0.000669)^2 \right) & -0.2 + 10 \left(\frac{0.04}{300} + \frac{0.8}{300}(0.000669) \right) 1.98 \end{bmatrix}$$

$$J = \begin{bmatrix} -0.2 - (0.0020269) & -0.0002675 \\ 10(0.0020269) & -0.2 + 10(-0.0002675) \end{bmatrix}$$

$$J = \begin{bmatrix} -0.2020269 & -0.0002675 \\ 0.020269 & -0.202675 \end{bmatrix}$$

Now we find the eigenvalues by solving the characteristic equation of this matrix, which is the determinant of

$$\begin{bmatrix} -0.2020269 - \lambda & -0.0002675 \\ 0.020269 & -0.202675 - \lambda \end{bmatrix}$$

Multiplying out the determinant and setting it equal to zero gives

$$\lambda^2 + 0.4047019\lambda + 0.0409512 = 0$$

Applying the quadratic formula to this gives

$$\lambda = -0.202 \pm 0.0023i$$

Since both eigenvalues have a negative real part, the steady state is stable, as expected.

3. The second order, irreversible reaction $2A \rightarrow B$ 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 feed to the reactor has $C_{Ao} = 3$ moles/liter. The mean residence time of the reactor is 10 minutes. The reaction rate is given by

$$r = 2 C_A^2 \text{ mol liter}^{-1} \text{ hr}^{-1}, \text{ with } C_A \text{ in moles per liter.}$$

- (a) Derive the **dimensionless residence time distribution function** for two equally-sized perfectly-mixed tanks in series. (15 pts.)
 (b) Show how you would compute the **concentration** of A in the reactor effluent using a **segregated flow** model with the RTD derived in part (a). You should set up all of the equations and take the solution as far as you can, but you may not actually be able to get a numerical answer. (10 pts.)

Imagine we put a pulse input into the first tank at $t = 0$. The pulse will instantaneously be distributed in the perfectly mixed tank, and after that, the tracer concentration in the feed stream will be zero. The tracer concentration in the second tank will be zero at $t = 0$, and the inlet concentration for the second tank will be given by the concentration in the first tank. The transient CSTR balance equations for the two tanks (with no reaction for the tracer) are

$$\frac{dC_{t1}}{dt} = \frac{-C_{t1}}{\tau_1}$$

$$\frac{dC_{t2}}{dt} = \frac{C_{t1} - C_{t2}}{\tau_2}$$

where C_{t1} is the concentration of tracer in tank 1, C_{t2} is the tracer concentration in tank 2. If the initial pulse at $t = 0$ contained M moles of tracer, then at $t = 0$, the tracer concentration in tank 1 will be $C_{t1}(t = 0) = M/V_1$, where V_1 is the volume of tank one. Since the two tanks are equally-sized, we will have $\tau_1 = \tau_2 = \tau/2 = 5$ minutes.

Integrating the first equation, using this initial condition and definition of τ_1 , gives

$$C_{t1} = \frac{M}{V_1} \exp\left(\frac{-2t}{\tau}\right)$$

Substituting this into the equation for tank two gives

$$\frac{dC_{t2}}{dt} = \frac{2M}{V_1\tau} \exp\left(\frac{-2t}{\tau}\right) - \frac{2C_{t2}}{\tau}$$

We'll solve this by guessing that C_{t2} has the form $C_{t2} = f \exp(-2t/\tau)$, which gives

$$\frac{dC_{t2}}{dt} = f' \exp\left(\frac{-2t}{\tau}\right) - \frac{2f}{\tau} \exp\left(\frac{-2t}{\tau}\right) = \frac{2M}{V_1\tau} \exp\left(\frac{-2t}{\tau}\right) - \frac{2f}{\tau} \exp\left(\frac{-2t}{\tau}\right)$$

$$f' = \frac{2M}{V_1\tau}$$

$$f = \frac{2Mt}{V_1\tau} + \text{const.}$$

$$C_{t2} = \frac{2Mt}{V_1\tau} \exp\left(-\frac{2t}{\tau}\right) + \text{const.} \exp\left(-\frac{2t}{\tau}\right)$$

Using the initial condition that $C_{t2} = 0$ at $t = 0$ shows that the constant is 0, so we finally have

$$C_{t2} = \frac{2Mt}{V_1\tau} \exp\left(-\frac{2t}{\tau}\right)$$

The RTD function is simply proportional to the concentration of tracer in the outlet of the second reactor, normalized so that its integral from zero to infinity is one. That is

$$E = \frac{C_{t2}}{\int_0^{\infty} C_{t2} dt} = \frac{\frac{2Mt}{V_1\tau} \exp\left(-\frac{2t}{\tau}\right)}{\int_0^{\infty} \frac{2Mt}{V_1\tau} \exp\left(-\frac{2t}{\tau}\right) dt} = \frac{t \exp\left(-\frac{2t}{\tau}\right)}{\int_0^{\infty} t \exp\left(-\frac{2t}{\tau}\right) dt}$$

The denominator can be integrated by parts to get

$$\int_0^{\infty} t \exp\left(-\frac{2t}{\tau}\right) dt = \left(\frac{\tau}{2}\right)^2$$

So, the RTD for two tanks in series with total residence time τ is

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

(b) For the segregated flow model, we compute the concentration as

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

We know E , the residence time distribution function, but we need to compute C_A for a batch reactor as a function of time (the other part of the integral). For the second-order reaction in a batch reactor, we have

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

which is a separable equation that integrates to

$$\begin{aligned} \frac{1}{C_A} - \frac{1}{C_{A0}} &= kt \\ \frac{1}{C_A} &= \frac{1}{C_{A0}} + kt = \frac{1 + C_{A0}kt}{C_{A0}} \\ C_A &= \frac{C_{A0}}{1 + C_{A0}kt} \end{aligned}$$

so, we have

$$\bar{C}_A = \int_0^{\infty} \frac{C_{A0}}{1 + C_{A0}k\theta} \frac{4\theta}{\tau^2} \exp\left(-\frac{2\theta}{\tau}\right) d\theta = \frac{4C_{A0}}{\tau^2} \int_0^{\infty} \frac{\theta}{1 + C_{A0}k\theta} \exp\left(-\frac{2\theta}{\tau}\right) d\theta$$

We could go ahead and substitute in the numbers that we know, to get

$$\bar{C}_A = 0.12 \int_0^{\infty} \frac{\theta}{1 + 6\theta} \exp\left(-\frac{\theta}{5}\right) d\theta$$

This integral can be evaluated numerically, or analytically in terms of the exponential integral, but not during a test, I suppose. The answer comes out to be 0.0902.