

CE 561, Exam 2, December 11, 2003

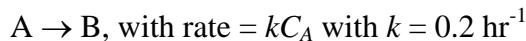
This exam consists of 3 questions, each with multiple parts. You should be careful not to get stuck on one part. If you do not know how to do a problem, move on and return to it if you have time at the end. If you cannot find the numerical answer to a problem, explain how you would find the answer if 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 irreversible first order reaction



is to be carried out in 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. 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 3 hours.

- (a) 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.)

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

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

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

$$\frac{d(V C_B)}{dt} = k C_A V$$

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  $V = Qt = 500t$  (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:

$$\frac{dN_A}{dt} = Q C_{A0} - k N_A$$

$$\frac{dN_B}{dt} = k N_A$$

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. Adding the above two equations, we see that

$$\frac{d}{dt}(N_A + N_B) = QC_{Ao}$$

Integrating this, and using the initial condition that  $N_A = N_B = 0$  at  $t = 0$  and substituting  $Q = 500$  liters/hr and  $C_{Ao} = 2$  mol/liter, we get

$$N_A + N_B = QC_{Ao}t = 1000t$$

Since the reaction is irreversible, the rate equation for A is independent of B, and we can solve the equation for A first, and then find B from  $N_B = 1000t - N_A$ . Our rate equation for A is:

$$\frac{dN_A}{dt} = QC_{Ao} - kN_A$$

As usual, we solve this sort of equation by assuming a solution of the form  $N_A = f(t)\exp(-kt)$

$$\frac{dN_A}{dt} = f' \exp(-kt) - kf \exp(-kt) = QC_{Ao} - kf \exp(-kt)$$

$$f' \exp(-kt) = QC_{Ao}$$

$$f' = QC_{Ao} \exp(kt)$$

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

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

Using the initial condition that  $N_A = 0$  at  $t = 0$ , we see that the constant of integration is  $-1$ , and

$$N_A = \frac{QC_{Ao}}{k} (1 - \exp(-kt)) = 5000(1 - \exp(-0.2t))$$

Then

$$N_B = QC_{Ao}t - N_A = 1000t - 5000(1 - \exp(-0.2t))$$

The above solution for  $N_A$  and  $N_B$  is valid for  $t = 0$  to  $t = 2$  hours. After that,  $Q = 0$  and we have

$$\frac{dN_A}{dt} = -kN_A$$

$$\frac{dN_B}{dt} = kN_A$$

Adding these shows that  $N_A + N_B$  is constant after  $t = 2$  hours. At  $t = 2$  hours,  $N_A + N_B = 1000t = 2000$  moles. So, after  $t = 2$  hours,  $N_B = 2000 - N_A$ . The equation for  $N_A$  is our favorite differential equation, except that we want to apply the initial condition at  $t = 2$  hours, at which time  $N_A = 5000(1 - \exp(-0.4)) = 1648.4$  moles. So, for times greater than 2 hours, we get  $N_A = 1648.4 \exp(-0.2(t - 2))$  and therefore  $N_B = 2000 - 1648.4 \exp(-0.2(t - 2))$ .

To summarize:

$N_A = 5000(1 - \exp(-0.2t))$  for  $0 < t < 2$  hours and  $N_A = 1648.4 \exp(-0.2(t - 2))$  for  $t > 2$  hours.

$N_B = 1000t - 5000(1 - \exp(-0.2t))$  for  $0 < t < 2$  hours and  $N_B = 2000 - 1648.4 \exp(-0.2(t - 2))$  for  $t > 2$  hours.

(b) Find the **batch time** that maximizes the average production rate of species B. (15 pts.)

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 time needed to empty and clean the reactor). So, the production rate is

$$\text{Prod. Rate} = \frac{1000t - 5000(1 - \exp(-0.2t))}{t + 3} \quad \text{for } 0 \leq t \leq 2$$

$$\text{Prod. Rate} = \frac{2000 - 1648.4 \exp(-0.2(t - 2))}{t + 3} \quad \text{for } t \geq 2$$

