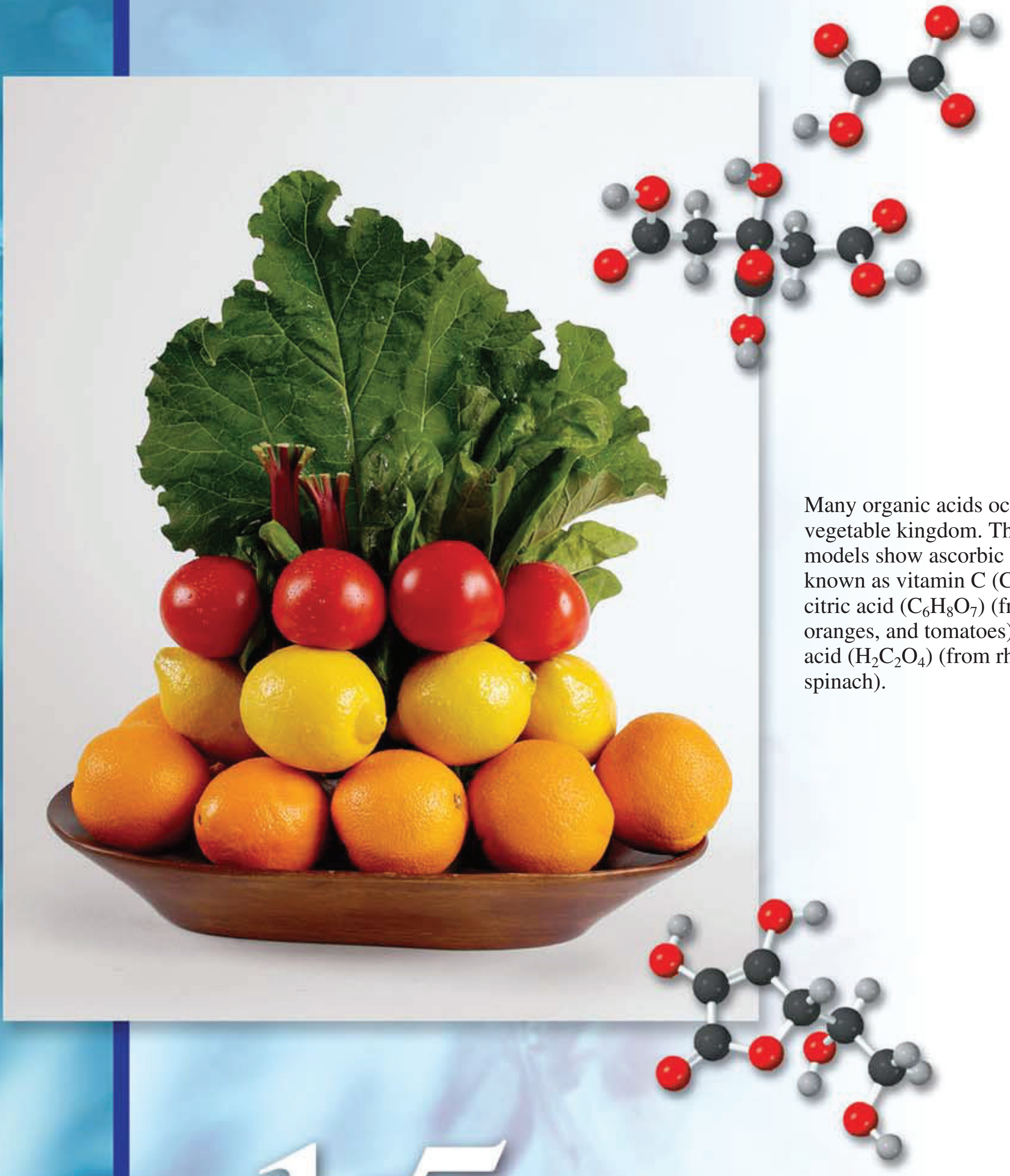
Acids and Bases



Many organic acids occur in the vegetable kingdom. The molecular models show ascorbic acid, also known as vitamin C ($C_6H_8O_6$), and citric acid ($C_6H_8O_7$) (from lemons, oranges, and tomatoes) and oxalic acid ($H_2C_2O_4$) (from rhubarb and spinach).

15

Chapter Outline

A Look Ahead

- We start by reviewing and extending Brønsted's definitions of acids and bases (in Chapter 4) in terms of acid-base conjugate pairs. (15.1)
- Next, we examine the acid-base properties of water and define the ion-product constant for the autoionization of water to give H^+ and OH^- ions. (15.2)
- We define pH as a measure of acidity and also introduce the pOH scale. We see that the acidity of a solution depends on the relative concentrations of H^+ and OH^- ions. (15.3)
- Acids and bases can be classified as strong or weak, depending on the extent of their ionization in solution. (15.4)
- We learn to calculate the pH of a weak acid solution from its concentration and ionization constant and to perform similar calculations for weak bases. (15.5 and 15.6)
- We derive an important relationship between the acid and base ionization constants of a conjugate pair. (15.7)
- We then study diprotic and polyprotic acids. (15.8)
- We continue by exploring the relationship between acid strength and molecular structure. (15.9)
- The reactions between salts and water can be studied in terms of acid and base ionizations of the individual cations and anions making up the salt. (15.10)
- Oxides and hydroxides can be classified as acidic, basic, and amphoteric. (15.11)

Some of the most important processes in chemical and biological systems are acid-base reactions in aqueous solutions. In this first of two chapters on the properties of acids and bases, we will study the definitions of acids and bases, the pH scale, the ionization of weak acids and weak bases, and the relationship between acid strength and molecular structure. We will also look at oxides that can act as acids and bases.

15.1 Brønsted Acids and Bases

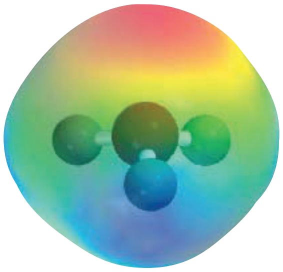
In Chapter 4 we defined a Brønsted acid as a substance capable of donating a proton, and a Brønsted base as a substance that can accept a proton. These definitions are generally suitable for a discussion of the properties and reactions of acids and bases.

Conjugate means "joined together."

An extension of the Brønsted definition of acids and bases is the concept of the ***conjugate acid-base pair,*** which can be defined as *an acid and its conjugate base or a base and its conjugate acid.* The conjugate base of a Brønsted acid is the species that remains when one proton has been removed from the acid. Conversely, a conjugate acid results from the addition of a proton to a Brønsted base.

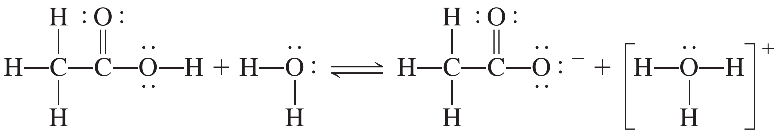
Every Brønsted acid has a conjugate base, and every Brønsted base has a conjugate acid. For example, the chloride ion (Cl^-) is the conjugate base formed from the acid HCl, and H_3O^+ (hydronium ion) is the conjugate acid of the base H_2O.

$$HCl + H_2O \longrightarrow H_3O^+ + Cl^-$$



The proton is always associated with water molecules in aqueous solution. The H_3O^+ ion is the simplest formula of a hydrated proton.

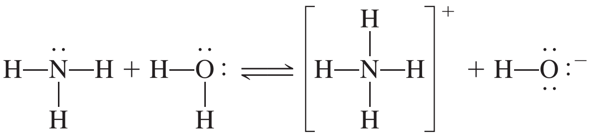
Similarly, the ionization of acetic acid can be represented as



$$\underset{\text{acid}_1}{CH_3COOH(aq)} + \underset{\text{base}_2}{H_2O(l)} \rightleftharpoons \underset{\text{base}_1}{CH_3COO^-(aq)} + \underset{\text{acid}_2}{H_3O^+(aq)}$$

The subscripts 1 and 2 designate the two conjugate acid-base pairs. Thus, the acetate ion (CH_3COO^-) is the conjugate base of CH_3COOH. Both the ionization of HCl (see Section 4.3) and the ionization of CH_3COOH are examples of Brønsted acid-base reactions.

The Brønsted definition also enables us to classify ammonia as a base because of its ability to accept a proton:



$$\underset{\text{base}_1}{NH_3(aq)} + \underset{\text{acid}_2}{H_2O(l)} \rightleftharpoons \underset{\text{acid}_1}{NH_4^+(aq)} + \underset{\text{base}_2}{OH^-(aq)}$$

In this case, NH_4^+ is the conjugate acid of the base NH_3, and the hydroxide ion OH^- is the conjugate base of the acid H_2O. Note that the atom in the Brønsted base that accepts a H^+ ion must have a lone pair.

In Example 15.1, we identify the conjugate pairs in an acid-base reaction.

EXAMPLE 15.1

Identify the conjugate acid-base pairs in the reaction between ammonia and hydrofluoric acid in aqueous solution

$$NH_3(aq) + HF(aq) \rightleftharpoons NH_4^+(aq) + F^-(aq)$$

(Continued)

Strategy Remember that a conjugate base always has one fewer H atom and one more negative charge (or one fewer positive charge) than the formula of the corresponding acid.

Solution NH_3 has one fewer H atom and one fewer positive charge than NH_4^+. F^- has one fewer H atom and one more negative charge than HF. Therefore, the conjugate acid-base pairs are (1) NH_4^+ and NH_3 and (2) HF and F^-.

Practice Exercise Identify the conjugate acid-base pairs for the reaction

$$CN^- + H_2O \rightleftharpoons HCN + OH^-$$

It is acceptable to represent the proton in aqueous solution either as H^+ or as H_3O^+. The formula H^+ is less cumbersome in calculations involving hydrogen ion concentrations and in calculations involving equilibrium constants, whereas H_3O^+ is more useful in a discussion of Brønsted acid-base properties.

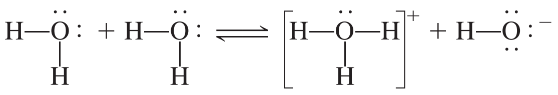
15.2 The Acid-Base Properties of Water

Water, as we know, is a unique solvent. One of its special properties is its ability to act either as an acid or as a base. Water functions as a base in reactions with acids such as HCl and CH_3COOH, and it functions as an acid in reactions with bases such as NH_3. Water is a very weak electrolyte and therefore a poor conductor of electricity, but it does undergo ionization to a small extent:

Tap water and water from underground sources do conduct electricity because they contain many dissolved ions.

$$H_2O(l) \rightleftharpoons H^+(aq) + OH^-(aq)$$

This reaction is sometimes called the *autoionization* of water. To describe the acid-base properties of water in the Brønsted framework, we express its autoionization as follows (also shown in Figure 15.1):



$$H-\underset{\underset{\textstyle H}{|}}{\ddot{O}}: + H-\underset{\underset{\textstyle H}{|}}{\ddot{O}}: \rightleftharpoons \left[H-\underset{\underset{\textstyle H}{|}}{\ddot{O}}-H\right]^+ + H-\underset{\cdot\cdot}{\ddot{O}}:^-$$

or

$$\underset{\text{acid}_1}{H_2O} + \underset{\text{base}_2}{H_2O} \rightleftharpoons \underset{\text{acid}_2}{H_3O^+} + \underset{\text{base}_1}{OH^-} \qquad (15.1)$$

The acid-base conjugate pairs are (1) H_2O (acid) and OH^- (base) and (2) H_3O^+ (acid) and H_2O (base).

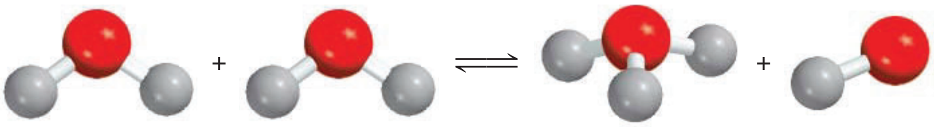


Figure 15.1 *Reaction between two water molecules to form hydronium and hydroxide ions.*

The Ion Product of Water

Recall that in pure water, $[H_2O] = 55.5\ M$ (see p. 621).

In the study of acid-base reactions, the hydrogen ion concentration is key; its value indicates the acidity or basicity of the solution. Because only a very small fraction of water molecules are ionized, the concentration of water, $[H_2O]$, remains virtually unchanged. Therefore, the equilibrium constant for the autoionization of water, according to Equation (15.1), is

$$K_c = [H_3O^+][OH^-]$$

Because we use $H^+(aq)$ and $H_3O^+(aq)$ interchangeably to represent the hydrated proton, the equilibrium constant can also be expressed as

$$K_c = [H^+][OH^-]$$

To indicate that the equilibrium constant refers to the autoionization of water, we replace K_c by K_w

$$K_w = [H_3O^+][OH^-] = [H^+][OH^-] \tag{15.2}$$

where K_w is called the ***ion-product constant,*** which is *the product of the molar concentrations of H^+ and OH^- ions at a particular temperature.*

If you could randomly remove and examine 10 particles (H_2O, H^+, or OH^-) per second from a liter of water, it would take you 2 years, working nonstop, to find one H^+ ion!

