

Chemical Reactor Analysis and Design Fundamentals

Errata for First Printing

November 18, 2017

- cover, change sign on \dot{W}_s term and add \dot{W}_b term to energy balance at bottom of cover.
- cover, remove minus sign in front of \mathcal{D}_j .
- p. 43, three lines above first equation, change "Equation 2.27" to "Reaction 2.26." Thanks to Manos Mavrikakis of UW for pointing out this erratum.
- p. 78, last equation, replace ΔC_p with ΔC_p° . Thanks to Carlos Henao of UW for pointing out this erratum.
- p. 91. Change $\varepsilon_1, \varepsilon_2$ to $\varepsilon'_1, \varepsilon'_2$, respectively, in second to last displayed equation and sentence preceding it.
- p. 91, last paragraph, change "the production of 2,2,4 is preferable" to "the production of 2,2,3 is preferable." Thanks to Manos Mavrikakis of UW for pointing out this erratum.
- p. 103, Exercise 3.10, change equation in (a) to

$$\frac{k_f}{k_r} = \frac{K}{RTz} \frac{\hat{\phi}_A}{\hat{\phi}_B^2}$$

in which z is the compressibility factor of the mixture.

- p. 103, Exercise 3.10 (b), change "ideal mixture" to "ideal-gas mixture."
- p. 104, line after Equation 3.86. Change $\pi(n-1)$ to $\pi(n+1)$.
- p. 104, last equation, change $\sum_j \mu_j n_j$ to $\sum_j \mu_j dn_j$.
- p. 106, in Exercise 3.14, matrix $\tilde{\mathbf{H}}$ is positive definite, but matrix \mathbf{H} is only positive semidefinite. Therefore change parts (c) and (e) to the following. Also include the definition of a positive semidefinite matrix in the problem statement.

A matrix \mathbf{H} is **positive semidefinite** if

$$\mathbf{x}^T \mathbf{H} \mathbf{x} \geq 0, \quad \text{for every } \mathbf{x} \neq \mathbf{0}$$

- (c) To show \mathbf{H} is positive semidefinite, we must show that the following quadratic form is nonnegative

$$\mathbf{x}^T \mathbf{H} \mathbf{x} = \sum_j \sum_l x_j H_{jl} x_l \geq 0, \quad \text{for every } \mathbf{x} \neq \mathbf{0}$$

Substitute Equation 3.92 into the above equation and show

$$\mathbf{x}^T \mathbf{H} \mathbf{x} = \frac{RT}{nT} \left[\sum_l \frac{x_l^2}{y_l} - \left(\sum_l x_l \right)^2 \right]$$

Next use the Cauchy inequality, Equation 3.31, to show the right-hand side is nonnegative. When is equality achieved in the Cauchy inequality? We have therefore shown \mathbf{H} is a positive semidefinite matrix. Note that it is not positive definite, however.

- (e) Finally, use the Cauchy inequality again to show that $\tilde{\mathbf{H}}$ is a positive definite matrix.
- p. 130, sentence after Equation 4.40, should read "One can divide Equation 4.39 through by $Q_f \dots$ ". Thanks to Nathan Knapp of Oregon State University for pointing out this erratum.
 - p. 135, sentence after Equation 4.51, should read "...replace a high-concentration species mole balance with the total mass balance ..." Thanks to Carlos Henao of UW for pointing out this erratum.
 - p. 159, exchange limits on integral
 - p. 165, sentence before r_1 and r_2 expressions; the underlined portion of the following sentences is missing. "The *probability* of reaction is assumed proportional to the number of combinations of the molecules that can be taken with the reaction stoichiometry. For a uni-molecular reaction, the number of combinations is simply the number of molecules, so the probabilities for the two reactions are"
 - p. 165, fifth sentence from bottom should read, "(ii) choose which reaction occurs at that time." Thanks to Jay Schieber of IIT for pointing out this erratum.
 - p. 166, first sentence of last paragraph should read, "If r_{tot} is the total reaction rate, $r_{\text{tot}} e^{-r_{\text{tot}} \tilde{t}}$ is the probability that a reaction has not occurred during time interval $\tilde{t} \dots$ "
 - p. 170, Equation 4.102, add units of 1/day to the rate constants. Thanks to Elise Huang of UW for pointing out this erratum.
 - p. 178, Exercise 4.6, Equation 4.115 is missing a term; it should read

