

Two reactors are available. One is a gray 200.0-dm<sup>3</sup> CSTR that can be heated to 77°C or cooled to 0°C, and the other is a white 800.0-dm<sup>3</sup> PFR operated at 300 K that cannot be heated or cooled but can be painted red or black. Note  $k = 0.07 \text{ dm}^3/\text{mol}\cdot\text{min}$  at 300 K and  $E = 20 \text{ kcal/mol}$ .

- Which reactor and what conditions do you recommend? Explain the reason for your choice (e.g., color, cost, space available, weather conditions). Back up your reasoning with the appropriate calculations.
- How long would it take to achieve 90% conversion in a 200-dm<sup>3</sup> batch reactor with  $C_{A0} = C_{B0} = 1 \text{ M}$  after mixing at a temperature of 77°C?
- What would your answer to part (b) be if the reactor were cooled to 0°C? (Ans. 2.5 days)
- What conversion would be obtained if the CSTR and PFR were operated at 300 K and connected in series? In parallel with 5 mol/min to each?
- Keeping Table 4-1 in mind, what batch reactor volume would be necessary to process the same amount of species A per day as the flow reactors while achieving 90% conversion? Referring to Table 1-1, estimate the cost of the batch reactor.
- Write a couple of sentences describing what you learned from the problem and what you believe to be the point of the problem.

P4-6<sub>n</sub>

Dibutyl phthalate (DBP), a plasticizer, has a potential market of 12 million lb/yr (*AICHE Student Contest Problem*) and is to be produced by reaction of *n*-butanol with monobutyl phthalate (MBP). The reaction follows an elementary rate law and is catalyzed by H<sub>2</sub>SO<sub>4</sub> (Figure P4-6). A stream containing MBP and butanol is to be mixed with the H<sub>2</sub>SO<sub>4</sub> catalyst immediately before the stream enters the reactor. The concentration of MBP in the stream entering the reactor is 0.2 lb mol/ft<sup>3</sup>, and the molar feed rate of butanol is five times that of MBP. The specific reaction rate at 100°F is 1.2 ft<sup>3</sup>/lb mol·h. There is a 1000-gallon CSTR and associated peripheral equipment available for use on this project for 30 days a year (operating 24 h/day).

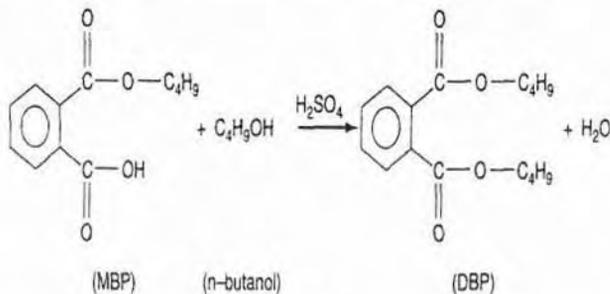
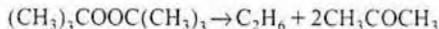
National AIChE  
Contest Problem

Figure P4-6

- Determine the exit conversion in the available 1000-gallon reactor if you were to produce 33% of the share (i.e., 4 million lb/yr) of the predicted market. (Ans.:  $X = 0.33$ )
- How might you increase the conversion for the same  $F_{A0}$ ? For example, what conversion would be achieved if a second 1000-gal CSTR were placed either in series or in parallel with the CSTR? [ $X_2 = 0.55$  (series)]

- (c) For the same temperature as part (a), what CSTR volume would be necessary to achieve a conversion of 85% for a molar feed rate of MBP of 1 lb mol/min?
- (d) *If possible*, calculate the tubular reactor volume necessary to achieve 85% conversion, when the reactor is oblong rather than cylindrical, with a major-to-minor axis ratio of 1.3 : 1.0. There are no radial gradients in either concentration or velocity. If it is not possible to calculate  $V_{PFR}$ , explain.
- (e) How would your results for parts (a) and (b) change if the temperature were raised to 150°F where  $k$  is now 5.0 ft<sup>3</sup>/lb mol · h but the reaction is reversible with  $K_C = 0.3$ ?
- (f) Keeping in mind the times given in Table 4-1 for filling, and other operations, how many 1000-gallon reactors operated in the batch mode would be necessary to meet the required production of 4 million pounds in a 30-day period? Estimate the cost of the reactors in the system. *Note:* Present in the feed stream may be some trace impurities, which you may lump as hexanol. The activation energy is believed to be somewhere around 25 kcal/mol. *Hint:* Plot number of reactors as a function of conversion. (*Ans.:* 5 reactors)
- (g) What generalizations can you make about what you learned in this problem that would apply to other problems?
- (h) Write a question that requires critical thinking and then explain why your question requires critical thinking. [*Hint:* See Preface, Section B.2]

P4-7<sub>A</sub> The elementary gas-phase reaction



is carried out isothermally in a flow reactor with no pressure drop. The specific reaction rate at 50°C is  $10^{-4} \text{ min}^{-1}$  (from pericosity data) and the activation energy is 85 kJ/mol. Pure di-*tert*-butyl peroxide enters the reactor at 10 atm and 127°C and a molar flow rate of 2.5 mol/min. Calculate the reactor volume and space time to achieve 90% conversion in:

- (a) a PFR (*Ans.:* 967 dm<sup>3</sup>)
- (b) a CSTR (*Ans.:* 4700 dm<sup>3</sup>)
- (c) **Pressure drop.** Plot  $X$ ,  $y$ , as a function of the PFR volume when  $\alpha = 0.001 \text{ dm}^{-3}$ . What are  $X$ , and  $y$  at  $V = 500 \text{ dm}^3$ ?
- (d) Write a question that requires critical thinking, and explain why it involves critical thinking.
- (e) If this reaction is to be carried out isothermally at 127°C and an initial pressure of 10 atm in a constant-volume batch mode with 90% conversion, what reactor size and cost would be required to process (2.5 mol/min × 60 min/h × 24 h/day) 3600 mol of di-*tert*-butyl peroxide per day? (*Hint:* Recall Table 4-1.)
- (f) Assume that the reaction is reversible with  $K_C = 0.025 \text{ mol}^2/\text{dm}^6$ , and calculate the equilibrium conversion; then redo (a) through (c) to achieve a conversion that is 90% of the equilibrium conversion.
- (g) **Membrane reactor.** Repeat Part (f) for the case when  $\text{C}_2\text{H}_6$  flows out through the sides of the reactor and the transport coefficient is  $k_C = 0.08 \text{ s}^{-1}$ .

