SOLUTIONS

Chapter 1

1. (a)

(b)

(c)

(d)

(e)

(f)

2. The functional groups are identified below.

Vitamin C

Nicotinic acid (niacin)

Coenzyme Q
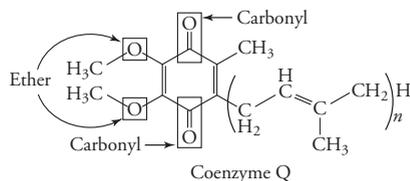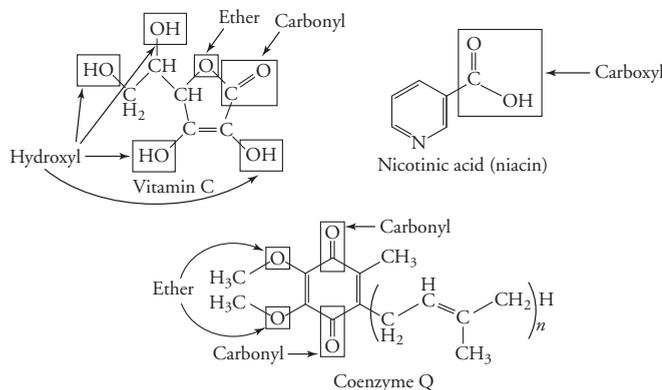
3. Amino acids, monosaccharides, nucleotides, and lipids are the four types of biological small molecules. Amino acids, monosaccharides, and nucleotides can form polymers of proteins, polysaccharides, and nucleic acids, respectively.

4. (a) *N*-acetylglucosamine is a monosaccharide.
(b) CMP is a nucleotide.
(c) Homocysteine is an amino acid.
(d) Cholesteryl ester is a lipid.

5. (a) Mainly C and H plus some O
(b) C, H, and O
(c) C, H, O, and N plus small amounts of S

6. It is a lipid (it is actually lecithin). It is mostly C and H, with relatively little O and only one N and one P. It has too little O to be a carbohydrate, too little N to be a protein, and too little P to be a nucleic acid.

7. (a) You should measure the nitrogen content, since this would indicate the presence of protein (neither lipids nor carbohydrates contain nitrogen).
(b) You could add the compound that contains the most nitrogen, compound B, which is melamine. (Melamine is a substance that has been

added to some pet foods and milk products from China so that they would appear to contain more protein. Melamine is toxic to pets and children.)
(c) Compound C is an amino acid, so it would already be present in protein-containing food.

8. A diet high in protein results in a high urea concentration, since urea is the body's method of ridding itself of extra nitrogen. Nitrogen is found in proteins but is not found in significant amounts in lipids or carbohydrates. A low-protein diet provides the patient with just enough protein for tissue repair and growth. In the absence of excess protein consumption, urea production decreases, and this puts less strain on the patient's weakened kidneys.

9. All amino acids have carboxylate groups. All have primary amino groups except for proline, which has a secondary amino group.

10. The carbon marked with an asterisk is chiral. This means that alanine has two possible enantiomers, or mirror-image isomers.
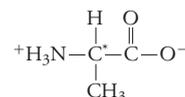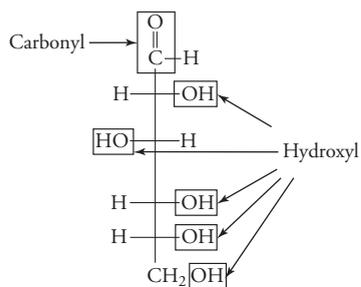

11. Asn has an amido group and Cys has a sulfhydryl group.

12. Two hydrogen atoms and one oxygen atom are lost when Asn and Cys form a dipeptide. This is an example of a condensation reaction. The carboxylate functional group on the Asn is lost and the amino functional group on the Cys is lost. An amido group is formed.
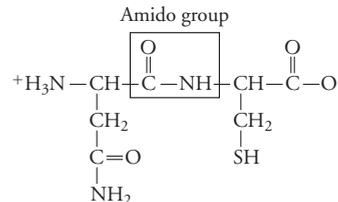
13.

14. (a) Fructose has the same molecular formula, $C_6H_{12}O_6$, as glucose.
(b) Fructose is a ketone, whereas glucose is an aldehyde.

15. Uracil has a carbonyl functional group, whereas cytosine has an amino functional group.

16. Nucleotides consist of a five-carbon sugar, a nitrogenous ring, and one or more phosphate groups linked covalently together.

17. As described in the text, palmitate and cholesterol are highly nonpolar and are therefore insoluble in water. Both are highly aliphatic. Alanine is water soluble because its amino group and carboxylate group are ionized, which render the molecule "saltlike." Glucose is also water soluble because its aldehyde group and many hydroxyl groups are able to form hydrogen bonds with water.

18. Glucose has several hydroxyl groups and is a polar molecule. As such, it will have difficulty crossing the nonpolar membrane. The 2,4-dinitrophenol molecule consists of a substituted benzene ring and has greater nonpolar character. Of the two molecules, the 2,4-dinitrophenol will traverse the membrane more easily.

19. DNA forms a more regular structure because DNA consists of only four different nucleotides, whereas proteins are made up of as many as 20 different amino acids. In addition, the 20 amino acids have much more individual variation in their structures than do the four nucleotides. Both of these factors result in a more regular structure for DNA. The cellular role of DNA relies on the *sequence* of the nucleotides that make up the DNA, not on the overall shape of the DNA molecule itself. Proteins, on the other hand, fold into unique shapes, as illustrated by endothelin in Figure 1-4. The ability of proteins to fold into a wide variety of shapes means that proteins can also serve a wide variety of biochemical roles in the cell. According to Table 1-2, the major roles of proteins in the cell are to carry out metabolic reactions and to support cellular structures.

20. Polysaccharides serve as fuel-storage molecules and can also serve as structural support for the cell.

21. The pancreatic amylase is unable to digest the glycosidic bonds that link the glucose residues together in cellulose. Figure 1-6 shows the structural differences between starch and cellulose. Pancreatic amylase binds to starch prior to catalyzing the hydrolysis of the glycosidic bond; thus, the enzyme and the starch must have shapes that are complementary. The enzyme would be unable to bind to the cellulose, whose structure is much different from that of starch.

22. Cellulose cannot be digested in mammals and therefore the energy yield is 0 kilocalories per gram. Although both starch and glycogen are polymers of glucose, the glucose residues are linked together differently in the two molecules and pancreatic amylase is unable to hydrolyze the glycosidic bonds (see Solution 21). Cellulose provides no energy to the diet but is an important component of the diet as fiber.

23. A positive entropy change indicates that the system has become more disordered; a negative entropy change indicates that the system has become more ordered.
  (a) negative   (b) positive
  (c) positive   (d) positive
  (e) negative

24. (a) decrease
  (b) increase

25. The polymeric molecule is more ordered and thus has less entropy. A mixture of constituent monomers has a large number of different arrangements (like the balls scattered on a pool table) and thus has greater entropy.

26. Entropy increases as the reactants (7 molecules) are converted to products (12 molecules).

27. The dissolution of ammonium nitrate in water is a highly endothermic process, as indicated by the positive value of ΔH. This means that when ammonium nitrate dissolves in water, the system absorbs heat from the surroundings and the surroundings become cold. The plastic bag containing the ammonium nitrate becomes cold and can be used as a cold pack to treat an injury.

28. The dissolution of calcium chloride in water is a highly exothermic process, as indicated by the negative value of ΔH. This means that when calcium chloride dissolves in water, the system loses heat to the surroundings and the surroundings become warm. The plastic bag holding the calcium chloride solution becomes warm and can be used as a hot pack by the hiker at cold temperatures.