In pure water at 25°C, the concentrations of H^+ and OH^- ions are equal and found to be $[H^+] = 1.0 \times 10^{-7}\ M$ and $[OH^-] = 1.0 \times 10^{-7}\ M$. Thus, from Equation (15.2), at 25°C

$$K_w = (1.0 \times 10^{-7})(1.0 \times 10^{-7}) = 1.0 \times 10^{-14}$$

Whether we have pure water or an aqueous solution of dissolved species, the following relation *always* holds at 25°C:

$$\boxed{K_w = [H^+][OH^-] = 1.0 \times 10^{-14}} \tag{15.3}$$

Whenever $[H^+] = [OH^-]$, the aqueous solution is said to be neutral. In an acidic solution there is an excess of H^+ ions and $[H^+] > [OH^-]$. In a basic solution there is an excess of hydroxide ions, so $[H^+] < [OH^-]$. In practice we can change the concentration of either H^+ or OH^- ions in solution, but we cannot vary both of them independently. If we adjust the solution so that $[H^+] = 1.0 \times 10^{-6}\ M$, the OH^- concentration *must* change to

$$[OH^-] = \frac{K_w}{[H^+]} = \frac{1.0 \times 10^{-14}}{1.0 \times 10^{-6}} = 1.0 \times 10^{-8}\,M$$

An application of Equation (15.3) is given in Example 15.2.

EXAMPLE 15.2

The concentration of OH^- ions in a certain household ammonia cleaning solution is $0.0025\ M$. Calculate the concentration of H^+ ions.

Strategy We are given the concentration of the OH^- ions and asked to calculate $[H^+]$. The relationship between $[H^+]$ and $[OH^-]$ in water or an aqueous solution is given by the ion-product of water, K_w [Equation (15.3)].

(Continued)

Solution Rearranging Equation (15.3), we write

$$[H^+] = \frac{K_w}{[OH^-]} = \frac{1.0 \times 10^{-14}}{0.0025} = 4.0 \times 10^{-12}\,M$$

Check Because $[H^+] < [OH^-]$, the solution is basic, as we would expect from the earlier discussion of the reaction of ammonia with water.

Practice Exercise Calculate the concentration of OH^- ions in a HCl solution whose hydrogen ion concentration is 1.3 *M*.

Similar problems: 15.15, 15.16.

15.3 pH—A Measure of Acidity

Because the concentrations of H^+ and OH^- ions in aqueous solutions are frequently very small numbers and therefore inconvenient to work with, Soren Sorensen[†] in 1909 proposed a more practical measure called pH. The ***pH*** of a solution is defined as *the negative logarithm of the hydrogen ion concentration (in mol/L):*

$$\text{pH} = -\log\,[H_3O^+] \quad \text{or} \quad \text{pH} = -\log\,[H^+] \tag{15.4}$$

Keep in mind that Equation (15.4) is simply a definition designed to give us convenient numbers to work with. The negative logarithm gives us a positive number for pH, which otherwise would be negative due to the small value of $[H^+]$. Furthermore, the term $[H^+]$ in Equation (15.4) pertains only to the *numerical part* of the expression for hydrogen ion concentration, for we cannot take the logarithm of units. Thus, like the equilibrium constant, the pH of a solution is a dimensionless quantity.

The pH of concentrated acid solutions can be negative. For example, the pH of a 2.0 *M* HCl solution is −0.30.

Because pH is simply a way to express hydrogen ion concentration, acidic and basic solutions at 25°C can be distinguished by their pH values, as follows:

Acidic solutions:	$[H^+] > 1.0 \times 10^{-7}\,M$, pH < 7.00
Basic solutions:	$[H^+] < 1.0 \times 10^{-7}\,M$, pH > 7.00
Neutral solutions:	$[H^+] = 1.0 \times 10^{-7}\,M$, pH $= 7.00$

Notice that pH increases as $[H^+]$ decreases.

Sometimes we may be given the pH value of a solution and asked to calculate the H^+ ion concentration. In that case, we need to take the antilog of Equation (15.4) as follows:

$$[H_3O^+] = 10^{-\text{pH}} \quad \text{or} \quad [H^+] = 10^{-\text{pH}} \tag{15.5}$$

Be aware that the definition of pH just shown, and indeed all the calculations involving solution concentrations (expressed either as molarity or molality) discussed in previous chapters, are subject to error because we have implicitly assumed ideal behavior. In reality, ion-pair formation and other types of intermolecular interactions may affect the actual concentrations of species in solution. The situation is analogous to the relationships between ideal gas behavior and the behavior of real gases discussed in Chapter 5. Depending on temperature, volume, and amount and type of gas present,

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[†] Soren Peer Lauritz Sorensen (1868–1939). Danish biochemist. Sorensen originally wrote the symbol as p_H and called p the "hydrogen ion exponent" (*Wasserstoffionexponent*); it is the initial letter of *Potenz* (German), *puissance* (French), and *power* (English). It is now customary to write the symbol as pH.

Figure 15.2 *A pH meter is commonly used in the laboratory to determine the pH of a solution. Although many pH meters have scales marked with values from 1 to 14, pH values can, in fact, be less than 1 and greater than 14.*

the measured gas pressure may differ from that calculated using the ideal gas equation. Similarly, the actual or "effective" concentration of a solute may not be what we think it is, knowing the amount of substance originally dissolved in solution. Just as we have the van der Waals and other equations to reconcile discrepancies between the ideal gas and nonideal gas behavior, we can account for nonideal behavior in solution.

One way is to replace the concentration term with *activity,* which is the effective concentration. Strictly speaking, then, the pH of solution should be defined as

$$\mathrm{pH} = -\log a_{\mathrm{H}^+} \tag{15.6}$$

where a_{H^+} is the activity of the H^+ ion. As mentioned in Chapter 14 (see p. 621), for an ideal solution activity is numerically equal to concentration. For real solutions, activity usually differs from concentration, sometimes appreciably. Knowing the solute concentration, there are reliable ways based on thermodynamics for estimating its activity, but the details are beyond the scope of this text. Keep in mind, therefore, that, except for dilute solutions, the measured pH is usually not the same as that calculated from Equation (15.4) because the concentration of the H^+ ion in molarity is not numerically equal to its activity value. Although we will continue to use concentration in our discussion, it is important to know that this approach will give us only an approximation of the chemical processes that actually take place in the solution phase.

In the laboratory, the pH of a solution is measured with a pH meter (Figure 15.2). Table 15.1 lists the pHs of a number of common fluids. As you can see, the pH of body fluids varies greatly, depending on location and function. The low pH (high acidity) of gastric juices facilitates digestion whereas a higher pH of blood is necessary for the transport of oxygen. These pH-dependent actions will be illustrated in Chemistry in Action essays in this chapter and Chapter 16.

A pOH scale analogous to the pH scale can be devised using the negative logarithm of the hydroxide ion concentration of a solution. Thus, we define pOH as

$$\mathrm{pOH} = -\log\,[\mathrm{OH}^-] \tag{15.7}$$

If we are given the pOH value of a solution and asked to calculate the OH^- ion concentration, we can take the antilog of Equation (15.7) as follows

$$[\mathrm{OH}^-] = 10^{-\mathrm{pOH}} \tag{15.8}$$

TABLE 15.1

The pHs of Some Common Fluids

Sample	pH Value
Gastric juice in the stomach	1.0–2.0
Lemon juice	2.4
Vinegar	3.0
Grapefruit juice	3.2
Orange juice	3.5
Urine	4.8–7.5
Water exposed to air*	5.5
Saliva	6.4–6.9
Milk	6.5
Pure water	7.0
Blood	7.35–7.45
Tears	7.4
Milk of magnesia	10.6
Household ammonia	11.5

*Water exposed to air for a long period of time absorbs atmospheric CO_2 to form carbonic acid, H_2CO_3.

Now consider again the ion-product constant for water at 25°C:

$$[\mathrm{H^+}][\mathrm{OH^-}] = K_\mathrm{w} = 1.0 \times 10^{-14}$$

Taking the negative logarithm of both sides, we obtain

$$-(\log\,[\mathrm{H^+}] + \log\,[\mathrm{OH^-}]) = -\log\,(1.0 \times 10^{-14})$$
$$-\log\,[\mathrm{H^+}] - \log\,[\mathrm{OH^-}] = 14.00$$

From the definitions of pH and pOH we obtain

$$\mathrm{pH} + \mathrm{pOH} = 14.00 \tag{15.9}$$

Equation (15.9) provides us with another way to express the relationship between the H^+ ion concentration and the OH^- ion concentration.

Examples 15.3, 15.4, and 15.5 illustrate calculations involving pH.

EXAMPLE 15.3

The concentration of H^+ ions in a bottle of table wine was 3.2×10^{-4} *M* right after the cork was removed. Only half of the wine was consumed. The other half, after it had been standing open to the air for a month, was found to have a hydrogen ion concentration equal to 1.0×10^{-3} *M*. Calculate the pH of the wine on these two occasions.

Strategy We are given the H^+ ion concentration and asked to calculate the pH of the solution. What is the definition of pH?

Solution According to Equation (15.4), $\mathrm{pH} = -\log\,[\mathrm{H^+}]$. When the bottle was first opened, $[\mathrm{H^+}] = 3.2 \times 10^{-4}$ *M*, which we substitute in Equation (15.4)

$$\begin{aligned}\mathrm{pH} &= -\log\,[\mathrm{H^+}]\\ &= -\log\,(3.2 \times 10^{-4}) = 3.49\end{aligned}$$

On the second occasion, $[\mathrm{H^+}] = 1.0 \times 10^{-3}$ *M*, so that

$$\mathrm{pH} = -\log\,(1.0 \times 10^{-3}) = 3.00$$

In each case, the pH has only two significant figures. The two digits to the right of the decimal in 3.49 tell us that there are two significant figures in the original number (see Appendix 4).

Comment The increase in hydrogen ion concentration (or decrease in pH) is largely the result of the conversion of some of the alcohol (ethanol) to acetic acid, a reaction that takes place in the presence of molecular oxygen.

Practice Exercise Nitric acid (HNO_3) is used in the production of fertilizer, dyes, drugs, and explosives. Calculate the pH of a HNO_3 solution having a hydrogen ion concentration of 0.76 *M*.

Similar problems: 15.17, 15.18.

EXAMPLE 15.4

The pH of rainwater collected in a certain region of the northeastern United States on a particular day was 4.82. Calculate the H^+ ion concentration of the rainwater.

Strategy Here we are given the pH of a solution and asked to calculate $[\mathrm{H^+}]$. Because pH is defined as $\mathrm{pH} = -\log\,[\mathrm{H^+}]$, we can solve for $[\mathrm{H^+}]$ by taking the antilog of the pH; that is, $[\mathrm{H^+}] = 10^{-\mathrm{pH}}$, as shown in Equation (15.5).

(Continued)

Solution From Equation (15.4)

$$\text{pH} = -\log [\text{H}^+] = 4.82$$

Therefore,

$$\log [\text{H}^+] = -4.82$$

Scientific calculators have an antilog function that is sometimes labeled INV log or 10^x.

To calculate $[\text{H}^+]$, we need to take the antilog of -4.82

$$[\text{H}^+] = 10^{-4.82} = 1.5 \times 10^{-5}\ M$$

Check Because the pH is between 4 and 5, we can expect $[\text{H}^+]$ to be between $1 \times 10^{-4}\ M$ and $1 \times 10^{-5}\ M$. Therefore, the answer is reasonable.

Practice Exercise The pH of a certain orange juice is 3.33. Calculate the H^+ ion concentration.

EXAMPLE 15.5

In a NaOH solution $[\text{OH}^-]$ is $2.9 \times 10^{-4}\ M$. Calculate the pH of the solution.

Strategy Solving this problem takes two steps. First, we need to calculate pOH using Equation (15.7). Next, we use Equation (15.9) to calculate the pH of the solution.

Solution We use Equation (15.7):

$$\begin{aligned}\text{pOH} &= -\log [\text{OH}^-]\\ &= -\log (2.9 \times 10^{-4})\\ &= 3.54\end{aligned}$$

Now we use Equation (15.9):

$$\begin{aligned}\text{pH} + \text{pOH} &= 14.00\\ \text{pH} &= 14.00 - \text{pOH}\\ &= 14.00 - 3.54 = 10.46\end{aligned}$$

Alternatively, we can use the ion-product constant of water, $K_w = [\text{H}^+][\text{OH}^-]$ to calculate $[\text{H}^+]$, and then we can calculate the pH from the $[\text{H}^+]$. Try it.

