Acids and Bases

13

Van Gogh Museum

The principal acid present in lemons is citric acid, $H_3C_6H_5O_2$. Citric acid is a triprotic acid capable of donating three protons.

There is nothing in the Universe
but alkali and acid,
From which Nature composes all
things.

—OTTO TACHENIUS (1671)

Among the solution reactions considered in Chapter 4 were those between acids and bases. In this chapter, we take a closer look at the properties of acidic and basic water solutions. In particular, we examine

- the ionization of water and the equilibrium between hydrated H^+ ions (H_3O^+ ions) and OH^- ions in water solution (Section 13-2).
- the quantities pH and pOH, used to describe the acidity or basicity of water solutions (Section 13-3).
- the types of species that act as weak acids and weak bases and the equilibria that apply in their water solutions (Sections 13-4 and 13-5).
- the acid-base properties of salt solutions (Section 13-6).
- the Lewis model, which expands the range of compounds that can be considered acids and bases (Section 13-7).

13-1 Brønsted-Lowry Acid-Base Model

In Chapter 4 we considered an acid to be a substance that produces an excess of H^+ ions in water. A base was similarly defined to be a substance that forms excess OH^- ions in water solution. This approach, first proposed by Svante Arrhenius in

Chapter Outline

1884, is a very practical one, but it has one disadvantage. It severely limits the number of reactions that qualify as acid-base.

The model of acids and bases in this chapter is a somewhat more general one developed independently by Johannes Brønsted (1879–1947) in Denmark and Thomas Lowry (1874–1936) in England in 1923. The *Brønsted-Lowry model* focuses on the nature of acids and bases and the reactions that take place between them. Specifically, it considers that

Sometimes called the Lowry-Brønsted model, at least in England.

- ***an* acid *is a proton (H^+ ion) donor.***
- ***a* base *is a proton (H^+ ion) acceptor.***
- ***in an acid-base reaction, a proton is transferred from an acid to a base.***

A Brønsted-Lowry acid-base reaction might be represented as

$$HB(aq) + A^-(aq) \rightleftharpoons HA(aq) + B^-(aq)$$

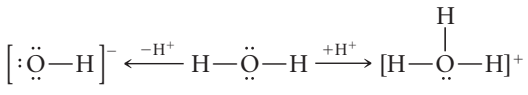
The species HB and HA both act as a **Brønsted-Lowry acid** in the forward and reverse reactions, respectively; A^- and B^- both act as a **Brønsted-Lowry base.**

The Brønsted-Lowry model introduces some new terminology.

1. The species formed when a proton is removed from an acid is referred to as the **conjugate base** of that acid; B^- is the conjugate base of HB. The species formed when a proton is added to a base is called the **conjugate acid** of that base: HA is the conjugate acid of A^-. In other words, conjugate acid-base pairs differ only in the presence or absence of a proton, H^+. A conjugate acid has one more proton than its conjugate base. Thus we have

Conjugate Acid	Conjugate Base
HF	F^-
HSO_4^-	SO_4^{2-}
NH_4^+	NH_3

2. A species that can either accept or donate a proton is referred to as an **amphiprotic species**. An example is the H_2O molecule, which can gain a proton to form the **hydronium ion,** H_3O^+, or lose a proton, leaving the hydroxide ion, OH^-.



EXAMPLE 13.1

Consider the following species: HNO_2, F^-, and HCO_3^-. Write the formula of the conjugate base for the weak acid, the conjugate acid for the weak base, and the conjugate acid and base of the amphiprotic ion.

STRATEGY

1. Form the conjugate base by removing one H atom. Decrease the charge by one unit (e.g., −1 to −2).
2. Form the conjugate acid by adding one H atom. Increase the charge by one unit (e.g., −1 to 0).

SOLUTION

HNO_2 conjugate base	$HNO_2 \longrightarrow NO_2^{0-1} \longrightarrow \boxed{NO_2^-}$
F^- conjugate acid	$F^- \longrightarrow HF^{-1+1} \longrightarrow \boxed{HF}$
HCO_3^- conjugate base	$HCO_3^- \longrightarrow CO_3^{-1-1} \longrightarrow \boxed{CO_3^{2-}}$
HCO_3^- conjugate acid	$HCO_3^- \longrightarrow H_2CO_3^{-1+1} \longrightarrow \boxed{H_2CO_3}$

13-2 The Ion Product of Water

The acidic and basic properties of aqueous solutions are dependent on an equilibrium that involves the solvent water. The reaction involved can be regarded as a Brønsted-Lowry acid-base reaction in which the H_2O molecule shows its amphiprotic nature:

$$H_2O + H_2O \rightleftharpoons H_3O^+(aq) + OH^-(aq)$$

Alternatively, and somewhat more simply, the reaction can be viewed as the ionization of a single H_2O molecule:

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

Recall (Chapter 12) that in the equilibrium constant expression for reactions in solution

- solutes enter as their molarity, [ ].
- the solvent, H_2O in this case, does not appear. Its concentration is essentially the same in all dilute solutions.

