

## Acids, Bases, and pH

## Chapter Preview

- 8.1** Explaining the Properties of Acids and Bases
- 8.2** The Equilibrium of Weak Acids and Bases
- 8.3** Bases and Buffers
- 8.4** Acid-Base Titration Curves


## Prerequisite Concepts and Skills

Before you begin this chapter, review the following concepts and skills:

- writing net ionic equations (Concepts and Skills Review)
- calculating molar concentrations (Concepts and Skills Review)
- solving equilibrium problems (Chapter 7, sections 7.3 and 7.4)
- explaining the mathematical properties of logarithms (previous studies)
- performing acid-base titrations (previous studies)

For many people, the word “acid” evokes the image of a fuming, highly corrosive, dangerous liquid. This image is fairly accurate for concentrated hydrochloric acid, a strong acid. Most acids, however, are not as corrosive as hydrochloric acid, although they may still be very hazardous. For example, hydrofluoric acid can cause deep, slow-healing tissue burns if it is handled carelessly. It is used by artists and artisans who etch glass. It reacts with the silica in glass to form a compound that dissolves, leaving the glass with a brilliant surface. Hydrofluoric acid is highly corrosive. Even a 1% solution is considered to be hazardous. Yet chemists classify hydrofluoric acid as a weak acid.

You learned about acids and bases in your previous chemistry course. In this chapter, you will extend your knowledge to learn how the structure of a compound determines whether it is an acid or a base. You will use the equilibrium constant of the reaction of an acid or base with water to determine whether the acid or base is strong or weak. You will apply your understanding of dissociation and pH to investigate buffer solutions: solutions that resist changes in pH. Finally, you will examine acid-base titrations that involve combinations of strong and weak acids and bases.



The hydrohalic acids ( $\text{HX}_{(\text{aq})}$ ), where X represents a halogen) include HF, HCl, HBr, and HI. Only HF is a weak acid. The rest are strong acids. What factors account for this difference?

# Explaining the Properties of Acids and Bases

## 8.1

Table 8.1 outlines properties of acids and bases that you have examined in previous courses. In this section, you will review two theories that help to explain these and other properties. As well, you will use your understanding of molecular structure to help you understand why acids and bases differ in strength.

**Table 8.1** Examples and Common Properties of Acids and Bases

Example	Acids	Bases
solid	acetyl salicylic acid	sodium hydroxide
liquid	acetic acid	aniline
gas	hydrogen chloride	ammonia
Property	Acids	Bases
taste <b>CAUTION</b> Never taste chemicals in a lab.	Acids taste sour.	Bases taste bitter.
texture of solution <b>CAUTION</b> Never deliberately touch chemicals. Strong, concentrated acids and bases will burn your skin.	Acids do not have a characteristic texture.	Bases feel slippery.
reaction with phenolphthalein	Acidic phenolphthalein is colourless.	Basic phenolphthalein is pink.
reaction with litmus paper	Acids turn blue litmus red.	Bases turn red litmus blue.
reaction with metals	Acids react with metals above hydrogen in the activity series to displace $H_{2(g)}$ .	Bases react with certain metals (such as Al) to form $H_{2(g)}$ .
reaction with carbonates	Carbon dioxide is formed.	No reaction occurs.
reaction with ammonium chloride	No reaction occurs.	Ammonia, $NH_3$ , a gas with a characteristic odour, is produced.
neutralization reaction	Acids neutralize basic solutions.	Bases neutralize acidic solutions.
reaction with fatty acids	No reaction occurs.	Bases react to form soap (a saponification reaction).
aqueous property of oxides	Non-metal oxides form acidic solutions: for example, $CO_{2(g)} + H_2O_{(l)} \rightarrow H_2CO_{3(aq)}$	Metal oxides form basic solutions: for example, $CaO_{(s)} + H_2O_{(l)} \rightarrow Ca(OH)_{2(aq)}$
amount of dissociation in aqueous solution (strength)	Strong acids dissociate completely. Weak acids dissociate only partially.	Strong bases dissociate completely. Weak bases dissociate only partially.

### Section Preview/ Specific Expectations

In this section, you will

- **compare** strong acids and bases, and weak acids and bases, in terms of equilibrium
- **identify** conjugate acid-base pairs
- **solve** problems that involve strong acids and strong bases
- **communicate** your understanding of the following terms: *hydronium ion* ( $H_3O^+_{(aq)}$ ), *conjugate acid-base pair*, *monoprotic acids*, *polyprotic acids*

The following ExpressLab highlights concepts that you will examine in this section, as well as later in the chapter.

## ExpressLab



## Comparing Acid-Base Reactions

You will perform three acid-base reactions. Before you begin, read the Procedure and make a prediction about the relative rates of these reactions.

### Safety Precautions



The solutions that are used in this lab are irritants and should be handled with care. Wash any spills on your skin or clothing with plenty of water. Inform your teacher immediately.

### Materials

powdered calcium carbonate,  $\text{CaCO}_{3(s)}$   
3 squeeze bottles, each containing one of the following solutions: 2.0 mol/L  $\text{HCl}_{(aq)}$ ;  
2.0 mol/L  $\text{CH}_3\text{COOH}_{(aq)}$ ; mixture of  
2.0 mol/L  $\text{CH}_3\text{COOH}_{(aq)}$  and 2.0 mol/L  $\text{NaCH}_3\text{COO}_{(aq)}$   
scoopula  
3 test tubes  
test tube rack  
labels or grease pencil

### Procedure

1. Label each test tube to identify the solution it will contain. Then fill each test tube with the corresponding solution, to a depth of about 2 cm.
2. Add a small amount of  $\text{CaCO}_{3(s)}$  (enough to cover the tip of a scoopula) to each test tube. Try to add the same amount of  $\text{CaCO}_{3(s)}$  to all three test tubes.
3. Record your observations. Rank the rates of the three reactions from fastest to slowest.

### Analysis

1. (a) What rate-related change did you observe in each test tube?  
(b) If you wanted to collect quantitative data for each reaction, how could you modify the experiment?
2. In all three test tubes, the following reaction occurred.  
$$\text{CaCO}_{3(s)} + 2\text{H}_3\text{O}^+_{(aq)} \rightarrow \text{CO}_{2(g)} + \text{Ca}^{2+}_{(aq)} + 3\text{H}_2\text{O}_{(l)}$$
  
The only difference between the test tubes was the concentration of  $\text{H}^+_{(aq)}$  in the acidic solutions that reacted with  $\text{CaCO}_{3(s)}$ . Explain your ranking of the rates of reaction in terms of  $[\text{H}_3\text{O}^+]$ .
3. The concentrations of  $\text{HCl}_{(aq)}$  and  $\text{CH}_3\text{COOH}_{(aq)}$  were identical. The following dissociation reactions occurred.  
$$\text{HCl}_{(aq)} + \text{H}_2\text{O}_{(l)} \rightleftharpoons \text{H}_3\text{O}^+_{(aq)} + \text{Cl}^-_{(aq)}$$
  
$$\text{CH}_3\text{COOH}_{(aq)} + \text{H}_2\text{O}_{(l)} \rightleftharpoons \text{H}_3\text{O}^+_{(aq)} + \text{CH}_3\text{COO}^-_{(aq)}$$
  
Explain your ranking of the  $[\text{H}_3\text{O}^+]$  in these solutions in terms of the extent of the equilibrium dissociation.
4. The third solution was a mixture of 2.0 mol/L  $\text{CH}_3\text{COOH}_{(aq)}$  and 2.0 mol/L  $\text{NaCH}_3\text{COO}_{(aq)}$ . How did the addition of sodium acetate affect the equilibrium of the dissociation reaction of acetic acid?
5. Explain your ranking of the rate of the reaction between calcium carbonate and the solution that was a mixture of acetic acid and sodium acetate.

## The Arrhenius Theory of Acids and Bases

According to the Arrhenius theory (1887), acids and bases are defined in terms of their structure and the ions produced when they dissolve in water.

- An acid is a substance that dissociates in water to form  $\text{H}^+_{(aq)}$ . Two examples of Arrhenius acids are hydrochloric acid,  $\text{HCl}$ , and sulfuric acid,  $\text{H}_2\text{SO}_4$ .
- A base is a substance that dissociates in water to form  $\text{OH}^-_{(aq)}$ . Two examples of Arrhenius bases are sodium hydroxide,  $\text{NaOH}$ , and potassium hydroxide,  $\text{KOH}$ .

The Arrhenius theory explains acid-base reactions as a combination of  $\text{H}^+_{(\text{aq})}$  and  $\text{OH}^-_{(\text{aq})}$ . It provides insight into the heat of neutralization for the reaction between a strong acid and a strong base. (Strong acids and bases dissociate completely into ions in solution.) For example, consider the following reaction.



The total ionic equation for this reaction is

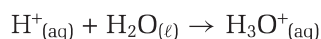


Subtracting spectator ions from both sides, the net ionic equation is

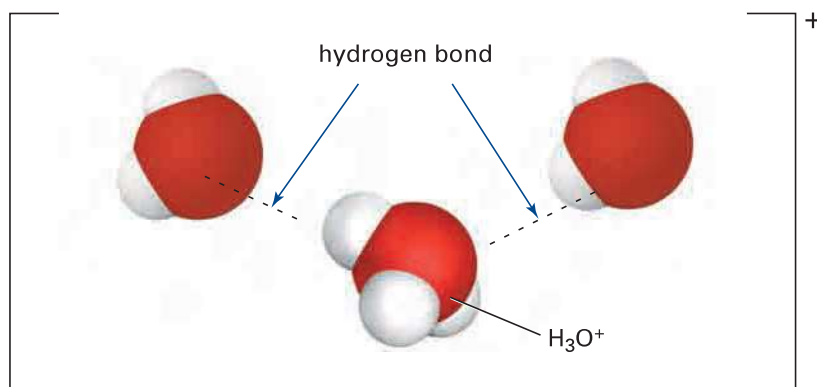


Different combinations of strong Arrhenius acids and bases react with the same exothermic result. Measurements always show the release of 56 kJ of energy per mole of water formed. This makes sense, because the net ionic equation is the same regardless of the specific neutralization reaction that occurs.

The Arrhenius theory has limitations, however. For example,  $\text{H}^+_{(\text{aq})}$ , a bare proton, does not exist in water. The positive charge on a proton is attracted to the region of negative charge on the lone pair of electrons on a water molecule's oxygen atom. The combination is a hydrated proton called a **hydronium ion**,  $\text{H}_3\text{O}^+_{(\text{aq})}$ .

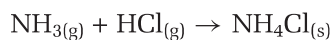


The hydronium ion, itself, forms hydrogen bonds with other water molecules. (See Figure 8.1.) Thus, a better formula for the ion that is present in acidic solutions is  $[\text{H}(\text{H}_2\text{O})_n]^+$ , where  $n$  is usually 4 or 5. For convenience, however, chemists usually use a single hydronium ion when writing equations.



**Figure 8.1** In aqueous solution, the hydronium ion,  $\text{H}_3\text{O}^+$ , forms hydrogen bonds with other water molecules.

The Arrhenius theory also has limitations for explaining certain reactions. For example, aqueous solutions of ammonia are basic. They react with acids in neutralization reactions, even though ammonia does not contain the hydroxide ion. Many aqueous solutions of salts with no hydroxide ions are basic, too. Some reactions take place without any liquid solvent. For example, ammonium chloride can be formed by the reaction between ammonia and hydrogen chloride, which are both gases:



## The Brønsted-Lowry Theory

The limitations of the Arrhenius theory of acids and bases are overcome by a more general theory, called the Brønsted-Lowry theory. This theory was proposed independently, in 1923, by Johannes Brønsted, a Danish chemist, and Thomas Lowry, an English chemist. It recognizes an acid-base reaction as a chemical equilibrium, having both a forward reaction and a reverse reaction that involve the transfer of a proton. The Brønsted-Lowry theory defines acids and bases as follows:

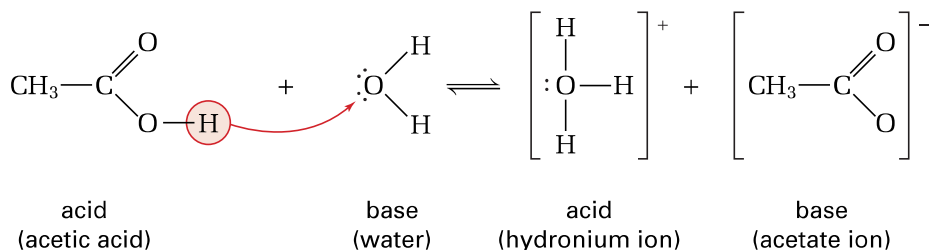
- An acid is a substance from which a proton can be removed. (Some chemists describe Brønsted-Lowry acids as “proton-donors.”)
- A base is a substance that can accept a proton. (Some chemists describe Brønsted-Lowry bases as “proton-acceptors.”)

Note that the word “proton” refers to the nucleus of a hydrogen atom — an  $\text{H}^+$  ion that has been removed from the acid molecule. It does not refer to a proton removed from the nucleus of another atom, such as oxygen or sulfur, that may be present in the acid molecule. As mentioned previously,  $\text{H}^+$  ions share electrons with any species (ion or molecule) that has a lone pair of electrons. In aqueous solution, the proton bonds with a water molecule to form the hydronium ion. Unlike the Arrhenius theory, however, the Brønsted-Lowry theory is not restricted to aqueous solutions. For example, the lone pair of electrons on an ammonia molecule can bond with  $\text{H}^+$ , and liquid ammonia can act as a base.

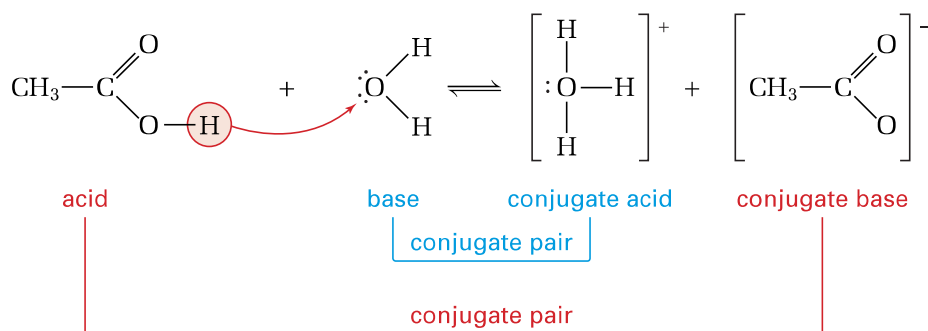
Definition Term	Arrhenius Theory	Brønsted-Lowry Theory
acid	a substance that contains hydrogen and dissociates in water to form $\text{H}^+_{(\text{aq})}$	a substance from which a proton can be removed
base	a substance that contains the hydroxide group and dissociates in water to form $\text{OH}^-_{(\text{aq})}$	a substance that can accept a proton from an acid

## Conjugate Acid-Base Pairs

The dissociation of acetic acid in water is represented in Figure 8.2. This dissociation is an equilibrium reaction because it proceeds in both directions. Acetic acid is weak, so only a few ions dissociate. The position of equilibrium lies to the left, and the reverse reaction is favoured. In the reverse reaction, the hydronium ion gives up a proton to the acetate ion. Thus, these ions are an acid and a base, respectively, as shown in Figure 8.3. The acid on the left ( $\text{CH}_3\text{COOH}$ ) and the base on the right ( $\text{CH}_3\text{COO}^-$ ) differ by one proton. They are called a **conjugate acid-base pair**. Similarly,  $\text{H}_2\text{O}$  and  $\text{H}_3\text{O}^+$  are a conjugate acid-base pair.

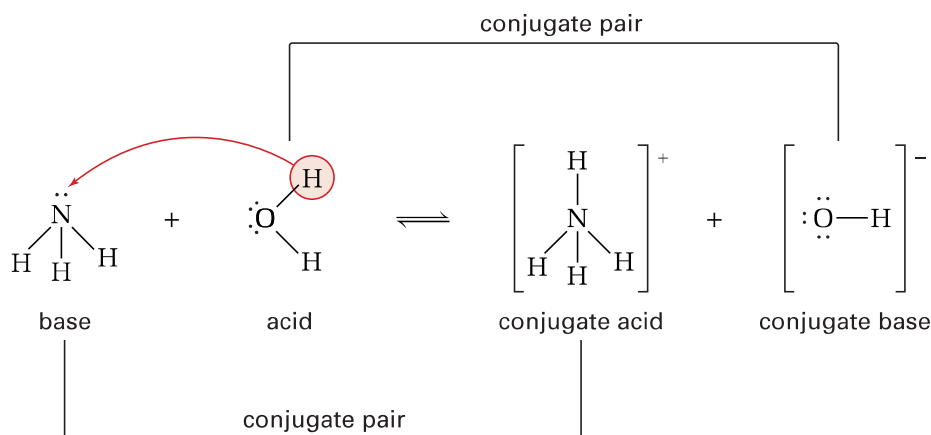


**Figure 8.2** The dissociation of acetic acid, a weak acid, in water



**Figure 8.3** Conjugate acid-base pairs in the dissociation of acetic acid in water

Unlike the Arrhenius theory, the Brønsted-Lowry theory of acids and bases can explain the basic properties of ammonia when it dissolves in water. See Figure 8.4.



