“How do I know what printing I have?” Look at the reverse side of the title page of your Study Guide and Solutions Manual, where you see all sorts of publication information. On the last line, you will see a series of digits. These digits will end with the number of your printing. Thus, 10 9 8 7 6 5 4 3 2 1 is a first printing; 10 9 8 7 6 5 4 3 2 is a second printing; and 10 9 8 7 6 5 4 3 is a third printing.

All items marked with $^2$ were corrected in the second printing.
All items marked with $^3$ were corrected in the third printing.
All items marked with $^4$ will be corrected in the fourth printing.

Chapter 1
p. 11 $^3$

Figure SG1.5. In the figure, the part (b) antibonding MO and bonding MO $H_2$ should be $H_2^-$.

Chapter 2
p. 34 $^3$

Solution 2.26 (b), 3,4-dimethylhexane is another possible answer. [Credit: Sae Rome Choi, student, University of Notre Dame]

p. 37 $^3$

Solution 2.33 (b). Should read “Compound B is 3-ethyl-2-methylhexane.” [Credit: Erin Jonasson, University of Notre Dame]

p. 37 $^3$

Solution 2.34 (b). This answer has been updated to reflect the correction to 2.33 (b). The corrected display and changes to the text are shown in bold below:

(b) The ethyl group on carbon-4 has to be gauche to either the ethyl group or the isopropyl group on carbon-3. Because the isopropyl group is larger, the ethyl group is gauche to the other ethyl group in the most stable conformation.

The ambiguity in drawing the structure is that it has a mirror image, which is not the same, although it has the same energy. (The issue of mirror-image structures is considered in Chapter 6.) If you drew the mirror-image structure, it is equally correct. As noted in the solution to Problem 2.33(b), the name of this compound is 3-ethyl-2-methylhexane.

[Credit: Erin Jonasson, University of Notre Dame]

p. 39 $^3$

Solution 2.38 (b). Should read “…viewing down the C3–C4 bond.” [Credit: Bruce Ganem, Cornell University]
Chapter 3

p. 66

Solution 3.53. The figure and caption to which this problem references is missing. It is shown below.

![Figure SG3.2](image)

**Figure SG3.2.** Free-energy diagram to accompany the solution to Problem 3.53. The dication is destabilized by the two nearby positive charges. (The neutral compounds, are arbitrarily placed at the same energy for comparison purposes.)

Chapter 4

p. 84

Solution 4.8, parts (c) and (d) should be switched. Part (c) should begin “The prefix “cyclo”…” and part (d) should begin “The suffix “triene”…”.

p. 85

Solution 4.10 (a). Depending on which printing of the textbook you have, formula D may or may not be reasonable. The answer should read:

(a) A way to tell whether a formula is reasonable is to calculate its unsaturation number using Eq. 4.7 on text p. 144. A formula that gives a negative or fractional unsaturation number is not possible. Formula A cannot be a correct formula, because a compound containing only C, H, and an odd number of nitrogens must have an odd number of hydrogens. Formula C also could not be the formula of an organic compound, because the maximum number of hydrogens possible in a compound containing 10 carbons, 3 nitrogens, and any number of oxygens is 25. Formulas B (C_{10}H_{20}N_{2}O_{2}) and D (C_{10}H_{16}O_{2}) are both reasonable, and could be organic compounds.

An early printing of the text had a formula D that was the same as formula A (C,H,N), which would make it unreasonable.

p. 85

Solution 4.10 (b). There are nine isomeric alcohols with the given formula. The answer should read:

(b) There are nine isomeric alcohols and one ketone with the formula C_{4}H_{8}O. The first three alcohols are called enols and, as you will learn in Chapter 14, they are in equilibrium with their corresponding ketone or aldehyde forms.

Figure SG4.1. The curves are mislabeled; “reaction A” and “reaction B” should be switched. [Credit: Maggie Doyle, student, University of Notre Dame]

Solution 4.46. The answers to parts (b) and (d) should be switched. Part (b) should be (E)-4,4,-dimethyl-2-pentene and part (d) should be 4-methylcycloheptene. [Credit: Roslyn Joseph, student, University of Notre Dame]

Solution 4.52. The cis isomer of the second compound shown is also a correct answer. The updated display is shown below.

any ONE of these

propylcyclohexane

Solution 4.61 (c). The last line should read “…by between 14.2 and 6.6 kJ mol⁻¹”.

