

# 2

## Water

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This chapter introduces you to the unique properties of water and to acid–base reactions. The discussion of water begins with a look at its structure and how its polarity provides a basis for understanding its powers as a solvent. You are then introduced to the hydrophobic effect, osmosis, and diffusion. The chemical properties of water are then described, beginning with the ionization of water, which sets the stage for a discussion of acid–base chemistry and the behavior of weak acids and buffers. This discussion includes the Brønsted–Lowry definition for acids and bases, the definition of pH, and the derivation of the Henderson–Hasselbalch equation. As we shall see in subsequent chapters, a solid understanding of acid–base equilibria is fundamental to understanding key aspects of amino acid biochemistry, protein structure, enzyme catalysis, transport across membranes, energy metabolism, and other metabolic transformations.

### **Essential Concepts**

1. Water is essential to biochemistry because:
  - (a) Biological macromolecules assume specific shapes in response to the chemical and physical properties of water.
  - (b) Biological molecules undergo chemical reactions in an aqueous environment.
  - (c) Water is a key reactant in many reactions, usually in the form of  $\text{H}^+$  and  $\text{OH}^-$  ions.
  - (d) Water is oxidized in photosynthesis to produce molecular oxygen,  $\text{O}_2$ , as part of the process that converts the sun's energy into usable chemical form. Expenditure of that energy under aerobic conditions leads to the reduction of  $\text{O}_2$  back to water.

### *Physical Properties of Water*

2. The structure of water closely approximates a tetrahedron with its two hydrogen atoms and the two lone pairs of electrons of its oxygen atom “occupying” the vertices of the tetrahedron.
3. The high electronegativity of oxygen relative to hydrogen results in the establishment of a permanent dipole in water molecules.
4. The polar nature of water results in negative portions of the molecule being attracted to the positive portions of neighboring water molecules by a largely electrostatic interaction known as the hydrogen bond.

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5. Hydrogen bonds are represented as  $D-H\cdots A$ , where  $D-H$  is a weakly acidic compound so that the hydrogen atom (H) has a partial positive charge, and A is a weakly basic group that bears lone pairs of electrons. A is often an oxygen atom or a nitrogen atom (occasionally sulfur).
6. Water is strongly hydrogen bonded, with each water molecule participating in four hydrogen bonds with its neighbors; two in which it donates and two in which it accepts. Hydrogen bonds commonly form between water molecules and the polar functional groups of biomolecules, or between the polar functional groups themselves.
7. The strongly hydrogen bonded character of water is responsible for many of its characteristic properties, most notably:
  - (a) A high heat of fusion, which allows water to act as a heat sink, such that greater heat loss is necessary for the freezing of water compared to other substances of similar molecular mass.
  - (b) A high heat of vaporization, such that relatively more heat must be input to vaporize water compared to other substances of similar molecular mass.
  - (c) An ability to dissolve most polar compounds.
  - (d) An open structure makes ice less dense than liquid water, thereby making ice float, insulating the water beneath it, and inhibiting total freezing of large bodies of water.
8. A variety of weak electrostatic interactions are critical to the structure and reactivity of biological molecules. These interactions include, in order of increasing strength, London dispersion forces, dipole–dipole interactions, hydrogen bonds, and ionic interactions (see Table 2-1).
9. Water is an excellent solvent of polar and ionic substances due to its property of surrounding polar molecules and ions with oriented shells of water, thereby attenuating the electrostatic forces between these molecules and ions.
10. The tendency of water to minimize its contact with nonpolar (hydrophobic) molecules is called the hydrophobic effect. This effect is largely driven by the increase in entropy caused by the necessity for water to order itself around nonpolar molecules. This causes the nonpolar molecules to aggregate, thereby reducing the surface area that water must order itself about. Consequently, nonpolar substances are poorly soluble in aqueous solution.
11. Many biological molecules have both polar (or charged) and nonpolar functional groups and are therefore simultaneously hydrophilic and hydrophobic. These molecules are said to be amphiphilic or amphipathic.
12. Osmosis is the movement of solvent across a semipermeable membrane from a region of lower concentration of solute to a region of higher concentration of solute. Osmotic pressure of a solution is the pressure that must be applied to the solution to prevent an inflow of solvent. Hence, an increase in solute concentration results in an increase in osmotic pressure.