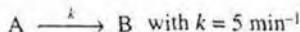
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Creative Thinking

### P4-8<sub>B</sub> Troubleshooting

- (a) A liquid-phase isomerization  $A \longrightarrow B$  is carried out in a 1000-gal CSTR that has a single impeller located halfway down the reactor. The liquid enters at the top of the reactor and exits at the bottom. The reaction is second order. Experimental data taken in a batch reactor predicted the CSTR conversion should be 50%. However, the conversion measured in the actual CSTR was 57%. Suggest reasons for the discrepancy and suggest something that would give closer agreement between the predicted and measured conversions. Back your suggestions with calculations. P.S. It was raining that day.
- (b) The first-order gas-phase isomerization reaction



is to be carried out in a tubular reactor. For a feed of pure A of  $5 \text{ dm}^3/\text{min}$ , the expected conversion in a PFR is 63.2%. However, when the reactor was put in operation, the conversion was only 58.6%. We should note that the straight tubular reactor would not fit in the available space. One engineer suggested that the reactor be cut in half and the two reactors be put side by side with equal feed to each. However, the chief engineer overrode this suggestion saying the tubular reactor had to be one piece so he bent the reactor in a U shape. The bend was not a good one. Brainstorm and make a list of things that could cause this off-design specification. Choose the most logical explanation/model, and carry out a calculation to show quantitatively that with your model the conversion is 58.6%. (An Ans: 57% of the total)

- (c) The liquid-phase reaction



was carried out in a CSTR. For an entering concentration of  $2 \text{ mol}/\text{dm}^3$ , the conversion was 40%. For the same reactor volume and entering conditions as the CSTR, the expected PFR conversion is 48.6%. However, the PFR conversion was amazingly 50% exactly. Brainstorm reasons for the disparity. Quantitatively show how these conversions came about (i.e., the expected conversion and the actual conversion).

- (d) The gas-phase reaction



is carried out in a packed bed reactor. When the particle size was decreased by 15%, the conversion remained unchanged. When the particle size was decreased by 20%, the conversion decreased. When the original particle size was increased by 15%, the conversion also decreased. In all cases, the temperature, the total catalyst weight, and all other conditions remained unchanged. What's going on here?

### P4-9<sub>B</sub>

A reversible liquid-phase isomerization  $A \rightleftharpoons B$  is carried out *isothermally* in a 1000-gal CSTR. The reaction is second order in both the forward and reverse directions. The liquid enters at the top of the reactor and exits at the bottom. Experimental data taken in a batch reactor shows the CSTR conversion to be 40%. The reaction is reversible with  $K_C = 3.0$  at 300 K, and



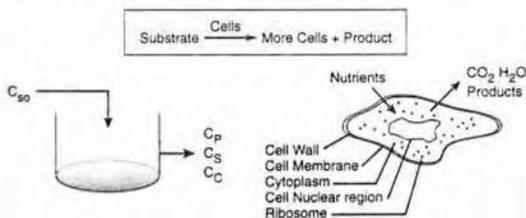
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$\Delta H_{R_x} = -25,000$  cal/mol. Assuming that the batch data taken at 300 K are accurate and that  $E = 15,000$  cal/mol, what CSTR temperature do you recommend to obtain maximum conversion? *Hint:* Read Appendix C. Assume  $\Delta C_p = 0$  in the appendix Equation (C-8):

$$K_c(T) = K_c(T_0) \exp \left[ \frac{\Delta H_{R_x}}{R} \left( \frac{1}{T_0} - \frac{1}{T} \right) \right]$$

Use Polymath to make a plot of  $X$  versus  $T$ . Does it go through a maximum? If so, explain why.

- P4-10** The growth of bacteria to form a product,  $P$ , is carried out in a 25 dm<sup>3</sup> CSTR (chemostat). The bacteria (e.g., *Zyomononas*) consumes the nutrient substrate (e.g., to generate more cells and the desired product—ethanol)



The CSTR was initially inoculated with bacteria and now has reached steady state. Only substrate (nutrient) is fed to the reactor at a volumetric rate of 5 dm<sup>3</sup>/h and a concentration of 30 g/dm<sup>3</sup>. The growth law  $r_g$  (g/hr dm<sup>3</sup>)

$$r_g = \frac{\mu_{\max} C_S C_C}{K_m + C_S}$$

and the rate of substrate consumption is related to growth rate by

$$-r_S = Y_{S/C} r_g$$

with the stoichiometric relationship

$$C_C = Y_{C/S} [C_{S0} - C_S]$$

- Write a mass balance on the cells and the substrate concentration in the CSTR operated at steady state.
- Solve the cell mass balance for the substrate concentration and calculate  $C_S$ .
- Calculate the cell concentration,  $C_C$ .
- How would your answers to (b) and (c) change if the volumetric flow rate were cut in half?
- How would your answers to (b) and (c) change if the CSTR volume were reduced by a factor of three?
- The reaction is now carried out in a 10 dm<sup>3</sup> batch reactor with initial concentrations of substrate  $C_{S0} = 30$  g/dm<sup>3</sup> and cells of  $C_{C0} = 0.1$  g/dm<sup>3</sup>. Plot  $C_S$ ,  $C_C$ ,  $r_g$ , and  $-r_S$  as a function of time.
- Repeat (f) for a 100 dm<sup>3</sup> reactor.