Hence for the ionization of water, the equilibrium constant expression can be written*

$$K_w = [H^+][OH^-] \qquad (13.1)$$

where K_w, referred to as the **ion product constant of water,** has a very small value. At 25°C,

$$K_w = 1.0 \times 10^{-14} \qquad (13.2)$$

This equation applies to *any* water solution at 25°C.

The concentrations of H^+ ($[H^+] = [H_3O^+]$) ions and OH^- ions in *pure water* at 25°C are readily calculated from K_w. Notice from the equation for ionization that these two ions are formed in equal numbers. Hence in pure H_2O,

$$[H^+] = [OH^-]$$
$$K_w = [H^+][OH^-] = [H^+]^2 = 1.0 \times 10^{-14}$$
$$[H^+] = 1.0 \times 10^{-7}\,M = [OH^-]$$

An aqueous solution in which $[H^+]$ *equals* $[OH^-]$ is called a **neutral solution**. It has an $[H^+]$ of $1.0 \times 10^{-7}\,M$ at 25°C.

In most water solutions, the concentrations of H^+ and OH^- are not equal. The equation $[H^+][OH^-] = 1.0 \times 10^{-14}$ indicates that these two quantities are inversely proportional to one another (Figure 13.1). When $[H^+]$ is very high, $[OH^-]$ is very low, and vice versa.

An aqueous solution in which $[H^+]$ is greater than $[OH^-]$ is termed acidic. An aqueous solution in which $[OH^-]$ is greater than $[H^+]$ is basic (alkaline). Therefore,

if $[H^+] > 1.0 \times 10^{-7}\,M$, $[OH^-] < 1.0 \times 10^{-7}\,M$, solution is acidic
if $[OH^-] > 1.0 \times 10^{-7}\,M$, $[H^+] < 1.0 \times 10^{-7}\,M$, solution is basic

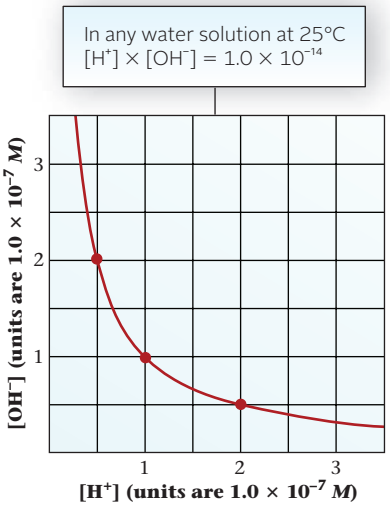


Figure 13.1 The $[H^+]$-$[OH^-]$ relationship. A graph of $[OH^-]$ versus $[H^+]$ looks very much like a graph of gas volume versus pressure. In both cases, the two variables are inversely proportional to one another. When $[H^+]$ gets larger, $[OH^-]$ gets smaller.

There are very few H^+ and OH^- ions in pure water.

13-3 pH and pOH

As just pointed out, the acidity or basicity of a solution can be described in terms of its H^+ concentration. In 1909, Søren Sørensen (1868–1939), a biochemist working at the Carlsberg Brewery in Copenhagen, proposed an alternative method of

*For simplicity, throughout this chapter, we will use H^+ rather than H_3O^+ in equilibrium constant expressions.