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. The derivatives, after a little simplification, are

$$\frac{d}{dt}(\text{Prod. Rate}) = \frac{-1000t \exp(-0.2t) + 8000(1 - \exp(-0.2t))}{(t + 3)^2} \quad \text{for } 0 \leq t \leq 2$$

$$\frac{d}{dt}(\text{Prod. Rate}) = \frac{329.7t \exp(-0.2(t - 2)) - 2000 + 2637.4 \exp(-0.2(t - 2))}{(t + 3)^2} \quad \text{for } t \geq 2$$

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. This is even easier to see if you have a graphing calculator with which to plot it from 0 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:

$$329.7t \exp(-0.2(t - 2)) - 2000 + 2637.4 \exp(-0.2(t - 2)) = 0$$

If we plot this using a graphing calculator, or just try a few values, we can see that it goes through zero near  $t = 6.3$  hours, and this can be refined by trial and error to give  $t = 6.281$ . Since this goes from positive to negative with increasing  $t$  the second derivative of production rate with respect to time (the slope of the first derivative vs. time) is negative, and this is, in fact a maximum and not a minimum.

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

(c) Evaluating the production rate for  $t = 6.281$  gives 140.1 moles/hour. Evaluating it for nearby values of  $t$  again confirms that this is a maximum in 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 =  $C_{Ao} = 1$  mol/liter

Heat of reaction =  $\Delta H = -418,000$  J/mol

Density =  $\rho = 1000$  g/liter

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

Feed flow rate =  $Q = 50$  liters  $\text{min}^{-1}$

Reactor volume =  $V = 100$  liters

The reaction rate constant can be expressed as

$$k = 10^{12} \exp(-10000/T) \text{ min}^{-1}$$

- (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.)

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

$$T - T_o - \tau (A \exp(-E_a/T))(JC_{Ao} - (T - T_o)) = 0$$

Putting in the rest of the numbers from the problem statement, we have  $\tau = 100$  liters/50 liters/min = 2 min and  $J = 418000/(1000*4.18) = 100$  K liter mol<sup>-1</sup> and

$$T - 300 - 2 \times 10^{12} \exp(-10000/T)(400 - T) = 0$$

The maximum temperature rise is  $J C_{Ao} = 100$  K, so we know that  $T$  will always be between 300 and 400 K. Plotting the above function shows that it crosses zero near 301 K, 356 K, and 395 K. These can be refined by trial and error or fixed point iteration to get 300.72 K, 356.18, and 395.41 K. The corresponding concentrations of A are given by

$$C_A = C_{Ao} - \frac{1}{J}(T - T_o) = 1 - 0.01(T - 300)$$

So, for  $T = 300.72$  K,  $C_A = 0.9928$  mol/liter, for  $T = 356.18$  K,  $C_A = 0.4382$  mol/liter, and for  $T = 395.41$  K,  $C_A = 0.0459$  mol/liter

- (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.)

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

$$\frac{dC_A}{dt} = \frac{C_{Ao} - C_A}{\tau} - A \exp\left(\frac{-E_a}{T}\right) C_A$$

$$\frac{dT}{dt} = \frac{T_o - T}{\tau} + JA \exp\left(\frac{-E_a}{T}\right) C_A$$

So, the Jacobian is

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

Putting in the numbers from the problem statement

$$J = \begin{bmatrix} -\frac{1}{2} - 10^{12} \exp(-10000/T) & -\left(\frac{10000}{T^2}\right) 10^{12} \exp(-10000/T) C_A \\ 10^{14} \exp(-10000/T) & -\frac{1}{2} + \left(\frac{10000}{T^2}\right) 10^{14} \exp(-10000/T) C_A \end{bmatrix}$$

For  $T = 300.72$  K,  $C_A = 0.9928$  mol/liter this becomes

$$J = \begin{bmatrix} -0.5036 & -0.0003969 \\ 0.3616 & -0.4603 \end{bmatrix}$$

To find the eigenvalues of this, we take the determinant of

$$J = \begin{bmatrix} -0.5036 - \lambda & -0.0003969 \\ 0.3616 & -0.4603 - \lambda \end{bmatrix}$$

Multiplying out the determinant and setting it equal to zero gives

$$\lambda^2 + 0.9639\lambda + 0.2320 = 0$$

Applying the quadratic formula to this gives

$$\lambda = -0.4986 \text{ or } \lambda = -0.4653$$

Since both eigenvalues are negative, the steady state is stable.

