

## ERRATA FOR 2<sup>ND</sup> PRINTING OF WATER CHEMISTRY

1. (2/22/05) Inside back cover: the final value shown for  $RT_{298.15K}$  should be 24.79 L-bar/mol (not 24.17 L-bar/mol).
2. (2/25/04) p.3. In Table 1.1., the concentration of  $Mg^{2+}$  in seawater should be given as 1280 mg/L, not 128 mg/L.
3. (1/16/02) p.30. In Table 1.4a, in the explanation of the terms in the Extended Debye-Huckel equation, the expression for  $B$  should be:  $B = 50.3(\epsilon T)^{-1/2}$  (in the book, the minus sign is missing from the exponent).
4. (10/04/06) p.53. Delete the first two sentences of Problem 7; start with “The activity coefficients...” Delete the word “concentration” from that sentence.
5. (10/01/03) p.77, second line from bottom: delete the word “and” after the comma.
6. (10/25/03) p.79, Equation 2.30: the left hand side should be  $\frac{dPE_{tot}}{dx}$ .
7. (10/25/03) p.110, first line: the reference to Equation (2.79) should be to Equation (2.80).
8. (10/08/03) p.111, Example 2.10. In the fourth line of the solution to part *a* (the second equation shown), the left hand side of the equation should be  $\Delta\bar{G}_r^o$  instead of  $\Delta\bar{G}_r$ .
9. (9/23/03) p.111-113, Example 2.10. In the problem statement, in part *b*, lines 1-2, replace the phrase “a system,” with “1.0 L of a solution.” At the end of that sentence, add the sentence: Assume that the molar volumes of  $H_2O$ ,  $HCrO_4^-$ , and  $Cr_2O_7^{2-}$  are all equal (1 L per 55.56 mol), so that the solution volume remains constant as the reaction proceeds.

On the first line of p.112, replace “Assuming that” with “Because.”

Revise footnote 13 as follows: Although the activity of water is very nearly 1.0 regardless of the distribution of Cr species, the number of moles of  $H_2O$  in the solution changes slightly when some of the Cr converts from one form to the other. As a result, the contribution of  $H_2O$  to  $G_{tot}$  changes as the reaction proceeds, and this change must be taken into account.

Revise Equation (2.92) by placing the  $V$  on the right hand side:

$$G_{\text{tot}} = V \left[ c_{\text{H}_2\text{O}} \left( \bar{G}_{\text{H}_2\text{O}}^{\circ} + RT \ln \frac{c_{\text{H}_2\text{O}}}{\sum c_i} \right) + c_{\text{HCrO}_4^-} \left( \bar{G}_{\text{HCrO}_4^-}^{\circ} + RT \ln c_{\text{HCrO}_4^-} \right) \right. \\ \left. + c_{\text{Cr}_2\text{O}_7^{2-}} \left( \bar{G}_{\text{Cr}_2\text{O}_7^{2-}}^{\circ} + RT \ln c_{\text{Cr}_2\text{O}_7^{2-}} \right) \right] \quad (2.92)$$

