CE 561, Exam 2, December 9, 2008

This exam consists of three 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. You may use three pages (2-sided) of hand-written notes.

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

   A → B, with rate = $k_1 C_A$
   B → C, with rate = $k_2 C_B$

   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 $k_1 = 1.0$ hr^{-1} and $k_2 = 1.5$ hr^{-1} at the operating temperature. At the start of each batch, the reactor is filled with a solution containing 5 moles of A per liter (and no B or C). The reactor volume is 1000 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. (15 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

$$C_A = C_{Ao}\exp(-k_1 t) = 5\exp(-1.0t)$$

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

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

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

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

which simplifies to

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

Integrating this gives

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

So we have

$$C_B = \frac{k_1 C_{Ao}}{k_2 - k_1}\exp\left(-k_1 t\right) + Const.\exp\left(-k_2 t\right)$$

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

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

So, finally, we have

$$C_B = \frac{k_1 C_{Ao}}{k_2 - k_1}\left(\exp\left(-k_1 t\right) - \exp\left(-k_2 t\right)\right)$$

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

$$C_B = \frac{1.0 * 5}{1.5 - 1.0}\left(\exp\left(-1.0t\right) - \exp\left(-1.5t\right)\right) = 10\left(\exp\left(-1.0t\right) - \exp\left(-1.5t\right)\right)$$

with C_B in moles per liter and t in hours.

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

$$C_C = 5\left(1 - \exp\left(-1.0t\right)\right) - 10\left(\exp\left(-1.0t\right) - \exp\left(-1.5t\right)\right)$$

$$C_C = 5\left(1 - 3\exp\left(-1.0t\right) + 2\exp\left(-1.5t\right)\right)$$

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

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

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

$$prod.\ rate = \frac{1000 * 10\left(\exp\left(-1.0t\right) - \exp\left(-1.5t\right)\right)}{t + 0.25} \quad \text{mol hr}^{-1}$$

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

$$\frac{d\left(prod.\ rate\right)}{dt} = 10000\frac{\left(t + 0.25\right)\left(1.5\exp\left(-1.5t\right) - 1.0\exp\left(-1.0t\right)\right) - \left(\exp\left(-1.0t\right) - \exp\left(-1.5t\right)\right)}{\left(t + 0.25\right)^2} \quad \text{mol hr}^{-2}$$

or $$\frac{d\left(prod.\ rate\right)}{dt} = 10000\frac{\left(1.5t + 1.375\right)\exp\left(-1.5t\right) - \left(t + 1.25\right)\exp\left(-1.0t\right)}{\left(t + 0.25\right)^2} \quad \text{mol hr}^{-2}$$

Setting this equal to zero, recognizing that this requires the numerator to be equal to zero, and multiplying the numerator by exp(-1.5t) gives us

$$1.5t + 1.375 - \left(t + 1.25\right)\exp\left(0.5t\right) = 0$$

or

$$t = \frac{1}{0.5}\ln\left(\frac{1.5t + 1.375}{t + 1.25}\right)$$

Starting with some initial guess for t, one can iterate on the above expression to get $t = 0.341$ hr.

(c) Evaluating the production rate at $t = 0.341$ hr gives

$$prod.\ rate = \frac{10000\left(\exp\left(-0.3406\right) - \exp\left(-0.5109\right)\right)}{0.5906}\ \ \text{mol hr}^{-1} = 1890\ \text{mol hr}^{-1}$$

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. The rate does go down slightly for $t = 0.33$ or $t = 0.35$ hr.