29. First, calculate ΔH and ΔS, as described in Sample Calculation 1-1:
$$\Delta H = H_B - H_A$$
$$\Delta H = 60 \text{ kJ} \cdot \text{mol}^{-1} - 54 \text{ kJ} \cdot \text{mol}^{-1}$$
$$\Delta H = 6 \text{ kJ} \cdot \text{mol}^{-1}$$
$$\Delta S = S_B - S_A$$
$$\Delta H = 43 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1} - 22 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$$
$$\Delta H = 21 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$$
  (a) $\Delta G = (6000 \text{ J} \cdot \text{mol}^{-1}) - (4 + 273 \text{ K})(21 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1})$
   $\Delta G = 180 \text{ J} \cdot \text{mol}^{-1}$

The reaction is not favorable at 4°C.
  (b) $\Delta G = (6000 \text{ J} \cdot \text{mol}^{-1}) - (37 + 273 \text{ K})(21 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1})$
   $\Delta G = -510 \text{ J} \cdot \text{mol}^{-1}$
The reaction is favorable at 37°C.

30. $0 > 15,000 \text{ J} \cdot \text{mol}^{-1} - (T)(51 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1})$
$-15,000 > -(T)(51 \text{ K}^{-1})$
$15,000 < (T)(51 \text{ K}^{-1})$
$294 \text{ K} < \text{T}$
The reaction is favorable at temperatures of 21°C and higher.

31. $0 > -14.3 \text{ kJ} \cdot \text{mol}^{-1} - (273 + 25 \text{ K})(\Delta S)$
$14.3 \text{ kJ} \cdot \text{mol}^{-1} > -(273 + 25 \text{ K})(\Delta S)$
$-48 \text{ J} \cdot \text{mol}^{-1} > \Delta S$
ΔS could be any positive value, or it could have a negative value smaller than $-48 \text{ J} \cdot \text{mol}^{-1}$.

32. $-63 \text{ kJ} \cdot \text{mol}^{-1} = \Delta H - (273 + 25 \text{ K})(190 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1})$
$\Delta H = -63 \text{ kJ} \cdot \text{mol}^{-1} + 56.6 \text{ kJ} \cdot \text{mol}^{-1}$
$\Delta H = -6.4 \text{ kJ} \cdot \text{mol}^{-1}$

The reaction is exothermic.

33. Process (d) is never spontaneous.

34. (a) Because the rubber band becomes cooler, it is absorbing heat. Therefore, its change in enthalpy is positive.
  (b) In order for ΔG to be negative (a spontaneous process), the entropy change must negative so that it can compensate for an unfavorable (positive) change in enthalpy.

35. The dissolution of urea in water is an endothermic process and has a positive ΔH value. In order to be spontaneous, the process must also have a positive ΔS value in order for the free energy change of the process to be negative. Solutions have a higher order of entropy than the solvent and solute alone.

**36.** (a) The reaction is exothermic because the value of ΔH is negative.
  (b) $\Delta G = \Delta H - T \Delta S$
   $-17200 \text{ J} \cdot \text{mol}^{-1} = -9500 \text{ J} \cdot \text{mol}^{-1} - (310 \text{ K})(\Delta S)$
   $\Delta S = 25 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$

The positive value of ΔS indicates that the reaction proceeds with an increase in entropy.
  (c) The ΔH term makes a greater contribution to the ΔG value. This indicates that the reaction is spontaneous largely because the reaction is exothermic.
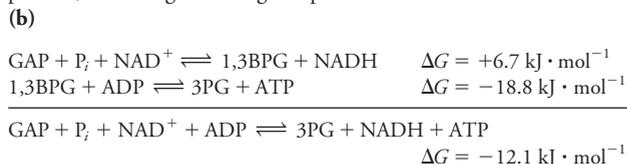
37. (a) The conversion of glucose to glucose-6-phosphate is not favorable because the ΔG value for the reaction is positive, indicating an endergonic process.
  (b) If the two reactions are coupled, the overall reaction would be the sum of the two individual reactions. The ΔG value would be the sum of the ΔG values for the two individual reactions.

ATP + glucose $\rightleftharpoons$ ADP + glucose-6-phosphate
$$\Delta G = -16.7 \text{ kJ} \cdot \text{mol}^{-1}$$
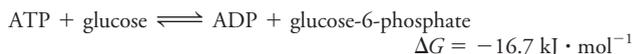
Coupling the conversion of glucose to glucose-6-phosphate with the hydrolysis of ATP has converted an unfavorable reaction to a favorable reaction. The ΔG value of the coupled reaction is negative, which indicates that the reaction as written is favorable.

38. (a) The reaction is not favorable because the ΔG value for the reaction is positive, indicating an endergonic process.
 (b)

GAP + P$_i$ + NAD$^+$ $\rightleftharpoons$ 1,3BPG + NADH	$\Delta G = +6.7 \text{ kJ} \cdot \text{mol}^{-1}$
1,3BPG + ADP $\rightleftharpoons$ 3PG + ATP	$\Delta G = -18.8 \text{ kJ} \cdot \text{mol}^{-1}$

GAP + P$_i$ + NAD$^+$ + ADP $\rightleftharpoons$ 3PG + NADH + ATP
$$\Delta G = -12.1 \text{ kJ} \cdot \text{mol}^{-1}$$

The coupled reaction is spontaneous because the ΔG value is negative.

**39.** C (most oxidized), A, B (most reduced)

40. (a) reduction
  (b) oxidation

41. (a) oxidized (b) oxidized
(c) oxidized (d) reduced

42. (a) oxidizing agent (b) oxidizing agent
(c) oxidizing agent (d) reducing agent

43. (a) Palmitate's carbon atoms, which have the formula —CH_2—, are more reduced than CO_2, so their reoxidation to CO_2 can release free energy.
(b) Because the —CH_2— groups of palmitate are more reduced than those of glucose (—HCOH—), their conversion to the fully oxidized CO_2 would be even more thermodynamically favorable (have a larger negative value of ΔG) than the conversion of glucose carbons to CO_2. Therefore, palmitate carbons could provide more free energy than glucose carbons.

44. The complete oxidation of stearate to CO_2 yields more energy because 17 of the 18 carbons of stearate are fully reduced. The conversion of these carbons to CO_2 provides more free energy than some of the carbons of α-linolenate, which participate in double bonds and are therefore already partially oxidized.

45. The experiment was significant because it demonstrated that it was possible to synthesize the building blocks of biological macromolecules (amino acids, carbohydrates, and nucleic acids) using only inorganic gases as starting materials and lightning as an energy source, that is, the conditions that most likely existed in the prebiotic world.

46. The first biological molecules would have had to polymerize, and they would have had to find some way to make copies of themselves.

47. Morphological differences, which are useful for classifying large organisms, are not useful for bacteria, which often look alike. Furthermore, microscopic organisms do not leave an easily interpreted imprint in the fossil record, as vertebrates do. Thus, molecular information is often the only means for tracing the evolutionary history of bacteria.

48. It is difficult to envision how a single engulfment event could have given rise to a stable and heritable association of the eukaryotic host and the bacterial dependent within a single generation. It is much more likely that natural selection gradually promoted the interdependence of the cells. Over many generations, genetic information supporting the association would have become widespread.

49. (a) H15 and H7 are closely related, as are H4 and H14.
(b) H4 and H14 are most closely related to H3

50.
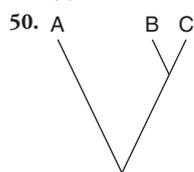
Chapter 2

1. The water molecule is not perfectly tetrahedral because the electrons in the nonbonding orbitals repel the electrons in the bonding orbitals more than the bonding electrons repel each other. The angle between the bonding orbitals is therefore slightly less than 109°.

2. Because the partial negative charges are arranged symmetrically (and the shape of the molecule is linear), the molecule as a whole is not polar.
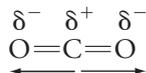

3. Ammonia is polar because it has one unshared electron pair. Its shape is trigonal pyramidal, and the molecule is not symmetrical. Nitrogen is more electronegative than hydrogen, so partial negative charges reside on the nitrogen and partial positive charges on the hydrogens.
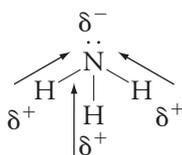

4. Water has the highest melting point because each water molecule forms hydrogen bonds with four neighboring water molecules, and hydrogen bonds are among the strongest intermolecular forces. Ammonia is also capable of forming hydrogen bonds, but they are not as strong (due to the electronegativity difference between hydrogen and nitrogen). Methane cannot form hydrogen bonds; the molecules are attracted to their neighbors only via weak London dispersion forces.

