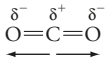
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SKU: 9781119713203-SOLUTIONS

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°.

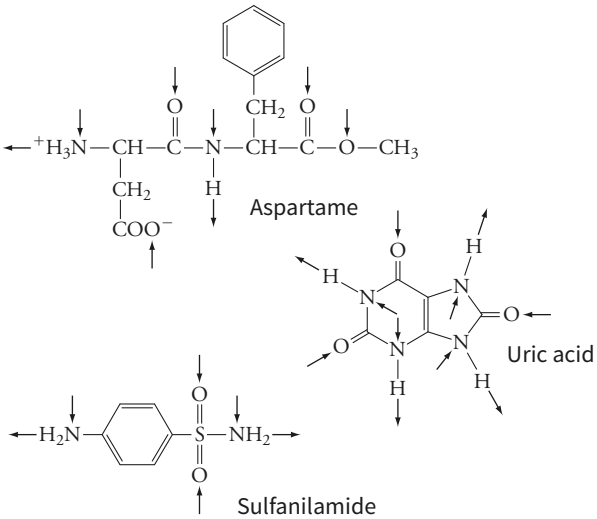
2. Because the partial negative charges are arranged symmetrically (and the shape of the molecule is linear), the molecule as a whole is not polar.



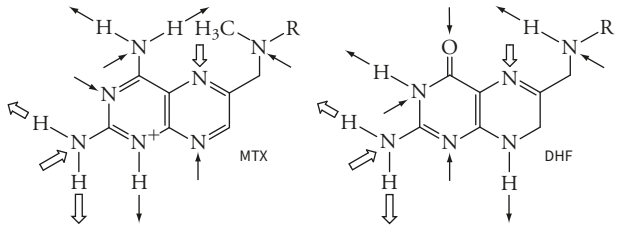
3. Water has the higher boiling point because, although each molecule has the same geometry and can form hydrogen bonds with its neighbors, the hydrogen bonds formed between water molecules are stronger than those formed between H_2S molecules. The electronegativity difference between H and O is greater than that between H and S and results in greater differences in the partial charges on the atoms in the water molecule.

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 smaller 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.

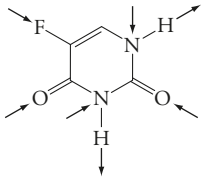


6. Arrows point toward hydrogen acceptors and away from hydrogen donors. [From Kubiny, H., in *3D QSAR in Drug Design: Volume 1: Theory Methods and Application,* Springer Science & Business Media (1993).]

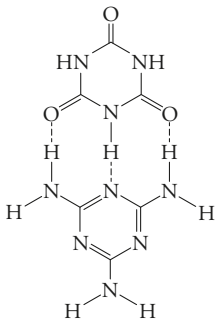


7. Identical hydrogen bonding patterns in the two molecules are shown as open arrows in Solution 6.

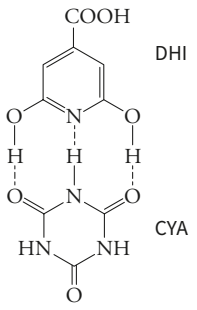
8. [From Taylor, R., *Acta Cryst B* 73, 474–488 (2017).]



9. [From Puschner, P. et al., *J. Vet. Diagn. Invest.* 19, 616–624 (2007).]



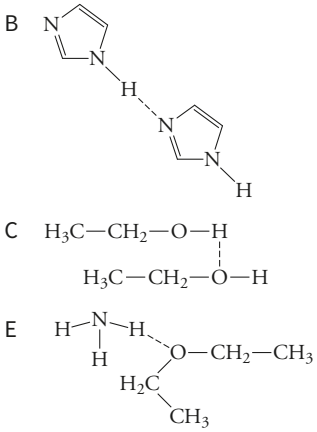
10. [From Chen, D. et al., *Sci. Adv.* 2, e1501240 (2016).]



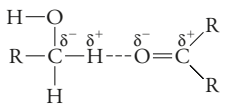
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11. The greater an atom's electronegativity, the more polar its bond with H and the greater its ability to act as a hydrogen bond acceptor. Thus, N, O, and F, which have relatively high electronegativities, can act as hydrogen bond acceptors, whereas C and S, whose electronegativities are only slightly greater than that of hydrogen, cannot.

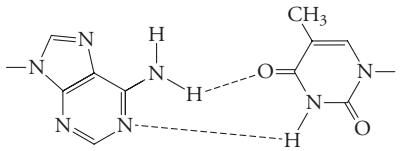
12. Compound A does not form hydrogen bonds (the molecule has a hydrogen bond acceptor but no hydrogen bond donor). Compounds B and C form hydrogen bonds as shown because each molecule contains at least one hydrogen bond donor and a hydrogen bond acceptor. The molecules in D do not form hydrogen bonds with each other because ethyl chloride lacks both a hydrogen bond donor and a hydrogen bond acceptor. The molecules in E do because ammonia has a hydrogen bond donor and diethyl ether has a hydrogen bond acceptor:



13. There are many possibilities. One example is



14.



15. a. van der Waals forces (dipole–dipole interactions); **b.** hydrogen bonding; **c.** van der Waals forces (London dispersion forces); **d.** ionic interactions.

16. a. Hydrogen bonding; **b.** ionic interactions; **c.** van der Waals forces (London dispersion forces).

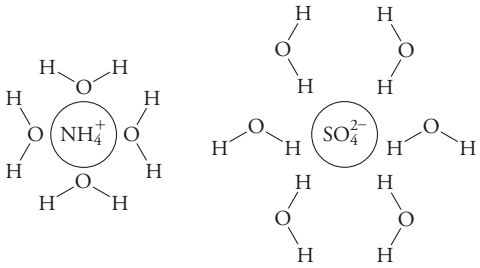
17. Solubility in water decreases as the number of carbons in the alcohol increases. The hydroxyl group of the alcohol is able to form hydrogen bonds with water, but water cannot interact favorably with the hydrocarbon chain. Increasing the length of the chain increases the number of potentially unfavorable interactions of the alcohol with water and solubility decreases as a result.

