

CE 561, Exam 2, December 10, 2007

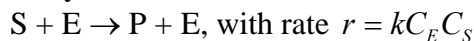
This exam consists of 3 questions, each with multiple parts. You should be careful not to get stuck on one part. If you do not know how to do a problem, move on and return to it if you have time at the end. If you cannot find the numerical answer to a problem, explain how you would find the answer if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

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

You will have 3 hours to complete the exam. *Please use a separate blue book for each exam problem.* Carefully explain any assumptions you make, label what part of what problem you are working on, and define the symbols that you use. The point value of each part is indicated – budget your effort accordingly. There are 100 points total.

Good luck.

1. The enzymatic 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 per liter of the substrate S and 0.05 moles per liter of the enzyme E. The feed flow rate is 50 liters per hour. The reactor volume is 100 liters, and when it is full, the feed is shut off. That is, the feed rate is 50 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. The rate constant is  $k = 5 \text{ liter}/(\text{mol hr})$ .

- (a) Find the **number of moles of substrate (S) and product (P)** 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). (15 pts.)

The enzyme concentration does not change due to reaction (it acts as a catalyst) and therefore we do not need to write a balance on it. We can simply write balances for the substrate (S) and product (P) and lump the constant enzyme concentration into the rate constant.

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

$$\begin{aligned}\frac{d(\rho V)}{dt} &= \rho Q \\ \frac{d(V C_S)}{dt} &= Q C_{S_0} - k C_E C_S V \\ \frac{d(V C_P)}{dt} &= k C_E C_S V\end{aligned}$$

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  $V = Qt = 50t$  (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  $N_S = VC_S$  and  $N_P = VC_P$ . In terms of  $N_S$  and  $N_P$ , the equations are:

$$\frac{dN_S}{dt} = QC_{S_0} - kC_E N_S$$

$$\frac{dN_P}{dt} = kC_E N_S$$

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

$$\frac{d}{dt}(N_S + N_P) = QC_{S_0}$$

Integrating this, and using the initial condition that  $N_S = N_P = 0$  at  $t = 0$  and substituting  $Q = 50$  liters/hr and  $C_{S_0} = 2$  mol/liter, we get

$$N_S + N_P = QC_{S_0}t = 100t$$

Since the reaction is irreversible, the rate equation for S is independent of P, and we can solve the equation for S first, and then find P from  $N_P = 100t - N_S$ . Our rate equation for S is:

$$\frac{dN_S}{dt} = QC_{S_0} - kC_E N_S$$

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

$$\frac{dN_S}{dt} = f' \exp(-kC_E t) - kC_E f \exp(-kC_E t) = QC_{S_0} - kC_E f \exp(-kC_E t)$$

$$f' \exp(-kC_E t) = QC_{S_0}$$

$$f' = QC_{S_0} \exp(kC_E t)$$

$$f = \frac{QC_{S_0}}{kC_E} (\exp(kC_E t) + \text{const.})$$

$$N_S = \frac{QC_{S_0}}{kC_E} (1 + \text{const.} \exp(-kC_E t))$$

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

$$N_S = \frac{QC_{A_0}}{kC_E} (1 - \exp(-kC_E t)) = 400(1 - \exp(-0.25t))$$

Then

$$N_P = QC_{S_0}t - N_S = 100t - 400(1 - \exp(-0.25t))$$

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

$$\frac{dN_S}{dt} = -kC_E N_S$$

$$\frac{dN_P}{dt} = kC_E N_S$$

Adding these shows that  $N_S + N_P$  is constant after  $t = 2$  hours. At  $t = 2$  hours,  $N_S + N_P = 100t = 200$  moles. So, after  $t = 2$  hours,  $N_P = 200 - N_S$ . The equation for  $N_S$  is our favorite differential equation, except that we want to apply the initial condition at  $t = 2$  hours, at

which time  $N_S = 400(1 - \exp(-0.5)) = 157.4$  moles. So, for times greater than 2 hours, we get  $N_S = 157.4 \exp(-0.25(t - 2))$  and therefore  $N_P = 200 - 157.4 \exp(-0.25(t - 2))$ .

To summarize:

$N_S = 400(1 - \exp(-0.25t))$  for  $0 < t < 2$  hours and  $N_S = 157.4 \exp(-0.25(t - 2))$  for  $t > 2$  hours.