5. The arrows point toward hydrogen acceptors and away from hydrogen donors.
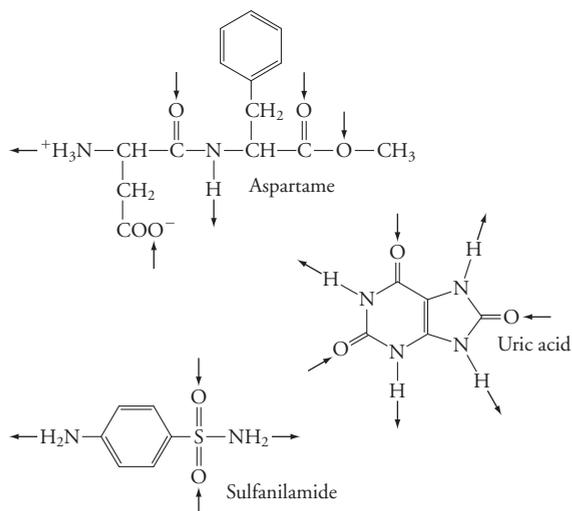
6. Compound A does not form hydrogen bonds (the molecule has a hydrogen bond acceptor but no hydrogen bond donor). Compounds B and C form hydrogen bonds as shown because each molecule contains at least one hydrogen bond donor and a hydrogen bond acceptor. The molecules in D do not form hydrogen bonds with each other, whereas the molecules in E do because ammonia has a hydrogen bond donor and diethyl ether has a hydrogen bond acceptor.
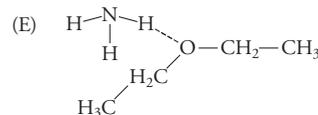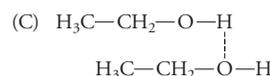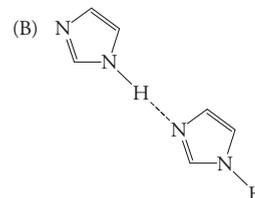
7. (a) van der Waals forces (dipole–dipole interactions)
(b) Hydrogen bonding
(c) van der Waals forces (London dispersion forces)
(d) Ionic interactions

8. (a) H < C < N < O < F
(b) The greater an atom's electronegativity, the more polar its bond with H and the greater its ability to act as a hydrogen bond acceptor. Thus, N, O, and F, which have relatively high electronegativity, can form hydrogen bonds, whereas C, whose electronegativity is only slightly greater than hydrogen's, cannot.

9. From the highest melting point to the lowest melting point: C, B, E, A, D. Compound C (urea, melting point 133°C) has three functional groups that can serve as hydrogen donors and/or acceptors. Compound B (acetamide, melting

point 80.16°C) has one less —NH group than Compound C and therefore forms fewer hydrogen bonds. Compound E (propionaldehyde, melting point −80°C) has one functional group that can serve as a hydrogen bond acceptor, but it has no donors, so dipole–dipole forces are the strongest intermolecular forces in a sample of this compound. Compound A (methyl ethyl ether, melting point −113°C) also has one functional group that can serve as a hydrogen bond acceptor (it has no donors), but it has hydrocarbon portions that interact with one another via London dispersion forces. Compound D (pentane, melting point −139.67°C) is nonpolar and experiences only London dispersion forces, so it has the lowest melting point in the group.

10. Compound D is completely nonpolar and cannot form hydrogen bonds, so it will most likely be insoluble in water. Compounds E, B, and A can form hydrogen bonds with water, but these molecules also have hydrocarbon portions that will not interact with water favorably, so they will be only slightly soluble in water. Compound C forms many hydrogen bonds with water and is likely to be very soluble in water.

11. Aquatic organisms that live in the pond are able to survive the winter. Since the water at the bottom of the pond remains in the liquid form instead of freezing, the organisms are able to move around. The ice on top of the pond also serves as an insulating layer from the cold winter air.

12. Water is unique in that its liquid form is more dense than its solid form. The weight of the skater puts pressure on the thin blade of the ice skate. The ice melts under the blade because of this increased pressure. A higher pressure favors the liquid form of water over the solid form because the liquid form is more dense and takes up less volume.

13. The positively charged ammonium ion is surrounded by a shell of water molecules that are oriented so that their partially negatively charged oxygen atoms interact with the positive charge on the ammonium ion. Similarly, the negatively charged sulfate ion is hydrated with water molecules oriented so that the partially positively charged hydrogen atoms interact with the negative charge on the sulfate anion. (Not shown in the diagram is the fact that the ammonium ions outnumber the sulfate ions by a 2:1 ratio. Also note that the exact number of water molecules shown is unimportant.)
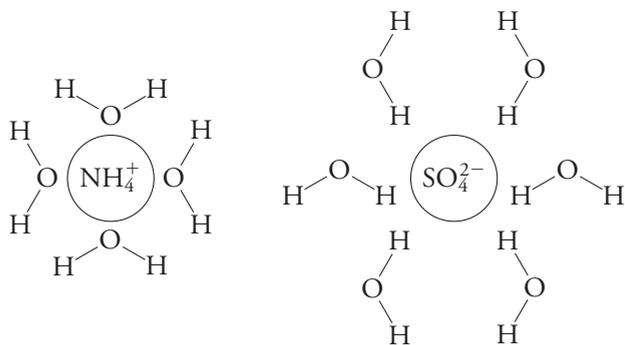
14. Structure A depicts a polar compound, while structure B depicts an ionic compound similar to a salt like sodium chloride. This is more consistent with glycine's physical properties as a white crystalline solid with a high melting point. While structure A could be water soluble because of its ability to form hydrogen bonds, the high solubility of glycine in water is more consistent with an ionic compound whose positively and negatively charged groups are hydrated in aqueous solution by water molecules.

15. (a) Surface tension is defined as the force that must be applied to surface molecules in a liquid so that they may experience the same forces as the molecules in the interior of the liquid. Water's surface tension is greater than ethanol's because the strength and number of water's intermolecular forces (hydrogen bonds) are both greater. Ethanol's —OH group also forms hydrogen bonds, but the hydrocarbon portion of the molecule cannot interact favorably with water, and weaker London dispersion forces form instead.
(b) The kinetic energy of the water molecules increases when temperature increases. Intermolecular forces are weaker in strength as a consequence of the increased molecular motion. Because surface tension increases when the strength of intermolecular forces increases, as described in part (a), surface tension decreases when temperature increases.

16. The waxed car is a hydrophobic surface. To minimize its interaction with the hydrophobic molecules (wax), each water drop minimizes its surface area by becoming a sphere (the geometrical shape with the lowest possible ratio of surface to volume). Water does not bead on glass, because the glass presents a hydrophilic surface with which the water molecules can interact. This allows the water to spread out.

17. Methanol, which has the highest dielectric constant, would be the best solvent for the cationic NH_4^+. The polarity of the alcohols, which all contain a primary —OH group, varies with the size of the hydrocarbon portion. 1-Butanol, with the largest hydrophobic group, is the least polar and therefore has the highest dielectric constant.

18. Isopropyl alcohol has intermolecular forces that are weaker and less numerous than those found in water. The isopropyl alcohol used to sponge off sweat would evaporate more quickly from the body than water, since less energy is required to convert the alcohol from the liquid to the gaseous phase.