**Figure 8.4** The dissociation of ammonia, a weak base, in water

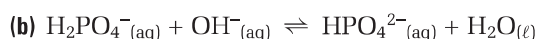
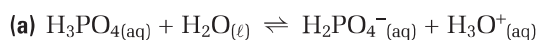
Aqueous ammonia is a weak base, so relatively few hydroxide ions form. The position of equilibrium lies to the left. In the forward reaction, the water molecule gives up a proton and acts as an acid. A substance that can act as a proton donor (an acid) in one reaction and a proton acceptor (a base) in another reaction is said to be *amphoteric*. (Water acts as an acid in the presence of a stronger base, and as a base in the presence of a stronger acid.)

## Sample Problem

### Identifying Conjugate Acid-Base Pairs

#### Problem

Identify the conjugate acid-base pair in each reaction.



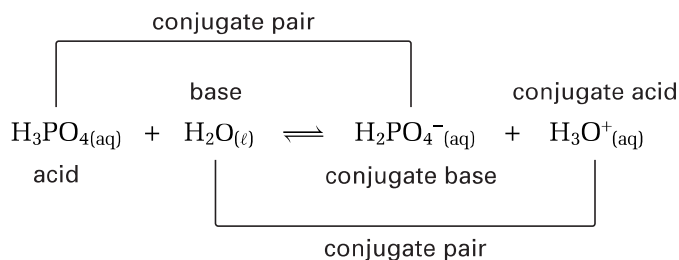
Continued ...



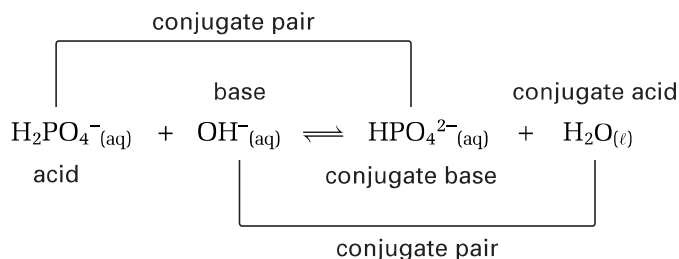
**Solution**

On the left side of the equation, the acid is the molecule or ion that donates a proton. The base is the molecule or ion that accepts the proton. On the right side of the equation, you can identify the conjugate acid and base by the difference of a single proton from the base and acid on the left side.

(a) The conjugate acid-base pairs are  $\text{H}_3\text{PO}_4/\text{H}_2\text{PO}_4^-$  and  $\text{H}_2\text{O}/\text{H}_3\text{O}^+$ .



(b) The conjugate acid-base pairs are  $\text{H}_2\text{PO}_4^-/\text{HPO}_4^{2-}$  and  $\text{OH}^-/\text{H}_2\text{O}$ .

**Check Your Solution**

In each case, the acid has one more proton than its conjugate base.

**Practice Problems**

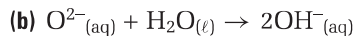
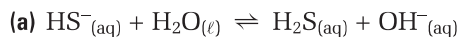
1. Name and write the formula of the conjugate base of each molecule or ion.

- (a)  $\text{HCl}$       (b)  $\text{HCO}_3^-$       (c)  $\text{H}_2\text{SO}_4$       (d)  $\text{N}_2\text{H}_5^+$

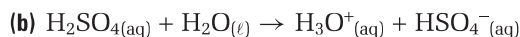
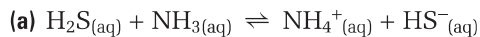
2. Name and write the formula of the conjugate acid of each molecule or ion.

- (a)  $\text{NO}_3^-$       (b)  $\text{OH}^-$       (c)  $\text{H}_2\text{O}$       (d)  $\text{HCO}_3^-$

3. Identify the conjugate acid-base pairs in each reaction.



4. Identify the conjugate acid-base pairs in each reaction.



## Molecular Structure and the Strength of Acids and Bases

When a strong acid or base dissolves in water, almost every acid or base molecule dissociates. While there are many acids and bases, most are weak. Thus, the number of strong acids and strong bases is fairly small.

### Strong Acids

- binary acids that have the general formula  $\text{HX}_{(\text{aq})}$ , where  $\text{X} = \text{Cl}$ ,  $\text{Br}$ , and  $\text{I}$  (but not  $\text{F}$ ): for example, hydrochloric acid,  $\text{HCl}$ , and hydrobromic acid,  $\text{HBr}$  ( $\text{HCl}$  and  $\text{HBr}$  are *hydrohalic acids*: acids that have hydrogen bonded to atoms of the halogen elements.)
- oxoacids (acids containing oxygen atoms) in which the number of oxygen atoms exceeds, by two or more, the number of protons that can be dissociated: for example, nitric acid,  $\text{HNO}_3$ , sulfuric acid,  $\text{H}_2\text{SO}_4$ , perchloric acid,  $\text{HClO}_4$ , and chloric acid,  $\text{HClO}_3$

The binary acids of non-metals exhibit periodic trends in their acid strength, as shown in Figure 8.5. Two factors are responsible for this trend: the electronegativity of the atom that is bonded to hydrogen, and the strength of the bond.

increasing acid strength increasing electronegativity					18(VIIIA)
13 (IIIA)	14 (IVA)	15 (VA)	16 (VIA)	17 (VIIA)	
	$\text{CH}_4$	$\text{NH}_3$	$\text{H}_2\text{O}$	$\text{HF}$	
			$\text{H}_2\text{S}$	$\text{HCl}$	
			$\text{H}_2\text{Se}$	$\text{HBr}$	
			$\text{H}_2\text{Te}$	$\text{HI}$	

decreasing bond strength  
increasing acid strength

**Figure 8.5** The binary acids show periodic trends, which are related to electronegativity and bond strength.

Across a period, electronegativity is the most important factor. The acid strength of hydrides increases as their electronegativity increases. This happens because an electronegative atom draws electrons away from the hydrogen atom, making it relatively positive. The negative pole of a water molecule then strongly attracts the hydrogen atom and pulls it away.

Down a group, bond strength is the most important factor. Acid strength increases as bond strength decreases. A weaker bond means that the hydrogen atom is more easily pulled away from the atom to which it is attached. For example, hydrofluoric acid is a stronger acid than water, but  $\text{HF}$  is the weakest of the hydrohalic acids because the  $\text{H-F}$  bond is relatively strong.



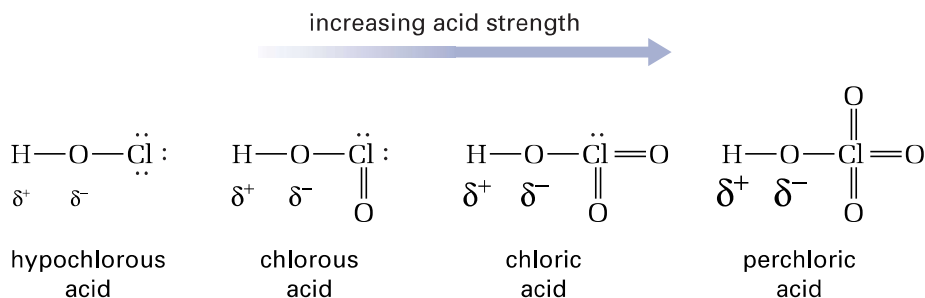


## CHEM

### FACT

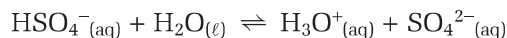
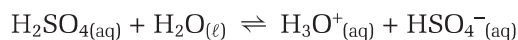
You might wonder how  $\text{HCl}_{(\text{aq})}$ ,  $\text{HBr}_{(\text{aq})}$ , and  $\text{HI}_{(\text{aq})}$  can be described as increasing in strength, since each acid dissociates completely in water. This trend becomes apparent if you add equal concentrations of the acids to a solvent that is less basic than water, such as pure acetic acid. You will find that the acids dissociate to different extents.

Oxoacids increase in strength with increasing numbers of oxygen atoms, as shown in Figure 8.6. The hydrogen atoms that dissociate in water are always attached to oxygen atoms. Oxygen is more electronegative than hydrogen, so oxygen atoms draw electrons away from hydrogen atoms. The more oxygen atoms there are in a molecule, the greater is the polarity of the bond between each hydrogen atom and the oxygen atom it is attached to, and the more easily the water molecule can tear the hydrogen atom away.



**Figure 8.6** The relative strength of oxoacids increases with the number of oxygen atoms.

Acids such as  $\text{HCl}$ ,  $\text{CH}_3\text{COOH}$ , and  $\text{HF}$  are **monoprotic acids**. They have only a single hydrogen atom that dissociates in water. Some acids have more than one hydrogen atom that dissociates. These acids are called **polyprotic acids**. For example, sulfuric acid has two hydrogen atoms that can dissociate.



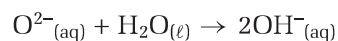
Sulfuric acid is a far stronger acid than the hydrogen sulfate ion, because much more energy is required to remove a proton from a negatively charged ion. *The strength of a polyprotic acid decreases as the number of hydrogen atoms that have dissociated increases.*

Strong bases are confined to the oxides and hydroxides from Groups 1 (IA) and 2 (IIA).

### Strong Bases

- all oxides and hydroxides of the alkali metals: for example, sodium hydroxide,  $\text{NaOH}$ , and potassium hydroxide,  $\text{KOH}$
- alkaline earth (Group 2 (IIA)) metal oxides and hydroxides below beryllium: for example, calcium hydroxide,  $\text{Ca}(\text{OH})_2$ , and barium hydroxide,  $\text{Ba}(\text{OH})_2$

The strong basic oxides have metal atoms with low electronegativity. Thus, the bond to oxygen is ionic and is relatively easily broken by the attraction of polar water molecules. The oxide ion always reacts with water molecules to produce hydroxide ions.



Magnesium oxide and magnesium hydroxide are not very soluble. They are strong bases, however, because the small amount that does dissolve dissociates almost completely into ions. Beryllium oxide is a weak base. (It is the exception in Group 2 (IIA).) It is a relatively small atom, so the bond to oxygen is strong and not easily broken by water molecules.

## Calculations That Involve Strong Acids and Bases

When a strong acid dissociates completely into ions in water, the concentration of  $\text{H}_3\text{O}^+_{(\text{aq})}$  is equal to the concentration of the strong acid. Similarly, when a strong base dissociates completely in water, the concentration of  $\text{OH}^-_{(\text{aq})}$  is equal to the concentration of the strong base.

### Sample Problem

#### Calculating Ion Concentrations in Acidic and Basic Solutions

##### Problem

During an experiment, a student pours 25.0 mL of 1.40 mol/L nitric acid into a beaker that contains 15.0 mL of 2.00 mol/L sodium hydroxide solution. Is the resulting solution acidic or basic? What is the concentration of the ion that causes the solution to be acidic or basic?

##### What Is Required?

You must determine the ion in excess and its concentration.

##### What Is Given?

You have the following data:

Volume of nitric acid = 25.0 mL

$[\text{HNO}_3] = 1.40 \text{ mol/L}$

Volume of sodium hydroxide = 15.0 mL

$[\text{NaOH}] = 2.00 \text{ mol/L}$

##### Plan Your Strategy

**Step 1** Write the chemical equation for the reaction.

**Step 2** Calculate the amount of each reactant using the following equation.

$$\text{Amount (in mol)} = \text{Concentration (in mol/L)} \times \text{Volume (in L)}$$

**Step 3** Determine the limiting reactant.

**Step 4** The reactant in excess is a strong acid or base. Thus, the excess amount results in the same amount of  $\text{H}_3\text{O}^+$  or  $\text{OH}^-$ .

**Step 5** Calculate the concentration of the excess ion by using the amount in excess and the total volume of the solution.

##### Act on Your Strategy

**Step 1**  $\text{HNO}_{3(\text{aq})} + \text{NaOH}_{(\text{aq})} \rightarrow \text{NaNO}_{3(\text{aq})} + \text{H}_2\text{O}_{(\ell)}$

**Step 2** Amount of  $\text{HNO}_3 = 1.40 \text{ mol/L} \times 0.0250 \text{ L}$   
 $= 0.0350 \text{ mol}$

Amount of  $\text{NaOH} = 2.00 \text{ mol/L} \times 0.0150 \text{ L}$   
 $= 0.0300 \text{ mol}$

**Step 3** The reactants combine in a 1:1 ratio. The amount of  $\text{NaOH}$  is less, so this reactant must be the limiting reactant.

**Step 4** Amount of excess  $\text{HNO}_{3(\text{aq})} = 0.0350 \text{ mol} - 0.0300 \text{ mol}$   
 $= 0.0050 \text{ mol}$

Therefore, the amount of  $\text{H}_3\text{O}^+_{(\text{aq})}$  is  $5.0 \times 10^{-3} \text{ mol}$ .

**Step 5** Total volume of solution = 25.0 mL + 15.0 mL = 40.0 mL

$$\begin{aligned} [\text{H}_3\text{O}^+] &= \frac{5.0 \times 10^{-3} \text{ mol}}{0.0400 \text{ L}} \\ &= 0.12 \text{ mol/L} \end{aligned}$$

Continued ...

The solution is acidic, and  $[\text{H}_3\text{O}^+]$  is 0.12 mol/L.

### Check Your Solution

The chemical equation has a 1:1 ratio between reactants. The amount of acid is greater than the amount of base. Therefore, the resulting solution should be acidic, which it is.

## Practice Problems

5. Calculate the concentration of hydronium ions in each solution.
  - (a) 4.5 mol/L  $\text{HCl}_{(\text{aq})}$
  - (b) 30.0 mL of 4.50 mol/L  $\text{HBr}_{(\text{aq})}$  diluted to 100.0 mL
  - (c) 18.6 mL of 2.60 mol/L  $\text{HClO}_{4(\text{aq})}$  added to 24.8 mL of 1.92 mol/L  $\text{NaOH}_{(\text{aq})}$
  - (d) 17.9 mL of 0.175 mol/L  $\text{HNO}_{3(\text{aq})}$  added to 35.4 mL of 0.0160 mol/L  $\text{Ca}(\text{OH})_{2(\text{aq})}$
6. Calculate the concentration of hydroxide ions in each solution.
  - (a) 3.1 mol/L  $\text{KOH}_{(\text{aq})}$
  - (b) 21.0 mL of 3.1 mol/L  $\text{KOH}$  diluted to 75.0 mL
  - (c) 23.2 mL of 1.58 mol/L  $\text{HCl}_{(\text{aq})}$  added to 18.9 mL of 3.50 mol/L  $\text{NaOH}_{(\text{aq})}$
  - (d) 16.5 mL of 1.50 mol/L  $\text{H}_2\text{SO}_{4(\text{aq})}$  added to 12.7 mL of 5.50 mol/L  $\text{NaOH}_{(\text{aq})}$
7. Determine whether reacting each pair of solutions results in an acidic solution or a basic solution. Then calculate the concentration of the ion that causes the solution to be acidic or basic. (Assume that the volumes in part (a) are additive. Assume that the volumes in part (b) stay the same.)
  - (a) 31.9 mL of 2.75 mol/L  $\text{HCl}_{(\text{aq})}$  added to 125 mL of 0.0500 mol/L  $\text{Mg}(\text{OH})_{2(\text{aq})}$
  - (b) 4.87 g of  $\text{NaOH}_{(\text{s})}$  added to 80.0 mL of 3.50 mol/L  $\text{HBr}_{(\text{aq})}$
8. 2.75 g of  $\text{MgO}_{(\text{s})}$  is added to 70.0 mL of 2.40 mol/L  $\text{HNO}_{3(\text{aq})}$ . Is the solution that results from the reaction acidic or basic? What is the concentration of the ion that is responsible for the character of the solution?

## Section Summary

Strong acids and bases (and strong electrolytes) dissociate completely in water. Therefore, you can use the concentrations of these compounds to determine the concentrations of the ions they form in aqueous solutions. You cannot, however, use the concentrations of weak acids, bases, and electrolytes in the same way. Their solutions contain some particles that have not dissociated into ions. Nevertheless, important changes in  $[\text{H}_3\text{O}^+]$  and  $[\text{OH}^-]$  take place because dissolved ions affect the dissociation of water.

In the next section, you will focus on the equilibrium of water. You will discover how the pH scale is related to the concentrations of the ions that form when water dissociates. As well, you will learn how to calculate the pH values of solutions of weak acids and bases.