18. Solubility in water and dielectric constants are correlated; low molecular weight alcohols are miscible with water and have a high dielectric constant; high molecular weight alcohols are not very soluble in water and have a low dielectric constant.

19. 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.

20. 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.

21. The positively charged ammonium ion is surrounded by a shell of water molecules that are oriented so that the 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.)



22. 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 lowest dielectric constant.

23. 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.

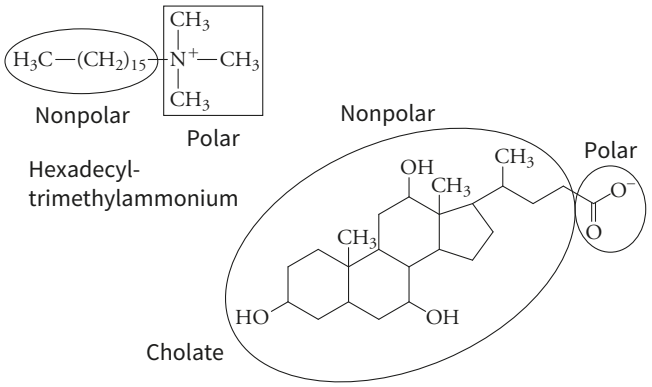
24. a. Surface tension is defined as the force that must be applied to surface molecules in a liquid so that they may experience the same forces as the molecules in the interior of the liquid. The surface tension of water is greater than that of ethanol because the strength and number of water's intermolecular 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.

25. 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.

26. The paper clip, although composed of a metal with a greater density than water, floats due to the strong hydrogen bonding that occurs among water molecules on the surface of the liquid. Soap disrupts these strong intermolecular forces and as a result the paper clip sinks to the bottom of the container.

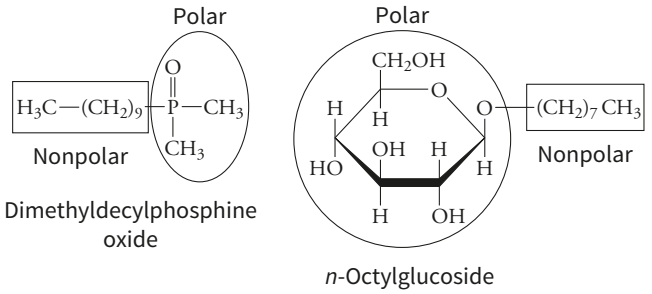
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27. Polar and nonpolar regions of the detergents are indicated.



28. The polar portion (boxed) of the hexadecyltrimethylammonium ion (see Solution 27) is able to form favorable dipole–dipole interactions with water. The polar portion (circled) of the cholate molecule (see Solution 27) is able to form both favorable dipole–dipole interactions and hydrogen bonds with water, with both oxygens serving as hydrogen bond acceptors.

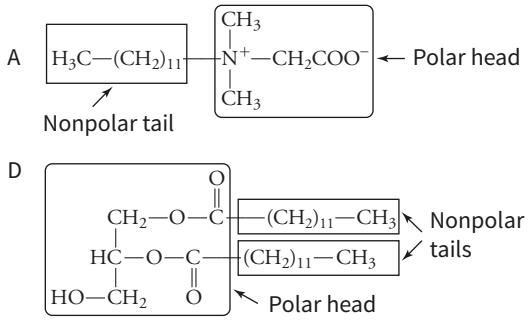
29. Polar and nonpolar regions of the detergents are indicated.



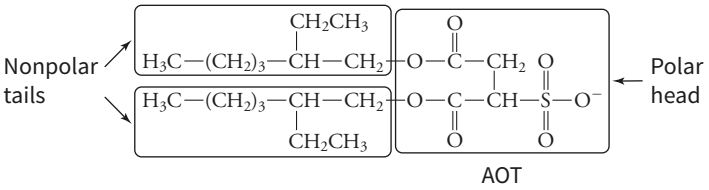
30. The polar portions (circled) of both detergents (see Solution 29) are able to form favorable dipole–dipole interactions with water. In addition, both polar portions can form a hydrogen bond with water, with the carbonyl group of dimethyldecylphosphine oxide serving as a hydrogen bond donor and the hydroxyl groups of *n*-octylglucoside serving as both hydrogen bond donors and hydrogen bond acceptors.

31. Compounds A and D are amphiphilic, compound B is nonpolar, and compounds C and E are polar.

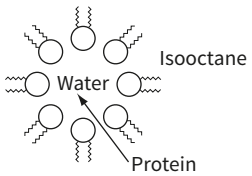
32. Compound A has a polar head and a nonpolar tail as indicated and can form a micelle (see Fig. 2.9). Compound D has a polar head and two nonpolar tails as indicated and can form a bilayer (see Fig. 2.10). Compounds B, C, and E form neither micelles nor bilayers.



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

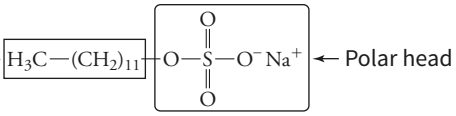


b. The protein, which contains numerous polar groups, interacts with the polar AOT groups in the micelle interior.