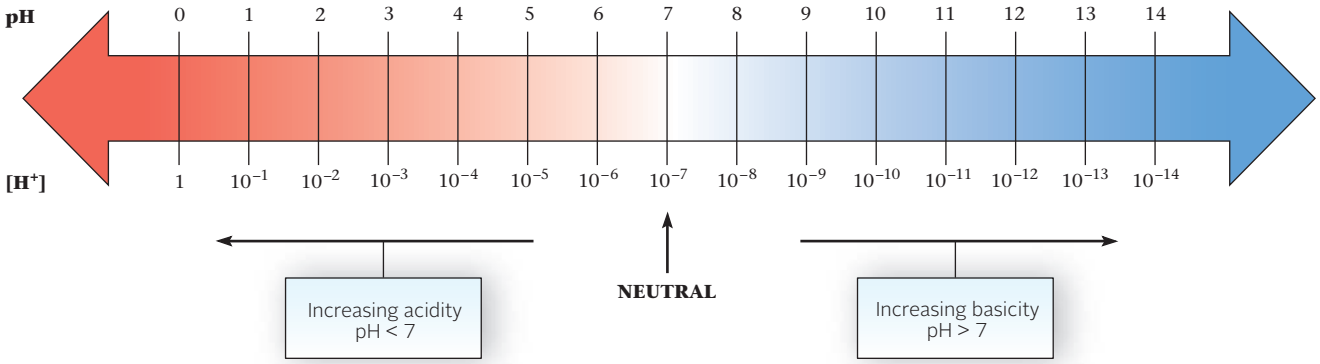


Figure 13.2 pH-[H⁺] relationship. Acidity is inversely related to pH; the higher the H^+ ion concentration, the lower the pH. In neutral solution, $[H^+] = [OH^-] = 1.0 \times 10^{-7}\ M$; pH = 7.00 at 25°C.

specifying the acidity of a solution. He defined a term called **pH** (for "power of the hydrogen ion"):

$$\text{pH} = -\log_{10}[H^+] = -\log_{10}[H_3O^+] \qquad (13.3)$$

or

$$[H^+] = [H_3O^+] = 10^{-\text{pH}}$$

Figure 13.2 shows the relationship between pH and $[H^+]$. Notice that, as the defining equation implies, pH increases by one unit when the concentration of H^+ decreases by a power of 10. Moreover, ***the higher the pH, the less acidic the solution.*** Most aqueous solutions have hydrogen ion concentrations between 1 and $10^{-14}\ M$ and hence have a pH between 0 and 14.

It is simpler to use numbers (pH = 4) than exponents ($[H^+] = 10^{-4}\ M$) to describe acidity.

The pH, like $[H^+]$ or $[OH^-]$, can be used to differentiate acidic, neutral, and basic solutions. At 25°C,

if pH < 7.0, solution is acidic
if pH = 7.0, solution is neutral
if pH > 7.0, solution is basic

Table 13.1 shows the pH of some common solutions.

A similar approach is used for the hydroxide ion concentration. The **pOH** of a solution is defined as

$$\text{pOH} = -\log_{10}[OH^-] \qquad (13.4)$$

Because $[H^+][OH^-] = 1.0 \times 10^{-14}$ at 25°C, it follows that at this temperature

$$\text{pH} + \text{pOH} = 14.00$$

Thus a solution that has a pH of 6.20 must have a pOH of 7.80, and vice versa.

Table 13.1 pH of Some Common Materials

Lemon juice	2.2–2.4	Urine, human	4.8–8.4
Wine	2.8–3.8	Cow's milk	6.3–6.6
Vinegar	3.0	Saliva, human	6.5–7.5
Tomato juice	4.0	Drinking water	5.5–8.0
Beer	4–5	Blood, human	7.3–7.5
Cheese	4.8–6.4	Seawater	8.3

EXAMPLE 13.2

Consider the following solutions at 25°C.

a Find the $[H^+]$ and pH of a tap water sample in which $[OH^-] = 2.0 \times 10^{-7}$.

ANALYSIS

Information given:	$[OH^-]$ $(2.0 \times 10^{-7}\ M)$
Information implied:	K_w value
Asked for:	$[H^+]$ and pH

STRATEGY

1. Substitute into Equation 13.1 to obtain $[H^+]$.
2. Substitute into Equation 13.3 to convert $[H^+]$ to pH.

SOLUTION

1. $[H^+]$

$$K_w = 1.0 \times 10^{-14} = [H^+][OH^-] = [H^+](2.0 \times 10^{-7})$$

$$[H^+] = \frac{1.0 \times 10^{-14}}{2.0 \times 10^{-7}} = 5.0 \times 10^{-8}\ M$$

Remember to enter the minus sign before pressing the 10^x key.

2. pH

$$\text{pH} = -\log_{10}[H^+] = -\log_{10}(5.0 \times 10^{-8}) = 7.30$$

b Find the $[H^+]$ and $[OH^-]$ of human blood at pH 7.40.

ANALYSIS

Information given:	pH (7.40)
Information implied:	K_w value
Asked for:	$[H^+]$ and $[OH^-]$

STRATEGY

1. Substitute into Equation 13.3 to convert pH to $[H^+]$.
2. Substitute into Equation 13.1 to obtain $[OH^-]$.

SOLUTION

1. $[H^+]$

$$\text{pH} = -\log_{10}[H^+] \longrightarrow 7.40 = -\log_{10}[H^+] \longrightarrow [H^+] = 10^{-7.40} = 4.0 \times 10^{-8}\ M$$

2. $[OH^-]$

$$1.0 \times 10^{-14} = [OH^-](4.0 \times 10^{-8}) \longrightarrow [OH^-] = 2.5 \times 10^{-7}\ M$$

c Find the pOH of a solution in which $[H^+] = (5.0)[OH^-]$.