$N_P = 100t - 400(1 - \exp(-0.25t))$  for  $0 < t < 2$  hours and  $N_P = 200 - 157.4 \exp(-0.25(t - 2))$  for  $t > 2$  hours.

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

The average production rate of P is equal to the total amount of P 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

$$\text{Prod. Rate} = \frac{100t - 400(1 - \exp(-0.25t))}{t + 1} \quad \text{for } 0 \leq t \leq 2$$

$$\text{Prod. Rate} = \frac{200 - 157.4 \exp(-0.25(t - 2))}{t + 1} \quad \text{for } t \geq 2$$

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  $N_P$  changes. The derivatives, after a little simplification, are

$$\frac{d}{dt}(\text{Prod. Rate}) = \frac{(t + 1)(100 + 100 \exp(-0.25t)) - 100t + 400(1 - \exp(-0.25t))}{(t + 1)^2} \quad \text{for } 0 \leq t \leq 2$$

$$\frac{d}{dt}(\text{Prod. Rate}) = \frac{500 + (100t - 300) \exp(-0.25t)}{(t + 1)^2} \quad \text{for } 0 \leq t \leq 2$$

$$\frac{d}{dt}(\text{Prod. Rate}) = \frac{(t + 1)(39.35 \exp(-0.25(t - 2))) - 200 + 157.4(\exp(-0.25(t - 2)))}{(t + 1)^2} \quad \text{for } t \geq 2$$

$$\frac{d}{dt}(\text{Prod. Rate}) = \frac{(39.35t + 196.7)(\exp(-0.25(t - 2))) - 200}{(t + 1)^2} \quad \text{for } t \geq 2$$

Evaluating the first expression at  $t = 0$ ,  $t = 1$  and at  $t = 2$  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:

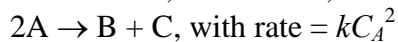
$$(39.35t + 196.7)(\exp(-0.25(t - 2))) - 200 = 0$$

If we plot this using a graphing calculator, or just try a few values, we can see that it goes through zero near  $t = 4.5$  hours, and this can be refined by trial and error to give  $t = 4.502$  hours. 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 product (P) for this optimal batch time. (5 pts.)

Evaluating the production rate for  $t = 4.502$  hr gives 21.05 moles/hour for the average production rate. Evaluating it for nearby values of  $t$  again confirms that this is a maximum in production rate.

2. The irreversible, exothermic, second-order reaction



is to be carried out in solution in a perfectly mixed adiabatic stirred tank reactor. Properties of the reaction and reactor are as follows:

Feed temperature =  $T_o = 290$  K

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

Heat of reaction =  $\Delta H = -83600$  J/mol

Density =  $\rho = 1000$  g/liter

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

Feed flow rate =  $Q = 20$  liters  $\text{min}^{-1}$

Reactor volume =  $V = 200$  liters

The reaction rate constant is given by

$$k = 5 \times 10^{25} \exp(-19000/T)$$

(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. (18 pts.)

The steady-state material and energy balances are just

$$Q(C_{Ao} - C_A) - 2VkC_A^2 = 0$$

$$\rho C_p Q(T_o - T) + (-\Delta H)VkC_A^2 = 0$$

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:

$$C_{Ao} - C_A = 2\tau k C_A^2$$

$$T - T_o = J\tau k C_A^2$$

From which we see that we have the usual type of relationship for an adiabatic reactor, except for the stoichiometric coefficient of 2 for A in the reaction:

$$C_{Ao} - C_A = \frac{2}{J}(T - T_o)$$

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

$$T - T_o - J\tau \left( A \exp(-E_a/T) \right) \left( C_{Ao} - \frac{2}{J}(T - T_o) \right)^2 = 0$$

Putting in the rest of the numbers from the problem statement, we have  $\tau = 200$  liters/20 liters/min = 10 min and  $J = 83600/(1000*4.18) = 20$  K liter  $\text{mol}^{-1}$  and

$$T - 290 - 10^{28} \exp(-19000/T) (2 - 0.1(T - 290))^2 = 0$$

The maximum temperature rise is  $J C_{A0}/2 = 20$  K, so we know that  $T$  will always be between 290 and 310 K. Plotting the above function shows that it crosses zero near 292 K. This can be refined by trial and error or iteration to get  $T = 291.73$  K. There is only a single steady state solution for the conditions selected.