Check The answer shows that the solution is basic ($\text{pH} > 7$), which is consistent with a NaOH solution.

Practice Exercise The OH^- ion concentration of a blood sample is $2.5 \times 10^{-7}\ M$. What is the pH of the blood?

15.4 Strength of Acids and Bases

In reality, no acids are known to ionize completely in water.

Strong acids *are strong electrolytes that,* for practical purposes, *are assumed to ionize completely in water* (Figure 15.3). Most of the strong acids are inorganic acids: hydrochloric acid (HCl), nitric acid (HNO_3), perchloric acid (HClO_4), and sulfuric acid (H_2SO_4):

$$\begin{aligned}\text{HCl}(aq) + \text{H}_2\text{O}(l) &\longrightarrow \text{H}_3\text{O}^+(aq) + \text{Cl}^-(aq)\\ \text{HNO}_3(aq) + \text{H}_2\text{O}(l) &\longrightarrow \text{H}_3\text{O}^+(aq) + \text{NO}_3^-(aq)\\ \text{HClO}_4(aq) + \text{H}_2\text{O}(l) &\longrightarrow \text{H}_3\text{O}^+(aq) + \text{ClO}_4^-(aq)\\ \text{H}_2\text{SO}_4(aq) + \text{H}_2\text{O}(l) &\longrightarrow \text{H}_3\text{O}^+(aq) + \text{HSO}_4^-(aq)\end{aligned}$$

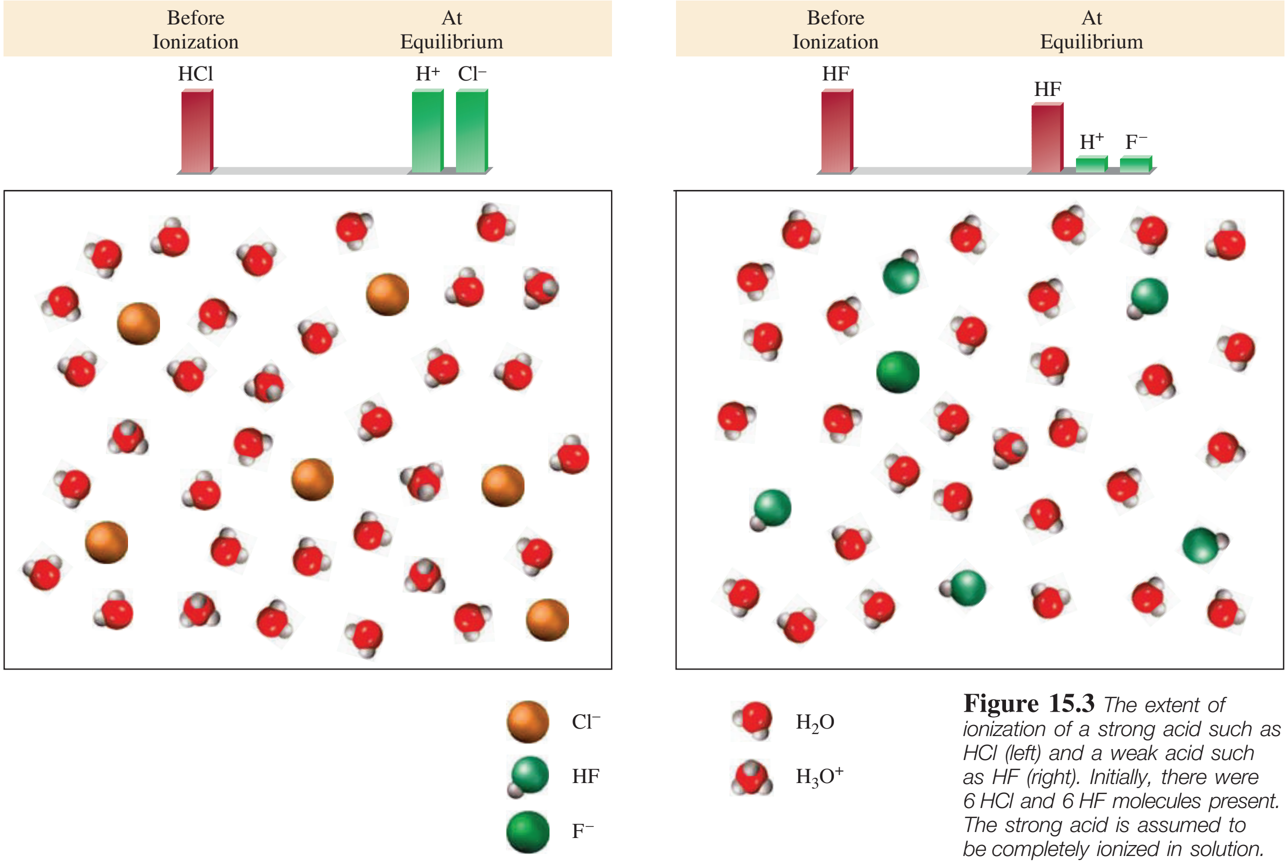


Figure 15.3 *The extent of ionization of a strong acid such as HCl (left) and a weak acid such as HF (right). Initially, there were 6 HCl and 6 HF molecules present. The strong acid is assumed to be completely ionized in solution. The proton exists in solution as the hydronium ion (H_3O^+).*

Note that H_2SO_4 is a diprotic acid; we show only the first stage of ionization here. At equilibrium, solutions of strong acids will not contain any nonionized acid molecules.

Most acids are ***weak acids,*** which *ionize only to a limited extent in water*. At equilibrium, aqueous solutions of weak acids contain a mixture of nonionized acid molecules, H_3O^+ ions, and the conjugate base. Examples of weak acids are hydrofluoric acid (HF), acetic acid (CH_3COOH), and the ammonium ion (NH_4^+). The limited ionization of weak acids is related to the equilibrium constant for ionization, which we will study in the next section.

Like strong acids, ***strong bases*** *are strong electrolytes that ionize completely in water.* Hydroxides of alkali metals and certain alkaline earth metals are strong bases. [All alkali metal hydroxides are soluble. Of the alkaline earth hydroxides, $Be(OH)_2$ and $Mg(OH)_2$ are insoluble; $Ca(OH)_2$ and $Sr(OH)_2$ are slightly soluble; and $Ba(OH)_2$ is soluble.] Some examples of strong bases are

$$\begin{aligned} NaOH(s) &\xrightarrow{H_2O} Na^+(aq) + OH^-(aq) \\ KOH(s) &\xrightarrow{H_2O} K^+(aq) + OH^-(aq) \\ Ba(OH)_2(s) &\xrightarrow{H_2O} Ba^{2+}(aq) + 2OH^-(aq) \end{aligned}$$

Strictly speaking, these metal hydroxides are not Brønsted bases because they cannot accept a proton. However, the hydroxide ion (OH^-) formed when they ionize *is* a Brønsted base because it can accept a proton:

$$H_3O^+(aq) + OH^-(aq) \longrightarrow 2H_2O(l)$$

Media Player
The Dissociation of Strong and Weak Acids

Zn reacts more vigorously with a strong acid like HCl (left) than with a weak acid like CH_3COOH (right) of the same concentration because there are more H^+ ions in the former solution.

TABLE 15.2 Relative Strengths of Conjugate Acid-Base Pairs

Acid strength increases ↑		Acid	Conjugate Base	Base strength increases ↓
	Strong acids	$HClO_4$ (perchloric acid)	ClO_4^- (perchlorate ion)	
		HI (hydroiodic acid)	I^- (iodide ion)	
		HBr (hydrobromic acid)	Br^- (bromide ion)	
		HCl (hydrochloric acid)	Cl^- (chloride ion)	
		H_2SO_4 (sulfuric acid)	HSO_4^- (hydrogen sulfate ion)	
		HNO_3 (nitric acid)	NO_3^- (nitrate ion)	
		H_3O^+ (hydronium ion)	H_2O (water)	
	Weak acids	HSO_4^- (hydrogen sulfate ion)	SO_4^{2-} (sulfate ion)	
		HF (hydrofluoric acid)	F^- (fluoride ion)	
		HNO_2 (nitrous acid)	NO_2^- (nitrite ion)	
		HCOOH (formic acid)	$HCOO^-$ (formate ion)	
		CH_3COOH (acetic acid)	CH_3COO^- (acetate ion)	
		NH_4^+ (ammonium ion)	NH_3 (ammonia)	
		HCN (hydrocyanic acid)	CN^- (cyanide ion)	
		H_2O (water)	OH^- (hydroxide ion)	
		NH_3 (ammonia)	NH_2^- (amide ion)	

Thus, when we call NaOH or any other metal hydroxide a base, we are actually referring to the OH^- species derived from the hydroxide.

Weak bases, like weak acids, *are weak electrolytes.* Ammonia is a weak base. It ionizes to a very limited extent in water:

$$NH_3(aq) + H_2O(l) \rightleftharpoons NH_4^+(aq) + OH^-(aq)$$

Note that, unlike acids, NH_3 does not donate a proton to water. Rather, NH_3 behaves as a base by accepting a proton from water to form NH_4^+ and OH^- ions.

Table 15.2 lists some important conjugate acid-base pairs, in order of their relative strengths. Conjugate acid-base pairs have the following properties:

1. If an acid is strong, its conjugate base has no measurable strength. Thus, the Cl^- ion, which is the conjugate base of the strong acid HCl, is an extremely weak base.
2. H_3O^+ is the strongest acid that can exist in aqueous solution. Acids stronger than H_3O^+ react with water to produce H_3O^+ and their conjugate bases. Thus, HCl, which is a stronger acid than H_3O^+, reacts with water completely to form H_3O^+ and Cl^-:

   $$HCl(aq) + H_2O(l) \longrightarrow H_3O^+(aq) + Cl^-(aq)$$

   Acids weaker than H_3O^+ react with water to a much smaller extent, producing H_3O^+ and their conjugate bases. For example, the following equilibrium lies primarily to the left:

   $$HF(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + F^-(aq)$$

3. The OH^- ion is the strongest base that can exist in aqueous solution. Bases stronger than OH^- react with water to produce OH^- and their conjugate acids.

For example, the oxide ion (O^{2-}) is a stronger base than OH^-, so it reacts with water completely as follows:

$$O^{2-}(aq) + H_2O(l) \longrightarrow 2OH^-(aq)$$

For this reason the oxide ion does not exist in aqueous solutions.

Example 15.6 shows calculations of pH for a solution containing a strong acid and a solution of a strong base.

EXAMPLE 15.6

Calculate the pH of (a) a 1.0×10^{-3} M HCl solution and (b) a 0.020 M $Ba(OH)_2$ solution.

Strategy Keep in mind that HCl is a strong acid and $Ba(OH)_2$ is a strong base. Thus, these species are completely ionized and no HCl or $Ba(OH)_2$ will be left in solution.

Solution (a) The ionization of HCl is

$$HCl(aq) \longrightarrow H^+(aq) + Cl^-(aq)$$

Recall that $H^+(aq)$ is the same as $H_3O^+(aq)$.

The concentrations of all the species (HCl, H^+, and Cl^-) before and after ionization can be represented as follows:

We use the ICE method for solving equilibrium concentrations as shown in Section 14.4 (p. 634).

	$HCl(aq)$	$\longrightarrow$	$H^+(aq)$	+	$Cl^-(aq)$
Initial (M):	1.0×10^{-3}		0.0		0.0
Change (M):	-1.0×10^{-3}		$+1.0 \times 10^{-3}$		$+1.0 \times 10^{-3}$
Final (M):	0.0		1.0×10^{-3}		1.0×10^{-3}

A positive (+) change represents an increase and a negative (−) change indicates a decrease in concentration. Thus,

$$\begin{aligned}[H^+] &= 1.0 \times 10^{-3}\,M \\ pH &= -\log(1.0 \times 10^{-3}) \\ &= 3.00\end{aligned}$$

(b) $Ba(OH)_2$ is a strong base; each $Ba(OH)_2$ unit produces two OH^- ions:

$$Ba(OH)_2(aq) \longrightarrow Ba^{2+}(aq) + 2OH^-(aq)$$

The changes in the concentrations of all the species can be represented as follows:

	$Ba(OH)_2(aq)$	$\longrightarrow$	$Ba^{2+}(aq)$	+	$2OH^-(aq)$
Initial (M):	0.020		0.00		0.00
Change (M):	−0.020		+0.020		+2(0.020)
Final (M):	0.00		0.020		0.040

Thus,

$$\begin{aligned}[OH^-] &= 0.040\,M \\ pOH &= -\log 0.040 = 1.40\end{aligned}$$

Therefore, from Equation (15.8),

$$\begin{aligned}pH &= 14.00 - pOH \\ &= 14.00 - 1.40 \\ &= 12.60\end{aligned}$$

(Continued)

Check Note that in both (a) and (b) we have neglected the contribution of the autoionization of water to $[H^+]$ and $[OH^-]$ because 1.0×10^{-7} *M* is so small compared with 1.0×10^{-3} *M* and 0.040 *M*.