Figure SG4.6. The second value, between 2-methyl-1-butene and 2-methyl-2-butene should be −6.6 kJ mol⁻¹, not −14.2. The corrected figure is shown below.

Chapter 5

Solution 5.4 (d). In the product, the last carbon in the chain should be CH₃, not CH₂. [Credit: Leigh Campbell, student, University of Notre Dame]
p. 124 Solution 5.7 (d). In the product, the last carbon in the chain should be CH₃, not CH₂. [Credit: Madison McCracken, student, University of Notre Dame]

p. 124 Solution 5.5. The product of the first reaction, acid catalyzed hydration, has one too many carbons in it. The corrected display is below. [Credit: Karl Schlaht, student, University of Notre Dame]

p. 127 Solution 5.14. The answers to parts (a) and (b) should be switched. Part (a) is cis- or trans-4-octene and (b) is 1-methylecycloheptene [Credit: Jori Goldberg and Clare Hannon, students, University of Notre Dame]

p. 129 Solution 5.20 (a). There is an extra methyl group attached to the carbon in the radical initiator (it should look like the product of Eq. 5.50 in the book) and the product (product should be NC-CH(CH₃)). [Credit: Chloe Hemm and Kyle Moon, students, University of Notre Dame]

p. 134 Solution 5.32 (i). Hydrogenation of 3-ethyl-2-pentene (or 3-ethyl-1-pentene, not shown) would give the desired alkane.

Chapter 6

p. 154 Solution 6.10 (e). The units for the answer should be deg mL g⁻¹ dm⁻¹, not deg mL⁻¹ g⁻¹ dm⁻¹. [Credit: Erin Jonasson, University of Notre Dame]

p. 158 Solution 6.27. The four stereoisomers should be: (2Z,4S), (2E,4S), (2Z,4R), and (2E,4R). [Credit: Nick Rossiter, student, University of Notre Dame]

p. 161 Solution 6.40. Compounds D and E can be resolved into enantiomers. The explanations should be: “Compounds D and E can be resolved because they contain asymmetric carbons (the ones bearing the phenyl group in each).” [Credit: Lilia Escobedo, student, Cornell University]

p. 163 Solution 6.46 (a). The first line should read “(See the solution to Problem 6.45…”

Chapter 7

p. 173 Further Exploration 7.4. First line should read “(p. 114 of this manual).”, not 107.

p. 181 Solution 7.16 (a). At the top of page 181, the caption under puckered trans-1,3-dibromocyclobutane should read C–Br bond dipoles do not cancel. [Credit: Erin Jonasson, University of Notre Dame]

p. 189 Solution 7.41 (a,b). The structures are correct, but compounds D and C should be named as cyclopentanols, not cyclohexanols. [Credit: Erin Jonasson, University of Notre Dame]

p. 194
Solution 7.54 (a). The end of the second sentence should read “...whereas an anti-addition will lead to the observed 2S,3R product.,” not 2R,3R.

p. 195
Solution 7.55 (b). The second product should contain an OH group (circled, below), not a second Br. [Credit: Leigh Campbell, student, University of Notre Dame]

p. 203
Solution 7.69 (b). The last sentence of the paragraph should read “…unusual cyclic bromonium radical (similar to…”, not ion. In the display, the bromine should bear a “partial electron”, not a partial positive charge. The corrected display is shown below.

p. 204
Solution 7.72 (a). Line 7 in the first paragraph should read, “that of a methyl–hydrogen gauche-butane interaction be $DG^\circ(\text{gauche}) = 3.7 \text{ kJ mol}^{-1}$,” not 2.8. Using this value, the first equation should be:

$$DG^\circ(\text{eq}) = DG^\circ(B) - DG^\circ(A) = 8.4 - 7.4 + 3.7 + DG^\circ(\text{Me–Me}) - 17.6$$

And solving for $DG^\circ$ (Me–Me) then gives:

$$DG^\circ(\text{Me–Me}) = 14.9 \text{ kJ mol}^{-1}(3.6 \text{ kcal mol}^{-1})$$

p. 205
Solution 7.73 (b). The last paragraph should be:

“In Equation (2), two Ph–H diaxial interactions (13.2 kJ mol⁻¹) and a gauche-butane interaction (3.7 kJ mol⁻¹) on the left side are balanced against four methyl–hydrogen diaxial interactions on the right (14.8 kJ mol⁻¹). The overall $DG^\circ$ for equation (2) is therefore $14.8 - 16.9 = -2.1 \text{ kJ mol}^{-1}$."