13. Diffusion is the random movement of molecules in solution (or in the gas phase). It is responsible for the movement of solutes from a region of high concentration to a region of low concentration.

*Chemical Properties of Water*

14. Water is a neutral, polar molecule that has a slight tendency to ionize into  $\text{H}^+$  and  $\text{OH}^-$ . However, the proton is never free and binds to a water molecule to form  $\text{H}_3\text{O}^+$  (hydronium ion).
15. The ionization of water is described as an equilibrium between the unionized water (reactant) and its ionized species (products)



In which

$$K = \frac{[\text{H}^+][\text{OH}^-]}{[\text{H}_2\text{O}]}$$

Since in dilute aqueous solution, the concentration of water is essentially constant (55.5 M), the concentration of  $\text{H}_2\text{O}$  is incorporated into the value of  $K$ , which is referred to as  $K_w$ , the ionization constant of water.

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

16. The values of both  $\text{H}^+$  and  $K$  are inconveniently small; hence, their values are more conveniently expressed as negative logarithms, so that

$$\text{pH} = -\log [\text{H}^+]$$

$$\text{p}K = -\log K$$

17. According to the Brønsted–Lowry definition, an acid is a substance that can donate a proton, and a base is a substance that can accept a proton. The strength of a weak acid is proportional to its dissociation constant, which is expressed as

$$K = \frac{[\text{H}^+][\text{A}^-]}{[\text{HA}]}$$

18. The pH of a solution of a weak acid is determined by the relative concentrations of the acid and its conjugate base. The equilibrium expression for the dissociation of a weak acid can be rearranged to

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

This relationship is known as the Henderson–Hasselbalch equation. When the concentration of a weak acid is equal to the concentration of its conjugate base,  $\text{pH} = \text{p}K$ . Hence, the stronger the acid, the lower its  $\text{p}K$  (see Table 2-4).

19. Solutions of a weak acid at  $\text{pH}$ 's near its  $\text{p}K$  resist large changes in  $\text{pH}$  as  $\text{OH}^-$  or  $\text{H}^+$  is added. Added protons react with the weak acid's conjugate base to reform the weak acid; whereas added  $\text{OH}^-$  combines with the acid to form its conjugate base and water. A solution of a weak acid and its conjugate base (in the form of a salt) is referred to as a buffer. Buffers are effective within 1  $\text{pH}$  unit of the  $\text{p}K$  of the component acid.

### Key Equation

Know how to use the Henderson–Hasselbalch equation:

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

### Guide to Study Exercises (text p. 38)

1. A water molecule in ice is linked to its four nearest neighbors to form a three-dimensional lattice in which the hydrogen-bonded atoms assume a tetrahedral arrangement (see Fig. 2-3). In liquid water, there are only slightly fewer hydrogen bonds between water molecules, but the bonds are no longer strictly tetrahedral, so that irregular groupings of hydrogen bonded molecules occur. (Section 2-1A)
2. Polar substances dissolve in water because the polar water molecules interact with the dipoles of the solute, thereby weakening the attractive forces between solute molecules. Nonpolar substances do not dissolve in water because they lack the bond dipoles that can interact with polar water molecules. (Section 2-1B)
3. The dispersion of a nonpolar substance in an aqueous medium is accompanied by a decrease in entropy due to the ordering of polar water molecules in cages around the nonpolar molecules. The entropy of this process is minimized by the aggregation of the nonpolar molecules, which reduces the area of the water cages and thus the number of ordered water molecules. The loss of entropy of the aggregated nonpolar substance is more than offset by the collective increase in the entropy of the water molecules. The aggregation and exclusion from aqueous solvent of the nonpolar solute is known as the hydrophobic effect. (Section 2-1C)
4. Amphiphiles form micelles in water in order that their nonpolar portions can aggregate by exclusion from water while their polar portions can interact with the polar water molecules. (Section 2-1C)
5. Osmosis is the movement of molecules across a semipermeable membrane from a region of relatively high concentration (e.g., pure water, which can pass through a membrane) to a region of relatively low concentration (e.g., water containing a dissolved solute that cannot