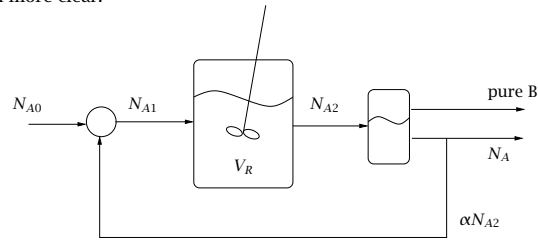
$$\mathbf{x}(t) = \mathbf{x}_0 e^{At} - \frac{b}{A} [1 - e^{At}] \quad (4.115)$$

and the partial fraction formula after Equation 4.115 is missing a minus sign; it should read

$$\frac{1}{s(s-A)} = -\frac{1}{A} \left[\frac{1}{s} - \frac{1}{s-A} \right]$$

- p. 179, Exercise 4.8, change units of E_a to kcal/mol. Thanks to Ryan West of UW for pointing out this erratum.
- p. 180, Exercise 4.8, part (a), change "production rate of propylene glycol" to "the total reactor production rate of propylene glycol"
- p. 181, Exercise 4.10, Add the phrase "starting with pure A" to the question in (a).

23. p. 182, Exercise 4.12 (b), change “gas flowrate” to “volumetric flowrate.” Thanks to Charlie Hill of UW for pointing out this erratum.
24. p. 183, Exercise 4.13, second line, should read “from 5% to 5 ppm.”
25. p. 183, Exercise 4.14, third sentence should read “What happens if one attempts to achieve a higher conversion than this limiting value by recycling more material?”
26. p. 183, Figure 4.36. Replace the figure with the following to make the separation more clear.



27. p. 184, Exercise 4.17, change units of k_1 from mol/L·min to L/mol·min. Thanks to Yong Ku Cho of UW for pointing out this erratum.
28. p. 212, change the two equations at the bottom of the page to
- $$\frac{d\varepsilon_1}{dt} = r_1 \quad \frac{d\varepsilon_2}{dt} = \frac{K_2}{1 + K_2} r_1$$
29. p. 246, Equation 5.140, change K_{CO} to K_1 . Thanks to Irene Chen of UW for pointing out this erratum.
30. p. 261, Exercise 5.6, 3 lines from end. Change the list (CH_3 , CH_3CO and CHO) to (CH_3 and CH_3CO). Thanks to Tania Deb and Chris Barrett of UW for pointing out this erratum.
31. p. 269, Exercise 5.19, first line. Change “hydrogen” to “ethane.” Thanks to Kevin Henneck of Princeton University for pointing out this erratum.
32. p. 270, add “+S” to the right-hand side of the last reaction in Exercise 5.19. Thanks to Andrew Stella of Princeton University for pointing out this erratum.
33. p. 297, change \dot{Q}_r under Equation 6.38 to $-\dot{Q}_r$
34. p. 300, change U° to $U^\circ A/V_R$ in Equation 6.40
35. p. 301, change U° to $U^\circ A/V_R$ in Equation 6.44
36. p. 305, Add $U^\circ A/V_R = 340 \text{ kJ}/(\text{m}^3 \text{ min K})$ to Table 6.3
37. p. 305, Add $T_a = 298 \text{ K}$ to Table 6.3. Thanks to Mike Donnelly of UW for pointing out this erratum.

