# ESSENTIALS OF CHEMICAL REACTION ENGINEERING

SECOND EDITION

H. SCOTT FOGLER

INTERNATIONAL SERIES IN THE
PHYSICAL AND CHEMICAL ENGINEERING SCIENCES

# *Essentials of Chemical Reaction Engineering*

*Second Edition*

other is a white, 800.0-dm$^3$ PFR operated at 300 K that cannot be heated or cooled but can be painted red or black. Note that $k = 0.07\ \text{dm}^3/\text{mol}\cdot\text{min}$ at 300 K and $E = 20\ \text{kcal/mol}$.

**(a)** 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.

**(b)** How long would it take to achieve 90% conversion in a 200-dm$^3$ batch reactor with $C_{A0} = C_{B0} = 1\ M$ after mixing at a temperature of 77°C?

**(c)** What would your answer to part **(b)** be if the reactor were cooled to 0°C? (***Ans.:*** 2.5 days)

**(d)** 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?

**(e)** Keeping Table 4-3 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.

**(f)** Write a couple of sentences describing what you learned from the problem and what you believe to be the point of the problem.

**(g)** Apply one or more of the six ideas in Preface Table P-4, page xxvii, to this problem.

**P5-10$_B$ 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, e.g., a model, that would give closer agreement between the predicted and measured conversions. Back your suggestions with calculations. P.S. It was raining *very* hard that day.

**(b)** The liquid-phase reaction

$$\mathrm{A} \longrightarrow \mathrm{B}$$

was carried out in a CSTR. For an entering concentration of 2 mol/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, 52.6% exactly. Brainstorm reasons for the disparity. Quantitatively show how these conversions came about (i.e., the expected conversion and the actual conversion). Part (b) is C-level difficulty.

**(c)** The gas-phase reaction

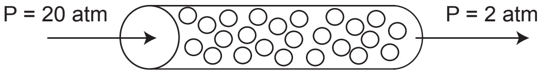
$$\mathrm{A} + \mathrm{B} \longrightarrow \mathrm{C} + \mathrm{D}$$

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?

**P5-11$_B$** The irreversible elementary gas-phase reaction

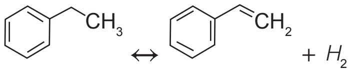
$$A + B \longrightarrow C + D$$

is carried out isothermally at 305 K in a packed-bed reactor with 100 kg of catalyst.



The entering pressure was 20 atm and the exit pressure is 2 atm. The feed is equal molar in A and B and the flow is in the turbulent flow regime, with $F_{A0} = 10$ mol/min and $C_{A0} = 0.4$ mol/dm$^3$. Currently 80% conversion is achieved. What would be the conversion if the catalyst particle size were doubled and everything else remained the same? (***Ans.:*** $X = 0.83$)

**P5-12$_B$** The reversible gas-phase elementary reaction



(*ethylbenzene* ↔ *styrene* + $H_2$)

is carried out in an isothermal CSTR with no pressure drop. The feed enters at a volumetric flow rate of $\upsilon_0 = 5000 \frac{\text{dm}^3}{\text{hour}}$. The feed consists of half ethyl benzene (i.e., A) and half inerts on a molar basis and is well mixed before it enters the reactor (I). The pressure in the reactor is 6 atm (so $P_{A0} = 3$ atm and $P_{I0} = 3$ atm, making the entering concentration of ethyl benzene, A, $C_{A0} = 0.04 \frac{\text{mol}}{\text{dm}^3}$). The molar flow rate of A is $F_{A0} = 200 \frac{\text{mol}}{\text{hr}}$. At the reaction temperature of 640°C, the rate constant, $k_A$, is $5.92 \frac{\text{mol}}{\text{dm}^3 \cdot \text{hr} \cdot \text{atm}}$. The equilibrium constant, $K_P$, is 9 atm and the corresponding equilibrium conversion is $X_e = 0.84$.

Reference: Won Jae Lee and Gilbert F. Froment. *Ind. Eng. Chem. Res.* 2008, 47, pp. 9183–9194.

- **(a)** Write out each step of the algorithm.
- **(b)** Write the rate of reaction, $-r_A$, solely as a function of $P_{A0}$ $X$, $K_P$ and $k$.
- **(c)** Calculate the reactor volume necessary to achieve 90% of the equilibrium conversion, $X_e$.
- **(d)** How would the conversion from part (a) be affected if the reactor diameter increased and height decreased but total volume remained the same? Explain.