For  $T = 356.18$  K,  $C_A = 0.4382$  mol/liter, the Jacobian becomes

$$J = \begin{bmatrix} -1.1410 & -0.02214 \\ 64.104 & 1.7142 \end{bmatrix}$$

To find the eigenvalues of this, we take the determinant of

$$J = \begin{bmatrix} -1.1410 - \lambda & -0.02214 \\ 64.104 & 1.7142 - \lambda \end{bmatrix}$$

Multiplying out the determinant and setting it equal to zero gives

$$\lambda^2 - 0.5732\lambda - 0.5366 = 0$$

Applying the quadratic formula to this gives

$$\lambda = -0.5 \text{ or } \lambda = 1.0732$$

Since one eigenvalue is positive, we conclude that this steady state is unstable.

Finally, for  $T = 395.41$  K,  $C_A = 0.0459$  mol/liter this becomes

$$J = \begin{bmatrix} -10.8897 & -0.0305 \\ 1038.97 & 2.5501 \end{bmatrix}$$

To find the eigenvalues of this, we take the determinant of

$$J = \begin{bmatrix} -10.8897 - \lambda & -0.0305 \\ 1038.97 & 2.5501 - \lambda \end{bmatrix}$$

Multiplying out the determinant and setting it equal to zero gives

$$\lambda^2 + 8.3396\lambda + 3.9188 = 0$$

Applying the quadratic formula to this gives

$$\lambda = -0.4999 \text{ or } \lambda = -7.839$$

Since both eigenvalues are negative, the steady state is stable.

- (3) Consider the production of  $\text{SO}_3$  from  $\text{SO}_2$  in a fixed bed tubular reactor. The overall reaction is  $\text{SO}_2 + \frac{1}{2} \text{O}_2 \leftrightarrow \text{SO}_3$ . The feed to the reactor is 5.0% by volume  $\text{SO}_2$  and 95.0% by volume dry air (79%  $\text{N}_2$ , 21%  $\text{O}_2$ ) at  $450^\circ\text{C}$  and 2 bar total pressure. The total feed flow rate is 500 kg/hr. The reactor will be a 50 cm diameter cylindrical vessel filled with catalyst pellets. The platinum on alumina catalyst is in the form of 4 mm diameter cylindrical pellets (ranging from 15 to 50 mm long), with a catalyst density of  $1.0 \text{ g cm}^{-3}$ , a pore volume of  $0.4 \text{ cm}^3 \text{ g}^{-1}$ , and a specific surface area of  $150 \text{ m}^2 \text{ g}^{-1}$ . The density of the catalyst bed, as packed in the reactor, is  $0.6 \text{ (kg catalyst) m}^{-3}$ . The pressure drop through the reactor is negligible. The reaction rate, in the absence of any diffusion limitations, is

$$r = k_1 C_{\text{SO}_2} - k_2 C_{\text{SO}_3}, \text{ with}$$

$$k_1 = 1.0 \times 10^6 e^{(-12000/T)} \text{ m}^3 \text{ s}^{-1} \text{ (kg catalyst)}^{-1} \text{ and } k_2 = 1.0 \times 10^{13} e^{(-24000/T)} \text{ m}^3 \text{ s}^{-1} \text{ (kg catalyst)}^{-1}.$$

The specific heat of the gas mixture can be assumed constant at  $1.0 \text{ kJ kg}^{-1} \text{ K}^{-1}$ . The atomic weights of sulfur, oxygen, and nitrogen are 32, 16, and 14  $\text{g mol}^{-1}$ , respectively.

- (a) Write the steady-state reactant ( $\text{SO}_2$ ) mole balance equation and the enthalpy balance equation, including appropriate boundary conditions, for the fixed bed reactor for each of the following cases. Identify the variables in the equations and the units in which they are measured. Give their numerical values where possible. Where numerical values are not available from the problem statement, suggest how they might be obtained. For each part, give a brief description of how the balance equations could be solved numerically.

