

1. Which of these statements about hydrogen bonds is *not* true?
 - A) Hydrogen bonds account for the anomalously high boiling point of water.
 - B) In liquid water, the average water molecule forms hydrogen bonds with three to four other water molecules.
 - C) Individual hydrogen bonds are much weaker than covalent bonds.
 - D) Individual hydrogen bonds in liquid water exist for many seconds and sometimes for minutes.
 - E) The strength of a hydrogen bond depends on the linearity of the three atoms involved in the bond.

2. A *true* statement about hydrophobic interactions is that they:
 - A) are the driving force in the formation of micelles of amphipathic compounds in water.
 - B) do not contribute to the structure of water-soluble proteins.
 - C) have bonding energies of approximately 20–40 Kjoule per mole.
 - D) involve the ability of water to denature proteins.
 - E) primarily involve the effect of polar solutes on the entropy of aqueous systems.

3. Hydrophobic interactions make important energetic contributions to:
 - A) binding of a hormone to its receptor protein.
 - B) enzyme-substrate interactions.
 - C) membrane structure.
 - D) three-dimensional folding of a polypeptide chain.
 - E) All of the above are true.

4. Dissolved solutes alter some physical (colligative) properties of the solvent water because they change the:
 - A) concentration of the water.
 - B) hydrogen bonding of the water.
 - C) ionic bonding of the water.
 - D) pH of the water.
 - E) temperature of the water.

5. Osmosis is movement of a:
 - A) charged solute molecule (ion) across a membrane.
 - B) gas molecule across a membrane.
 - C) nonpolar solute molecule across a membrane.
 - D) polar solute molecule across a membrane.
 - E) water molecule across a membrane.

6. A hydronium ion:
- A) has the structure H_3O^+ .
 - B) is a hydrated hydrogen ion.
 - C) is a hydrated proton.
 - D) is the usual form of one of the dissociation products of water in solution.
 - E) All of the above are true.
7. The pH of a solution of 1 M HCl is:
- A) 0.
 - B) 0.1.
 - C) 1.
 - D) 10.
 - E) -1.
8. The pH of a solution of 0.1 M NaOH is:
- A) 0.1.
 - B) 1.0.
 - C) 12.8.
 - D) 13.
 - E) 14.
9. Which of the following is *true* about the properties of aqueous solutions?
- A) A pH change from 5.0 to 6.0 reflects an increase in the hydroxide ion concentration ($[\text{OH}^-]$) of 20%.
 - B) A pH change from 8.0 to 6.0 reflects a decrease in the proton concentration ($[\text{H}^+]$) by a factor of 100.
 - C) Charged molecules are generally insoluble in water.
 - D) Hydrogen bonds form readily in aqueous solutions.
 - E) The pH can be calculated by adding 7 to the value of the pOH.
10. The pH of a sample of blood is 7.4, while gastric juice is pH 1.4. The blood sample has:
- A) 0.189 times the $[\text{H}^+]$ as the gastric juice.
 - B) 5.29 times lower $[\text{H}^+]$ than the gastric juice.
 - C) 6 times lower $[\text{H}^+]$ than the gastric juice.
 - D) 6000 times lower $[\text{H}^+]$ than the gastric juice.
 - E) one million times lower $[\text{H}^+]$ than the gastric juice.