**P5-13$_B$** World famous Inspector Sgt. Nigel Ambercromby was called in from Scotland Yard when the body of Ian Shoemaker, an English businessman, was discovered outside his home at 6 AM the morning of April 1st. Mr. Shoemaker was in the process of investigating why there was money missing from the chemical engineers' pension fund on March 31st. He met individually over coffee with each of the four employees who had access to the fund on March 31st, to confirm his suspicions before he pressed charges. However, the guilty one must have discovered Shoemaker's suspicions beforehand and wanted to keep their identity secret by murdering him.

***Who done it?***

During the autopsy the coroner determined Mr. Shoemaker was poisoned by a chemical known as Iocane powder. Iocane stops the heart from beating and is virtually undetectable, but it decomposes in the blood to form the detectable compound Optoid, according to the reaction

$$\text{Iocane} + \text{RBC} \rightarrow \text{Optoid}$$

Because of the high concentration of red blood cells, $C_{RBC}$, the rate law between Iocane and the red blood cells can be modeled as a pseudo first-order reaction in terms of the concentration of Iocane, $C_A$,

$$-r_A = k'_A C_{RBC} C_A \cong k_A C_A$$

The coroner told Inspector Ambercromby that during the autopsy at 11 AM on April 1st, he found that the concentration of Optoid was 0.01 mol/dm$^3$.

According to his calendar, Shoemaker had meetings the previous day, March 31st, at the following times:

1:30 PM (21.5 hours prior) with Mr. Gafhari
3:00 PM (20 hours prior) with Mr. Ross
5:00 PM (18 hours prior) with Ms. Patel
8:00 PM (15 hours prior) with Mr. Jenkins

These four individuals are now the prime suspects. Iocane is available over the counter as a rat poison in powder capsules, each containing 18 g (56.25 g/mol), and a capsule could have easily been put in Shoemaker's coffee.

*Additional information:*

Volume of blood: 5 $dm^3$
$k_A = 0.00944\ hr^{-1}$ at 310 K (body temperature)
E = 20.5 kcal/mol
Assume the poison goes virtually immediately into the blood.

**(a)** Calculate the initial concentration $C_{A0}$ of Iocane in the blood in gmol/$dm^3$ after ingesting one capsule.

**(b)** Knowing $C_{A0}$ and the concentration of Optoid at 11 AM, calculate the time Shoemaker was poisoned. Whom should Ambercromby arrest?

**(c)** After calculating the time the poison was put in the coffee and arresting the alleged killer, Shoemaker's wife mentioned that Shoemaker was running a fever of 311.7 K (101.4 F) that morning. Knowing Shoemaker had a fever, do you think Nigel arrested the right suspect? If not, whom should he arrest?

(Eric O'Neill, U of M, class of 2018)

**P5-14$_B$** The dehydration butanol on alumina is carried out over a silica-alumina catalyst at 680 K.

$$CH_3CH_2CH_2CH_2OH \xrightarrow[cat]{} CH_3CH{=}CHCH_3 + H_2O$$

The rate law is

$$-r'_{Bu} = \frac{kP_{Bu}}{\left(1+K_{Bu}P_{Bu}\right)^2}$$

with $k = 0.054$ mol/gcat•h•atm and $K_{Bu} = 0.32\ atm^{-1}$. Pure butanol enters a thin-tubed, packed-bed reactor at a molar flow rate of 50 kmol/hr and a pressure of 10 atm (1013•kPa).

**(a)** What PBR catalyst weight is necessary to achieve 80% conversion in the absence of pressure drop? Plot and analyze $X$, $p$, $f$ (i.e., $(v/v_0)$) and reaction rate, $-r'_A$, as a function of catalyst weight.

**(b)** What "fluidized CSTR" catalyst weight is necessary to achieve 80% conversion?

**(c)** Repeat **(a)** when there is pressure drop, with the pressure-drop parameter $\alpha = 0.0006\ kg^{-1}$. Do you observe a maximum in the rate of reaction, and if so, why? What catalyst weight is necessary to achieve 70% conversion? Compare this weight with that for no pressure drop to achieve the same conversion.

**(d)** What generalizations can you make about this problem?

**(e)** Write a question for this problem that requires critical thinking and then explain why your question requires critical thinking. (*Hint:* See Preface Section G.2)

**P5-15$_B$** The gaseous reaction A → B has a unimolecular reaction rate constant of 0.0015 $min^{-1}$ at 80°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°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. Source: From California Professional Engineers' Exam.

**P5-16$_B$** **(a)** The irreversible elementary reaction 2A → 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? Source: From California Professional Engineers' Exam.

**(b)** Write a question that requires critical thinking, and explain why it involves critical thinking. (See Preface Section G.2.)