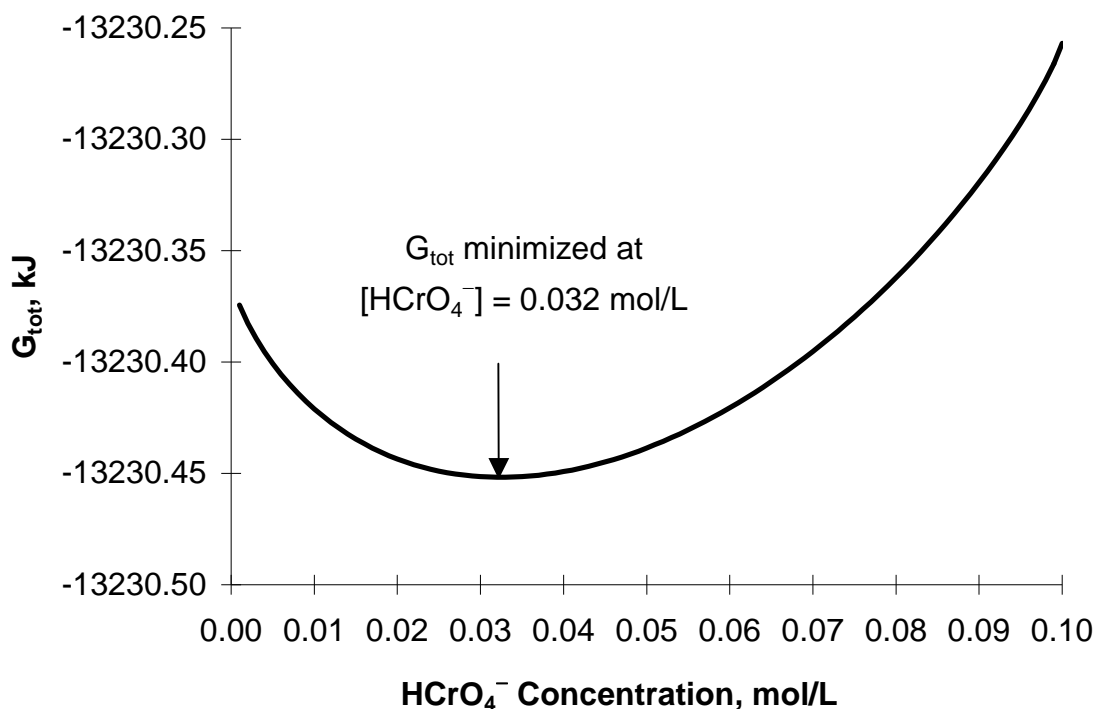
In the second line below Equation (2.92) replace “water” with “total species.”

Revise Equation (2.94) as follows:

$$a_{\text{H}_2\text{O}} = \frac{55.56 - c_{\text{HCrO}_4^-} - c_{\text{Cr}_2\text{O}_7^{2-}}}{55.56} = \frac{55.56 - c_{\text{HCrO}_4^-} - 0.5(0.10 - c_{\text{HCrO}_4^-})}{55.56} \\ = \frac{55.51 - 0.5c_{\text{HCrO}_4^-}}{55.56} \quad (2.94)$$

In the second line below Equation (2.94), delete “per unit volume of solution.” In the third and fourth lines below the equation, change “ $G_{\text{tot}}/V$ ” to “ $G_{\text{tot}}$ .”

Replace Figure 2.8 and its caption with the following figure (note: the values on the y axis have changed, and the y axis label now represents  $G_{\text{tot}}$ , not  $G_{\text{tot}}/V$ ).



**Figure 2.8** Total Gibbs energy of 1.0 L of a solution containing  $10^{-1} M c_{\text{Cr,tot}}$ , as a function of the  $\text{HCrO}_4^-$  concentration.

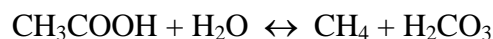
10. (10/25/03) p.116, first equation in solution to Example 2.12: replace 16.40 with 16.32.
11. (10/25/03) p.124, solution to Example 2.14: In last equation in part *b* and both equations in part *c*, replace 3.03 with 2.96, and 1.74 with 1.72.
12. (10/29/07) p.128, Problem 3. In the parenthetical in the first line following Reaction 2, replace “TOTNH<sub>3</sub>” with “the sum of the concentrations of NH<sub>4</sub><sup>+</sup> and NH<sub>3</sub>”.
13. (10/11/05) p.128, Problem 3. At the end of the paragraph preceding part *a*, add: Reaction 1 is at equilibrium, but Reaction 2 might not be.
14. (11/13/03) p.135: In Equation 3.5, change  $10^{-1}$  to 1.
15. (10/25/03) p.136, second line of caption to Figure 3.3: replace Al<sup>3+</sup> with Cu<sup>2+</sup>.
16. (10/23/08) p.139, Table 3.2: For arsenous acid (H<sub>3</sub>AsO<sub>3</sub>), the value of  $\text{p}K_{a3}$  should be 13.41. Make the same change in the copy of this table on p.642.
17. (12/06/05) p.139. The value of  $\text{p}K_{a2}$  for Zinc ion should be 7.94, not 8.94. Make the same change in the copy of this table on p.642.
18. (2/14/03) p.160, line 2. “undergoes *k*” should be “undergoes *n*”

