

Extra Exercises
for
Chemical Reactor
Analysis and Design
Fundamentals

James B. Rawlings
Department of Chemical and Biological
Engineering
University of Wisconsin
Madison, Wisconsin

John G. Ekerdt
Department of Chemical Engineering
The University of Texas
Austin, Texas

August 3, 2016

Nob Hill Publishing

Madison, Wisconsin

The extra exercises were set in Lucida using L^AT_EX.

Copyright © 2016 by Nob Hill Publishing, LLC

All rights reserved.

Nob Hill Publishing, LLC
Cheryl M. Rawlings, publisher
Madison, WI 53705
orders@nobhillpublishing.com
<http://www.nobhillpublishing.com>

The extra exercises are intended for use by students and course instructors.

This document has been posted electronically on the website: www.che.wisc.edu/~jbraw/chemreacfun.

2

The Stoichiometry of Reactions

Exercise 2.16: Element balances

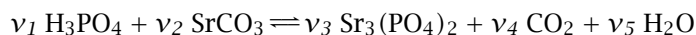
Consider a chemical reaction between the species P_4 , Cl_2 and PCl_5



- Write the element matrix \mathcal{A} for this reaction.
- What is the rank of \mathcal{A} ? How many linearly independent reactions can satisfy Reaction 2.73?
- Write all of the possible stoichiometries for these species using the smallest possible integers for ν .

Exercise 2.17: More element balances

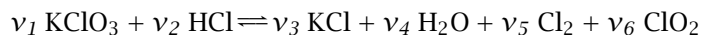
Consider the reaction



- Write the element matrix \mathcal{A} for this reaction.
- How many linearly independent reactions are possible with these species?
- Write all of the possible stoichiometries for these species using the smallest possible integers for ν .

Exercise 2.18: A 10th grade stoichiometry problem

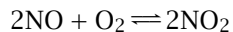
Consider the reaction



- (a) Write the element matrix \mathcal{A} for this reaction.
- (b) How many linearly independent reactions are possible with these species?
- (c) Write all possible stoichiometries for these species.
 Hint: you will not obtain integer coefficients if you use standard software to find null space of \mathcal{A}^T because the vectors of the null space are made into an orthonormal set. Try the Octave program `nullint` which gives an integer-valued null space.

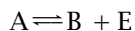
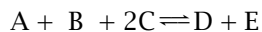
Exercise 2.19: Stoichiometry short questions

- (a) What is the difference between a set of reactions that is linearly independent and a set of reactions that is linearly dependent?
- (b) For the reaction



is it likely that this overall reaction would occur also as a molecular event? Why or why not?

- (c) Consider the set of reactions



- Write out the species list and stoichiometric matrix. For ease of grading, please keep the species in alphabetical order in the species list.
- By inspection, what is the rank of this matrix? Explain your answer.

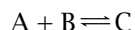
3

Review of Chemical Equilibrium

Exercise 3.16: Confusion over reaction equilibrium with multiple phases

A student in your class asks for your help with the following difficult she is having.

I have a gas/liquid two-phase system with the chemical reaction



I assume the gas phase is an ideal-gas mixture and the liquid phase is an ideal-liquid solution. The phase rule says that I have two free intensive variables

$$f = n + 2 - \pi - r$$

$$f = 3 + 2 - 2 - 1$$

$$f = 2$$

so I fix T and P and try to find the phase compositions, y_j , and x_j , $j = A, B, C$. I have $6 - 2 = 4$ unknowns since the mole fractions in each phase sum to one. I equate the chemical potentials for each component in the two phases

$$\mu_j^{\text{liq}} = \mu_j^{\text{gas}} \quad j = A, B, C$$

for three equations, and I know the condition for reaction equilibrium is

$$K = \prod_{j=1}^n a_j^{y_j}$$

for the fourth equation. But if I express the reaction equilibrium equation for the gas phase, I get a different equation than for the liquid phase

$$\prod_j a_j^{y_j} = \frac{y_C}{P y_A y_B} \quad \text{gas-phase}$$

$$\prod_j a_j^{y_j} = \frac{x_C}{x_A x_B} \quad \text{liquid-phase}$$

in which I have ignored the Poynting correction for the liquid phase because the pressure is low. These cannot give the same solution because the phase equilibrium relations are

$$Py_j = P_j^0 x_j \quad j = A, B, C$$

in which P_j^0 is the vapor pressure of component j at the system T . Using the gas phase for the reaction equilibrium gives

$$\begin{aligned} K &= \frac{y_C}{Py_A y_B} \\ &= \frac{Py_C}{(Py_A)(Py_B)} \\ &= \frac{P_C^0 x_C}{(P_A^0 x_A)(P_B^0 x_B)} \\ &= \left(\frac{P_C^0}{P_A^0 P_B^0} \right) \left(\frac{x_C}{x_A x_B} \right) \\ K &\neq \frac{x_C}{x_A x_B} \end{aligned}$$

which does not agree with the choice of using the liquid phase for the reaction equilibrium. Can I conclude that the component vapor pressures must be related by

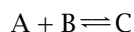
$$\frac{P_C^0}{P_A^0 P_B^0} = 1$$

If not, how do I get consistent results for the equilibrium composition? Nature doesn't know which phase I choose when I do my equilibrium calculation!

How do you respond to this student?

Exercise 3.17: Equilibrium, friend or foe?

The following reaction takes place at low pressure in the gas phase



You charge a batch reactor with equal amounts of A and B and no C, run the reactor for a long time at a given temperature and pressure, and then open it up and find that you have converted about 50 percent of the starting materials.

But you need to reach 75 percent conversion for this process to be profitable. Your boss asks you to troubleshoot this process and make suggestions to save the project, which is about to be canceled. What do you tell your boss? Here are some options to consider. Feel free to choose one or more of these, or suggest your own options. The important point is to explain and justify your choice.

- (a) Just run the reactor for a longer time. Eventually it will reach 75 percent conversion, guaranteed. You just have to be patient. State what other thermochemical data you require, if any, to justify this approach.
- (b) Change the operating temperature. If you choose this option, what new temperature do you select? State what other thermochemical data you require, if any, to select the new temperature, and calculate the new temperature assuming whatever new data you require is available in your company's thermochemical database.
- (c) Change the operating pressure. If you choose this option, what new pressure do you select? Again state what other thermochemical data, if any, you require to select the new pressure, and calculate the new pressure assuming whatever new data you require is available in your company's thermochemical database.

4

The Material Balance for Chemical Reactors

Exercise 4.23: Short answers on microscopic and macroscopic balances

Consider the volume element V of total volume V_R with bounding surface S and outward normal n depicted in Figure 4.39. The volume element has one entrance and one exit stream, and otherwise moves to contain chemical species $j = 1, \dots, n_s$ with velocities v_j relative to some fixed laboratory coordinates. The velocity of the element's outer bounding surface is v_s . Decide whether the following statements are true or false, and give a short explanation justifying your answer.

(a) $\int_{V(t)} \frac{\partial c_j}{\partial t} d\Omega = \frac{d}{dt} \int_{V(t)} c_j d\Omega$ if the volume element is well-mixed

(b) $\int_{V(t)} \frac{\partial c_j}{\partial t} d\Omega = \frac{dc_j}{dt} V_R$ if the volume element is well-mixed

(c) $\frac{d}{dt} \int_{V(t)} c_j d\Omega = \int_{V(t)} \frac{\partial c_j}{\partial t} d\Omega + \int_{S(t)} c_j (v_s \cdot n) d\sigma$

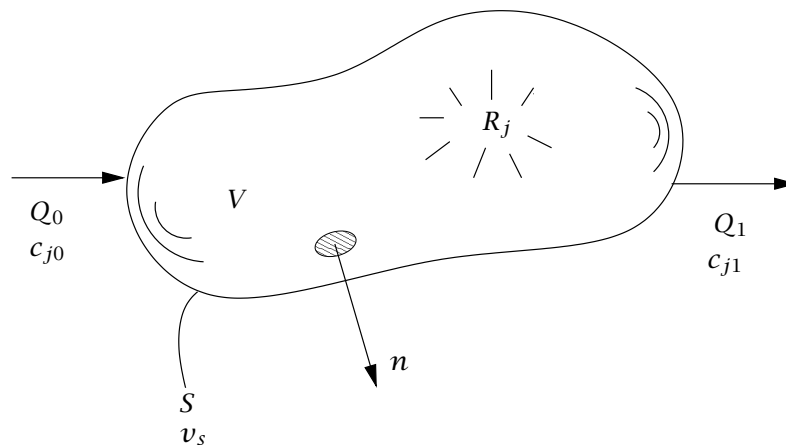


Figure 4.39: Volume element V with one entrance stream and one exit stream. The bounding surface is S and moves with velocity v_s .

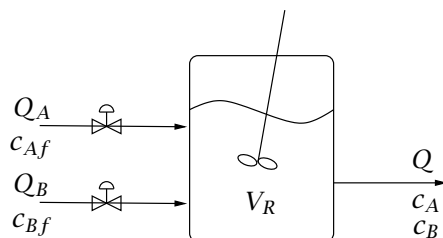


Figure 4.40: Organic acid and base streams fed into a CSTR.

- (d) $\int_{S(t)} c_j(v_j \cdot n) d\sigma = -Q_0 c_{j0} + Q_1 c_j$ if the volume element is well-mixed
- (e) $\int_{S(t)} c_j(v_j \cdot n) d\sigma = -Q_0 c_{j0} + Q_1 c_j + c_j \frac{dV_R}{dt}$ if the volume element is well-mixed
- (f) $\frac{d}{dt} \int_{V(t)} c_j d\Omega = - \int_{S(t)} c_j(v_j - v_s) \cdot n d\sigma + \int_{V(t)} R_j d\Omega$

Exercise 4.24: Esterification in a CSTR

Consider the liquid-phase organic esterification reaction taking place in a CSTR depicted in Figure 4.40. Two streams, an acid stream containing no base, and a base stream containing no acid, are fed into the CSTR. The esterification reaction and its rate are given by



in which A is the organic acid and B is the organic base. The acid and base are dissolved in an organic solvent and the acid and base feed streams have feed concentrations c_{Af} and c_{Bf} , respectively. You may assume that the density of the fluid is independent of concentration over the concentration range of interest here. The reactor's volume is constant during the entire operation.

- What are the units of k ?
- What is the volumetric flowrate Q of the effluent stream in terms of the feed stream flowrates Q_A and Q_B ? Show your reasoning.
- Write out the *transient* material balances for components A and B. You should have differential equations for dc_A/dt , dc_B/dt when you are finished. What initial conditions do you require for these two differential equations.
- Now consider the steady-state problem. Write the steady-state balances for the acid and base concentrations in the reactor, c_{As} , c_{Bs} .

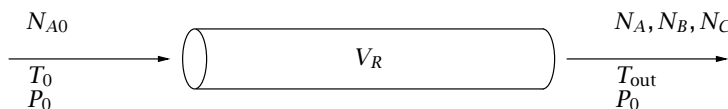


Figure 4.41: PFR with nonconstant number of moles and nonconstant temperature.

- (e) Can you solve these two equations for c_{As} , c_{Bs} in the general form for all values of the parameters? Is this steady-state solution unique?
- (f) Whether or not you were able to solve the equations in the general form, given the following specific parameter values, find the steady-state reactor concentrations c_{As} , c_{Bs}

$$\tau = 10 \text{ min} \quad Q_A = Q_B \quad c_{Af} = 8 \text{ mol/L} \quad c_{Bf} = 4 \text{ mol/L}$$

$$k = 0.1 \text{ (in units of min, mol, L)}$$

- (g) What are the steady-state molar conversions of A and B for these specific parameter values?

Exercise 4.25: PFR with changing flowrate

Consider the gas-phase PFR depicted in Figure 4.41 in which the following reaction takes place



The feed is pure A with molar flow N_{A0} at temperature T_0 , pressure P_0 and volumetric flowrate Q_0 . The outlet of the reactor is at temperature T_{out} . Neglect pressure drop in the tube ($P = P_0$). The gas may be assumed to be an ideal gas over this temperatures range at this pressure. The rate constant may be assumed independent of temperature over the temperature range $T_0 \leq T \leq T_{\text{out}}$.