ANALYSIS

Information given:	$[H^+]$ and $[OH^-]$ relation $([H^+] = 5.0\ [OH^-])$
Information implied:	K_w value
Asked for:	pOH

STRATEGY

1. Substitute into Equation 13.1 to obtain $[OH^-]$.
2. Substitute into Equation 13.4 to convert $[OH^-]$ to pOH.

SOLUTION

1. $[OH^-]$

$$1.0 \times 10^{-14} = [OH^-][H^+] = [OH^-](5.0[OH^-]) = 5.0[OH^-]^2$$

$$[OH^-]^2 = \frac{1.0 \times 10^{-14}}{5.0} \longrightarrow [OH^-] = 4.5 \times 10^{-8}\ M$$

2. pOH

$$\text{pOH} = -\log_{10}[OH^-] = -\log_{10}(4.5 \times 10^{-8}) = 7.35$$

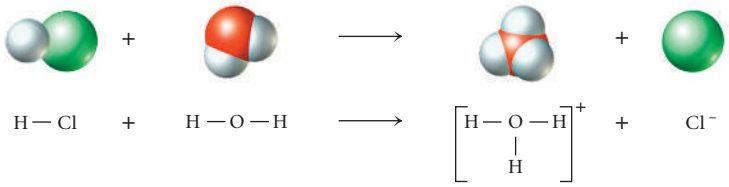


Figure 13.3 Ionization of a strong acid. When HCl is added to water, there is a proton transfer from HCl to an H_2O molecule, forming a Cl^- ion and an H_3O^+ ion. In the reaction, HCl acts as a Brønsted-Lowry acid, H_2O as a Brønsted-Lowry base.

The number calculated in part (b) for the concentration of H^+ in blood, 4.0×10^{-8} *M*, is very small. You may wonder what difference it makes whether $[H^+]$ is 4.0×10^{-8} *M*, 4.0×10^{-7} *M*, or some other such tiny quantity. In practice, it makes a great deal of difference because a large number of biological processes involve H^+ as a reactant, so the rates of these processes depend on its concentration. If $[H^+]$ increases from 4.0×10^{-8} *M* to 4.0×10^{-7} *M*, the rate of a first-order reaction involving H^+ increases by a factor of 10. Indeed, if $[H^+]$ in blood increases by a much smaller amount, from 4.0×10^{-8} *M* to 5.0×10^{-8} *M* (pH 7.40 ⟶ 7.30), a condition called *acidosis* develops. The nervous system is depressed; fainting and even coma can result.

pH of Strong Acids and Strong Bases

As pointed out in Chapter 4, the following acids are strong

HCl	HBr	HI
$HClO_4$	HNO_3	H_2SO_4*

in the sense that they are completely ionized in water. The reaction of the strong acid HCl with water can be represented by the equation (Figure 13.3)

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

Because this reaction goes to completion, it follows that a 0.10 *M* solution of HCl is 0.10 *M* in both H_3O^+ (i.e., H^+) and Cl^- ions.

1 *M* HCl has a pH of 0, 1 *M* NaOH a pH of 14.

The strong bases

LiOH	NaOH	KOH
$Ca(OH)_2$	$Sr(OH)_2$	$Ba(OH)_2$

are completely ionized in dilute water solution. A 0.10 *M* solution of NaOH is 0.10 *M* in both Na^+ and OH^- ions.

The fact that strong acids and bases are completely ionized in water makes it relatively easy to calculate the pH of their solutions (Example 13.3).

*The *first* ionization of H_2SO_4 is complete:

$$H_2SO_4(aq) \longrightarrow H^+(aq) + HSO_4^-(aq)$$

The *second* ionization is reversible:

$$HSO_4^-(aq) \rightleftharpoons H^+(aq) + SO_4^{2-}(aq)$$

EXAMPLE 13.3 GRADED

Consider barium hydroxide, $Ba(OH)_2$, a white powdery substance used in the treatment of waste water. A student is asked by his TA to prepare 455 mL of a solution containing 4.23 g of $Ba(OH)_2$.

a What is the calculated pH of the prepared solution?