The corresponding concentration of A is given by

$$C_A = C_{A0} - \frac{2}{J}(T - T_0) = 2 - 0.1(T - 290)$$

So, for  $T = 291.73$  K,  $C_A = 1.827$  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**. (18 pts.)

When there is only one steady state, we generally expect that it will be stable, but that does not have to always be the case. So, we can still carry out the formal stability analysis. 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

$$\frac{dC_A}{dt} = \frac{C_{A0} - C_A}{\tau} - 2A \exp\left(\frac{-E_a}{T}\right) C_A^2$$

$$\frac{dT}{dt} = \frac{T_0 - T}{\tau} + JA \exp\left(\frac{-E_a}{T}\right) C_A^2$$

So, the Jacobian is

$$\underline{\underline{J}} = \begin{bmatrix} -\frac{1}{\tau} - 4A \exp(-E_a/T) C_A & -2\left(\frac{E_a}{T^2}\right) A \exp(-E_a/T) C_A^2 \\ 2JA \exp(-E_a/T) C_A & -\frac{1}{\tau} + J\left(\frac{E_a}{T^2}\right) A \exp(-E_a/T) C_A^2 \end{bmatrix}$$

Putting in the numbers from the problem statement

$$\underline{\underline{J}} = \begin{bmatrix} -\frac{1}{10} - 2 \times 10^{26} \exp(-19000/T) C_A & -\left(\frac{1.9 \times 10^{30}}{T^2}\right) \exp(-19000/T) C_A^2 \\ 2 \times 10^{27} \exp(-19000/T) C_A & -\frac{1}{10} + \left(\frac{1.9 \times 10^{31}}{T^2}\right) \exp(-19000/T) C_A^2 \end{bmatrix}$$

For  $T = 291.73$  K,  $C_A = 1.827$  mol/liter this becomes

$$\underline{\underline{J}} = \begin{bmatrix} -0.11896 & -0.0038665 \\ 0.18961 & -0.061335 \end{bmatrix}$$

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

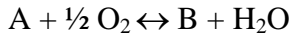
$$\underline{\underline{J}} = \begin{bmatrix} -0.11896 - \lambda & -0.0038665 \\ 0.18961 & -0.061335 - \lambda \end{bmatrix}$$

Multiplying out the determinant and setting it equal to zero gives

$$\lambda^2 + 0.1803\lambda + 0.008020 = 0$$

Applying the quadratic formula, or otherwise solving this gives  $\lambda_1 = -0.1$  and  $\lambda_2 = -0.0803$ . As expected, both eigenvalues are negative, and the steady state is stable.

3. Consider the oxidative dehydrogenation of A to B in an adiabatic packed bed catalytic reactor:



Data for the reaction are as follows:

Feed temperature = 500 K

Feed pressure = 4 bar

Molar flow of A in the feed = 50 mol s<sup>-1</sup>

Molar flow of O<sub>2</sub> in the feed = 500 mol s<sup>-1</sup>

Molar flow of B in the feed = 0 mol s<sup>-1</sup>

Molar flow of H<sub>2</sub>O in the feed = 1000 mol s<sup>-1</sup>

Reaction rate =  $k (p_A p_{O_2}^{0.5} - p_B p_{H_2O}/K)$  mol (g catalyst)<sup>-1</sup> s<sup>-1</sup>  
with  $k = 10^{13} \exp(-10000/T)$  mol (g catalyst)<sup>-1</sup> s<sup>-1</sup> bar<sup>-1.5</sup>

(in the absence of any pore diffusion limitations)

and  $K = 10^{12} \exp(-12000/T)$  bar<sup>0.5</sup>

heat of reaction = -100 kJ mol<sup>-1</sup>

specific heat of feed mixture = 2.0 J g<sup>-1</sup> K<sup>-1</sup>

molecular weight of A = 100 g mol<sup>-1</sup>

- (a) If the molar flow rate of B at the reactor exit is 30 mol s<sup>-1</sup>, what is the **temperature at the reactor exit**? (5 pts.)