Practice Exercise Calculate the pH of a 1.8×10^{-2} *M* $Ba(OH)_2$ solution.

If we know the relative strengths of two acids, we can predict the position of equilibrium between one of the acids and the conjugate base of the other, as illustrated in Example 15.7.

EXAMPLE 15.7

Predict the direction of the following reaction in aqueous solution:

$$HNO_2(aq) + CN^-(aq) \rightleftharpoons HCN(aq) + NO_2^-(aq)$$

Strategy The problem is to determine whether, at equilibrium, the reaction will be shifted to the right, favoring HCN and NO_2^-, or to the left, favoring HNO_2 and CN^-. Which of the two is a stronger acid and hence a stronger proton donor: HNO_2 or HCN? Which of the two is a stronger base and hence a stronger proton acceptor: CN^- or NO_2^-? Remember that the stronger the acid, the weaker its conjugate base.

Solution In Table 15.2 we see that HNO_2 is a stronger acid than HCN. Thus, CN^- is a stronger base than NO_2^-. The net reaction will proceed from left to right as written because HNO_2 is a better proton donor than HCN (and CN^- is a better proton acceptor than NO_2^-).

Practice Exercise Predict whether the equilibrium constant for the following reaction is greater than or smaller than 1:

$$CH_3COOH(aq) + HCOO^-(aq) \rightleftharpoons CH_3COO^-(aq) + HCOOH(aq)$$

15.5 Weak Acids and Acid Ionization Constants

As we have seen, there are relatively few strong acids. The vast majority of acids are weak acids. Consider a weak monoprotic acid, HA. Its ionization in water is represented by

$$HA(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + A^-(aq)$$

or simply

$$HA(aq) \rightleftharpoons H^+(aq) + A^-(aq)$$

The equilibrium expression for this ionization is

$$K_a = \frac{[H_3O^+][A^-]}{[HA]} \quad \text{or} \quad K_a = \frac{[H^+][A^-]}{[HA]} \qquad (15.10)$$

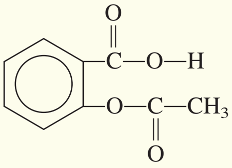
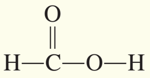
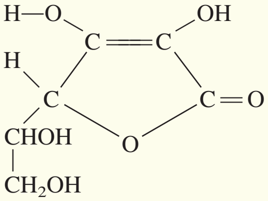
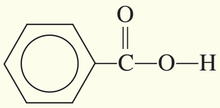
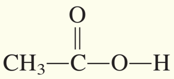
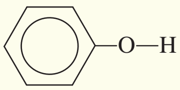
All concentrations in this equation are equilibrium concentrations.

where K_a, the ***acid ionization constant,*** is the *equilibrium constant for the ionization of an acid*. At a given temperature, the strength of the acid HA is measured quantitatively by the magnitude of K_a. The larger K_a, the stronger the acid—that is, the greater the concentration of H^+ ions at equilibrium due to its ionization. Keep in mind, however, that only weak acids have K_a values associated with them.

Table 15.3 lists a number of weak acids and their K_a values at 25°C in order of decreasing acid strength. Although all these acids are weak, within the group there is great variation in their strengths. For example, K_a for HF (7.1×10^{-4}) is about 1.5 million times that for HCN (4.9×10^{-10}).

Generally, we can calculate the hydrogen ion concentration or pH of an acid solution at equilibrium, given the initial concentration of the acid and its K_a value.

TABLE 15.3 Ionization Constants of Some Weak Acids and Their Conjugate Bases at 25°C

Name of Acid	Formula	Structure	K_a	Conjugate Base	K_b†
Hydrofluoric acid	HF	H—F	7.1×10^{-4}	F^-	1.4×10^{-11}
Nitrous acid	HNO_2	O═N—O—H	4.5×10^{-4}	NO_2^-	2.2×10^{-11}
Acetylsalicylic acid (aspirin)	$C_9H_8O_4$		3.0×10^{-4}	$C_9H_7O_4^-$	3.3×10^{-11}
Formic acid	HCOOH	 $H-\overset{\overset{\large O}{\|}}{C}-O-H$	1.7×10^{-4}	$HCOO^-$	5.9×10^{-11}
Ascorbic acid*	$C_6H_8O_6$		8.0×10^{-5}	$C_6H_7O_6^-$	1.3×10^{-10}
Benzoic acid	C_6H_5COOH		6.5×10^{-5}	$C_6H_5COO^-$	1.5×10^{-10}
Acetic acid	CH_3COOH	 $CH_3-\overset{\overset{\large O}{\|}}{C}-O-H$	1.8×10^{-5}	CH_3COO^-	5.6×10^{-10}
Hydrocyanic acid	HCN	H—C≡N	4.9×10^{-10}	CN^-	2.0×10^{-5}
Phenol	C_6H_5OH		1.3×10^{-10}	$C_6H_5O^-$	7.7×10^{-5}

*For ascorbic acid it is the upper left hydroxyl group that is associated with this ionization constant.

†The base ionization constant K_b is discussed in Section 15.6.

Alternatively, if we know the pH of a weak acid solution and its initial concentration, we can determine its K_a. The basic approach for solving these problems, which deal with equilibrium concentrations, is the same one outlined in Chapter 14. However, because acid ionization represents a major category of chemical equilibrium in aqueous solution, we will develop a systematic procedure for solving this type of problem that will also help us to understand the chemistry involved.

Suppose we are asked to calculate the pH of a 0.50 *M* HF solution at 25°C. The ionization of HF is given by

$$\mathrm{HF}(aq) \rightleftharpoons \mathrm{H}^+(aq) + \mathrm{F}^-(aq)$$

From Table 15.3 we write

$$K_a = \frac{[\mathrm{H}^+][\mathrm{F}^-]}{[\mathrm{HF}]} = 7.1 \times 10^{-4}$$

The first step is to identify all the species present in solution that may affect its pH. Because weak acids ionize to a small extent, at equilibrium the major species present are nonionized HF and some H^+ and F^- ions. Another major species is H_2O, but its very small K_w (1.0×10^{-14}) means that water is not a significant contributor to the H^+ ion concentration. Therefore, unless otherwise stated, we will always ignore the H^+ ions produced by the autoionization of water. Note that we need not be concerned with the OH^- ions that are also present in solution. The OH^- concentration can be determined from Equation (15.3) after we have calculated $[H^+]$.

We can summarize the changes in the concentrations of HF, H^+, and F^- according to the steps shown on p. 635 as follows:

$$\begin{array}{lcccc}
 & \mathrm{HF}(aq) & \rightleftharpoons & \mathrm{H}^+(aq) & + \ \mathrm{F}^-(aq) \\
\text{Initial } (M): & 0.50 & & 0.00 & 0.00 \\
\text{Change } (M): & -x & & +x & +x \\
\hline
\text{Equilibrium } (M): & 0.50 - x & & x & x
\end{array}$$

The equilibrium concentrations of HF, H^+, and F^-, expressed in terms of the unknown *x*, are substituted into the ionization constant expression to give

$$K_a = \frac{(x)(x)}{0.50 - x} = 7.1 \times 10^{-4}$$

Rearranging this expression, we write

$$x^2 + 7.1 \times 10^{-4}x - 3.6 \times 10^{-4} = 0$$

This is a quadratic equation which can be solved using the quadratic formula (see Appendix 4). Or we can try using a shortcut to solve for *x*. Because HF is a weak acid and weak acids ionize only to a slight extent, we reason that *x* must be small compared to 0.50. Therefore, we can make the approximation

$$0.50 - x \approx 0.50$$

The sign ≈ means "approximately equal to." An analogy of the approximation is a truck loaded with coal. Losing a few lumps of coal on a delivery trip will not appreciably change the overall mass of the load.

Now the ionization constant expression becomes

$$\frac{x^2}{0.50 - x} \approx \frac{x^2}{0.50} = 7.1 \times 10^{-4}$$

Rearranging, we get

$$x^2 = (0.50)(7.1 \times 10^{-4}) = 3.55 \times 10^{-4}$$
$$x = \sqrt{3.55 \times 10^{-4}} = 0.019\ M$$

Thus, we have solved for x without having to use the quadratic equation. At equilibrium, we have

$$[\text{HF}] = (0.50 - 0.019)\ M = 0.48\ M$$
$$[\text{H}^+] = 0.019\ M$$
$$[\text{F}^-] = 0.019\ M$$

and the pH of the solution is

$$\text{pH} = -\log(0.019) = 1.72$$

How good is this approximation? Because K_a values for weak acids are generally known to an accuracy of only ±5%, it is reasonable to require x to be less than 5% of 0.50, the number from which it is subtracted. In other words, the approximation is valid if the following expression is equal to or less than 5%:

$$\frac{0.019\ M}{0.50\ M} \times 100\% = 3.8\%$$

Thus, the approximation we made is acceptable.

Now consider a different situation. If the initial concentration of HF is 0.050 M, and we use the above procedure to solve for x, we would get $6.0 \times 10^{-3}\ M$. However, the following test shows that this answer is not a valid approximation because it is greater than 5% of 0.050 M:

$$\frac{6.0 \times 10^{-3}\ M}{0.050\ M} \times 100\% = 12\%$$

In this case, we can get an accurate value for x by solving the quadratic equation.

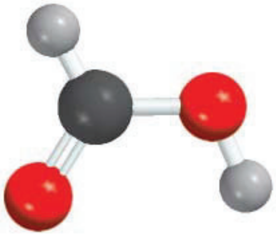
The Quadratic Equation... No AP question will require the quadratic equation.

$$x^2$$

In summary, the main steps for solving weak acid ionization problems are:

1. Identify the major species that can affect the pH of the solution. In most cases we can ignore the ionization of water. We omit the hydroxide ion because its concentration is determined by that of the H^+ ion.
2. Express the equilibrium concentrations of these species in terms of the initial concentration of the acid and a single unknown x, which represents the change in concentration.
3. Write the weak acid ionization and express the ionization constant K_a in terms of the equilibrium concentrations of H^+, the conjugate base, and the unionized acid. First solve for x by the approximate method. If the approximate method is not valid, use the quadratic equation to solve for x. **No AP Question will require the Quadratic Equation.**
4. Having solved for x, calculate the equilibrium concentrations of all species and/or the pH of the solution.

One way to determine K_a of an acid is to measure the pH of the acid solution of known concentration at equilibrium. Example 15.9 shows this approach.

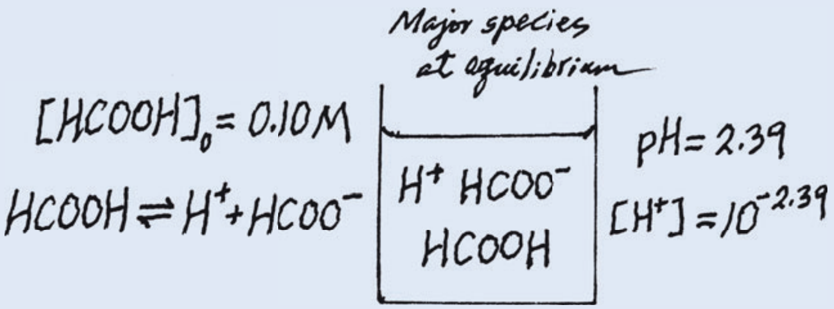


HCOOH

EXAMPLE 15.9

The pH of a 0.10 *M* solution of formic acid (HCOOH) is 2.39. What is the K_a of the acid?

Strategy Formic acid is a weak acid. It only partially ionizes in water. Note that the concentration of formic acid refers to the initial concentration, before ionization has started. The pH of the solution, on the other hand, refers to the equilibrium state. To calculate K_a, then, we need to know the concentrations of all three species: $[H^+]$, $[HCOO^-]$, and [HCOOH] at equilibrium. As usual, we ignore the ionization of water. The following sketch summarizes the situation.



Solution We proceed as follows.

Step 1: The major species in solution are HCOOH, H^+, and the conjugate base $HCOO^-$.