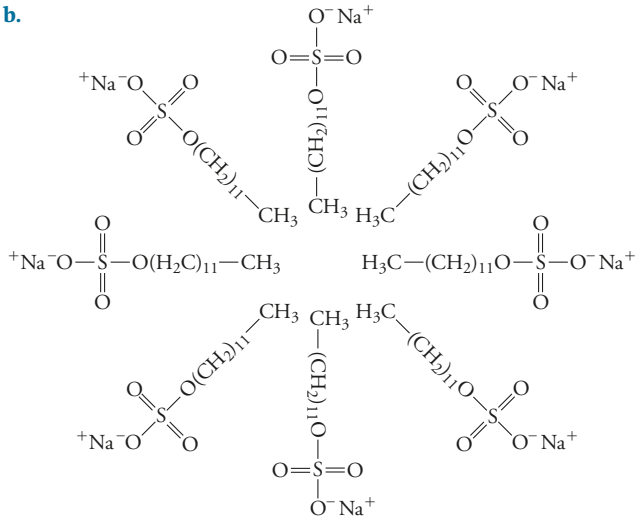


34.

a. Nonpolar tail → 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.

35. 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. 2.12). 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.

36. 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 35. This is a non-spontaneous process that requires an input of energy in order to proceed, unlike osmosis, which occurs spontaneously, without input of energy.

37. Compounds **a** and **b** are polar and **d** is ionic; as these substances are highly hydrated, none of them would be able to cross a lipid bilayer. Compound **c** is nonpolar and would be able to cross a bilayer.

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38. 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.

39. 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 from 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.

40. 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 (Box 2.B), is

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

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

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

42. *E. coli* accumulates water when grown in a low-salt 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-salt 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).]

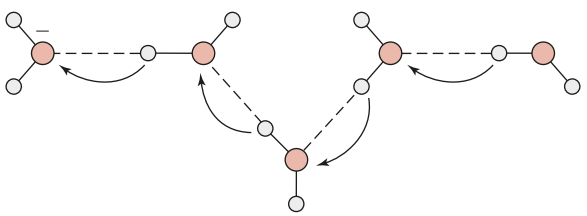
43. Since the molecular mass of H_2O is 18.0 g · mol^{-1}, a given volume (for example, 1 L or 1000 g) has a molar concentration of 1000 g · L^{-1} ÷ 18.0 g · mol^{-1} = 55.5 M. By definition, a liter of water at pH 7.0 has a hydrogen ion concentration of 1.0×10^{-7} M. Therefore, the ratio of $[H_2O]$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

44.
$$[H^+] = [OH^-] = 1.47 \times 10^{-14}$$
$$[H^+] = \sqrt{1.47 \times 10^{-14}}$$
$$[H^+] = 1.21 \times 10^{-7}\ \text{M}$$
$$\text{pH} = -\log(1.21 \times 10^{-7}) = 6.92$$

45. 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. However, 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.

46. The pH of this solution is 7.0 (see Solution 45). 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.

47.



48.

	Acid, base, or neutral?	pH	$[H^+]$ (M)	$[OH^-]$ (M)
Pancreatic juice	base	7.89	1.3×10^{-8}	7.7×10^{-7}
Blood	base	7.42	3.8×10^{-8}	2.6×10^{-7}
Saliva	neutral	7.00	1.0×10^{-7}	1.0×10^{-7}
Urine	acid	6.80	1.6×10^{-7}	6.3×10^{-8}
Gastric juice	acid	2.10	7.9×10^{-3}	1.3×10^{-12}

49. 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.

50. The carbonate ions accept protons from water and form hydroxide ions (as shown in the equation below), resulting in basic urine.

$$CO_3^{2-}(aq) + H_2O(l) \rightleftharpoons HCO_3^-(aq) + OH^-(aq)$$

51. 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-}

52. 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

53. a. The final concentration of HNO_3 is (0.020 L)(1.0 M) ÷ 0.520 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.)

$$\text{pH} = -\log[H^+]$$
$$\text{pH} = -\log(0.038)$$
$$\text{pH} = 1.4$$

b. The final concentration of KOH is (0.015 L)(1.0 M) ÷ 0.515 L = 0.029 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.)

$$K_w = 1.0 \times 10^{-14} = [H^+][OH^-]$$
$$[H^+] = \frac{1.0 \times 10^{-14}}{[OH^-]}$$
$$[H^+] = \frac{1.0 \times 10^{-14}}{(0.029\ \text{M})}$$
$$[H^+] = 3.4 \times 10^{-13}\ \text{M}$$
$$\text{pH} = -\log[H^+]$$
$$\text{pH} = -\log(3.4 \times 10^{-13})$$
$$\text{pH} = 12.5$$

54. a. The final concentration of HCl is (0.0015 L)(3.0 M) ÷ 1.0015 L = 0.0045 M. Since HCl is a strong acid and dissociates completely, the added $[H^+]$ is equal to [HCl]. (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.)

$$\text{pH} = -\log[H^+]$$
$$\text{pH} = -\log(0.0045)$$
$$\text{pH} = 2.3$$

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b. The final concentration of NaOH is (0.0015 L)(3.0 M) ÷ 1.0015 L = 0.0045 M. Since NaOH dissociates completely, the added [OH^-] is equal to the [NaOH]. (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.)

$$K_w = 1.0 \times 10^{-14} = [H^+][OH^-]$$
$$[H^+] = \frac{1.0 \times 10^{-14}}{[OH^-]}$$
$$[H^+] = \frac{1.0 \times 10^{-14}}{(0.0045\ M)}$$
$$[H^+] = 2.2 \times 10^{-12}\ M$$
$$pH = -\log[H^+]$$
$$pH = -\log(2.2 \times 10^{-12})$$
$$pH = 11.6$$

55. a. The final concentration of HBr is (0.010 L)(0.50 M) ÷ 0.510 L = 0.0098 M. Since HBr is a strong acid and dissociates completely, the added [H^+] is equal to [HBr]. (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 HBr.)