Additional Information:

$$\mu_{\max} = 0.5 \text{ hr}^{-1}, \quad K_m = 5 \text{ g/dm}^3$$

$$Y_{C/S} = 0.8 \text{ g cell formed/g substrate consumed} = 1/Y_{S/C}$$



- P4-11<sub>B</sub>** The gaseous reaction  $A \longrightarrow B$  has a unimolecular reaction rate constant of  $0.0015 \text{ min}^{-1}$  at  $80^\circ\text{F}$ . This reaction is to be carried out in *parallel tubes* 10 ft long and 1 in. inside diameter under a pressure of 132 psig at  $260^\circ\text{F}$ . A production rate of 1000 lb/h of B is required. Assuming an activation energy of 25,000 cal/mol, how many tubes are needed if the conversion of A is to be 90%? Assume perfect gas laws. A and B each have molecular weights of 58. (From California Professional Engineers Exam.)



- P4-12<sub>B</sub>** (a) The irreversible elementary reaction  $2A \longrightarrow B$  takes place in the gas phase in an *isothermal tubular (plug-flow) reactor*. Reactant A and a diluent C are fed in equimolar ratio, and conversion of A is 80%. If the molar feed rate of A is cut in half, what is the conversion of A assuming that the feed rate of C is left unchanged? Assume ideal behavior and that the reactor temperature remains unchanged. What was the point of this problem? (From California Professional Engineers Exam.)

(b) Write a question that requires critical thinking, and explain why it involves critical thinking.



- P4-13<sub>B</sub>** Compound A undergoes a reversible isomerization reaction,  $A \rightleftharpoons B$ , over a supported metal catalyst. Under pertinent conditions, A and B are liquid, miscible, and of nearly identical density; the equilibrium constant for the reaction (in concentration units) is 5.8. In a *fixed-bed isothermal flow reactor* in which backmixing is negligible (i.e., plug flow), a feed of pure A undergoes a net conversion to B of 55%. The reaction is elementary. If a second, identical flow reactor at the same temperature is placed downstream from the first, what overall conversion of A would you expect if:

(a) The reactors are directly connected in series? (Ans.:  $X = 0.74$ .)

(b) The products from the first reactor are separated by appropriate processing and only the unconverted A is fed to the second reactor?

(From California Professional Engineers Exam.)



- P4-14<sub>C</sub>** A total of 2500 gal/h of metaxylene is being isomerized to a mixture of orthoxylene, metaxylene, and paraxylene in a reactor containing 1000 ft<sup>3</sup> of catalyst. The reaction is being carried out at  $750^\circ\text{F}$  and 300 psig. Under these conditions, 37% of the metaxylene fed to the reactor is isomerized. At a flow rate of 1667 gal/h, 50% of the metaxylene is isomerized at the same temperature and pressure. Energy changes are negligible.

It is now proposed that a second plant be built to process 5500 gal/h of metaxylene at the same temperature and pressure as described earlier. What size reactor (i.e., what volume of catalyst) is required if conversion in the new plant is to be 46% instead of 37%? Justify any assumptions made for the scale-up calculation. (Ans.: 2931 ft<sup>3</sup> of catalyst.) (From California Professional Engineers Exam.) Make a list of the things you learned from this problem.



- P4-15<sub>A</sub>** It is desired to carry out the gaseous reaction  $A \longrightarrow B$  in an existing *tubular reactor* consisting of 50 parallel tubes 40 ft long with a 0.75-in. inside diameter. Bench-scale experiments have given the reaction rate constant for this first-order reaction as  $0.00152 \text{ s}^{-1}$  at  $200^\circ\text{F}$  and  $0.0740 \text{ s}^{-1}$  at  $300^\circ\text{F}$ . At what temperature should the reactor be operated to give a conversion of A of 80% with a feed rate of 500 lb/h of pure A and an operating pressure of 100 psig? A has a molecular weight of 73. Departures from perfect gas behavior may be neglected, and the reverse reaction is insignificant at these conditions. (Ans.:  $T = 275^\circ\text{F}$ .) (From California Professional Engineers Exam.)

**P4-16<sub>A</sub>** The reversible isomerization

follows an elementary rate law. If  $X_e$  is the equilibrium conversion,

(a) Show for a batch and a PFR:  $t = \tau_{\text{PFR}} = \frac{X_e}{k} \ln \frac{X_e}{X_e - X}$

(b) Show for a CSTR:  $\tau_{\text{PFR}} = \frac{X_e}{k} \left( \frac{X_e}{X_e - X} \right)$

(c) Show that the volume efficiency is

$$\frac{V_{\text{PFR}}}{V_{\text{CSTR}}} = \frac{(X_e - X) \ln \left( \frac{X_e}{X_e - X} \right)}{X_e}$$

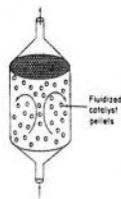
and then plot the volume efficiency as a function of the ratio ( $X/X_e$ ) from 0 to 1.

(d) What would be the volume efficiency for two CSTRs in series with the sum of the two CSTR volumes being the same as the PFR volume?

**P4-17<sub>B</sub>** The gas-phase dimerization

follows an elementary rate law and takes place isothermally in a PBR charged with 1.0 kg of catalyst. The feed, consisting of pure A, enters the PBR at a pressure of 20 atm. The conversion exiting the PBR is 0.3, and the pressure at the exit of the PBR is 5 atm.