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

$$\frac{dF_A}{dz} = -\Omega r$$

$$\frac{dF_B}{dz} = \Omega r$$

$$\frac{dF_{O_2}}{dz} = -0.5\Omega r$$

$$\frac{dF_{H_2O}}{dz} = \Omega r$$

where  $F_A$ ,  $F_B$ ,  $F_{O_2}$  and  $F_{H_2O}$  are the molar flow rates of A, B, oxygen and steam,  $\Omega$  is the reactor cross-sectional area, and  $r$  is the rate of reaction in moles per volume per time,

$$r = \rho_B k (p_A p_{O_2}^{0.5} - p_B p_{H_2O}/K) \text{ mol m}^{-3} \text{ s}^{-1}$$

where  $\rho_B$  is the density of the packed bed (kg catalyst per m<sup>3</sup> 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

$$\frac{dF_A}{dz} = 2 \frac{dF_{O_2}}{dz} = -\frac{dF_B}{dz} = -\frac{dF_{H_2O}}{dz}$$

which reflects the stoichiometric constraint that  $(F_{A,o} - F_A) = 2(F_{O_2,o} - F_{O_2}) = F_B = F_{H_2O}$ .

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

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

Because 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

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

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

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

This is the relationship that is needed to compute the reactor outlet temperature from the outlet feed composition. The group  $\rho_o u_{s,o} \Omega$  is the total mass flow entering the reactor. This mass flow rate is obtained by summing the molar flow rates multiplied by their molecular weights:

$$\rho_o u_{s,o} \Omega = 50 \cdot 100 + 500 \cdot 32 + 1000 \cdot 18 = 39,000 \text{ g/s}$$

If the flow rate of B at the outlet is 30 mol/s, then the flow rate of A is 20 mol/s. Thus,

$$T = 500 + \frac{100000}{39000 \cdot 2} (50 - 20) = 538.5 \text{ K}$$

- (b) Calculate the **mass of catalyst** required to achieve a molar flow rate of B of 30 mol s<sup>-1</sup> at the reactor exit. (15 pts.)

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

$$T = T_o + \frac{-\Delta H}{\rho_o u_{s,o} \hat{C}_p \Omega} (F_{A,o} - F_A) = 500 + 1.282(50 - F_A)$$

From stoichiometry, we have

$$F_B = F_{A,o} - F_A = 50 - F_A \text{ mol s}^{-1}$$

$$F_{O_2} = F_{O_2,o} - \frac{1}{2}(F_{A,o} - F_A) = 475 + 0.5F_A \text{ mol s}^{-1}$$

$$F_{H_2O} = F_{H_2O,o} + (F_{A,o} - F_A) = 1050 - F_A \text{ mol s}^{-1}$$

$$F_{total} = F_A + F_B + F_{O_2} + F_{H_2O} = 1575 - 0.5F_A \text{ mol s}^{-1}$$

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

$$p_A = p_{total} \left( \frac{F_A}{F_{total}} \right) = 4 \left( \frac{F_A}{1575 - 0.5F_A} \right) \text{ bar}$$

$$p_B = p_{total} \left( \frac{F_B}{F_{total}} \right) = 4 \left( \frac{50 - F_A}{1575 - 0.5F_A} \right) \text{ bar}$$

$$p_{O_2} = p_{total} \left( \frac{F_{O_2}}{F_{total}} \right) = 4 \left( \frac{475 + 0.5F_A}{1575 - 0.5F_A} \right) \text{ bar}$$

$$p_{H_2O} = p_{total} \left( \frac{F_{H_2O}}{F_{total}} \right) = 4 \left( \frac{1050 - F_A}{1575 - 0.5F_A} \right) \text{ bar}$$

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 A can then be written as

$$\frac{dF_A}{dz} = -\Omega \rho_B k \left( p_A p_{O_2}^{0.5} - p_B p_{H_2O} / K \right)$$

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

$$\frac{dF_A}{dW} = -k \left( p_A p_{O_2}^{0.5} - p_B p_{H_2O} / K \right)$$

Substituting into this the expressions for the partial pressures gives

$$\frac{dF_A}{dW} = -k \left( \frac{8F_A (475 + 0.5F_A)^{0.5}}{(1575 - 0.5F_A)^{1.5}} - \frac{16(50 - F_A)(1050 - F_A)}{K (1575 - 0.5F_A)^2} \right)$$