19. (a) First, calculate the number of moles of protein using Avogadro's number:

$$1000 \text{ molecules} \times \frac{1 \text{ mole}}{6.02 \times 10^{23} \text{ molecules}} = 1.66 \times 10^{-21} \text{ moles}$$

Next, calculate the volume of the cell, expressing r in centimeters:

$$\text{volume} = \frac{4\pi r^3}{3} = \frac{4\pi(5 \times 10^{-5} \text{ cm})^3}{3} = 5.2 \times 10^{-13} \text{ cm}^3$$

Since $1 \text{ cm}^3 = 1 \text{ mL}$, the volume is $5.2 \times 10^{-13} \text{ mL}$, or $5.2 \times 10^{-16} \text{ L}$. Therefore, the concentration of the protein is

$$\frac{1.66 \times 10^{-21} \text{ moles}}{5.2 \times 10^{-16} \text{ L}} = 3.3 \times 10^{-6} \text{ M, or } 3.2 \text{ } \mu\text{M}$$

(b) $\dfrac{5 \times 10^{-3} \text{ moles}}{\text{L}} \times \dfrac{6.02 \times 10^{23} \text{ molecules}}{\text{mole}}$
$\times 5.2 \times 10^{-16} \text{ L} = 1.6 \times 10^6 \text{ molecules}$

20. (a) A 30X dilution is equivalent to multiplying one-tenth (10^{-1}) by itself 30 times: $(10^{-1})^{30} = 10^{-30}$. The concentration would be 10^{-30} M.
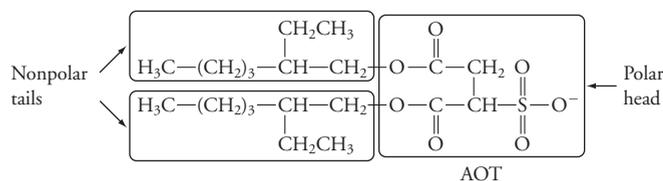**(b)** Use Avogadro's number and multiply the concentration by the volume to show that there is much less than one molecule present in 1 mL:
$(0.001 \text{ L})(10^{-30} \text{ moles/L})(6.02 \times 10^{23} \text{ molecules/mole})$
$$= 6.02 \times 10^{-10} \text{ molecules}$$
(c) The ability of water molecules to form a hydrogen-bonded coating, or cage, around a solute molecule, particularly a hydrophobic one, might support the idea of water's memory. However, water molecules are constantly in motion, so a group of water molecules that have been in contact with a solute do not retain an imprint of it.

21. Compound A is amphiphilic and has a polar head and a nonpolar tail as indicated and can form a micelle (see Fig. 2-10). Compound B is nonpolar and cannot form a micelle or a bilayer. Compound C is polar (ionic) and cannot form a micelle or a bilayer. Compound D is amphiphilic and has a polar head and two nonpolar tails as indicated and can form a bilayer (see Fig. 2-11). Compound E is polar and forms neither a micelle nor a bilayer.
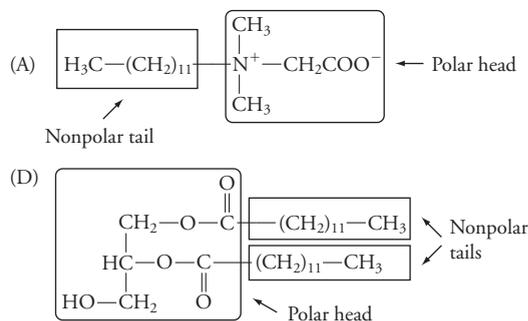

22. (a) In the nonpolar solvent, AOT's polar head group faces the interior of the micelle, and its nonpolar tails face the solvent.

Nonpolar tails

$H_3C-(CH_2)_3-CH-CH_2$ (with CH_2CH_3 substituents) $-O-C-CH_2$ O
$H_3C-(CH_2)_3-CH-CH_2$ (with CH_2CH_3 substituents) $-O-C-CH-S-O^-$

Polar head

AOT

(b) The protein, which contains numerous polar groups, interacts with the polar AOT groups in the micelle interior.

Isooctane

Water

Protein

23.

(a) Nonpolar tail ⟶ $H_3C-(CH_2)_{11}-O-S-O^-Na^+$ ⟵ Polar head

(b)
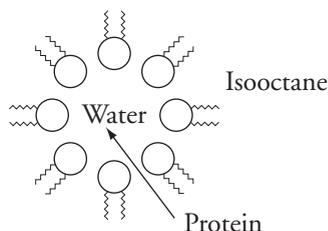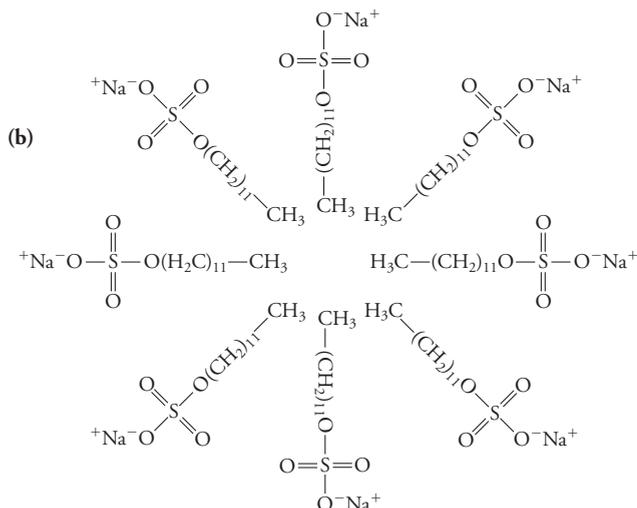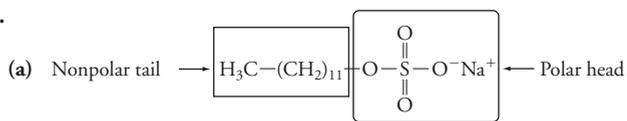
(c) The hydrophobic grease can move into the hydrophobic core of the water-soluble soap micelle. The "dissolved" grease can then be washed away with the micelle.

24. (a) It is doubtful that the contents of the ball could influence the behavior of external water molecules separated by layers of rubber and plastic.
(b) Even if water clusters were disrupted (which they are not), the removal of dirt requires more than one individual water molecule. In order for a dirt molecule to be washed away, it must be surrounded (solubilized) by many water molecules.
(c) Hot water, because of the higher energy of its water molecules, has intrinsically better dirt-solubilizing power than cold water, regardless of the presence or absence of detergent. In the absence of detergent, hot water has significant cleaning power on its own, which could be attributed to the presence of a laundry ball.

25. (a) The nonpolar core of the lipid bilayer helps prevent the passage of water since the polar water molecules cannot easily penetrate the hydrophobic core of the bilayer.
(b) Most human cells are surrounded by a fluid containing about 150 mM Na^+ and slightly less Cl^- (see Fig. 2-13). A solution containing 150 mM NaCl mimics the extracellular fluid and therefore helps maintain the isolated cells in near-normal conditions. If the cells were placed in pure water, water would tend to enter the cells by osmosis; this might cause the cells to burst.

26. In reverse osmosis, water moves from an area of low concentration (high solute concentration) to an area of high concentration (low solute concentration). This movement is opposite that described for osmosis in Problem 25. This is a nonspontaneous process that requires an input of energy in order to proceed, unlike osmosis, which occurs spontaneously without input of energy.

27. (a) CO_2 is nonpolar and would be able to cross a bilayer.
(b) Glucose is polar and would not be able to pass through a bilayer because the presence of the hydroxyl groups means glucose is highly hydrated and would not be able to pass through the nonpolar tails of the molecules forming the bilayer.
(c) DNP is nonpolar and would be able to cross a bilayer.
(d) Calcium ions are charged and are, like glucose, highly hydrated and would not be able to cross a lipid bilayer.

28. Vesicles consist of a lipid bilayer that closes up to enclose an aqueous compartment. The polar drug readily dissolves in this aqueous compartment. Delivery to the cell is accomplished when the vesicle membrane fuses with the cell membrane, releasing the drug into the cytosol.

29. Substances present at high concentration move to an area of low concentration spontaneously, or "down" a concentration gradient in a process that increases their entropy. The export of Na^+ ions out of the cell requires that the sodium ions be transported from an area of low concentration to an area of high concentration. The same is true for potassium transport. Thus, these processes are not spontaneous, and an input of cellular energy is required to accomplish the transport.