ANALYSIS

Information given:	mass $Ba(OH)_2$ (4.23 g); volume of solution (455 mL)
Information implied:	molar mass of $Ba(OH)_2$; K_w
Asked for:	pH of the solution

continued

STRATEGY

1. Start by expressing the concentration in g $Ba(OH)_2$/L of solution.
2. Follow the pathway:

$$\text{mass } Ba(OH)_2/L \xrightarrow{MM} [Ba(OH)_2] \xrightarrow{2[OH^-]/[Ba(OH)_2]} [OH^-] \xrightarrow{K_w} [H^+] \xrightarrow{\text{Eq 13.3}} \text{pH}$$

SOLUTION

$[OH^-]$	$\frac{4.23\text{ g } Ba(OH)_2}{0.455\text{ L}} \times \frac{1\text{ mol } Ba(OH)_2}{171.3\text{ g}} \times \frac{2\text{ mol } OH^-}{1\text{ mol } Ba(OH)_2} = 0.109\text{ mol/L} = 0.109\ M$
$[H^+]$	$[H^+] = \frac{1.0 \times 10^{-14}}{0.109} = 9.2 \times 10^{-14}\ M$
pH	$\text{pH} = -\log_{10}(9.2 \times 10^{-14}) = 13.04$

b His TA measures the pH of the prepared solution with a pH meter and finds it to be 12.91. How much $Ba(OH)_2$ did the student really add?

ANALYSIS

Information given:	pH (12.91) mass $Ba(OH)_2$ to be added (4.23 g); volume of solution (455 mL)
Information implied:	molar mass of $Ba(OH)_2$; K_w
Asked for:	mass $Ba(OH)_2$ added compared to student's calculation

STRATEGY

The pathway to follow is the reverse of that in (a):

$$\text{pH} \xrightarrow{\text{Eq 13.3}} [H^+] \xrightarrow{K_w} [OH^-] \xrightarrow{2[OH^-]/[Ba(OH)_2]} [Ba(OH)_2] \xrightarrow{V} \text{mol } Ba(OH)_2 \xrightarrow{MM} \text{mass}$$

SOLUTION

$[OH^-]$	$[H^+] = 10^{-12.91} = 1.2 \times 10^{-13}\ M$; $[OH^-] = \frac{1.0 \times 10^{-14}}{1.2 \times 10^{-13}} = 0.081\ M$
mass $Ba(OH)_2$ really added	$\frac{0.081\text{ mol } OH^-}{1\text{ L}} \times \frac{1\text{ mol } Ba(OH)_2}{2\text{ mol } OH^-} \times 0.455\text{ L} \times \frac{171.3\text{ g } Ba(OH)_2}{1\text{ mol}} = 3.16\text{ g}$

c The TA added 0.50 g of NaOH to the prepared solution to increase the pH. What is the pH of the prepared solution after the addition of NaOH?

ANALYSIS

Information given:	from (b) $[OH^-]$ due to $Ba(OH)_2$ (0.081 *M*); volume of solution (455 mL) mass of NaOH added (0.50 g)
Information implied:	molar mass of NaOH; K_w
Asked for:	pH of the solution

STRATEGY

1. Find moles OH^- contributed by $Ba(OH)_2$ from (b).
2. Find moles OH^- contributed by NaOH.
3. Find $[OH^-]$ after NaOH addition.

$$\frac{(\text{mol } OH^-)_{NaOH} + (\text{mol } OH^-)_{Ba(OH)_2}}{V}$$

4. Find $[H^+]$ and pH.

continued

SOLUTION

1. mol OH^- from $Ba(OH)_2$

$$\frac{0.081 \text{ mol } OH^-}{1 \text{ L}} \times 0.455 \text{ L} = 0.0369$$

2. mol OH^- from NaOH

$$0.50 \text{ g NaOH} \times \frac{1 \text{ mol}}{40.0 \text{ g}} \times \frac{1 \text{ mol } OH^-}{1 \text{ mol NaOH}} = 0.0125$$

3. $[OH^-]$

$$\frac{0.0369 \text{ mol} + 0.0125 \text{ mol}}{0.455 \text{ L}} = 0.108 \, M$$

4. $[H^+]$ and pH

$$[H^+] = \frac{1.0 \times 10^{-14}}{0.108} = 9.2 \times 10^{-14} \, M$$

$$\text{pH} = -\log_{10}(9.2 \times 10^{-14}) = 13.04$$

Measuring pH

The pH of a solution can be measured by an instrument called a pH meter. A pH meter translates the H^+ ion concentration of a solution into an electrical signal that is converted into either a digital display or a deflection on a meter that reads pH directly (Figure 13.4). Later, in Chapter 17, we will consider the principle on which the pH meter works.

A less accurate but more colorful way to measure pH uses a universal indicator, which is a mixture of acid-base indicators that shows changes in color at different pH values (Figure 13.5). A similar principle is used with pH paper.

One type of paper, pH paper, is also known as litmus paper.

Strips of this paper are coated with a mixture of pH-sensitive dyes; these strips are widely used to test the pH of biological fluids, groundwater, and foods. Depending on the indicators used, a test strip can measure pH over a wide or narrow range.