- (i) Ideal plug flow, no radial or axial mixing, no heat flow through the reactor walls. (10 points)

For ideal plug flow with no mixing, the mole balance on  $\text{SO}_2$  can be written as

$$\frac{dF_{\text{SO}_2}}{dz} = -\rho_B \Omega (k_1 C_{\text{SO}_2} - k_2 C_{\text{SO}_3})$$

or it can be written as

$$\frac{d(u_s C_{\text{SO}_2})}{dz} = -\rho_B (k_1 C_{\text{SO}_2} - k_2 C_{\text{SO}_3})$$

The enthalpy balance can be written as

$$\rho_g \hat{c}_p u_s \frac{dT}{dz} = (-\Delta H_{rxn}) \rho_B (k_1 C_{\text{SO}_2} - k_2 C_{\text{SO}_3})$$

The boundary conditions for these equations at the reactor inlet are  $F_{\text{SO}_2} = F_{\text{SO}_2,o}$ , or  $C_{\text{SO}_2} = C_{\text{SO}_2,o}$  and  $T = T_o$  at  $z = 0$ .

The variables in these equations are

$$F_{\text{SO}_2} = \text{molar flow rate of } \text{SO}_2 \text{ (mol s}^{-1}\text{)}$$

$$z = \text{axial position in the reactor (m)}$$

$$\rho_B = \text{catalyst bed density} = 0.6 \text{ (kg catalyst m}^{-3}\text{)}$$

$\Omega$  = reactor cross-sectional area = 0.196 m<sup>2</sup>

$k_1$  = forward first-order rate constant =  $1.0 \times 10^6 e^{(-12000/T)}$  m<sup>3</sup> s<sup>-1</sup> (kg catalyst)<sup>-1</sup>

$k_2$  = reverse first-order rate constant =  $1.0 \times 10^{13} e^{(-24000/T)}$  m<sup>3</sup> s<sup>-1</sup> (kg catalyst)<sup>-1</sup>

$C_{SO_2}$  = concentration of SO<sub>2</sub> (mol m<sup>-3</sup>)

$C_{SO_3}$  = concentration of SO<sub>3</sub> (mol m<sup>-3</sup>). It is related to the concentration of SO<sub>2</sub> by stoichiometry. The molar flow rates are related by  $F_{SO_3} = F_{SO_2,o} - F_{SO_2}$ . The molar flow rate is the concentration times the velocity times the reactor cross-sectional area.

So, we can relate the concentrations by  $C_{SO_3} = \frac{u_{s,o}}{u_s} C_{SO_2,o} - C_{SO_2}$

$u_s$  = superficial velocity (volumetric flow rate/reactor cross-sectional area) (m s<sup>-1</sup>) This is the total molar flow rate divided by the total concentration (which can be determined from the ideal gas law) divided by the reactor cross-sectional area. This is

$$u_s = \frac{F_{N_2} + F_{O_2} + F_{SO_2} + F_{SO_3}}{\Omega} \left( \frac{RT}{p} \right) = \frac{F_{N_2,o} + F_{O_2,o} + F_{SO_2,o} - \frac{1}{2}(F_{SO_2,o} - F_{SO_2})}{\Omega} \left( \frac{RT}{p} \right)$$

$$u_s = u_{s,o} \frac{F_{N_2,o} + F_{O_2,o} + \frac{1}{2}F_{SO_2,o} - \frac{1}{2}F_{SO_2}}{F_{N_2,o} + F_{O_2,o} + F_{SO_2,o}} \left( \frac{T}{T_o} \right)$$

$\rho_g$  = gas density (kg m<sup>-3</sup>) This can be calculated from the ideal gas law as

$$\rho_g = \frac{\bar{M}p}{RT} = \rho_{g,o} \frac{\bar{M}T_o}{\bar{M}_o T} = \rho_{g,o} \left( \frac{F_{N_2,o} + F_{O_2,o} + F_{SO_2,o}}{F_{N_2,o} + F_{O_2,o} + \frac{1}{2}F_{SO_2,o} - \frac{1}{2}F_{SO_2}} \right) \frac{T_o}{T}$$

$\hat{c}_p$  = specific heat of gas mixture = 1.0 kJ kg<sup>-1</sup> K<sup>-1</sup>

$T$  = temperature (K)

$\Delta H_{rxn}$  = heat of reaction = forward activation energy – reverse activation energy = -12000 R = -99.8 kJ mol<sup>-1</sup>

$\bar{M}_o$  = mean molecular weight of the feed (kg mol<sup>-1</sup>) = 0.005\*0.064 + 0.995\*0.79\*0.028 + 0.995\*0.21\*0.032 = 0.0290 kg mol<sup>-1</sup>