## Section Review

- 1 **K/U** Phosphoric acid,  $\text{H}_3\text{PO}_{4(\text{aq})}$  is triprotic. It has three hydrogen ions that may be dissociated.
  - (a) Write an equation to show the dissociation of each proton.
  - (b) Show that  $\text{H}_2\text{PO}_4^-$  can act as either an acid or a base.
  - (c) Which is the stronger acid,  $\text{H}_3\text{PO}_{4(\text{aq})}$  or  $\text{H}_2\text{PO}_4^-$ ? Explain your answer.
- 2 **K/U** Para-aminobenzoic acid (PABA) is a weak monoprotic acid that is used in some sunscreen lotions. Its formula is  $\text{C}_6\text{H}_4\text{NH}_2\text{COOH}$ . What is the formula of the conjugate base of PABA?
- 3 **K/U** Boric acid,  $\text{B}(\text{OH})_{3(\text{aq})}$ , is used as a mild antiseptic in eye-wash solutions. The following reaction takes place in aqueous solution.
$$\text{B}(\text{OH})_{3(\text{aq})} + 2\text{H}_2\text{O}_{(\ell)} \rightleftharpoons \text{B}(\text{OH})_{4(\text{aq})}^- + \text{H}_3\text{O}_{(\text{aq})}^+$$
  - (a) Identify the conjugate acid-base pairs.
  - (b) Is boric acid strong or weak? How do you know?
- 4 **K/U** Classify each compound as a strong acid, weak acid, strong base, or weak base.
  - (a) butyric acid,  $\text{CH}_3\text{CH}_2\text{CH}_2\text{COOH}$  (responsible for the odour of rancid butter)
  - (b) hydroiodic acid,  $\text{HI}_{(\text{aq})}$  (added to some cough syrups)
  - (c) potassium hydroxide,  $\text{KOH}$  (used in the manufacture of soft soaps)
  - (d) red iron oxide,  $\text{Fe}_2\text{O}_3$  (used as a colouring pigment in paints)
- 5 **C** Distinguish between a concentrated solution of a weak base, and a dilute solution of a strong base. Give an example of each.

## 8.2

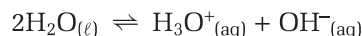
## The Equilibrium of Weak Acids and Bases

Section Preview/  
Specific Expectations

In this section, you will

- **define and perform** calculations that involve the ion product constant for water,  $K_w$ , and the acid dissociation constant,  $K_a$
- **compare** strong acids and bases in terms of equilibrium
- **compare** weak acids and bases in terms of equilibrium
- **communicate** your understanding of the following terms: *ion product constant for water ( $K_w$ ), pH, pOH, acid dissociation constant ( $K_a$ ), percent dissociation*

The dissociation of an acidic or basic compound in aqueous solution produces ions that interact with water. The pH of the aqueous solution is determined by the position of equilibrium in reactions between the ions that are present in solution and the water molecules. Pure water contains a few ions, produced by the dissociation of water molecules:



At 25°C, only about two water molecules in one billion dissociate. This is why pure water is such a poor conductor of electricity. In neutral water, at 25°C, the concentration of hydronium ions is the same as the concentration of hydroxide ions:  $1.0 \times 10^{-7}$  mol/L. These concentrations must be the same because the dissociation of water produces equal numbers of hydronium and hydroxide ions. Because this is an equilibrium reaction, and because the position of equilibrium of all reactions changes with temperature,  $[\text{H}_3\text{O}^+]$  is not  $1.0 \times 10^{-7}$  mol/L at other temperatures. The same is true of  $[\text{OH}^-]$ .

## The Ion Product Constant for Water

The equilibrium constant,  $K_c$ , for the dissociation of water is given by the following expression.

$$K_c = \frac{[\text{H}_3\text{O}^+][\text{OH}^-]}{[\text{H}_2\text{O}]^2}$$

So few ions form that the concentration of water is essentially constant. The product  $K_c[\text{H}_2\text{O}]^2$  is equal to the product of the concentrations of hydronium ions and hydroxide ions. The equilibrium value of the concentration ion product  $[\text{H}_3\text{O}^+][\text{OH}^-]$  at 25°C is called the **ion product constant for water**. It is given the symbol  $K_w$ .

$$\begin{aligned} K_c[\text{H}_2\text{O}]^2 &= [\text{H}_3\text{O}^+][\text{OH}^-] \\ &= 1.0 \times 10^{-7} \text{ mol/L} \times 1.0 \times 10^{-7} \text{ mol/L} \\ &= 1.0 \times 10^{-14} \\ &= K_w \end{aligned}$$

The units are commonly dropped, as in other equilibrium expressions you have encountered.

The concentration of  $\text{H}_3\text{O}^+$  in the solution of a strong acid is equal to the concentration of the dissolved acid, unless the solution is very dilute. Consider  $[\text{H}_3\text{O}^+]$  in a solution of 0.1 mol/L hydrochloric acid. All the molecules of HCl dissociate in water, forming a hydronium ion concentration that equals 0.1 mol/L. The increased  $[\text{H}_3\text{O}^+]$  pushes the dissociation reaction between water molecules to the left, in accordance with Le Châtelier's principle. Consequently, the concentration of hydronium ions that results from the dissociation of water is even less than  $1 \times 10^{-7}$  mol/L. This  $[\text{H}_3\text{O}^+]$  is negligible compared with the 0.1 mol/L concentration of the hydrochloric acid. Unless the solution is very dilute (about  $1 \times 10^{-7}$  mol/L), the dissociation of water molecules can be ignored when determining  $[\text{H}_3\text{O}^+]$  of a strong acid.

Similarly, the concentration of hydroxide ions can be determined from the concentration of the dissolved base. If the solution is a strong base, you can ignore the dissociation of water molecules when determining  $[\text{OH}^-]$ , unless the solution is very dilute. When either  $[\text{H}_3\text{O}^+]$  or  $[\text{OH}^-]$  is known, you can use the ion product constant for water,  $K_w$ , to determine the concentration of the other ion. Although the value of  $K_w$  for water is  $1.0 \times 10^{-14}$  at  $25^\circ\text{C}$  only, you can use this value unless another value is given for a different temperature.

#### **$[\text{H}_3\text{O}^+]$ and $[\text{OH}^-]$ in Aqueous Solutions at $25^\circ\text{C}$**

In an acidic solution,  $[\text{H}_3\text{O}^+]$  is greater than  $1.0 \times 10^{-7}$  mol/L and  $[\text{OH}^-]$  is less than  $1.0 \times 10^{-7}$  mol/L.

In a neutral solution, both  $[\text{H}_3\text{O}^+]$  and  $[\text{OH}^-]$  are equal to  $1.0 \times 10^{-7}$  mol/L.

In a basic solution,  $[\text{H}_3\text{O}^+]$  is less than  $1.0 \times 10^{-7}$  mol/L and  $[\text{OH}^-]$  is greater than  $1.0 \times 10^{-7}$  mol/L.

### **Sample Problem**

#### **Determining $[\text{H}_3\text{O}^+]$ and $[\text{OH}^-]$**

##### **Problem**

Find  $[\text{H}_3\text{O}^+]$  and  $[\text{OH}^-]$  in each solution.

(a) 2.5 mol/L nitric acid

(b) 0.16 mol/L barium hydroxide

##### **Solution**

You know that nitric acid is a strong acid and barium hydroxide is a strong base. Since both dissociate completely in aqueous solutions, you can use their molar concentrations to determine  $[\text{H}_3\text{O}^+]$  or  $[\text{OH}^-]$ . You can find the concentration of the other ion using  $K_w$ :

$$\begin{aligned} K_w &= 1.0 \times 10^{-14} \\ &= [\text{H}_3\text{O}^+][\text{OH}^-] \end{aligned}$$

(a)  $[\text{HNO}_3] = 2.5$  mol/L, so  $[\text{H}_3\text{O}^+] = 2.5$  mol/L

$$\begin{aligned} [\text{OH}^-] &= \frac{1.0 \times 10^{-14} \text{ mol/L}}{2.5} \\ &= 4.0 \times 10^{-15} \text{ mol/L} \end{aligned}$$

(b)  $\text{Ba}(\text{OH})_2 \xrightarrow{\text{H}_2\text{O}} \text{Ba}^{2+}_{(\text{aq})} + 2\text{OH}^{-}_{(\text{aq})}$

Each mole of  $\text{Ba}(\text{OH})_2$  in solution forms two moles of  $\text{OH}^-$  ions.

$$\therefore [\text{OH}^-] = 2 \times 0.16 = 0.32 \text{ mol/L}$$

$$\begin{aligned} [\text{H}_3\text{O}^+] &= \frac{1.0 \times 10^{-14} \text{ mol/L}}{0.32} \\ &= 3.1 \times 10^{-14} \text{ mol/L} \end{aligned}$$

##### **Check Your Solution**

For a solution of a strong acid, as in part (a),  $[\text{H}_3\text{O}^+]$  should be greater than  $1.0 \times 10^{-7}$  and  $[\text{OH}^-]$  should be less than  $1.0 \times 10^{-7}$ . For a solution of strong base,  $[\text{OH}^-]$  should be greater than, and  $[\text{H}_3\text{O}^+]$  should be less than,  $1.0 \times 10^{-7}$ .



## CONCEPT CHECK

Sulfuric acid is the only common strong diprotic acid. Explain why the concentration of hydronium ions in a solution of 1.0 mol/L  $\text{H}_2\text{SO}_{4(\text{aq})}$  is 1.0 mol/L, not 2.0 mol/L.

## Practice Problems

9. Determine  $[\text{H}_3\text{O}^+]$  and  $[\text{OH}^-]$  in each solution.
  - (a) 0.45 mol/L hydrochloric acid
  - (b) 1.1 mol/L sodium hydroxide
10. Determine  $[\text{H}_3\text{O}^+]$  and  $[\text{OH}^-]$  in each solution.
  - (a) 0.95 mol/L hydrobromic acid
  - (b) 0.012 mol/L calcium hydroxide
11.  $[\text{OH}^-]$  is  $5.6 \times 10^{-14}$  mol/L in a solution of hydrochloric acid. What is the molar concentration of the  $\text{HCl}_{(\text{aq})}$ ?
12.  $[\text{H}_3\text{O}^+]$  is  $1.7 \times 10^{-14}$  in a solution of calcium hydroxide. What is the molar concentration of the  $\text{Ca}(\text{OH})_{2(\text{aq})}$ ?

## pH and pOH

You can describe the acidity of an aqueous solution quantitatively by stating the concentration of the hydronium ions that are present.  $[\text{H}_3\text{O}^+]$  is often, however, a very small number. The pH scale was devised by a Danish biochemist named Søren Sørensen as a convenient way to represent acidity (and, by extension, basicity). The scale is logarithmic, based on 10. Think of the letter *p* as a mathematical operation representing  $-\log$ . The **pH** of a solution is the exponential power of hydrogen (or hydronium) ions, in moles per litre. It can therefore be expressed as follows:

$$\text{pH} = -\log[\text{H}_3\text{O}^+]$$

The *practical* range of the pH scale, shown in Figure 8.7, is from 0 to 14. A solution of a strong acid that is more concentrated than 1.0 mol/L would give a negative pH. Since you can determine  $[\text{H}_3\text{O}^+]$  of such solutions directly from the concentration of the acid, the pH scale offers no advantage. Similarly, the pH of a strong base that is more concentrated than 1.0 mol/L is greater than 14. Note that pH is a dimensionless quantity. In other words, it has no units.

You can calculate the **pOH** (the power of hydroxide ions) of a solution from the  $[\text{OH}^-]$ .

$$\text{pOH} = -\log[\text{OH}^-]$$

$$K_w = [\text{H}_3\text{O}^+][\text{OH}^-] = 1.0 \times 10^{-14} \text{ at } 25^\circ\text{C}$$

$$\therefore \text{pH} + \text{pOH} = 14$$

### Web LINK

[www.mcgrawhill.ca/links/chemistry12](http://www.mcgrawhill.ca/links/chemistry12)

Many people, for both personal and professional reasons, rely on pH meters to provide quick, reliable pH measurements. Use the Internet to find out how a pH meter works, and what jobs or tasks it is used for. To start your research, go to the web site above and click on **Web Links**. Prepare a brief report, a web page, or a brochure to present your findings.

### Math LINK

Prove the relationship  $\text{pH} + \text{pOH} = 14$  as follows. Record the ion product equation and its value at  $25^\circ\text{C}$ . Take the logarithm of both sides. Then reverse the sign of each term. What is your result?

## Sample Problem

### Calculating pH and pOH

#### Problem

A liquid shampoo has a hydroxide ion concentration of  $6.8 \times 10^{-5}$  mol/L at  $25^\circ\text{C}$ .

- (a) Is the shampoo acidic, basic, or neutral?
- (b) Calculate the hydronium ion concentration.
- (c) What is the pH and the pOH of the shampoo?

### Solution

- (a) Compare  $[\text{OH}^-]$  in the shampoo with  $[\text{OH}^-]$  in neutral water at  $25^\circ\text{C}$ .

$[\text{OH}^-] = 6.8 \times 10^{-5} \text{ mol/L}$ , which is greater than  $1 \times 10^{-7} \text{ mol/L}$ .

Therefore, the shampoo is basic.

- (b) Use the equation  $[\text{H}_3\text{O}^+] = \frac{1.0 \times 10^{-14}}{[\text{OH}^-]}$  to find the hydronium ion concentration.

$$\begin{aligned} [\text{H}_3\text{O}^+] &= \frac{1.0 \times 10^{-14}}{6.8 \times 10^{-5}} \\ &= 1.5 \times 10^{-10} \text{ mol/L} \end{aligned}$$

- (c) Substitute known values into the equations  $\text{pH} = -\log[\text{H}_3\text{O}^+]$  and  $\text{pOH} = -\log[\text{OH}^-]$ .

$$\begin{aligned} \text{pH} &= -\log(1.5 \times 10^{-10}) \\ &= 9.83 \end{aligned}$$

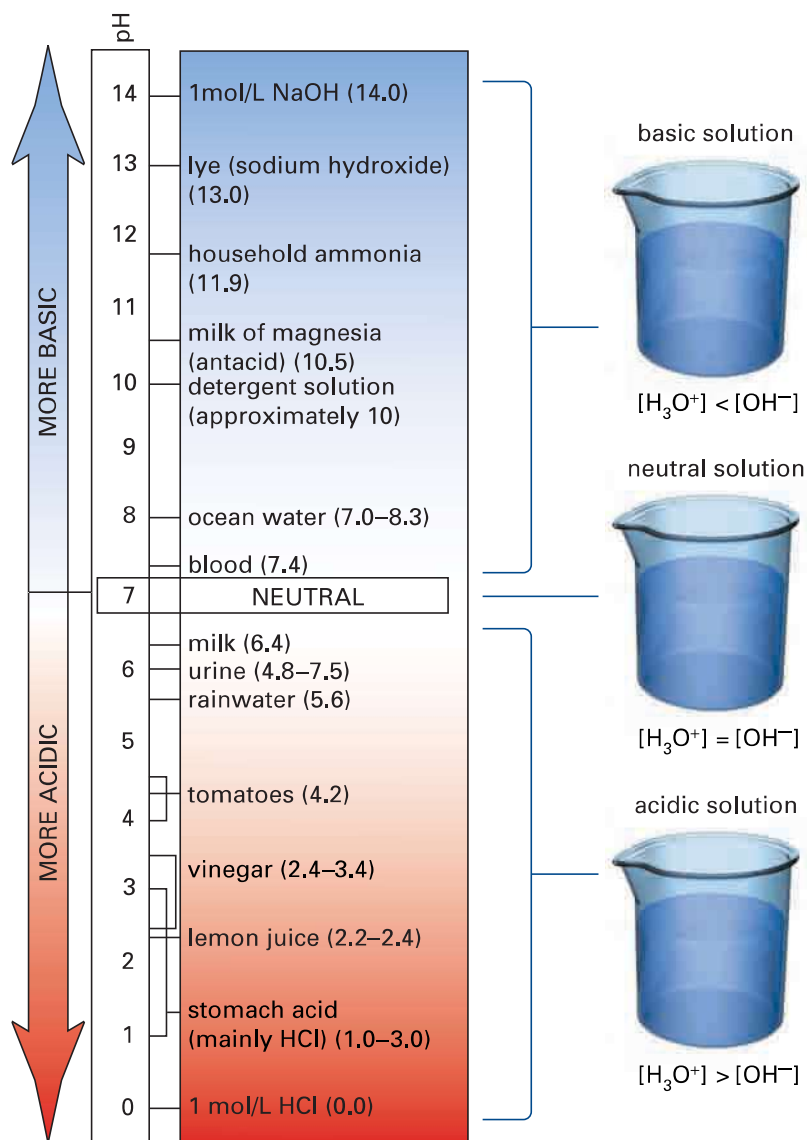
$$\begin{aligned} \text{pOH} &= -\log(6.8 \times 10^{-5}) \\ &= 4.17 \end{aligned}$$

### Check Your Solution

$$\text{pH} + \text{pOH} = 14$$

### PROBLEM TIP

When you work with logarithms, the number of significant digits in a number must equal the number of digits after the decimal in the number's logarithm. Here  $1.5 \times 10^{-10}$  has two significant digits. Therefore, the calculated pH, 9.83, must have two significant digits after the decimal.



**Figure 8.7** The pH scale is logarithmic. Each change by one unit on the scale represents a change of 10 in the hydronium ion concentration of a solution.