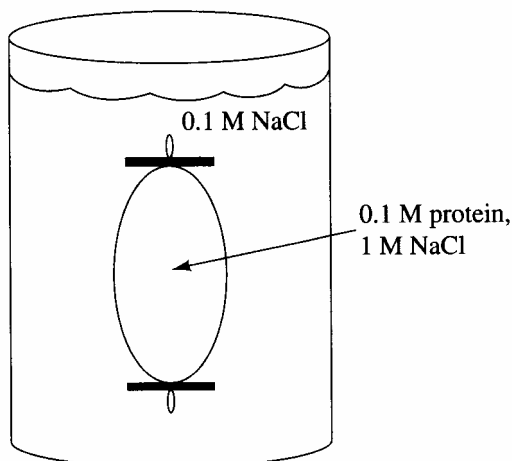
pass through the membrane). Diffusion is the random movement of molecules in solution (or in a gas) from a region of higher solute concentration to a region of lower solute concentration. (Section 2-1D)

6. In both the Arrhenius and Brønsted–Lowry definitions, an acid is a substance that can donate a proton. The Arrhenius definition of a base is somewhat limited: an Arrhenius base is a substance that can donate a hydroxide ion. The Brønsted–Lowry definition of a base is more general: a Brønsted–Lowry base is a substance that can accept a proton and hence includes substances that don't contain hydroxyl groups. (Section 2-2B)
7. Because HCl is a strong acid, it dissociates completely in solution. Therefore, the  $[H^+]$  of 1 M HCl is 1 M. Since  $pH = -\log [H^+]$ , the pH of a 1 M solution of HCl is 0. (Section 2-2B)

## Questions

### *Physical Properties of Water*

1. Draw a 3-dimensional structure of a water molecule, including any lone pairs of electrons, and indicate the dipole moment. What is the name of the geometrical figure you have drawn?
2. Which gas in each of the following pairs would you expect to be more soluble in water? Why?
  - (a) oxygen and carbon dioxide
  - (b) nitrogen and ammonia
  - (c) methane and hydrogen sulfide
3. Why do bottles of beer break when placed in a freezer?
4. Distinguish between hydrophilic, hydrophobic, and amphipathic substances.
5. Mixing olive oil with vinegar creates a salad dressing that is an emulsion, a mixture of vinegar with many tiny oil droplets. However, in a few minutes, the olive oil separates entirely from the vinegar. Describe the changes in entropy that occur during the initial mixing and the subsequent separation of the olive oil and vinegar.
6. Shown on the next page is a beaker that contains a solution of 0.1 M NaCl. Floating inside is a cellulose bag that is permeable to water and small ions like  $Na^+$  and  $Cl^-$  but is impermeable to protein. The bag contains 1 M NaCl and 0.1 M protein. Describe the movement of solutes and solvent.



### Chemical Properties of Water

7. In the most general definition of an acid and a base, a Lewis acid is a compound that can accept an electron pair, and a Lewis base is a compound that can donate an electron pair. Which of the following compounds can be classified as Brønsted–Lowry acids and bases and which as Lewis acids and bases?