- (a) If the PBR were replaced by a “fluidized” CSTR with 1 kg of catalyst, what will be the conversion at the exit of the CSTR? You may assume that there is no pressure drop in the CSTR. (*Ans.*:  $X = 0.4$ .)
- (b) What would be the conversion in the PBR if the mass flow rate were decreased by a factor of 4 and particle size were doubled? Assume turbulent flow. (*Final exam*)
- (c) Discuss what you learned from this problem as well as the strengths and weaknesses of using this as a final exam problem.
- (d) Write a question on critical thinking and explain why it involves critical thinking.



Fluidized CSTR reactor

**P4-18<sub>B</sub>** The irreversible first-order (wrt partial pressure of A) gas-phase reaction

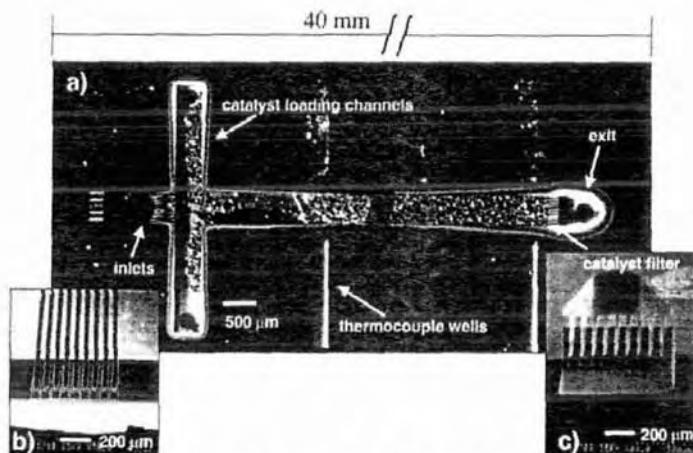
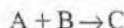
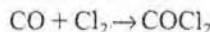
is carried out isothermally in a “fluidized” catalytic CSTR containing 50 kg of catalyst (Figure in margin). ·

Currently 50% conversion is realized for pure A entering at pressure of 20 atm. There is virtually no pressure drop in the CSTR. It is proposed to put a PBR containing the same catalyst weight in series with the CSTR. The pressure drop parameter for the PBR  $\alpha$ , given by Equation (4-33) is  $\alpha = 0.018 \text{ kg}^{-1}$ . The particle size is 0.2 mm, the bed porosity is 40%, and the viscosity is the same as that of air at 200°C.

- (a) Should the PBR be placed upstream or downstream of the CSTR in order to achieve the highest conversion? Explain qualitatively using concepts you learned in Chapter 2.

- (b) What is the conversion exiting the last reactor?  
 (c) What is the pressure at the exit of the packed bed?  
 (d) How would your answers change if the catalyst diameter were decreased by a factor of 2 and the PBR diameter were increased by 50% assuming turbulent flow?

**P4-19** A microreactor similar to the one shown in Figure P4-19 from the MIT group is used to produce phosgene in the gas phase.



**Figure P4-19** Microreactor (Courtesy of S. K. Ajmera, M. W. Losey, K. F. Jensen, and M. A. Schmidt, *AIChE J.* 47, 1639 (2001)).

The microreactor is 20 mm long, 500  $\mu\text{m}$  in diameter, and packed with catalyst particles 35  $\mu\text{m}$  in diameter. The entering pressure is 830 kPa (8.2 atm), and the entering flow to each microreactor is equimolar. The molar flow rate of CO is  $2 \times 10^{-5}$  mol/s and the volumetric flow is  $2.83 \times 10^{-7}$  m<sup>3</sup>/s. The weight of catalyst in one microreactor:  $W = 3.5 \times 10^{-6}$  kg. The reactor is kept isothermal at 120°C. Because the catalyst is also slightly different than the one in Figure P4-19, the rate law is different as well:

$$-r'_A = k_A C_A C_B$$

- (a) Plot the molar flow rates  $F_A$ ,  $F_B$ , and  $F_C$ , the conversion  $X$ , and pressure ratio  $y$  along the length of the reactor.  
 (b) Calculate the number of microreactors in parallel to produce 10,000 kg/year phosgene.  
 (c) Repeat part (a) for the case when the catalyst weight remains the same but the particle diameter is cut in half. If possible compare your answer with part (a) and describe what you find, noting anything unusual.  
 (d) How would your answers to part (a) change if the reaction were reversible with  $K_C = 0.4$  dm<sup>3</sup>/mol? Describe what you find.

- (e) What are the advantages and disadvantages of using an array of microreactors over using one conventional packed bed reactor that provides the same yield and conversion?
- (f) Write a question that involves critical thinking, and explain what the question involves critical thinking.
- (g) Discuss what you learned from this problem and what you believe to be the point of the problem.

*Additional information:*

$$\alpha = 3.55 \times 10^5 / \text{kg catalyst (based on properties of air and } \phi = 0.4)$$

$$k = 0.004 \text{ m}^6/\text{mol} \cdot \text{s} \cdot \text{kg catalyst at } 120^\circ\text{C}$$

$$u_0 = 2.83 \cdot 10^{-7} \text{ m}^3/\text{s}, \rho = 7 \text{ kg/m}^3, \mu = 1.94 \cdot 10^{-5} \text{ kg/m} \cdot \text{s},$$

$$A_c = 1.96 \cdot 10^{-7} \text{ m}^2, G = 10.1 \text{ kg/m}^2 \cdot \text{s}$$

**P4-20c** The elementary gas-phase reaction



is carried out in a packed-bed reactor. Currently, catalyst particles 1 mm diameter are packed into 4-in. schedule 40 pipe ( $A_c = 0.82126 \text{ dm}^2$ ). The value of  $\beta_0$  in the pressure drop equation is 0.001 atm/dm. A stoichiometric mixture of A and B enters the reactor at a total molar flow rate of 10 mol/hr at a temperature of 590 K, and a pressure of 20 atm. Flow is turbulent through the bed. Currently, only 12% conversion is achieved with 100 kg of catalyst.