30. The amount of Na^+ (atomic weight 23 g · mol^{-1}) lost in 15 minutes, assuming a fluid loss rate of 2 L per hour and a sweat Na^+ concentration of 50 mM, is

$$0.25\ h \times \frac{2\ L}{h} \times \frac{0.05\ mol}{L} \times \frac{23\ g}{mol} \times \frac{1000\ mg\ Na^+}{g\ Na^+}$$
$$\times \frac{1\ oz\ chips}{200\ mg\ Na^+} = 2.9\ oz\ chips$$

It would take 2.9 ounces of potato chips (about a handful) to replace the lost sodium ions.

31. In a high-solute medium, the cytoplasm loses water; therefore its volume decreases. In a low-solute medium, the cytoplasm gains water and therefore its volume increases.

32. *E. coli* accumulates water when grown in a low-osmolarity medium. However, regulation of water content only would cause a large increase in cytoplasmic volume. To avoid this large increase in volume, *E. coli* also exports K^+ ions. The opposite occurs when *E. coli* is grown in a high-osmolarity medium—the cytoplasmic water content is decreased, but cytoplasmic osmolarity increases as *E. coli* imports K^+ ions. [From Record, M. T., et al., *Trends Biochem. Sci.* **23**, 143–148 (1998).]

33. Since the molecular mass of H_2O is 18.0 g · mol^{-1}, a given volume (for example, 1 L or 1000 g) has a molar concentration of 1000 g · L^{-1} ÷18.0 g · mol^{-1} = 55.5 M. By definition, a liter of water at pH 7.0 has a hydrogen ion concentration of 1.0×10^{-7} M. Therefore, the ratio of $[H_2O]$ to $[H^+]$ is 55.5 M/$(1.0 \times 10^{-7}$ M$)$ = 5.55×10^8.

34. $[H^+] \times [OH^-] = 1.47 \times 10^{-14}$ and $[H^+] = [OH^-]$
$[H^+] = \sqrt{1.47 \times 10^{-14}}$
$[H^+] = 1.21 \times 10^{-7}$ M
pH $= -\log(1.21 \times 10^{-7}$ M$)$
pH $= 6.92$

35. The HCl is a strong acid and dissociates completely. This means that the concentration of hydrogen ions contributed by the HCl is 1.0×10^{-9} M. But the concentration of the hydrogen ions contributed by the dissociation of water is 100-fold greater than this: 1.0×10^{-7} M. The concentration of the hydrogen ions contributed by the HCl is negligible in comparison. Therefore, the pH of the solution is equal to 7.0.

36. The pH of this solution is 7.0 (see Solution 35). The concentration of hydroxide ions contributed by the dissociation of water is 100-fold greater than that contributed by the dissociation of the dilute NaOH.

37. In aqueous solution, where virtually all biochemical reactions take place, an extremely strong acid such as HCl dissociates completely, so that all its

protons are donated to water: $HCl + H_2O \rightarrow H_3O^+ + Cl^-$. This leaves H_3O^+ as the only acidic species remaining.

38.
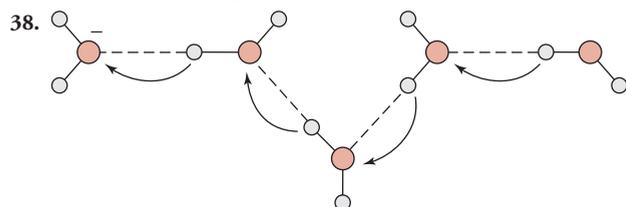
39. Since $pH = -\log[H^+]$, $[H^+] = 10^{-pH}$
For saliva, $[H^+] = 10^{-6.6} = 2.5 \times 10^{-7}$ M
For urine, $[H^+] = 10^{-5.5} = 3.2 \times 10^{-6}$ M

40.

	Acid, base, or neutral?	pH	$[H^+]$ (M)	$[OH^-]$ (M)
A	acid	5.60	2.5×10^{-6}	4.0×10^{-9}
B	base	7.65	2.2×10^{-8}	4.5×10^{-7}
C	neutral	7.00	1.0×10^{-7}	1.0×10^{-7}
D	acid	2.68	2.1×10^{-3}	4.8×10^{-12}

41. (a) The final concentration of HNO_3 is $\dfrac{(0.020 \text{ L})(1.0 \text{ M})}{0.520 \text{ L}} = 0.038$ M
Since HNO_3 is a strong acid and dissociates completely, the added $[H^+]$ is equal to $[HNO_3]$. (The existing hydrogen ion concentration in the water itself, 1.0×10^{-7} M, can be ignored because it is much smaller than the hydrogen ion concentration contributed by the nitric acid.)
$$pH = -\log[H^+]$$
$$pH = -\log(0.038)$$
$$pH = 1.4$$
(b) The final concentration of KOH is
$$\frac{(0.015 \text{ L})(1.0 \text{ M})}{0.515 \text{ L}} = 0.029 \text{ M}$$
Since KOH dissociates completely, the added $[OH^-]$ is equal to the $[KOH]$. (The existing hydroxide ion concentration in the water itself, 1.0×10^{-7} M, can be ignored because it is much smaller than the hydroxide ion concentration contributed by the KOH.)
$$K_w = 1.0 \times 10^{-14} = [H^+][OH^-]$$
$$[H^+] = \frac{1.0 \times 10^{-14}}{[OH^-]}$$
$$[H^+] = \frac{1.0 \times 10^{-14}}{(0.029 \text{ M})}$$
$$[H^+] = 3.4 \times 10^{-13} \text{ M}$$
$$pH = -\log[H^+]$$
$$pH = -\log(3.4 \times 10^{-13})$$
$$pH = 12.5$$

42. (a) Since HCl is a strong acid and dissociates completely, the added $[H^+]$ is equal to $[HCl]$. The final concentration of HCl is $(0.0015 \text{ L})(3.0 \text{ M})/$ 1 L $= 0.0045$ M. (The existing hydrogen ion concentration in the water itself, 1.0×10^{-7} M, can be ignored because it is much smaller than the hydrogen ion concentration contributed by the hydrochloric acid.)
$$pH = -\log[H^+]$$
$$pH = -\log(0.0045)$$
$$pH = 2.3$$
**(b)** Since NaOH dissociates completely, the added $[OH^-]$ is equal to the $[NaOH]$. The final concentration of NaOH is $(0.0015 \text{ L})(3.0 \text{ M})/$ 1 L $= 0.0045$ M. (The existing hydroxide ion concentration in the water itself, 1.0×10^{-7} M, can be ignored because it is much smaller than the hydroxide ion concentration contributed by the NaOH.)
$$K_w = 1.0 \times 10^{-14} = [H^+][OH^-]$$
$$[H^+] = \frac{1.0 \times 10^{-14}}{[OH^-]}$$
$$[H^+] = \frac{1.0 \times 10^{-14}}{(0.0045 \text{ M})}$$

$$[H^+] = 2.2 \times 10^{-12} \text{ M}$$
$$pH = -\log[H^+]$$
$$pH = -\log(2.2 \times 10^{-12})$$
$$pH = 11.6$$

43. The stomach contents have a low pH due to the contribution of gastric juice (pH 1.5–3.0). When the partially digested material enters the small intestine, the addition of pancreatic juice (pH 7.8–8.0) neutralizes the acid and increases the pH.

44. The carbonate ions accept protons from water and form hydroxide ions (as shown in the equation below), resulting in basic urine.
$$CO_3^{2-}(aq) + H_2O(l) \rightarrow HCO_3^-(aq) + OH^-(aq)$$
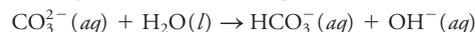
45. (a) $C_2O_4^{2-}$ **(b)** SO_3^{2-} **(c)** HPO_4^{2-} **(d)** CO_3^{2-}
(e) AsO_4^{3-} **(f)** PO_4^{3-} **(g)** O_2^{2-}

46. (a) $H_2C_2O_4$ **(b)** H_2SO_3 **(c)** H_3PO_4 **(d)** H_2CO_3
(e) $H_2AsO_4^-$ **(f)** $H_2PO_4^-$ **(g)** H_2O_2

47.