19. (10/29/07) p.161. In the middle of the page, in the equation following the sentence “Alternatively,  $\alpha_1$  can be derived...” change the  $K_1$  at the end of the equation to  $K_{a1}$ .
20. (10/25/03) p.168, first line of last paragraph: replace “nine” with “seven.”
21. (11/12/03) p.184-185. On the bottom line of the table on p.184, the pH of the solution with  $[\text{NaCl}] = 0.1 \text{ M}$  should be 3.30. Also, add a line to the bottom of that table, for the species “ $\log [\text{H}^+]$ ”. On this line, below the values of 3.26 and 3.30 on the “pH” line, put values of  $-3.26$  and  $-3.19$ , respectively.

Revise paragraph at bottom of p.184 and top of p.185 as follows: The water with NaCl has slightly higher  $\text{H}^+$  and  $\text{F}^-$  concentrations than the salt-free solution, because the salt decreases the activity coefficients of these two species. Since the activity coefficient of HF is 1.0 in both solutions, the decreases in  $\gamma_{\text{H}^+}$  and  $\gamma_{\text{F}^-}$  force more HF to dissociate to satisfy the  $K_a$  expression, and this extra dissociation releases more  $\text{H}^+$  and  $\text{F}^-$  to solution. Correspondingly, the concentration of HF that remains undissociated declines. Despite the increase in the concentrations of  $\text{H}^+$  and  $\text{F}^-$ , the activity of each of these species declines, because their activity coefficients decline. The resulting, fractional decline in the product  $\{\text{H}^+\}\{\text{F}^-\}$  is exactly equal to the fractional decline in  $\{\text{HF}\}$ , so the ratio  $\{\text{H}^+\}\{\text{F}^-\}/\{\text{HF}\}$  is the same as in the solution with no NaCl, and equal to  $K_a$ . Because  $\{\text{H}^+\}$  is lower in the salty solution, pH is higher, as indicated. The effect of the salt would be greater if more highly charged species were involved (for example,  $\text{CO}_3^{2-}$  or  $\text{PO}_4^{3-}$ ).

22. (9/25/03) p.187. In question 5, the correct formula for ascorbic acid is  $\text{C}_6\text{H}_8\text{O}_6$ .
23. (2/06/07) p.187. In the second line of Problem 9, replace “Example 1.6” with “Problem 1.7”.
24. (10/16/03) p.195. In the equation just above the horizontal line, the fraction and final result should be  $\frac{(10^{-7.95})(10^{-3.00})}{10^{-6.05}} = 10^{-4.90}$ .
25. (10/26/05) p.199, part a, last equation: should be “(where  $\{\text{H}^+\} = \{\text{OCl}^-\}$ )” instead of “(where  $\{\text{H}^+\} + \{\text{OCl}^-\}$ )”.
26. (10/25/03) p.202, final line: Last two terms in the equality should be  $10^{1.77}$  and 58.9, instead of  $10^{-1.77}$  and 0.017.
27. (10/21/03) p.217-218. In the table near the bottom and the equation immediately below it, the values  $1.0 \times 10^{-10}$  and  $1.0 \times 10^{-4}$  should be replaced by  $7.94 \times 10^{-11}$  and  $1.26 \times 10^{-4}$ , respectively. Also, in the table, the values  $0.56 \times 10^{-4}$  and  $0.44 \times 10^{-4}$  should be reversed.
- In addition, on the last line of the page, the value  $-1.56 \times 10^{-4}$  should be replaced by  $-1.82 \times 10^{-4}$ . The same replacement should be made on p.218 in the third-to-last line of the example, and the value  $1.12 \times 10^{-4}$  in the final two lines should be replaced by  $1.13 \times 10^{-4}$ .