$F_o$  = total molar flow rate of the feed = 500 kg hr<sup>-1</sup>/3600 s hr<sup>-1</sup>/(0.0290 kg mol<sup>-1</sup>) = 4.79 mol s<sup>-1</sup>

$$\rho_{g,o} = \text{density of the feed stream} = \frac{\bar{M}_o p}{RT_o} = \frac{(0.0290)(200000)}{(8.314)(723)} = 0.965 \frac{\text{kg}}{\text{m}^3}$$

$\bar{M}$  = mean molecular weight (kg mol<sup>-1</sup>)

$$= 0.028F_{N_2} + 0.032F_{O_2} + 0.064F_{SO_2} + 0.080F_{SO_3}$$

$F_{SO_2,o}$  = feed molar flow rate of SO<sub>2</sub> = 0.005\*4.79 = 0.0239 mol s<sup>-1</sup>

$F_{O_2,o}$  = feed molar flow rate of O<sub>2</sub> = 0.995\*0.21\*4.79 = 1.000 mol s<sup>-1</sup>

$F_{N_2,o}$  = feed molar flow rate of N<sub>2</sub> = 0.995\*0.79\*4.79 = 3.763 mol s<sup>-1</sup>

$C_{SO_2,o}$  = feed concentration of SO<sub>2</sub> = 0.005\*total concentration = 0.005\*( $p/RT$ ) = 0.005\*(200000/8.314/723) = 0.1664 mol m<sup>-3</sup>

$T_o$  = feed temperature = 450 °C = 723 K

$u_{s,o}$  = the inlet superficial velocity ( $\text{m s}^{-1}$ ). It can be calculated as the volumetric flowrate divided by the cross-sectional area at inlet conditions. This gives  $u_{s,o} = 4.79 \times 8.314 \times 723 / 200000 / 0.196 = 0.735 \text{ m s}^{-1}$ .

Mathematically, these balance equations form an initial value problem. They can be solved using one of the Euler methods, a Runge-Kutta method, Gear's method, or any of the other methods that we learned for 1<sup>st</sup> order ODE's.

- (ii) Plug flow with mixing in the axial direction due to flow around the catalyst pellets, but still no heat flow through the reactor walls. (5 points)

If we also consider axial mixing, then the equations become

$$\frac{d(u_s C_{SO_2})}{dz} = \frac{d}{dz} \left( D_{e,z} \frac{dC_{SO_2}}{dz} \right) - \rho_B (k_1 C_{SO_2} - k_2 C_{SO_3})$$

and

$$\rho_g \hat{c}_p u_s \frac{dT}{dz} = \frac{d}{dz} \left( \lambda_{e,z} \frac{dT}{dz} \right) + (-\Delta H_{rxn}) \rho_B (k_1 C_{SO_2} - k_2 C_{SO_3})$$

Now boundary conditions are needed at both the inlet and the outlet of the reactor. These could be  $C_{SO_2} = C_{SO_2,o}$  and  $T = T_o$  at  $z = 0$  and  $\frac{dC_{SO_2}}{dz} = 0$  and  $\frac{dT}{dz} = 0$  at  $z = L$ , or they could be the 'Danckwerts' boundary conditions,

$$u_s C_{SO_2} - D_{e,z} \frac{dC_{SO_2}}{dz} = u_{s,o} C_{SO_2,o} \text{ and } \rho \hat{c}_p u_s T - \lambda_{e,z} \frac{dT}{dz} = \rho_o \hat{c}_p u_{s,o} T_o \text{ at } z = 0 \text{ and}$$

$$\frac{dC_{SO_2}}{dz} = 0 \text{ and } \frac{dT}{dz} = 0 \text{ at } z = L.$$

The variables are defined as in part (i). New variables are

$D_{e,z}$  = effective axial dispersion coefficient ( $\text{m}^2 \text{s}^{-1}$ ). No value for this is given. It is best found by performing a tracer experiment.

$\lambda_{e,z}$  = effective axial thermal conductivity ( $\text{kJ m}^{-1} \text{s}^{-1} \text{K}^{-1}$ ). No value for this is given. It is best found from experiment.