2. The irreversible, liquid phase, exothermic reaction

   A + B → C, with rate = $k_1 C_A C_B$

   is to be carried out in a perfectly mixed adiabatic stirred tank reactor. A solution containing equal amounts of A and B is fed to the reactor (mixing just prior to entering the reactor). The rate parameters, reactor properties, and physical properties are as follows:

   Feed concentration of A = Feed concentration of B = 10 mol/L
   Feed temperature = 300 K
   Density of feed = Density of product = 1.0 kg/L
   Specific Heat of feed = Specific Heat of product = 4.2 kJ kg^{-1} K^{-1}
   Heat of reaction = -42 kJ/mol
   Rate constant = $k_1 = 3\times10^{11}$ exp(-10000/T) L mol^{-1} hr^{-1}
   Feed flow rate = 100 liters hr^{-1}
   Reactor volume = 300 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. (15 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. (20 pts.)

From stoichiometry, $C_{Ao} - C_A = C_{Bo} - C_B = C_C$. Thus, $C_A = C_B$ and it is sufficient to solve for only species A and the temperature.

At steady state, the species mole balance for A and the enthalpy balance are

In – out + production = 0

$$Q_o\left(C_{Ao} - C_A\right) + V\left(-k_1 C_A C_B\right) = 0$$

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

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

then we have

$$C_{Ao} - C_A = \tau\left(k_1 C_A C_B\right)$$

$$T_o - T = \tau J\left(k_1 C_A C_B\right)$$

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 $C_B = C_A$ and $T = T_o + J(C_{Ao} - C_A)$, as well as well as the Arrhenius expressions for the rate constants, into the species mole balance for A gives

$$C_{Ao} - C_A = \tau\left(A\exp\left(\frac{-E/R}{T_o + J\left(C_{Ao} - C_A\right)}\right)C_A^2\right)$$

From the numbers in the problem statement, $\tau = 3$ hr and $J = 10$ K liter mol^{-1}. Putting in these and the rest of the numbers gives

$$10 - C_A = 3\left(3\times 10^{11}\exp\left(\frac{-10000}{300+10\left(10-C_A\right)}\right)C_A^2\right)$$

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

$$x = 9\times 10^{11}\exp\left(\frac{-10000}{300+10x}\right)\left(10-x\right)^2$$

The possible range of x is x=0 to x=10 mol liter^{-1}. 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

$x = 0.447$, $x = 2.947$, and $x = 8.747$

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

(1) $C_A = C_B = 9.553$ mol liter^{-1}, $C_C = 0.447$ mol liter^{-1}, $T = 304.5$ K
(2) $C_A = C_B = 7.053$ mol liter^{-1}, $C_C = 2.947$ mol liter^{-1}, $T = 329.5$ K
(3) $C_A = C_B = 1.253$ mol liter^{-1}, $C_C = 8.747$ mol liter^{-1}, $T = 387.5$ 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

$$V\frac{dC_A}{dt} = Q_o\left(C_{Ao} - C_A\right) + V\left(-k_1 C_A^2\right)$$

$$\rho\hat{C}_p V\frac{dT}{dt} = \rho\hat{C}_p Q_o\left(T_o - T\right) + \left(-\Delta H\right)V\left(k_1 C_A^2\right)$$

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

$$\frac{dC_A}{dt} = \frac{C_{Ao} - C_A}{\tau} - A\exp\left(\frac{-E/R}{T}\right)C_A^2$$

$$\frac{dT}{dt} = \frac{T_o - T}{\tau} + JA\exp\left(\frac{-E/R}{T}\right)C_A^2$$

and substituting in the numbers

$$\frac{dC_A}{dt} = \frac{10 - C_A}{3} - 3\times 10^{11}\exp\left(\frac{-10000}{T}\right)C_A^2$$

$$\frac{dT}{dt} = \frac{300 - T}{3} + 3\times 10^{12}\exp\left(\frac{-10000}{T}\right)C_A^2$$

taking all 4 partial derivatives, the Jacobian of this set of equations is

$$\underline{\underline{J}} = \begin{bmatrix} -\frac{1}{3} - 6\times 10^{11}\exp\left(\frac{-10000}{T}\right)C_A & -\frac{10000}{T^2}3\times 10^{11}\exp\left(\frac{-10000}{T}\right)C_A^2 \\ 6\times 10^{12}\exp\left(\frac{-10000}{T}\right)C_A & -\frac{1}{3} + \frac{10000}{T^2}3\times 10^{12}\exp\left(\frac{-10000}{T}\right)C_A^2 \end{bmatrix}$$