**P5-17$_B$** Compound A undergoes a reversible isomerization reaction, A $\rightleftarrows$ 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?

**(c)** Apply one or more of the six ideas in Preface Table P-4, page xxvii, to this problem.

**P5-18$_B$** 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$^3$ of catalyst. The reaction is being carried out at 750°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$^3$ of catalyst.] Source: From California Professional Engineers' Exam. Make a list of the things you learned from this problem.

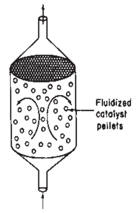
**P5-19$_B$** It is desired to carry out the gaseous reaction A → B in an existing *tubular reactor* consisting of 50 parallel tubes 40 ft long with a 0.75-in. inside diameter. Bench-scale experiments have given the reaction rate constant for this first-order reaction as 0.00152 s$^{-1}$ at 200°F and 0.0740 s$^{-1}$ at 300°F. At what temperature should the reactor be operated to give a conversion of A of 80% with a feed rate of 500 lb m/h of pure A and an operating pressure of 100 psig? A has a molecular weight of 73 Daltons. Departures from perfect gas behavior may be neglected, and the reverse reaction is insignificant at these conditions. [***Ans.:*** $T = 278$°F.] Source: From California Professional Engineers' Exam.

**P5-20$_B$** The irreversible first-order (wrt partial pressure of A) gas-phase reaction

$$A \rightarrow B$$

is carried out isothermally in a "fluidized" catalytic CSTR containing 50 kg of catalyst.

Currently, 50% conversion is realized for pure A entering at a 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 (5-29) is $\alpha = 0.018$ 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.



Fluidized CSTR

**(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 coming out of the first reactor?

**(c)** What is the conversion exiting the last reactor? (***Ans.:*** $X = 0.76$)

**(d)** What is the pressure at the exit of the packed bed? (***Ans.:*** $P = 6.32$ atm)

**(e)** 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?

**P5-21$_B$** A microreactor from the MIT group similar to the one shown in Figure P5-21$_B$ was used to produce phosgene in the gas phase. We continue our discussion on micro reactors in Chapter 6.

$$CO + Cl_2 \rightarrow COCl_2$$

$$A + B \rightarrow C$$

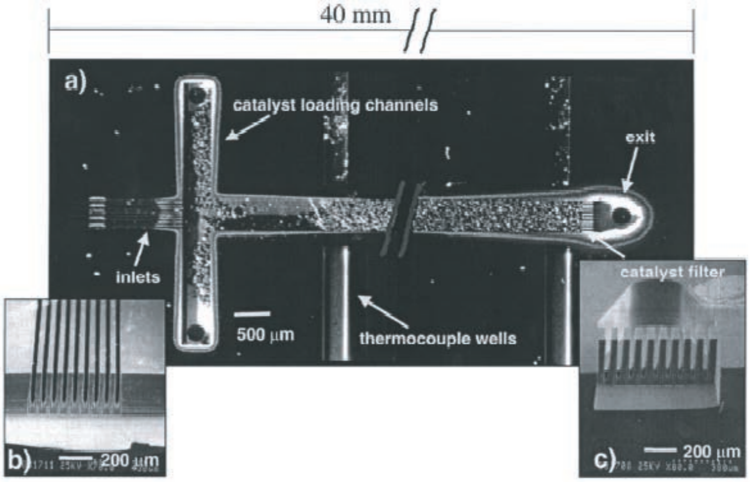


**Figure P5-21$_B$** Microreactor. Source: Courtesy of S. K. Ajmera, M. W. Losey, K. F. Jensen, and M. A. Schmidt, *AIChE J. 47*, 1639 (2001). (Article titled "Microfabricated cross-flow chemical reactor for catalyst testing.")

The microreactor is 20 mm long, 500 μm in diameter, and packed with catalyst particles 35 μm in diameter. The entering partial pressure of A is 231 kPa (2.29 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$^3$/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 P5-21$_B$, the rate law is different as well:

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

*Additional information:*

$\alpha = 3.55 \times 10^5$/kg catalyst (based on properties of air and $\phi = 0.4$)
$k = 0.004$ m$^6$/(mol · s · kg catalyst) at 120°C
$\upsilon_0 = 2.83 \cdot 10^{-7}$ m$^3$/s, $\rho = 7$ kg/m$^3$, $\mu = 1.94 \cdot 10^{-5}$ kg/m · s
$A_c = 1.96 \cdot 10^{-7}$ m$^2$, $G = 10.1$ kg/m$^2$ · s

**(a)** Plot the molar flow rates $F_A$, $F_B$, and $F_C$, the conversion $X$, and pressure ratio $p$ along the length (i.e., catalyst weight, $W$) of the reactor.
**(b)** Calculate the number of microreactors in parallel needed 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$^3$/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 why it involves critical thinking. (See Preface, Tables P-3 and P-4.)
**(g)** Apply one or more of the six ideas in Preface Table P-4, page xxvii, to this problem.

