Chemical Reactor Analysis and Design Fundamentals

Errata for First Printing

January 2, 2011

1. cover, change sign on $\dot{W}_s$ term and add $\dot{W}_b$ term to energy balance at bottom of cover.

2. cover, remove minus sign in front of $D_j$.

3. 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.

4. p. 78, last equation, replace $\Delta C_P$ with $\Delta C_P^\circ$. Thanks to Carlos Henao of UW for pointing out this erratum.

5. 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.

6. p. 103, Exercise 3.10, change equation in (a) to

$$\frac{k_f}{k_r} = \frac{K \phi_A}{RTz \phi_B^2}$$

in which $z$ is the compressibility factor of the mixture.

7. p. 103, Exercise 3.10 (b), change “ideal mixture” to “ideal-gas mixture.”

8. p. 104, last equation, change $\sum_j \mu_j n_j$ to $\sum_j \mu_j dn_j$.

9. p. 106, in Exercise 3.14, matrix $\tilde{H}$ is positive definite, but matrix $H$ 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 $H$ is **positive semidefinite** if

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

(c) To show $H$ is positive semidefinite, we must show that the following quadratic form is nonnegative

$$x^T H x = \sum_{j} \sum_{l} x_j H_{jl} x_l \geq 0, \quad \text{for every } x \neq 0$$

Substitute Equation 3.92 into the above equation and show

$$x^T H x = \frac{RT}{n_r} \left[ \sum_{l} \frac{x_l^2}{y_l} - \left( \sum_{l} x_l \right)^2 \right]$$

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 $H$ is a positive semidefinite matrix. Note that it is not positive definite, however.
(e) Finally, use the Cauchy inequality again to show that $\tilde{H}$ is a positive definite matrix.

10. p. 130, sentence after Equation 4.40, should read “One can divide Equation 4.39 through by $Q_f$ …”. Thanks to Nathan Knapp of Oregon State University for pointing out this erratum.

11. 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.

12. p. 159, exchange limits on integral

13. 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”

14. 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.

15. p. 166, first sentence of last paragraph should read, “If $r_{tot}$ is the total reaction rate, $r_{tot}e^{-r_{tot}t}$ is the probability that a reaction has not occurred during time interval $\tilde{t}$ …”

16. 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.

17. p. 178, Exercise 4.6, Equation 4.115 is missing a term; it should read

$$x(t) = x_0 e^{At} - \frac{b}{A} \left[ 1 - e^{At} \right]$$

(4.115)

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

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

18. p. 179, Exercise 4.8, change units of $E_a$ to kcal/mol. Thanks to Ryan West of UW for pointing out this erratum.

19. p. 180, Exercise 4.8, part (a), change “production rate of propylene glycol” to “the total reactor production rate of propylene glycol”

20. p. 181, Exercise 4.10, Add the phrase “starting with pure A” to the question in (a).

21. p. 182, Exercise 4.12 (b), change “gas flowrate” to “volumetric flowrate.” Thanks to Charlie Hill of UW for pointing out this erratum.

22. p. 183, Exercise 4.13, second line, should read “from 5% to 5 ppm.”
23. 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?”

24. p. 183, Figure 4.36. Replace the figure with the following to make the separation more clear.

![Diagram](image_url)

25. 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.

26. p. 212, change the two equations at the bottom of the page to

$$\frac{d\varepsilon_1}{dt} = r_1 \quad \frac{d\varepsilon_2}{dt} = \frac{K_2}{1 + K_2} r_1$$

27. p. 246, Equation 5.140, change $K_{CO}$ to $K_1$. Thanks to Irene Chen of UW for pointing out this erratum.

28. p. 261, Exercise 5.6, 3 lines from end. Change the list (CH$_3$, CH$_3$CO and CHO) to (CH$_3$ and CH$_3$CO). Thanks to Tania Deb and Chris Barrett of UW for pointing out this erratum.

29. p. 297, change $Q_r$ under Equation 6.38 to $-\dot{Q}_r$

30. p. 300, change $U^0$ to $U^0 A/V_R$ in Equation 6.40

31. p. 301, change $U^0$ to $U^0 A/V_R$ in Equation 6.44

32. p. 305, Add $U^0 A/V_R = 340$ kJ/(m$^3$ min K) to Table 6.3

33. p. 305, Add $T_a = 298$ K to Table 6.3. Thanks to Mike Donnelly of UW for pointing out this erratum.