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

$$\frac{dF_A}{dW} = -10^{13} \exp(-10000/(500 + 1.282(50 - F_A))) \left( \frac{8F_A (475 + 0.5F_A)^{0.5}}{(1575 - 0.5F_A)^{1.5}} - \frac{16(50 - F_A)(1050 - F_A)}{10^{12} \exp(-12000/(500 + 1.282(50 - F_A)))(1575 - 0.5F_A)^2} \right)$$

This can be rearranged to give

$$dW = \left( -10^{13} \exp(-10000/(500 + 1.282(50 - F_A))) \left( \frac{8F_A (475 + 0.5F_A)^{0.5}}{(1575 - 0.5F_A)^{1.5}} - \frac{16(50 - F_A)(1050 - F_A)}{10^{12} \exp(-12000/(500 + 1.282(50 - F_A)))(1575 - 0.5F_A)^2} \right) \right)^{-1} dF_A$$

The catalyst mass required is obtained by integrating this from  $F_A = 50$  to  $F_A = 20$  (or integrating the negative of it from 20 to 50).

$$W = \int_{20}^{50} \left( 10^{13} \exp(-10000/(500 + 1.282(50 - F_A))) \left( \frac{8F_A (475 + 0.5F_A)^{0.5}}{(1575 - 0.5F_A)^{1.5}} - \frac{16(50 - F_A)(1050 - F_A)}{10^{12} \exp(-12000/(500 + 1.282(50 - F_A)))(1575 - 0.5F_A)^2} \right) \right)^{-1} dF_A$$

You can probably evaluate this integral using a function on your calculator. If not, you could evaluate the rate for a few values of  $F_A$ , and realize that it doesn't change much. Then, you could approximate the integral using an average rate over the range. Integrating it with my calculator, I got  $W = 0.0073$  g catalyst. This is not a realistic number, given a mass flow rate of 39 kg/s of gas flowing through the reactor. Nonetheless, for the given rate expression, it seems to be correct.

- (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  $2.0 \text{ g cm}^{-3}$ . The effective diffusion coefficient for A in the catalyst pores is about  $0.1 \text{ cm}^2 \text{ s}^{-1}$  in the temperature range in which the reactor is operated. (9 pts).

Pore diffusion becomes important when the Thiele modulus is about 1. If  $k$  is the intrinsic first-order rate constant per catalyst mass,  $\rho_s$  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 1<sup>st</sup> 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. The reaction in question here is not strictly first-order, but is nearly so, since the oxygen is present in large excess. So, the oxygen partial pressure can be lumped into the effective rate constant. The effective first-order rate constant is

$$k_{eff} = 10^{13} \cdot \exp(-10000/520) \cdot (4 \cdot (500/1550))^{0.5} = 50,500 \text{ mol (g catalyst)}^{-1} \text{ s}^{-1} \text{ bar}^{-1}$$

I evaluated the rate constant at a representative temperature in the reactor (520 K, between the feed temperature of 500 K and the exit temperature from part (a)). At this temperature,  $k_{eff} = 50,500 \text{ mol (g catalyst)}^{-1} \text{ s}^{-1} \text{ bar}^{-1}$ . 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' 1<sup>st</sup> 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 4 bar and the reaction conditions. Using the ideal gas law, we find that at 520 K, a pressure of 4 bar corresponds to a concentration of  $92.5 \text{ moles m}^{-3}$ . Dividing the rate constant by this conversion factor gives  $k = 546 \text{ m}^3 (\text{g catalyst})^{-1} \text{ s}^{-1}$ .

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

$$\phi = \frac{d}{6} \sqrt{\frac{546 \text{ m}^3 (\text{g catalyst})^{-1} \text{ s}^{-1} \times 2000000 (\text{g catalyst}) \text{ m}^{-3}}{0.1 \text{ cm}^2 \text{ s}^{-1} \times 10^{-4} \text{ m}^2 \text{ cm}^{-2}}}$$
$$\phi = \frac{d}{6} (1.04 \times 10^7 \text{ m}^{-1})$$

Setting this equal to 1 and solving for  $d$  gives  $d = 5.7 \times 10^{-7}$  m, or about 0.6 microns. Thus, for these conditions where the rate constant is extremely high, there will be strong pore diffusion limitations for any practical particle size.