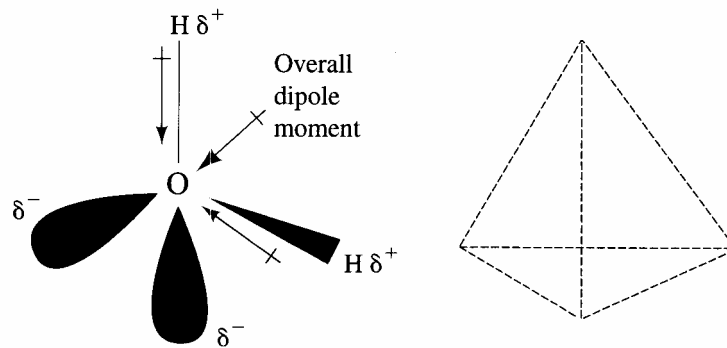


8. Define  $pK$  and  $pH$ , and write the Henderson–Hasselbalch equation that relates the two.
9. The  $pK$ 's of trichloroacetic acid and acetic acid are 0.7 and 4.76, respectively. Which is the stronger acid? What is the dissociation constant of each?
10. What is the  $[\text{OH}^-]$  in a 0.05 M HCl solution? What is the  $pH$ ?
11. A solution of 0.1 M HCl has a  $pH$  of 1. A solution of 0.1 M acetic acid has a  $pH$  of 2.8. How much 1 M NaOH is needed to titrate a 100 mL sample of each acid to its respective equivalence point? Hint: It may be useful to review Le Chatelier's principle.
12. A 0.01 M solution of a weak acid in water is 0.05% ionized at 25°C. What is its  $pK$ ?
13. What is a buffer? How does it work? What compounds act as buffers in cells?
14. What is the  $pH$  of a 0.1 M solution of cacodylic acid ( $pK = 6.27$ )?
15. How would the  $pH$  of a 0.1 M solution of acetic acid be affected by the addition of a 4.5 M solution of sodium acetate (NaOAc)? NaOAc is a relatively strong base (weak acids have strong conjugate bases). Hint: Consider Le Chatelier's principle.
16. A 0.02 M solution of lactic acid ( $pK = 3.86$ ) is mixed with an equal volume of a 0.05 M solution of sodium lactate. What is the  $pH$  of the final solution?

17. You need a KOAc solution at pH 5, which is 3 M in  $K^+$ . Such a solution is used in bacterial plasmid DNA isolation. How many moles of KOAc and acetic acid (HOAc) do you need to make 500 mL of this solution?
18. What are the predominant phosphate ions in a neutral pH phosphate buffer?
19. A beaker of pure distilled water sitting out on your lab bench is slightly acidic. Explain. Hint: see Box 2-2.

### Answers to Questions

1.



The molecule forms a tetrahedron.

2. (a) Carbon dioxide ( $O = C = O$ ), which is more polarizable than oxygen ( $O = O$ ). (b) Ammonia ( $NH_3$ ), which is more polar than nitrogen ( $N = N$ ). (c) Hydrogen sulfide ( $HS$ ), which is more polar than methane ( $CH_4$ ).
3. Water expands upon freezing. Full bottles of beer have little room for expansion and the frozen liquid expands beyond the boundaries of the glass and cap. Similarly, bottles of wine lose their corks in the freezer.
4. Hydrophilic substances are polar compounds that are readily soluble in water. Hydrophobic substances are nonpolar compounds that are insoluble in water. Amphipathic substances have both polar and nonpolar segments; they form micelles or bilayers in aqueous solution in which the polar groups face the water and the nonpolar groups exclude water and face each other (see Figure 2-11).
5. When the olive oil and vinegar (which is an aqueous solution) are mixed, the entropy of the solution decreases (the action of mixing is an input of energy that drives this process). Mechanical mixing results in an ordering of water around the thousands of oil droplets. Once the mixing has stopped, the system moves toward equilibrium, which maximizes entropy. As the oil droplets fuse, the surface-to-volume ratio of all of the oil decreases, thereby decreasing the amount of ordered water. Consequently, the entropy of the solution increases.