28. (10/28/05) p.229. In the table, in the row with the  $\text{Cu}(\text{NH}_3)_x^{2+}$  species, the entry under  $-2$  should be  $\text{Cu}(\text{NH}_3)_4^{2+}$ , and the entry under  $+1$  should be  $\text{Cu}(\text{NH}_3)^{2+}$ .
29. (10/24/06) p.230. In the last sentence of Problem 1, replace “charge balance” with “ $K_a$ ”.
30. (1/27/03) p.231. Most of question 4a is irrelevant, since the values were inadvertently printed on the axes.
31. (10/29/07) p.235. Problem 13. In the fifth line of the problem statement, change ‘CuS’ to ‘sulfide minerals’.
32. (10/25/03) p.249, solution to Example 5.2: In the fourth line of the second paragraph, replace  $2.67 \times 10^{-3}$  and  $0.67$  with  $3.32 \times 10^{-3}$  and  $0.83$ , respectively. Later in the paragraph, replace  $4.92 \times 10^{-3}$  with  $5.57 \times 10^{-3}$ . Make the corresponding changes ( $3.32$  for  $2.67$  and  $5.57$  for  $4.92$  in the summation at the end of the example.
33. (10/25/03) p.254, fourth line from bottom: replace “large” with “wide.”
34. (10/28/03) p.255. In the last line on the page,  $\text{H}_2\text{CO}_2$  should be  $\text{H}_2\text{CO}_3$ .
35. (10/28/05) p.264. In the table, the entries for  $\text{Cl}^-$  and  $\text{HCl}$  should not be italicized.
36. (11/17/06) p.267. In the last row of the third paragraph, the values  $9.0$  and  $4.7$  should be reversed.
37. (10/25/03) p.272. In the second line of the *Solution*, part *a*, replace “base” with “acid.”
38. (10/27/03) p.284. In part *b* of the answer to Example 5.10, the reference shown to Table 5.5 should actually be to Table 5.6.
39. (10/28/03) p.284. In part *b*, in the equation for  $\beta_{\text{PO}_4}$ , the value  $10^{-3}$  should be  $10^{-2}$ .
40. (10/28/03) p.285. In the table at the top of the page,  $\beta_{\text{NH}_3}$  at pH 9.25 (the last entry in the last column) should be  $1.73 \times 10^{-2}$ .
41. (10/28/03) p.286. In part *b* of the answer to Example 5.11, the reference shown to Table 5.5 should actually be to Table 5.6.
42. (10/28/07) p.288. Problem 1(a): Change “needed to adjust the pH of all three of these solutions to 8.0.” to “that was added to each of the solutions.”
43. (10/28/05) p.288. Problem 2(a)(vi):  $\text{p}K_{a1}$ ,  $\text{p}K_{a2}$ , and  $\text{p}K_{a3}$  should be  $3.13$ ,  $4.72$ , and  $6.33$ , respectively.
44. (2/13/03) p.290. In problem 9, the first reaction shown should be:

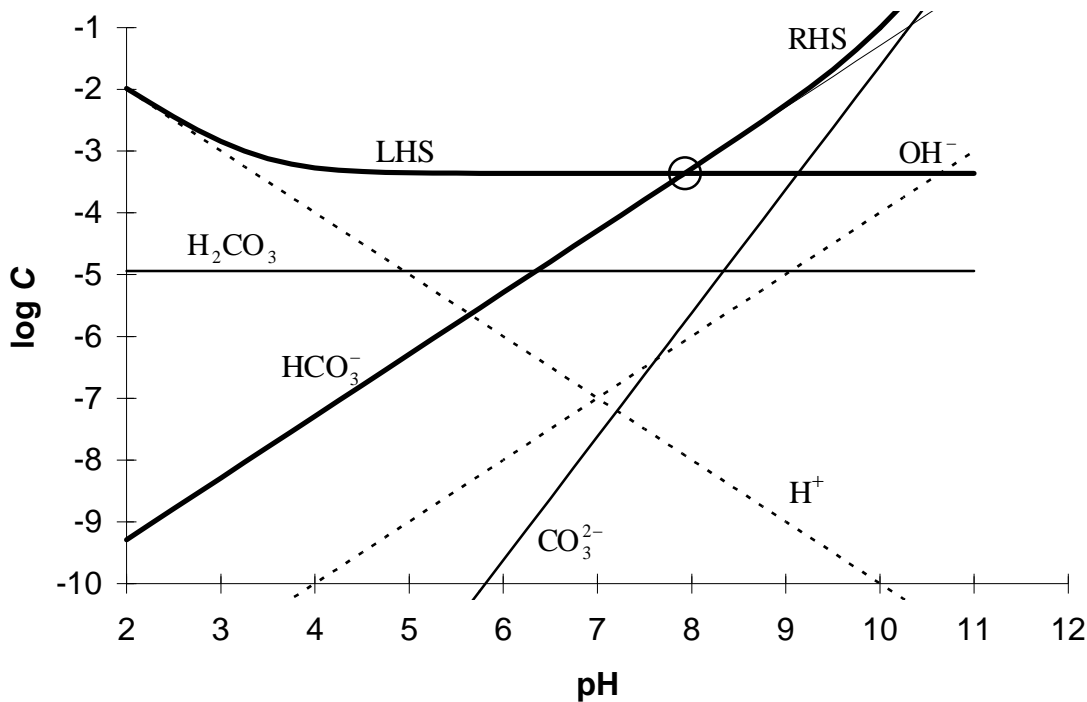


Part *b* of the question should be reworded as follows: What would the solution pH be if all the sulfite were destroyed by the second reaction, and then all the acetic acid that remained was destroyed by the first reaction?

45. (2/13/03) p.290. In problem 11, line 4, the word “strong” should be inserted before the word “acid.”
46. (11/08/04) p.292. In Problem 14, second paragraph, second sentence: replace “contains negligible  $\text{Ca}^{2+}$  and alkalinity” with “can be represented as a mixture of water,  $\text{H}_2\text{NOM}$ , and  $\text{NaCl}$ ”.
47. (10/31/03) p.299: In the chemical reaction shown at the bottom of the page, the coefficient 1 for  $\text{H}^+$  should be underlined.
48. (10/31/03) p.301: In the table near the top of the page, the heading **Stoichiometric Coefficient** should be centered over the three columns labeled  $\text{H}_2\text{O}$ ,  $\text{OH}^-$ , and  $\text{HAc}$ , and the underline under that heading should extend only over those three columns.
49. (11/02/06) p.310. In the Log K column of the first table near the bottom, change 4.13 to 3.17.
50. (11/17/06) p.317: The value in the final column, second row, should be  $1.00 \times 10^{-4}$ , not  $1.00 \times 10^{-3}$ .
51. (11/13/03) p.332. In the footnote to Table 7.2, change  $20^\circ\text{C}$  to  $25^\circ\text{C}$ . Make the same change in the copy of the table on p.643.
52. (2/7/03) p.334. In the fourth line of the caption for Figure 7.2, change “that concentration of  $\text{Cl}^-$  and” to “the concentration of  $\text{Cl}^-$  indicated, and”
53. (11/13/03) p.336: In the first equation in the solution to Example 7.3, in both places where  $^\circ\text{C}$  appears in the denominator of the fraction, it should be change to K (Kelvins).
54. (10/21/02) p.341. In the equation just above 7.22, the coefficient “2” preceding  $\{\text{HAc}\}$  should be deleted.
55. (2/7/03) p.342. The second paragraph in the Solution to Example 7.6 should begin, “Rather than write a charge balance...”
56. (11/10/03) p.347. In the PC table, the first two values in the right hand column should be  $2.96 \times 10^{-5}$  and  $4.44 \times 10^{-5}$ .
57. (11/13/06) p.347. The first and third equations below the PC table should be:

$$\begin{aligned} \text{TOT}_{\text{H}_{\text{in}}} &= 10^{-10.5} - 10^{-3.5} - 2.96 \times 10^{-5} - (2)(4.44 \times 10^{-5}) = -4.35 \times 10^{-4} \\ \{\text{H}^+\} + 4.35 \times 10^{-4} &= \{\text{OH}^-\} + \{\text{HCO}_3^-\} + 2\{\text{CO}_3^{2-}\} \end{aligned}$$