38. p. 316, First paragraph of Section 6.4. Should read “...Equations 6.82–6.83 in the semi-batch reactor Table 6.9 are identical to the corresponding Equations 6.73–6.74 in the CSTR Table 6.8.”
39. p. 324, E/R in Table 6.5 should be E_a/R or simply E .
40. pp. 324–325. Table 6.5, change k_m value from 1922.6 to 2.0822; change ΔH_R value from -1.361×10^3 to -1.284×10^6 . With these changes the corrected Figures 6.35 and 6.36 are shown here. Thanks to Matt Kipper of Colorado State for pointing out this erratum.
41. p. 327, Partial pressures in Equation 6.55 are divided by 1.0 atm.
42. p. 329, Table 6.6, units of k_{-10} are atm/s.
43. p. 329, Add $x_{Af} = 0.015$, $x_{Nf} = 0.985 \cdot (1/4)$, $x_{Hf} = 0.985 \cdot (3/4)$ to Table 6.6. The feed consists of 1.5% ammonia and 98.5% stoichiometric mixture of nitrogen and hydrogen. Thanks to graduate student Jim Pfaendtner of Northwestern for pointing out this omission and the next typo.
44. p. 329, Change the sign of ΔG° in Table 6.6.
45. p. 328, Table 6.6. Change Q_f to $0.05713 \text{ m}^3/\text{s}$.
46. p. 329. Figure 6.38 is not quite correct. The corrected figure is shown here in Figure 6.38.
47. p. 330. The middle steady-state profiles in Figures 6.39 and 6.40 are not quite correct. The corrected figures are shown here in Figures 6.39 and 6.40.
48. p. 332, Equation 6.65, change V to V_R
49. p. 333, Equation 6.75, change α to αT
50. p. 333, missing terms in Equation 6.75 and Equation 6.76 of Table 6.8 are underlined below. Note $P_{n_j} = (\partial P/\partial n_j)_{T,V,n_k}$ has been added to the list of symbols.
- b. Constant-volume reactor**
- $$V_R \rho \hat{C}_V \frac{dT}{dt} = - \sum_i (\Delta H_{Ri} - \alpha T V_R \sum_j \nu_{ij} P_{n_j}) r_i V_R + \sum_j c_{jf} Q_f (H_{jf} - H_j) + \alpha T V_R \sum_j P_{n_j} (c_{jf} Q_f - c_j Q) + \dot{Q} \quad (6.75)$$
- b.1 Constant-volume reactor, ideal gas**
- $$V_R \rho \hat{C}_V \frac{dT}{dt} = - \sum_i (\Delta H_{Ri} - RT \bar{\nu}_i) r_i V_R + \sum_j c_{jf} Q_f (H_{jf} - H_j) + RT \sum_j (c_{jf} Q_f - c_j Q) + \dot{Q} \quad (6.76)$$
51. p. 342, replace A_h with A in the table for Exercise 6.6.

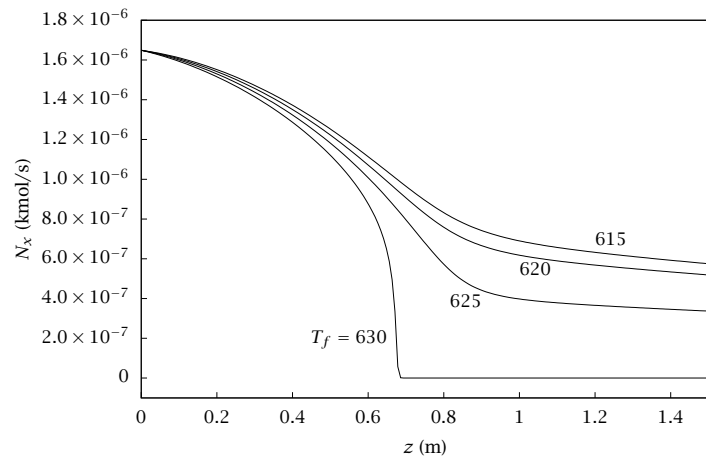


Figure 6.35: Molar flow of o-xylene versus reactor length for different feed temperatures.