It is suggested that conversion could be increased by changing the catalyst particle diameter. Use the following data to correlate the specific reaction rate as a function of particle diameter. Then use this correlator to determine the catalyst size that gives the highest conversion. As you will learn in Chapter 12,  $k'$  for first-order reaction is expected to vary according to the following relationship

$$k' = \eta k = \frac{3}{\Phi^2} (\Phi \coth \Phi - 1) k \quad (\text{P4-21})$$

where  $\Phi$  varies directly with particle diameter,  $\Phi = c D_p$ . Although the reaction is not first order, one notes from Figure 12-5 the functionality for a second-order reaction is similar to Equation (P4-20.1).

- (a) Show that when the flow is turbulent

$$\alpha(D_p) = \alpha_0 \left( \frac{D_{p0}}{D_p} \right)^2$$

and that  $\alpha_0 = 0.8 \times 10^{-4} \text{ atm/kg}$  and also show that  $c = 75 \text{ min}^{-1}$ .

- (b) Plot the specific reaction rate  $k'$  as a function of  $D_p$ , and compare your plot with Figure 12-5.
- (c) Make a plot of conversion as a function of catalyst size.
- (d) Discuss how your answer would change if you had used the effectiveness factor for a second-order reaction rather than a first-order reaction.
- (e) How would your answer to (b) change if both the particle diameter and the pipe diameter were increased by 50% when
- (1) the flow is laminar.
  - (2) the flow is turbulent.
- (f) Write a few sentences describing and explaining what would happen to the pressure drop parameter  $\alpha$  if it is varied.



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- (g) What generalizations can you make about what you learned in this problem that would apply to other problems?
- (h) Discuss what you learned from this problem and what you believe to be the point of the problem.

*Additional information:*

Void fraction = 0.35      Solid catalyst density = 2.35 kg/dm<sup>3</sup>

Bulk density:  $\rho_B = (1 - \phi) \rho_C = (0.35)(2.35) = 0.822$

Catalyst Diameter, $d_p$ (mm)	2	1	0.4	0.1	0.02	0.002
$k'$ (dm <sup>6</sup> /mol·min·kg cat)	0.06	0.12	0.30	1.2	2.64	3.00

[Hint: You could use Equation (P4.20-1), which would include  $D_p$  and an unknown proportionality constant that you could evaluate from the data. For very small values of the Thiele modulus we know  $\eta = 1$ , and for very large values of the Thiele modulus we know that  $\eta = 3/\Phi = 3/cD_p$ .]

P4-21<sub>A</sub>



Nutrition is an important part of ready-to-eat cereal. To make cereal healthier, many nutrients are added. Unfortunately, nutrients degrade over time, making it necessary to add more than the declared amount to assure enough for the life of the cereal. Vitamin  $V_1$  is declared at a level of 20% of the Recommended Daily Allowance per serving size (serving size = 30 g). The Recommended Daily Allowance is 6500 IU ( $1.7 \times 10^6$  IU = 1 g). It has been found that the degradation of this nutrient is first order in the amount of nutrients. Accelerated storage tests have been conducted on this cereal, with the following results:

Temperature (°C)	45	55	65
$k$ (week <sup>-1</sup> )	0.0061	0.0097	0.0185

- (a) Given this information and the fact that the cereal needs to have a vitamin level above the declared value of 6500 IU for 1 year at 25°C, what IU should be present in the cereal at the time it is manufactured? Your answer may also be reported in percent overuse: (Ans. 12%)

$$\%OU = \frac{C(t=0) - C(t=1 \text{ yr})}{C(t=1 \text{ yr})} \times 100$$

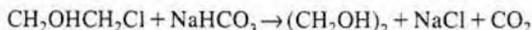
- (b) At what percent of declared value of 6500 IU must you apply the vitamin? If 10,000,000 lb/yr of the cereal is made and the nutrient cost is \$100 per pound, how much will this overuse cost?
- (c) If this were your factory, what percent overuse would you actually apply and why?
- (d) How would your answers change if you stored the material in a Bangkok warehouse for 6 months, where the daily temperature is 40°C, before moving it to the supermarket? (Table of results of accelerated storage tests on cereal; and Problem of vitamin level of cereal after storage courtesy of General Mills, Minneapolis, MN.)

4-22<sub>A</sub>

A very proprietary industrial waste reaction, which we'll code as  $A \rightarrow B + S$  is to be carried out in a 10-dm<sup>3</sup> CSTR followed by 10-dm<sup>3</sup> PFR. The reaction is elementary, but A, which enters at a concentration of 0.001 mol/dm<sup>3</sup> and a molar flow rate of 20 mol/min, has trouble decomposing. The specific reaction rate at 42°C (i.e., room temperature in the Mojave desert) is 0.0001 s<sup>-1</sup>.

However, we don't know the activation energy; therefore, we cannot carry out this reaction in the winter in Michigan. Consequently this reaction, while important, is not worth your time to study. Therefore, perhaps you want to take a break and go watch a movie such as *Dances with Wolves* (a favorite of the author), *Bride and Prejudice*, or *Finding Neverland*.