Step 2: First we need to calculate the hydrogen ion concentration from the pH value

$$\begin{aligned} \text{pH} &= -\log [H^+] \\ 2.39 &= -\log [H^+] \end{aligned}$$

Taking the antilog of both sides, we get

$$[H^+] = 10^{-2.39} = 4.1 \times 10^{-3}\ M$$

Next we summarize the changes:

	$HCOOH(aq)$	$\rightleftharpoons$	$H^+(aq)$	+	$HCOO^-(aq)$
Initial (*M*):	0.10		0.00		0.00
Change (*M*):	-4.1×10^{-3}		$+4.1 \times 10^{-3}$		$+4.1 \times 10^{-3}$
Equilibrium (*M*):	$(0.10 - 4.1 \times 10^{-3})$		4.1×10^{-3}		4.1×10^{-3}

Note that because the pH and hence the H^+ ion concentration is known, it follows that we also know the concentrations of HCOOH and $HCOO^-$ at equilibrium.

Step 3: The ionization constant of formic acid is given by

$$\begin{aligned} K_a &= \frac{[H^+][HCOO^-]}{[HCOOH]} \\ &= \frac{(4.1 \times 10^{-3})(4.1 \times 10^{-3})}{(0.10 - 4.1 \times 10^{-3})} \\ &= 1.8 \times 10^{-4} \end{aligned}$$

(Continued)

Check The K_a value differs slightly from the one listed in Table 15.3 because of the rounding-off procedure we used in the calculation.

Practice Exercise The pH of a 0.060 *M* weak monoprotic acid is 3.44. Calculate the K_a of the acid.

Percent Ionization

We have seen that the magnitude of K_a indicates the strength of an acid. Another measure of the strength of an acid is its ***percent ionization,*** which is defined as

$$\text{percent ionization} = \frac{\text{ionized acid concentration at equilibrium}}{\text{initial concentration of acid}} \times 100\% \qquad (15.11)$$

We can compare the strengths of acids in terms of percent ionization only if concentrations of the acids are the same.

The stronger the acid, the greater the percent ionization. For a monoprotic acid HA, the concentration of the acid that undergoes ionization is equal to the concentration of the H^+ ions or the concentration of the A^- ions at equilibrium. Therefore, we can write the percent ionization as

$$\text{percent ionization} = \frac{[H^+]}{[HA]_0} \times 100\%$$

where $[H^+]$ is the concentration at equilibrium and $[HA]_0$ is the initial concentration.

Referring to Example 15.8, we see that the percent ionization of a 0.036 *M* HNO_2 solution is

$$\text{percent ionization} = \frac{3.8 \times 10^{-3}\,M}{0.036\,M} \times 100\% = 11\%$$

Thus, only about one out of every 9 HNO_2 molecules has ionized. This is consistent with the fact that HNO_2 is a weak acid.

The extent to which a weak acid ionizes depends on the initial concentration of the acid. The more dilute the solution, the greater the percentage ionization (Figure 15.4). In qualitative terms, when an acid is diluted, the concentration of the "particles" in the solution is reduced. According to Le Châtelier's principle (see Section 14.5), this reduction in particle concentration (the stress) is counteracted by shifting the reaction to the side with more particles; that is, the equilibrium shifts from the nonionized acid side (one particle) to the side containing H^+ ions and the conjugate base (two particles): $HA \rightleftharpoons H^+ + A^-$. Consequently, the concentration of "particles" increases in the solution.

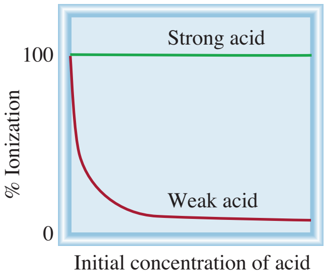


Figure 15.4 *Dependence of percent ionization on initial concentration of acid. Note that at very low concentrations, all acids (weak and strong) are almost completely ionized.*

The dependence of percent ionization on initial concentration can be illustrated by the HF case discussed on page 672:

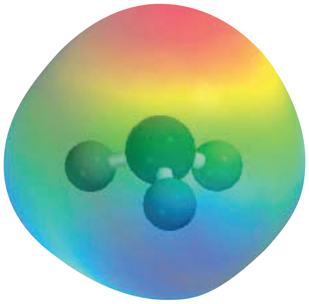
0.50 *M* HF

$$\text{percent ionization} = \frac{0.019\,M}{0.50\,M} \times 100\% = 3.8\%$$

0.050 *M* HF

$$\text{percent ionization} = \frac{5.6 \times 10^{-3}\,M}{0.050\,M} \times 100\% = 11\%$$

We see that, as expected, a more dilute HF solution has a greater percent ionization of the acid.



The lone pair (red color) on the N atom accounts for ammonia's basicity.

Animation
Base Ionization

15.6 Weak Bases and Base Ionization Constants

The ionization of weak bases is treated in the same way as the ionization of weak acids. When ammonia dissolves in water, it undergoes the reaction

$$NH_3(aq) + H_2O(l) \rightleftharpoons NH_4^+(aq) + OH^-(aq)$$

The equilibrium constant is given by

$$K = \frac{[NH_4^+][OH^-]}{[NH_3][H_2O]}$$

Compared with the total concentration of water, very few water molecules are consumed by this reaction, so we can treat $[H_2O]$ as a constant. Thus, we can write the ***base ionization constant (K_b),*** which is *the equilibrium constant for the ionization reaction,* as

$$\begin{aligned} K_b = K[H_2O] &= \frac{[NH_4^+][OH^-]}{[NH_3]} \\ &= 1.8 \times 10^{-5} \end{aligned}$$

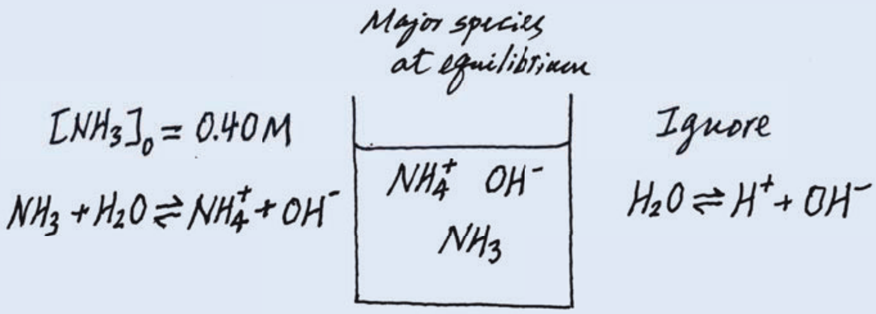
Table 15.4 lists a number of common weak bases and their ionization constants. Note that the basicity of all these compounds is attributable to the lone pair of electrons on the nitrogen atom. The ability of the lone pair to accept a H^+ ion makes these substances Brønsted bases.

In solving problems involving weak bases, we follow the same procedure we used for weak acids. The main difference is that we calculate $[OH^-]$ first, rather than $[H^+]$. Example 15.10 shows this approach.

EXAMPLE 15.10

What is the pH of a 0.40 *M* ammonia solution?

Strategy The procedure here is similar to the one used for a weak acid (see Example 15.8). From the ionization of ammonia, we see that the major species in solution at equilibrium are NH_3, NH_4^+, and OH^-. The hydrogen ion concentration is very small as we would expect from a basic solution, so it is present as a minor species. As before, we ignore the ionization of water. We make a sketch to keep track of the pertinent species as follows:

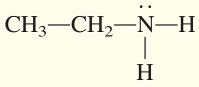
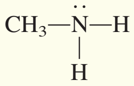
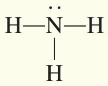
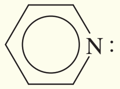
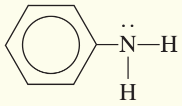
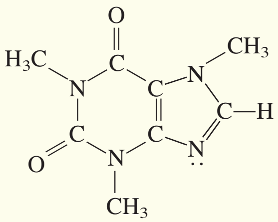
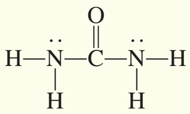


Solution We proceed according to the following steps.

Step 1: The major species in an ammonia solution are NH_3, NH_4^+, and OH^-. We ignore the very small contribution to OH^- concentration by water.

(Continued)

TABLE 15.4 Ionization Constants of Some Weak Bases and Their Conjugate Acids at 25°C

Name of Base	Formula	Structure	K_b*	Conjugate Acid	K_a
Ethylamine	$C_2H_5NH_2$	 $CH_3{-}CH_2{-}\underset{\underset{H}{\vert}}{\overset{\cdot\cdot}{N}}{-}H$	5.6×10^{-4}	$C_2H_5\overset{+}{N}H_3$	1.8×10^{-11}
Methylamine	CH_3NH_2	 $CH_3{-}\underset{\underset{H}{\vert}}{\overset{\cdot\cdot}{N}}{-}H$	4.4×10^{-4}	$CH_3\overset{+}{N}H_3$	2.3×10^{-11}
Ammonia	NH_3	 $H{-}\underset{\underset{H}{\vert}}{\overset{\cdot\cdot}{N}}{-}H$	1.8×10^{-5}	NH_4^+	5.6×10^{-10}
Pyridine	C_5H_5N		1.7×10^{-9}	$C_5H_5\overset{+}{N}H$	5.9×10^{-6}
Aniline	$C_6H_5NH_2$		3.8×10^{-10}	$C_6H_5\overset{+}{N}H_3$	2.6×10^{-5}
Caffeine	$C_8H_{10}N_4O_2$		5.3×10^{-14}	$C_8H_{11}\overset{+}{N}_4O_2$	0.19
Urea	$(NH_2)_2CO$	 $H{-}\underset{\underset{H}{\vert}}{\overset{\cdot\cdot}{N}}{-}\overset{\overset{O}{\Vert}}{C}{-}\underset{\underset{H}{\vert}}{\overset{\cdot\cdot}{N}}{-}H$	1.5×10^{-14}	$H_2NCO\overset{+}{N}H_3$	0.67

*The nitrogen atom with the lone pair accounts for each compound's basicity. In the case of urea, K_b can be associated with either nitrogen atom.

Step 2: Letting x be the equilibrium concentration of NH_4^+ and OH^- ions in mol/L, we summarize:

	$NH_3(aq) + H_2O(l) \rightleftharpoons$	$NH_4^+(aq)$ +	$OH^-(aq)$
Initial (M):	0.40	0.00	0.00
Change (M):	$-x$	$+x$	$+x$
Equilibrium (M):	$0.40 - x$	x	x

Step 3: Table 15.4 gives us K_b:

$$K_b = \frac{[NH_4^+][OH^-]}{[NH_3]}$$

$$1.8 \times 10^{-5} = \frac{x^2}{0.40 - x}$$

(Continued)

Applying the approximation $0.40 - x \approx 0.40$, we obtain

$$
\begin{aligned}
1.8 \times 10^{-5} &= \frac{x^2}{0.40 - x} \approx \frac{x^2}{0.40} \\
x^2 &= 7.2 \times 10^{-6} \\
x &= 2.7 \times 10^{-3}\,M
\end{aligned}
$$

To test the approximation, we write

$$\frac{2.7 \times 10^{-3}\,M}{0.40\,M} \times 100\% = 0.68\%$$

The 5 percent rule (p. 673) also applies to bases.

Therefore, the approximation is valid.

Step 4: At equilibrium, $[\text{OH}^-] = 2.7 \times 10^{-3}\,M$. Thus,

$$
\begin{aligned}
\text{pOH} &= -\log(2.7 \times 10^{-3}) \\
&= 2.57 \\
\text{pH} &= 14.00 - 2.57 \\
&= 11.43
\end{aligned}
$$

Check Note that the pH calculated is basic, which is what we would expect from a weak base solution. Compare the calculated pH with that of a 0.40 *M* strong base solution, such as KOH, to convince yourself of the difference between a strong base and a weak base.

Practice Exercise Calculate the pH of a 0.26 *M* methylamine solution (see Table 15.4).

15.7 The Relationship Between the Ionization Constants of Acids and Their Conjugate Bases

An important relationship between the acid ionization constant and the ionization constant of its conjugate base can be derived as follows, using acetic acid as an example:

$$\text{CH}_3\text{COOH}(aq) \rightleftharpoons \text{H}^+(aq) + \text{CH}_3\text{COO}^-(aq)$$

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

The conjugate base, CH_3COO^-, supplied by a sodium acetate (CH_3COONa) solution, reacts with water according to the equation

$$\text{CH}_3\text{COO}^-(aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{CH}_3\text{COOH}(aq) + \text{OH}^-(aq)$$

and we can write the base ionization constant as

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

The product of these two ionization constants is given by

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

This result may seem strange at first, but if we add the two equations we see that the sum is simply the autoionization of water.

$$\begin{array}{llcll}
(1) & CH_3COOH(aq) & \rightleftharpoons & H^+(aq) + CH_3COO^-(aq) & K_a \\
(2) & CH_3COO^-(aq) + H_2O(l) & \rightleftharpoons & CH_3COOH(aq) + OH^-(aq) & K_b \\
\hline
(3) & H_2O(l) & \rightleftharpoons & H^+(aq) + OH^-(aq) & K_w
\end{array}$$

This example illustrates one of the rules for chemical equilibria: When two reactions are added to give a third reaction, the equilibrium constant for the third reaction is the product of the equilibrium constants for the two added reactions (see Section 14.2). Thus, for any conjugate acid-base pair it is always true that

$$\boxed{K_aK_b = K_w} \tag{15.12}$$

Expressing Equation (15.12) as

$$K_a = \frac{K_w}{K_b} \qquad K_b = \frac{K_w}{K_a}$$

enables us to draw an important conclusion: The stronger the acid (the larger K_a), the weaker its conjugate base (the smaller K_b), and vice versa (see Tables 15.3 and 15.4).