34. 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.”

35. p. 324, $E/R$ in Table 6.5 should be $E_a/R$ or simply $E$.

36. pp. 324–325. Table 6.5, change $k_m$ value from 1922.6 to 2.0822; change $\Delta H_R$ value from $-1.361 \times 10^3$ to $-1.284 \times 10^6$. 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.

37. p. 327, Partial pressures in Equation 6.55 are divided by 1.0 atm.
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).

38. p. 329, Table 6.6, units of $k_{-10}$ are atm/s.

39. 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.

40. p. 329, Change the sign of $\Delta G^\circ$ in Table 6.6.

41. p. 328, Table 6.6. Change $Q_f$ to 0.05713 m$^3$/s.

42. p. 329. Figure 6.38 is not quite correct. The corrected figure is shown here in Figure 6.38.

43. 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.

44. p. 332, Equation 6.65, change $V$ to $V_R$

45. p. 333, Equation 6.75, change $\alpha$ to $\alpha T$

46. 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.
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.
b. Constant-volume reactor

\[ V_R \rho \hat{C}_V \frac{dT}{dt} = - \sum_i (\Delta H_{Ri} - \alpha T V_R \sum_j \nu_i P_{n_j}) r_i V_R + \sum_j c_{ij} Q_f (H_{j_f} - H_j) + \alpha T V_R \sum_j P_{n_j} (c_{ij} Q_f - c_j Q) + \hat{Q} \]  

(6.75)

b.1 Constant-volume reactor, ideal gas

\[ V_R \rho \hat{C}_V \frac{dT}{dt} = - \sum_i (\Delta H_{Ri} - RT \hat{v}_i) r_i V_R + \sum_j c_{ij} Q_f (H_{j_f} - H_j) + RT \sum_j (c_{ij} Q_f - c_j Q) + \hat{Q} \]  

(6.76)

47. p. 342, replace \( A_h \) with \( A \) in the table for Exercise 6.6.


49. 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.”

50. p. 346, Exercise 6.16, replace “in a PFR” with “in an adiabatic PFR.”

51. p. 350, Figure 6.41 is not quite correct. The corrected figure is shown here in Figure 6.41.

52. p. 373, add \( \times 10^{-5} \) after \(-2.125\) in second equation after Equation 7.37.

53. p. 382, change the upper limit of integration from \( c \) to \( \bar{c} \) in the equation preceding Equation 7.56.

54. 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.

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

\[ \bar{c} = \frac{c_A}{c_{A_s}} \quad \bar{T} = \frac{T - T_s}{T_s} \]

to the definitions of dimensionless parameters \( \gamma \), \( \beta \), and \( \Phi \).

56. p. 393, in Equation 7.74, \( d\bar{c}/d\bar{r} = 0 \) at \( \bar{r} = 0 \), and \( \bar{c} = 1 \) at \( \bar{r} = 3 \).

57. 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.
58. 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.

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

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

61. 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.

62. p. 409, Example 7.6:
(a) change the rate constant to \(k = 1.048 \times 10^{12} \exp(-13,500/T)\) cm\(^3\)/mol s.
(b) Change the reactor feed sentence to, “The feed to the reactor consists of 16.7 mol% CO, 83.3 mol% O\(_2\) and zero CO\(_2\), with volumetric flowrate \(Q_f = 60\) cm\(^3\)/s.”

Thanks to Khalifa Yousif of UW for pointing out the errata in Example 7.6.

63. p. 412, Table 7.6, delete K in the units of the two heats of reaction, \(\Delta H_{R1}\), \(\Delta H_{R2}\).

64. p. 418. Change \(k_{jm}\) to \(k_{mj}\). Thanks to Robert Erickson of UW for pointing out this erratum.
Errata

65. p. 422, Exercise 7.4, change the units on the rate constant to cm$^3$/mol s.

66. p. 429, Exercise 7.18 (b), change “…two derivatives with respect to $\tau$…” to “…two derivatives with respect to $z$…”

67. 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 $P_f = 1.5$ atm, $T_f = 570$ 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 $u_f = 5$ 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$_3$H$_6$ 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, $u_f = 0.75$ m/s exhaust pipe velocity at the entrance to the catalytic converter. What is the conversion CO and C$_3$H$_6$ at the end of the bed? What is the pressure drop across the bed?