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6.  $\text{Na}^+$  and  $\text{Cl}^-$  ions diffuse out of the bag down their concentration gradient across the cellulose membrane. Water moves into the bag via osmosis since its concentration inside the bag is relatively lower due to the presence of the protein that cannot traverse the membrane (and initially due to the higher  $[\text{NaCl}]$  inside the bag—which eventually equalizes with the  $[\text{NaCl}]$  outside the bag). The bag expands as water enters. This setup is called dialysis and is used to remove or add salts to solutions of macromolecules.
7.  $\text{BF}_3$ ,  $\text{Zn}^{2+}$ ,  $\text{HCOOH}$ ,  $\text{NH}_4^+$ , and  $\text{H}_2\text{O}$  are Lewis acids; however, only  $\text{HCOOH}$ ,  $\text{NH}_4^+$ , and  $\text{H}_2\text{O}$  are Brønsted–Lowry acids.  $\text{NH}_3$ ,  $\text{OH}^-$  and  $\text{Cl}^-$  are considered bases under both definitions.
8.  $\text{p}K$  is the negative logarithm of the dissociation constant of a weak acid.  $\text{pH}$  is the negative logarithm of the  $[\text{H}^+]$ . The Henderson–Hasselbalch equation is

$$\text{pH} = \text{p}K + \log \frac{[\text{conjugate base}]}{[\text{acid}]}$$

9.  $\text{p}K$  is the negative logarithm of the dissociation constant,  $K$ , so the smaller the value of  $\text{p}K$ , the larger the value of  $K$ . The larger the value of  $K$ , the greater the dissociation of the acid in water. Therefore, trichloroacetic acid is the stronger acid since it has a lower  $\text{p}K$  than acetic acid.

For trichloroacetic acid,  $\text{p}K = -\log K$

Therefore,  $K = 10^{-0.7} = 0.2$

Similarly for acetic acid,

$$\begin{aligned}\log K &= -4.76 \\ K &= 10^{-4.76} = 1.74 \times 10^{-5}\end{aligned}$$

10.  $\text{HCl}$  is a strong acid and completely dissociates in water, so  $[\text{HCl}] = [\text{H}^+] = 0.05 \text{ M}$ . The  $\text{pH}$  is given by

$$\begin{aligned}\text{pH} &= -\log [\text{H}^+] \\ &= -\log 0.05 \\ &= 1.3\end{aligned}$$

Since  $[\text{H}^+][\text{OH}^-] = K_w$ ,

$$\begin{aligned}[\text{OH}^-] &= \frac{K_w}{[\text{H}^+]} \\ &= \frac{10^{-14}}{0.05} \\ &= 2 \times 10^{-13} \text{ M}\end{aligned}$$



11. By Le Chatelier's principle, the equilibrium for the dissociation of a weak acid is shifted toward the dissociation of the acid by removal of  $H^+$ . Therefore, as  $H^+$  is removed by titration with  $OH^-$ , more acid dissociates, until there is no acid remaining. Hence, the amount of  $OH^-$  needed to titrate equivalent amounts of all monovalent acids is the same. In this case, 10 mL of 1 M NaOH will bring the titration of each acid to its end point. (Note: 10 mL of 1 M NaOH provides 0.01 moles of  $OH^-$  to neutralize the 0.01 moles of  $H^+$ .)
12. The equilibrium constant for a weak acid is

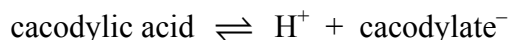
$$K = \frac{[H^+][A^-]}{[HA]}$$

The concentration of each of the dissociated ions is 0.05% of 0.01 M, or  $0.0005 \times 0.01 \text{ M} = 5 \times 10^{-6} \text{ M}$ . Because only 0.05% of the acid is ionized, we can assume that  $[HA]$  does not change. We then calculate

$$K = \frac{(5 \times 10^{-6})(5 \times 10^{-6})}{0.01} = 2.5 \times 10^{-9}$$

$$pK = -\log(2.5 \times 10^{-9}) = 8.6$$

13. A buffer is a solution of a weak acid and its conjugate base. A buffer works by "absorbing" base or acid equivalents within about one pH unit of its  $pK$ . For example, when a small amount of  $OH^-$  is added, it reacts with HA to form water and  $A^-$ , with little change in pH. Similarly, a small amount of  $H^+$  reacts with  $A^-$  to form HA. In biological systems, protons produced during catabolic reactions must be buffered by the cell. Phosphate and carbonate ions, as well as proteins, nucleic acids, and fatty acids, serve as buffers in cells.
14. Since  $pK = 6.27$ ,  $K = 10^{-6.27} = 5.37 \times 10^{-7}$ . For the dissociation of cacodylic acid



we can approximate  $[H^+] = [\text{cacodylate}^-] = x$ .