We can use Equation (15.12) to calculate the K_b of the conjugate base (CH_3COO^-) of CH_3COOH as follows. We find the K_a value of CH_3COOH in Table 15.3 and write

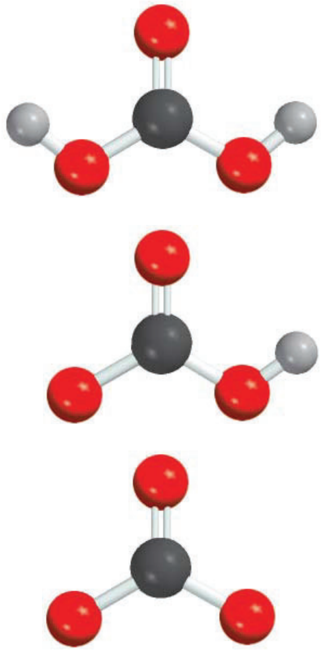
$$\begin{aligned}
K_b &= \frac{K_w}{K_a} \\
&= \frac{1.0 \times 10^{-14}}{1.8 \times 10^{-5}} \\
&= 5.6 \times 10^{-10}
\end{aligned}$$

15.8 Diprotic and Polyprotic Acids

The treatment of diprotic and polyprotic acids is more involved than that of monoprotic acids because these substances may yield more than one hydrogen ion per molecule. These acids ionize in a stepwise manner; that is, they lose one proton at a time. An ionization constant expression can be written for each ionization stage. Consequently, two or more equilibrium constant expressions must often be used to calculate the concentrations of species in the acid solution. For example, for carbonic acid, H_2CO_3, we write

$$H_2CO_3(aq) \rightleftharpoons H^+(aq) + HCO_3^-(aq) \qquad K_{a_1} = \frac{[H^+][HCO_3^-]}{[H_2CO_3]}$$

$$HCO_3^-(aq) \rightleftharpoons H^+(aq) + CO_3^{2-}(aq) \qquad K_{a_2} = \frac{[H^+][CO_3^{2-}]}{[HCO_3^-]}$$



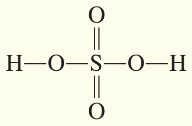
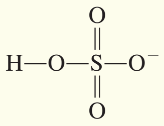
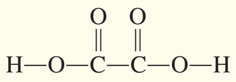
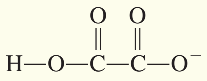
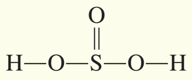
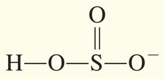
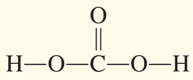
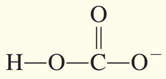
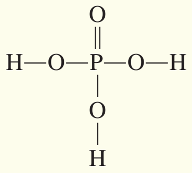
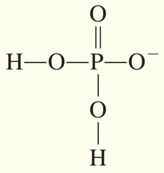
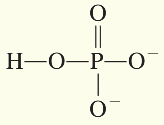
Top to bottom: H_2CO_3, HCO_3^-, and CO_3^{2-}.

Note that the conjugate base in the first ionization stage becomes the acid in the second ionization stage.

Table 15.5 on p. 683 shows the ionization constants of several diprotic acids and one polyprotic acid. For a given acid, the first ionization constant is much larger than the second ionization constant, and so on. This trend is reasonable because it is easier to remove a H^+ ion from a neutral molecule than to remove another H^+ ion from a negatively charged ion derived from the molecule.

In Example 15.11 we calculate the equilibrium concentrations of all the species of a diprotic acid in aqueous solution.

TABLE 15.5 Ionization Constants of Some Diprotic Acids and a Polyprotic Acid and Their Conjugate Bases at 25°C

Name of Acid	Formula	Structure	K_a	Conjugate Base	K_b
Sulfuric acid	H_2SO_4	 $\mathrm{H{-}O{-}\overset{\begin{array}{c}O\\\Vert\end{array}}{\underset{\begin{array}{c}\Vert\\O\end{array}}{S}}{-}O{-}H}$	very large	HSO_4^-	very small
Hydrogen sulfate ion	HSO_4^-	 $\mathrm{H{-}O{-}\overset{\begin{array}{c}O\\\Vert\end{array}}{\underset{\begin{array}{c}\Vert\\O\end{array}}{S}}{-}O^-}$	1.3×10^{-2}	SO_4^{2-}	7.7×10^{-13}
Oxalic acid	$H_2C_2O_4$	 $\mathrm{H{-}O{-}\overset{\begin{array}{c}O\\\Vert\end{array}}{C}{-}\overset{\begin{array}{c}O\\\Vert\end{array}}{C}{-}O{-}H}$	6.5×10^{-2}	$HC_2O_4^-$	1.5×10^{-13}
Hydrogen oxalate ion	$HC_2O_4^-$	 $\mathrm{H{-}O{-}\overset{\begin{array}{c}O\\\Vert\end{array}}{C}{-}\overset{\begin{array}{c}O\\\Vert\end{array}}{C}{-}O^-}$	6.1×10^{-5}	$C_2O_4^{2-}$	1.6×10^{-10}
Sulfurous acid*	H_2SO_3	 $\mathrm{H{-}O{-}\overset{\begin{array}{c}O\\\Vert\end{array}}{S}{-}O{-}H}$	1.3×10^{-2}	HSO_3^-	7.7×10^{-13}
Hydrogen sulfite ion	HSO_3^-	 $\mathrm{H{-}O{-}\overset{\begin{array}{c}O\\\Vert\end{array}}{S}{-}O^-}$	6.3×10^{-8}	SO_3^{2-}	1.6×10^{-7}
Carbonic acid	H_2CO_3	 $\mathrm{H{-}O{-}\overset{\begin{array}{c}O\\\Vert\end{array}}{C}{-}O{-}H}$	4.2×10^{-7}	HCO_3^-	2.4×10^{-8}
Hydrogen carbonate ion	HCO_3^-	 $\mathrm{H{-}O{-}\overset{\begin{array}{c}O\\\Vert\end{array}}{C}{-}O^-}$	4.8×10^{-11}	CO_3^{2-}	2.1×10^{-4}
Hydrosulfuric acid	H_2S	$\mathrm{H{-}S{-}H}$	9.5×10^{-8}	HS^-	1.1×10^{-7}
Hydrogen sulfide ion[†]	HS^-	$\mathrm{H{-}S^-}$	1×10^{-19}	S^{2-}	1×10^5
Phosphoric acid	H_3PO_4	 $\mathrm{H{-}O{-}\overset{\begin{array}{c}O\\\Vert\end{array}}{\underset{\begin{array}{c}\vert\\O\\\vert\\H\end{array}}{P}}{-}O{-}H}$	7.5×10^{-3}	$H_2PO_4^-$	1.3×10^{-12}
Dihydrogen phosphate ion	$H_2PO_4^-$	 $\mathrm{H{-}O{-}\overset{\begin{array}{c}O\\\Vert\end{array}}{\underset{\begin{array}{c}\vert\\O\\\vert\\H\end{array}}{P}}{-}O^-}$	6.2×10^{-8}	HPO_4^{2-}	1.6×10^{-7}
Hydrogen phosphate ion	HPO_4^{2-}	 $\mathrm{H{-}O{-}\overset{\begin{array}{c}O\\\Vert\end{array}}{\underset{\begin{array}{c}\vert\\O^-\end{array}}{P}}{-}O^-}$	4.8×10^{-13}	PO_4^{3-}	2.1×10^{-2}

---

*H_2SO_3 has never been isolated and exists in only minute concentration in aqueous solution of SO_2. The K_a value here refers to the process $SO_2(g) + H_2O(l) \rightleftharpoons H^+(aq) + HSO_3^-(aq)$.

[†] The ionization constant of HS^- is very low and difficult to measure. The value listed here is only an estimate.

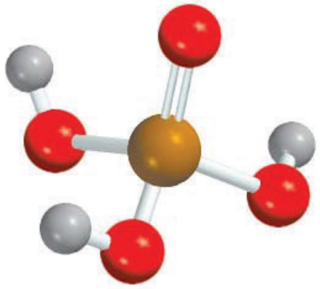
For diprotic acids, if $K_{a_1} \gg K_{a_2}$, then we can assume that the concentration of H^+ ions is the product of only the first stage of ionization. Furthermore, the concentration of the conjugate base for the second-stage ionization is *numerically* equal to K_{a_2}.

Phosphoric acid (H_3PO_4) is a polyprotic acid with three ionizable hydrogen atoms:

$$H_3PO_4(aq) \rightleftharpoons H^+(aq) + H_2PO_4^-(aq) \qquad K_{a_1} = \frac{[H^+][H_2PO_4^-]}{[H_3PO_4]} = 7.5 \times 10^{-3}$$

$$H_2PO_4^-(aq) \rightleftharpoons H^+(aq) + HPO_4^{2-}(aq) \qquad K_{a_2} = \frac{[H^+][HPO_4^{2-}]}{[H_2PO_4^-]} = 6.2 \times 10^{-8}$$

$$HPO_4^{2-}(aq) \rightleftharpoons H^+(aq) + PO_4^{3-}(aq) \qquad K_{a_3} = \frac{[H^+][PO_4^{3-}]}{[HPO_4^{2-}]} = 4.8 \times 10^{-13}$$



H_3PO_4

We see that phosphoric acid is a weak polyprotic acid and that its ionization constants decrease markedly for the second and third stages. Thus, we can predict that, in a solution containing phosphoric acid, the concentration of the nonionized acid is the highest, and the only other species present in significant concentrations are H^+ and $H_2PO_4^-$ ions.

15.9 Molecular Structure and the Strength of Acids

The strength of an acid depends on a number of factors, such as the properties of the solvent, the temperature, and, of course, the molecular structure of the acid. When we compare the strengths of two acids, we can eliminate some variables by considering their properties in the same solvent and at the same temperature and concentration. Then we can focus on the structure of the acids.

Let us consider a certain acid HX. The strength of the acid is measured by its tendency to ionize:

$$HX \longrightarrow H^+ + X^-$$

TABLE 15.6 Bond Enthalpies for Hydrogen Halides and Acid Strengths for Hydrohalic Acids

Bond	Bond Enthalpy (kJ/mol)	Acid Strength
H—F	568.2	weak
H—Cl	431.9	strong
H—Br	366.1	strong
H—I	298.3	strong

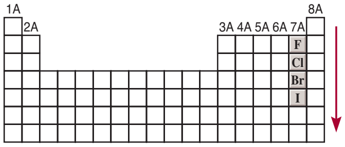
Two factors influence the extent to which the acid undergoes ionization. One is the strength of the H—X bond—the stronger the bond, the more difficult it is for the HX molecule to break up and hence the *weaker* the acid. The other factor is the polarity of the H—X bond. The difference in the electronegativities between H and X results in a polar bond like

$$\overset{\delta+}{\mathrm{H}}\text{—}\overset{\delta-}{\mathrm{X}}$$

If the bond is highly polarized, that is, if there is a large accumulation of positive and negative charges on the H and X atoms, HX will tend to break up into H^+ and X^- ions. So a high degree of polarity characterizes a *stronger* acid. Below we will consider some examples in which either bond strength or bond polarity plays a prominent role in determining acid strength.

Hydrohalic Acids

The halogens form a series of binary acids called the hydrohalic acids (HF, HCl, HBr, and HI). Of this series, which factor (bond strength or bond polarity) is the predominant factor in determining the strength of the binary acids? Consider first the strength of the H—X bond in each of these acids. Table 15.6 shows that HF has the highest bond enthalpy of the four hydrogen halides, and HI has the lowest bond enthalpy. It takes 568.2 kJ/mol to break the H—F bond and only 298.3 kJ/mol to break the H—I bond. Based on bond enthalpy, HI should be the strongest acid because it is easiest to break the bond and form the H^+ and I^- ions. Second, consider the polarity of the H—X bond. In this series of acids, the polarity of the bond decreases from HF to HI because F is the most electronegative of the halogens (see Figure 9.5). Based on bond polarity, then, HF should be the strongest acid because of the largest accumulation of positive and negative charges on the H and F atoms. Thus, we have two competing factors to consider in determining the strength of binary acids. The fact that HI is a strong acid and that HF is a weak acid indicates that bond enthalpy is the predominant factor in determining the acid strength of binary acids. In this series of binary acids, the weaker the bond, the stronger the acid so that the strength of the acids increases as follows:



Strength of hydrohalic acids increases from HF to HI.

$$\mathrm{HF} \ll \mathrm{HCl} < \mathrm{HBr} < \mathrm{HI}$$

Oxoacids

To review the nomenclature of inorganic acids, see Section 2.8 (p. 66).