$$pH = -\log[H^+]$$
$$pH = -\log(0.0098)$$
$$pH = 2.0$$

b. The final concentration of NaOH is (0.025 L)(0.25 M) ÷ 0.525 L = 0.012 M. Since NaOH dissociates completely, the added [OH^-] is equal to the [NaOH]. (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.)

$$K_w = 1.0 \times 10^{-14} = [H^+][OH^-]$$
$$[H^+] = \frac{1.0 \times 10^{-14}}{[OH^-]}$$
$$[H^+] = \frac{1.0 \times 10^{-14}}{0.012\ M}$$
$$[H^+] = 8.3 \times 10^{-13}\ M$$
$$pH = -\log[H^+]$$
$$pH = -\log(8.3 \times 10^{-13})$$
$$pH = 12.1$$

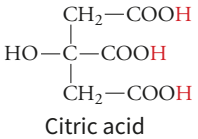
56. a. The final concentration of HI is (0.015 L)(2.0 M) ÷ 1.015 L = 0.030 M. Since HI is a strong acid and dissociates completely, the added [H^+] is equal to [HI]. (The existing hydrogen ion concentration in the water itself, 1.0×10^{-7} M, can be ignored because it is much smaller than the hydrogen ion concentration contributed by the HI.)

$$pH = -\log[H^+]$$
$$pH = -\log(0.030)$$
$$pH = 1.5$$

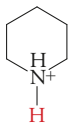
b. The final concentration of $Ba(OH)_2$ is (0.025 L)(2.0 M) ÷ 1.025 L = 0.049 M. Since $Ba(OH)_2$ dissociates completely and because each mole of $Ba(OH)_2$ yields two moles of hydroxide ions, the added [OH^-] is 0.050 M. (The existing hydroxide ion concentration in the water itself, 1.0×10^{-7} M, can be ignored because it is much smaller than the hydroxide ion concentration contributed by the $Ba(OH)_2$.)

$$K_w = 1.0 \times 10^{-14} = [H^+][OH^-]$$
$$[H^+] = \frac{1.0 \times 10^{-14}}{[OH^-]}$$
$$[H^+] = \frac{1.0 \times 10^{-14}}{0.049\ M}$$
$$[H^+] = 2.0 \times 10^{-13}\ M$$
$$pH = -\log[H^+]$$
$$pH = -\log(2.0 \times 10^{-13})$$
$$pH = 12.7$$

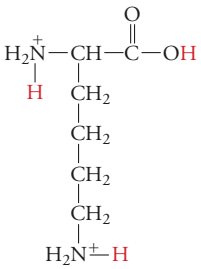
57.



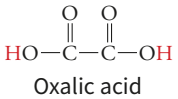
Citric acid



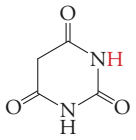
Piperidine



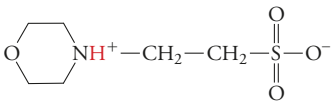
Lysine



Oxalic acid



Barbituric acid

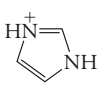


4-Morphine ethanesulfonic acid (MES)

58. 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.

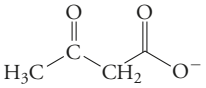
	Acid	K_a	pK
A	Citrate	1.74×10^{-5}	4.76
B	Succinic acid	6.17×10^{-5}	4.21
C	Succinate	2.29×10^{-6}	5.64
D	Formic acid	1.78×10^{-4}	3.75
E	Citric acid	7.41×10^{-4}	3.13

59. At pH 7.4, imidazole is protonated (there is more than one way to draw the structure).



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60. The carboxyl group at right is an acidic group. At pH 7.4, it is ionized.



Acetoacetate

61. First, calculate the final concentrations of boric acid (HA) and borate (A^-). Note that sodium is a spectator ion. The final volume of the solution is 500 mL + 10 mL + 20 mL = 530 mL = 0.53 L.

$$[HA] = \frac{(0.010\ L)(0.050\ M)}{(0.53\ L)} = 9.4 \times 10^{-4}\ M$$

$$[A^-] = \frac{(0.020\ L)(0.020\ M)}{(0.53\ L)} = 7.5 \times 10^{-4}\ M$$

Next, substitute these values into the Henderson–Hasselbalch equation using the pK for boric acid given in Table 2.4 and as shown in Sample Calculation 2.2:

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

$$= 9.24 + \log\frac{7.5 \times 10^{-4}}{9.4 \times 10^{-4}}$$

$$= 9.24 - 0.10 = 9.14$$

62. First, calculate the final concentrations of glycinamide hydrochloride (HA) and glycinamide (A^-). Note that chloride is a spectator ion. The final volume of the solution is 500 mL + 20 mL + 35 mL = 555 mL = 0.555 L.

$$[HA] = \frac{(0.020\ L)(0.100\ M)}{(0.555\ L)} = 3.6 \times 10^{-3}\ M$$

$$[A^-] = \frac{(0.035\ L)(0.050\ M)}{(0.555\ L)} = 3.2 \times 10^{-3}\ M$$

Next, substitute these values into the Henderson–Hasselbalch equation using the pK for glycinamide given in Table 2.4 and as shown in Sample Calculation 2.2:

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

$$= 8.20 + \log\frac{3.2 \times 10^{-3}}{3.6 \times 10^{-3}}$$

$$= 8.20 - 0.05 = 8.15$$

63. First, calculate the final concentrations of $H_2PO_4^-$ (HA) and HPO_4^{2-} (A^-). Note that K^+ is a spectator ion.

$$[HA] = \frac{(0.025\ L)(2.0\ M)}{(0.200\ L)} = 0.25\ M$$

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

Next, substitute these values into the Henderson–Hasselbalch equation using the pK value for dihydrogen phosphate given in Table 2.4 and as shown in Sample Calculation 2.2:

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

$$pH = 6.82 + \log\frac{0.50}{0.25}$$

$$pH = 6.82 + 0.30$$

$$pH = 7.12$$

64. First, calculate the final concentrations of $H_2PO_4^-$ (HA) and HPO_4^{2-} (A^-). Note that K^+ is a spectator ion.

$$[HA] = \frac{(0.050\ L)(2.0\ M)}{(0.200\ L)} = 0.50\ M$$

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

Next, substitute these values into the Henderson–Hasselbalch equation using the pK value for dihydrogen phosphate given in Table 2.4 and as shown in Sample Calculation 2.2:

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

$$pH = 6.82 + \log\frac{0.25}{0.50}$$

$$pH = 6.82 - 0.30$$

$$pH = 6.52$$

65. Since the acid is only 1% dissociated, $[A^-]/[HA] = 0.01$. Use the Henderson–Hasselbalch equation and the pK value for formic acid given in Table 2.4 to calculate the pH as shown in Sample Calculation 2.2:

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

$$= 3.75 + \log(0.01)$$

$$= 3.75 + (-2)$$

$$= 1.75$$

[From Dussourd, D.E. et al., *PLoS ONE* 14, e0218994 (2019).]

66. Since the acid is 10% dissociated, $[A^-]/[HA] = 0.1$. Use the Henderson–Hasselbalch equation and the pK value for butyric acid to calculate the pH as shown in Sample Calculation 2.2:

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

$$= 4.82 + \log(0.1)$$

$$= 4.82 + (-1)$$

$$= 3.82$$

[From Dussourd, D.E. et al., *PLoS ONE* 14, e0218994 (2019).]

67. Use the Henderson–Hasselbalch equation to determine the ratio of acetate (A^-) to acetic acid (HA) at pH 5.0, using the pK value for acetic acid given in Table 2.4 and as shown in Sample Calculation 2.3:

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

$$\log\frac{[A^-]}{[HA]} = pH - pK = 5.0 - 4.76 = 0.24$$

$$\frac{[A^-]}{[HA]} = 1.74 \text{ or } [A^-] = 1.74\ [HA]$$

$$[A^-] = 1.74[HA] = 1.74(0.05\ M - [A^-])$$

$$[A^-] = 0.087 - 1.74[A^-]$$

$$2.74[A^-] = 0.087\ M$$

$$[A^-] = 0.032\ M \text{ or } 32\ mM$$

68. Use the Henderson–Hasselbalch equation to determine the ratio of HPO_4^{2-} (A^-) to $H_2PO_4^-$ (HA) at pH 7.5, using the pK value for $H_2PO_4^-$ given in Table 2.4 and as shown in Sample Calculation 2.3:

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

$$\log\frac{[\text{A}^-]}{[\text{HA}]} = \text{pH} - \text{p}K = 7.50 - 6.82 = 0.68$$

$$\frac{[\text{A}^-]}{[\text{HA}]} = 4.79 \text{ or } [\text{A}^-] = 4.79[\text{HA}]$$

$$[\text{A}^-] = 4.79[\text{HA}] = 4.79(0.100\text{ M} - [\text{A}^-])$$

$$[\text{A}^-] = 0.479 - 4.79[\text{A}^-]$$

$$5.79[\text{A}^-] = 0.479\text{ M}$$

$$[\text{A}^-] = 0.083\text{ M or }83\text{ mM}$$

69.

$CH_2—COOH$	$CH_2—COOH$	$CH_2—COO^-$
$CH_2—COOH$	$CH_2—COO^-$	$CH_2—COO^-$
pH 2	pH 5	pH 7

One of the carboxylic acid groups has a pK of 4.21; the second has a pK of 5.64. Compare the pK values for each group with the pH (as demonstrated in Sample Calculation 2.4). At pH 2, both groups are protonated since the pH is below both pK values. At pH 5, the pH is above pK_1 and below pK_2, so the group with the lower pK is ionized and the group with the higher pK is protonated. At pH 7, the pH is greater than both pK values, so both groups are ionized.

70.

pH 2 $^+H_3N—CH_2—COOH$

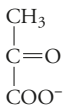
pH 7 $^+H_3N—CH_2—COO^-$

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. Compare the pK values for each group to the pH (as shown in Sample Calculation 2.4). At pH 2, the pH is below both pK values, so both functional groups are 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 unprotonated.

71. 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.

72. a.



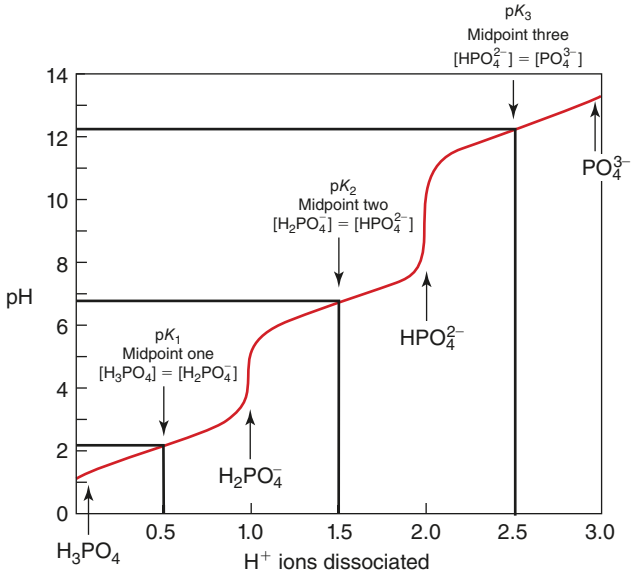
Pyruvate

b. Pyruvate predominates 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.

73. 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. Both a weak acid and a conjugate base are required buffer constituents. Neither the weak acid alone (boric acid) nor the conjugate base alone (sodium borate) can serve as an effective buffer.