Home gardeners frequently measure and adjust soil pH in an effort to improve the yield and quality of grass, vegetables, and flowers. Interestingly enough, the colors of many flowers depend on pH; among these are dahlias, delphiniums, and, in particular, hydrangeas (Figure 13.6). The first research in this area was carried out by Robert Boyle of gas-law fame, who published a paper on the relation between flower color and acidity in 1664.

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Figure 13.4 A pH meter with a digital readout. With a pH of 3.12, cola drinks are quite acidic.

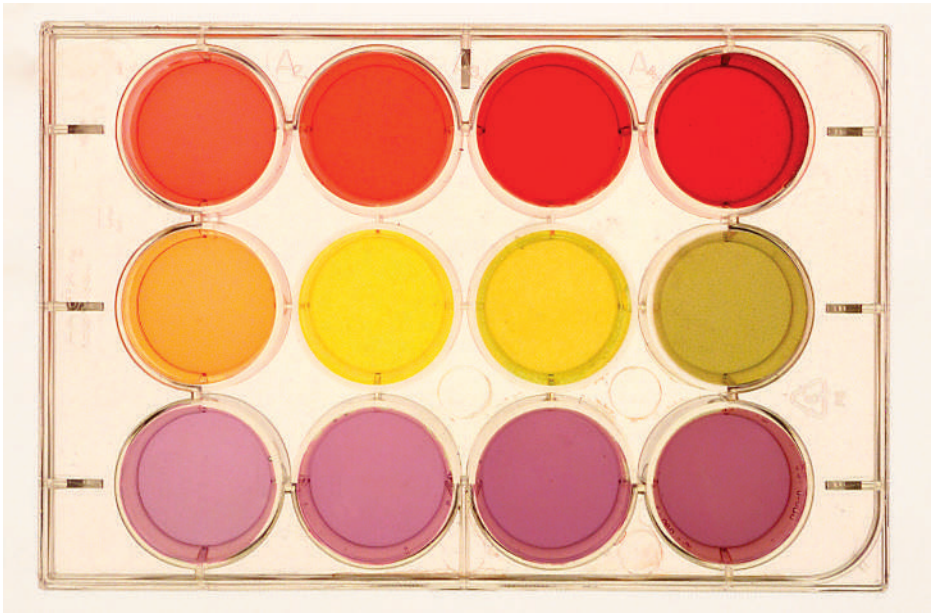

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Figure 13.5 pH as shown by a universal indicator. Universal indicator is deep red in strongly acidic solution *(upper left)*. It changes to yellow and green at pH 6 to 8, and then to deep violet in strongly basic solution *(lower right)*.

13-4 Weak Acids and Their Equilibrium Constants

Many solutes behave as weak acids; that is, they react reversibly with water to form H_3O^+ ions. Using HB to represent a weak acid, its Brønsted-Lowry reaction with water is

$$HB(aq) + H_2O \longrightarrow H_3O^+(aq) + B^-(aq)$$

Typically, this reaction occurs to a very small extent; usually, fewer than 1% of the HB molecules are converted to ions.

Most weak acids (Figure 13.7) fall into one of two categories:

1. *Molecules containing an ionizable hydrogen atom.* This type of weak acid was discussed in Chapter 4. There are literally thousands of molecular weak acids, most of them organic in nature. Among the molecular inorganic weak acids is nitrous acid:

$$HNO_2(aq) + H_2O \rightleftharpoons H_3O^+(aq) + NO_2^-(aq)$$

2. *Cations* (acidic ion). The ammonium ion, NH_4^+, behaves as a weak acid in water; a 0.10 *M* solution of NH_4Cl has a pH of about 5. The process by which the NH_4^+ ion lowers the pH of water can be represented by the (Brønsted-Lowry) equation:

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

Comparing this equation with the one above for HNO_2, you can see that they are very similar. In both cases, a weak acid (HNO_2, NH_4^+) is converted to its conjugate base (NO_2^-, NH_3). The fact that the NH_4^+ ion has a +1 charge, whereas the HNO_2 molecule is neutral, is really irrelevant here.

You may be surprised to learn that many metal cations act as weak acids in water solution. A 0.10 *M* solution of $Al_2(SO_4)_3$ has a pH close to 3; you can change the color of hydrangeas from red to blue by adding aluminum salts to soil. At first glance it is not at all obvious how a cation such as Al^{3+} can make a water solution acidic. However, the aluminum cation in water solution is really a hydrated species, $Al(H_2O)_6^{3+}$, in which six water molecules are bonded to the central Al^{3+} ion. This species can transfer a proton to a solvent water molecule to form an H_3O^+ ion:

$$Al(H_2O)_6^{3+}(aq) + H_2O \rightleftharpoons H_3O^+(aq) + Al(H_2O)_5(OH)^{2+}(aq)$$

Figure 13.8 shows the structures of the $Al(H_2O)_6^{3+}$ cation and its conjugate base, $Al(H_2O)_5(OH)^{2+}$.