### Another Way to Find $[\text{H}_3\text{O}^+]$ and $[\text{OH}^-]$

You can calculate  $[\text{H}_3\text{O}^+]$  or  $[\text{OH}^-]$  by finding the *antilog* of the pH or pOH.

$$[\text{H}_3\text{O}^+] = 10^{-\text{pH}}$$

$$[\text{OH}^-] = 10^{-\text{pOH}}$$

If you are using a calculator, you can use it to find the antilog of a number in one of two ways. If the logarithm is entered in the calculator, you can press the two keys  $\boxed{\text{INV}}$  and  $\boxed{\text{LOG}}$  in sequence. (Some calculators may have a  $\boxed{10^x}$  button instead.) Alternatively, since  $[\text{H}_3\text{O}^+] = 10^{-\text{pH}}$  and  $[\text{OH}^-] = 10^{-\text{pOH}}$ , you can enter 10, press the  $\boxed{y^x}$  button, enter the negative value of pH (or pOH), and then press  $\boxed{=}$ .

### Sample Problem

#### Finding pOH, $[\text{H}_3\text{O}^+]$ , and $[\text{OH}^-]$

##### Problem

If the pH of urine is outside the normal range of values, this can indicate medical problems. Suppose that the pH of a urine sample was measured to be 5.53 at 25°C. Calculate pOH,  $[\text{H}_3\text{O}^+]$ , and  $[\text{OH}^-]$  for the sample.

##### Solution

You use the known value, pH = 5.53, to calculate the required values.

$$\begin{aligned}\text{pOH} &= 14.00 - 5.53 \\ &= 8.47\end{aligned}$$

$$\begin{aligned}[\text{H}_3\text{O}^+] &= 10^{-5.53} \\ &= 3.0 \times 10^{-6} \text{ mol/L}\end{aligned}$$

$$\begin{aligned}[\text{OH}^-] &= 10^{-8.47} \\ &= 3.4 \times 10^{-9} \text{ mol/L}\end{aligned}$$

##### Check Your Solution

In this problem, the ion product constant is a useful check:

$$\begin{aligned}[\text{H}_3\text{O}^+][\text{OH}^-] &= (3.0 \times 10^{-6}) \times (3.4 \times 10^{-9}) \\ &= 1.0 \times 10^{-14}\end{aligned}$$

This value equals the expected value for  $K_w$  at 25°C.

### Practice Problems

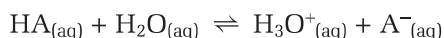
- $[\text{H}_3\text{O}^+]$  of a sample of milk is found to be  $3.98 \times 10^{-7}$  mol/L. Is the milk acidic, neutral, or basic? Calculate the pH and  $[\text{OH}^-]$  of the sample.
- A sample of household ammonia has a pH of 11.9. What is the pOH and  $[\text{OH}^-]$  of the sample?
- Phenol,  $\text{C}_6\text{H}_5\text{OH}$ , is used as a disinfectant. An aqueous solution of phenol was found to have a pH of 4.72. Is phenol acidic, neutral, or basic? Calculate  $[\text{H}_3\text{O}^+]$ ,  $[\text{OH}^-]$ , and pOH of the solution.
- At normal body temperature, 37°C, the value of  $K_w$  for water is  $2.5 \times 10^{-14}$ . Calculate  $[\text{H}_3\text{O}^+]$  and  $[\text{OH}^-]$  at this temperature. Is pure water at 37°C acidic, neutral, or basic?

17. A sample of baking soda was dissolved in water and the pOH of the solution was found to be 5.81 at 25°C. Is the solution acidic, basic, or neutral? Calculate the pH,  $[\text{H}_3\text{O}^+]$ , and  $[\text{OH}^-]$  of the solution.
18. A chemist dissolved some Aspirin<sup>TM</sup> in water. The chemist then measured the pH of the solution and found it to be 2.73 at 25°C. What are  $[\text{H}_3\text{O}^+]$  and  $[\text{OH}^-]$  of the solution?

## The Acid Dissociation Constant

Many common foods (such as citrus fruits), pharmaceuticals (such as Aspirin<sup>TM</sup>), and some vitamins (such as niacin, vitamin B3) are weak acids. When a weak acid dissolves in water, it does not completely dissociate. The concentration of the hydronium ions, and the concentration of the conjugate base of the acid that is formed in solution, depend on the initial concentration of the acid and the amount of acid that dissociates.

You can represent any weak monoprotic acid with the general formula HA. The equilibrium of a weak monoprotic acid in aqueous solution can be expressed as follows:



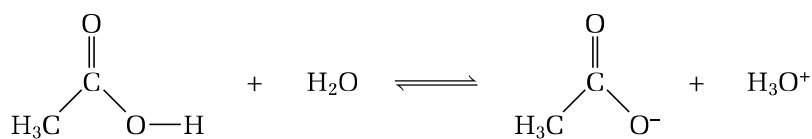
The equilibrium expression for this reaction is

$$K_c = \frac{[\text{H}_3\text{O}^+][\text{A}^-]}{[\text{HA}][\text{H}_2\text{O}]}$$

In dilute solutions, the concentration of water is almost constant. Multiplying both sides of the equilibrium expression by  $[\text{H}_2\text{O}]$  gives the product of two constants on the left side. This new constant is called the **acid dissociation constant**,  $K_a$ . (Some chemists refer to the acid dissociation constant as the *acid ionization constant*. With either name, the symbol is  $K_a$ .)

$$K_c[\text{H}_2\text{O}] = K_a = \frac{[\text{H}_3\text{O}^+][\text{A}^-]}{[\text{HA}]}$$

You can determine the value of  $K_a$  for a particular acid by measuring the pH of a solution. In the following investigation, you will add sodium hydroxide to acetic acid, which is a weak acid. (See Figure 8.8.) By graphing pH against the volume of sodium hydroxide that you added, you will be able to calculate the concentration of the acetic acid. Then you will be able to determine the acid dissociation constant,  $K_a$ , for this acid.



**Figure 8.8** Acetic acid is a weak monoprotic acid.



### CHEM

### FACT

Niacin is found in many foods, including corn. The niacin in corn, however, cannot be absorbed in the intestinal tract. In regions of the world where corn is a major part of the diet, niacin deficiency can occur. If you add calcium oxide or wood ash to the water in which you boil corn, the resulting basic solution allows the niacin to be absorbed. The flour for making corn tortillas is commonly prepared using this method.

## Investigation 8-A

### SKILL FOCUS

Predicting

Performing and recording

Analyzing and interpreting

# $K_a$ of Acetic Acid

In your previous chemistry course, you learned how to determine the molar concentration of an acid by adding a basic solution of known concentration and measuring the volume of the basic solution required to reach the endpoint. This procedure is called a titration. The endpoint is the point at which an indicator changes colour.

In this investigation, you will be given a sample of acetic acid with an unknown concentration. Instead of measuring the volume of the basic solution required to reach the endpoint, however, you will measure the pH. Then you will graph the data you collected and use the graph to calculate the molar concentration of the acetic acid and its  $K_a$ .

### Question

In a solution of acetic acid, how does the concentration of hydronium ions compare with the concentration of acetic acid?

### Materials

25 mL pipette and pipette bulb  
retort stand  
burette and burette clamp  
2 beakers (150 mL)  
Erlenmeyer flask (150 mL)  
labels  
meniscus reader  
sheet of white paper  
funnel  
acetic acid,  $\text{CH}_3\text{COOH}$ , solution  
sodium hydroxide,  $\text{NaOH}$ , solution  
dropper bottle containing phenolphthalein  
pH meter or pH paper

### Safety Precautions



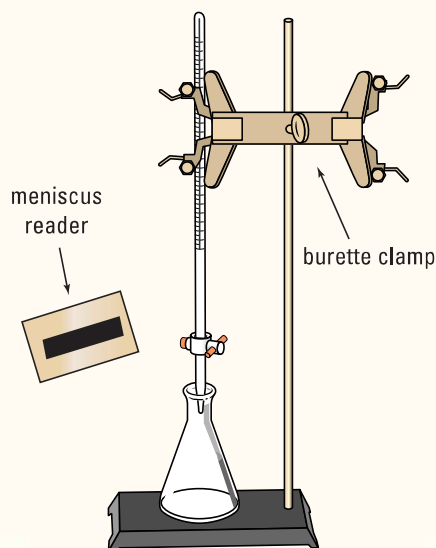
Both  $\text{CH}_3\text{COOH}$  and  $\text{NaOH}$  are corrosive. Wash any spills on your skin or clothing with plenty of cool water. Inform your teacher immediately.

### Procedure

1. Your teacher will give you the molar concentration of the  $\text{NaOH}$  solution. Record this concentration in your notebook, as well as the volume of the pipette (in mL).
2. Copy the table below into your notebook, to record your observations. Leave plenty of space. You will collect 15 to 30 sets of data, depending on the concentration of the acid.

Volume of $\text{NaOH}$ added (mL)	pH
0.00	

3. Label a clean, dry beaker for each liquid. Obtain about 40 mL of acetic acid and about 70 mL of  $\text{NaOH}$  solution.
4. Rinse a clean burette with about 10 mL of  $\text{NaOH}$  solution. Discard the rinse with plenty of water. Then set up a retort stand, burette clamp, meniscus reader, and funnel. Fill the burette with  $\text{NaOH}$  solution. Make sure that the solution fills the tube below the tap with no air bubbles. Remove the funnel.





5. Obtain a clean 25 mL pipette and a suction bulb. Rinse the pipette with 5 mL to 10 mL of  $\text{CH}_3\text{COOH}$ , and discard the rinse with plenty of water. Pipette 25.00 mL of  $\text{CH}_3\text{COOH}$  into an Erlenmeyer flask. Add two or three drops of phenolphthalein indicator.
  6. Record the initial pH of the solution. Make sure that the glass electrode is immersed deeply enough to get an accurate reading. If necessary, tip the flask to one side. Place a sheet of white paper under the flask.
  7. Add 2 mL of NaOH from the burette. Record the volume carefully, correct to two decimal places. Swirl the contents of the Erlenmeyer flask, then measure the pH of the solution.
  8. Repeat step 7 until the pH rises above 2.0. Add 1 mL amounts until the pH reaches 5.0.
  9. Above pH = 5.0, add NaOH in 0.2 mL or 0.1 mL portions. Continue to swirl the contents of the flask and take pH readings. Record the volume at which the phenolphthalein changes from colourless to pink.
  10. Above pH = 11, add 1 mL portions until the pH reaches at least 12.
  11. Wash the liquids down the sink with plenty of water. Rinse the pipette and burette with distilled water. Leave the burette tap open.
3. Calculate the molar concentration of the  $\text{CH}_3\text{COOH}$ . Use the ratio in which the acid and base react, determined from the chemical equation. You can use the following equation to find the amount of a chemical in solution.  
Amount (in mol) = Concentration (in mol/L)  $\times$  Volume (in L)  
Determine the amount of NaOH added, using its concentration (given by your teacher) and the volume on your graph (from question 2).
  4. Write the expression for  $K_a$  for the dissociation of  $\text{CH}_3\text{COOH}$  in water.
  5. Use the initial pH of the  $\text{CH}_3\text{COOH}$  (before you added any base) to find the initial  $[\text{H}_3\text{O}^+]$ . What was the initial  $[\text{CH}_3\text{COO}^-]$ ?
  6. Assume that the amount of  $\text{CH}_3\text{COOH}$  that dissociates is small compared with the initial concentration of the acid. If this is true, the equilibrium value of  $[\text{CH}_3\text{COOH}]$  is equal to the initial concentration of the acid. Use your values of  $[\text{H}_3\text{O}^+]$ ,  $[\text{CH}_3\text{COO}^-]$ , and  $[\text{CH}_3\text{COOH}]$  to calculate  $K_a$  for acetic acid. **Hint:**  $[\text{H}_3\text{O}^+] = [\text{CH}_3\text{COO}^-]$
  7. Refer to the volume of NaOH on your graph (from question 2). Calculate half this volume. On your graph, find the pH when the solution was half-neutralized.
  8. Calculate  $[\text{H}_3\text{O}^+]$  when the  $\text{CH}_3\text{COOH}$  was half-neutralized. How does this value compare with your value of  $K_a$  for  $\text{CH}_3\text{COOH}$ ?

### Analysis

1. Write the chemical equation for the neutralization reaction you observed.
2. Plot a graph of your data, with pH on the vertical axis and volume of NaOH on the horizontal axis. Your graph should show a steep rise in pH as the volume of NaOH becomes enough to neutralize all the  $\text{CH}_3\text{COOH}$ . Take the midpoint on the graph (where the graph rises steeply) and read off the volume of NaOH. This is the volume of NaOH that was needed to neutralize all the  $\text{CH}_3\text{COOH}$ . Compare the volume on your graph with the volume you recorded when the phenolphthalein indicator first turned pink.

### Conclusion

9. Calculate the percent difference between your value for  $K_a$  and the accepted value. State two sources of error that might account for any differences.

### Application

10. Do the values you calculated for  $[\text{H}_3\text{O}^+]$  and  $[\text{CH}_3\text{COOH}]$  prove that  $\text{CH}_3\text{COOH}$  is a weak acid? Explain.



## pH and $K_a$ of a Weak Acid

Table 8.2 lists the acid dissociation constants for selected acids at 25°C. Notice that weak acids have  $K_a$  values that are between 1 and about  $1 \times 10^{-16}$ . Very weak acids have  $K_a$  values that are less than  $1 \times 10^{-16}$ . The smaller the value of  $K_a$ , the less the acid ionizes in aqueous solution.

Problems that involve the concentrations of ions formed in aqueous solutions are considered to be equilibrium problems. The steps for solving acid and base equilibrium problems are similar to the steps you learned in Chapter 7 for solving equilibrium problems.

### Solving Equilibrium Problems That Involve Acids and Bases

The steps that you will use to solve acid and base equilibrium problems will vary depending on the problem. Below are a few general steps to guide you.

- Write the chemical equation. Use the chemical equation to set up an ICE table for the reacting substances. Enter any values that are given in the problem. (**Note:** For the problems in this textbook, you can assume that the concentrations of hydronium ions and hydroxide ions in pure water are negligible compared with the concentrations of these ions when a weak acid or weak base is dissolved in water.)
- Let  $x$  represent the change in concentration of the substance with the smallest coefficient in the chemical equation.
- For problems that give the initial concentration of the acid,  $[HA]$ , compare the initial concentration of the acid with the acid dissociation constant,  $K_a$ .
- If  $\frac{[HA]}{K_a} > 500$ , the change in the initial concentration,  $x$ , is negligible and can be ignored.
- If  $\frac{[HA]}{K_a} < 500$ , the change in the initial concentration,  $x$ , may not be negligible. The equilibrium equation will be more complex, possibly requiring the solution of a quadratic equation.

**Table 8.2** Some Acid Dissociation Constants for Weak Acids at 25°C

Acid	Formula	Acid dissociation constant, $K_a$
acetic acid	$\text{CH}_3\text{COOH}$	$1.8 \times 10^{-5}$
chlorous acid	$\text{HClO}_2$	$1.1 \times 10^{-2}$
formic acid	$\text{HCOOH}$	$1.8 \times 10^{-4}$
hydrocyanic acid	$\text{HCN}$	$6.2 \times 10^{-10}$
hydrofluoric acid	$\text{HF}$	$6.6 \times 10^{-4}$
hydrogen oxide (water)	$\text{H}_2\text{O}$	$1.0 \times 10^{-14}$
lactic acid	$\text{CH}_3\text{CHOHCOOH}$	$1.4 \times 10^{-4}$
nitrous acid	$\text{HNO}_2$	$7.2 \times 10^{-4}$
phenol	$\text{C}_6\text{H}_5\text{OH}$	$1.3 \times 10^{-10}$

## Percent Dissociation

The **percent dissociation** of a weak acid is the fraction of acid molecules that dissociate compared with the initial concentration of the acid, expressed as a percent. (Some chemists refer to percent dissociation as *percent of dissociation*.) The percent dissociation depends on the value of  $K_a$  for the acid, as well as the initial concentration of the weak acid. The following Sample Problems show how to solve problems that involve percent dissociation.

### Sample Problem

#### Determining $K_a$ and Percent Dissociation

##### Problem

Propanoic acid,  $\text{CH}_3\text{CH}_2\text{COOH}$ , is a weak monoprotic acid that is used to inhibit mould formation in bread. A student prepared a 0.10 mol/L solution of propanoic acid and found that the pH was 2.96. What is the acid dissociation constant for propanoic acid? What percent of its molecules were dissociated in the solution?

##### What Is Required?

You need to find  $K_a$  and the percent dissociation for propanoic acid.