Now let us consider the oxoacids. Oxoacids, as we learned in Chapter 2, contain hydrogen, oxygen, and one other element Z, which occupies a central position. Figure 15.5 shows the Lewis structures of several common oxoacids. As you can see, these acids

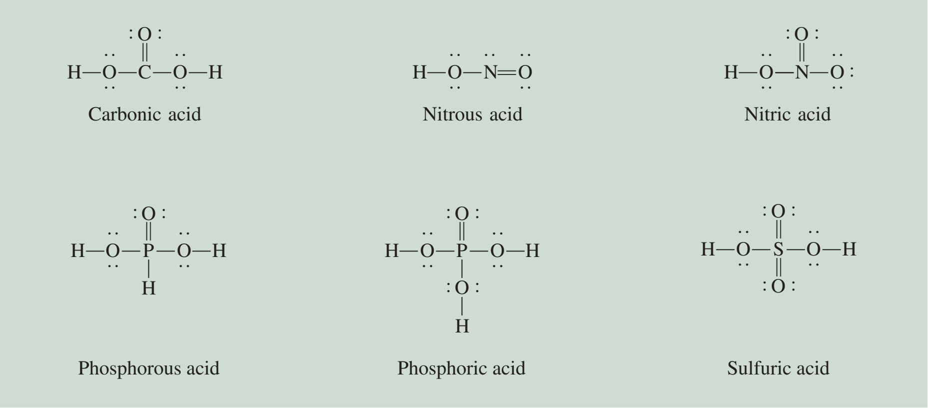
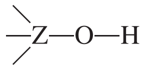


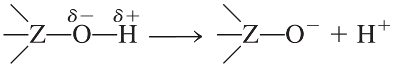
Figure 15.5 *Lewis structures of some common oxoacids. For simplicity, the formal charges have been omitted.*

are characterized by the presence of one or more O—H bonds. The central atom Z might also have other groups attached to it:



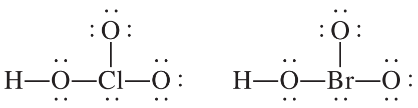
If Z is an electronegative element, or is in a high oxidation state, it will attract electrons, thus making the Z—O bond more covalent and the O—H bond more polar. Consequently, the tendency for the hydrogen to be donated as a H^+ ion increases:

As the oxidation number of an atom becomes larger, its ability to draw electrons in a bond toward itself increases.



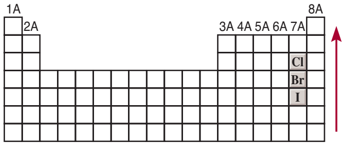
To compare their strengths, it is convenient to divide the oxoacids into two groups.

1. *Oxoacids Having Different Central Atoms That Are from the Same Group of the Periodic Table and That Have the Same Oxidation Number*. Within this group, acid strength increases with increasing electronegativity of the central atom, as $HClO_3$ and $HBrO_3$ illustrate:



Cl and Br have the same oxidation number, +5. However, because Cl is more electronegative than Br, it attracts the electron pair it shares with oxygen (in the Cl—O—H group) to a greater extent than Br does. Consequently, the O—H bond is more polar in chloric acid than in bromic acid and ionizes more readily. Thus, the relative acid strengths are

$$HClO_3 > HBrO_3$$



Strength of halogen-containing oxoacids having the same number of O atoms increases from bottom to top.

2. *Oxoacids Having the Same Central Atom but Different Numbers of Attached Groups*. Within this group, acid strength increases as the oxidation number of the central atom increases. Consider the oxoacids of chlorine shown in Figure 15.6. In this series the ability of chlorine to draw electrons away from the OH group (thus making the O—H bond more polar) increases with the number of electronegative O atoms attached to Cl. Thus, $HClO_4$ is the strongest acid because it

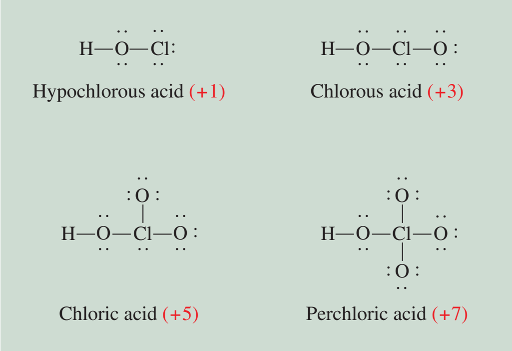


Figure 15.6 *Lewis structures of the oxoacids of chlorine. The oxidation number of the Cl atom is shown in parentheses. For simplicity, the formal charges have been omitted. Note that although hypochlorous acid is written as HClO, the H atom is bonded to the O atom.*

has the largest number of O atoms attached to Cl, and the acid strength decreases as follows:

$$HClO_4 > HClO_3 > HClO_2 > HClO$$

Example 15.12 compares the strengths of acids based on their molecular structures.

EXAMPLE 15.12

Predict the relative strengths of the oxoacids in each of the following groups: (a) HClO, HBrO, and HIO; (b) HNO_3 and HNO_2.

Strategy Examine the molecular structure. In (a) the two acids have similar structure but differ only in the central atom (Cl, Br, and I). Which central atom is the most electronegative? In (b) the acids have the same central atom (N) but differ in the number of O atoms. What is the oxidation number of N in each of these two acids?

Solution (a) These acids all have the same structure, and the halogens all have the same oxidation number (+1). Because the electronegativity decreases from Cl to I, the Cl atom attracts the electron pair it shares with the O atom to the greatest extent. Consequently, the O—H bond is the most polar in HClO and least polar in HIO. Thus, the acid strength decreases as follows:

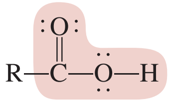
$$HClO > HBrO > HIO$$

(b) The structures of HNO_3 and HNO_2 are shown in Figure 15.5. Because the oxidation number of N is +5 in HNO_3 and +3 in HNO_2, HNO_3 is a stronger acid than HNO_2.

Practice Exercise Which of the following acids is weaker: $HClO_2$ or $HClO_3$?

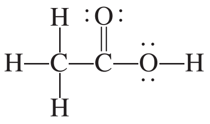
Carboxylic Acids

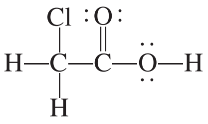
So far the discussion has focused on inorganic acids. A group of organic acids that also deserves attention is the carboxylic acids, whose Lewis structures can be represented by



$$R—\overset{\overset{\textstyle :\ddot{O}:}{\|}}{C}—\ddot{\underset{\cdot\cdot}{O}}—H$$

where R is part of the acid molecule and the shaded portion represents the *carboxyl* group, —COOH. The strength of carboxylic acids depends on the nature of the R group. Consider, for example, acetic acid and chloroacetic acid:

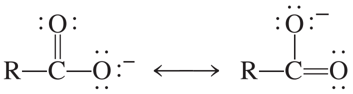

acetic acid ($K_a = 1.8 \times 10^{-5}$)


chloroacetic acid ($K_a = 1.4 \times 10^{-3}$)

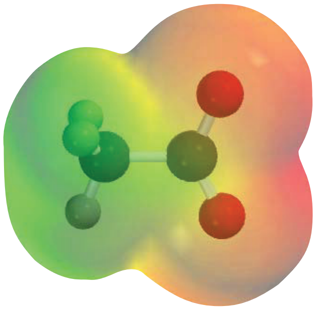
The presence of the electronegative Cl atom in chloroacetic acid shifts electron density toward the R group, thereby making the O—H bond more polar. Consequently, there is a greater tendency for the acid to ionize:

$$\mathrm{CH_2ClCOOH}(aq) \rightleftharpoons \mathrm{CH_2ClCOO^-}(aq) + \mathrm{H^+}(aq)$$

The conjugate base of the carboxylic acid, called the carboxylate anion ($\mathrm{RCOO^-}$), can exhibit resonance:



In the language of molecular orbital theory, we attribute the stability of the anion to its ability to spread or delocalize the electron density over several atoms. The greater the extent of electron delocalization, the more stable the anion and the greater the tendency for the acid to undergo ionization. Thus, benzoic acid ($\mathrm{C_6H_5COOH}$, $K_a = 6.5 \times 10^{-5}$) is a stronger acid than acetic acid because the benzene ring (see p. 449) facilitates electron delocalization, so that the benzoate anion ($\mathrm{C_6H_5COO^-}$) is more stable than the acetate anion ($\mathrm{CH_3COO^-}$).


Electrostatic potential map of the acetate ion. The electron density is evenly distributed between the two O atoms.

15.10 Acid-Base Properties of Salts

As defined in Section 4.3, a salt is an ionic compound formed by the reaction between an acid and a base. Salts are strong electrolytes that completely dissociate into ions in water. The term ***salt hydrolysis*** describes *the reaction of an anion or a cation of a salt, or both, with water*. Salt hydrolysis usually affects the pH of a solution.

The word "hydrolysis" is derived from the Greek words *hydro,* meaning "water," and *lysis,* meaning "to split apart."

Salts That Produce Neutral Solutions

It is generally true that salts containing an alkali metal ion or alkaline earth metal ion (except $\mathrm{Be^{2+}}$) and the conjugate base of a strong acid (for example, $\mathrm{Cl^-}$, $\mathrm{Br^-}$, and $\mathrm{NO_3^-}$) do not undergo hydrolysis to an appreciable extent, and their solutions are assumed to be neutral. For instance, when $\mathrm{NaNO_3}$, a salt formed by the reaction of NaOH with $\mathrm{HNO_3}$, dissolves in water, it dissociates completely as follows:

In reality, all positive ions give acid solutions in water.

$$\mathrm{NaNO_3}(s) \xrightarrow{\mathrm{H_2O}} \mathrm{Na^+}(aq) + \mathrm{NO_3^-}(aq)$$

The hydrated $\mathrm{Na^+}$ ion neither donates nor accepts $\mathrm{H^+}$ ions. The $\mathrm{NO_3^-}$ ion is the conjugate base of the strong acid $\mathrm{HNO_3}$, and it has no affinity for $\mathrm{H^+}$ ions. Consequently, a solution containing $\mathrm{Na^+}$ and $\mathrm{NO_3^-}$ ions is neutral, with a pH of about 7.

Salts That Produce Basic Solutions

The solution of a salt derived from a strong base and a weak acid is basic. For example, the dissociation of sodium acetate ($\mathrm{CH_3COONa}$) in water is given by

$$\mathrm{CH_3COONa}(s) \xrightarrow{\mathrm{H_2O}} \mathrm{Na^+}(aq) + \mathrm{CH_3COO^-}(aq)$$

The mechanism by which metal ions produce acid solutions is discussed on p. 692.

The hydrated Na^+ ion has no acidic or basic properties. The acetate ion CH_3COO^-, however, is the conjugate base of the weak acid CH_3COOH and therefore has an affinity for H^+ ions. The hydrolysis reaction is given by

$$CH_3COO^-(aq) + H_2O(l) \rightleftharpoons CH_3COOH(aq) + OH^-(aq)$$

Because this reaction produces OH^- ions, the sodium acetate solution will be basic. The equilibrium constant for this hydrolysis reaction is the same as the base ionization constant expression for CH_3COO^-, so we write (see p. 681)

$$K_b = \frac{[CH_3COOH][OH^-]}{[CH_3COO^-]} = 5.6 \times 10^{-10}$$

Because each CH_3COO^- ion that hydrolyzes produces one OH^- ion, the concentration of OH^- at equilibrium is the same as the concentration of CH_3COO^- that hydrolyzed. We can define the *percent hydrolysis* as

$$\begin{aligned}\%\ \text{hydrolysis} &= \frac{[CH_3COO^-]_{\text{hydrolyzed}}}{[CH_3COO^-]_{\text{initial}}} \times 100\% \\ &= \frac{[OH^-]_{\text{equilibrium}}}{[CH_3COO^-]_{\text{initial}}} \times 100\%\end{aligned}$$

A calculation based on the hydrolysis of CH_3COONa is illustrated in Example 15.13. In solving salt hydrolysis problems, we follow the same procedure we used for weak acids and weak bases.

EXAMPLE 15.13

Calculate the pH of a 0.15 *M* solution of sodium acetate (CH_3COONa). What is the percent hydrolysis?