- (a) List the ideal gas equation of state relating temperature T , pressure P and total molar concentration c ?
- (b) What is the relationship between total molar flow N , volumetric flowrate Q , temperature T , and pressure P for the ideal gas equation of state?
- (c) For this reaction stoichiometry, what is the total molar flow N expressed solely in terms of the molar flowrate of component A N_A , i.e. an expression not involving N_B and N_C ?

- (d) Assume first that the volumetric flowrate does not depend on the change in the number of moles with reaction, nor on the temperature, i.e. $Q(V) = Q_0$. Find the reactor volume, V_R , required to achieve 90% conversion of A. Call this volume V_{R1} . It should be in terms of k, R, T_0, P_0, N_{A0} and the chosen conversion (or N_A at the outlet).
- (e) Assume next that the tube is isothermal, but account for the change in volumetric flowrate due to change in the number of moles with reaction. What reactor volume is required to achieve 90% conversion? Call this volume V_{R2} . Find the ratio V_{R2}/V_{R1} . You can obtain a numerical value for this ratio with the given information. Which reactor is larger, V_{R1} or V_{R2} ? Why?
- (f) Finally, assume the change in temperature is well approximated by the linear relationship

$$T(V) = T_0 + (T_{\text{out}} - T_0) \frac{V}{V_R}$$

Solve the problem again accounting for both the change in temperature and the change in the number of moles with reaction. Assume the reactor temperature at the outlet is one and a half times the temperature at the inlet

$$T_{\text{out}} = 1.5 T_0 \quad \text{for } T \text{ in absolute temperature units}$$

What reactor volume is required to achieve 90% conversion? Call this volume V_{R3} . Find the ratio V_{R3}/V_{R2} . You can obtain a numerical value for this ratio with the given information. Which reactor is larger, V_{R2} or V_{R3} ? Why?

- (g) For this stoichiometry, conversion and temperature change, which effect has more impact on the reactor size, changing the number of moles by reaction or changing the temperature of the gas?

Exercise 4.26: Solving the transient nonconstant density reactor

Revisit Exercise 4.8, but solve the transient reactor starting from a water-filled reactor of 1000 L assuming an ideal mixture. Be sure to plot the molar numbers of all components, the reactor volume and the effluent flowrate for each case below.

- (a) First assume the reactor is operated at constant volume. Plot the solution to the model showing the transient approach to steady state. Which set of reactor balances from Tables 4.1 and 4.2 do you choose and why? You may want to read Exercise 4.19 to get some ideas on what is going on with these different model forms.
- (b) Next assume the reactor has a fixed and constant outlet flowrate

$$Q = \alpha Q_f$$

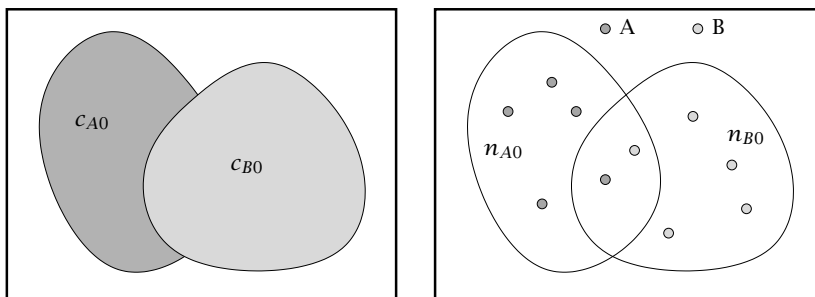


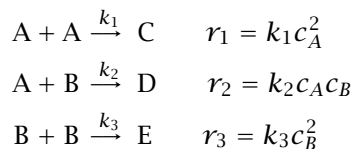
Figure 4.42: Species A and B in a well-mixed volume element. Continuum and molecular settings.

For what range of α does the model admit a steady-state solution? Provide a closed-form solution for the steady-state reactor volume as a function of α valid over this range. Plot this steady-state reactor volume versus α over this range. You may want to display this result using a semi-log plot for the y -axis.

- (c) Choose $\alpha = 0.987$ and simulate the transient reactor behavior. Which set of reactor balances from Tables 4.1 and 4.2 work for this situation?

Exercise 4.27: What happened to my rate?

Consider a well-mixed continuum setting in which we have positive, real-valued concentrations of reacting molecules of two types, A and B, as depicted in Figure 4.42. Let the concentration of A and B molecules in the volume of interest be denoted c_{A0} , c_{B0} . Consider the three possible irreversible reactions between these species using the elementary rate expressions



Consider also the total rate of reaction

$$r = r_1 + r_2 + r_3$$

- (a) If the A and B species are chemically similar so the different reactions' rate constants are all similar, $k_1 = k_2 = k_3 = k$, and the concentrations of A and B are initially equal, the total rate is given by

$$r = 3k c_{A0}^2$$

Reactor	Volume
Small A	100 mL
Small B	200 mL
Medium A	1 L
Medium B	2 L
Large	50 L

Other data: $T = 200$ C, $k = 1500$ L/mol hr, $R = 0.08314$ L bar/mol K; all components are in the gas phase at the reactor temperature and pressure.

- Write out the mass balances for the four components.
- What is Q in terms of the feed conditions and N_A ?
- Assuming pure reactants in the feed with $N_{Af} = N_{O_2f}$ solve the PFR mass balance for component A.
- What molar feed of A and O_2 is required to get 90% conversion in each of the reactors given in the table.
- You need to produce 105 mol/yr of phenol (100 mol/yr for downstream processes and 5 mol/yr to cover losses). What single reactor do you recommend to minimize reactor down time?
- If you can use multiple reactors, what reactors do you recommend to minimize both the number of reactors and the reactor down time? (i.e., how close can you get to 105 mol/yr production rate using the minimal number of reactors). You can use the same reactor type multiple times if desired.

Exercise 4.29: CSTRs and recycle

The following liquid-phase reaction



is taking place in the single CSTR system shown in Figure 4.43(a). You need to increase the steady-state conversion without lowering the overall production rate. A creative but slightly unstable colleague has proposed the modification using a second reactor shown in Figure 4.43(b). The following parameter values are known

$$kV_{R1}/Q_f = 1 \quad kV_{R2}/Q_f = 2$$

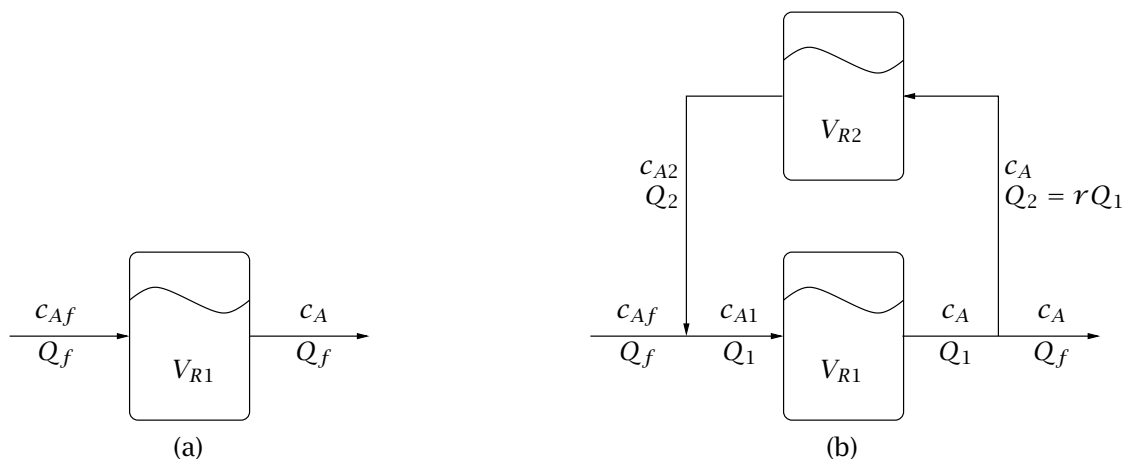
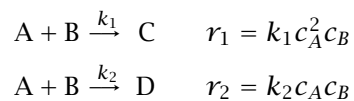


Figure 4.43: (a) Original single CSTR system. (b) Modified two-CSTR system with recycle.

- Compute the steady-state exit dimensionless concentration c_A/c_{Af} for the single CSTR. What is the steady-state conversion?
- Write a total mass balance at the splitting point and determine Q_1 and Q_2 as a function of Q_f and the recycle ratio $r = Q_2/Q_1$.
- Write component A mass balances over both reactors and find the concentrations at the exits of the two CSTRs, c_A/c_{Af} and c_{A2}/c_{Af} .
- Evaluate the steady-state overall conversion of A using the two CSTRs for recycle ratio, $r = 1/2$. Which conversion is higher, the single CSTR or the two-CSTR with recycle? Try again for $r = 3/4$ and $r = 1/4$.
- What do you think is the best recycle ratio to use to maximize the conversion? What are the advantages and disadvantages of your colleague's proposal to use the second reactor? Can you suggest a better use of the second reactor?

Exercise 4.30: Selectivity of competing first-order and second-order reactions

The following two reactions take place in a constant-volume batch reactor



There is a large excess of reactant B initially, and therefore we can assume that c_B is approximately constant throughout the batch time. Note that, despite the stoichiometry, the first reaction is second-order in A, but the second reaction is first-order in A.

- Write out the component balance for species A in the reactor. How does it simplify when noting that B is in large excess?
- Solve the component balance for $c_A(t)$. Check that your solution satisfies the initial condition.
- Draw a sketch of $c_A(t)$ versus t .
- How would you define the *instantaneous* selectivity of product C, s_C (production of C relative to consumption of A). Explain in physical terms what this selectivity is measuring.
- How would you define the *overall* selectivity of product C, S_C as a function of the batch time, t . Explain in physical terms what this selectivity is measuring.
Are the two selectivities you have defined the same for this application? Why or why not?
- How would you define overall conversion of A for this reactor, x_A ? Explain in physical terms what this conversion is measuring.

Hint: if you need to integrate something like

$$\int \frac{dx}{(x+a)(x+b)}$$

and, since WolframAlpha is unreachable, instead notice that you can express

$$\frac{1}{(x+a)(x+b)} = \frac{1}{b-a} \left[\frac{1}{x+a} - \frac{1}{x+b} \right]$$

and you know how to integrate both terms on the right-hand side. This is called a partial fraction expansion, and you will use it later in CBE 470.

Exercise 4.31: Optimizing selectivity and conversion

Revisit Exercise 4.30 and answer the following.

- Solve the problem numerically for $c_A(t)$, $c_C(t)$, $c_D(t)$ using the following parameter values

$$c_{A0} = 1 \text{ mol/L} \quad (k_1 c_{B0}) = 2 \text{ L}/(\text{mol}\cdot\text{hr}) \quad (k_2 c_{B0}) = 1 \text{ hr}^{-1}$$

Check your analytical solution for $c_A(t)$ from Exam 1

(b) Define

$$s_C = \frac{R_C}{-R_A} \quad S_C = \frac{n_C - n_{C0}}{n_{A0} - n_A} \quad x_A = \frac{n_{A0} - n_A}{n_{A0}}$$

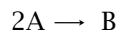
Plot s_C, S_C, x_A versus time from your numerical solution.

(c) Let's say that you have done an economic analysis of this process and decided that you need greater than 80 percent conversion of A and greater than 50 percent yield of C. Are these two requirements feasible? If so, what batch time do you choose for this application?

(d) Make a plot of x_A versus S_C . What is the largest yield of C possible for 80 percent or higher conversion of A? What is the largest conversion of A possible for 50 percent or higher yield of C?

Exercise 4.32: Gas-phase reaction in a PFR

The following elementary, gas-phase reaction takes place in a PFR.