A very similar equation can explain why solutions of zinc salts are acidic. Here it appears that the hydrated cation in water solution contains four H_2O molecules bonded to a central Zn^{2+} ion. The Brønsted-Lowry equation is

$$Zn(H_2O)_4^{2+}(aq) + H_2O \rightleftharpoons H_3O^+(aq) + Zn(H_2O)_3(OH)^+(aq)$$

The Equilibrium Constant for a Weak Acid

In discussing the equilibrium involved when a weak acid is added to water, it is convenient to represent the proton transfer

$$HB(aq) + H_2O \rightleftharpoons H_3O^+(aq) + B^-(aq)$$

as a simple ionization

$$HB(aq) \rightleftharpoons H^+(aq) + B^-(aq)$$

in which case the expression for the equilibrium constant becomes

$$K_a = \frac{[H^+][B^-]}{[HB]} \qquad (13.5)$$

You can assume that all common acids other than HCl, HBr, HI, HNO_3, $HClO_4$, and H_2SO_4 are weak.

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Figure 13.6 Influence of acidic or basic soil. Hydrangeas grown in strongly acidic soil (below pH 5) are blue. When they are grown in neutral or basic soil, the flowers are rosy pink.

The color change of hydrangeas is exactly the opposite of that for litmus.

To get red hydrangeas, add lime (CaO).

All transition metal cations behave this way.

Figure 13.7 Some household weak acids. Vinegar contains acetic acid. Fruit juices and sodas contain citric acid. Baking powder contains the Al^{3+} ion.

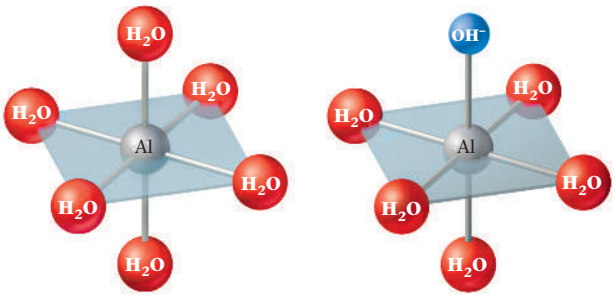


Figure 13.8 A weakly acidic cation. In water solution, the Al^{3+} ion is bonded to six water molecules in the $Al(H_2O)_6^{3+}$ ion *(left)*. In the $Al(H_2O)_5OH^{2+}$ ion *(right)*, one of the H_2O molecules has been replaced by an OH^- ion.

The equilibrium constant K_a is called, logically enough, the **acid equilibrium constant** of the weak acid HB. Table 13.2 lists the K_a values of some weak acids in order of decreasing strength. The weaker the acid, the smaller the value of K_a.

Table 13.2 Equilibrium Constants for Weak Acids and Their Conjugate Bases

	Acid	K_a	Base	K_b
Sulfurous acid	H_2SO_3	1.7×10^{-2}	HSO_3^-	5.9×10^{-13}
Hydrogen sulfate ion	HSO_4^-	1.0×10^{-2}	SO_4^{2-}	1.0×10^{-12}
Phosphoric acid	H_3PO_4	7.1×10^{-3}	$H_2PO_4^-$	1.4×10^{-12}
Hexaaquairon(III) ion	$Fe(H_2O)_6^{3+}$	6.7×10^{-3}	$Fe(H_2O)_5OH^{2+}$	1.5×10^{-12}
Hydrofluoric acid	HF	6.9×10^{-4}	F^-	1.4×10^{-11}
Nitrous acid	HNO_2	6.0×10^{-4}	NO_2^-	1.7×10^{-11}
Formic acid	$HCHO_2$	1.9×10^{-4}	CHO_2^-	5.3×10^{-11}
Lactic acid	$HC_3H_5O_3$	1.4×10^{-4}	$C_3H_5O_3^-$	7.1×10^{-11}
Benzoic acid	$HC_7H_5O_2$	6.6×10^{-5}	$C_7H_5O_2^-$	1.5×10^{-10}
Acetic acid	$HC_2H_3O_2$	1.8×10^{-5}	$C_2H_3O_2^-$	5.6×10^{-10}
Hexaaquaaluminum (III) ion	$Al(H_2O)_6^{3+}$	1.2×10^{-5}	$Al(H_2O)_5OH^{2+}$	8.3×10^{-10}
Carbonic acid	H_2CO_3	4.4×10^{-7}	HCO_3^-	2.3×10^{-8}
Dihydrogen phosphate ion	$H_2PO_4^-$	6.2×10^{-8}	HPO_4^{2-}	1.6×10^{-7}
Hydrogen sulfite ion	HSO_3^-	6.0×10^{-8}	SO_3^{2-}	1.7×10^{-7}
Hypochlorous acid	HClO	2.8×10^{-8}	ClO^-	3.6×10^{-7}
Hydrocyanic acid	HCN	5.8×10^{-10}	CN^-	1.7×10^{-5}
Ammonium ion	NH_4^+	5.6×10^{-10}	NH_3	1.8×10^{-5}
Tetraaquazinc(II) ion	$Zn(H_2O)_4^{2+}$	3.3×10^{-10}	$Zn(H_2O)_3OH^+$	3.0×10^{-5}
Hydrogen carbonate ion	HCO_3^-	4.7×10^{-11}	CO_3^{2-}	2.1×10^{-4}
Hydrogen phosphate ion	HPO_4^{2-}	4.5×10^{-13}	PO_4^{3-}	2.2×10^{-2}