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)

$$\underline{\underline{J}} = \begin{bmatrix} -\frac{1}{3} - 2kC_A & -\frac{10000}{T^2}kC_A^2 \\ 20kC_A & -\frac{1}{3} + \frac{100000}{T^2}kC_A^2 \end{bmatrix}$$

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

The characteristic polynomial for this matrix is

$$\left(-\frac{1}{3} - 2kC_A - \lambda\right)\left(-\frac{1}{3} + \frac{100000}{T^2}kC_A^2 - \lambda\right) + \frac{10000}{T^2}kC_A^2 \times 20kC_A = 0$$

$$\frac{1}{9} - \frac{100000kC_A^2}{3T^2} + \frac{\lambda}{3} + \frac{2kC_A}{3} - \frac{200000k^2C_A^3}{T^2} + 2kC_A\lambda + \frac{\lambda}{3} - \frac{100000kC_A^2}{T^2}\lambda + \lambda^2 + \frac{10000}{T^2}kC_A^2 \times 20kC_A = 0$$

$$\lambda^2 + \left(\frac{2}{3} + 2kC_A - \frac{100000kC_A^2}{T^2}\right)\lambda + \frac{1}{9} + \frac{2kC_A}{3} - \frac{100000kC_A^2}{3T^2} = 0$$

For $C_A = 9.553$ mol liter^{-1}, $T = 304.5$ K, we have $k = 0.00163$ hr^{-1}

$$\lambda^2 + 0.5370\lambda + 0.06789 = 0$$

Applying the quadratic formula gives $\lambda = -0.2037$ or $\lambda = -0.3333$.
The fact that these are both negative shows that this steady state **is stable**.

For $C_A = 7.053$ mol liter^{-1}, $T = 329.5$ K, $k = 0.01975$ hr^{-1} and we have

$$\lambda^2 + 04027\lambda - 0.09769 = 0$$

Applying the quadratic formula gives $\lambda = 0.2931$ or $\lambda = -0.3333$.
The fact that one of these is positive shows that this steady state **is unstable**.

For $C_A = 1.253$ mol liter^{-1}, $T = 387.5$ K, $k = 1.856$ hr^{-1} and we have

$$\lambda^2 + 3.377\lambda + 1.015 = 0$$

and the eigenvalues are –3.044 and –0.3333.
The fact that these are both negative shows that this steady state **is stable**.

3. Now, something a little different. Answer the following questions in a few sentences each:

(a) Describe how, experimentally, you would determine whether internal diffusion limitations are important for a reaction being carried out using a high surface area porous heterogeneous catalyst. (5 points)

The most straightforward experimental approach is to do experiments with catalyst pellets of different sizes or, if using pre-formed pellets, with the original pellets and crushed pellets. If the apparent reaction rate changes with pellet size, then diffusion limitations are important. If the rate (per unit mass of catalyst) is independent of pellet size, then diffusion limitations are not important for the conditions being considered.

(b) Explain how you would go about measuring an experimental residence time distribution for a reactor with an unknown degree of mixing. (5 points)

A residence time distribution is measured by injecting a pulse of a non-reactive tracer compound at the reactor inlet and measuring its concentration at the outlet. Ideally, this should be repeated with different tracer compounds to ensure that no reaction or retention (reversible adsorption on solid surfaces) is occurring. The residence time distribution is directly proportional to the concentration leaving the reactor:

$$E(\theta)d\theta = \frac{\text{Amount coming out between } \theta \text{ and } \theta + d\theta}{\text{Total amount of tracer}} = \frac{QC(\theta)d\theta}{M} = \frac{QC(\theta)d\theta}{Q\int_0^\infty C(\theta)d\theta} \text{, so}$$

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

Where $E(\theta)$ is the residence time distribution, Q is the volumetric flowrate through the reactor, θ is time, measured from the instant when the tracer was injected, and M is the total amount of tracer injected (in units consistent with those for concentration and flowrate).