The reactor is fed with a mixture of reactant A and inert diluent I at feedrates N_{Af} and N_{If} at total molar concentration c_f . The feed conditions and rate constant are

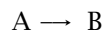
$$c_f = 0.2 \text{ mol/L} \quad N_{Af} = 2.0 \text{ mol/min} \quad N_{If}/N_{Af} = 3 \quad k = 20.0 \text{ L/mol} \cdot \text{min}$$

The pressure and temperature are constant in the PFR, and the gas may be assumed to behave as an ideal-gas mixture.

- (a) Write a balance for the steady-state molar flow of A, N_A . Make sure that your right-hand side is a function of only N_A and known parameters. What is the initial condition for this differential equation?
- (b) What reactor size is required to achieve 85 percent conversion?
- (c) What happens to this reactor size if you
 1. Double the rate constant k ?
 2. Double the feed flows N_{Af} and N_{If} , but keep feed concentration constant?
 3. Double the feed concentration, but keep the feed flows constant?

Exercise 4.33: PFR and CSTR size comparison

Even for a simple stoichiometry like



depending on the mechanism, we will derive a reaction rate expression in Chapter 5 as complex as

$$r = \frac{kc_A}{(1 + Kc_A)^2}$$

- What are the units of k and K ? Draw a sketch of $r(c_A)$ as a function of c_A . Show what happens at both low c_A concentration and high c_A concentration.
- Draw a sketch of $1/r(c_A)$ as a function of c_A . Find the minimum of $1/r(c_A)$. Draw this point also on your sketch.
- Assume we run this reaction in liquid phase in a CSTR and also in a PFR.

To achieve a conversion of A of 50 percent, and with the following parameter values, which reactor has more volume, the CSTR or the PFR?

$$c_{Af} = 1.4 \text{ mol/L} \quad K = 2.0 \text{ L/mol}$$

Justify your answer. You might find your sketch of $1/r(c_A)$ in the previous part useful.

- To achieve the same 50 percent conversion of A and with the following parameter values, which reactor has more volume, the CSTR or the PFR?

$$c_{Af} = 0.6 \text{ mol/L} \quad K = 1.0 \text{ L/mol}$$

Justify your answer. You might find your sketch of $1/r(c_A)$ in the previous part useful.

Exercise 4.34: Make PFR and CSTR the same size!

Let's revisit Exercise 4.33 and see if we can make the PFR and CSTR reactors the same size.

- For the first case with parameter values

$$c_{Af} = 1.4 \text{ mol/L} \quad K = 2.0 \text{ L/mol}$$

What conversion can you choose so that the sizes of the PFR and CSTR are identical?

(b) For the second case with parameter values

$$c_{Af} = 0.6 \text{ mol/L} \quad K = 1.0 \text{ L/mol}$$

what inlet feed concentration can you choose so that the sizes of the PFR and CSTR are identical (keep the conversion at 50 percent).

(c) Why do you not need to know the reactor rate constant k in Exercise 4.33 and this exercise?

5

Chemical Kinetics

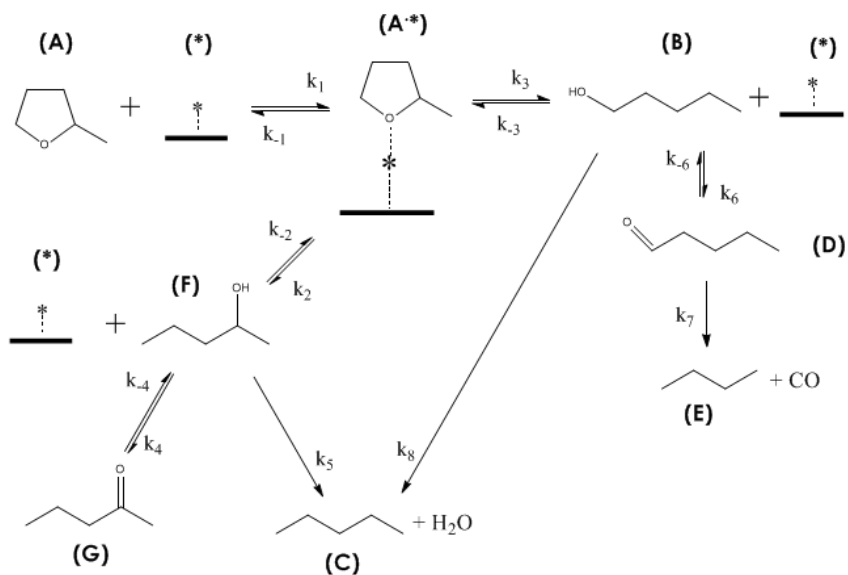


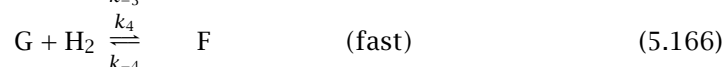
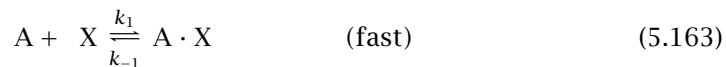
Figure 5.26: Mechanism for hydrogenolysis of 2-methyltetrahydrofuran on platinum. The H_2 are not shown in the diagram for clarity but are listed in the mechanism below.

species	A	A·X	G	F	B	D	E	C	H ₂ O	H ₂	CO
mole percent	20	0	23	2	0	0	10	14	14	7	10

Table 5.9: Steady-state gas-phase mole percentages at 545 K, 1.3 bar in the effluent of a flow reactor. Adsorbed methyl THF (A·X) is adsorbed on the catalyst and is not present in the effluent, but is present in the reactor in nonnegligible amount.

Exercise 5.20: Hydrogenolysis of 2-methyltetrahydrofuran

Consider the reaction mechanism depicted in Figure 5.26 consisting of the following reactions [2]



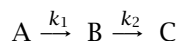
The rates of reactions 1 and 4 are known to be fast, so these two reactions may be assumed to be at equilibrium with respect to the other six reactions. A gas-phase CSTR containing a platinum catalyst is used to collect data. The feed consists of A and H₂. Typical steady-state concentrations of the gas-phase species in the effluent are listed in the table.

- From the table, what species are good candidates for making the quasi-steady-state assumption in order to simplify the reaction mechanism. Explain your choice.
- Apply the QSSA to these species and the equilibrium assumption to reactions 1 and 4 and express the production rate of butane (E) in terms of reactants and products present in large concentration in the gas phase (greater than 5 mole percent).

- (c) Find the production rate of n-pentane (C) in terms of reactants and products present in large concentration in the gas phase (greater than 5 mole percent).

Exercise 5.21: QSSA as the outer solution in a two-time-scale singular perturbation

Consider the following simple reaction mechanism taking place in a well-mixed, constant-volume, batch reactor



and assume $k_2 \gg k_1$ so B is a low-concentration species for which we wish to examine the QSSA.

- (a) Solve A's material balance and show

$$c_{As} = c_{A0}e^{-k_1t}$$

Apply the usual QSSA approach, set $R_B = 0$ and show that

$$c_{Bs} = \frac{k_1}{k_2}c_{As} = c_{A0}\frac{k_1}{k_2}e^{-k_1t}$$

The concentration of C is always available if desired from the total species balance

$$c_{Cs}(t) = c_A(0) + c_B(0) + c_C(0) - c_{As}(t) - c_{Bs}(t)$$

These results are in agreement with Equations 5.61-5.63.

- (b) The B species has two-time-scale behavior. On the fast time scale, it changes rapidly from initial concentration c_{B0} to the quasi-steady-state value for which $R_B \approx 0$. Divide B's material balance by k_2 , define the fast time-scale time as $\tau = k_2t$, and obtain for B's material balance

$$\frac{dc_B}{d\tau} = \epsilon k_1 c_A - c_B \quad \epsilon = \frac{1}{k_2}$$

We wish to find an asymptotic solution for small ϵ . We try a series expansion in powers of ϵ for the inner solution (fast time scale)

$$c_{Bi} = Y_0 + \epsilon Y_1 + \epsilon^2 Y_2 + \dots$$

The initial condition, $c_{Bi} = c_{B0}$, must be valid for all ϵ , which gives for the initial conditions of the Y_n

$$Y_0(0) = c_{B0} \quad Y_n(0) = 0, \quad n = 1, 2, \dots$$

Substitute the series expansion into B's material balance, collect like powers of ϵ and show the following differential equations govern the Y_n

$$\begin{aligned}\epsilon^0 : \quad & \frac{dY_0}{d\tau} = -Y_0 \\ \epsilon^1 : \quad & \frac{dY_1}{d\tau} = k_1 c_A - Y_1 \\ \epsilon^n : \quad & \frac{dY_n}{d\tau} = -Y_n \quad n \geq 2\end{aligned}$$

(c) Solve these differential equations and show

$$\begin{aligned}Y_0 &= c_{B0} e^{-\tau} \\ Y_1 &= c_{A0} \frac{k_1}{k_1/k_2 - 1} (e^{-\tau} - e^{-k_1\tau/k_2}) \\ Y_n &= 0 \quad n \geq 2\end{aligned}$$

Because Y_n vanishes for $n \geq 2$, show you obtain the exact solution for the B concentration for all ϵ by using the first two terms. Compare your result to Equation 5.59.

(d) Next we analyze B's large-time-scale behavior, also called the outer solution. Divide B's material balance by k_2 again but do not rescale time and obtain

$$\epsilon \frac{dc_B}{dt} = \epsilon k_1 c_A - c_B$$

Expand c_B again in a power series of ϵ

$$c_{B0} = B_0 + \epsilon B_1 + \epsilon^2 B_2 + \dots$$

Substitute the power series into the material balance and collect like powers of ϵ to obtain the following equations

$$\begin{aligned}\epsilon^0 : \quad & B_0 = 0 \\ \epsilon^1 : \quad & \frac{dB_0}{dt} = k_1 c_A - B_1 \\ \epsilon^n : \quad & \frac{dB_n}{dt} = -B_{n+1} \quad n \geq 1\end{aligned}$$

Solve these equations and show

$$\begin{aligned}B_0 &= 0 \\ B_1 &= k_1 c_A \\ B_n &= k_1^n c_A \quad n \geq 2\end{aligned}$$

So we see the zero-order outer solution is $C_{B0} = 0$, which is appropriate for a QSSA species, but a rather rough approximation.

- (e) Show that the classic QSSA analysis is the first-order outer solution.
- (f) To obtain a uniform solution valid for both short and long times, we add the inner and outer solution and subtract any common terms. Plot the uniform zeroth-order and first-order solutions for the following parameter values

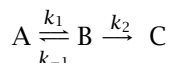
$$c_{A0} = 1 \quad c_{B0} = 1/2 \quad k_1 = 1 \quad k_2 = 10$$

Compare to the exact solution and the first-order outer solution (QSSA solution).

- (g) Show that the infinite order uniform solution is also the exact solution.

Exercise 5.22: QSSA and matching conditions in singular perturbation

Consider again Exercise 5.21 with a slightly more complex reaction mechanism



and assume that either $k_{-1} \gg k_1$ or $k_2 \gg k_1$ (or both) so B is again a low-concentration species for which we wish to examine the QSSA. Notice that either k_{-1} or k_2 may be large with respect to the other without invalidating the QSSA assumption for B. Only if $k_{-1} \gg k_1 \gg k_2$ is the reaction equilibrium assumption also valid for this mechanism.

- (a) Apply the QSSA on species B and show

$$c_{As} = \left(c_{A0} + c_{B0} \frac{1}{1 + K_2} \right) e^{-\frac{k_1 K_2}{1 + K_2} t}$$

$$c_{Bs} = \frac{1}{k_{-1}} \frac{k_1}{1 + K_2} \left(c_{A0} + c_{B0} \frac{1}{1 + K_2} \right) e^{-\frac{k_1 K_2}{1 + K_2} t}$$

in which $K_2 = k_2/k_{-1}$. Notice that these are in agreement with but more general than Equations 5.70 and 5.71, which have assumed in addition that $c_{B0} = 0$.