74. a. 10 mM acetic acid buffer, because its pK is closer to the desired pH. **b.** 20 mM acetic acid buffer because the higher 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. Neither the weak acid alone (acetic acid) nor the conjugate base alone (sodium acetate) can serve as an effective buffer.

75. 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.

$$H_3PO_4 \rightleftharpoons H^+ + H_2PO_4^-$$

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

$$HPO_4^{2-} \rightleftharpoons H^+ + PO_4^{3-}$$

c. 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 base is HPO_4^{2-}. **d.** 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).

76. 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.

77. Use the pK value in Table 2.4 and the Henderson–Hasselbalch equation to calculate the ratio of the concentrations of imidazole (A^-) to the imidazolium ion (HA):

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

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

$$\frac{[\text{A}^-]}{[\text{HA}]} = 10^{(\text{pH} - \text{p}K)}$$

$$\frac{[\text{A}^-]}{[\text{HA}]} = 10^{(7.4-7.0)} = \frac{2.5}{1}$$

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78.

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

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

$$\frac{[\text{A}^-]}{[\text{HA}]} = 10^{(\text{pH}-\text{p}K)}$$

$$\frac{[\text{A}^-]}{[\text{HA}]} = 10^{(6.5\,-\,7.0)} = 10^{-0.5} = 0.316$$

Since the starting solution contains (0.50 L)(0.010 mol · L^{-1}) = 0.0050 mole of imidazole (A^-), the amount of imidazolium chloride (HA) needed is 0.0050 mol/0.316 = 0.016 moles. The stock imidazolium chloride is 2 M, so the volume of imidazolium chloride to be added is 0.016 mol ÷ 2.0 mol · L^{-1} = 0.008 L = 8 mL.

79. Use the pK value in Table 2.4 and the Henderson–Hasselbalch equation to calculate the ratio of methylammonia (A^-) to the methylammonium ion (HA) as shown in Sample Calculation 2.5:

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

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

$$\frac{[\text{A}^-]}{[\text{HA}]} = 10^{(\text{pH}-\text{p}K)}$$

$$\frac{[\text{A}^-]}{[\text{HA}]} = 10^{(10.5-10.6)} = \frac{0.79}{1}$$

80. The ratio of methylamine (A^-) to the methylammonium ion (HA) at pH 10.5 is 0.79:1 (see Solution 79). The concentration of the methylamine solution provided by the manufacturer is 40 g · 100 mL^{-1} × (1 mol ÷ 31.1 g) = 0.013 mol · mL^{-1} = 13 M. Since the starting solution contains (1.0 L)(0.050 mol · L^{-1}) = 0.050 mole of methylammonium bromide (HA), the amount of methylamine (A^-) needed is 0.79 × 0.050 mol = 0.0395 moles, as shown in Sample Calculation 2.5. The stock methylamine solution is 13 M, so the volume to be added is 0.0395 mol ÷ 13 mol · L^{-1} = 0.003 L = 3 mL.

81. The ratio of acetate (A^-) to acetic acid (HA) at pH 5.0 is 1.74 (see Solution 67). The moles of acetate (A^-) already present is determined: (0.50 L)(0.20 mol · L^{-1}) = 0.10 moles acetate. Next, calculate the moles of acetic acid needed, based on the calculated ratio as shown in Sample Calculation 2.5:

$$\frac{[\text{A}^-]}{[\text{HA}]} = \frac{1.74}{1}$$

$$[\text{HA}] = \frac{0.10\text{ moles}}{1.74}$$

$$[\text{HA}] = 0.057\text{ moles}$$

The volume of glacial acetic acid needed is 0.057 mol ÷ 17.4 mol · L^{-1} = 0.0033 L = 3.3 mL. The addition of 3.3 mL to a 500-mL solution dilutes the solution by less than 1%, which does not introduce significant error.

82. Adding NaOH to the acetic acid will convert some of the acetic acid (HA) to acetate (A^-):

$$\text{NaOH} + \text{CH}_3\text{COOH} \rightarrow \text{Na}^+ + \text{CH}_3\text{COO}^- + \text{H}_2\text{O}$$

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. Calculate the initial amount of acetic acid, using the $[A^-]/[HA]$ ratio determined in Solution 67. The initial amount of acetic acid is 0.10 mol, so the final amount of acetic acid will be 0.10 mol − x.

$$\frac{[\text{A}^-]}{[\text{HA}]} = 1.74 = \frac{x}{0.10\text{ mol} - x}$$

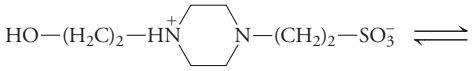
$$x = 1.74(0.10\text{ mol} - x) = 0.174\text{ mol} - 1.74x$$

$$2.74x = 0.174\text{ mol}$$

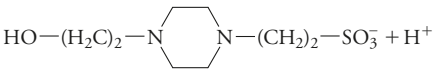
$$x = 0.174\text{ mol}/2.74 = 0.0635\text{ mol}$$

The mass of NaOH to add is calculated: 0.0635 mol × 40 g · mol^{-1} = 2.54 g.

83. a.



Weak acid (HA)



Conjugate base (A)

b. The pK for HEPES is 7.55 (see Table 2.4); therefore, its effective buffering range is 6.55–8.55.

c. $1.0\text{ L} \times \frac{0.10\text{ mole}}{\text{L}} \times \frac{260.3\text{ g}}{\text{mol}} = 26\text{ g}$

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,

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

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 L)(0.10 mol · L^{-1}) = 0.10 moles. After the HCl is added, the amount of A^- will be 0.10 moles − x and the amount of HA will be x. Consequently,

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

$$2.82x = 0.10\text{ mol} - x$$

$$3.82x = 0.10\text{ mol}$$

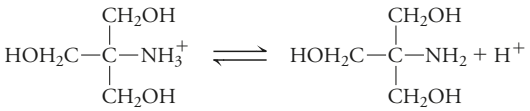
$$x = 0.10\text{ mol} \div 3.82 = 0.0262\text{ mol}$$

The amount of 6.0 M HCl to add is 0.0262 mol ÷ 6.0 mol · L^{-1} = 0.0044 L = 4.4 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.