11. The aqueous solution with the lowest pH is:
A) 0.01 M HCl.
B) 0.1 M acetic acid ($pK_a = 4.86$).
C) 0.1 M formic acid ($pK_a = 3.75$).
D) 0.1 M HCl.
E) 10^{-12} M NaOH.
12. The aqueous solution with the highest pH is:
A) 1 M HCl.
B) 1 M NH_3 ($pK_a = 9.25$).
C) 0.5 M $NaHCO_3$ ($pK_a = 3.77$).
D) 0.1 M NaOH.
E) 0.001 M NaOH.
13. Phosphoric acid is tribasic, with pK_a 's of 2.14, 6.86, and 12.4. The ionic form that predominates at pH 3.2 is:
A) H_3PO_4 .
B) $H_2PO_4^-$.
C) HPO_4^{2-} .
D) PO_4^{3-} .
E) None of the above.
14. Which of the following statements about buffers is *true*?
A) A buffer composed of a weak acid of $pK_a = 5$ is stronger at pH 4 than at pH 6.
B) At pH values lower than the pK_a , the salt concentration is higher than that of the acid.
C) The pH of a buffered solution remains constant no matter how much acid or base is added to the solution.
D) The strongest buffers are those composed of strong acids and strong bases.
E) When $pH = pK_a$, the weak acid and salt concentrations in a buffer are equal.
15. A compound has a pK_a of 7.4. To 100 mL of a 1.0 M solution of this compound at pH 8.0 is added 30 mL of 1.0 M hydrochloric acid. The resulting solution is pH:
A) 6.5.
B) 6.8.
C) 7.2.
D) 7.4.
E) 7.5.

16. The Henderson-Hasselbalch equation:
- A) allows the graphic determination of the molecular weight of a weak acid from its pH alone.
 - B) does not explain the behavior of di- or tri-basic weak acids.
 - C) employs the same value for pK_a for all weak acids.
 - D) is equally useful with solutions of acetic acid and of hydrochloric acid.
 - E) relates the pH of a solution to the pK_a and the concentrations of acid and conjugate base.
17. Consider an acetate buffer, initially at the same pH as its pK_a (4.76). When sodium hydroxide (NaOH) is mixed with this buffer, the:
- A) pH remains constant.
 - B) pH rises more than if an equal amount of NaOH is added to an acetate buffer initially at pH 6.76.
 - C) pH rises more than if an equal amount of NaOH is added to unbuffered water at pH 4.76.
 - D) ratio of acetic acid to sodium acetate in the buffer falls.
 - E) sodium acetate formed precipitates because it is less soluble than acetic acid.
18. A compound is known to have a free amino group with a pK_a of 8.8, and one other ionizable group with a pK_a between 5 and 7. To 100 mL of a 0.2 M solution of this compound at pH 8.2 was added 40 mL of a solution of 0.2 M hydrochloric acid. The pH changed to 6.2. The pK_a of the second ionizable group is:
- A) The pH cannot be determined from this information.
 - B) 5.4.
 - C) 5.6.
 - D) 6.0.
 - E) 6.2.

19. Three buffers are made by combining a 1 M solution of acetic acid with a 1 M solution of sodium acetate in the ratios shown below.

	<u>1 M acetic acid</u>	<u>1 M sodium acetate</u>
Buffer 1:	10 mL	90 mL
Buffer 2:	50 mL	50 mL
Buffer 3:	90 mL	10 mL

Which of these statements is *true* of the resulting buffers?

- A) pH of buffer 1 < pH of buffer 2 < pH of buffer 3
 - B) pH of buffer 1 = pH of buffer 2 = pH of buffer 3
 - C) pH of buffer 1 > pH of buffer 2 > pH of buffer 3
 - D) The problem cannot be solved without knowing the value of pK_a .
 - E) None of the above
20. A 1.0 M solution of a compound with 2 ionizable groups (pK_a 's = 6.2 and 9.5; 100 mL total) has a pH of 6.8. If a biochemist adds 60 mL of 1.0 M HCl to this solution, the solution will change to pH:
- A) 5.60.
 - B) 8.90.
 - C) 9.13.
 - D) 9.32.
 - E) The pH cannot be determined from this information.
21. You want to maintain pH = 7.0 for an enzyme-catalyzed reaction that will produce hydrogen ions along with the desired product. At equal concentrations, which weak acid, if any, will serve as the better buffer for the reaction: Acid A, with $pK_a = 6.5$ or Acid B, with $pK_a = 7.5$?
- A) Acid A
 - B) Water is as good as either of the acids available.
 - C) Acid B
 - D) Both are equally effective.
22. In which reaction below does water *not* participate as a reactant (rather than as a product)?
- A) Conversion of an acid anhydride to two acids
 - B) Conversion of an ester to an acid and an alcohol
 - C) Conversion of ATP to ADP
 - D) Photosynthesis
 - E) Production of gaseous carbon dioxide from bicarbonate