- (b) With this mechanism, both the A and B species have two-time-scale behavior, so we use a series expansion for both c_A and c_B . Let the inner solution be given by

$$c_{Ai} = X_0 + \epsilon X_1 + \epsilon^2 X_2 + \dots$$

$$c_{Bi} = Y_0 + \epsilon Y_1 + \epsilon^2 Y_2 + \dots$$

in which the small parameter ϵ is the inverse of the largest rate constant in the mechanism. In the following we assume k_{-1} is largest and $\epsilon = 1/k_{-1}$. Define $K_2 = k_2/k_{-1}$ and we assume that K_2 is order unity or smaller. If K_2 were large, we

should have chosen $\epsilon = 1/k_2$ as the small parameter. Collect terms of like power of ϵ and show

$$\begin{aligned} \epsilon^0 : \quad & \frac{dX_0}{d\tau} = Y_0 & \frac{dY_0}{d\tau} &= -(1 + K_2)Y_0 \\ \epsilon^1 : \quad & \frac{dX_1}{d\tau} = -k_1X_0 + Y_1 & \frac{dY_1}{d\tau} &= k_1X_0 - (1 + K_2)Y_1 \\ \epsilon^n : \quad & \frac{dX_n}{d\tau} = -k_1X_{n-1} + Y_n & \frac{dY_n}{d\tau} &= k_1X_{n-1} - (1 + K_2)Y_n \quad n \geq 1 \end{aligned}$$

What are the initial conditions for the X_n and Y_n variables?

(c) Solve these for the zero-order inner solution and show

$$X_0 = c_{A0} + c_{B0} \frac{1}{1 + K_2} \left(1 - e^{-(1+K_2)\tau}\right) \quad Y_0 = c_{B0} e^{-(1+K_2)\tau}$$

(d) Next we construct the outer solution valid for large times. Postulate a series expansion of the form

$$\begin{aligned} c_{A0} &= A_0 + \epsilon A_1 + \epsilon^2 A_2 + \dots \\ c_{B0} &= B_0 + \epsilon B_1 + \epsilon^2 B_2 + \dots \end{aligned}$$

Substitute these into the A and B material balances and show

$$\begin{aligned} \epsilon^0 : \quad & B_0 = 0 & (1 + K_2)B_0 &= 0 \\ \epsilon^1 : \quad & \frac{dA_0}{dt} = -k_1A_0 + B_1 & \frac{dB_0}{dt} &= k_1A_0 - (1 + K_2)B_1 \\ \epsilon^n : \quad & \frac{dA_{n-1}}{dt} = -k_1A_n + B_n & \frac{dB_{n-1}}{dt} &= k_1A_{n-1} - (1 + K_2)B_n \quad n \geq 1 \end{aligned}$$

(e) Solve these and show for zero order

$$A_0 = A_0(0)e^{-\frac{k_1K_2}{1+K_2}t} \quad B_0 = 0$$

Again we see that to zero order, the B concentration is zero after a short time.

Note also that, unlike in Exercise 5.21, we *require an initial condition for the outer solution* A_n differential equations. We obtain the missing initial condition by matching with the inner solution as follows

$$\lim_{\tau \rightarrow \infty} X_0(\tau) = \lim_{t \rightarrow 0} A_0(t)$$

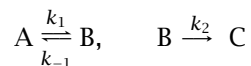
In other words, the long-time solution (steady state) on the fast-time scale is the short-time solution (initial condition) on the slow-time scale. Using this matching condition show

$$A_0(0) = c_{A0} + c_{B0} \frac{1}{1 + K_2}$$

- (f) Find also the first-order solution, B_1 , and show that the QSSA solution corresponds to the zero-order outer solution for c_A and the first-order outer solution for c_B .

Exercise 5.23: Reaction equilibrium assumption as a singular perturbation

Consider again the reaction equilibrium assumption and the following reactions



in which rate constants k_1, k_{-1} are much larger than the rate constants k_2 , so the first reaction equilibrates quickly.

- (a) Apply the method discussed in Chapter 5 to obtain differential equations for c_A and c_B valid on the slow time scale. What are the correct initial conditions for these slow-time-scale differential equations?
- (b) Now consider the problem using the singular perturbation approach of Exercises 5.21 and 5.22. Assume k_{-1} is the largest rate constant and define the fast time scale as

$$\tau = \frac{t}{k_{-1}} \quad K_1 = \frac{k_1}{k_{-1}}$$

Expand c_A and c_B on the fast time scale as

$$c_A = X_0 + \epsilon X_1 + \epsilon^2 X_2 + \dots \quad c_B = Y_0 + \epsilon Y_1 + \epsilon^2 Y_2 + \dots$$

Show the fast time-scale model for zero order is

$$\begin{aligned} \frac{dX_0}{d\tau} &= -K_1 X_0 + Y_0 & X_0(0) &= c_{A0} \\ \frac{dY_0}{d\tau} &= K_1 X_0 - Y_0 & Y_0(0) &= c_{B0} \end{aligned}$$

- (c) Solve these differential equations and show

$$\begin{aligned} X_0 &= c_{A0} e^{-(1+K_1)\tau} + (c_{A0} + c_{B0}) \frac{1}{1 + K_1} (1 - e^{-(1+K_1)\tau}) \\ Y_0 &= c_{B0} e^{-(1+K_1)\tau} + (c_{A0} + c_{B0}) \frac{K_1}{1 + K_1} (1 - e^{-(1+K_1)\tau}) \end{aligned}$$

(d) For the slow time scale, expand c_A and c_B as

$$c_A = A_0 + \epsilon A_1 + \epsilon^2 A_2 + \dots \quad c_B = B_0 + \epsilon B_1 + \epsilon^2 B_2 + \dots$$

Show the zero order terms give the single algebraic equation

$$0 = K_1 A_0 - B_0$$

and the first order terms give the two differential equations

$$\begin{aligned} \frac{dA_0}{dt} &= -K_1 A_0 + B_1 \\ \frac{dB_0}{dt} &= K_1 A_0 - B_1 - k_2 B_0 \end{aligned}$$

Use the matching conditions with the fast time scale solution to derive the initial conditions for the slow-time-scale differential equations and show

$$A_0(0) = (c_{A0} + c_{B0}) \frac{1}{1 + K_1} \quad B_0(0) = (c_{A0} + c_{B0}) \frac{K_1}{1 + K_1}$$

(e) We now wish to eliminate the first-order term B_1 appearing in the zero-order differential equations. Add the two zero-order differential equations to remove B_1 .¹ Use the algebraic equation and show the two zero-order differential equations can be rewritten as

$$\begin{aligned} \frac{dA_0}{dt} &= -\frac{k_2 K_1}{1 + K_1} A_0 \\ \frac{dB_0}{dt} &= -\frac{k_2 K_1}{1 + K_1} B_0 \end{aligned}$$

(f) Solve these differential equations and show the zero-order outer solution is

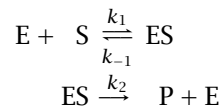
$$\begin{aligned} c_{A0} &= (c_{A0} + c_{B0}) \frac{1}{1 + K_1} e^{-\frac{k_2 K_1}{1 + K_1} t} \\ c_{B0} &= (c_{A0} + c_{B0}) \frac{K_1}{1 + K_1} e^{-\frac{k_2 K_1}{1 + K_1} t} \end{aligned}$$

Compare this solution to the reaction equilibrium solution of the first part. What conclusions do you draw from this comparison?

¹Notice that this addition of the two equations to remove the unknown B_1 is analogous to the step that eliminated r_2 and led to Equation 5.45 in the discussion in Chapter 5.

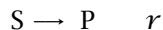
Exercise 5.24: Michaelis-Menten kinetics as QSSA

Consider the enzyme kinetics



in which the free enzyme E binds with substrate S to form bound substrate ES in the first reaction, and the bound substrate is converted to product P and releases free enzyme in the second reaction. This mechanism has become known as Michaelis-Menten kinetics [6], but it was proposed earlier by Henri [4]. If the rates of these two reactions are such that either the free or bound enzyme is present in small concentration, the mechanism is a candidate for model reduction with the QSSA.

Assume $k_1 \gg k_{-1}, k_2$ so E is present in small concentration. Apply the QSSA and show that the slow-time-scale model reduces to a first-order, irreversible decomposition of S to P



- (a) For a well-stirred batch reactor, show the total enzyme concentration satisfies

$$c_E(t) + c_{ES}(t) = c_E(0) + c_{ES}(0)$$

- (b) Find an expression for the QSS concentration of E. What is the corresponding concentration of ES?

- (c) Show the rate expression for the reduced model's single reaction is

$$r = \frac{k c_S}{1 + K c_S} \quad k = k_2 K E_0 \quad K = \frac{k_1}{k_{-1} + k_2} \quad E_0 = c_E(0) + c_{ES}(0) \quad (5.171)$$

which depends solely on the substrate concentration. The inverse of the constant K is known as the Michaelis constant. The production rates of reactant S and product P in the reduced model are then simply

$$R_S = -r \quad R_P = r$$

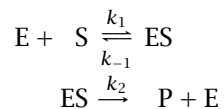
Notice we have reduced the number of reactions from two to one; we have reduced the number of rate constants from three (k_1, k_{-1}, k_2) to two (k, K).

- (d) Plot the concentrations versus time for the full model and QSSA model for the following values of the rate constants and initial conditions.

$$\begin{array}{l} k_1 = 5 \quad k_{-1} = 1 \quad k_2 = 10 \\ c_E(0) = 1 \quad c_{ES}(0) = 0 \quad c_S(0) = 50 \quad c_P(0) = 0 \end{array}$$

Exercise 5.25: Michaelis-Menten kinetics as reaction equilibrium

Consider again the enzyme kinetics given in Exercise 5.24.



Now assume the rate constants satisfy $k_1, k_{-1} \gg k_2$ so that the first reaction is at equilibrium on the time scale of the second reaction.

- (a) Find the equilibrium concentrations of E and ES
 (b) Show the production rate of P is given by

$$R_P = \frac{\tilde{k}c_S}{1 + K_1c_S} \quad \tilde{k} = k_2K_1E_0 \quad K_1 = k_1/k_{-1} \quad (5.172)$$

in which K_1 is the equilibrium constant for the first reaction. Notice this form is identical to the production rate of P given in the QSSA approach. For this reason, these two assumptions for reducing enzyme kinetics are often mistakenly labeled as the same approach. This second reaction equilibrium approach is sometimes considered a special case of the QSSA [3, p.97]. That viewpoint is erroneous because neither E nor ES need to be in low concentration when assuming reaction equilibrium, but do need to be in low concentration when assuming QSS.

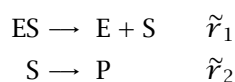
It is interesting to note that in their original work in 1913, Michaelis and Menten proposed the reaction equilibrium approximation to describe enzyme kinetics, in which the second step is slow compared to the first step [6]. Michaelis and Menten credit Henri with proposing this mechanism to explain the experimental observations that (i) production rate of P increases linearly with substrate at low substrate concentration and (ii) production rate of P is independent of substrate concentration at high substrate concentration [4].

The QSSA analysis of enzyme kinetics was introduced by Briggs and Haldane in 1925, in which the enzyme concentration is assumed small compared to the substrate [1]. Since that time, the QSSA approach has become the more popular explanation of the observed dependence of substrate in the production rate of product R_P in Equation 5.171 and Equation 5.172 [8].

Boyde provides a fascinating and detailed historical account of the contributions of Henri, Michaelis and Menten, and Briggs and Haldane, and includes English translations of Henri's 1901 paper in French[5] and Michaelis and Menten's 1913 paper in German [7]. Boyde concludes that Henri's pioneering contribution has been largely overlooked in favor of Michaelis and Menten, despite Michaelis and Menten's own explicit attribution to Henri.

The reader should be aware that either approximation may be appropriate depending on the values of the rate constants and initial conditions. Although both reduced models give the same form for the production rate of P, they are often quite different in other respects. Finally, for some values of rate constants, in particular $k_{-1} \gg k_1 \gg k_2$, both the QSS assumption and the reaction equilibrium assumption apply.