68. p. 451, add the phrase “for the reaction

\[ A \rightarrow B \quad r = k c_A^2 \]

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

69. p. 452, Figure 8.12, time should have units of minutes. Thanks to Ralph White of U. South Carolina, for pointing out this erratum.

70. p. 453, change $p(\theta)$ to $P(\theta)$ (two places).

71. p. 453, change $t$ to $\theta$ in both $P(\theta)$ equations (two places in each equation).

72. p. 461, change $x$ to $\lambda$ in first two equations after the start of the numerical solution section (two places).

73. p. 461, change $\theta$ to $\lambda$ two lines before Example 8.3.

74. p. 462, change $\theta$ to $\lambda$ starting with the third equation to the end of the page (two places). Change $x$ to $\overline{X}$ in the same area of the page (nine places).

75. p. 467, change $c_A(\theta)$ to $c_{Af}$ in first line after the two unnumbered equations. Thanks to Manos Mavrikakis of UW for pointing out this erratum.

76. p. 480, add $c_{Af} = c_{Bf} = 1$ mol/L to Table 8.3.

77. p. 491, Exercise 8.3, change $kc/(1 + kc)$ to $k \frac{Kc}{1 + KC}$.

78. p. 492, change $\theta$ to $\lambda$ in Exercise 8.6.

79. p. 493, replace $\delta_i \leq 1$ with $0 \leq \delta_i \leq 1$ in last equation for $r(c)$.
80. P. 496, Exercise 8.12 (c), change “15 possible reactor configurations” to “20 possible reactor configurations.”

81. p. 497, Exercise 8.13, change “maximize” to “minimize,” fourth line from top of page.

82. 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”

83. p. 535, equation should read

\[ T_m = \frac{2}{\frac{1}{300} + \frac{1}{500}} = 375 \text{ K} \]

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

84. 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.

85. p. 567, insert a minus sign on right-hand side of \( r_1 \) equation in item 1.

86. 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 …”.

87. p. 587, Example A.2, Equation A.12, replace \(- t k c A_0 e^{-kt}\) with \(- t c A_0 e^{-kt}\).

88. p. 590, change \( \sum_{i=1} \) to \( \sum_{j=1} \) (two places).

89. p. 590, integral should read \( \int_0^1 f(r) \, dr = \sum_{j=1}^{n_c} Q_j f(r_j) \).

90. 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

January 2, 2011

1. The parameter \( V_R/Q_f \) is now denoted by \( \tau \) instead of \( \theta \) in Chapters 4 and 6. The variable \( \theta \) 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.

<table>
<thead>
<tr>
<th>First Printing</th>
<th>Second Printing</th>
<th>Title</th>
</tr>
</thead>
<tbody>
<tr>
<td>9.1 new</td>
<td>9.1</td>
<td>Estimating activation energy and pre-exponential factor</td>
</tr>
<tr>
<td>9.2</td>
<td>9.3</td>
<td>Estimation without differentiation</td>
</tr>
<tr>
<td>9.3 new</td>
<td>9.4</td>
<td></td>
</tr>
<tr>
<td>9.4</td>
<td>9.6</td>
<td>Estimating rate constant from catalyzed CSTR reaction data</td>
</tr>
<tr>
<td>9.5</td>
<td>9.7</td>
<td></td>
</tr>
<tr>
<td>9.6 new</td>
<td>9.8</td>
<td>Least-squares estimate formula</td>
</tr>
<tr>
<td>9.7</td>
<td>9.9</td>
<td>Linear transformation of a normal is normal</td>
</tr>
<tr>
<td>9.8</td>
<td>9.10</td>
<td></td>
</tr>
<tr>
<td>9.9</td>
<td>9.11</td>
<td></td>
</tr>
<tr>
<td>9.10</td>
<td>9.12</td>
<td></td>
</tr>
<tr>
<td>new</td>
<td>9.13</td>
<td></td>
</tr>
<tr>
<td>new</td>
<td>9.14</td>
<td></td>
</tr>
</tbody>
</table>