84. a. To prepare 250 mL of HA, you would need 0.25 L × 1.0 mol · L^{-1} × 238.3 g · mol^{-1} = 59.6 g. Similarly, to prepare 250 mL of A^-, you would need 0.25 L × 1.0 mol · L^{-1} × 260.3 g · mol^{-1} = 65 g. Prepare the solutions by weighing out the appropriate mass of solid, transferring to a beaker to dissolve, then diluting to a final volume of 250 mL using a volumetric flask. **b.** The ratio of A^- to HA required for the buffer is 2.82:1 at pH 8.0. The final concentration of the buffer is 0.10 M. Thus 0.026 moles of HA (see Solution 83d) and (0.10 mol − 0.026 mol) = 0.074 mol of A^- are required per liter. To prepare the buffer from the stock solutions, combine (1.0 L)(0.074 M) ÷ 1.0 M = 0.074 L = 74 mL of A^- and (1.0 L)(0.026 M) ÷ 1.0 M = 0.026 L = 26 mL of HA. Dilute to a final volume of 1.0 L.

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85. a.



Weak acid (HA) Conjugate base (A^-)

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, $[A^-] = 0.10\text{ M} - [HA]$,

and $$\frac{(0.10\text{ M} - [HA])}{[HA]} = 0.79$$

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

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

$$[HA] = \frac{0.10\text{ M}}{1.79} = 0.056\text{ M} = 56\text{ mM}$$

$[A^-] + [HA] = 0.10\text{ M} = 100\text{ mM}$, so $[A^-] = 44$ 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 mol · 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:

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

$$pH = 8.3 + \log\frac{39.5\text{ mmol} \div 1001.5\text{ mL}}{60.5\text{ mmol} \div 1001.5\text{ mL}}$$

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

$$pH = 8.1$$

The buffer is effective. The pH decreases about 0.1 unit (from 8.2 to 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, results in a pH change from approximately 7.0 to 2.3 (see Solution 54a).

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 mol · 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:

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

$$pH = 8.3 + \log\frac{48.5\text{ mmol} \div 1001.5\text{ mL}}{51.5\text{ mmol} \div 1001.5\text{ mL}}$$

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

$$pH = 8.27$$

The buffer is effective. The pH increases only 0.07 units (from 8.2 to 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, results in a pH change from approximately 7.0 to 11.6 (see Solution 54b).

86. 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 L)(3.0 mol · L^{-1}) = 0.0045 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 (1.0×10^{-2} M), for a total concentration of 0.0145 M.

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

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 mol · 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:

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

$$pH = 8.3 + \log\frac{4.5\text{ mmol} \div 1001.5\text{ mL}}{95.5\text{ mmol} \div 1001.5\text{ mL}}$$

$$pH = 8.3 + (-1.3) = 7.0$$

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.

87. a. The amount of imidazole required is 1.0 L × 0.10 mol · L^{-1} × 68.1 g · mol^{-1} = 6.81 g. Weigh 6.81 g of imidazole 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). **b.** At the final pH, the ratio of imidazole (A^-) to the imidazolium ion (HA) is 2.5:1 (see Solution 77). For each mole of HCl added, x, one mole of imidazole (A^-) will be converted to a mole of imidazolium (HA). The starting amount of A^- is (1.0 L)(0.10 mol · L^{-1}) = 0.10 moles. After the HCl is added, the amount of A^- will be 0.10 moles − x and the amount of HA will be x. Consequently,

$$\frac{[A^-]}{[HA]} = \frac{2.5}{1} = \frac{0.10\text{ mol} - x}{x}$$

$$2.5\,x = 0.10\text{ mol} - x$$

$$3.5\,x = 0.10\text{ mol}$$

$$x = \frac{0.10\text{ mol}}{3.5} = 0.029\text{ mol}$$

The amount of 6.0 M HCl to add is 0.029 mol ÷ 6.0 mol · L^{-1} = 0.0048 L = 4.8 mL. To make the buffer, dissolve 6.81 g of imidazole (see part **a**) in

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less than 1.0 L. Add 4.8 mL of 6.0 M HCl, then add water to bring the final volume to 1.0 L.

88. a. To prepare 100 mL of imidazolium hydrobromide, you would need $0.10\ \text{L} \times 1.0\ \text{mol} \cdot \text{L}^{-1} \times 149\ \text{g} \cdot \text{mol}^{-1} = 14.9\ \text{g}$. Similarly, to prepare 100 mL of imidazole you would need $0.10\ \text{L} \times 1.0\ \text{mol} \cdot \text{L}^{-1} \times 68.1\ \text{g} \cdot \text{mol}^{-1} = 6.81\ \text{g}$. Prepare the solutions by weighing out the appropriate mass of solid, transferring to a beaker to dissolve, then diluting to a final volume of 100 mL using a volumetric flask. **b.** The ratio of A^- to HA required for the buffer is 2.5:1 at pH 7.0 (see Solution 77). The final concentration of the buffer is 0.10 M. Thus 0.029 moles of HA (see Solution 87b) and (0.10 mol − 0.029 mol) = 0.071 mol of A^- are required per liter. To prepare the buffer from the stock solutions, combine (1.0 L)(0.071 M) ÷ 1.0 M = 0.071 L = 71 mL of A^- and (1.0 L)(0.029 M) ÷ 1.0 M = 0.029 L = 29 mL of HA. Dilute to a final volume of 1.0 L.