- (c) Show that the slow-time-scale reduced model for the reaction equilibrium assumption can be summarized by two irreversible reactions



with the following rate expressions

$$\begin{aligned} \tilde{r}_1 &= \left(\frac{K_1 c_E}{1 + K_1(c_E + c_S)} \right) \left(\frac{\tilde{k} c_S}{1 + K_1 c_S} \right) & \tilde{k} &= k_2 K_1 E_0 \\ \tilde{r}_2 &= \frac{\tilde{k} c_S}{1 + K_1 c_S} & K_1 &= k_1 / k_{-1} \end{aligned}$$

Notice here we have not reduced the number of reactions; we still have two reactions, but as before we have reduced the number of rate constants from three (k_1, k_{-1}, k_2) to two (\tilde{k}, K_1). The first rate expression here depends on c_S and c_E rather than only c_S as in the previous QSSA reduction. Therefore the production rates of E, ES and S depend on c_E as well as c_S . Only the production rate of P ($R_P = \tilde{r}_2$) loses the c_E dependence.

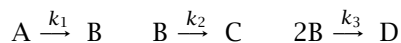
- (d) Plot the concentrations versus time for the full model and reaction equilibrium model for the following values of the rate constants and initial conditions.

$$\begin{aligned} k_1 &= 0.5 & k_{-1} &= 1 & k_2 &= 0.5 \\ c_E(0) &= 20 & c_{ES}(0) &= 10 & c_S(0) &= 50 & c_P(0) &= 0 \end{aligned}$$

Recall that you must modify the initial conditions for the slow-time-scale model by equilibrating the first reaction from these starting values.

Exercise 5.26: Highly reactive intermediates

Consider the following three elementary reactions

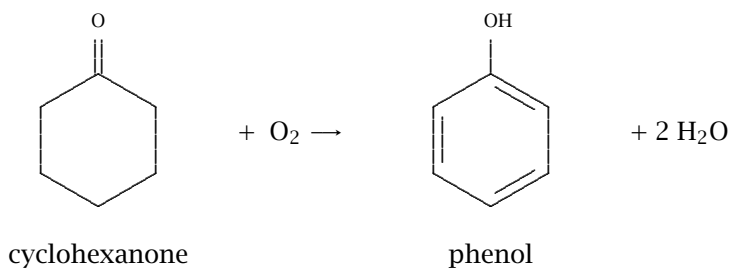


taking place in a well-mixed batch reactor of constant volume.

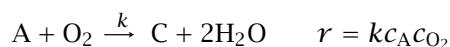
- Write the material balances for all four species: A, B, C, and D.
- Assume species B is a highly reactive intermediate species. Write down the algebraic equation that applies in this situation.
- Solve this equation for intermediate B's concentration in terms of concentrations of reactants and products A, C, and D.
- Remove the concentration of B from the material balances of reactants and products and write the reduced model for the time evolution of the concentrations of A, C and D.
- For what ranges of rate constants k_1 , k_2 , k_3 do you expect this reduced model to agree closely with the full model?

Exercise 5.27: Catalytic reaction mechanism

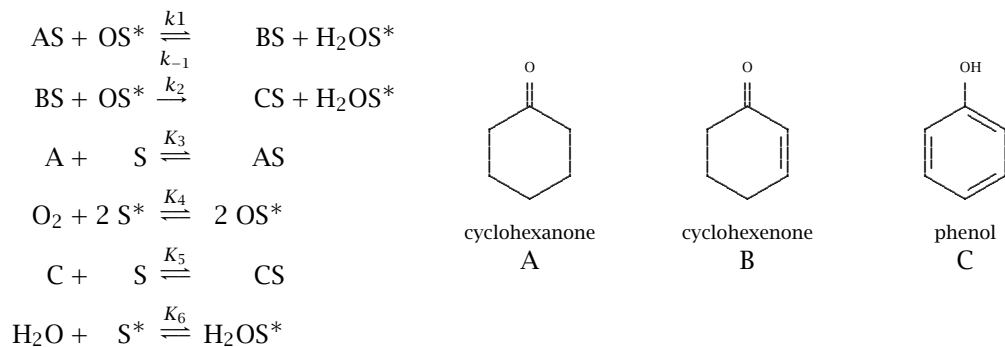
You have been continuing studies on the following reaction and have noticed limitations in the previously given rate expression



or



Your chemist colleague does some experiments and comes up with the following mechanism consisting of six reactions involving two different types of catalyst sites S and S*



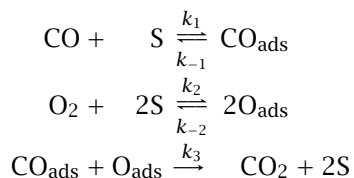
We make the following assumptions

1. Reaction 2 is irreversible.
2. All adsorption/desorption reactions are in equilibrium.
3. Species BS is an intermediate and the QSSA can be used.
4. A, B, and C adsorb on surface sites S due to their large molecular sizes.
5. O₂ and H₂O adsorb on surface sites S* due to their small molecular sizes.

You have a measurement device that is calibrated to detect the total concentration of phenyl groups in the system, both in the gas phase and on the surface. What is the production rate of phenyl groups in the above mechanism in terms of gas-phase concentrations c_A , c_C , c_{O_2} , c_{H_2O} , rate/equilibrium constants k_i , k_{-i} , K_i , and total metal sites c_m (for S) and c_{m^*} (for S*)? No surface species concentration should appear in your final rate expression.

Exercise 5.28: Reduced model for catalytic CO conversion

Consider again the following mechanism for the oxidation of CO on a Pd catalyst



- (a) Express the full kinetic model for these reactions taking place in a well-mixed batch reactor. Write balances for all six species: CO, O₂, CO₂, CO_{ads}, O_{ads}, and S, the vacant surface sites. Solve the full model using the initial condition of an equimolar concentration of CO and O in the gas phase and a bare catalyst surface. Use the following parameter values (expressed in some consistent set of units)

$$\begin{aligned} c_{\text{CO}}(0) = 1, \quad c_{\text{O}}(0) = 1, \quad \bar{c}_{\text{CO}} = \bar{c}_{\text{O}} = 0, \quad \bar{c}_v = \bar{c}_m \\ \bar{c}_m = 1, \quad k_1 = k_2 = 0.01, \quad k_{-1} = k_{-2} = 0.05, \quad k_3 = 1 \end{aligned}$$

Solve the resulting ODE model with Octave or MATLAB. Plot all species concentrations versus time.

- (b) Next increase the rate constants of the first two reactions by two orders of magnitude

$$k_1 = k_2 = 1, \quad k_{-1} = k_{-2} = 5, \quad k_3 = 1$$

and solve the model again. Does the solution indicate that it is reasonable to assume that the first two reactions are always at equilibrium?

- (c) Derive the reduced model that eliminates the first two fast reactions' rate constants and replaces them with the ratios

$$K_1 = k_1/k_{-1}, \quad K_2 = k_2/k_{-2}$$

Note that your reduced model will be a mixture of differential equations and algebraic equations. Use an *implicit* ODE solver to solve this model. See the computational appendix for a discussion of implicit ODE solvers available in Octave or MATLAB.

Hint: note that before solving the reduced model, you need to adjust the initial conditions by equilibrating the two fast reactions. This step requires that you adjust the given vector of initial concentrations to a set of equilibrium concentrations, and use these equilibrated concentrations as the *initial* conditions for the reduced model. We have that

$$\mathbf{c}_{\text{eq}} = \mathbf{c}(0) + \mathbf{v}^T \boldsymbol{\varepsilon}$$

We are keeping the slow third reaction extent ε_3 fixed at zero, so we have two unknowns, $\varepsilon_1, \varepsilon_2$. We have two constraints, the equilibrium conditions for the fast reactions,

$$\bar{c}_{\text{CO}} - K_1 c_{\text{CO}} \bar{c}_{\text{v}} = 0, \quad \bar{c}_{\text{O}} - K_2 c_{\text{O}} \bar{c}_{\text{v}}^2 = 0$$

Solve the reduced model using \mathbf{c}_{eq} as the initial condition. Does your reduced model agree with the full model? Explain why or why not.

Exercise 5.29: Reduced model for catalytic CO conversion in a CSTR

Revisit Exercise 5.28, but this time let the reactions takes place in a constant volume CSTR. Assume the reactor is initially charged with inert N_2 and a bare catalyst surface, the feed is equimolar concentrations of CO and O_2 , $c_{\text{CO}f} = c_{\text{O}_2f} = 1$, the residence time of the CSTR is $\tau = 10$. Assume that the inert N_2 feed concentration is large enough that we may assume $Q = Q_f$ without significant error (even though moles are not conserved in these reactions).

Repeat the steps of Exercise 5.28.

6

The Energy Balance for Chemical Reactors

Exercise 6.24: Mass and energy balances with multiple phases¹

Consider the process depicted in Figure 6.43 in which the reactor contents and the streams entering and leaving the reactor consist of multiple, well-mixed phases. Without loss of generality, we shall consider two phases: α and β . Consider the state of the reactor to be described by the following set of $2(n_s + 2)$ intensive variables and 2 extensive variables

$$T^\alpha, P^\alpha, m^\alpha, c_j^\alpha \quad j = 1, \dots, n_s$$

$$T^\beta, P^\beta, m^\beta, c_j^\beta \quad j = 1, \dots, n_s$$

in which m^α, m^β are the masses of the α and β phases, respectively.

Let us assume the phases equilibrate with each other even though the reactor is not assumed to be at complete chemical equilibrium. As discussed in Chapter 3, the conditions of phase equilibrium, Equations 3.50, imply that both phases are at the same temperature, T , and both phases are at the same pressure, P , which allows us

¹JBR would like to thank Vasilios Manousiouthakis of UCLA for helpful discussion of this and the next two exercises.

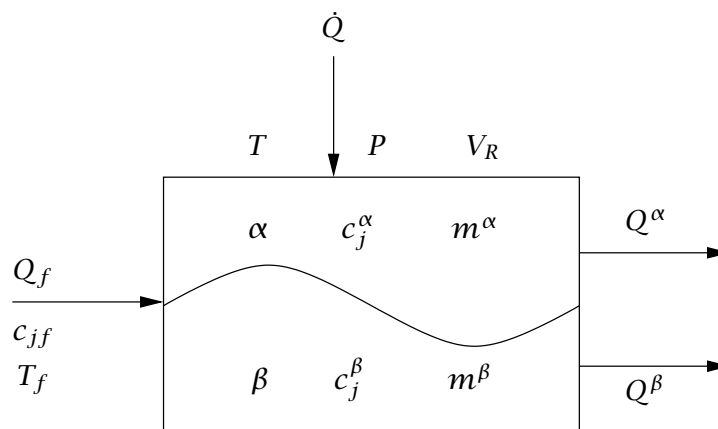


Figure 6.43: Reactor containing two well-mixed phases of matter.

to describe the state of the reactor with $2n_s + 2$ intensive variables and 2 extensive variables

$$T, P, m^\alpha, m^\beta, c_j^\alpha, c_j^\beta \quad j = 1, \dots, n_s$$

Since the process in Figure 6.43 is an open system, we also have the two effluent flowrates and the rate of heat transfer to the system

$$Q^\alpha, Q^\beta, \dot{Q}$$

that need to be determined, bringing the total number of unknown variables to $2n_s + 7$. We assume we have specified the feed conditions, Q_f, c_{jf}, T_f . Let us also assume that the the system pressure and volume are known constants and the rate of heat transferred to the system is specified. So we have specified two of our unknown variables

$$P, \dot{Q}$$

which brings us back to $2n_s + 5$ unknowns, and we have one constraint on the total system volume.

- (a) Is the process now fully specified? If so, write the $2n_s + 5$ equations that fully determine the system.
- (b) Let's apply this result to a simple system consisting of a single species that does not undergo chemical reaction. An example would be a boiler fed with a pure water stream in which liquid water and steam are the two different phase effluent streams. For this case, we have $2n_s + 5 = 7$ unknowns.

Can you write seven independent equations to specify this system? If so, write the equations that specify the boiler system.