(c) Write the balance equations for a single reaction in an adiabatic plug flow reactor with axial mixing, and explain how you would approach solving these equations. (5 points)

The species mole balance on a reactant is:

$$-v_x \frac{dC}{dx} + D\frac{d^2C}{dx^2} - r = 0$$

Where C is the concentration of the reactant, v_x is the axial velocity, D is the dispersion coefficient, and r is the reaction rate, which depends on both concentration and temperature. The above assumes that the reaction is written so that the species under consideration has a stoichiometric coefficient of -1.

The energy balance is

$$-\rho\hat{C}_p v_x \frac{dT}{dx} + \lambda\frac{d^2T}{dx^2} - \Delta H r = 0$$

Where ρ is the fluid density, C_p is the specific heat (assumed constant), T is the temperature, ΔH is the enthalpy of reaction, and λ is the effective thermal conductivity. The above expressions assume that the dispersion coefficient is the same for all species, and that all properties are independent of composition and temperature.

These can be solved by discretizing the first and second derivatives with finite differences and then applying Newton's method to solve the resulting set of algebraic equations for the concentration and temperature at discrete points within the reactor.

(d) Write an equation for the pressure drop in a fixed-bed catalytic reactor, and explain how you would determine the parameter(s) that appear in the equation. (5 points)

The pressure drop is usually computed from a simplified momentum balance like

$$\frac{dp}{dz} = -f\frac{\rho_g u_s^2}{d_p}$$

Where p is pressure, z is axial position, ρ_g is the fluid density, u_s is the superficial velocity, and d_p is the catalyst pellet diameter (or equivalent diameter). f is a friction factor that is generally determined from correlations like the Ergun equation:

$$f = \frac{(1-\varepsilon)^2}{\varepsilon^3}\frac{150}{d_p\rho_g u_s/\mu}, \text{ with } d_p = \frac{6(1-\varepsilon)}{a_v}$$

In which ε is the void fraction of the bed, μ is the viscosity of the fluid, and a_v is the external surface area per unit volume of the catalyst pellet (which would be $6/d_p$ for a sphere).

(e) Describe the first calculations you would make if you were assigned the task of designing a fixed-bed catalytic reactor for a new process. (5 points)

The first calculation to be done is to find the adiabatic reaction temperature, and determine from it, and the kinetics, whether the reaction can be carried out in a single adiabatic bed. If heat removal is needed, then one must decide whether it can be accomplished with a few adiabatic beds in series, with inter-bed cooling, or if continuous cooling is required. Use of an inert diluents to reduce the temperature rise or fall should also be considered.

(f) Explain why an inert diluent such as nitrogen might be added to the feed to a fixed bed reactor in which an exothermic reaction is taking place. (5 points)

An inert diluent is most often used to reduce the effect of the heat of reaction, by increasing the heat capacity of the stream flowing through the reactor. It does this at the cost of reducing the reaction rate (by lowering reactant concentrations) and increasing cost by the cost of adding the diluent and separating it after the reactor. However, this is advantageous if it allows the reaction to be carried out in one (or a few) adiabatic stages rather than in a reactor with continuous heat addition or removal.

(g) Describe a situation in which it would be advantageous to use a batch reactor rather than a continuous reactor, and explain why it is advantageous. (5 points)

Batch reactors can be advantageous when many different products or grades of product are to be produced in the same set of equipment (as in some specialty chemical manufacture) or when individual batches must be certified by lot number, etc. as in some pharmaceutical, food, and beverage applications. Batch reactors are also sometimes used because they are viewed as being easier to scale up from (batch) laboratory experiments than a continuous process.