In the subsequent paragraph, the value of the equilibrium pH should be 7.96 (not 7.34), the value of  $\text{TOTCO}_3$  should be  $4.39 \times 10^{-4}$  (not  $1.29 \times 10^{-4}$ ), and the amount of  $\text{CO}_2(\text{g})$  that dissolves should be  $3.64 \times 10^{-4}$  ( $5.5 \times 10^{-5}$ ). The graph on p.348 should be replaced with the following one:



58. (11/10/03) p.348. In Equation (7.23), the subscript on the first  $\{\text{OH}^-\}$  in the equation should be changed from fii to fin.
59. (11/13/03) p.354: In the table at the bottom, the equilibrium concentration of  $\text{HCO}_3^-$  should be  $1.95 \times 10^{-3}$ .
60. (11/13/07) p.358: In problem 8a, replace the second sentence with the sentence: Consider  $\text{Ca}^{2+}$  to be a weak acid with  $\text{p}K_{a1} = 12.60$ .
61. (11/13/03) p.358: In problem 8c, the mass balance should state that the rate at which sulfur enters the column (moles of S per unit time), considering both inlet streams, equals the rate at which it leaves, considering both outlet streams, i.e.,  

$$(Q_{\text{gas,in}} c_{\text{S,gas,in}} + Q_{\text{aq,in}} c_{\text{S,aq,in}} = Q_{\text{gas,out}} c_{\text{S,gas,out}} + Q_{\text{aq,out}} c_{\text{S,aq,out}} .$$
62. (10/29/07) p.359. In Problem 9, part *b*, after the words *pH 4.5*, insert the phrase: *and that no  $\text{H}_2\text{S}$  enters or leaves the solution during the titration.*
63. (11/13/03) p.361: In Problem 16, line 3: change Example to Problem.
64. (11/21/03) p.368: In Table 8.2,  $\text{Log } \beta_3$  for  $\text{Hg}^{2+}$  should be 32.16, and  $\text{Log } * \beta_3$  should be  $-9.84$ . The same corrections are needed on the copy of Table 8.2 on p.644.
65. (11/22/04) p.375. In Table 8.3, the values in the  $\text{NH}_3$  column in the rows corresponding to  $\text{Zn}^{2+}$  should be 2.2, 4.5, 7.0, and 9.0 for  $\text{ZnL}$ ,  $\text{ZnL}_2$ ,  $\text{ZnL}_3$ , and  $\text{ZnL}_4$ , respectively. The same changes should be made in the copy of Table 8.3 on p.646.
66. (12/05/04) p.398. In Table 8.7, add the following entries to the table:  $\text{SiO}_2(s)$ ,  $\text{log } K_{s0} = -2.74$ ;  $\text{ZnO}(s)$ ,  $\text{log } K_{s0} = -16.12$ . Also,  $\text{Log } K_{s0}$  for Hematite ( $\alpha\text{-Fe}_2\text{O}_3$ ) should be  $-81.26$ ,