$L$  = the total length of the reactor

Mathematically, these equations give a 1-dimensional boundary value problem. It would be solved by replacing the derivatives with finite differences, then using Newton's method to solve the resulting set of algebraic equations.

- (iii) Plug flow with both radial and axial mixing due to flow around the catalyst pellets and heat transfer through the reactor wall to condensing steam at 200 °C. (5 points)

If we also consider radial mixing, then the equations become

$$\frac{\partial(u_s C_{SO_2})}{\partial z} = \frac{\partial}{\partial z} \left( D_{e,z} \frac{\partial C_{SO_2}}{\partial z} \right) + \frac{1}{r} \frac{\partial}{\partial r} \left( r D_{e,r} \frac{\partial C_{SO_2}}{\partial r} \right) - \rho_B (k_1 C_{SO_2} - k_2 C_{SO_3})$$

and

$$\rho_g \hat{c}_p u_s \frac{\partial T}{\partial z} = \frac{\partial}{\partial z} \left( \lambda_{e,z} \frac{\partial T}{\partial z} \right) + \frac{1}{r} \frac{\partial}{\partial r} \left( r \lambda_{e,r} \frac{\partial T}{\partial r} \right) + (-\Delta H_{rxn}) \rho_B (k_1 C_{SO_2} - k_2 C_{SO_3})$$

With inlet and outlet boundary conditions:

$$u_s C_{SO_2} - D_{e,z} \frac{\partial C_{SO_2}}{\partial z} = u_{s,o} C_{SO_2,o} \text{ and } \rho \hat{c}_p u_s T - \lambda_{e,z} \frac{\partial T}{\partial z} = \rho_o \hat{c}_p u_{s,o} T_o \text{ at } z = 0$$

$$\text{and } \frac{\partial C_{SO_2}}{\partial z} = 0 \text{ and } \frac{\partial T}{\partial z} = 0 \text{ at } z = L.$$

and radial boundary conditions

$$\frac{\partial C_{SO_2}}{\partial r} = 0 \text{ and } \frac{\partial T}{\partial r} = 0 \text{ at } r = 0$$

$$\text{and } \frac{\partial C_{SO_2}}{\partial r} = 0 \text{ and } -\lambda_{e,r} \frac{\partial T}{\partial r} = h_f (T - T_r) \text{ at } r = R_t$$

The variables are defined as in parts (i) and (ii). New variables are  $D_{e,r}$  = effective radial dispersion coefficient ( $m^2 s^{-1}$ ). No value for this is given. It is best found from experiment.

$\lambda_{e,r}$  = effective radial thermal conductivity ( $kJ m^{-1} s^{-1} K^{-1}$ ). No value for this is given. It is best found from experiment.

$R_t$  = the tube radius = 0.25 m

$h_f$  = heat transfer coefficient from the fluid near the wall to the condensing steam ( $kJ s^{-1} K^{-1} m^{-2}$ ). This is not given. It could be determined from experiment or from correlations.

Mathematically, these equations give a 2-dimensional boundary value problem. This would also be solved by replacing the derivatives with finite differences, then using Newton's method to solve the resulting set of algebraic equations. However, the problem would be larger and more complex than the 1-D problem in part (ii).

- (b) For *adiabatic operation* of the reactor with ideal plug flow and no radial or axial mixing, derive a relationship between the reactor temperature and the SO<sub>2</sub> conversion. Estimate the maximum temperature that could be reached in the reactor. What are the concentrations of SO<sub>2</sub> and SO<sub>3</sub> when this maximum temperature is reached? (10 points)

We start from the balance equations for the ideal adiabatic plug flow reactor given in part (a):

$$\frac{d(u_s C_{SO_2})}{dz} = -\rho_B (k_1 C_{SO_2} - k_2 C_{SO_3})$$

$$\rho_g \hat{c}_p u_s \frac{dT}{dz} = (-\Delta H_{rxn}) \rho_B (k_1 C_{SO_2} - k_2 C_{SO_3})$$

From the overall continuity equation, we know that the product  $\rho_g u_s$  is constant, and we are assuming that the heat of reaction and specific heat are constant, so we can take these all inside the derivative in the energy equation and write

$$\frac{d}{dz} (u_s C_{SO_2}) = \frac{d}{dz} \left( \frac{\rho_g \hat{c}_p u_s}{\Delta H_{rxn}} T \right)$$