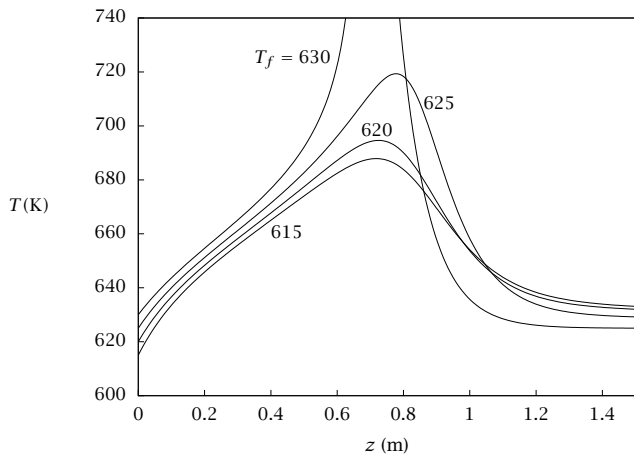


Figure 6.36: Reactor temperature versus length for different feed temperatures.

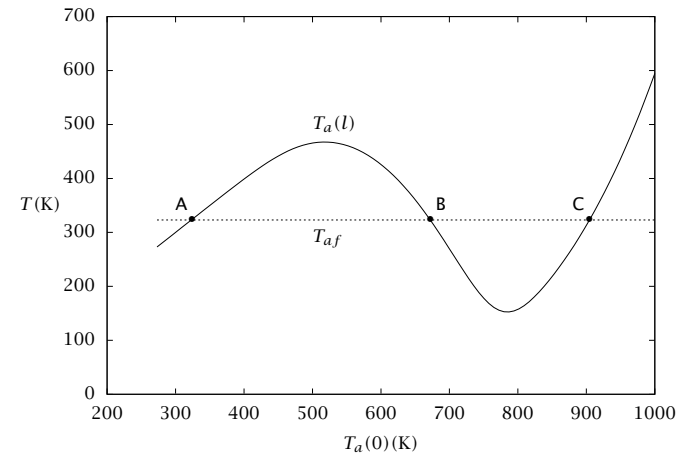


Figure 6.38: Coolant temperature at reactor outlet versus temperature at reactor inlet, $T_a(l)$ versus $T_a(0)$; intersection with coolant feed temperature T_{af} indicates three steady-state solutions (A,B,C).

52. p. 345, Exercise 6.13. Change Equation 6.72 to Equation 6.73 and change Equation 6.81 to Equation 6.82.
53. p. 345, Exercise 6.14 (e). replace
 "If the equilibrium conversion of component A determined in 6.14d is achieved in the *adiabatic* reactor, calculate the outlet temperature using the inlet conditions specified in 6.14d."
 with
 "Calculate the minimal inlet temperature of an *adiabatic* reactor required to achieve the equilibrium conversion of component A determined in 6.14d."
54. p. 346, Exercise 6.16, replace "in a PFR" with "in an adiabatic PFR."
55. p. 350, Figure 6.41 is not quite correct. The corrected figure is shown here in Figure 6.41.
56. p. 373, add $\times 10^{-5}$ after -2.125 in second equation after Equation 7.37.
57. p. 382, change the upper limit of integration from c to \bar{c} in the equation preceding Equation 7.56.
58. p. 391, Replace the last sentence of the first paragraph with the following.

We even obtain an incorrect reaction order: the first-order reaction is correct, but a second-order reaction appears 3/2 order, and so on.