Chapter 8

p. 215
Solution 8.28. The fourth structure, 3-methyl-1-butanol, has an extra hydrogen on carbon-3. The correct display should be as follows. [Credit: Alison Ou, student, Purdue University]

p. 220

Solution 8.47. This solution has been expanded for clarity:

“The structure of propofol is largely hydrocarbon-like, even though it contains a polar OH group, which is why it is insoluble in water. The lecithin/soybean oil mixture forms phospholipid vesicles. The propofol is incorporated into the vesicles near the aqueous interface so that the OH group can H-bond to solvent water and the apolar portion can interact with the apolar region of the vesicles.”

p. 220

Solution 8.51 (c). This solution has been expanded for clarity:

“As the hint suggests, the boiling point is a measure of the tendency of a molecule to escape from its liquid state. The solubility in water is a combination of the escaping tendency from the pure alcohol phase and solvation in the aqueous phase. Both of these factors work in the same direction. The tertiary alcohol has a greater escaping tendency and requires a less negative entropy of solvation in water.”

p. 221

Solution 8.52 (d). This solution has been expanded for clarity:

“As described in the solution to 8.51 (c), solubility in water is composed of two factors: escape of a molecule from its own liquid phase and solvation by water. Although 1-pentanol can be both a hydrogen bond donor and acceptor, this favorable interaction must be outweighed by the fact that the molecules are attracted to each other through hydrophobic interactions of the five-carbon alkyl chain. The relative boiling points tell us that the intrinsic escaping tendency of the ether from its own liquid phase is much greater than that of the alcohol. Even though the alcohol can donate hydrogen bonds, it seems that the escaping tendency is more important. Thus, diethyl ether, with its hydrogen bond-accepting ability, smaller alkyl chains, and lower boiling point, is more soluble in water.”
Chapter 9

p. 236  Figure SG9.1. The description of the lower curve should read “has smaller magnitude at longer times.” The corrected figure is shown below.

p. 247  Solution 9.46 (c). The text reference page is missing. It should refer to text p. 191.

p. 248  Solution 9.48 (a). The last sentence in the explanation should read, “The only one that gives only one chiral monochlorinated product and one achiral monochlorinated product is 2,3-dimethylbutane.” The structures are correct. [Credit: Daniel Staros, student, Bloomsburg University]

p. 248  Solution 9.52 (c). The answer should have one additional carbon than what is shown: Na⁺ OCH₂CH₂CH₂CH₂OCH₃ [Credit: Hannah Choset, student, Cornell University]

p. 263  Solution 9.87 (a). On the second line of the reaction mechanism, the carbon has one too many chlorines. \( \text{Cl}_2\text{C}^- \) should be \( \text{Cl}_2\text{C}^- \)

[Credit: Susan Li, student, University of Notre Dame]

Chapter 10

p. 271  Reaction Review II. B. 5. is incomplete. It should read as follows:
“Because all these methods have an \( \text{S}_\text{n}2 \) mechanism as their basis, alcohols with a significant amount of \( \beta \)-branching (that is, alkyl substituents at the \( \beta \)-position) will react more slowly or not at all, with one exception. The exception is \( \text{Ph}_3\text{PBr}_2 \), as described on p. 471, will react even with neopentyl alcohols.”

p. 284  Solution 10.33 (e). \( \text{H}^+ \) and \( \text{H}^- \) (and \( \text{H}^+ \) and \( \text{H}^- \)) are enantiotopic, not homotopic. The second sentence should read, “\( \text{H}^+ \) and \( \text{H}^- \) are also constitutionally equivalent and enantiotopic, as are \( \text{H}^+ \) and \( \text{H}^- \).” [Credit: Alexander Seed, Kent State University]

p. 289  Solution 10.49 (b). The reagent mentioned should be \( \text{Ph}_3\text{PBr}_2 \), not \( \text{PBr}_3 \).

p. 294  Solution 10.59 (f). This reaction proceeds by \( \text{E}_1 \), not \( \text{E}_2 \). The solution should read:
(f) Treatment of the alcohol with strong acid protonates the hydroxy group making it a good leaving group. Once the water leaves, there are two different but equivalent protons adjacent to the positively charged carbon. Since there is an equal opportunity to remove either one leading to one of two enantiomers, a racemic mixture of E1 elimination products is generated.