23. Which of the following properties of water does *not* contribute to the fitness of the aqueous environment for living organisms?
- Cohesion of liquid water due to hydrogen bonding
 - High heat of vaporization
 - High specific heat
 - The density of water is greater than the density of ice
 - The very low molecular weight of water
24. Name and briefly define five types of noncovalent interactions that occur between biological molecules.
25. Explain the fact that ethanol ($\text{CH}_3\text{CH}_2\text{OH}$) is more soluble in water than is ethane (CH_3CH_3).
26. Explain the fact that triethylammonium chloride ($(\text{CH}_3\text{CH}_2)_3\text{N-HCl}$) is more soluble in water than is triethylamine ($(\text{CH}_3\text{CH}_2)_3\text{N}$).
27. Explain with an appropriate diagram why amphipathic molecules tend to form micelles in water. What force drives micelle formation?
28. (a) Briefly define “isotonic,” “hypotonic,” and “hypertonic” solutions.
 (b) Describe what happens when a cell is placed in each of these types of solutions.
29. For each of the pairs below, circle the conjugate base.

RCOOH	RCOO^-
RNH_2	RNH_3^+
H_2PO_4^-	H_3PO_4
H_2CO_3	HCO_3^-

30. Phosphoric acid (H_3PO_4) has three dissociable protons, with the $\text{p}K_a$'s shown below. Which form of phosphoric acid predominates in a solution at pH 4? Explain your answer.

<u>Acid</u>	<u>$\text{p}K_a$</u>
H_3PO_4	2.14
H_2PO_4^-	6.86
HPO_4^{2-}	12.4

31. Define pK_a for a weak acid in the following two ways: (1) in relation to its acid dissociation constant, K_a , and (2) by reference to a titration curve for the weak acid.
32. Give the general Henderson-Hasselbalch equation and sketch the plot it describes (pH against amount of NaOH added to a weak acid). On your curve, label the pK_a for the weak acid and indicate the region in which the buffering capacity of the system is greatest.
33. Draw the titration curve for a weak acid, HA, whose pK_a is 3.2. Label the axes properly. Indicate with an arrow where on the curve the ratio of salt (A^-) to acid (HA) is 3:1. What is the pH at this point?
34. What is the pH of a solution containing 0.2 M acetic acid ($pK_a = 4.7$) and 0.1 M sodium acetate?
35. You have just made a solution by combining 50 mL of a 0.1 M sodium acetate solution with 150 mL of 1 M acetic acid ($pK_a = 4.7$). What is the pH of the resulting solution?
36. For a weak acid with a pK_a of 6.0, show how you would calculate the ratio of acid to salt at pH 5.
37. Suppose you have just added 100 mL of a solution containing 0.5 mol of acetic acid per liter to 400 mL of 0.5 M NaOH. What is the final pH? (The pK_a of acetic acid is 4.7.)
38. A weak acid HA, has a pK_a of 5.0. If 1.0 mol of this acid and 0.1 mol of NaOH were dissolved in one liter of water, what would the final pH be?
39. In proteins, the amino acid histidine (His) plays an important role in many biological reactions. The pK_a for the protonation of His to form $HisH^+$ = 6.0. When pH = 7.0, what is the fraction of total histidine that will be in the $HisH^+$ form?
40. Severe diarrhea is accompanied by a loss of HCO_3^- . If untreated, will the condition result in acidosis or alkalosis? Use the bicarbonate buffer system given in the scheme below and Le Chatelier's Principle to explain your answer.