Strategy What is a salt? In solution, CH_3COONa dissociates completely into Na^+ and CH_3COO^- ions. The Na^+ ion, as we saw earlier, does not react with water and has no effect on the pH of the solution. The CH_3COO^- ion is the conjugate base of the weak acid CH_3COOH. Therefore, we expect that it will react to a certain extent with water to produce CH_3COOH and OH^-, and the solution will be basic.

Solution

Step 1: Because we started with a 0.15 *M* sodium acetate solution, the concentrations of the ions are also equal to 0.15 *M* after dissociation:

	$CH_3COONa(aq)$ $\longrightarrow$	$Na^+(aq)$ +	$CH_3COO^-(aq)$
Initial (*M*):	0.15	0	0
Change (*M*):	−0.15	+0.15	+0.15
Final (*M*):	0	0.15	0.15

Of these ions, only the acetate ion will react with water

$$CH_3COO^-(aq) + H_2O(l) \rightleftharpoons CH_3COOH(aq) + OH^-(aq)$$

At equilibrium, the major species in solution are CH_3COOH, CH_3COO^-, and OH^-. The concentration of the H^+ ion is very small as we would expect for a basic solution, so it is treated as a minor species. We ignore the ionization of water.

(Continued)

Step 2: Let x be the equilibrium concentration of CH_3COOH and OH^- ions in mol/L, we summarize:

	$CH_3COO^-(aq)$	$+\ H_2O(l) \rightleftharpoons$	$CH_3COOH(aq)$	$+\ OH^-(aq)$
Initial (M):	0.15		0.00	0.00
Change (M):	$-x$		$+x$	$+x$
Equilibrium (M):	$0.15 - x$		x	x

Step 3: From the preceding discussion and Table 15.3 we write the equilibrium constant of hydrolysis, or the base ionization constant, as

$$K_b = \frac{[CH_3COOH][OH^-]}{[CH_3COO^-]}$$

$$5.6 \times 10^{-10} = \frac{x^2}{0.15 - x}$$

Because K_b is very small and the initial concentration of the base is large, we can apply the approximation $0.15 - x \approx 0.15$:

$$5.6 \times 10^{-10} = \frac{x^2}{0.15 - x} \approx \frac{x^2}{0.15}$$

$$x = 9.2 \times 10^{-6}\ M$$

Step 4: At equilibrium:

$$\begin{aligned} [OH^-] &= 9.2 \times 10^{-6}\ M \\ pOH &= -\log(9.2 \times 10^{-6}) \\ &= 5.04 \\ pH &= 14.00 - 5.04 \\ &= 8.96 \end{aligned}$$

Thus the solution is basic, as we would expect. The percent hydrolysis is given by

$$\begin{aligned} \%\ \text{hydrolysis} &= \frac{9.2 \times 10^{-6}\ M}{0.15\ M} \times 100\% \\ &= 0.0061\% \end{aligned}$$

Check The result shows that only a very small amount of the anion undergoes hydrolysis. Note that the calculation of percent hydrolysis takes the same form as the test for the approximation, which is valid in this case.

Practice Exercise Calculate the pH of a 0.24 M sodium formate solution (HCOONa).

Similar Problem: 15.79.

ARIS

Salts That Produce Acidic Solutions

When a salt derived from a strong acid such as HCl and a weak base such as NH_3 dissolves in water, the solution becomes acidic. For example, consider the process

$$NH_4Cl(s) \xrightarrow{H_2O} NH_4^+(aq) + Cl^-(aq)$$

The Cl^- ion, being the conjugate base of a strong acid, has no affinity for H^+ and no tendency to hydrolyze. The ammonium ion NH_4^+ is the weak conjugate acid of the weak base NH_3 and ionizes as follows:

$$NH_4^+(aq) + H_2O(l) \rightleftharpoons NH_3(aq) + H_3O^+(aq)$$

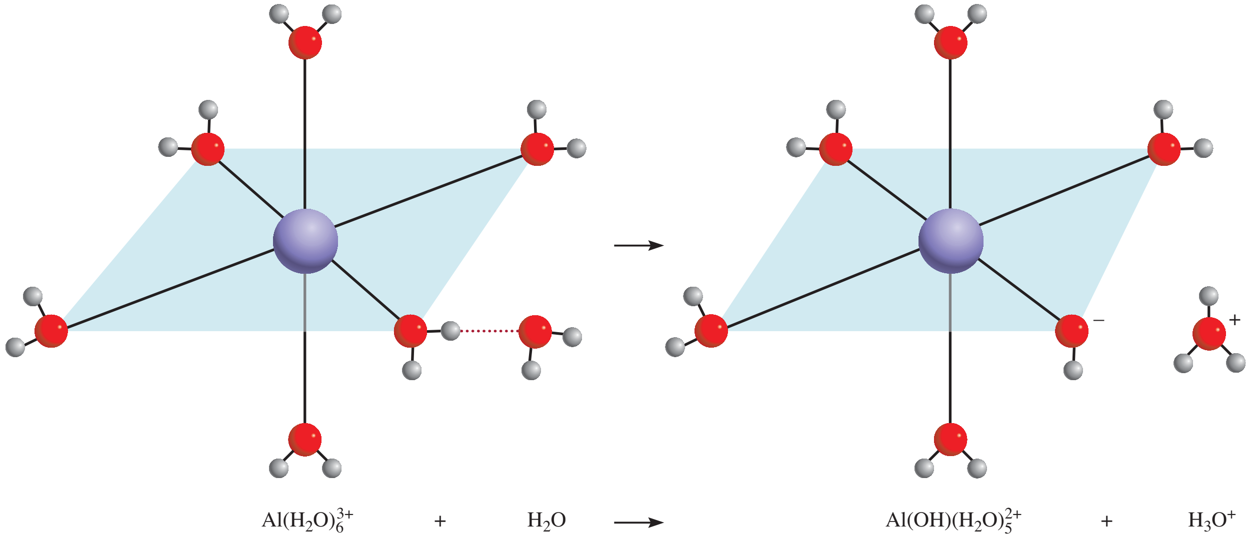


Figure 15.7 *The six H_2O molecules surround the Al^{3+} ion octahedrally. The attraction of the small Al^{3+} ion for the lone pairs on the oxygen atoms is so great that the O—H bonds in a H_2O molecule attached to the metal cation are weakened, allowing the loss of a proton (H^+) to an incoming H_2O molecule. This hydrolysis of the metal cation makes the solution acidic.*

or simply

$$NH_4^+(aq) \rightleftharpoons NH_3(aq) + H^+(aq)$$

Note that this reaction also represents the hydrolysis of the NH_4^+ ion. Because H^+ ions are produced, the pH of the solution decreases. The equilibrium constant (or ionization constant) for this process is given by

By coincidence, K_a of NH_4^+ has the same numerical value as K_b of CH_3COO^-.

$$K_a = \frac{[NH_3][H^+]}{[NH_4^+]} = \frac{K_w}{K_b} = \frac{1.0 \times 10^{-14}}{1.8 \times 10^{-5}} = 5.6 \times 10^{-10}$$

and we can calculate the pH of an ammonium chloride solution following the same procedure used in Example 15.13.

TABLE 15.7 Acid-Base Properties of Salts

Type of Salt	Examples	Ions That Undergo Hydrolysis	pH of Solution
Cation from strong base; anion from strong acid	NaCl, KI, KNO_3, RbBr, $BaCl_2$	None	≈ 7
Cation from strong base; anion from weak acid	CH_3COONa, KNO_2	Anion	> 7
Cation from weak base; anion from strong acid	NH_4Cl, NH_4NO_3	Cation	< 7
Cation from weak base; anion from weak acid	NH_4NO_2, CH_3COONH_4, NH_4CN	Anion and cation	< 7 if $K_b < K_a$ ≈ 7 if $K_b \approx K_a$ > 7 if $K_b > K_a$
Small, highly charged cation; anion from strong acid	$AlCl_3$, $Fe(NO_3)_3$	Hydrated cation	< 7

EXAMPLE 15.14

Predict whether the following solutions will be acidic, basic, or nearly neutral: (a) NH_4I, (b) $NaNO_2$, (c) $FeCl_3$, (d) NH_4F.

Strategy In deciding whether a salt will undergo hydrolysis, ask yourself the following questions: Is the cation a highly charged metal ion or an ammonium ion? Is the anion the conjugate base of a weak acid? If yes to either question, then hydrolysis will occur. In cases where both the cation and the anion react with water, the pH of the solution will depend on the relative magnitudes of K_a for the cation and K_b for the anion (see Table 15.7).

Solution We first break up the salt into its cation and anion components and then examine the possible reaction of each ion with water.

(a) The cation is NH_4^+, which will hydrolyze to produce NH_3 and H^+. The I^- anion is the conjugate base of the strong acid HI. Therefore, I^- will not hydrolyze and the solution is acidic.

(b) The Na^+ cation does not hydrolyze. The NO_2^- is the conjugate base of the weak acid HNO_2 and will hydrolyze to give HNO_2 and OH^-. The solution will be basic.

(c) Fe^{3+} is a small metal ion with a high charge and hydrolyzes to produce H^+ ions. The Cl^- does not hydrolyze. Consequently, the solution will be acidic.

(d) Both the NH_4^+ and F^- ions will hydrolyze. From Tables 15.3 and 15.4 we see that the K_a of NH_4^+ (5.6×10^{-10}) is greater than the K_b for F^- (1.4×10^{-11}). Therefore, the solution will be acidic.

Practice Exercise Predict whether the following solutions will be acidic, basic, or nearly neutral: (a) $LiClO_4$, (b) Na_3PO_4, (c) $Bi(NO_3)_3$, (d) NH_4CN.

Key Equations

$K_w = [H^+][OH^-]$	(15.3)	Ion-product constant of water.
$pH = -\log [H^+]$	(15.4)	Definition of pH of a solution.
$[H^+] = 10^{-pH}$	(15.5)	Calculating H^+ ion concentration from pH.
$pOH = -\log [OH^-]$	(15.7)	Definition of pOH of a solution.
$[OH^-] = 10^{-pOH}$	(15.8)	Calculating OH^- ion concentration from pOH.
$pH + pOH = 14.00$	(15.9)	Another form of Equation (15.3).
$\text{percent ionization} = \frac{\text{ionized acid concentration at equilibrium}}{\text{initial concentration of acid}} \times 100\%$	(15.11)	
$K_a K_b = K_w$	(15.12)	Relationship between the acid and base ionization constants of a conjugate acid-base pair.

Summary of Facts and Concepts

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Chapter Summary

1. Brønsted acids donate protons, and Brønsted bases accept protons. These are the definitions that normally underlie the use of the terms "acid" and "base."
2. The acidity of an aqueous solution is expressed as its pH, which is defined as the negative logarithm of the hydrogen ion concentration (in mol/L).
3. At 25°C, an acidic solution has $pH < 7$, a basic solution has $pH > 7$, and a neutral solution has $pH = 7$.
4. In aqueous solution, the following are classified as strong acids: $HClO_4$, HI, HBr, HCl, H_2SO_4 (first stage of ionization), and HNO_3. Strong bases in aqueous solution include hydroxides of alkali metals and of alkaline earth metals (except beryllium).
5. The acid ionization constant K_a increases with acid strength. K_b similarly expresses the strengths of bases.
6. Percent ionization is another measure of the strength of acids. The more dilute a solution of a weak acid, the greater the percent ionization of the acid.
7. The product of the ionization constant of an acid and the ionization constant of its conjugate base is equal to the ion-product constant of water.
8. The relative strengths of acids can be explained qualitatively in terms of their molecular structures.
9. Most salts are strong electrolytes that dissociate completely into ions in solution. The reaction of these ions with water, called salt hydrolysis, can produce acidic or basic solutions. In salt hydrolysis, the conjugate bases of weak acids yield basic solutions, and the conjugate acids of weak bases yield acidic solutions.

Answers to Practice Exercises

15.1 (1) H_2O (acid) and OH^- (base); (2) HCN (acid) and CN^- (base). **15.2** 7.7×10^{-15} *M*. **15.3** 0.12. **15.4** 4.7×10^{-4} *M*. **15.5** 7.40. **15.6** 12.56. **15.7** Smaller than 1. **15.8** 2.09. **15.9** 2.2×10^{-6}. **15.10** 12.03. **15.11** $[H_2C_2O_4] = 0.11$ *M*, $[HC_2O_4^-] = 0.086$ *M*, $[C_2O_4^{2-}] = 6.1 \times 10^{-5}$ *M*, $[H^+] = 0.086$ *M*. **15.12** $HClO_2$. **15.13** 8.58. **15.14** (a) pH $\approx$ 7, (b) pH $>$ 7, (c) pH $<$ 7, (d) pH $>$ 7. **15.15** Lewis acid: Co^{3+}; Lewis base: NH_3.