If not, provide a physical argument for the boiler that shows the system is underdetermined. If underdetermined, what natural additional constraint(s) would you apply in order to fully specify the boiler system?

Exercise 6.25: Writing DAE models for systems with multiple phases

- (a) Describe the system of Exercise 6.24 with a set of DAEs of the form

$$\begin{aligned} \frac{d\mathbf{x}}{dt} &= \mathbf{f}(\mathbf{x}, \mathbf{y}) \\ \mathbf{0} &= \mathbf{g}(\mathbf{x}, \mathbf{y}) \end{aligned}$$

in which \mathbf{x} are the differential states and \mathbf{y} are the algebraic states. Be sure that \mathbf{f} and \mathbf{g} are functions of only \mathbf{x} , \mathbf{y} , and other, known variables. Assume you have access to complete thermochemical data, which means you can evaluate any intensive thermodynamic variable of a phase given the set T, P, c_j of that phase.

(b) Identify the variables that comprise \mathbf{x} and \mathbf{y} .

Notice that neither the heat of reaction nor the heat of phase change are required in the energy balance when one has complete thermochemical data available. These two enthalpy changes are only useful for simplifying the required thermochemical data. When full thermochemical data are available on the other hand, using heats of reaction and phase change merely complicates the energy balance, and their use should therefore be avoided. Experience indicates that always using heat of reaction and heat of phase change can be a difficult habit for chemical engineers to break. It seems new training on how to express energy balances would be useful given the current wide availability of computer-based thermochemical databases.

Exercise 6.26: Using thermochemical databases that contain reference states

Many thermochemical databases provide energies relative to some internal reference state. Say a given database has defined a particular reference pressure, temperature, composition and phase of matter, which determines all intensive thermochemical properties. Denote the specific internal energy and enthalpy of the reference state by

$$\hat{U}_{\text{ref}} \quad \hat{H}_{\text{ref}}$$

which are related by

$$\hat{U}_{\text{ref}} = \hat{H}_{\text{ref}} + \frac{P_{\text{ref}}}{\rho_{\text{ref}}}$$

Consider these common material and energy balances for a two-phase system

$$\begin{aligned} \frac{dn_j}{dt} &= Q_f c_{jf} - Q^\alpha c_j^\alpha - Q^\beta c_j^\beta + \sum_i v_{ij} (r_i^\alpha + r_i^\beta) \quad j = 1, \dots, n_s \\ \frac{dU}{dt} + P \frac{dV_R}{dt} &= Q_f \rho_f \hat{H}_f - Q^\alpha \rho^\alpha \hat{H}^\alpha - Q^\beta \rho^\beta \hat{H}^\beta + \dot{Q} \end{aligned}$$

Now define the following shifted internal energies and enthalpies

$$\tilde{U}^\alpha = \hat{U}^\alpha - \hat{U}_{\text{ref}} \quad \tilde{U}^\beta = \hat{U}^\beta - \hat{U}_{\text{ref}} \quad \tilde{H}^\alpha = \hat{H}^\alpha - \hat{H}_{\text{ref}} \quad \tilde{H}^\beta = \hat{H}^\beta - \hat{H}_{\text{ref}}$$

Calling the thermochemical database functions returns these shifted quantities. Define the shifted total internal energy by

$$\begin{aligned} \tilde{U} &= m^\alpha (\hat{U}^\alpha - \hat{U}_{\text{ref}}) + m^\beta (\hat{U}^\beta - \hat{U}_{\text{ref}}) \\ &= m^\alpha \hat{U}^\alpha + m^\beta \hat{U}^\beta - (m^\alpha + m^\beta) \hat{U}_{\text{ref}} \\ \tilde{U} &= U - m \hat{U}_{\text{ref}} \end{aligned}$$

in which $m = m^\alpha + m^\beta$ is the total mass of the system.

- (a) We would like to use a new energy balance expressed in terms of these shifted variables. Is the following shifted energy balance correct?

$$\frac{d\tilde{U}}{dt} + P \frac{dV_R}{dt} = Q_f \rho_f \tilde{H}_f - Q^\alpha \rho^\alpha \tilde{H}^\alpha - Q^\beta \rho^\beta \tilde{H}^\beta + \dot{Q} \quad (6.95)$$

If so, provide a derivation. If not, derive a correct form.

- (b) Consider a second approach in which the same reference energy, \hat{E}_{ref} is subtracted from all energies (both the internal energy and enthalpy)

$$\begin{aligned} \tilde{U}^\alpha &= \hat{U}^\alpha - \hat{E}_{\text{ref}} & \tilde{U}^\beta &= \hat{U}^\beta - \hat{E}_{\text{ref}} & \tilde{H}^\alpha &= \hat{H}^\alpha - \hat{E}_{\text{ref}} & \tilde{H}^\beta &= \hat{H}^\beta - \hat{E}_{\text{ref}} \\ \tilde{U} &= U - m\hat{E}_{\text{ref}} \end{aligned}$$

Is the shifted energy balance, Equation 6.95, correct with these defined quantities? If so, provide a derivation. If not, derive a correct form.

Exercise 6.27: Equal time for internal energy

In deriving the energy balances in Chapter 6, we often found enthalpy rather than internal energy to be the more convenient energy function. For situations in which internal energy is more convenient, provide derivations for the following useful relations

- (a)

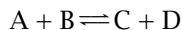
$$\left(\frac{\partial U}{\partial P}\right)_{T, n_j} = -\alpha TV + PV\kappa_T$$

- (b)

$$\left(\frac{\partial U}{\partial n_j}\right)_{T, V, n_{k \neq j}} = \bar{H}_j - \frac{\alpha}{\kappa_T} T \bar{V}_j$$

Exercise 6.28: Nonisothermal plug-flow reactor

The reaction



is carried out adiabatically in a series of tubular reactors with interstage cooling as shown in Figure 6.44. The feed is equimolar in A and B and enters each reactor at 27°C. The heat removed between the reactors is -87.5 kcal/min.

- What is the outlet temperature of the first reactor?
- What is the conversion of A at the outlet of the first reactor?
- Is the first reactor close to equilibrium at the exit?

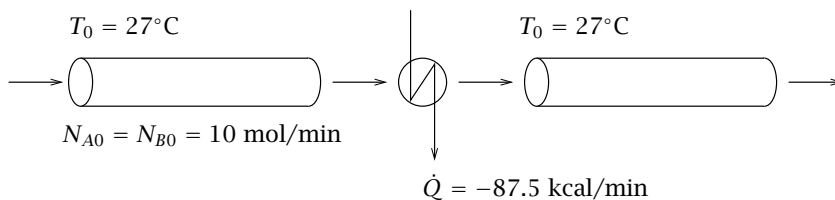


Figure 6.44: Tubular Reactors with Interstage Cooling.

State any assumptions that you make while solving the problem.

Data:

ΔH_R	-30 kcal/mol
C_p	25 cal/mol·K
K at 50°C	5.0×10^5
N_{A0}, N_{B0}	10 mol/min
\dot{Q}	-87.5 kcal/min
R	1.987 cal/mol·K

Exercise 6.29: A colleague's batch reactor energy balance

A colleague presents you with the following derivation of the energy balance for a constant-volume batch reactor.

You know, the people writing our textbooks sure make things complicated. I found a much simpler energy balance for the constant-volume batch reactor. Here's how it goes. Because you cannot do work on a closed system at constant volume, the total energy balance is simply

$$\frac{dU}{dt} = \dot{Q} \quad (6.96)$$

For a single-phase system, internal energy $U(T, V, n_j)$ changes due to changes in T , V and n_j by

$$dU = \left(\frac{\partial U}{\partial T}\right)_{V, n_j} dT + \left(\frac{\partial U}{\partial V}\right)_{T, n_j} dV + \sum_j \left(\frac{\partial U}{\partial n_j}\right)_{T, V, n_{k \neq j}} dn_j \quad (6.97)$$

The definitions of constant volume heat capacity and partial molar internal energy are

$$C_V = \left(\frac{\partial U}{\partial T}\right)_{V, n_j} \quad (6.98)$$

$$\bar{U}_j = \left(\frac{\partial U}{\partial n_j}\right)_{T, V, n_{k \neq j}} \quad (6.99)$$

Since the reactor volume is constant, $dV = 0$, and forming the time derivative of the internal energy from Equation 6.97 reduces to

$$\frac{dU}{dt} = C_V \frac{dT}{dt} + \sum_j \bar{U}_j \frac{dn_j}{dt} \quad (6.100)$$

From the definition of enthalpy ($H = U + PV$), we know that

$$\bar{H}_j = \bar{U}_j + P\bar{V}_j \quad (6.101)$$

in which \bar{H}_j is the partial molar enthalpy and \bar{V}_j is the partial molar volume. The material balance for the batch reactor is

$$\frac{dn_j}{dt} = R_j V_R = \sum_i \nu_{ij} r_i V_R, \quad j = 1, \dots, n_s \quad (6.102)$$

in which r_i is the reaction rate per reactor volume and ν_{ij} is the stoichiometric coefficient for species j in reaction i . We can define the change in enthalpy and change in volume for reaction i by

$$\Delta H_{Ri} = \sum_{j=1}^{n_s} \nu_{ij} \bar{H}_j \quad \Delta V_{Ri} = \sum_{j=1}^{n_s} \nu_{ij} \bar{V}_j \quad (6.103)$$

I put the material balance and these definitions in Equation 6.100 and I obtain

$$\boxed{C_V \frac{dT}{dt} = - \sum_i (\Delta H_{Ri} - P \Delta V_{Ri}) r_i V_R + \dot{Q}} \quad (6.104)$$

Notice that my result doesn't agree with Equation 6.66 in our text!

$$\boxed{C_V \frac{dT}{dt} = - \sum_i (\Delta H_{Ri} - \frac{\alpha}{\kappa_T} T \Delta V_{Ri}) r_i V_R + \dot{Q}}$$

What's going on here?

Answer the following questions yes or no and provide a short justification.

- Is Equation 6.96 correct for the constant-volume batch reactor given the other assumptions?
- Is Equation 6.97 correct for this situation?
- Do Equations 6.98 and 6.99 agree with the usual definitions of constant-volume heat capacity and partial molar internal energy?
- Is Equation 6.100 a correct rearrangement of the previous equations?

- (e) Is Equation 6.101 valid also for partial molar properties?
- (f) Is Equation 6.102 a correct statement of the material balance for the batch reactor?
- (g) Does Equation 6.103 agree with the usual definitions of enthalpy change and volume change upon reaction?
- (h) Is Equation 6.104 a correct rearrangement of the previous equations?
- (i) Provide a short discussion of the apparent energy balance contradiction.
- If your answers to all questions above were yes, do you think the two energy balances are equivalent? If so, how would you show this equivalence?
- If your answers to some of the questions above were no, how would you repair your colleague's derivation?

Exercise 6.30: Dynamic plug-flow reactor energy balance

Start with the plug-flow energy balance of Section 6.5, rewritten here,

$$\frac{\partial}{\partial t}(\rho \hat{U}) = -\frac{\partial}{\partial V}(Q\rho \hat{H}) + \dot{q}$$

- (a) Derive the dynamic energy balance in the variables T, P, c_j for a single-phase system.²
- (b) Does your dynamic energy balance reduce at steady state to Equation 6.50? Discuss why or why not.

Exercise 6.31: Solving the autothermal plug-flow reactor with collocation

Revisit the ammonia synthesis in an autothermal plug-flow reactor described in Example 6.6.

- (a) Solve the resulting boundary-value problem for the parameters given in Table 6.6 with collocation and compare your three steady-state profiles to the results given in Figures 6.39 and 6.40. Be sure to note that the flowrate should be $Q_f = 0.05713 \text{ m}^3/\text{s}$ in Table 6.6, and that the the middle steady-state profile (B) in Figures 6.39 and 6.40 is shifted somewhat from the correct answer. See the errata posted on www.che.wisc.edu/~jbrow/chemreacfun for the correct profiles.