**P4-23<sub>B</sub>** The production of ethylene glycol from ethylene chlorohydrin and sodium bicarbonate



is carried out in a semibatch reactor. A 1.5 molar solution of ethylene chlorohydrin is fed at a rate 0.1 mole/minute to 1500 dm<sup>3</sup> of a 0.75 molar solution of sodium bicarbonate. The reaction is elementary and carried out isothermally at 30°C where the specific reaction rate is 5.1 dm<sup>3</sup>/mol/h. Higher temperatures produce unwanted side reactions. The reactor can hold a maximum of 2500 dm<sup>3</sup> of liquid. Assume constant density.

- Plot the conversion, reaction rate, concentration of reactants and products, and number of moles of glycol formed as a function of time.
- Suppose you could vary the flow rate between 0.01 and 2 mol/min, what flow a rate would and holding time you choose to make the greatest number of moles of ethylene glycol in 24 hours keeping in mind the downtimes for cleaning, filling, etc., shown in Table 4-1.
- Suppose the ethylene chlorohydrin is fed at a rate of 0.15 mol/min until the reactor is full and then shut in. Plot the conversion as a function of time.
- Discuss what you learned from this problem and what you believe to be the point of this problem.

**P4-24<sub>C</sub>** The following reaction is to be carried out in the liquid phase



The initial concentrations are 0.2 M in NaOH and 0.25 M in CH<sub>3</sub>COOC<sub>2</sub>H<sub>5</sub> with  $k = 5.2 \times 10^{-5}$  m<sup>3</sup>/mol·s at 20°C with  $E = 42,810$  J/mol. Design a set of operating conditions to produce 200 mol/day of ethanol in a semibatch reactor and not operate above 35°C and below a concentration of NaOH of 0.02 molar.<sup>12</sup> The semibatch reactor you have available is 1.5 m in diameter and 2.5 m tall.

**P4-25<sub>C</sub>** (*Membrane reactor*) The first-order, reversible reaction



is taking place in a membrane reactor. Pure A enters the reactor, and B diffuses through the membrane. Unfortunately, some of the reactant A also diffuses through the membrane.

- Plot the flow rates of A, B, and C down the reactor, as well as the flow rates of A and B through the membrane.
- Compare the conversion profiles of a conventional PFR with those of an IMRCF. What generalizations can you make?

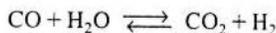
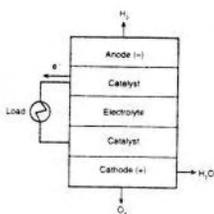
<sup>12</sup> Manual of Chemical Engineering Laboratory, University of Nancy, Nancy, France. 1994. *eric@ist.uni-stuttgart.de*. *www.sysbio.del/AICHE*

- (c) Would the conversion of A be greater or smaller if C were diffusing out instead of B?
- (d) Discuss how your curves would change if the temperature were increased significantly or decreased significantly for an exothermic reaction and for an endothermic reaction.

Additional information:

$$\begin{aligned}
 k &= 10 \text{ min}^{-1} & F_{A0} &= 100 \text{ mol/min} \\
 K_C &= 0.01 \text{ mol}^2/\text{dm}^6 & v_0 &= 100 \text{ dm}^3/\text{min} \\
 k_{CA} &= 1 \text{ min}^{-1} & V_{\text{reactor}} &= 20 \text{ dm}^3 \\
 k_{CB} &= 40 \text{ min}^{-1}
 \end{aligned}$$

- P4-26<sub>B</sub>** As we move toward a hydrogen-based energy economy for use in fuel cells. The use of fuel cells to operate appliances ranging from computers to automobiles is rapidly becoming a reality. In the immediate future, fuel cells will use hydrogen to produce electricity, which some have said will lead to a hydrogen-based economy instead of a petroleum-based economy. A large component in the processing train for fuel cells is the water gas shift membrane reactor. (M. Gummala, N. Gupta, B. Olsomer, and Z. Dardas, **Paper 103c**, 2003, AIChE National Meeting, New Orleans, LA.)



Here CO and water are fed to the membrane reactor containing the catalyst. Hydrogen can diffuse out the sides of the membrane while CO, H<sub>2</sub>O, and CO<sub>2</sub> cannot. Based on the following information, plot the concentrations and molar flow rates of each of the reacting species down the length of the membrane reactor. Assume the following. The volumetric feed is 10 dm<sup>3</sup>/min at 10 atm, and the equimolar feed of CO and water vapor with C<sub>T0</sub> = 0.4 mol/dm<sup>3</sup>. The equilibrium constant is K<sub>e</sub> = 1.44. The k specific reaction rate constant is 1.37 dm<sup>6</sup>/mol kg cat · min, and the mass transfer coefficient for hydrogen, k<sub>CH<sub>2</sub></sub> = 0.1 dm<sup>3</sup>/kg cat · min. What is the reactor volume necessary to achieve 85% conversion of CO? Compare with a PFR. For that same reactor volume, what would be the conversion if the feed rate were doubled?

- P4-27** Go to Professor Herz's **Reactor Lab** on the CD-ROM or on the web at [www.reactorlab.net](http://www.reactorlab.net). Load Division 2, Lab 2 of The Reactor Lab concerning a packed-bed reactor (labeled PFR) in which a gas with the physical properties of air flows over spherical catalyst pellets. Perform experiments here to get a feeling for how pressure drop varies with input parameters such as reactor diameter, pellet diameter, gas flow rate, and temperature. In order to get significant pressure drop, you may need to change some of the input values substantially from those shown when you enter the lab. If you get a notice that you can't get the desired flow, then you need to increase the inlet pressure. In Chapters 10–12, you will learn how to analyze the conversion results in such a reactor.