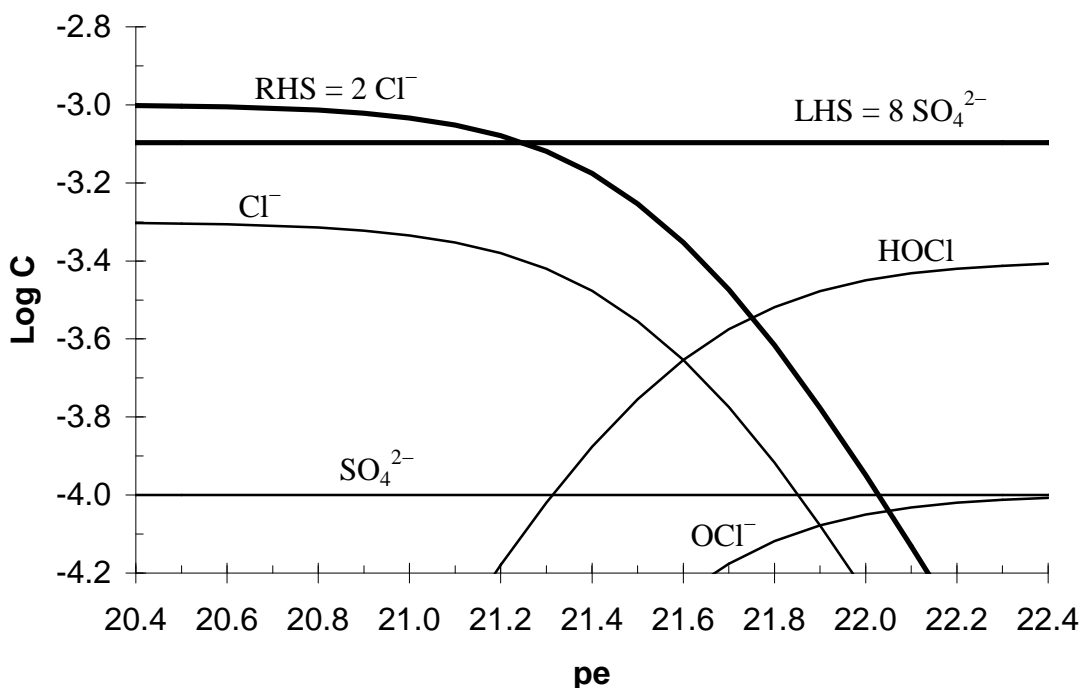
and Log  $K_{s0}$  for Hydroxyl apatite ( $\text{Ca}_5(\text{OH})(\text{PO}_4)_3(s)$ ) should be  $-58.2$ . The same changes should be made to the copy of Table 8.7 on p.647.

67. (12/04/03) p.418, 3<sup>rd</sup> line of final paragraph: change  $10^{-13.73}$  to  $10^{-14.73}$ .
68. (11/29/03) p.420, line 9: change Figure 8.10 to Figure 8.12.
69. (2/27/03) p.454. In problem 4, line 3, Cu should be  $\text{Cu}^{2+}$ . Also, in part *c*, add the words, “showing all species that are present at  $>10^{-6} M$ ” to the end of the question.
70. (2/25/03) p.455. In Problem 7, for Species B, the coefficient for  $\text{NH}_4^+$  should be 0, and the log K should be 6.35.
71. (12/16/05) p.455. In Problem 10, after  $\text{PO}_4\text{-P}$ , insert: (i.e.,  $\text{TOTPO}_4\text{-P}$ ). Similarly, after  $\text{NH}_4\text{-N}$ , insert: (i.e.,  $\text{TOTNH}_4\text{-N}$ ).
72. (12/06/05) p.456. In Problem 10, the chemical shown as  $\text{Fe}_2(\text{NH}_4)\text{PO}_4(s)$  should not have the ‘2’; it should be  $\text{Fe}(\text{NH}_4)\text{PO}_4(s)$ .
73. (12/05/04) p.456. In Problem 11, right before the last sentence, add: Ignore hydrolysis of  $\text{Ca}^{2+}$ .
74. (9/23/03) p.456. In Problem 13b, before the parenthetical remark about hydrolysis reactions, add the statement: Ignore formation of Al- $\text{SO}_4$  complexes.
75. (12/16/05) p.458. At the end of Problem 16c, add:  $K_{s0}$  for  $\text{ZnO}(s)$  is for the reaction  $\text{Zn}^{2+} + \text{H}_2\text{O} \leftrightarrow \text{Zn}^{2+} + 2 \text{OH}^-$ .
76. (3/5/03) p.459. In the second paragraph of Problem 19, replace the wording at the end of the problem, starting with the sentence that begins “Carry out the calculations...” as follows: Carry out the calculations twice, using first one and then the other of the following two assumptions. (1) The rain is in equilibrium with the atmosphere before striking the monument, but no more gases dissolve as the rain drips down the monument’s surface; (2) The rainwater is in continuous equilibrium with the atmosphere as the water drips.  
  