![Chemical structures](image)

[Credit: Albert Wang, student, Cornell University]

p. 295^3 Solution 10.61 (c). This part of the answer is incomplete; it doesn’t take into account the details given in the problem involving deuterium. The corrected answer is shown below.

(c) To solve this problem, first write out the reaction that occurs with deuterium-labeled alcohol:

\[ R-\overset{D}{C}-\overset{\delta}{O}\overset{\delta}{S}(CH_3)_2 \rightarrow R-\overset{D}{C}-D + H_3C-\overset{\delta}{S}-CH_2D \]

Since deuterium ends up incorporated into one of the methyl groups on sulfur, one of those hydrogens must have been removed at some point. Use triethylamine to remove a proton, generating an intermediate called a sulfur ylide. The sulfur ylide then can react intramolecularly to remove a deuterium from the nearby carbon, oxidizing that carbon, and eliminating dimethyl sulfide containing deuterium. The sulfur ultimately accepts electrons so it is oxidized, as noted in the solution to part (b).

![Chemical structures](image)

p. 297^2 Solution 10.64 (a). This reaction is two-electron oxidation, not one. The solution should read:

“Following the steps in Sec. 10.5A, we can balance the equation. First, we don’t need to add any water because no oxygens are involved. Next, we add one H\(^+\) to the right side to replace the one that was lost from serotonin. Finally, we add two electrons to the right side to cancel the plus charges. Thus, two electrons were lost, or, we can say this reaction is a two-electron oxidation.”

p. 299^3 Solution 10.67 (c). Initially, the phosphorus adds to the bromine, then the displaced CBr\(_3^-\) deprotonates the alcohol, as shown below.
Further Exploration 11.1. At the top of p. 305, the osmium in the second resonance structure should be neutral, not negative. The corrected display is shown below.

Solution 11.16 (d). The reference in this problem should be to Sec. 11.1, text p. 512.

Solution 11.27 (b). The structure of phenylacetaldehyde should be PhCH₂CH=O, not PhCH₂=O. [Credit: Jamieson Abrams, student, University of Notre Dame]

Solution 11.40 (d). In the last two structures, the lower ethoxy groups should be methyl groups. The corrected display is shown below.

Solution 11.45 (h,i). Corrected structures and/or names are shown below.

(h) \((\pm)-3\text{-ethoxy-3-methylhexane}\)

(i) \((\pm)-3\text{-methoxy-3-methylhexane}\)
p. 334

Solution 11.57. Compounds A and B are mislabeled, and should be switched. The corrected display is shown below.

![Chemical structure](image)

(3S,4S)-4-methoxy-3-methyl-1-pentene

compound A
(meso; therefore achiral and optically inactive)

compound B
(optically active)

p. 337

Solution 11.61 (l). The final reagent in the sequence should be HIO, not 1) O; 2) H2O.

Chapter 12

p. 352

Second to last paragraph. Should read “But Eq. SG12.4 states that…”.

p. 355

Solution 12.5. The answer should be 0.39, not −0.39.

p. 366

Solution 12.44 (c). The explanation given is inappropriate for this part, and should be ignored. The correct answer is shown by the mechanism below.

![Mechanism](image)

1-butyl radical
allyl cation

Chapter 13

p. 382

Solution 13.25. The first paragraph of this solution should read:

“The two protons in the 4.6–4.8 region are vinylic protons, and they are not chemically equivalent. Their very small splitting is consistent only with geminal (that is, H2CA) protons. Thus, we have the partial structure”

p. 388

Solution 13.40 (f). Ignore the first sentence. The second line, containing chemical shifts and integrations, can also be ignored because it is just a restatement from the problem and unnecessary for the solution. This solution should read simply as follows:

(f) The compound has one degree of unsaturation and a tert-butyl group. This, plus the requirement for two chlorines and a partial structure CH2—CH required by the splitting leaves only the following possibility:

(CH3)2C—CH2—CH=CCl2

1,1-dichloro-4,4-dimethyl-1-pentene

p. 394

Solution 13.52 (a). The structure is incorrect, and should be as is shown below. The explanation is correct.