48. (a)
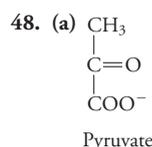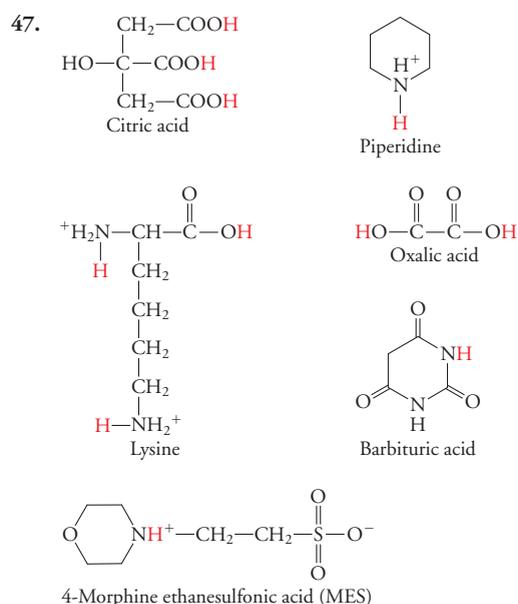
Pyruvate

(b) The structure of pyruvate will predominate in the cell at pH 7.4. The pK values for carboxylic acid groups are typically in the 2–3 range; therefore, the carboxylate group will be unprotonated at physiological pH.

49.
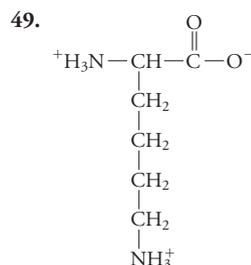
50. Convert all the data to either K_a or pK values to evaluate ($pK = -\log K_a$). The greater the K_a value, the stronger the acid—that is, the greater the tendency for the proton to be donated. (The lower the pK value, the stronger the acid.) From strongest to weakest acid: E, D, B, A, C. Note that the stronger the acid, the weaker its conjugate base. For example, citric

acid is a stronger acid than citrate, and succinic acid is a stronger acid than succinate.

	Acid	K_a	pK
A	citrate	1.74×10^{-5}	4.76
B	succinic acid	6.17×10^{-5}	4.21
C	succinate	2.29×10^{-6}	5.64
D	formic acid	1.78×10^{-4}	3.75
E	citric acid	7.41×10^{-4}	3.13

51. The pK of the fluorinated compound would be lower (it is 9.0); that is, the compound becomes less basic and more acidic. This occurs because the F atom, which is highly electronegative, pulls on the nitrogen's electrons, loosening its hold on the proton.

52. pH 2 $^+H_3N—CH_2—COOH$
pH 7 $^+H_3N—CH_2—COO^-$
pH 10 $H_2N—CH_2—COO^-$

The carboxylic acid group has a pK of 2.35, and the amino group has a pK of 9.78. The Henderson–Hasselbalch equation can be used to calculate the exact percentage of protonated/unprotonated forms of each functional group, but that really isn't necessary. Instead, the pK values for each group should be compared to the pH. At pH = 2, the pH is below both pK values, so both functional groups are mostly protonated. At pH = 7, the pH is well above the pK for the carboxylic acid group but below the pK for the amino group. Therefore the carboxylic acid group is unprotonated and the amino group is protonated. At pH = 10, the pH is above the pK values of both functional groups. Thus, both groups are mostly unprotonated.

53. **(a)** 10 mM glycinamide buffer because its pK is closer to the desired pH.
(b) 20 mM Tris buffer because the higher the concentration of the buffering species, the more acid or base it can neutralize.
(c) Neither; each solution will contain an equilibrium mixture of the boric acid and its conjugate base (borate).

54. **(a)** 10 mM acetic acid buffer because its pK is closer to the desired pH.
(b) 20 mM acetic acid buffer because the higher the concentration of buffer species will allow it to neutralize a greater amount of acid or base.
(c) Neither. Both a weak acid and a conjugate base are required buffer constituents. The weak acid alone (acetic acid) or the conjugate base alone (sodium acetate) cannot serve as an effective buffer.

55. Because it is small and nonpolar (see Solution 2), CO_2 can quickly diffuse across cell membranes to exit the tissues and enter red blood cells.

56. **(a)** $H_2CO_3(aq) \rightarrow H^+(aq) + HCO_3^-(aq)$
$HCO_3^-(aq) \rightarrow H^+(aq) + CO_3^{2-}(aq)$
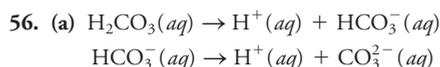
(b) The pK of the first dissociation is closer to the pH; therefore the weak acid present in blood is H_2CO_3 and the conjugate base is HCO_3^-.

57. **(a)** The three ionizable protons of phosphoric acid have pK values of 2.15, 6.82, and 12.38 (Table 2-4). The pK values are the midpoints of the titration curve.
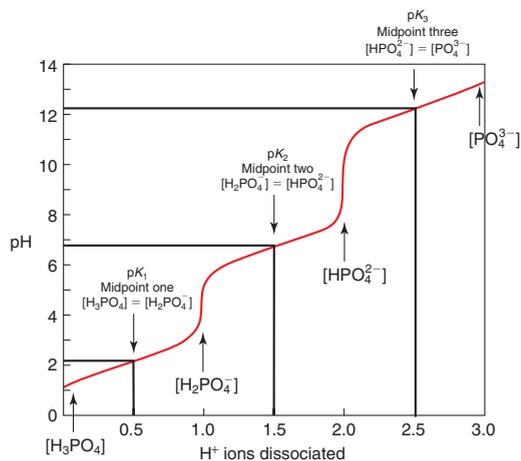
(b) The dissociation of the second proton has a pK of 6.82, which is closest to the pH of blood. Therefore, the weak acid present in blood is $H_2PO_4^-$ and the weak acid is HPO_4^{2-}.
(c) The dissociation of the third proton has a pK of 12.38. Therefore, a buffer solution at pH 11 would consist of the weak acid HPO_4^{2-} and its conjugate base, PO_4^{3-} (supplied as the sodium salts Na_2HPO_4 and Na_3PO_4).

58. The aspirin is more likely to be absorbed in the stomach at pH 2. At this pH, the carboxylate group is mostly protonated and uncharged. This allows the aspirin to pass more easily through the nonpolar lipid bilayer. At the pH of the small intestine, the carboxylate group is mostly in the ionized form and will be negatively charged. Charged species are more polar than uncharged species (and are likely to be hydrated) and will have difficulty traversing a lipid bilayer.

59. Calculate the final concentrations of the weak acid ($H_2PO_4^-$) and conjugate base (HPO_4^{2-}). Note that K^+ is a spectator ion.

$$[H_2PO_4^-] = \frac{(0.025 \text{ L})(2.0 \text{ M})}{0.200 \text{ L}} = 0.25 \text{ M}$$

$$[HPO_4^{2-}] = \frac{(0.050 \text{ L})(2.0 \text{ M})}{0.200 \text{ L}} = 0.50 \text{ M}$$

Next, substitute these values into the Henderson–Hasselbalch equation using the pK values in Table 2-4:

$$pH = pK + \log\frac{[A^-]}{[HA]}$$
$$pH = 6.82 + \log(0.50 \text{ M})/(0.25 \text{ M})$$
$$pH = 6.82 + 0.30$$
$$pH = 7.12$$

60. Use the pK value in Table 2-4 and the Henderson–Hasselbalch equation to calculate the ratio of imidazole (A^-) and the imidazolium ion (HA):

$$pH = pK + \log\left(\frac{[A^-]}{[HA]}\right)$$
$$\log\left(\frac{[A^-]}{[HA]}\right) = pH - pK$$
$$\frac{[A^-]}{[HA]} = 10^{(pH-pK)}$$
$$\frac{[A^-]}{[HA]} = 10^{(7.4-7.0)}$$
$$\frac{[A^-]}{[HA]} = \frac{2.5}{1}$$