Integrating this (and using the values at the inlet) gives

$$u_s C_{SO_2} - u_{s,o} C_{SO_2,o} = \frac{\hat{c}_p \rho_{g,o} u_{s,o}}{\Delta H_{rxn}} (T - T_o)$$

Solving this for  $T$  gives

$$T = T_o + \frac{-\Delta H_{rxn}}{\rho_{g,o} \hat{c}_p} \left( C_{SO_2,o} - \frac{u_s}{u_{s,o}} C_{SO_2} \right)$$

If the reaction were irreversible, then the maximum temperature would be achieved when  $C_{SO_2}$  goes to zero. This would be

$$T_{\max,irrev} = 723.15 + \frac{99.8}{0.995 \cdot 1.0} (0.1664) = 740.35 \text{ K}$$

The maximum possible temperature rise is 17.2 K. For this case, the factor  $u_s/u_{s,o}$  would be

$$\frac{u_s}{u_{s,o}} = \frac{F_{N_2,o} + F_{O_2,o} + \frac{1}{2} F_{SO_2,o}}{F_{N_2,o} + F_{O_2,o} + F_{SO_2,o}} \left( \frac{T}{T_o} \right) = 0.995 \left( \frac{740}{723} \right) = 1.018$$

This makes it clear that we can neglect this factor, and write our usual expression for a constant density adiabatic reactor,

$$T = T_o + \frac{-\Delta H_{rxn}}{\rho_{g,o} \hat{c}_p} (C_{SO_2,o} - C_{SO_2})$$

Since the reaction is reversible, we cannot, in fact, go to an  $SO_2$  concentration of zero, but only to the equilibrium composition. The equilibrium composition is given by

$$k_1 C_{SO_2,eq} - k_2 C_{SO_3,eq} = 0, \text{ or } k_1 C_{SO_2,eq} = k_2 (C_{SO_2,o} - C_{SO_2,eq})$$

$$\text{from which } \frac{C_{SO_2,eq}}{C_{SO_2,o}} = \frac{k_2}{k_1 + k_2} = \frac{k_1/k_2}{1 + k_1/k_2} = \frac{1 \times 10^{-7} e^{12000/T}}{1 + 1 \times 10^{-7} e^{12000/T}}$$

At 723 K, this gives  $\frac{C_{SO_2,eq}}{C_{SO_2,o}} = 0.6176$ , and at 740 K, this gives  $\frac{C_{SO_2,eq}}{C_{SO_2,o}} = 0.5245$ , so we expect to

get between 38% and 48% conversion at equilibrium. 43% of the temperature rise for complete conversion would be 7.4 K, so we predict a maximum temperature for adiabatic operation of about 730.5 K. If we wanted to compute the temperature rise more precisely, we could substitute the expression for  $T$  into the expression for the equilibrium composition to get

$$\frac{C_{SO_2,eq}}{C_{SO_2,o}} = \frac{1 \times 10^{-7} e^{12000 / \left( 723.15 + 17.2 \left( 1 - \frac{C_{SO_2,eq}}{C_{SO_2,o}} \right) \right)}}{1 + 1 \times 10^{-7} e^{12000 / \left( 723.15 + 17.2 \left( 1 - \frac{C_{SO_2,eq}}{C_{SO_2,o}} \right) \right)}}$$

and solve iteratively for  $\frac{C_{SO_2,eq}}{C_{SO_2,o}}$ . This would give  $\frac{C_{SO_2,eq}}{C_{SO_2,o}} = 0.5762$  and  $T_{\max} = 730.4 \text{ K}$

- (c) Assuming there are no diffusional limitations, estimate the amount of catalyst and the reactor length (catalyst bed depth) required to achieve 80% of the maximum possible conversion of  $SO_2$  to  $SO_3$  in this reactor. (10 points)

We saw in part (b) that the maximum possible conversion is  $1 - .5762 = 0.4238$  or 42%. 80% of this is 33.9% conversion, or  $\frac{C_{SO_2}}{C_{SO_2,o}} = 1 - 0.339 = 0.661$ . The feed concentration of  $SO_2$  is  $0.1664$