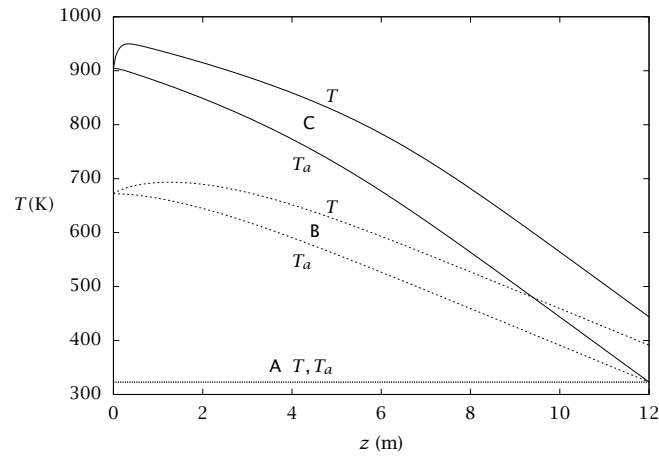


Figure 6.39: Reactor and coolant temperature profiles versus reactor length; lower (A), unstable middle (B), and upper (C) steady states.

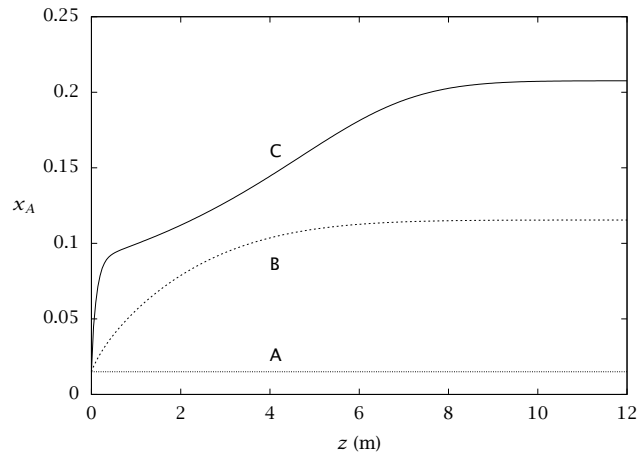


Figure 6.40: Ammonia mole fraction versus reactor length; lower (A), unstable middle (B), and upper (C) steady states.

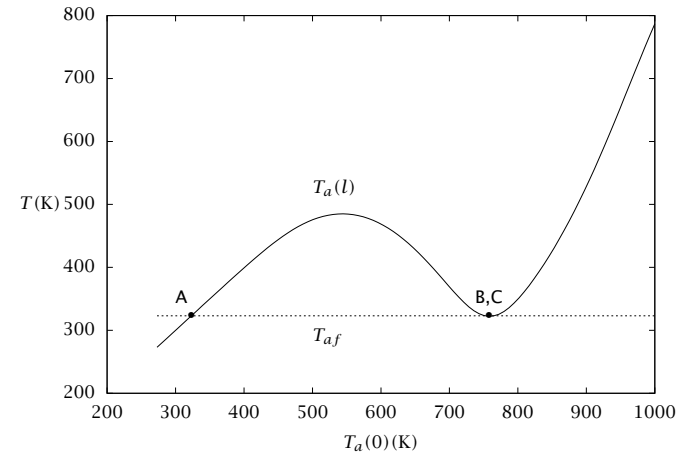


Figure 6.41: Coolant temperature at reactor outlet versus temperature at reactor inlet, $T_a(l)$ versus $T_a(0)$, at the critical value of heat-transfer coefficient; upper and middle steady-state solutions have coalesced.

59. p. 393, Add the definitions of dimensionless variables,

$$\bar{c} = \frac{c_A}{c_{As}} \quad \bar{T} = \frac{T - T_s}{T_s}$$

to the definitions of dimensionless parameters γ , β , and Φ^2 .

60. p. 393, in Equation 7.74, $d\bar{c}/d\bar{T} = 0$ at $\bar{T} = 0$, and $\bar{c} = 1$ at $\bar{T} = 3$.

61. p. 399, Table 7.5, change the units of k_{10} and k_{20} to $\text{cm}^3/\text{mol}\cdot\text{s}$. Thanks to Ralph White of South Carolina for pointing out this erratum.

62. p. 400, third equation. Insert a minus sign on the right-hand side. Fourth and fifth equations: change minus sign to plus sign. Thanks to Ralph White of South Carolina for pointing out this erratum.