δ 3.4 (triplet that disappears after D2O shake)
δ 3.8 (quartet that becomes a triplet after D2O shake)
δ 3.2 (singlet)
δ 3.1 (singlet)
δ 3.4 (triplet)

p. 397

Solution 13.58. The first paragraph at the top of the page should be replaced with the following, which contains a few minor changes (noted in bold).
“The two doublets centered at \( \delta \) 6.2 are assigned to the diene protons 1 and 2. These protons are split by each other, but not significantly by any other protons. (Coupling constants depend on dihedral angle, and the large splitting evidently suggests an anti relationship about the single bond.) The two resonances centered at \( \delta \) 4.9 are assigned to the geminal alkene protons 3 and 4. These two protons are diastereotopic, and are therefore chemically nonequivalent. Their splitting, although not expanded, is evidently the small splitting typical of geminal alkene protons (Table 13.3, text. p. 647). The multiplet just below \( \delta \) 4 is assigned to the \( \alpha \)-alcohol methane proton 6. We are given no information about a \( \text{D}_2\text{O} \) shake, so the proton 5 is not identified; it is probably within the complex pattern between \( \delta \) 1 and \( \delta \) 3. Within the inset on the right, the doublet integrating for three protons probably corresponds to a methyl group. The only \( \text{CH}_3\text{—CH} \) group are the methyl protons 8. In the inset, the doublet of doublets corresponds to six protons, which corresponds to the two diastereotopic methyl groups 9 and 10, each split by the adjacent methine hydrogen and having slightly different chemical shifts. The resonance at \( \delta \) 0.5 is due to an unsplit methyl group and must correspond to protons 7.”

p. 400
Solution 13.66 (c). The answer given is correct, but it should be calculated differently. It is calculated using the natural log equation for free energy, and given in kcal. The answer calculated using the log equation for free energy, and given in kilojoules, is shown below.

(c) One conformation is present in 3.39 times greater concentration than the other. The equilibrium constant, \( K_{eq} \), is the ratio of the two conformations, 3.39:1, or 3.39. Using this value, the temperature, \( T \), of 193 K (remember to convert Celsius to kelvins), and the gas constant of \( 8.314 \times 10^{-3} \text{kJ mol}^{-1} \text{K}^{-1} \), we can solve for \( \Delta G \).

\[
\Delta G = -2.3RT \log K_{eq} \\
= -2.3(8.134 \times 10^{-3} \text{kJ mol}^{-1} \text{K}^{-1})(193 \text{ K})\log 3.39 \\
= -1.96 \text{ kJ mol}^{-1}
\]

Chapter 14
p. 408
Solution 14.3 (d). The correct answer: \((E)\)-7-methoxy-3-propyl-5-hepten-1-yne

p. 416
Solution 14.33 (h). The synthesis shown gives trans-5-decene. The corrected synthesis, giving trans-3-decene is:

![trans-3-decene diagram]

[Credit: Katie Adlaka, student, University of Notre Dame]

Chapter 15
p. 442
Solution 15.31 (c) is missing. It should be as follows. [Credit: Madison McCracken, student, University of Notre Dame]

(c) Both ions have two resonance structures. However, the ion on the right (ion \( B \) below) is more stable because one of its resonance contributors is a secondary carbocation, whereas both contributors for the ion on the right (ion \( A \) below) are primary carbocations.
p. 450

Solution 15.55. The correct answer is as follows:

The energy difference between the two waves can be calculated using Eq. 15.3. The 109 term at the end of the solution is to convert the difference in reciprocal wavelengths from nm to m.

\[
\Delta E = \frac{hc}{\lambda_1} - \frac{hc}{\lambda_2} = \frac{hc}{\lambda_1} \left(1 - \frac{1}{\lambda_2/\lambda_1}\right) = (3.99 \times 10^{-13} \text{kJ mol}^{-1} \text{s})(3 \times 10^8 \text{ m s}^{-1}) \left(\frac{1}{488} - \frac{1}{510}\right)
\]

\[
= (12 \times 10^{-5} \text{ kJ mol}^{-1})(8.8 \times 10^{-5} \text{ nm}^{-1})(10^8 \text{ nm m}^{-1}) = 10.6 \text{ kJ mol}^{-1}
\]

p. 458

Solution 15.71. The 1,4-addition product is missing a carbon. The correct display is below.