$\text{mol m}^{-3}$ , so at 33.9% conversion, the concentration of  $SO_2$  is  $0.110 \text{ mol/m}^3$ . To find the residence time required to reach this conversion, we must integrate the  $SO_2$  mole balance for the adiabatic plug flow reactor. This is

$$\frac{d(u_s C_{SO_2})}{dz} = -\rho_B (k_1 C_{SO_2} - k_2 C_{SO_3})$$

and we saw in part (b) that changes in the superficial velocity would be negligible, so that we can define  $\tau = z/u_s$  and write

$$\frac{dC_{SO_2}}{d\tau} = -\rho_B (k_1 C_{SO_2} - k_2 C_{SO_3})$$

Rearranging this and integrating it gives

$$\tau \rho_B = \int_{C_{SO_2,o}}^{C_{SO_2}} \frac{-dC_{SO_2}}{k_1 C_{SO_2} - k_2 C_{SO_3}} = \int_{C_{SO_2,o}}^{C_{SO_2}} \frac{-dC_{SO_2}}{k_1 C_{SO_2} - k_2 (C_{SO_2,o} - C_{SO_2})}$$

Letting  $x = 1 - \frac{C_{SO_2}}{C_{SO_2,o}}$  and setting the limits to the desired 33.9% conversion, this becomes

$$\tau \rho_B = \int_0^{0.339} \frac{-dx}{k_1 (1-x) - k_2 x}$$

Substituting the expressions for the rate constants, this is

$$\tau \rho_B = \int_0^{0.339} \frac{-dx}{1 \times 10^6 \exp(-12000/T)(1-x) - 1 \times 10^{13} \exp(-24000/T)x}$$

From part (b), we have the relationship

$$T = T_o + \frac{-\Delta H_{rxn}}{\rho_{g,o} \hat{C}_p} (C_{SO_2,o} - C_{SO_2}) = 723.15 + 17.2x$$

Substituting this into the integral gives

$$\tau \rho_B = \int_0^{0.339} \frac{-dx}{1 \times 10^6 \exp\left(-\frac{12000}{723.15 + 17.2x}\right)(1-x) - 1 \times 10^{13} \exp\left(-\frac{24000}{723.15 + 17.2x}\right)x}$$

Oh no! We can't do this integral! But, we saw in part (b) that the reactor was almost isothermal. If it were isothermal, then the integral would just be

$$\tau \rho_B = \int_0^{0.339} \frac{-dx}{k_1 (1-x) - k_2 x} = \left[ \frac{1}{k_1 + k_2} \ln(k_1 (1-x) - k_2 x) \right]_0^{0.339} = \frac{1}{k_1 + k_2} \ln\left(\frac{k_1}{0.661k_1 - 0.339k_2}\right)$$

The temperature goes from 723.15 K at  $x = 0$  to 729 K at  $x = 0.339$ . At 723.15, the rate constants are  $k_1 = 0.0619 \text{ m}^3 \text{ s}^{-1} (\text{kg catalyst})^{-1}$ , and  $k_2 = 0.0383 \text{ m}^3 \text{ s}^{-1} (\text{kg catalyst})^{-1}$ . At 729 K, they are  $k_1 = 0.0710 \text{ m}^3 \text{ s}^{-1} (\text{kg catalyst})^{-1}$ , and  $k_2 = 0.0504 \text{ m}^3 \text{ s}^{-1} (\text{kg catalyst})^{-1}$ .

For isothermal operation at 723.15, this would give  $\tau \rho_B = 7.94 \text{ s (kg catalyst) m}^{-3}$ , and for isothermal operation at 729 K, this would give  $\tau \rho_B = 7.14 \text{ s (kg catalyst) m}^{-3}$ . So, a reasonable estimate is  $\tau \rho_B = 7.5 \text{ s (kg catalyst) m}^{-3}$ . Multiplying by the total feed rate of  $0.144 \text{ m}^3 \text{ s}^{-1}$  gives a

total catalyst requirement of 1.08 kg, which corresponds to a reactor volume of 1.8 m<sup>3</sup> and a residence time of 12.5 s. For the 50 cm diameter reactor, this gives a bed depth of 9.2 m.

If you are paying attention, you may have noticed that the catalyst bed density value was physically unrealistic. 0.6 kg/m<sup>3</sup> is lower than the gas density! Oops – got the units wrong!