63. p. 405, replace $(1 - \epsilon_B)$ in second equation with $1/(1 - \epsilon_B)$.

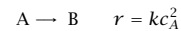
64. p. 405, replace $\left(\frac{0.6}{0.85}\right)$ in third equation with $\left(\frac{0.85}{0.6}\right)$.

65. p. 408, displayed equation before Equation 7.104. Factor of $\sqrt{2}$ missing from numerator. Thanks to Amy Claas of UW for pointing out this erratum.

66. pp. 409–411, Example 7.6. Change the reactor feed sentence to, “The feed to the reactor consists of 16.7 mol% CO, 83.3 mol% O₂ and zero CO₂, with volumetric flowrate $Q_f = 792 \text{ L/s}$.” Thanks to Khalifa Yousif of UW for reporting

this erratum. The rate constant should be $k = 1.3828 \times 10^{19} \exp(-13,500/T)$. With the adjusted rate constant and flowrate given above, the reactor volume should be $V_R = 233 \text{ cm}^3$ instead of L. Also change the units on the x-axis from L to cm^3 in Figures 7.27 and 7.28. Thanks to Jason Haugh and the students at NC State for reporting this erratum.

67. p. 409, seventh line from bottom. Replace “The catalyst pellet radius is 0.1 cm.” with, “The spherical catalyst pellet radius is 0.1 cm, and the densities are $\rho_p = 0.68, \rho_B = 0.60 \text{ g/cm}^3$.”
68. p. 412, Table 7.6, delete K in the units of the two heats of reaction, $\Delta H_{R1}, \Delta H_{R2}$.
69. p. 418. Change k_{jm} to k_{mj} . Thanks to Robert Erickson of UW for pointing out this erratum.
70. p. 422, Exercise 7.4, change the units on the rate constant to $\text{cm}^3/(\text{mol s})$.
71. p. 429, Exercise 7.18 (b), change “... two derivatives with respect to \bar{c} ...” to “... two derivatives with respect to z ...”
72. p. 430, Exercise 7.19. In order to make the simulation more realistic, change the second paragraph to the following.
In order to get reasonable pressure drops at these higher engine loads, let’s assume the catalyst bed porosity is $\epsilon_B = 0.4$, and the inlet pressure and temperature are $P_f = 1.5 \text{ atm}, T_f = 570 \text{ K}$. Assume the cross-section of the catalytic converter bed has a diameter four times as large as the exhaust pipe. Therefore the velocity in the entrance to the converter is 1/4 the velocity in the exhaust pipe.
- (a) Calculate the fluid and pellet profiles in the bed for $u_f = 5 \text{ m/s}$ exhaust pipe velocity at the entrance to the catalytic converter. How much catalyst is required to reach 97.0% conversion of CO and C_3H_6 under the new engine operation? What is the pressure drop for this case?
- (b) Using the bed size from the previous part, resolve the problem with the idling speed, $u_f = 0.75 \text{ m/s}$ exhaust pipe velocity at the entrance to the catalytic converter. What is the conversion CO and C_3H_6 at the end of the bed? What is the pressure drop across the bed?
73. p. 451, add the phrase “for the reaction



with second-order, irreversible kinetics” to the last sentence on page 451.

74. p. 452, Figure 8.12, time should have units of minutes. Thanks to Ralph White of U. South Carolina, for pointing out this erratum.
75. p. 453, change $p(\theta)$ to $P(\theta)$ (two places).
76. p. 453, change t to θ in both $P(\theta)$ equations (two places in each equation).
77. p. 461, change x to λ in first two equations after the start of the numerical solution section (two places).