61. First, determine the ratio of $[A^-]$ to $[HA]$:

$$pH = pK + \log\frac{[A^-]}{[HA]}$$
$$\log\frac{[A^-]}{[HA]} = pH - pK$$
$$\frac{[A^-]}{[HA]} = 10^{(pH-pK)}$$

Substitute the values for the desired pH (5.0) and the pK (4.76):

$$\frac{[A^-]}{[HA]} = 10^{(5.0-4.76)} = 10^{0.24} = 1.74$$

Calculate the number of moles of acetate (A^-) already present:

$$(0.50 \text{ L})(0.20 \text{ mol} \cdot L^{-1}) = 0.10 \text{ moles acetate}$$

Calculate the moles of acetic acid needed, based on the calculated ratio:

$$\frac{[A^-]}{[HA]} = 1.74$$
$$[HA] = \frac{0.10 \text{ moles}}{1.74}$$
$$[HA] = 0.057 \text{ moles}$$
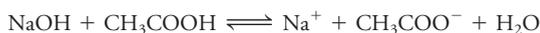
Finally, calculate the volume of glacial acetic acid needed:

$$\frac{0.057 \text{ moles}}{17.4 \text{ mol} \cdot \text{L}^{-1}} = 0.0033 \text{ L, or } 3.3 \text{ mL}$$

The addition of 3.3 mL to a 500-mL solution dilutes the solution by less than 1%, which doesn't introduce significant error.

62. Adding NaOH to the acetic acid will convert some of the acetic acid (HA) to acetate (A^-):
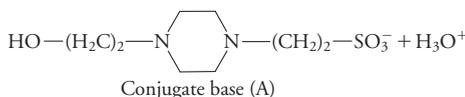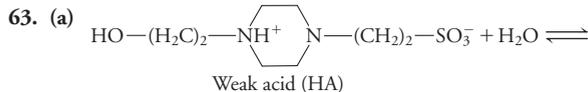
$$NaOH + CH_3COOH \rightleftharpoons Na^+ + CH_3COO^- + H_2O$$

For every mole of NaOH added, one mole of CH_3COOH will be consumed and one mole of CH_3COO^- will be generated. If x is the number of moles of NaOH added, then x will also be the number of moles of A^- generated. The initial amount of acetic acid is 0.10 mol, so the final amount of acetic acid will be 0.10 mol $- x$.

$$\frac{[A^-]}{[HA]} = 1.74 = \frac{x}{0.10 \text{ mol} - x}$$
$$x = 1.74(0.10 \text{ mol} - x) = 0.174 \text{ mol} - 1.74x$$
$$2.74x = 0.174 \text{ mol}$$
$$x = 0.174 \text{ mol}/2.74 = 0.0635 \text{ mol}$$

Calculate the mass of NaOH to add:

$$\frac{0.0635 \text{ mol}}{40 \text{ g} \cdot \text{mol}^{-1}} = 1.58 \text{ g}$$

63. (a)

HO—(H₂C)₂—NH⁺   N—(CH₂)₂—SO₃⁻ + H₂O ⇌

Weak acid (HA)

HO—(H₂C)₂—N   N—(CH₂)₂—SO₃⁻ + H₃O⁺

Conjugate base (A)

(b) The pK for HEPES is 7.55; therefore, its effective buffering range is 6.55–8.55.

(c) $1.0 \text{ L} \times \dfrac{0.10 \text{ mole}}{\text{L}} \times \dfrac{260.3 \text{ g}}{\text{mol}} = 26 \text{ g}$

Weigh 26 g of the HEPES salt and add to a beaker. Dissolve in slightly less than 1.0 liter of water (leave "room" for the HCl solution that will be added in the next step).

(d) At the final pH,

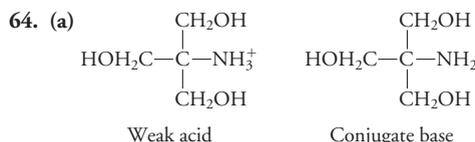$$\frac{[A^-]}{[HA]} = 10^{(pH - pK)} = 10^{(8.0 - 7.55)} = 10^{0.45} = 2.82$$

For each mole of HCl added, x, one mole of HEPES salt (A^-) will be converted to a mole of HEPES acid (HA). The starting amount of A^- is $(1.0 \text{ L})(0.10 \text{ mol} \cdot \text{L}^{-1}) = 0.10$ mole. After the HCl is added, the amount of A^- will be 0.10 mole $- x$, and the amount of HA will be x. Consequently,

$$\frac{[A^-]}{[HA]} = 2.82 = \frac{0.10 \text{ mole} - x}{x}$$
$$2.82x = 0.10 \text{ mol} - x$$
$$3.82x = 0.10 \text{ mol}$$
$$x = 0.10 \text{ mol}/3.82 = 0.0262 \text{ mol}$$

Calculate how much 6.0 M HCl to add:

$$\frac{0.0262 \text{ mol}}{6.0 \text{ mol} \cdot \text{L}^{-1}} = 0.0044 \text{ L, or } 4.4 \text{ mL}$$

To make the buffer, dissolve 26 g of HEPES salt [see part (c)] in less than 1.0 L. Add 4.4 mL of 6.0 M HCl, then add water to bring the final volume to 1.0 L.

64. (a)

CH₂OH   CH₂OH
 | |
HOH₂C—C—NH₃⁺   HOH₂C—C—NH₂
 | |
CH₂OH   CH₂OH

Weak acid   Conjugate base

(b) The pK of Tris is 8.30; therefore, its effective buffering range is 7.30–9.30.

(c) Rearranging the Henderson–Hasselbalch equation gives

$$\frac{[A^-]}{[HA]} = 10^{(pH - pK)} = 10^{(8.2 - 8.3)} = 10^{-0.1} = 0.79$$

Since $[A^-] + [HA] = 0.10$ M, $[A^-] = 0.10$ M $-$ [HA], and
$\dfrac{(0.10 \text{ M} - [HA])}{[HA]} = 0.79$

$$0.79[HA] = 0.10 \text{ M} - [HA]$$
$$1.79[HA] = 0.10 \text{ M}$$

$$[HA] = \frac{0.10 \text{ M}}{1.79} = 0.056 \text{ M} = 56 \text{ mM}$$
$$[A^-] + [HA] = 0.10 \text{ M} = 100 \text{ mM, so } [A^-] = 44 \text{ mM}$$

(d) When HCl is added, an equivalent amount of Tris base (A^-) is converted to Tris acid (HA). Let x = moles of H^+ added = (0.0015 L) $(3.0 \text{ mol} \cdot \text{L}^{-1}) = 0.0045$ moles = 4.5 mmol.
The final amount of A^- is 44 mmol $-$ 4.5 mmol = 39.5 mmol.
The final amount of HA is 56 mmol $+$ 4.5 mmol = 60.5 mmol.
Use the Henderson–Hasselbalch equation to calculate the new pH:

$$pH = pK + \log\left(\frac{[A^-]}{[HA]}\right)$$

$$pH = 8.3 + \log\left(\frac{39.5 \text{ mmol} \cdot 1001.5 \text{ mL}^{-1}}{60.5 \text{ mmol} \cdot 1001.5 \text{ mL}^{-1}}\right)$$

$$pH = 8.3 + (-0.2)$$
$$pH = 8.1$$

The buffer has been effective: The pH has declined about 0.1 unit (from pH 8.2 to pH 8.1) with the addition of the strong acid. In comparison, the addition of the same amount of acid to water, which is not buffered, resulted in a pH change from approximately 7.0 to 2.35 (see Problem 42a).