Also, at the end of the problem, add the following. Hint: for the systems that do not equilibrate continuously with the atmosphere, make a guess for the amount of solid that dissolves, and iterate on that guess until it is consistent with the charge balance.
77. (12/1/04) p.459. In Problem 20c, at the end of the first sentence, add:  $K_{s0} = 10^{-2.74}$ .
78. (12/2/03) p.473: in the solution to Example 9.4, part *a*, in the last line of text, delete the word ‘is’.
79. (12/10/03) p.487 and 499. At the bottom of Figures 9.4 and 9.5, the line for the  $\text{H}^+/\text{H}_2(g)$  system should say pH 10.5, not pH 7.

80. (12/2/03) p.500. In Table 9.5, entry #5, in the expression for  $\Delta pe$ , the final term should not have  $RT$  in the numerator; the expression should be as follows (note: the same correction is needed in the copy of Table 9.5 on page 652):

$$\Delta pe = \Delta pe^\circ - \frac{1}{n_e} \log Q$$

81. (12/2/03) p.501, lines 2-3: The term  $\bar{G}_e^-$  should be on one line.
82. (3/10/03) p.505. In the last equation on the page, above the final two paragraphs of text, the left hand side of the equation should be  $8pe^\circ(W)$ , not  $8pe^\circ$ .
83. (3/10/03) p.508. Figure 9.9 is missing curves for HOCl and  $OCl^-$ . The correct figure is shown below.



84. (12/22/06) p.518. Toward the end of the first full paragraph, in the expressions “ $pe > 3.8$ ” and “ $pe = 3.8$ ,” the values should be changed from 3.8 to  $-3.8$ .
85. (3/5/03) p.546. At the end of Problem 2, before the parenthetical remark, add the sentence: Consider HOCl,  $OCl^-$ , and  $Cl^-$  as the only significant Cl species.
86. (3/5/03) p.546. In Problem 3, paragraph 2,  $TOTHg$  should be  $TOTHg(II)$ .

87. **(3/10/03)** p.547. At the end of part a in Problem 6, add the sentence: Assume that the acid/ base reactions in the system reach equilibrium quickly.
88. **(12/19/01)** p.549. Add the following statement to problem 11, before the parenthetical note at the end: Ignore redox reactions of water.
89. **(4/28/05)** p.596. The fractions in Equations 10.47 and 10.48 should all be inverted. The same fractions appear in the bottom of Table 10.6 on p.604, and the same corrections should be made to them.
90. **(10/28/02)** p.604. The minus sign should be removed from the exponential argument in the equation for  $K_{A,int,o}$ .
91. **(4/15/05)** p.607. The third and fourth equations in the middle of the page are both missing a term equal to  $\{H^+\}^{-1}$  on the right-hand side. This term should appear in the middle of the equation, after the term  $\{A^{2+}\}$ .
92. **(12/05/04)** p.647. Add values of  $-25.55$  for  $\log K_{s0}$  of  $HgO(s)$  and  $-39.28$  for  $\log K_{s0}$  of  $Hg(CN)_2(s)$  to Table 8.7. Also,  $\text{Log } K_{s0}$  for Hematite ( $\alpha\text{-Fe}_2\text{O}_3$ ) should be  $-81.26$ , and  $\text{Log } K_{s0}$  for Hydroxyl apatite ( $Ca_5(OH)(PO_4)_3(s)$ ) should be  $-58.2$ .