²The following is one form the answer can take.

$$(\rho \hat{C}_P - \alpha P) \frac{\partial T}{\partial t} + (P\kappa_T - \alpha T) \frac{\partial P}{\partial t} - \sum_j P \bar{V}_j \frac{\partial c_j}{\partial t} = -Q \left(\rho \hat{C}_P \frac{\partial T}{\partial V} + (1 - \alpha T) \frac{\partial P}{\partial V} \right) - \sum_i \Delta H_{Ri} r_i + \dot{q}$$

- (b) What initial guesses for the collocation equations did you use to converge to the three steady-state profiles?
- (c) Vary the number of collocation points and demonstrate convergence for the upper steady-state solution. How many collocation points are required for a reasonably accurate solution?
- (d) Describe the advantages and disadvantages of the shooting method versus collocation for solving this boundary-value problem.

Exercise 6.32: Finite-sized PFRs and interstage cooling

Reconsider Example 6.4. The reaction



takes place in two adiabatic PFRs with interstage cooling as depicted in Figure 6.33. In Example 6.4 the PFRs were assumed to be long and the reaction reached equilibrium at the exit of both reactors. We determined the heat duty to be

$$\dot{Q} = -200,000 \text{ BTU/hr}$$

to reach the conversion $x_A = 0.7$ at the exit of the second reactor.

Here we consider two finite-sized reactors, each with volume

$$V_t = 2.22 \text{ ft}^3$$

The forward rate constant and activation energy are given by

$$k_1 = 3.47 \text{ s}^{-1} \quad \text{at } T = T_f \quad E_a/R = 9000 \text{ }^\circ\text{R}$$

- (a) Solve for the N_A and T profiles in both reactors. Plot N_A and T versus reactor volume for both reactors. Compute the conversion at the exit of each reactor and compare to the answers given in Figure 6.34. You should see that the overall conversion has dropped to $x_{A2} = 0.653$ due to the finite-sized reactors.
- (b) Next let's see if we can achieve $x_{A2} = 0.7$ by changing the heat duty. Vary \dot{Q} between $-125,000$ and $-250,000$ BTU/hr, and make a plot of x_{A2} versus \dot{Q} over this range. Can you reach $x_{A2} = 0.7$ by changing the heat duty? If so, what value of \dot{Q} do you use? If not, why not?

Exercise 6.33: Maximum rate of heat release in series reaction

Consider the elementary reactions in series



starting with no B or C. It was shown previously that for an isothermal, constant volume batch reactor

$$c_A = c_{A0}e^{-k_1t} \quad c_B = c_{A0} \frac{k_1}{k_2 - k_1} (e^{-k_1t} - e^{-k_2t})$$

We wish to maintain an isothermal reactor, but the reactions are quite exothermic. To size the heat exchange equipment appropriately, we must know how much heat to remove over time, as this quantity varies considerably.

- Give an expression for \dot{Q} , the heat removed by the heat exchanger. You may use the parameters V_R , c_{A0} , ΔH_{R1} , ΔH_{R2} , k_1 , and k_2 .
- At what time is the maximum heat generated in the reactor? Do not assume numerical values for the parameters. Obtain the general result.
- Consider next the following parameter values.

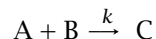
$$V_R = 1000 \text{ L} \quad c_{A0} = 3 \text{ mol/L} \\ \Delta H_{R1} = 150 \text{ kcal/mol} \quad \Delta H_{R2} = 100 \text{ kcal/mol} \quad k_1 = 1 \text{ min}^{-1} \quad k_2 = 2 \text{ min}^{-1}$$

How much heat should the heat exchanger be able to remove? When does the maximum occur? If you were not able to answer part (b) analytically, estimate the maximum heat removal rate and time of the maximum for the parameter values given.

- After the reaction has gone for 3 min, how many moles of A have reacted? Moles of B? How much total energy has the heat exchanger removed?

Exercise 6.34: Managing the heat in a CSTR

The exothermic liquid-phase reaction



takes place in a CSTR equipped with a heat exchanger. The feed consists of A and B dissolved in an inert solvent. An inhibitor is stripped from the feed just before addition to the reactor.

- You plan to start up the CSTR with a solvent filled reactor at the feed temperature. Simulate the reactor behavior ($c_A(t)$, $c_B(t)$, $T(t)$) for six hours after start up.

- (b) Simulate the reactor again for the following situation. After running for one hour, the coolant pump fails for 2 1/2 hours (the reactor runs adiabatically), and then the pump is restored. Simulate the response of the reactor for the six-hour start up period. Does the system return to the steady state observed in part (a)? Explain why or why not.
- (c) Calculate the adiabatic temperature rise for the feed. Start the reactor filled with solvent with initial temperature equal to the feed temperature plus the adiabatic temperature rise of the feed. Simulate for six hours. Compare the steady state achieved with the results in (a) and (b).

The reaction parameters are listed in the following table in which $k(T) = k_m e^{-E(1/T-1/T_m)}$ and $\alpha = (U^\circ A)/(\rho \hat{C}_p V_R)$.

Parameter	Value	Units
k_m	5×10^{-4}	min^{-1}
T_m	298	K
E	8000	K
ΔH_R	-3×10^5	kJ/kmol
ρ	1000	kg/m^3
\hat{C}_p	4.0	$\text{kJ/kg} \cdot \text{K}$
α	0.015	min^{-1}
T_a	298	K
T_f	298	K
c_{Af}	3.0	kmol/m^3
c_{Bf}	2.0	kmol/m^3
τ	30	min

7

Fixed-Bed Catalytic Reactors

Exercise 7.22: Changing catalyst and temperature

The production rate of a heterogeneously catalyzed, first-order reaction in a 0.75-cm diameter spherical pellet is $R_{Ap} = -3.25 \times 10^{-5} \text{ mol/cm}^3 \cdot \text{s}$ when the catalyst is exposed to pure, gaseous A at a pressure of 1 atm and a temperature of 525 K. This reaction's activation energy is $E_a = 18,600 \text{ cal/mol}$. Further, the effective diffusivity of A in the pellet is $D_A = 0.009 \text{ cm}^2/\text{s}$ at 525 K and that diffusion is in the regime of Knudsen flow. The bulk fluid and the external surface concentrations can be assumed the same. Find the production rate if the catalyst is changed to a cylindrical pellet that is 0.5 cm in diameter and 1.0 cm in length, and the temperature is increased to 600 K.

Exercise 7.23: Diffusion, external mass transfer, and reaction rates

The following second order liquid-phase catalytic reaction is conducted in an isothermal fixed-bed reactor:



The intrinsic rate constant is $16 \text{ L/mol} \cdot \text{s}$. The feed is 0.8 L/s of a solution of A with the concentration of A at 4 mol/L . Spherical catalyst pellets of radius 0.12 cm are used to pack the reactor. The catalyst has a pellet density of 0.88 g/cm^3 , and the reactor bed density is 0.5 g/cm^3 . The effective diffusivity of A inside the catalyst pellet is $3.14 \times 10^{-3} \text{ cm}^2/\text{s}$. You wish to achieve 99.9% conversion of A.

- First neglect both diffusional resistance and mass transfer resistance. What is the mass of catalyst required to achieve the desired conversion?
- Next consider diffusional resistance but neglect mass transfer resistance. What are the Thiele modulus and effectiveness factor at the entrance of the reactor? What are the Thiele modulus and effectiveness factor at the exit of the reactor?
Given these two effectiveness factors, compute an upper bound and a lower bound on the mass of catalyst required to achieve the desired conversion.
- Next consider both diffusional resistance and mass transfer resistance. Assume that we have estimated the mass transfer coefficient to be $k_m = 0.35 \text{ cm/s}$. Find

the effectiveness factor at the entrance of the reactor. Find the effectiveness factor at the exit of the reactor.

Given these two effectiveness factors, compute an upper bound and a lower bound on the mass of catalyst required to achieve the desired conversion.

- (d) Compare your answers to parts (a)–(c). Discuss whether diffusion and/or mass transfer limitations are important in this packed bed reactor.

8

Mixing in Chemical Reactors

Exercise 8.16: PFRs, CSTRs, and mixing

Consider the following irreversible, liquid-phase reaction with 1/2-order kinetics



Assume this reaction takes place in the the PFR in Figure 8.44, which is operating at steady state with residence time τ and feed A concentration c_{Af} . The total overall reaction rate is r_1 , which is the moles of A converted per time in the entire reactor volume, divided by the volume of the reactor. At time zero, we turn on a stirrer and perfectly mix the reactor contents. Immediately upon mixing the reactor achieves an overall reaction rate r_2 . Also consider the steady-state overall reaction rate achieved at long times by the mixed reactor, r_3 .

- Rank order the three overall reaction rates, r_1 , r_2 and r_3 . Justify your answer.
- Calculate the exact values of r_1 , r_2 , and r_3 for the following parameters: $k = 1 \text{ (mol/L)}^{1/2}\text{(1/hr)}$; $\tau = 1 \text{ hr}$; $c_{Af} = 1 \text{ mol/L}$.

Exercise 8.17: Dispersed PFR

You have been continuing studies on aromatization of cyclohexanone to phenol, when your chemistry colleague comes to you with a catalytic breakthrough. By using a ho-

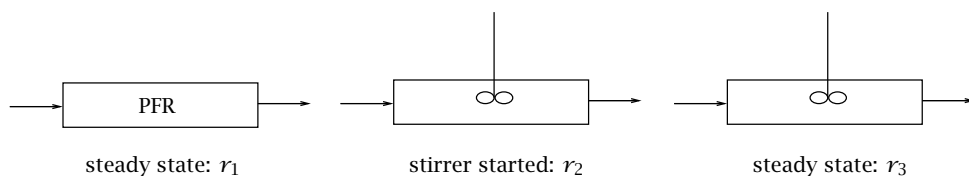
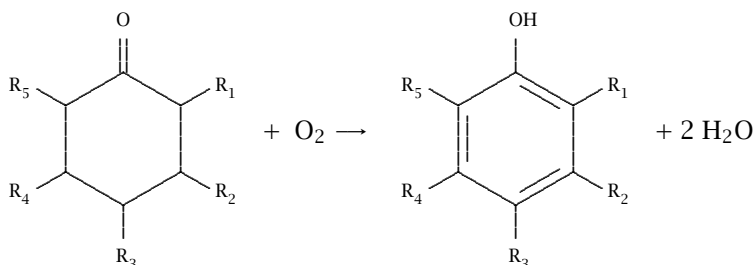


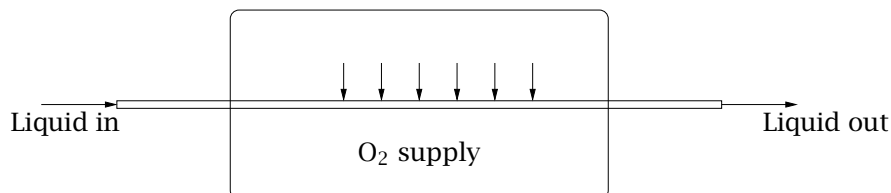
Figure 8.44: Reactor in three conditions: PRF at steady state, just after a perfect stirrer is started, and stirred reactor at steady state. The overall reaction rates are: r_1 , r_2 and r_3 , respectively.

homogeneous catalyst the reaction can now tolerate various substituents on the cyclohexanone ring



This new reaction has a downside though. The substituted cyclohexanones and phenols can no longer tolerate high temperatures and must remain in the liquid phase, but the O_2 is still in the gas phase. These new issues now need to be understood.

Assume the reaction rate is given by $r = kc_A$ when excess O_2 is present. To provide the required O_2 the reaction takes place in an isothermal, isobaric tubular membrane reactor inside a large cylinder with a continuous supply of O_2 as shown in the following schematic.