89. a.

$$H_2CO_3 \rightleftharpoons H^+ + HCO_3^-$$
$$HCO_3^- \rightleftharpoons H^+ + CO_3^{2-}$$

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^-.

c.

$$\text{pH} = \text{p}K + \log\frac{[HCO_3^-]}{[H_2CO_3]}$$
$$\log\frac{[HCO_3^-]}{[H_2CO_3]} = \text{pH} - \text{p}K$$
$$\log\frac{[HCO_3^-]}{[H_2CO_3]} = 7.4 - 6.1 = 1.3$$
$$\frac{[HCO_3^-]}{[H_2CO_3]} = 10^{1.3} = \frac{20}{1}$$
$$\frac{24 \times 10^{-3}\ \text{M}}{[H_2CO_3]} = \frac{20}{1}$$
$$[H_2CO_3] = 1.2 \times 10^{-3} = 1.2\ \text{mM}$$

90. $H^+(aq) + HCO_3^-(aq) \rightleftharpoons H_2CO_3(aq) \rightleftharpoons H_2O(l) + CO_2(aq)$

Failure to eliminate CO_2 in the lungs causes a buildup of $CO_2(aq)$. This shifts the equilibrium of the above equations to the left. The increase in $CO_2(aq)$ increases the production of carbonic acid, which in turn dissociates to form additional hydrogen ions, causing acidosis.

91. Mechanical hyperventilation removes CO_2 from the patient's lungs. Carbonic acid in the blood produces more water and CO_2 to make up for the loss of CO_2. This in turn causes additional hydrogen ions and bicarbonate ions to form more carbonic acid. The loss of hydrogen ions results in an increased pH, bringing the patient's pH back to normal.

92. a. The additional bicarbonate combines with hydrogen ions to form carbonic acid. The additional carbonic acid dissociates to form water and carbon dioxide. This helps alleviate the acidosis because the bicarbonate combines with excess hydrogen ions, thus decreasing the hydrogen ion concentration and increasing the pH. However, it is not acceptable for use in patients with ALI because of the increased production of aqueous CO_2 in the blood. The CO_2 produced would need to be exhaled in the lungs, which would be difficult in patients with ALI. **b.** Tris becomes protonated to form its conjugate acid (see Solution 85), removing H^+ from circulation and bringing the pH back to normal. The protonated form of Tris is excreted in the urine. This method of acidosis treatment does not involve exhalation of CO_2 and is therefore an acceptable treatment for patients with ALI. [From Kallet, R.H. et al., *Am. J. Respir. Crit. Care Med.* 161, 1149–1153 (2000).]

93. During hyperventilation, too much CO_2 (which is equivalent to H^+ in the form of carbonic acid) is given off, resulting in respiratory alkalosis. By repeatedly inhaling the expired air, the individual can recover some of this CO_2 and restore acid–base balance.

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

$$\text{pH} = \text{p}K + \log\frac{[HCO_3^-]}{[H_2CO_3]}$$
$$\log\frac{[HCO_3^-]}{[H_2CO_3]} = \text{pH} - \text{p}K$$
$$\log\frac{[HCO_3^-]}{[H_2CO_3]} = 7.5 - 6.1 = 1.4$$
$$\frac{[HCO_3^-]}{[H_2CO_3]} = 10^{1.4} = \frac{25}{1}$$

The ratio of bicarbonate to carbonic acid at pH 7.4 is 20:1 (see Solution 89c). 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 bicarbonate (conjugate base) concentration is too high relative to the carbonic acid (weak acid) concentration; thus the relative amount of weak acid is insufficient. [From Krause, D.S. et al., *Ther. Drug Monit.* 14, 441–445 (1992).]

95. Ammonia and ammonium ions are in equilibrium: $NH_4^+ \rightleftharpoons H^+ + NH_3$. Carbonic acid and bicarbonate ions are in equilibrium: $H_2CO_3 \rightleftharpoons H^+ + HCO_3^-$. Phosphate ions are in equilibrium: $H_2PO_4^- \rightleftharpoons H^+ + HPO_4^{2-}$. 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 excretes $H_2PO_4^-$ and ammonium ions and reabsorbs bicarbonate ions. The result is a decrease in the concentration of protons and an increase in blood pH.

96. The relevant equations are shown in Solution 95. 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^-.

97. The concentrations of both Na^+ and Cl^- are greater outside the cell than inside (see Fig. 2.12). Therefore, the movement of these ions into the cell is thermodynamically favorable. Na^+ movement into the cell drives the exit of H^+ via an exchange protein in the plasma membrane (the favorable movement of Na^+ into the cell "pays for" the unfavorable movement of H^+ out of the cell). Similarly, the movement of Cl^- into the cell drives the movement of HCO_3^- out of the cell through another exchange protein.

98. Acetoacetate is ionized at physiological pH (see Solution 60). The accumulation of the ketone bodies therefore causes metabolic acidosis. The body attempts to compensate by increasing the breathing rate in order to eliminate more CO_2.

99. The cell-surface carbonic anhydrase catalyzes the conversion of $H^+ + HCO_3^-$ to CO_2, which can then diffuse into the cell (the ionic H^+ and HCO_3^- cannot cross the hydrophobic lipid bilayer on their own). Inside the cell, carbonic anhydrase converts the CO_2 back to $H^+ + HCO_3^-$.

100. The lungs can compensate for metabolic acidosis through an increase in the breathing rate in order to eliminate more CO_2. The kidneys can compensate for respiratory acidosis by increasing the breakdown of glutamine to produce NH_3 (excreted in urine as NH_4^+; see Solution 95); however, this mechanism requires the synthesis of enzymes, which takes several hours at least.

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