### Good Alternatives on the CD and on the Web

The following problems are either similar to the ones already presented or use different reactions or have a number of figures that would require a lot of text space. Consequently, the full problem statements are on the CD-ROM

- P4-28** Pressure drop in a PBR with a first-order reaction using real data: What questions asked. [3rd Ed. P4-18]
- P4-29** *Good Troubleshooting Problem.* Inspector Sergeant Ambercromby investigates possible fraud at Worthless Chemical. [3rd Ed. P4-9]
- P4-30** The first-order reaction



is to be carried out in a packed bed reactor with pressure drop where the rate constant varies inversely with  $k \sim (1/D_p)$ . One can also choose from various pipe sizes to get the maximum conversion. Similar to Problems P4-22 and P4-23. [3rd Ed. P4-20]

- P4-31** Pressure drop in a packed bed reactor to make alkylated cyclohexanols. [3rd Ed. P4-22]

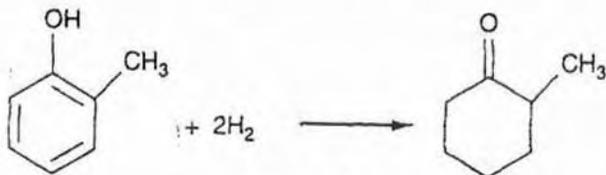


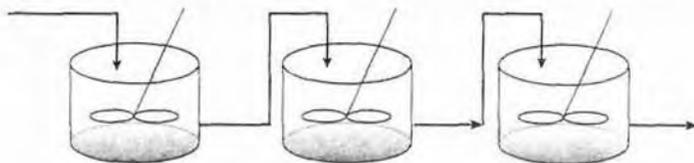
Figure P4-31

- P4-32** A semibatch reactor is used to carry out the reaction



Similar to problems 4-26 and 4-27. [3rd Ed. P4-26]

- P4-33** A CSTR with two impellers is modeled as three CSTRs in series. [3rd Ed. p4-2





## SOME THOUGHTS ON CRITIQUING WHAT YOU READ

Your textbooks after your graduation will be, in part, the professional journals that you read. As you read the journals, it is important that you study them with a critical eye. You need to learn if the author's conclusion is supported by the data, if the article is new or novel, if it advances our understanding, and to learn if the analysis is current. To develop this technique, one of the major assignments used in the graduate course in chemical reaction engineering at the University of Michigan for the past 25 years has been an in-depth analysis and critique of a journal article related to the course material. Significant effort is made to ensure that a cursory or superficial review is not carried out. Students are asked to analyze and critique ideas rather than ask questions such as: Was the pressure measured accurately? They have been told that they are not required to find an error or inconsistency in the article to receive a good grade, but if they do find such things, it just makes the assignment that much more enjoyable. Beginning with Chapter 4, a number of the problems at the end of each chapter in this book are based on students' analyses and critiques of journal articles and are designated with a C (e.g., P4C-1). These problems involve the analysis of journal articles that may have minor or major inconsistencies. A discussion on critiquing journal articles can be found in Professional Reference Shelf R4.4 on the CD-ROM.

### JOURNAL CRITIQUE PROBLEMS

- P4C-1** In *Water Research*, 33 (9), 2130 (1999), is there a disparity in the rate law obtained by batch experiments and continuous flow experiments?
- P4C-2** In the article describing the liquid reaction of isoprene and maleic anhydride under pressure [*AIChE J.*, 16(5), 766 (1970)], the authors show the reaction rate to be greatly accelerated by the application of pressure. For an equimolar feed they write the second-order reaction rate expression in terms of the mole fraction  $y$ :

$$\frac{dy}{dt} = -k_y y^2$$

and then show the effect of pressure on  $k_y$  ( $s^{-1}$ ). Derive this expression from first principles and suggest a possible logical explanation for the increase in the true specific reaction rate constant  $k$  ( $dm^3/mol \cdot s$ ) with pressure that is different from the author's. Make a quick check to verify your challenge.

- P4C-3** The reduction of NO by char was carried out in a fixed bed between 500 and 845°C [*Int. Chem. Eng.*, 20(2), 239 (1980)]. It was concluded that the reaction is first order with respect to the concentration of NO feed (300 to 1000 ppm) over the temperature range studied. It was also found that activation energy begins to increase at about 680°C. Is first order the true reaction order? If there were discrepancies in this article, what might be the reasons for them?
- P4C-4** In the article describing vapor phase esterification of acetic acid with ethanol to form ethyl acetate and water [*Ind. Eng. Chem. Res.*, 26(2), 198 (1987)], the pressure drop in the reactor was accounted for in a most unusual manner [i.e.,  $P = P_0(1 - fX)$ , where  $f$  is a constant].

- Using the Ergun equation along with estimating some of the parameter values (e.g.,  $\phi = 0.4$ ), calculate the value of  $\alpha$  in the packed-bed reactor (2 cm i.d. by 67 cm long).
- Using the value of  $\alpha$ , redo part (a) accounting for pressure drop along the lines described in this chapter.
- Finally, if possible, estimate the value of  $f$  used in these equations.