41. Give an example of a biological reaction in which water participates as a reactant and a reaction in which it participates as a product.
42. If ice were denser than water, how would that affect life on earth?

Answer Key

1. D
2. A
3. E
4. A
5. E
6. E
7. A
8. D
9. D
10. E
11. D
12. D
13. B
14. E
15. D
16. E
17. D
18. C
19. C
20. A
21. A
22. E
23. E
24. (1) Hydrogen bonds: weak electrostatic attractions between one electronegative atom (such as oxygen or nitrogen) and a hydrogen atom covalently linked to a second electronegative atom; (2) electrostatic interactions: relatively weak charge-charge interactions (attractions of opposite charges, repulsions of like charges) between two ionized groups; (3) hydrophobic interactions: the forces that tend to bring two hydrophobic groups together, reducing the total area of the two groups that is exposed to surrounding molecules of the polar solvent (water); (4) van der Waals interactions: weak interactions between the electric dipoles that two close-spaced atoms induce in each other; (5) tightly bound water molecules can form as an essential part of the binding site in a protein for its ligand.
25. Ethanol can form hydrogen bonds with water molecules, but ethane cannot. When ethanol dissolves, the decrease in the system's entropy that results from formation of ordered arrays of water around the CH_3CH_2^- group is partly compensated by the favorable interactions (hydrogen bonds) of the hydroxyl group of ethanol with water molecules. Ethane cannot form such hydrogen bonds.
26. The positive charge on the N atom in triethylammonium chloride is more polar than the uncharged N atom in triethylamine. This increased polarity leads to stronger interactions with water, leading to increased solubility.
27. Micelle formation minimizes the area of the hydrophobic part of amphipathic molecules that contacts the polar solvent, water. Hydrophobic interactions between hydrophobic moieties are the driving force for micelle formation. When amphipathic molecules

form micelles in water, the entropy decrease due to the formation of ordered arrays of water molecules around the hydrophobic moieties is minimized. (See Fig. 2-7, p. 48.)

28. (a) An isotonic solution has the same osmolarity as the solution to which it is being compared. A hypotonic solution has a lower osmolarity than the solution to which it is being compared. A hypertonic solution has a higher osmolarity than the solution to which it is being compared.
 (b) Higher osmolarity results in osmotic pressure, which generally leads to movement of water across a membrane. In an isotonic solution, in which the osmolarity of the solution is the same as the cell cytoplasm, there will be no net water movement. In a hypotonic solution, water will move into the cell, causing the cell to swell and possibly burst. In a hypertonic solution, water will move out of the cell and it will shrink.

29. RCOO^- , RNH_2 , H_2PO_4^- , HCO_3^-

30. At pH 4, the first dissociable proton ($\text{p}K_a = 2.14$) has been titrated completely, and the second ($\text{p}K_a = 6.86$) has just started to be titrated. The dominant form at pH 4 is therefore H_2PO_4^- , the form with one dissociated proton (see Fig. 2-15).

31. (1) $\text{p}K_a = -\log K_a$. (2) See Fig. 2-17, p. 59; $\text{p}K_a$ is the value of pH at the inflection point in a plot of pH vs. extent of titration of the weak acid. At the $\text{p}K_a$, the concentration of ionized acid equals the concentration of un-ionized acid.

32. The inflection point, which occurs when the weak acid has been exactly one half titrated with NaOH, occurs at a pH equal to the $\text{p}K_a$ of the weak acid. The region of greatest buffering capacity (where the titration curve is flattest) occurs at pH values of $\text{p}K_a \pm 1$. (See Fig. 2-17, p. 59.)