##### What Is Given?

You have the following data:

Initial  $[\text{CH}_3\text{CH}_2\text{COOH}] = 0.10 \text{ mol/L}$

pH = 2.96

##### Plan Your Strategy

**Step 1** Write the equation for the dissociation equilibrium of propanoic acid in water. Then set up an ICE table.

**Step 2** Write the equation for the acid dissociation constant. Substitute equilibrium terms into the equation.

**Step 3** Calculate  $[\text{H}_3\text{O}^+]$  using  $[\text{H}_3\text{O}^+] = 10^{-\text{pH}}$

**Step 4** Use the stoichiometry of the equation and  $[\text{H}_3\text{O}^+]$  to substitute for the unknown term,  $x$ , and calculate  $K_a$ .

**Step 5** Calculate the percent dissociation by expressing the fraction of molecules that dissociate out of 100.

##### Act on Your Strategy

**Step 1** Use the equation for the dissociation equilibrium of propanoic acid in water to set up an ICE table.

Concentration (mol/L)	$\text{CH}_3\text{CH}_2\text{COOH}_{(\text{aq})}$	$+$	$\text{H}_2\text{O}_{(\ell)}$	$\rightleftharpoons$	$\text{CH}_3\text{CH}_2\text{COO}^{-}_{(\text{aq})}$	$+$	$\text{H}_3\text{O}^{+}_{(\text{aq})}$
Initial	0.10				0		$\sim 0$
Change	$-x$				$+x$		$+x$
Equilibrium	$0.10 - x$				$+x$		$+x$

Continued ...

Continued ...

$$\begin{aligned}\text{Step 2 } K_a &= \frac{[\text{CH}_3\text{CH}_2\text{COO}^-][\text{H}_3\text{O}^+]}{[\text{CH}_3\text{CH}_2\text{COOH}]} \\ &= \frac{(x)(x)}{(0.10 - x)}\end{aligned}$$

**Step 3** The value of  $x$  is equal to  $[\text{H}_3\text{O}^+]$  and  $[\text{CH}_3\text{CH}_2\text{COOH}]$ .

$$\begin{aligned}[\text{H}_3\text{O}^+] &= 10^{-2.96} \\ &= 1.1 \times 10^{-3} \text{ mol/L}\end{aligned}$$

$$\begin{aligned}\text{Step 4 } K_a &= \frac{(1.1 \times 10^{-3})^2}{0.10 - (1.1 \times 10^{-3})} \\ &= 1.2 \times 10^{-5}\end{aligned}$$

$$\begin{aligned}\text{Step 5 } \text{Percent dissociation} &= \frac{1.1 \times 10^{-3} \text{ mol/L}}{0.10 \text{ mol/L}} \times 100 \\ &= 1.1\%\end{aligned}$$

### Check Your Solution

The value of  $K_a$  and the percent dissociation are reasonable for a weak acid.

## Sample Problem

### Calculating pH

#### Problem

Formic acid,  $\text{HCOOH}$ , is present in the sting of certain ants. What is the pH of a  $0.025 \text{ mol/L}$  solution of formic acid?

#### What Is Required?

You need to calculate the pH of the solution.

#### What Is Given?

You know the concentration of formic acid:

$$[\text{HCOOH}] = 0.025 \text{ mol/L}$$

The acid dissociation constant for formic acid is listed in Table 8.2:

$$K_a = 1.8 \times 10^{-4}$$

#### Plan Your Strategy

**Step 1** Write the equation for the dissociation equilibrium of formic acid in water. Then set up an ICE table.

**Step 2** Write the equation for the acid dissociation constant. Substitute equilibrium terms into the equation.

**Step 3** Check the value of  $\frac{[\text{HCOOH}]}{K_a}$  to see whether or not the amount that dissociates is negligible compared with the initial concentration of the acid.

**Step 4** Solve the equation for  $x$ . If the amount that dissociates is not negligible compared with the initial concentration of acid, you will need to use a quadratic equation.

**Step 5**  $\text{pH} = -\log [\text{H}_3\text{O}^+]$

### Act on Your Strategy

#### Step 1

Concentration (mol/L)	$\text{HCOOH}_{(\text{aq})}$	$+$	$\text{H}_2\text{O}_{(\ell)}$	$\rightleftharpoons$	$\text{HCOO}^-_{(\text{aq})}$	$+$	$\text{H}_3\text{O}^+_{(\text{aq})}$
Initial	0.025				0		$\sim 0$
Change	$-x$				$+x$		$+x$
Equilibrium	$0.025 - x$				$+x$		$+x$

$$\begin{aligned}\text{Step 2 } K_a &= \frac{[\text{HCOO}^-][\text{H}_3\text{O}^+]}{[\text{HCOOH}]} \\ &= \frac{(x)(x)}{(0.025 - x)} \\ &= 1.8 \times 10^{-4}\end{aligned}$$

$$\begin{aligned}\text{Step 3 } \frac{[\text{HCOOH}]}{K_a} &= \frac{0.025}{1.8 \times 10^{-4}} \\ &= 139\end{aligned}$$

Since this value is less than 500, the amount that dissociates is not negligible compared with the initial concentration of the acid.

**Step 4** Rearrange the equation into a quadratic equation.

$$\begin{aligned}\frac{x^2}{(0.025 - x)} &= 1.8 \times 10^{-4} \\ x^2 + (1.8 \times 10^{-4})x - (4.5 \times 10^{-6}) &= 0 \\ x &= \frac{-b \pm \sqrt{b^2 - 4ac}}{2a} \\ &= \frac{-(1.8 \times 10^{-4}) \pm \sqrt{(1.8 \times 10^{-4})^2 - 4 \times 1 \times (-4.5 \times 10^{-6})}}{2 \times 1} \\ x &= 0.0020 \text{ or } x = -0.002\end{aligned}$$

The negative value is not reasonable, since a concentration term cannot be negative.

$$\therefore x = 0.0020 \text{ mol/L} = [\text{H}_3\text{O}^+]$$

$$\begin{aligned}\text{Step 5 } \text{pH} &= -\log 0.0020 \\ &= 2.70\end{aligned}$$

The pH of a solution of 0.025 mol/L formic acid is 2.70.

### Check Your Solution

The pH indicates an acidic solution, as expected. Data that was given in the problem has two significant digits, and the pH has two digits following the decimal place. It is easy to make a mistake when solving a quadratic equation. You can estimate a solution to this problem, by assuming that  $(0.025 - x)$  is approximately equal to 0.025.

$$\begin{aligned}\frac{x^2}{0.025} &= 1.8 \times 10^{-4} \\ x^2 &= 4.5 \times 10^{-6} \\ x &= 2.1 \times 10^{-3} \text{ mol/L}\end{aligned}$$

This answer is very close to the answer obtained by solving the quadratic equation. Therefore, the solution is probably correct.

## Practice Problems

19. Calculate the pH of a sample of vinegar that contains 0.83 mol/L acetic acid. What is the percent dissociation of the vinegar?
20. In low doses, barbiturates act as sedatives. Barbiturates are made from barbituric acid, a weak monoprotic acid that was first prepared by the German chemist Adolph von Baeyer in 1864. The formula of barbituric acid is  $\text{C}_4\text{H}_4\text{N}_2\text{O}_3$ . A chemist prepares a 0.10 mol/L solution of barbituric acid. The chemist finds the pH of the solution to be 2.50. What is the acid dissociation constant for barbituric acid? What percent of its molecules dissociate?
21. A solution of hydrofluoric acid has a molar concentration of 0.0100 mol/L. What is the pH of this solution?
22. Hypochlorous acid,  $\text{HOCl}$ , is used as a bleach and a germ-killer. A chemist finds that 0.027% of hypochlorous acid molecules are dissociated in a 0.40 mol/L solution of the acid. What is the value of  $K_a$  for the acid?
23. The word “butter” comes from the Greek *butyros*. Butanoic acid (common name: butyric acid) gives rancid butter its distinctive odour. Calculate the pH of a  $1.0 \times 10^{-2}$  mol/L solution of butanoic acid ( $K_a = 1.51 \times 10^{-5}$ ).
24. Caproic acid,  $\text{C}_5\text{H}_{11}\text{COOH}$ , occurs naturally in coconut and palm oil. It is a weak monoprotic acid, with  $K_a = 1.3 \times 10^{-5}$ . A certain aqueous solution of caproic acid has a pH of 2.94. How much acid was dissolved to make 100 mL of this solution?

## Polyprotic Acids

As you know, polyprotic acids have more than one hydrogen atom that dissociates. Each dissociation has a corresponding acid dissociation constant. How can you calculate the pH of a solution of a polyprotic acid?

Problems that involve polyprotic acids can be divided into as many sub-problems as there are hydrogen atoms that dissociate. The ion concentrations that are calculated for the first dissociation are substituted as initial ion concentrations for the second dissociation, and so on. You can see this in the following Sample Problem.

### Sample Problem

#### Calculations That Involve Polyprotic Acids

##### Problem

Phosphoric acid,  $\text{H}_3\text{PO}_4$ , is one of the world's most important industrial chemicals. It is mainly used to manufacture phosphate fertilizers. It is also the ingredient that gives cola drinks their tart, biting taste. Calculate the pH,  $[\text{H}_2\text{PO}_4^-]$ , and  $[\text{HPO}_4^{2-}]$  of a 3.5 mol/L aqueous solution of phosphoric acid.

##### What Is Required?

You need to find pH and  $[\text{H}_2\text{PO}_4^-]$ .

### What Is Given?

You know that  $[\text{H}_3\text{PO}_4] = 3.5 \text{ mol/L}$ . From data tables, you can find  $K_{a_1} = 7.0 \times 10^{-3}$  and  $K_{a_2} = 6.3 \times 10^{-8}$ .

### Plan Your Strategy

- Step 1** Write the equation for the dissociation equilibrium of phosphoric acid in water. Then set up an ICE table.
- Step 2** Write the dissociation equation for  $K_{a_1}$ .
- Step 3** Determine whether or not the dissociation of  $\text{H}_3\text{PO}_4$  is negligible, compared with the initial concentration.
- Step 4** Solve the equation for  $x$ .
- Step 5** Write the equation for the dissociation equilibrium of  $\text{H}_2\text{PO}_4^-$  in water. Set up an ICE table using the concentrations you calculated for the first dissociation as initial concentrations here.
- Step 6** Write the dissociation equation for  $K_{a_2}$ .
- Step 7** Determine whether or not the dissociation of  $\text{H}_2\text{PO}_4^-$  is negligible, compared with the initial concentration.
- Step 8** Solve the equation for  $x$ .
- Step 9** Calculate  $[\text{H}_3\text{O}^+]$  and pH.
- Step 10** Calculate  $[\text{H}_2\text{PO}_4^-]$ .

### Act on Your Strategy

#### Step 1

Concentration (mol/L)	$\text{H}_3\text{PO}_{4(aq)} + \text{H}_2\text{O}_{(l)} \rightleftharpoons \text{H}_2\text{PO}_4^{-}(aq) + \text{H}_3\text{O}^{+}(aq)$		
Initial	3.5	0	$\sim 0$
Change	$-x$	$+x$	$+x$
Equilibrium	$3.5 - x$	$x$	$x$

$$\begin{aligned}\text{Step 2 } K_{a_1} &= \frac{[\text{H}_2\text{PO}_4^-][\text{H}_3\text{O}^+]}{[\text{H}_3\text{PO}_4]} \\ &= 7.0 \times 10^{-3} \\ &= \frac{(x)(x)}{(3.5 - x)}\end{aligned}$$

$$\begin{aligned}\text{Step 3 } \frac{[\text{H}_3\text{PO}_4]}{K_{a_1}} &= \frac{3.5}{7.0 \times 10^{-3}} \\ &= 500\end{aligned}$$

Therefore,  $x$  is probably negligible, compared with 3.5.

$$\begin{aligned}\text{Step 4 } 7.0 \times 10^{-3} &= \frac{x^2}{3.5} \\ x &= 0.16 \text{ mol/L}\end{aligned}$$

#### Step 5

Concentration (mol/L)	$\text{H}_2\text{PO}_4^{-}(aq) + \text{H}_2\text{O}_{(l)} \rightleftharpoons \text{HPO}_4^{2-}(aq) + \text{H}_3\text{O}^{+}(aq)$		
Initial	0.16	0	0.16
Change	$-x$	$+x$	$+x$
Equilibrium	$0.16 - x$	$x$	$(0.16 + x)$

Continued ...



$$\begin{aligned}\text{Step 6 } K_{a2} &= \frac{[\text{HPO}_4^{2-}][\text{H}_3\text{O}^+]}{[\text{H}_2\text{PO}_4^-]} \\ &= \frac{(x)(0.16 + x)}{(0.16 - x)}\end{aligned}$$

$$\text{Step 7 } \frac{[\text{H}_2\text{PO}_4^-]}{K_{a2}} = \frac{0.16}{6.3 \times 10^{-8}} = 2.5 \times 10^6$$

This is much greater than 500, so  $x$  is negligible compared with 0.16.

$$\begin{aligned}\text{Step 8 } K_{a2} &= 6.3 \times 10^{-8} = \frac{(x)(\cancel{0.16})}{(\cancel{0.16})} = x \\ x &= [\text{HPO}_4^{2-}] \\ &= 6.3 \times 10^{-8}\end{aligned}$$

$$\begin{aligned}\text{Step 9 } \text{pH} &= -\log 0.16 \\ &= 0.80\end{aligned}$$

$$\text{Step 10 } [\text{H}_2\text{PO}_4^-] = 0.16 - x = 0.16 \text{ (because } x \text{ is negligible)}$$

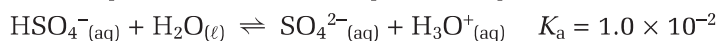
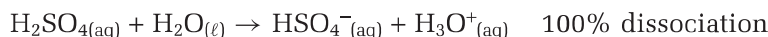
### Check Your Solution

$[\text{H}_3\text{O}^+]$  results from the first dissociation of phosphoric acid, so the second dissociation has a negligible effect on the concentration of hydronium ions or the pH of the solution. You would expect this, because the second dissociation is much weaker than the first.

## Polyprotic Acids and $[\text{H}_3\text{O}^+]$

All polyprotic acids, except sulfuric acid, are weak. Their second dissociation is much weaker than their first dissociation. For this reason, when calculating  $[\text{H}_3\text{O}^+]$  and pH of a polyprotic acid, only the first dissociation needs to be considered. The calculation is then the same as the calculation for any weak monoprotic acid. In the Sample Problem,  $[\text{HPO}_4^{2-}]$  was found to be the same as the second dissociation constant,  $K_{a2}$ . *The concentration of the anions formed in the second dissociation of a polyprotic acid is equal to  $K_{a2}$ .*

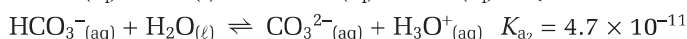
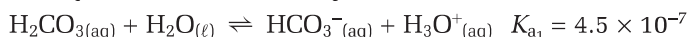
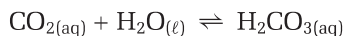
The only common strong polyprotic acid is sulfuric acid. Nevertheless, it is strong only for the first dissociation. Like the second dissociation of other polyprotic acids, the second dissociation of sulfuric acid is weak.



$[\text{H}_3\text{O}^+]$  in a solution of sulfuric acid is equal to the concentration of the acid. Only in dilute solutions (less than 1.0 mol/L) does the second dissociation of sulfuric acid contribute to the hydronium ion concentration.

### Practice Problems

25. Carbonated beverages contain a solution of carbonic acid. Carbonic acid is also important for forming the ions that are present in blood.



Calculate the pH of a solution of  $5.0 \times 10^{-4}$  mol/L carbonic acid. What is  $[\text{CO}_3^{2-}]$  in the solution?

26. Adipic acid is a diprotic acid that is used to manufacture nylon. Its formula can be abbreviated to  $\text{H}_2\text{Ad}$ . The acid dissociation constants for adipic acid are  $K_{a1} = 3.71 \times 10^{-5}$  and  $K_{a2} = 3.87 \times 10^{-6}$ . What is the pH of a 0.085 mol/L solution of adipic acid?
27. Hydrosulfuric acid,  $\text{H}_2\text{S}_{(\text{aq})}$ , is a weak diprotic acid that is sometimes used in analytical work. It is used to precipitate metal sulfides, which tend to be very insoluble. Calculate the pH and  $[\text{HS}^-_{(\text{aq})}]$  of a  $7.5 \times 10^{-3}$  mol/L solution.
28. What is the value of  $K_a$  when water acts as a Brønsted-Lowry acid? Write the expression for  $K_{a2}$  if water acts as a diprotic acid.

## Section Summary

In this section, you learned about the relationship between the pH scale and the concentrations of the ions that form when water and weak acids dissociate. In the next section, you will learn that the equilibrium of weak bases is similar to the equilibrium of weak acids. As you will see, solutions that contain a mixture of a weak acid and a salt of its conjugate base have properties with important biochemical and industrial applications.

## Section Review

- 1 **K/U** Complete the following table by calculating the missing values and indicating whether each solution is acidic or basic.