[H2C=CH-CH=CH2 → H2C—CH—CH=CH2 + ClCH2—CH=CH2—Cl]

1,4-addition product

1,2-addition product

Chapter 16

p. 476

Solution 16.2. Parts (f) and (h) are should be switched; i.e. (f) should be benzyl methyl ether, and (h) should be o-cresol.

p. 481

Solution 16.16. The tert-butyl groups in the last two structures should be (CH3)3C—, not (CH3)C—. [Credit: Katie Adlaka, student, University of Notre Dame]

p. 491

Solution 16.43 (g). The name of the product should be 2,6-dibromo-4-nitrotoluene, not 2,6-dibromo-1-nitrotoluene. [Credit: AJ Lepore, PhD student, University of Notre Dame]

p. 493

Solution 16.45 (d). The final structure is incorrect, the nitro group should be ortho to the phenyl ring and para to the methoxy group. The correct display is shown below. [Credit: Leigh Campbell, student, University of Notre Dame]

Chapter 17

p. 538

Solution 17.47. Part (e) should be deleted, and part (f) should be the answer to part (e).
Chapter 18

p. 550 Reaction Review I.A.1. The alkyne in the product has an extra H on the left carbon.

p. 575 Solution 18.40 (b). The second product is incorrect. The two products should be:

![Chemical structures](image)

[Credit: Corinne O'Connor, student, University of Notre Dame]

p. 579 Solution 18.49 (b). The benzyl alcohol structure is missing double bonds. The corrected display is:

![Chemical structures](image)

Chapter 19

p. 646 Solution 19.52 (m). The final product should contain CH₃, not CD₃:

![Chemical structure](image)

p. 646 Solution 19.69 (b) is missing. It should be as follows.

(b) Allow benzyl phenyl ketone to react with LiAlD₄.

![Chemical reaction](image)

p. 657 Solution 19.70 (c). The corrected solution is:

(c) Compound A exhibits a very weak carbonyl stretch in IR because very little of it is in the aldehyde form; rather, the molecule exists largely as a cyclic hemiacetal.

![Chemical structures](image)

Chapter 20

p. 689 Solution 20.51 (a). In the last step, the reference over the arrow (Eqs. 19.18a–b) is incorrect and should be ignored. The correct reference is in the solution text: Eqs. 19.20a–b.
Chapter 22

p. 797\textsuperscript{4} Solution 22.64 (a). The second structure in part (b), shown below, should be associated with part (a).

\[
\begin{align*}
\text{CH}_3\text{C} & \quad \text{O} \\
\text{O} & \quad \text{C} \quad \text{CCH}_3 \\
\text{Ph} & \\
\text{conjugate-base anion} & \\
\text{of the most acidic compound} &
\end{align*}
\]

p. 797\textsuperscript{4} Solution 22.64 (b). Only the first structure (shown below) should be associated with part (b). The second structure belongs with part (a).

\[
\begin{align*}
\text{H}_2\text{C} & \quad \text{=} \quad \text{CHCHCCH}_3 \\
\text{conjugate-base anion} & \\
\text{of the most acidic compound} &
\end{align*}
\]

p. 801\textsuperscript{4} Solution 22.74 (c). In the first step, the reference over the arrow (Problem 22.63) is incorrect and should be ignored. The correct reference is in the solution text: Problem 22.73.

Chapter 23

p. 840\textsuperscript{4} Solution 23.8 is missing. It should be:

23.8 From Table 23.1, text p. 1190, we see that the basicity order is as follows:

\[A < B < C\]

The basicities of all these amines are reduced by resonance interaction of the nitrogen unshared electron pair with the ring. The electron-withdrawing polar effect of the nitro group lowers basicity further, and resonance interaction of the nitrogen unshared pair with the \(p\)-nitro group stabilizes \(p\)-nitroaniline and lowers its basicity even more. (Resonance structures depicting this interaction are shown in the solution to Problem 23.3(a) on p. 838 of this manual.)