The following parameter values are known.

$$\begin{aligned}
 V_R &= 66 \text{ mL}, & Q_f &= 3 \text{ mL/min}, & c_{Af} &= 0.1 \text{ mol/L}, & c_A(V_R) &= 0.01 \text{ mol/L}, \\
 T &= 80 \text{ C}, & P &= 3 \text{ MPa}, & R &= 8.314 \text{ (MPa} \cdot \text{cm}^3\text{)/(mol} \cdot \text{K)}
 \end{aligned}$$

- (a) **Ideal PFR.** What is the residence time for this reactor? Solve the steady-state PFR material balance. Given the steady-state outlet concentration of A is $c_A(V_R) = 0.01 \text{ mol/L}$, what is the value of the rate constant k ?
- (b) **Nonideal flow.** To perform an RTD step test on the reactor, two inert solvents are used, toluene and cyclohexane. The reactor (PFR) begins with toluene flowing through at steady state. At time $t = 0$ a valve is turned introducing the cyclohexane flow and cutting off the toluene flow. The measured RTD is shown in Figures 8.45 and 8.46.

What is the mean residence time for the reactor?

- (c) **Dispersion number.** From Figure 8.47, which is similar to Figure 8.10 in the text, and the experimental data shown in Figures 8.45 and 8.46, estimate the dimensionless dispersion number, D , describing this reactor.
- (d) **Dispersed PFR model.** What differential equations would you use to model the dispersed PFR? Include all required boundary conditions. Make sure that all parameters appearing in your model are known.
- How would you solve this model? Describe what you would do; you do not need to actually solve it. Do you need any additional information to solve the problem? If so, what?
- (e) **Engineering intuition.** Would you expect the outlet A concentration to be higher, lower, or the same as the ideal PFR case? Assume both cases have the same mean residence times, flow rates, rate constants, temperatures, pressures, etc. and base your argument on only the nonideal flow and dispersion. Justify your answer.

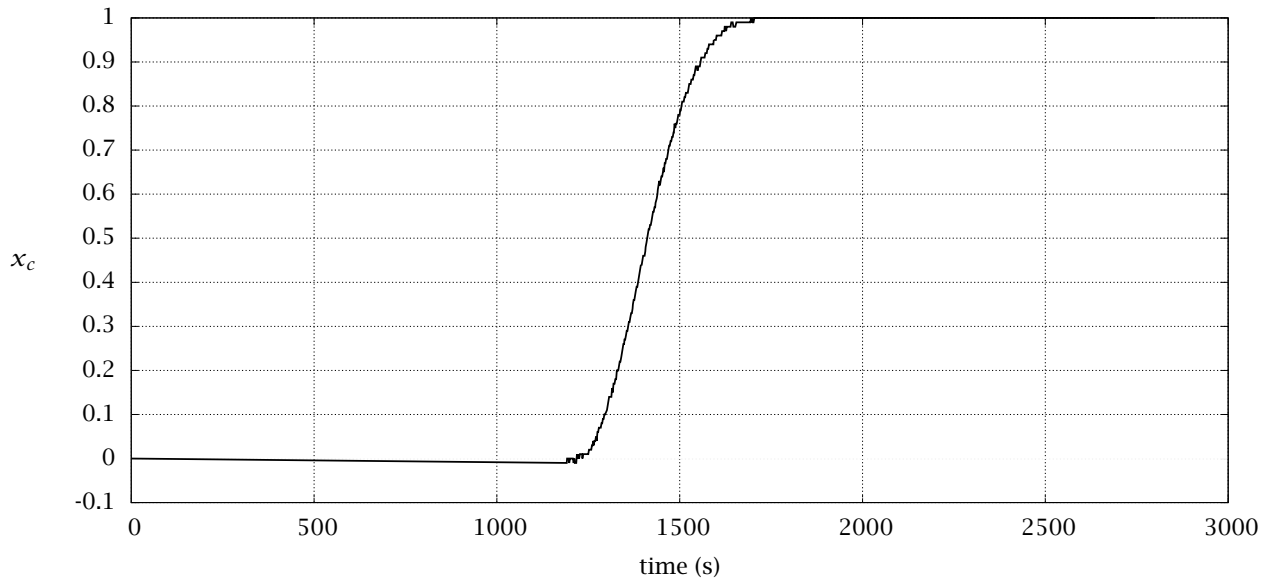


Figure 8.45: Mole fraction of cyclohexane in the effluent versus time after step change at $t = 0$.

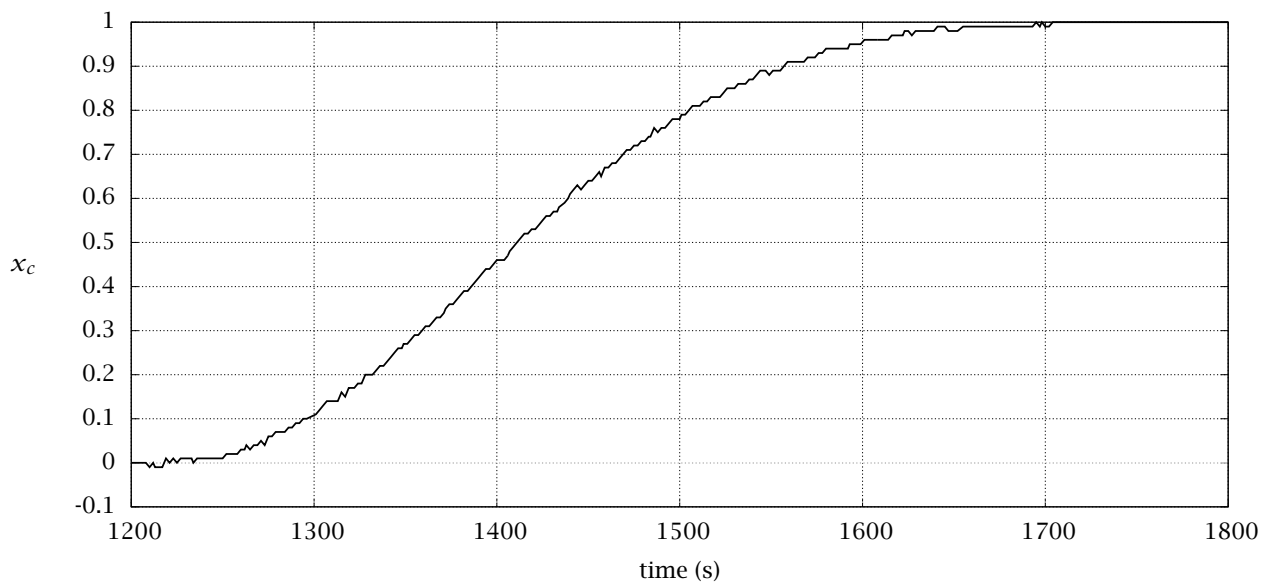


Figure 8.46: Mole fraction of cyclohexane in the effluent versus time after step change at $t = 0$; expanded time scale.

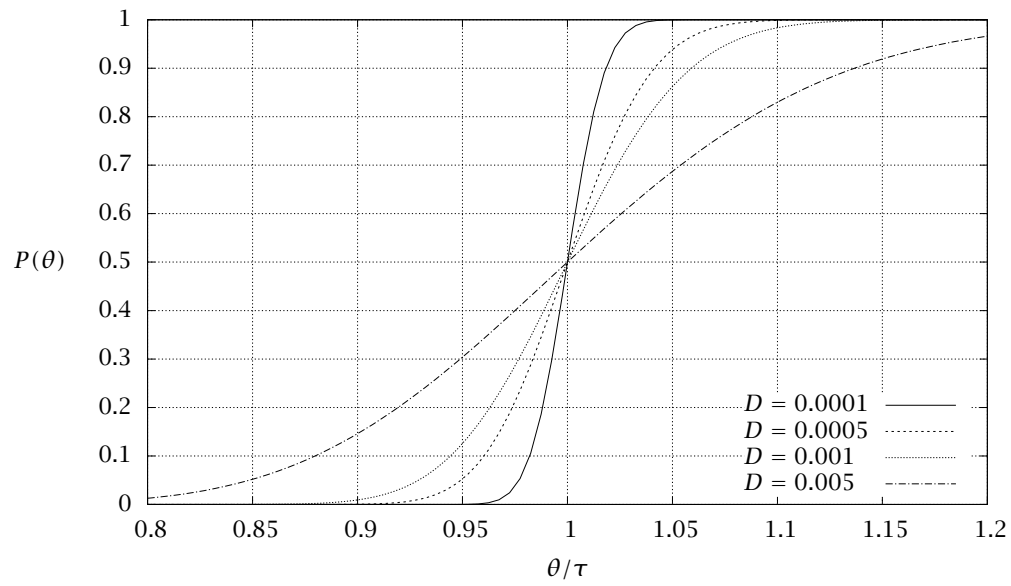


Figure 8.47: $P(\theta)$ versus θ/τ for dispersed plug flow with different dispersion number D .

9

Parameter Estimation for Reactor Models

Exercise 9.16: Least squares estimation and estimating measurement variance from data

Consider the following reaction mechanism



with reaction rates and production rates given by

$$r = \begin{bmatrix} r_1 \\ r_2 \end{bmatrix} \quad R = \begin{bmatrix} R_{\text{H}} \\ R_{\text{H}_2} \\ R_{\text{OH}} \\ R_{\text{H}_2\text{O}} \\ R_{\text{CO}} \\ R_{\text{CO}_2} \end{bmatrix}$$

We have replicate measurements of the six species production rates. We wish to estimate the two reaction rates. Twenty replicate measurements are given on the class website in the Exams folder. I also list the actual variance of the measurement error, Q_{ac} . Download the file `confestvar_measurements.dat` and load these into Octave using the load command; you should obtain two matrices, Q_{ac} and R_{meas} . Perform the following analysis.

- (a) Assume we do not know Q_{ac} (the usual case) so we assume the measurement error variance is an identity matrix, $Q = I$. Find the least-squares estimate of r for each of the 20 measurements. Calculate the mean over the 20 estimates. Plot all 20 estimates, and the 95% confidence interval with center located at the mean estimate.

Notice you should use Q_{ac} to compute the confidence interval, not $Q = I$. We want to analyze how the estimates are actually distributed, not how they would be distributed if $Q = I$. Ask me if this point is not clear.

- (b) Next calculate the covariance matrix for the twenty measurement samples. Call this matrix Q_{est} . Print out this matrix.

- (c) Next using $Q = Q_{\text{est}}$, reestimate the values of r using weighted least squares. Plot all twenty estimates and the 95% confidence intervals with center located at the mean estimate. How different are the mean estimates using $Q = I$ and $Q = Q_{\text{est}}$?
- (d) Finally, using zero as the center, plot the 95% confidence intervals for estimates using $Q = I$, $Q = Q_{\text{est}}$, and $Q = Q_{\text{ac}}$. How do these ellipses compare in size? Do you obtain tighter confidence interval (smaller variance) when you use Q_{est} instead of I in the least-squares estimate? How does the confidence interval using Q_{est} compare to the one using Q_{ac} ? Why?

Bibliography

- [1] G. E. Briggs and J. B. S. Haldane. A note on the kinetics of enzyme action. *Biochem. J.*, 19:338-339, 1925.
- [2] U. Gennari, R. Kramer, and H. Gruber. Hydrogenolysis of methyltetrahydrofurane on platinum. *Applied Catalysis*, 11:341-351, 1984.
- [3] G. G. Hammes. *Thermodynamics and Kinetics for the Biological Sciences*. Wiley-Interscience, New York, 2000.
- [4] M. V. Henri. Théorie générale de l'action de quelques diastases. *Comptes Rendu*, 135:916-919, 1901.
- [5] M. V. Henri. General theory of the action of certain enzymes. In T. R. C. Boyde, editor, *Foundation Stones of Biochemistry*. Voile et Aviron, Hong Kong, 1980. English translation.
- [6] L. Michaelis and M. L. Menten. Die Kinetik der Invertinwirkung. *Biochem. Z.*, 49:333-369, 1913.
- [7] L. Michaelis and M. L. Menten. The kinetics of invertin action. In T. R. C. Boyde, editor, *Foundation Stones of Biochemistry*. Voile et Aviron, Hong Kong, 1980. English translation.
- [8] D. L. Nelson and M. M. Cox. *Lehninger Principles of Biochemistry*. Worth Publishers, New York, third edition, 2000.