$[\text{H}_3\text{O}^+]$ (mol/L)	pH	$[\text{OH}^-]$ (mol/L)	pOH	Acidic or basic?
$3.7 \times 10^{-5}$	(a)	(b)	(c)	(d)
(e)	10.41	(f)	(g)	(h)
(i)	(j)	$7.0 \times 10^{-2}$	(k)	(l)
(m)	(n)	(o)	8.9	(p)

- 2 **I** Lactic acid,  $\text{CH}_3\text{CHOHCOOH}$ , is a monoprotic acid that is produced by muscle activity. It is also produced from milk by the action of bacteria. What is the pH of a 0.12 mol/L solution of lactic acid?
- 3 **I** A 0.10 mol/L solution of a weak acid was found to be 5.0% dissociated. Calculate  $K_a$ .
- 4 **I** Oxalic acid,  $\text{HOOC}\text{COOH}$ , is a weak diprotic acid that occurs naturally in some foods, including rhubarb. Calculate the pH of a solution of oxalic acid that is prepared by dissolving 2.5 g in 1.0 L of water. What is the concentration of hydrogen oxalate,  $\text{HOOC}\text{COO}^-$ , in the solution?
- 5 **I** A sample of blood was taken from a patient and sent to a laboratory for testing. Chemists found that the blood pH was 7.40. They also found that the hydrogen carbonate ion concentration was  $2.6 \times 10^{-2}$  mol/L. What was the concentration of carbonic acid in the blood?

# 8.3

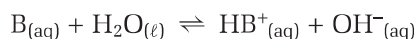
## Bases and Buffers

### Section Preview/ Specific Expectations

In this section, you will

- **solve** problems that involve the base dissociation constant,  $K_b$
- **describe** the properties and components of a buffer solution
- **identify** systems in which buffer solutions are found, and **explain** how they function
- **communicate** your understanding of the following terms: *base dissociation constant ( $K_b$ ), buffer solution, buffer capacity*

Many compounds that are present in plants are weak bases. Caffeine in coffee and piperidine in black pepper are two examples. A weak base, represented by B, reacts with water to form an equilibrium solution of ions.



The equilibrium expression for this general reaction is given as follows:

$$K_c = \frac{[HB^+][OH^-]}{[B][H_2O]}$$

The concentration of water is almost constant in dilute solutions.

Multiplying both sides of the equilibrium expression by  $[H_2O]$  gives the product of two constants on the left side. The new constant is called the **base dissociation constant,  $K_b$** .

$$K_c[H_2O] = \frac{[HB^+][OH^-]}{[B]} = K_b$$

Table 8.3 lists the base dissociation constants for several weak bases at 25°C. Nitrogen-containing compounds are Brønsted-Lowry bases, because the lone pair of electrons on a nitrogen atom can bond with  $H^+$  from water. The steps for solving problems that involve weak bases are similar to the steps you learned for solving problems that involve weak acids.

**Table 8.3** Some Base Dissociation Constants at 25°C

Base	Formula	Base dissociation constant, $K_b$
ethylenediamine	$NH_2CH_2CH_2NH_2$	$5.2 \times 10^{-4}$
dimethylamine	$(CH_3)_2NH$	$5.1 \times 10^{-4}$
methylamine	$CH_3NH_2$	$4.4 \times 10^{-4}$
trimethylamine	$(CH_3)_3N$	$6.5 \times 10^{-5}$
ammonia	$NH_3$	$1.8 \times 10^{-5}$
hydrazine	$N_2H_4$	$1.7 \times 10^{-6}$
pyridine	$C_5H_5N$	$1.4 \times 10^{-9}$
aniline	$C_6H_5NH_2$	$4.2 \times 10^{-10}$
urea	$NH_2CONH_2$	$1.5 \times 10^{-14}$

### Sample Problem

#### Solving Problems Involving $K_b$

##### Problem

The characteristic taste of tonic water is due to the addition of quinine. Quinine is a naturally occurring compound that is also used to treat malaria. The base dissociation constant,  $K_b$ , for quinine is  $3.3 \times 10^{-6}$ . Calculate  $[OH^-]$  and the pH of a  $1.7 \times 10^{-3}$  mol/L solution of quinine.

##### What Is Required?

You need to find  $[OH^-]$  and pH.

### What Is Given?

$$K_b = 3.3 \times 10^{-6}$$

$$\text{Concentration of quinine} = 1.7 \times 10^{-3} \text{ mol/L}$$

### Plan Your Strategy

**Step 1** Let Q represent the formula of quinine. Write the equation for the equilibrium reaction of quinine in water. Then set up an ICE table.

**Step 2** Write the equation for the base dissociation constant. Substitute equilibrium terms into the equation.

**Step 3** Calculate the value of  $\frac{[Q]}{K_b}$  to determine whether or not the amount of quinine that dissociates is negligible compared with the initial concentration.

**Step 4** Solve the equation for x. If the amount that dissociates is not negligible compared with the initial concentration of the base, you will need to use a quadratic equation.

**Step 5**  $\text{pOH} = -\log [\text{OH}^-]$   
 $\text{pH} = 14.00 - \text{pOH}$

### Act on Your Strategy

#### Step 1

Concentration (mol/L)	$\text{Q}_{(\text{aq})}$	+	$\text{H}_2\text{O}_{(\ell)}$	$\rightleftharpoons$	$\text{HQ}^+_{(\text{aq})}$	+	$\text{OH}^-_{(\text{aq})}$
Initial	$1.7 \times 10^{-3}$				0		$\sim 0$
Change	$-x$				$+x$		$+x$
Equilibrium	$(1.7 \times 10^{-3}) - x$				$x$		$x$

**Step 2** 
$$K_b = \frac{[\text{HQ}^+][\text{OH}^-]}{[\text{Q}]}$$
$$3.3 \times 10^{-6} = \frac{(x)(x)}{(1.7 \times 10^{-3}) - x}$$

**Step 3** 
$$\frac{[\text{Q}]}{K_b} = \frac{1.7 \times 10^{-3}}{3.3 \times 10^{-6}}$$
$$= 515$$

Since this value is greater than 500, the amount that dissociates is probably negligible, compared with the initial concentration of the base.

**Step 4** 
$$3.3 \times 10^{-6} = \frac{x^2}{1.7 \times 10^{-3}}$$
$$x = \pm 7.5 \times 10^{-5}$$

The negative root is not reasonable.  
 $\therefore x = 7.5 \times 10^{-5} \text{ mol/L} = [\text{OH}^-]$

**Step 5** 
$$\text{pOH} = -\log 7.5 \times 10^{-5}$$
$$= 4.13$$
$$\text{pH} = 14.00 - \text{pOH}$$
$$\therefore \text{pH} = 9.87$$

### Check Your Solution

The pH of the solution is greater than 7, as expected for a basic solution.

## Sample Problem

### Calculating $K_b$

#### Problem

Pyridine,  $C_5H_5N$ , is used to manufacture medications and vitamins. Calculate the base dissociation constant for pyridine if a 0.125 mol/L aqueous solution has a pH of 9.10.

#### What Is Required?

You need to find  $K_b$ .

#### What Is Given?

$$[C_5H_5N] = 0.125 \text{ mol/L}$$

$$\text{pH} = 9.10$$

#### Plan Your Strategy

**Step 1** Write the equation for the equilibrium reaction of pyridine in water. Then set up an ICE table.

**Step 2** Write the equation for the base dissociation constant. Substitute equilibrium terms into the equation.

**Step 3**  $\text{pOH} = 14.0 - \text{pH}$

**Step 4**  $[\text{OH}^-] = 10^{-\text{pOH}}$

**Step 5** Substitute for  $x$  into the equilibrium equation. Calculate the value of  $K_b$ .

#### Act on Your Strategy

##### Step 1

Concentration (mol/L)	$C_5H_5N_{(aq)}$	$+ H_2O_{(l)}$	$\rightleftharpoons C_5H_5NH^+_{(aq)}$	$+ OH^-_{(aq)}$
Initial	0.125		0	~0
Change	-x		+x	+x
Equilibrium	$0.125 - x$		x	x

**Step 2** 
$$K_b = \frac{[C_5H_5NH^+][OH^-]}{[C_5H_5N]}$$
$$= \frac{(x)(x)}{(0.125 - x)}$$

**Step 3**  $\text{pOH} = 14.00 - 9.10 = 4.90$

**Step 4**  $[\text{OH}^-] = 10^{-4.90}$ 
$$= 1.3 \times 10^{-5} \text{ mol/L}$$

**Step 5**  $0.125 - (1.3 \times 10^{-5}) = 0.125$

$$K_b = \frac{(1.3 \times 10^{-5})^2}{0.125}$$
$$= 1.4 \times 10^{-9}$$

#### Check Your Solution

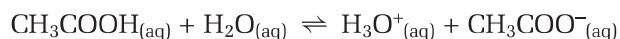
The value of  $K_b$  is reasonable for a weak organic base. The final answer has two significant digits, consistent with the two decimal places in the given pH.

## Practice Problems

29. An aqueous solution of household ammonia has a molar concentration of 0.105 mol/L. Calculate the pH of the solution.
30. Hydrazine,  $\text{N}_2\text{H}_4$ , has been used as a rocket fuel. The concentration of an aqueous solution of hydrazine is  $5.9 \times 10^{-2}$  mol/L. Calculate the pH of the solution.
31. Morphine,  $\text{C}_{17}\text{H}_{19}\text{NO}_3$ , is a naturally occurring base that is used to control pain. A  $4.5 \times 10^{-3}$  mol/L solution has a pH of 9.93. Calculate  $K_b$  for morphine.
32. Methylamine,  $\text{CH}_3\text{NH}_2$ , is a fishy-smelling gas at room temperature. It is used to manufacture several prescription drugs, including methamphetamine. Calculate  $[\text{OH}^-]$  and pOH of a 0.25 mol/L aqueous solution of methylamine.
33. At room temperature, trimethylamine,  $(\text{CH}_3)_3\text{N}$ , is a gas with a strong ammonia-like odour. Calculate  $[\text{OH}^-]$  and the percent of trimethylamine molecules that react with water in a 0.22 mol/L aqueous solution.
34. An aqueous solution of ammonia has a pH of 10.85. What is the concentration of the solution?

## Acids and Their Conjugate Bases

There is an important relationship between the dissociation constant for an acid,  $K_a$ , and the dissociation constant for its conjugate base,  $K_b$ . Consider acetic acid and its dissociation in water.



$K_a$  is given by the following expression.

$$K_a = \frac{[\text{CH}_3\text{COO}^-][\text{H}_3\text{O}^+]}{[\text{CH}_3\text{COOH}]}$$

The acetate ion is the conjugate base of acetic acid. A soluble salt of the conjugate base, such as sodium acetate, forms acetate ions in solution. The solution acts as a base with water.



$K_b$  is given by the expression below.

$$K_b = \frac{[\text{CH}_3\text{COOH}][\text{OH}^-]}{[\text{CH}_3\text{COO}^-]}$$

The product  $K_a K_b$  gives an interesting result.

$$\begin{aligned} K_a K_b &= \frac{[\text{H}_3\text{O}^+][\text{CH}_3\text{COO}^-]}{[\text{CH}_3\text{COOH}]} \times \frac{[\text{CH}_3\text{COOH}][\text{OH}^-]}{[\text{CH}_3\text{COO}^-]} \\ &= [\text{H}_3\text{O}^+][\text{OH}^-] \\ &= K_w \end{aligned}$$

Thus, for an acid and its conjugate base (or a base and its conjugate acid),  $K_a K_b = K_w$ . One interpretation of the result is the stronger an acid, the weaker its conjugate base must be. This makes sense chemically, because a strong acid gives up a proton from each molecule. Therefore, its conjugate base does not bond with the proton. In summary, then, the strength of an acid and its conjugate base are inversely related. *The conjugate of a strong acid is always a weak base, and, conversely, the conjugate of a strong base is always a weak acid.*



## Sample Problem

### Solving Problems Involving $K_a$ and $K_b$

#### Problem

Sodium acetate,  $\text{CH}_3\text{COONa}$ , is used for developing photographs. Find the value of  $K_b$  for the acetate ion. Then calculate the pH of a solution that contains 12.5 g of sodium acetate dissolved in 1.00 L of water. (Only the acetate ion affects the pH of the solution.)

#### What Is Required?

You need to find  $K_b$  and pH.

#### What Is Given?

$K_a$  for acetic acid =  $1.81 \times 10^{-5}$

12.5 g of  $\text{CH}_3\text{COONa}$  is dissolved in 1.00 L of water.

#### Plan Your Strategy

**Step 1** Find  $K_b$  using the relationship  $K_a K_b = K_w$

**Step 2** Calculate  $[\text{CH}_3\text{COO}^-]$ .

**Step 3** Write the chemical equation for the acetate ion acting as a base. Then set up an ICE table.

**Step 4** Write the dissociation equation for  $K_b$ , and substitute equilibrium values.

**Step 5** Determine whether or not the dissociation of the acetate ions is negligible compared with its initial concentration.

**Step 6** Solve the equation for  $x$ .

**Step 7** Calculate  $[\text{H}_3\text{O}^+]$  using  $K_w = [\text{H}_3\text{O}^+][\text{OH}^-]$ .

**Step 8** Calculate pH from  $\text{pH} = -\log[\text{H}_3\text{O}^+]$

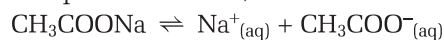
#### Act on Your Strategy

$$\begin{aligned}\text{Step 1 } K_b \text{ for } \text{CH}_3\text{COO}^- &= \frac{K_w}{K_a} \\ &= \frac{1.0 \times 10^{-14}}{1.8 \times 10^{-5}} \\ &= 5.6 \times 10^{-10}\end{aligned}$$

**Step 2**  $M(\text{CH}_3\text{COONa}) = 82.0 \text{ g/mol}$

$$\begin{aligned}\text{Amount} &= \frac{12.5 \text{ g}}{82.0 \text{ g/mol}} \\ &= 0.152 \text{ mol/L}\end{aligned}$$

In aqueous solution,



$$\therefore [\text{CH}_3\text{COO}^-] = 0.152 \text{ mol/L}$$

**Step 3**

Concentration (mol/L)	$\text{CH}_3\text{COO}^-_{(\text{aq})}$	+	$\text{H}_2\text{O}_{(\ell)}$	$\rightleftharpoons$	$\text{CH}_3\text{COOH}_{(\text{aq})}$	+	$\text{OH}^-_{(\text{aq})}$
Initial	0.152				0		~0
Change	-x				+x		+x
Equilibrium	$0.152 - x$				x		x

$$\begin{aligned}\text{Step 4 } K_b &= \frac{[\text{CH}_3\text{COOH}][\text{OH}^-]}{[\text{CH}_3\text{COO}^-]} \\ &= \frac{(x)(x)}{0.152 - x}\end{aligned}$$

$$\text{Step 5 } \frac{[\text{CH}_3\text{COO}^-]}{K_b} = \frac{0.152}{5.6 \times 10^{-10}} > 500$$

Therefore,  $x$  is negligible compared with the initial concentration.

$$\text{Step 6 } 5.6 \times 10^{-10} = \frac{x^2}{0.152}$$

Solving the equation (since only the positive root is reasonable),  
 $x = 9.2 \times 10^{-6} = [\text{OH}^-]$

$$\begin{aligned}\text{Step 7 } [\text{H}_3\text{O}^+] &= \frac{K_w}{[\text{OH}^-]} \\ &= \frac{1.0 \times 10^{-14}}{9.2 \times 10^{-6}} \\ &= 1.1 \times 10^{-9} \text{ mol/L}\end{aligned}$$

$$\begin{aligned}\text{Step 8 } \text{pH} &= -\log[\text{H}_3\text{O}^+] \\ &= -\log 1.1 \times 10^{-9} \\ &= 8.96\end{aligned}$$

### Check Your Solution

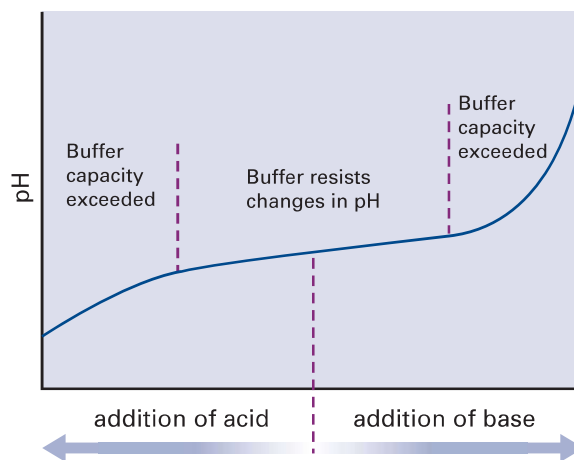
The solution is weakly basic. The acetate ion is a very weak base, so the answer is reasonable.