We approximate  $[\text{cacodylic acid}]$  by  $0.1 - x$ . Therefore,

$$K = \frac{[H^+][\text{cacodylate}^-]}{[\text{cacodylic acid}]}$$

$$5.37 \times 10^{-7} = \frac{x^2}{0.1 - x}$$

$$0 = x^2 + (5.37 \times 10^{-7})x - (5.37 \times 10^{-8})$$

Solve for  $x$  using the quadratic equation

$$x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}$$

$$x = \frac{-(5.37 \times 10^{-7}) \pm \sqrt{(5.37 \times 10^{-7})^2 + 4(5.37 \times 10^{-8})}}{2}$$

$$x = -2.32 \times 10^{-4} \text{ or } 2.31 \times 10^{-4}$$

The result can only be  $2.31 \times 10^{-4}$  since there is no such thing as a negative concentration.

Therefore,  $x = [\text{H}^+] = 2.31 \times 10^{-4} \text{ M}$  and

$$\text{pH} = 3.64$$

Note that for weak acids with  $\text{p}K > 5$ , one can approximate the pH by ignoring the change in acid concentration due to its dissociation. Thus,  $[\text{cacodylic acid}] = 0.1 \text{ M}$  and

$$5.37 \times 10^{-7} = \frac{x^2}{0.1}$$

Therefore,  $x = 2.32 \times 10^{-4} \text{ M}$

15. By Le Chatelier's principle, the added acetate anion drives the reaction toward the formation of undissociated acid, thereby causing a decrease in  $[\text{H}^+]$  and an increase in pH.
16. The final concentrations are  $[\text{lactic acid}] = 0.01 \text{ M}$  and  $[\text{lactate}] = 0.025 \text{ M}$ . Use the Henderson–Hasselbalch equation to calculate the pH:

$$\begin{aligned} \text{pH} &= \text{p}K + \log \frac{[\text{lactate}]}{[\text{lactic acid}]} \\ &= 3.86 + \log 2.5 \\ &= 3.86 + 0.398 \\ &= 4.26 \end{aligned}$$

17. Use the Henderson–Hasselbalch equation to calculate the concentration of acetic acid ( $x$ ) necessary to obtain a solution of pH 5 that contains 3 M  $K^+$  (3 M KOAc). The  $pK$  of acetic acid is 4.76 (Table 2-4).

$$\begin{aligned} \text{pH} &= \text{p}K + \log \frac{[\text{KOAc}]}{[\text{HOAc}]} \\ 5 &= 4.76 + \log \frac{3}{x} \\ 0.24 &= \log 3 - \log x \\ 0.24 - 0.48 &= -\log x \\ 0.24 &= \log x \\ x &= 1.73 \text{ M} \end{aligned}$$

Therefore, for a 500 mL solution, the amount of acetic acid added should be  $1.73/2$  or 0.86 moles. The amount of KOAc should be  $3/2$  or 1.5 moles.

18. At pH 7,  $\text{H}_2\text{PO}_4^-$  is in equilibrium with  $\text{HPO}_4^{2-}$  at nearly a 1:1 ratio since pH 7 is near  $pK_2$  (6.82). See Figure 2-18 and Table 2-4.
19. Atmospheric carbon dioxide reacts with the distilled water in the beaker to form carbonic acid. The carbonic acid dissociates into protons and bicarbonate with a  $pK$  of about 6. These protons make the distilled water slightly acidic.