78. p. 461, change θ to λ two lines before Example 8.3.
79. p. 462, change θ to λ starting with the third equation to the end of the page (two places). Change x to $\bar{\lambda}$ in the same area of the page (nine places).
80. p. 467, change $c_A(\theta)$ to c_{At} in first line after the two unnumbered equations. Thanks to Manos Mavrikakis of UW for pointing out this erratum.
81. p. 480, add $c_{Af} = c_{Bf} = 1 \text{ mol/L}$ to Table 8.3.
82. p. 491, Exercise 8.3, change $kc/(1+kc)$ to $k\frac{KC}{1+KC}$.
83. p. 492, change θ to λ in Exercise 8.6.
84. p. 493, replace $\delta_i \leq 1$ with $0 \leq \delta_i \leq 1$ in last equation for $r(c)$.
85. P. 496, Exercise 8.12 (c), change “15 possible reactor configurations” to “20 possible reactor configurations.”
86. p. 497, Exercise 8.13, change “maximize” to “minimize,” fourth line from top of page.
87. p. 519, First sentence should read “... we can show the parameter estimates also are normally distributed

$$\hat{\theta} \sim N(\theta, P)$$

in which the mean is the true value of the parameters and the covariance is”

88. p. 535, equation should read

$$T_m = \frac{2}{1/300 + 1/500} = 375 \text{ K}$$

Thanks to Henning Stotz of UW for pointing out this erratum.

89. p. 553, change right-hand side of Equation 9.67 to $k_2 c_C c_B V_R$. Thanks to Manos Mavrikakis of UW for pointing out this erratum.
90. p. 567, insert a minus sign on right-hand side of r_1 equation in item 1.
91. p. 568, Exercise 9.4. Change “Use the least squares method of this chapter and find ...” to “Use an ODE/sensitivity solver and optimizer to find ...”.
92. p. 587, Example A.2, Equation A.12, replace $-tk_{CA0}e^{-kt}$ with $-tc_{A0}e^{-kt}$.
93. p. 590, change $\sum_{i=1}$ to $\sum_{j=1}$ (two places).
94. p. 590, integral should read $\int_0^1 f(r)dr = \sum_{j=1}^{n_c} Q_j f(r_j)$.
95. p. 596, Exercise A.5, change $\beta = 0.7$ to $\beta = 0.85$.

Chemical Reactor Analysis and Design Fundamentals

Other Changes from the First to Second Printing

November 18, 2017

1. The parameter V_R/Q_f is now denoted by τ instead of θ in Chapters 4 and 6. The variable θ is now mainly used in Chapter 8 as the residence time variable.
2. We adopted the overbar notation to denote partial molar quantities such as partial molar volume, enthalpy, entropy, Gibbs energy and heat capacity.
3. One example was added to Chapter 6, Example 6.3, which shows how to write the mass and energy balances for systems with multiple phases.
4. One section was added to Chapter 7, Section 7.7.2, which shows how to use a logarithmic transformation to calculate the catalyst pellet concentrations when there are steep concentration profiles.
5. One new exercise was added to Chapter 6. Exercise 6.22, "CSTR steady-state isola."
6. One new exercise was added to Chapter 7. Exercise 7.20, "Logarithmic transformation."
7. Noise was added to the data in Exercise 9.6, the title of the exercise was changed to "Estimating rate constant from catalyzed CSTR reaction data," and the exercise now asks for a plot of the model's fit to the data.
8. Four new exercises were added to Chapter 9. The corresponding exercise numbers are listed below.

| First Printing | Second Printing | Title |
|----------------|-----------------|--|
| 9.1 | 9.1 | Estimating activation energy and preexponential factor |
| new | 9.2 | |
| 9.2 | 9.3 | Estimation without differentiation |
| 9.3 | 9.4 | |
| new | 9.5 | |
| 9.4 | 9.6 | Estimating rate constant from catalyzed CSTR reaction data |
| 9.5 | 9.7 | |
| 9.6 | 9.8 | |
| 9.7 | 9.9 | |
| 9.8 | 9.10 | Least-squares estimate formula |
| 9.9 | 9.11 | |
| 9.10 | 9.12 | |
| new | 9.13 | |
| new | 9.14 | Linear transformation of a normal is normal |