## Practice Problems

35. Use the table of  $K_a$  values in Appendix E to list the conjugate bases of the following acids in order of increasing base strength: formic acid,  $\text{HCOOH}$ ; hydrofluoric acid,  $\text{HF}_{(\text{aq})}$ ; benzoic acid,  $\text{C}_6\text{H}_5\text{COOH}$ ; phenol,  $\text{C}_6\text{H}_5\text{OH}$ .
36.  $K_b$  for ammonia,  $\text{NH}_3$ , is  $1.8 \times 10^{-5}$ .  $K_b$  for trimethylamine,  $(\text{CH}_3)_3\text{N}$ , is  $6.5 \times 10^{-5}$ . Which is the stronger acid,  $\text{NH}_4^+$  or  $(\text{CH}_3)_3\text{NH}^+$ ?
37. Sodium benzoate is used as a food preservative. Calculate the pH of a 1.0 mol/L aqueous solution of sodium benzoate. (Only the benzoate ion affects the pH of the solution.)
38. The hydrogen sulfite ion,  $\text{HSO}_3^-$ , is amphoteric. Write chemical equations to show how it acts first as an acid and then as a base.

## Buffer Solutions

A solution that contains a weak acid/conjugate base mixture or a weak base/conjugate acid mixture is called a **buffer solution**. A buffer solution resists changes in pH when a moderate amount of an acid or a base is added to it. (See Figure 8.9.) For example, adding 10 mL of 1.0 mol/L hydrochloric acid to 1 L of water changes the pH from 7 to about 3, a difference of 4 units. Adding the same amount of acid to 1 L of buffered solution might change the pH by only 0.1 unit.



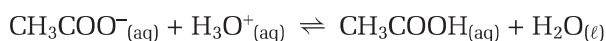
**Figure 8.9** Adding a moderate amount of an acid or a base to a buffer solution causes little change in pH.

Buffer solutions can be made in two different ways:

1. by using a weak acid and one of its salts: for example, by mixing acetic acid and sodium acetate
2. by using a weak base and one of its salts: for example, by mixing ammonia and ammonium chloride

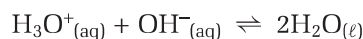
How does a buffer solution resist changes in pH when an acid or a base is added? Consider a buffer solution that is made using acetic acid and sodium acetate. Acetic acid is weak, so most of its molecules are not dissociated and  $[\text{CH}_3\text{COOH}]$  is high. Sodium acetate is soluble and a good electrolyte, so  $[\text{CH}_3\text{COO}^-]$  is also high. Adding an acid or a base has little effect because the added  $\text{H}_3\text{O}^+$  or  $\text{OH}^-$  ions are removed by one of the components in the buffer solution. The equilibrium of the reactions between the ions in solution shifts, as predicted by Le Châtelier's principle and described below.

- Adding an acid to a buffer: Acetate ions react with the hydronium ions added to the solution.

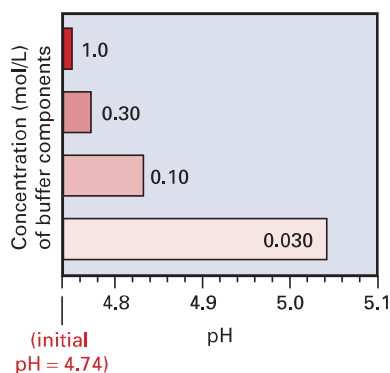


The position of equilibrium shifts to the right. Here hydronium ions are removed, by acetate ions, from the sodium acetate component.

- Adding a base to a buffer: Hydroxide ions react with the hydronium ions that are formed by the dissociation of acetic acid.



The position of this water equilibrium shifts to the right, replacing hydronium ions.

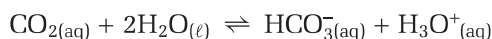


**Figure 8.10** These four buffer solutions have the same initial pH but different concentrations (shown by the numbers beside or on the bars). The pH increases with the addition of a certain amount of strong base. The more concentrated the buffer solution is (that is, the higher its buffer capacity), the smaller the change in pH is.

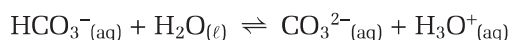
Buffer solutions have two important characteristics. One of these characteristics is the pH of the solution. The other is its **buffer capacity**: the amount of acid or base that can be added before considerable change occurs to the pH. The buffer capacity depends on the concentration of the acid/conjugate base (or the base/conjugate acid) in the buffer solution. When the ratio of the concentration of the buffer components is close to 1, the buffer capacity has reached its maximum. As well, a buffer that is more concentrated resists changes to pH more than a buffer that is more dilute. This idea is illustrated in Figure 8.10, with buffer solutions of acetic acid and acetate of different concentrations.

## Buffers in the Blood

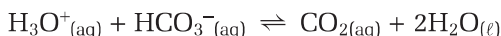
Buffers are extremely important in biological systems. The pH of arterial blood is about 7.4. The pH of the blood in your veins is just slightly less. If the pH of blood drops to 7.0, or rises above 7.5, life-threatening problems develop. To maintain its pH within a narrow range, blood contains a number of buffer systems. The most important buffer system in the blood depends on an equilibrium between hydrogen carbonate ions and carbonate ions. Dissolved carbon dioxide reacts with water to form hydrogen carbonate ions.



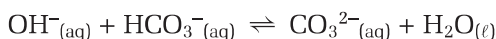
The  $\text{HCO}_3^-$  dissociates in water to form  $\text{CO}_3^{2-}$ .



If metabolic changes add  $\text{H}_3\text{O}^+$  ions to the blood, the excess  $\text{H}_3\text{O}^+$  ions are removed by combining with  $\text{HCO}_3^-$  ions.



If excess  $\text{OH}^-$  ions enter the blood, they are removed by reacting with the hydrogen carbonate,  $\text{HCO}_3^-$ , ions.



## Section Summary

In this section, you compared strong and weak acids and bases using your understanding of chemical equilibrium, and you solved problems involving their concentrations and pH. Then you considered the effect on pH of buffer solutions: solutions that contain a mixture of acid ions and base ions. In the next section, you will compare pH changes that occur when solutions of acids and bases with different strengths react together.

Web  LINK

[www.mcgrawhill.ca/links/chemistry12](http://www.mcgrawhill.ca/links/chemistry12)

Some aspirin products are sold in buffered form. Infer the reasoning behind this practice. Is there clinical evidence to support it? To find out, go to the web site above and click on **Web Links**. Conduct further research to investigate whether there is more recent evidence either in support of or disproving the effectiveness of buffering aspirin.

## Section Review

- 1** **I** Phenol,  $\text{C}_6\text{H}_5\text{OH}$ , is an aromatic alcohol with weak basic properties. It is used as a disinfectant and cleanser. Calculate the molar concentration of  $\text{OH}^-$  ions in a 0.75 mol/L solution of phenolate,  $\text{C}_6\text{H}_5\text{O}^-$ , ions ( $K_b = 7.7 \times 10^{-5}$ ). What is the pH of the solution?
- 2** **I** Potassium sorbate is a common additive in foods. It is used to inhibit the formation of mould. A solution contains 1.82 g of sorbate,  $\text{C}_6\text{H}_7\text{O}_2^-$ , ions ( $K_a = 1.7 \times 10^{-5}$ ) dissolved in 250 mL of water. What is the pH of the solution?
- 3** **I** Write the chemical formula for the conjugate base of hypobromous acid,  $\text{HOBr}$ . Calculate  $K_b$  for this ion.
- 4** **K/U** Describe how a buffer solution differs from an aqueous acidic or basic solution.
- 5** **MC** Explain the function and importance of buffers in blood.
- 6** **C** Explain why an aqueous mixture of  $\text{NaCl}$  and  $\text{HCl}$  does not act as a buffer, but an aqueous mixture of  $\text{NH}_3$  and  $\text{NH}_4\text{Cl}$  does.

# 8.4

## Acid-Base Titration Curves

### Section Preview/ Specific Expectations

In this section, you will

- **interpret** acid-base titration curves and the pH at the equivalence point
- **communicate** your understanding of the following terms: *acid-base titration curve*, *equivalence point*

In Investigation 8-A, you performed a titration and graphed the changes in the pH of acetic acid solution as sodium hydroxide solution was added. A graph of the pH of an acid (or base) against the volume of an added base (or acid) is called an **acid-base titration curve**.

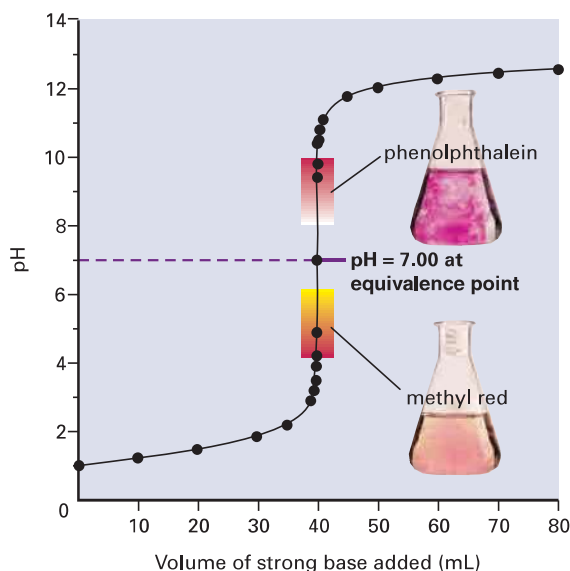
Titration is a common analytical procedure that chemists perform, with the usual goal of determining the concentration of one of the reactants. The **equivalence point** is the point in a titration when the acid and base that are present completely react with each other. If chemists know the volumes of both solutions at the equivalence point, and the concentration of one of them, they can calculate the unknown concentration.

As you can see in Figure 8.11, the equivalence point is the middle of the steep rise that occurs in a titration curve. The endpoint of a titration occurs when the indicator changes colour, which happens over a range of about 2 pH units. The pH changes rapidly near the equivalence point. Therefore, the change in colour usually takes place in a fraction of a millilitre, with the addition of a single drop of solution. Chemists have access to a variety of indicators that change colour at different pH values. The colour changes and ranges for three common indicators are given in Table 8.4.

**Table 8.4** Data on the Endpoints of Three Common Acid-Base Indicators

Indicator	Colour change at endpoint	Approximate range
bromocresol green	yellow to blue	3.8–5.2
methyl red	red to yellow	4.3–6.2
phenolphthalein	colourless to pink	8.2–10.0

When an indicator is used in a titration, the range of pH values at which its endpoint occurs must include, or be close to, the equivalence point. Some representative acid-base titration curves, shown in Figures 8.11, 8.12, and 8.13, will illustrate this point.



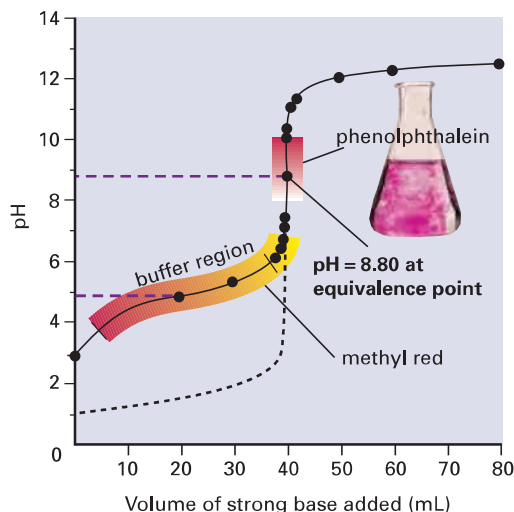
### Titration Curve for a Strong Acid With a Strong Base

These titrations have a pH of 7 at equivalence. Indicators such as phenolphthalein, methyl red, and bromocresol green can be used, because their endpoints are close to the equivalence point. Many chemists prefer phenolphthalein because the change from colourless to pink is easy to see.

**Figure 8.11** The curve for a strong acid-strong base titration

## Titration Curve for a Weak Acid With a Strong Base

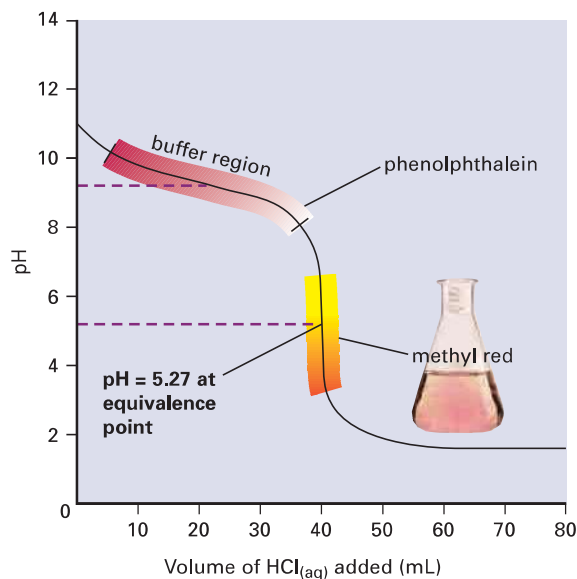
These titrations have pH values that are greater than 7 at equivalence. In the titration shown in Figure 8.12, the equivalence point occurs at a pH of 8.80. Therefore, phenolphthalein is a good indicator for this titration. Methyl red is not, because its endpoint is too far from the equivalence point.



**Figure 8.12** The curve for a weak acid-strong base titration: The weak acid here is propanoic acid,  $\text{CH}_3\text{CH}_2\text{COOH}$ .

## Titration Curve for a Weak Base With a Strong Acid

These titrations have pH values that are less than 7 at the equivalence point. The equivalence point in the titration shown in Figure 8.13, involving ammonia and hydrochloric acid, occurs at a pH of 5.27. Either methyl red or bromocresol green could be used as an indicator, but not phenolphthalein.



**Figure 8.13** The curve for a weak base-strong acid titration

## Section Summary

In this section, you examined acid-base titration curves for combinations of strong and weak acids and bases. You may have noticed the absence of a curve for the reaction of a weak acid with a weak base. A weak acid-weak base titration curve is difficult to describe quantitatively, because it has competing equilibria. You may learn about this curve in future chemistry courses.

In the next chapter, you will extend your knowledge of equilibria involving aqueous ions. You will learn how to calculate the pH at an equivalence point, so you can select an appropriate indicator for any acid-base titration. You will also learn why equilibrium is important to the solubility of compounds that are slightly soluble, and how to predict whether a precipitate will form as the result of a reaction between ions in solution.

## Section Review

- 1 **K/U** In this section, you examined acid-base titration curves.
  - (a) Distinguish between the equivalence point and the endpoint for a titration.
  - (b) When choosing an indicator, do the pH values of the two points need to coincide exactly? Explain.
- 2 **K/U** In a titration, a basic solution is added to an acidic solution, and measurements of pH are taken. Compare a strong acid-strong base titration and a strong acid-weak base titration in terms of
  - (a) the initial pH
  - (b) the quantity of base that is needed to reach the equivalence point
  - (c) the pH at the equivalence pointAssume that the concentrations of the two solutions are identical.
- 3 **C** Sketch the pH curve for the titration of a weak acid with a strong base. Show the equivalence point on your sketch. Suggest an indicator that might be used, and explain your selection.
- 4 **C** Suggest an indicator that could be used for the titration of potassium hydroxide with nitrous acid. Explain your suggestion.
- 5 **I** Estimate the pH of a solution in which bromocresol green is blue, and methyl red is orange.



## Reflecting on Chapter 8

Summarize this chapter in the format of your choice. Here are a few ideas to use as guidelines:

- Relate the microscopic properties of acids and bases to their macroscopic properties.
- Identify conjugate acid-base pairs for selected acid-base reactions, and compare their strengths.
- State the relationship among  $K_a$ ,  $K_b$ , and  $K_w$ .
- Outline the relationship among  $[H_3O^+]$ , pH,  $[OH^-]$ , and pOH.
- Describe two examples of buffer solutions in your daily life, and explain how they function.