[Credit: Maeve Flatley, student, University of Notre Dame]

p. 849\textsuperscript{4} Solution 23.35 is mislabeled as 23.29. The solution given is correct.

Chapter 25

p. 920\textsuperscript{2} Solution 25.1b. Should be \textit{S-isopropyl butanethioate}.

p. 921\textsuperscript{2} Solution 25.10. The text is irrelevant, and can be ignored. The reaction mechanism is correct.

p. 924\textsuperscript{2} Solution 25.15a. The text is irrelevant, and can be ignored. The reaction mechanism is correct.

p. 926\textsuperscript{2} Solution 25.19. The answer is incorrect. It should be \(-48.29 \text{ kJ/mol}\). The solution should read as follows:

If the concentrations of ATP, ADP, and phosphate are all 0.001 mM, then by Eq. 25.37 on text p. 1318, \(\Delta G^\circ = -48.29 \text{ kJ mol}^{-1}\) (see Study Problem 25.1 for a similar example).

p. 930\textsuperscript{2} Solution 25.29. The solution has been expanded. After the reaction mechanisms, additional explanation is as follows:

“Now consider the final part of the question. Sulfonate ions are much less basic than carboxylate ions, and are therefore better leaving groups than carboxylate ions, which is why the nucleophile reacts with the methyl group in reaction (a) and with the carbonyl in reaction (b). For reaction (c), the reaction could occur at either phosphorus (Sec. 25.7A) or the methyl group (Sec. 25.7C). Since we know that the isotope is
incorporated into compound $F$, we could argue that steric interference of the isopropyl groups precludes reaction at the phosphorus, and reaction at the methyl carbon is preferred.”

Solution 25.30. The mechanism has been corrected, and is shown below:

\[
\begin{align*}
\text{CH}_3\text{O}-\text{PO(O)}\text{CH}_3 + \text{H}_2\text{O} &\xrightarrow{\text{H}_2\text{O}^+} \text{CH}_3\text{O}-\text{PO(O)}\text{CH}_3 + \text{H}_2\text{O}^+ \\
&\xrightarrow{\text{H}^+} \text{CH}_3\text{O}-\text{PO}^+ \text{O} + \text{CH}_3\text{OH} \\
\end{align*}
\]

Solution 25.32. The explanation has been revised for clarity, and should read as follows:

“Nitrate ion can react with hydroxide to form orthonitrate, but the reaction is unfavorable. Nitrate ion is stabilized by resonance, which distributes the negative charge around to all three oxygen atoms equally. After reaction with hydroxide at the nitrogen, the product is very unstable for a few reasons. First, the resonance of the nitrate ion is lost—it is tetrahedral and the three oxygens bear three formal negative charges because no delocalization is possible. Also, its formation is unfavorable, because approach of the hydroxide is repelled by the nearby negative charges on the oxygens. Additionally, the product has a 2− charge, with negative charges localized on three oxygens. Finally, the three negative charges are pushed closer together in a tetrahedral arrangement than in the trigonal planar nitrate ion, further destabilizing the product.”

Solution 25.38. The solution for this problem has been corrected to match the corrected wording of the problem in the text, and should read as follows:

“As noted in Sec. 25.5A, thioesters are about as reactive as the corresponding oxygen esters, that is, not very reactive. At pH = 7, hydrolysis can proceed only with water, which is not a very good nucleophile, and the rate of the reaction is very slow. At pH = 10, hydroxide is present, and it is a much more reactive nucleophile than water. Additionally, after reaction at the carbonyl and expulsion of the leaving group, CoASH reacts with the acetic acid which drives the equilibrium to the right (see Eq. 25.3, text p. 1291, and Sec. 21.7A, text p. 1061). Therefore, $\Delta G^\circ$ would be more negative at pH = 11, and the reaction would be more favorable.”

Solution 25.39b. The text in this part is irrelevant, and can be ignored. The reaction mechanism is correct.