**P5-22$_A$** A very proprietary industrial-waste reaction, which we'll code as $A \rightarrow B + S$, is to be carried out in a 10-dm$^3$ CSTR followed by a 10-dm$^3$ PFR. The reaction is elementary, but A, which enters at a concentration of 0.001 mol/dm$^3$ 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$^{-1}$. 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* (all-time favorite of the author), *La La Land, The Fate of the Furious, Blade Runner 2049, or Despicable Me 3*. As a side note, the Jofostan film festival is held the last week in January in Riça, Jofostan. But don't try to attend the Jofostan film festival as it's only "A-List" celebrities such as Denzel Washington, Meryl Streep, and Sven Köttlov.

**P5-23$_B$** Walter White, Jesse Pinkman, and Mike Ehrmantraut stole 1000 gallons of methylamine during an episode of the TV series *Breaking Bad*. Shortly thereafter, Jesse and Mike decided they would get out of the cooking business and sell their shares of the methylamine. Walter wanted to keep all of the methylamine for future meth cooks and not let Jesse and Mike have their shares. Suppose Jesse and Mike decided to sabotage Walter's cooking operation by ruining the methylamine using the following gas phase reaction:

$$2\,CH_3NH_2 \leftrightarrow (CH_3)_2NH + NH_3$$

or, in short:

$$2A \rightleftarrows B + C$$

This reaction converts the methylamine to dimethylamine, using a silica-alumina catalyst. The molar flow rate into a packed-bed reactor is 23.6 mol/s and the entering pressure is 18 atm. Assume there is no pressure drop or temperature change in the reactor. The reaction rate follows an elementary rate law in terms of partial pressure.

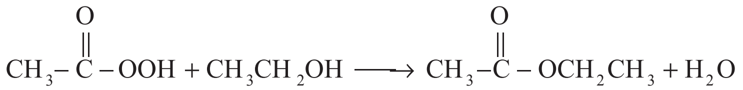
$$k_1 = 4.25 \times 10^{-6}\ \frac{\text{mol}}{\text{atm}^2 \cdot \text{gcatalyst} \cdot \text{s}} \quad \text{and } K_e = 2.5$$

**(a)** Write the mole balance.
**(b)** Write the rate law in terms of partial pressures.
**(c)** Set up a stoichiometric table for this reaction.
**(d)** Write the partial pressures in terms of conversion.
**(e)** Write the rate law solely in terms of conversion.
**(f)** What is the equilibrium conversion, $X_e$?
**(g)** Write out your algorithm in terms of conversion.
**(h)** How many kilograms of catalyst would Jesse need to load in a PBR to obtain a conversion of $0.9^*X_e$? For $X = 0.75\ X_e$?

***Who done it?***

**(i)** How many kilograms of catalyst would be needed to obtain 90% of the equilibrium conversion in a fluidized-bed reactor? If this weight is very, very large, what might you suggest to reduce the weight? (***Ans.:*** $W$ = 207.2 kg catalyst)
**(j)** What conversion would be achieved in a 100 kg PBR with pressure drop and $\alpha = 0.0098$ kg$^{-1}$? At what catalyst weight does the exit pressure fall below 1.0 atm?
**(k)** Repeat (j) when pressure drop is accounted for with $\alpha = 6 \times 10^{-4}$ kg$^{-1}$.
Ph.D. student Julia Faeth created this problem using modified data from J. W. Mitchell, et al., *Ind. Eng. Chem. Res. 33*, 1994, pp. 181–184.

**P5-24$_B$** Ethyl acetate is an extensively used solvent and can be formed by the vapor-phase esterification of acetic acid and ethanol.



$$CH_3-\overset{\overset{\large O}{\|}}{C}-OOH + CH_3CH_2OH \longrightarrow CH_3-\overset{\overset{\large O}{\|}}{C}-OCH_2CH_3 + H_2O$$

The reaction was studied using a microporous resin as a catalyst in a *packed-bed microreactor* [*Ind. Eng. Chem. Res., 26*(2), 198(1987)]. The reaction is first-order in ethanol and pseudo-zero-order in acetic acid. The total volumetric feed rate is 25 dm$^3$/min, the initial pressure is 10 atm, the temperature is