#### • Additional Homework Problems

- CDP4-A<sub>B</sub>** A sinister looking gentlemen is interested in producing methyl perchlorate in a batch reactor. The reactor has a strange and unsettling rate law. [2nd Ed. P4-28] (Solution Included)



Solved Problems

#### Bioreactors and Reactions

- CDP4-B<sub>C</sub>** (*Ecological Engineering*) A much more complicated version of Problem 4-17 uses actual pond (CSTR) sizes and flow rates in modeling the site with CSTRs for the Des Plaines River experimental wetlands site (EW3) in order to degrade atrazine. [ See Web Module on CD or WWW]
- CDP4-C<sub>B</sub>** The rate of binding ligands to receptors is studied in this application of reaction kinetics to *bioengineering*. The time to bind 50% of the ligands to the receptors is required. [2nd Ed. P4-34] J. Lindemann, University of Michigan

#### Batch Reactors

- CDP4-D<sub>B</sub>** A *batch reactor* is used for the bromination of *p*-chlorophenyl isopropyl ether. Calculate the batch reaction time. [2nd Ed. P4-29]
- CDP4-E<sub>B</sub>** California Professional Engineers Exam Problem, in which the reaction



is carried out in a batch reactor. [2nd Ed. P4-15]

- CDP4-F<sub>A</sub>** Verify that the liquid-phase reaction of 5,6-benzoquinoline with hydrogen is pseudo first order. [2nd Ed. P4-7]



#### Flow Reactors

- CDP4-G<sub>B</sub>** Radial flow reactors can be used to good advantage for exothermic reactions with large heats of reaction. The radial velocity is

$$U = \frac{U_0 R_0}{r} (1 + \varepsilon X) \frac{P_0}{P} \frac{T}{T_0}$$

- Vary the parameters and plot  $X$  as a function of  $r$ . [2nd Ed. P4-31]
- CDP4-H<sub>A</sub>** Designed to reinforce the basic CRE principles through very straightforward calculations of CSTR and PFR volumes and batch reactor time. This problem was one of the most frequently assigned problems from the 2nd Edition. [2nd Ed. P4-4]
- CDP4-I<sub>B</sub>** Formation of diphenyl in a batch, CSTR, and PFR. [3rd Ed. P4-10]

**Packed Bed Reactors**

- CDP4-J<sub>B</sub>  $n$ -Pentane  $\longrightarrow$   $i$ -pentane in a packed bed reactor. [3rd Ed. P4-21]  
 CDP4-K<sub>C</sub> Packed bed spherical reactor. [3rd Ed. P4-20]  
 CDP4-L<sub>B</sub> The reaction of  $A \rightleftharpoons B$  is carried out in a membrane reactor where B diffuses out.

**Recycle Reactors**

- CDP4-M<sub>B</sub> The overall conversion is required in a *packed-bed reactor with recycle*. [2nd Ed. P4-22]  
 CDP4-N<sub>C</sub> Excellent reversible reaction with recycle. Good problem by Professor H.S. Shankar, IIT—Bombay. [3rd Ed. P4-28]

**Really Difficult Problems**

- CDP-O<sub>C</sub> DQE April 1999  
 $A \longrightarrow B$  in a PFR and CSTR with unknown order. (30 minutes to solve)  
 CDP-P<sub>D</sub> A Dr. Probjot Singh Problem  
 $A \longrightarrow B \rightleftharpoons C$  Species C starts and ends at the same concentration.

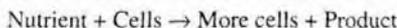
## Green Engineering

**New Problems on the Web**

- CDP4-New From time to time new problems relating Chapter 4 material to everyday interests or emerging technologies will be placed on the web. Solutions to these problems can be obtained by e-mailing the author. Also, one can go on the web site, [www.rowan.edu/greenengineering](http://www.rowan.edu/greenengineering), and work the home problem specific to this chapter.

**These Problems Were on CD-ROM for 3rd Edition but Not in Book for 3rd Edition**

- CDP4-Q<sub>A</sub> The gas-phase reaction  $A + 2B \longrightarrow 2D$  has the rate law  $-r_A = 2.5C_A^{0.5}C_B$ . Reactor volumes of PFRs and CSTRs are required in this multipart problem. [2nd Ed. P4-8]  
 CDP4-R<sub>B</sub> What type and arrangement of flow reactors should you use for a decomposition reaction with the rate law  $-r_A = k_1C_A^{0.5}/(1 + k_2C_A)$ ? [1st Ed. P4-14]  
 CDP4-S<sub>B</sub> The liquid-phase reaction  $2A + B \rightleftharpoons C + D$  is carried out in a semi-batch reactor. Plot the conversion, volume, and species concentrations as a function of time. Reactive distillation is also considered in part (e). [2nd Ed. P4-27]  
 CDP4-T<sub>B</sub> The growth of a bacterium is to be carried out in excess nutrient.



$$\text{The growth rate law is } r_B = \mu_m C_B \left( 1 - \frac{C_B}{C_{B\max}} \right) \quad [2\text{nd Ed. P4-35}]$$



- CDP4-U<sub>B</sub>** California Registration Examination Problem. Second-order reaction in different CSTR and PFR arrangements. [2nd Ed. P4-11]
- CDP4-V<sub>B</sub>** An unremarkable semibatch reactor problem, but it does require assessing which equation to use.

## SUPPLEMENTARY READING

- DAVIS, M. E., and R. J. DAVIS, *Fundamentals of Chemical Reaction Engineering*. New York: McGraw Hill, 2003.
- HILL, C. G., *An Introduction to Chemical Engineering Kinetics and Reactor Design*. New York: Wiley, 1977, Chap. 8.
- LEVENSPIEL, O., *Chemical Reaction Engineering*, 3rd ed. New York: Wiley, 1998, Chaps. 4 and 5.
- SMITH, J. M., *Chemical Engineering Kinetics*, 3rd ed. New York: McGraw Hill, 1981.
- ULRICH, G. D., *A Guide to Chemical Engineering Reactor Design and Kinetics*. Printed and bound by Braun-Brumfield, Inc., Ann Arbor, Mich., 1993.
- WALAS, S. M., *Reaction Kinetics for Chemical Engineers*. New York: McGraw Hill, 1970.

Recent information on reactor design can usually be found in the following journals: *Chemical Engineering Science*, *Chemical Engineering Communications*, *Industrial and Engineering Chemistry Research*, *Canadian Journal of Chemical Engineering*, *AIChE Journal*, *Chemical Engineering Progress*.