(e) When NaOH is added, an equivalent amount of Tris acid (HA) is converted to Tris base (A^-). Let x = moles of OH^- added = (0.0015 L) $(3.0 \text{ mol} \cdot \text{L}^{-1}) = 0.0045$ moles = 4.5 mmol.
The final amount of A^- is 44 mmol $+$ 4.5 mmol = 48.5 mmol.
The final amount of HA is 56 mmol $-$ 4.5 mmol = 51.5 mmol.
Use the Henderson–Hasselbalch equation to calculate the new pH:

$$pH = pK + \log\left(\frac{[A^-]}{[HA]}\right)$$

$$pH = 8.3 + \log\left(\frac{48.5 \text{ mmol} \cdot 1001.5 \text{ mL}^{-1}}{51.5 \text{ mmol} \cdot 1001.5 \text{ mL}^{-1}}\right)$$

$$pH = 8.3 + (-0.026)$$
$$pH = 8.27$$

The buffer has been effective: The pH has increased only 0.07 unit (from pH 8.2 to pH 8.27) with the addition of the strong base. In comparison, the addition of the same amount of base to water, which is not buffered, resulted in a pH change from approximately 7.0 to 11.6 (see Problem 42b).

65. (a) First, calculate the ratio of $[A^-]$ to [HA]. Rearranging the Henderson–Hasselbalch equation gives

$$\frac{[A^-]}{[HA]} = 10^{(pH - pK)} = 10^{(2.0 - 8.3)} = 10^{-6.3} = 5 \times 10^{-7}$$

Virtually all of the Tris is in the weak acid form. Therefore, the concentration of the weak acid, HA, is 0.10 M and the concentration of the conjugate base, A^-, is 5.0×10^{-8} M.

(b) The added HCl dissociates completely, so the amount of H^+ added is $(0.0015 \text{ L})(3.0 \text{ mol} \cdot \text{L}^{-1}) = 0.0045 \text{ mol}$. In an effective buffer, the acid would convert some of the conjugate Tris base to weak acid. But the concentration of conjugate base is already negligible. Therefore, the moles of additional H^+ should be added to the concentration of hydrogen ions already present $(1.0 \times 10^{-2} \text{ M})$, for a total concentration of 0.0145 M.

$$\text{pH} = -\log[H^+] = \log(0.0145 \text{ M}) = 1.84$$

The buffer has not functioned effectively. There was not enough conjugate base to react with the additional hydrogen ions added. The result is a decrease in pH from 2.0 to 1.84.

(c) When NaOH is added, an equivalent amount of Tris acid (HA) is converted to Tris base (A^-). Let x = moles of OH^- added = (0.0015 L) $(3.0 \text{ mol} \cdot \text{L}^{-1}) = 0.0045$ moles = 4.5 mmol.
The final amount of A^- is 5.0×10^{-8} mol + 4.5 mmol = 4.5 mmol.
The final amount of HA is 100 mmol − 4.5 mmol = 95.5 mmol.
The new pH is determined by substituting the new concentrations of H^- and HA into the Henderson–Hasselbalch equation:

$$\text{pH} = \text{p}K + \log\frac{[A^-]}{[HA]}$$

$$\text{pH} = 8.3 + \log\frac{(4.5 \text{ mmol})}{(95.5 \text{ mmol})}$$

$$\text{pH} = 8.3 + (-1.3) = 7.0$$

Tris is not an effective buffer at pH = 2.0, a pH more than 6 units lower than its pK value. Virtually all of the Tris is in the weak acid form at this pH. If acid is added, there is not enough base to absorb the excess added hydrogen ions, and the pH decreases. If base is added, some of the weak acid is converted to the conjugate base and the pH approaches the value of the pK.

66. The ratio of bicarbonate to carbonic acid in the patient's blood can be determined using the Henderson–Hasselbalch equation:

$$\text{pH} = \text{p}K + \log\left(\frac{[A^-]}{[HA]}\right)$$

$$7.55 = 6.35 + \log\frac{[HCO_3^-]}{[H_2CO_3]}$$

$$10^{1.2} = \frac{[HCO_3^-]}{[H_2CO_3]}$$

$$\frac{[HCO_3^-]}{[H_2CO_3]} = \frac{15.8}{1}$$

Similarly, the ratio of bicarbonate to carbonic acid in a normal person's blood can be determined:

$$\text{pH} = \text{p}K + \log\left(\frac{[A^-]}{[HA]}\right)$$

$$7.4 = 6.35 + \log\left(\frac{[HCO_3^-]}{[H_2CO_3]}\right)$$

$$10^{1.05} = \frac{[HCO_3^-]}{[H_2CO_3]}$$

$$\frac{[HCO_3^-]}{[H_2CO_3]} = \frac{11.2}{1}$$

In order to serve as an effective buffer (i.e., absorb both added H^+ and OH^-), both a conjugate base and a weak acid must be present. In the patient, the ratio of conjugate base to weak acid does not lie within an effective buffering range. The bicarbonate concentration (conjugate base) is too high relative to the carbonic acid (weak acid) concentration; thus the relative amount of weak acid is insufficient.
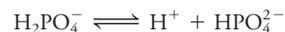
67. Ammonia and ammonium ions are in equilibrium, as represented by the following equation:

$$NH_4^+ \rightleftharpoons H^+ + NH_3$$
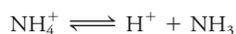
Carbonic acid and bicarbonate ions are in equilibrium, as represented by the following equation:

$$H_2CO_3 \rightleftharpoons H^+ + HCO_3^-$$
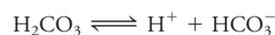
Phosphate ions are in equilibrium, according to the following equation:

$$H_2PO_4^- \rightleftharpoons H^+ + HPO_4^{2-}$$

In metabolic acidosis, the concentration of protons increases, so the equilibrium shifts to form $H_2PO_4^-$, carbonic acid and ammonium ions. In order to bring the pH back to normal, the kidney will excrete $H_2PO_4^-$ and ammonium ions and bicarbonate ions will be reabsorbed. The result is a decrease in the concentration of protons and an increase in blood pH.

68. The relevant equations are shown in Solution 67. In metabolic alkalosis there is an excess of hydroxide ions, which react with protons to form water. This causes the equilibria to shift to form HPO_4^{2-}, NH_3 and HCO_3^-. In order to bring the pH back to normal, the kidney reabsorbs NH_4^+ and $H_2PO_4^-$ and excretes HCO_3^-.

Chapter 3

1. The heat treatment destroys the polysaccharide capsule of the wild-type *Pneumococcus*, but the DNA survives the heat treatment. The DNA then "invades" the mutant *Pneumococcus* and supplies the genes encoding the enzymes needed for the capsule synthetic pathway that the mutant lacks. The mutant is now able to synthesize a capsule and has the capacity to cause disease, which results in the death of the mice and the appearance of encapsulated *Pneumococcus* in the mouse tissue.

2. These experiments showed that the transforming factor was neither a protein nor RNA.

3. Some of the labeled "parent" DNA appears in the progeny, but none of the labeled protein appears in the progeny. This indicates that the bacteriophage DNA is involved in the production of progeny bacteriophages, but bacteriophage protein is not required.

4. The triple-helical model is not consistent with the hydrophobic effect, which suggests that the nonpolar nitrogenous bases would reside in the center of the DNA structure and the hydrophilic phosphates would reside on the surface. The triple-helical model also assumes that the phosphate groups are protonated and form stabilizing hydrogen bonds in the DNA interior. But the pK value for phosphate is well below 7, so the phosphate groups would not be protonated at physiological pH. In the absence of hydrogen bonds, there are no additional forces that would hold the strands of the triple helix together.

5.

5-Methylcytosine

6. (a)
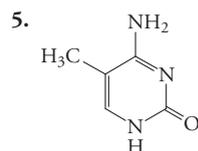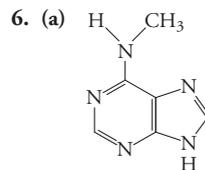
N^6-Methyladenine

(b) The N^6-DNA methyltransferase might be a good drug target. If methylation of certain adenine residues is required for virulence, then it is possible that inhibition of the bacterial transferase enzyme might prevent adenine methylation and thus prevent disease caused by pathogenic bacteria.

7. The base, 5-chlorouracil, is a substitute for thymine (5-methyluracil).

8. A chlorine is substituted for a hydrogen in 5-chlorouracil, which closely resembles thymine (see Solution 7). Therefore, to real chlorouracil the culture