## Reviewing Key Terms

For each of the following terms, write a sentence that shows your understanding of its meaning.

hydronium ion ( $H_3O^+_{(aq)}$ )	conjugate acid-base pair
monoprotic acids	polyprotic acids
ion product constant for water ( $K_w$ )	pH
acid dissociation constant ( $K_a$ )	pOH
percent dissociation	base dissociation constant ( $K_b$ )
buffer solution	buffer capacity
acid-base titration curve	equivalence point

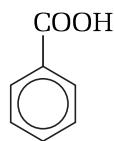
## Knowledge/Understanding

- Give two examples of each of the following acids and bases.
  - Arrhenius acids
  - Brønsted-Lowry bases
  - Brønsted-Lowry bases that are not Arrhenius bases
- Classify each compound as a strong acid, strong base, weak acid, or weak base.
  - phosphoric acid,  $H_3PO_4$  (used in cola beverages and rust-proofing products)
  - chromic acid,  $H_2CrO_4$  (used in the production of wood preservatives)
  - barium hydroxide,  $Ba(OH)_2$ , a white, toxic base (can be used to de-acidify paper)
  - $CH_3NH_2$ , commonly called methylamine (is responsible for the characteristic smell of fish that are no longer fresh)
- Write a chemical formula for each acid or base.
  - the conjugate base of  $OH^-$

- the conjugate acid of ammonia,  $NH_3$
  - the conjugate acid of  $HCO_3^-$
  - the conjugate base of  $HCO_3^-$
- Decide whether each statement is true or false, and explain your reasoning.
    - HBr is a stronger acid than HI.
    - $HBrO_2$  is a stronger acid than  $HBrO$ .
    - $H_2SO_3$  is a stronger acid than  $HSO_3^-$ .
  - Arrange the following aqueous solutions in order of pH, from lowest to highest: 2.0 mol/L  $HClO_4$ , 2.0 mol/L NaCl, 0.20 mol/L  $CH_3COOH$ , 0.02 mol/L HCl.
  - In each pair of bases, which is the stronger base?
    - $HSO_4^-_{(aq)}$  or  $SO_4^{2-}_{(aq)}$
    - $S^{2-}_{(aq)}$  or  $HS^-_{(aq)}$
    - $HPO_4^{2-}_{(aq)}$  or  $H_2PO_4^-_{(aq)}$
    - $HCO_3^-_{(aq)}$  or  $CO_3^{2-}_{(aq)}$
  - Use Appendix E to find the values of  $K_a$  for hydrosulfuric acid,  $HS^-_{(aq)}$ , and sulfurous acid,  $HSO_3^-_{(aq)}$ .
    - Write equations for the base dissociation constants of  $HS^-_{(aq)}$  and  $HSO_3^-_{(aq)}$ .
    - Calculate the value of  $K_b$  for each ion.
    - Which is the stronger base,  $HS^-_{(aq)}$  or  $HSO_3^-_{(aq)}$ ? Explain.
  - While the pH of blood must be maintained within strict limits, the pH of urine can vary. The sulfur in foods, such as eggs, is oxidized in the body and excreted in the urine. Does the presence of sulfide ions in urine tend to increase or decrease the pH? Explain.
  - Sodium methanoate,  $NaHCOO$ , and methanoic acid,  $HCOOH$ , can be used to make a buffer solution. Explain how this combination resists changes in pH when small amounts of acid or base are added.
  - Oxoacids contain an atom that is bonded to one or more oxygen atoms. One or more of these oxygen atoms may also be bonded to hydrogen. Consider the following oxoacids:  $HBrO_{3(aq)}$ ,  $HClO_{3(aq)}$ ,  $HClO_{4(aq)}$ , and  $H_2SO_{3(aq)}$ .
    - What factors are used to predict the strengths of oxoacids?
    - Arrange the oxoacids above in the order of increasing acid strength.

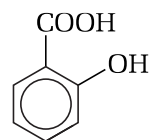
## Inquiry

11. What is the pH of a mixture of equal volumes of 0.040 mol/L hydrochloric acid and 0.020 mol/L sodium hydroxide?
12. Suppose that 15.0 mL of sulfuric acid just neutralized 18.0 mL of 0.500 mol/L sodium hydroxide solution. What is the concentration of the sulfuric acid?
13. A student dissolved 5.0 g of vitamin C in 250 mL of water. The molar mass of ascorbic acid is 176 g/mol, and its  $K_a$  is  $8.0 \times 10^{-5}$ . Calculate the pH of the solution. **Note:** Abbreviate the formula of ascorbic acid to  $H_{Asc}$ .
14. Benzoic acid is a weak, monoprotic acid ( $K_a = 6.3 \times 10^{-5}$ ). Its structure is shown below. Calculate the pH and the percent dissociation of each of the following solutions of benzoic acid. Then use Le Châtelier's principle to explain the trend in percent dissociation of the acid as the solution becomes more dilute.  
(a) 1.0 mol/L (b) 0.10 mol/L (c) 0.01 mol/L



15. Hypochlorous acid, HOCl, is a weak acid that is found in household bleach. It is made by dissolving chlorine gas in water.  
 $Cl_{2(g)} + 2H_2O_{(l)} \rightleftharpoons H_3O^+_{(aq)} + Cl^-_{(aq)} + HOCl_{(aq)}$   
(a) Calculate the pH and the percent dissociation of a 0.065 mol/L solution of hypochlorous acid.  
(b) What is the conjugate base of hypochlorous acid? What is its value for  $K_b$ ?
16. Calculate the pH of a 1.0 mol/L aqueous solution of sodium benzoate. **Note:** Only the benzoate ion affects the pH of the solution.
17. Calculate the pH of a 0.10 mol/L aqueous solution of sodium nitrite,  $NaNO_2$ . **Note:** Only the nitrite ion affects the pH of the solution.
18. A student prepared a saturated solution of salicylic acid and measured the pH of the solution. The student then carefully evaporated 100 mL of the solution and collected the solid. If the pH of the solution was 2.43, and 0.22 g was collected after evaporating 100 mL of the

solution, what is the acid dissociation constant for salicylic acid?

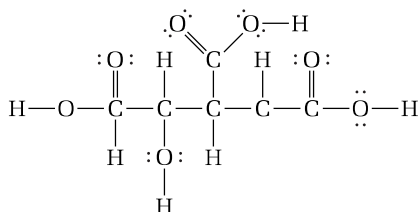


## Communication

19. List the oxoacids of bromine ( $HOBr$ ,  $HBrO_2$ ,  $HBrO_3$ , and  $HBrO_4$ ) in order of increasing strength. What is the order of increasing strength for the conjugate bases of these acids?
20. Consider the following acid-base reactions.  
 $HBrO_{2(aq)} + CH_3COO^-_{(aq)} \rightleftharpoons CH_3COOH_{(aq)} + BrO^-_{2(aq)}$   
 $H_2S_{(aq)} + OH^-_{(aq)} \rightleftharpoons HS^-_{(aq)} + H_2O_{(l)}$   
 $HS^-_{(aq)} + CH_3COOH_{(aq)} \rightleftharpoons H_2S_{(aq)} + CH_3COO^-_{(aq)}$   
If each equilibrium lies to the right, arrange the following compounds in order of increasing acid strength:  $HBrO_2$ ,  $CH_3COOH$ ,  $H_2S$ ,  $H_2O$ .
21. Discuss the factors that can be used to predict the relative strength of different oxoacids.
22. The formula of methyl red indicator can be abbreviated to HMr. Like most indicators, methyl red is a weak acid.  
 $HMr_{(aq)} + H_2O_{(l)} \rightleftharpoons H_3O^+_{(aq)} + Mr^-_{(aq)}$   
The change between colours (when the indicator colour is orange) occurs at a pH of 5.4. What is the equilibrium constant for the reaction?
23. Gallic acid is the common name for 3,4,5-trihydroxybenzoic acid.  
(a) Draw the structure of gallic acid.  
(b)  $K_a$  for gallic acid is  $3.9 \times 10^{-5}$ . Calculate  $K_b$  for the conjugate base of gallic acid. Then write the formula of the ion.
24. (a) Sketch the pH curves you would expect if you titrated
- a strong acid with a strong base
  - a strong acid with a weak base
  - a weak acid with a strong base
- (b) Congo red changes colour over a pH range of 3.0 to 5.0. For which of the above titrations would Congo red be a good indicator to use?

## Making Connections

25. Citric acid can be added to candy to give a sour taste. The structure of citric acid is shown below.



- (a) Identify the acidic hydrogen atoms that are removed by water in aqueous solution. Why do water molecules pull these hydrogen atoms away, rather than other hydrogen atoms in citric acid?
- (b) Why does citric acid not form  $\text{OH}^-$  ions in aqueous solution, and act as a base?
- (c) When citric acid and sodium hydrogen carbonate are used in bubble gum, the bubble gum foams when chewed. Suggest a reason why this happens.
26. (a) Imagine that you have collected a sample of rainwater in your community. The pH of your sample is 4.52. Unpolluted rainwater has a pH of about 5.6. How many more hydronium ions are present in your sample, compared with normal rainwater? Calculate the ratio of the concentration of hydronium ions in your sample to the concentration of hydronium ions in unpolluted rainwater.
- (b) You have been invited to a community meeting to explain your findings to local residents. No one at the meeting has a background in chemistry. In a paragraph, write what you would say at this meeting.
- (c) Suggest at least two possible factors that could be responsible for the pH you measured. What observations would you want to make, and what data would you want to collect, to help you gain confidence that one of these factors is responsible?

### Answers to Practice Problems and Short Answers to Section Review Questions

**Practice Problems:** 1.(a) chloride ion,  $\text{Cl}^-$  (b) carbonate ion,  $\text{CO}_3^{2-}$  (c) hydrogen sulfate ion,  $\text{HSO}_4^-$  (d) hydrazine,  $\text{N}_2\text{H}_4$   
 2.(a) nitric acid,  $\text{HNO}_3$  (b) water,  $\text{H}_2\text{O}$  (c) hydronium ion,  $\text{H}_3\text{O}^+$  (d) carbonic acid,  $\text{H}_2\text{CO}_3$  3.(a)  $\text{HS}^-/\text{H}_2\text{S}$  and  $\text{H}_2\text{O}/\text{OH}^-$

- (b)  $\text{O}^{2-}/\text{OH}^-$  and  $\text{H}_2\text{O}/\text{OH}^-$  4.(a)  $\text{H}_2\text{S}/\text{HS}^-$  and  $\text{NH}_3/\text{NH}_4^+$   
 (b)  $\text{H}_2\text{SO}_4/\text{HSO}_4^-$  and  $\text{H}_2\text{O}/\text{H}_3\text{O}^+$  5.(a) 4.5 mol/L (b) 1.35 mol/L  
 (c) 0.02 mol/L (d) 0.0375 mol/L 6.(a) 3.1 mol/L  
 (b) 0.87 mol/L (c) 0.701 mol/L (d) 0.697 mol/L 7.(a) acidic solution;  $[\text{H}_3\text{O}^+] = 0.479 \text{ mol/L}$  (b) acidic solution;  $[\text{H}_3\text{O}^+] = 1.98 \text{ mol/L}$  8. acidic solution;  $[\text{H}_3\text{O}^+] = 0.46 \text{ mol/L}$   
 9.(a)  $[\text{H}_3\text{O}^+] = 0.45 \text{ mol/L}$ ;  $[\text{OH}^-] = 2.2 \times 10^{-14} \text{ mol/L}$   
 (b)  $[\text{OH}^-] = 1.1 \text{ mol/L}$ ;  $[\text{H}_3\text{O}^+] = 9.1 \times 10^{-15} \text{ mol/L}$   
 10.(a)  $[\text{H}_3\text{O}^+] = 0.95 \text{ mol/L}$ ;  $[\text{OH}^-] = 1.1 \times 10^{-14} \text{ mol/L}$   
 (b)  $[\text{OH}^-] = 0.024 \text{ mol/L}$ ;  $[\text{H}_3\text{O}^+] = 4.2 \times 10^{-13} \text{ mol/L}$   
 11.  $[\text{HCl}] = 0.18 \text{ mol/L}$  12.  $[\text{Ca}(\text{OH})_2] = 0.29 \text{ mol/L}$  13. acidic;  $\text{pH} = 6.400$ ;  $[\text{OH}^-] = 2.51 \times 10^{-8} \text{ mol/L}$  14.  $\text{pOH} = 2.1$ ;  $[\text{OH}^-] = 8 \times 10^{-3} \text{ mol/L}$  15. acidic;  $[\text{H}_3\text{O}^+] = 1.9 \times 10^{-5} \text{ mol/L}$ ;  $[\text{OH}^-] = 5.2 \times 10^{-10}$ ;  $\text{pOH} = 9.28$   
 16.  $[\text{H}_3\text{O}^+] = [\text{OH}^-] = 1.6 \times 10^{-7}$ ; neutral  
 17. basic;  $\text{pH} = 8.19$ ;  $[\text{H}_3\text{O}^+] = 6.5 \times 10^{-9} \text{ mol/L}$ ;  $[\text{OH}^-] = 1.5 \times 10^{-6} \text{ mol/L}$  18.  $[\text{H}_3\text{O}^+] = 1.9 \times 10^{-3} \text{ mol/L}$ ;  $[\text{OH}^-] = 5.4 \times 10^{-12} \text{ mol/L}$  19.  $\text{pH} = 2.41$ ; 0.46% dissociation  
 20.  $K_a = 1.0 \times 10^{-4}$ ; percent dissociation = 3.2%  
 21.  $\text{pH} = 2.65$  22.  $K_a = 2.9 \times 10^{-8}$  23.  $\text{pH} = 3.411$  24. 1.2 g  
 25.  $\text{pH} = 4.82$ ;  $[\text{CO}_3^{2-}] = 4.7 \times 10^{-11} \text{ mol/L}$  26.  $\text{pH} = 2.74$   
 27.  $\text{pH} = 4.59$ ;  $[\text{HS}^-] = 2.6 \times 10^{-5} \text{ mol/L}$  28.  $K_a = 1.0 \times 10^{-14}$ ;  
 $K_{a2} = \frac{[\text{O}^{2-}][\text{H}_3\text{O}^+]}{[\text{OH}^-]}$  29.  $\text{pH} = 11.14$  30.  $\text{pH} = 10.50$   
 31.  $K_b = 1.6 \times 10^{-6}$  32.  $[\text{OH}^-] = 1.0 \times 10^{-2} \text{ mol/L}$ ;  $\text{pOH} = 1.98$   
 33.  $[\text{OH}^-] = 3.8 \times 10^{-3} \text{ mol/L}$ ; percent dissociation = 1.7%  
 34.  $[\text{NH}_3] = 2.8 \times 10^{-2} \text{ mol/L}$   
 35.  $\text{C}_6\text{H}_5\text{O}^- > \text{C}_6\text{H}_5\text{COO}^- > \text{HCOO}^- > \text{F}^-$  36.  $\text{NH}_4^+$   
 37.  $\text{pH} = 9.10$  38. as an acid:  
 $\text{HSO}_3^-(\text{aq}) + \text{H}_2\text{O}(\ell) \rightleftharpoons \text{H}_3\text{O}^+(\text{aq}) + \text{SO}_3^{2-}(\text{aq})$ ; as a base:  
 $\text{HSO}_3^-(\text{aq}) + \text{H}_2\text{O}(\ell) \rightleftharpoons \text{OH}^-(\text{aq}) + \text{H}_2\text{SO}_3(\text{aq})$

### Section Review: 8.1:

- 1.(a)  $\text{H}_3\text{PO}_4(\text{aq}) + \text{H}_2\text{O}(\text{aq}) \rightleftharpoons \text{H}_2\text{PO}_4^-(\text{aq}) + \text{H}_3\text{O}^+(\text{aq})$ ;  
 $\text{H}_2\text{PO}_4^-(\text{aq}) + \text{H}_2\text{O}(\text{aq}) \rightleftharpoons \text{HPO}_4^{2-}(\text{aq}) + \text{H}_3\text{O}^+(\text{aq})$ ;  
 $\text{HPO}_4^{2-}(\text{aq}) + \text{H}_2\text{O}(\text{aq}) \rightleftharpoons \text{PO}_4^{3-}(\text{aq}) + \text{H}_3\text{O}^+(\text{aq})$   
 (b) as an acid:  $\text{H}_2\text{PO}_4^-(\text{aq}) + \text{H}_2\text{O}(\text{aq}) \rightleftharpoons \text{HPO}_4^{2-}(\text{aq}) + \text{H}_3\text{O}^+(\text{aq})$ ;  
 as a base:  $\text{H}_2\text{PO}_4^-(\text{aq}) + \text{H}_3\text{O}^+(\text{aq}) \rightleftharpoons \text{H}_3\text{PO}_4(\text{aq}) + \text{H}_2\text{O}(\text{aq})$   
 (c)  $\text{H}_3\text{PO}_4(\text{aq})$  is much stronger (although it is still a weak acid) than  $\text{H}_2\text{PO}_4^-(\text{aq})$ . 2.  $\text{C}_6\text{H}_4\text{NH}_2\text{COO}^-$  3.(a)  $\text{B}(\text{OH})_3/\text{B}(\text{OH})_4^-$  and  $\text{H}_2\text{O}/\text{H}_3\text{O}^+$  (b) weak 4.(a) weak acid  
 (b) strong acid (c) strong base (d) weak base  
 8.2: 1.(a) 4.43 (b)  $2.70 \times 10^{-10}$  (c) 9.57 (d) acidic (e)  $3.9 \times 10^{-11}$   
 (f)  $2.6 \times 10^{-4}$  (g) 3.59 (h) basic (i)  $1.4 \times 10^{-13}$  (j) 12.85 (k) 1.15  
 (l) basic (m)  $8 \times 10^{-6}$  (n) 5.1 (o)  $1 \times 10^{-9}$  (p) acidic 2.  $\text{pH} = 2.39$   
 3.  $K_a = 2.5 \times 10^{-4}$  4.  $\text{pH} = 1.70$ ;  
 $[\text{HOCCOO}^-] = 5.4 \times 10^{-5} \text{ mol/L}$   
 5.  $[\text{H}_2\text{CO}_3] = 2.3 \times 10^{-3} \text{ mol/L}$   
 8.3: 1.  $[\text{OH}^-] = 7.6 \times 10^{-3} \text{ mol/L}$ ;  $\text{pH} = 11.88$  2.  $\text{pH} = 8.80$   
 3.  $\text{OBr}^-$ ;  $K_b = 3.6 \times 10^{-6}$  8.4: 4. phenolphthalein 5.  $\text{pH} \sim 5.0$