33. The plot of pH versus added base should have the general shape of those shown in Fig. 2-17, p. 59, with the midpoint of the titration (inflection point) at pH 3.2. The ratio of A^- to HA is 3 when 0.75 equivalents of base have been added. From the Henderson-Hasselbalch equation, the pH at this point can be calculated:

$$\text{pH} = \text{p}K_a + \log \frac{[\text{conjugate base}]}{[\text{acid}]} = 3.2 + \log 3 = 3.2 + 0.48 = 3.68$$

34.
$$\text{pH} = \text{p}K_a + \log \frac{[\text{conjugate base}]}{[\text{acid}]} = 4.7 + \log (0.1/0.2)$$

$$= 4.7 - 0.3 = 4.4$$

35.
$$\text{pH} = \text{p}K_a + \log \frac{[\text{conjugate base}]}{[\text{acid}]} = 4.7 + \log (5/150)$$

$$= 4.7 - 1.48 = 3.22$$

36.
$$\text{pH} = \text{p}K_a + \log \frac{[\text{conjugate base}]}{[\text{acid}]}, \text{ so } \text{p}K_a - \text{pH} = -\log \frac{[\text{conjugate base}]}{[\text{acid}]}$$

$$= \log \frac{[\text{acid}]}{[\text{conjugate base}]}$$

$$6.0 - 5.0 = \log \frac{[\text{acid}]}{[\text{conjugate base}]} ; \frac{[\text{acid}]}{[\text{conjugate base}]} = \text{antilog } 1 = 10$$

37. Addition of 200 mmol of NaOH ($400 \text{ mL} \times 0.5 \text{ M}$) to 50 mmol of acetic acid ($100 \text{ mL} \times 0.5 \text{ M}$) completely titrates the acid so that it can no longer act as a buffer and leaves 150 mmol of NaOH dissolved in 500 mL, an $[\text{OH}^-]$ of 0.3 M. Given $[\text{OH}^-]$, $[\text{H}^+]$ can be calculated from the water constant:

$$[\text{H}^+][\text{OH}^-] = 10^{-14}$$

$$[\text{H}^+] = 10^{-14} \text{ M}^2 / 0.3 \text{ M}$$

pH is, by definition, $\log (1/[\text{H}^+])$.

$$\text{pH} = \log (0.3 \text{ M} / 10^{-14} \text{ M}^2) = 12.48.$$

38. Combining 1 mol of weak acid with 0.1 mol of NaOH yields 0.9 mol of weak acid and 0.1 mol of salt.

$$\text{pH} = \text{p}K_a + \log \frac{[\text{conjugatebase}]}{[\text{acid}]} = 5.0 + \log (0.1/0.9) = 4.05$$

39. Use the Henderson-Hasselbalch equation to determine the *ratio* of [His] to [HisH⁺].

$$\text{pH} = \text{p}K_a + \log ([\text{His}] / [\text{HisH}^+])$$

$$7.0 = 6.0 + \log ([\text{His}] / [\text{HisH}^+])$$

$$1.0 = \log ([\text{His}] / [\text{HisH}^+])$$

$$[\text{His}] / [\text{HisH}^+] = \text{antilog} (1) = 10$$

To determine the *fraction* of the total in the HisH⁺ form, $[\text{His}]_{\text{total}} = [\text{His}] + [\text{HisH}^+]$,

$$\text{fraction} = [\text{HisH}^+] / [\text{His}]_{\text{total}}$$

$$= [\text{HisH}^+] / ([\text{His}] + [\text{HisH}^+])$$

substitute from ratio calculated above

$$= [\text{HisH}^+] / (10[\text{HisH}^+] + [\text{HisH}^+])$$

$$= \mathbf{1/11, \text{ or } 0.09}$$

40. Acidosis. The removal of HCO₃⁻ will pull the equilibria in the direction of HCO₃⁻, which will produce H⁺, thereby lowering the pH.
41. See page 65 for examples such as condensation and hydrolysis reactions.
42. Ice that formed at the surface of bodies of water would sink; hence, streams, ponds, lakes, and so on would freeze from the bottom up. With a reservoir of ice at the bottom, they would be perpetually cold, and in the limit they would freeze solid, precluding life as we know it.