$$HB(aq) \rightleftharpoons H^+(aq) + B^-(aq) \qquad K_a = \frac{[H^+] \times [B^-]}{[HB]}$$

$$B^-(aq) + H_2O \rightleftharpoons HB(aq) + OH^-(aq) \qquad K_b = \frac{[HB] \times [OH^-]}{[B^-]}$$

For example, HCN ($K_a = 5.8 \times 10^{-10}$) is a weaker acid than HNO_2, for which $K_a = 6.0 \times 10^{-4}$.

We sometimes refer to the **pK_a** value of a weak acid

$$pK_a = -\log_{10} K_a \qquad (13.6)$$

HNO_2	$K_a = 6.0 \times 10^{-4}$	$pK_a = 3.22$
HCN	$K_a = 5.8 \times 10^{-10}$	$pK_a = 9.24$

EXAMPLE 13.4

Consider acetic acid, $HC_2H_3O_2$, and the hydrated zinc cation, $Zn(H_2O)_4^{2+}$.

a Write equations to show why these species are acidic.

STRATEGY AND SOLUTION

1. To prove that a species is acidic, you must produce a hydronium ion (H_3O^+) obtained by transferring an H atom to water.

transfers to H_2O

$$HC_2H_3O_2(aq) + H_2O \rightleftharpoons C_2H_3O_2^-(aq) + HH_2O$$
$$(H_3O^+)$$

$$HC_2H_3O_2(aq) + H_2O \rightleftharpoons C_2H_3O_2^-(aq) + H_3O^+$$

2. For the hydrated cation, one of the water molecules in the ion donates an H atom to an unattached water molecule. Think of $Zn(H_2O)_4^{2+}$ as $Zn(H_2O)(H_2O)_3^{2+}$.

transfers to H_2O

$$Zn(H_2O)(H_2O)_3^{2+}(aq) + H_2O \rightleftharpoons Zn(OH^-)(H_2O)_3^{2+}(aq) + HH_2O$$
$$(Zn(OH)(H_2O)_3^+) \qquad (H_3O^+)$$

$$Zn(H_2O)(H_2O)_3^{2+}(aq) + H_2O \rightleftharpoons Zn(OH)(H_2O)_3^+(aq) + H_3O^+$$

b Which is the stronger acid?

SOLUTION

K_a values from Table 13.2	$HC_2H_3O_2(K_a = 1.8 \times 10^{-5})$ vs $Zn(H_2O)_4^{2+}(K_a = 3.3 \times 10^{-10})$
	$1.8 \times 10^{-5} > 3.3 \times 10^{-10}$ $HC_2H_3O_2$ is the stronger acid.

c What is the pK_a of $Zn(H_2O)_4^{2+}$?

SOLUTION

pK_a	$pK_a = -\log_{10} K_a = -\log_{10}(3.3 \times 10^{-10}) = 9.48$

There are several ways to determine K_a of a weak acid. A simple approach involves measuring $[H^+]$ or pH in a solution prepared by dissolving a known amount of the weak acid to form a given volume of solution.

EXAMPLE 13.5

Aspirin, a commonly used pain reliever, is a weak organic acid whose molecular formula may be written as $HC_9H_7O_4$. An aqueous solution of aspirin has total volume 350.0 mL and contains 1.26 g of aspirin. The pH of the solution is found to be 2.60. Calculate K_a for aspirin.

continued

ANALYSIS

Information given:	molecular formula for aspirin ($HC_9H_7O_4$); mass of aspirin (1.26 g); volume of solution (350.0 mL); pH of solution (2.60)
Information implied:	molar mass of aspirin; $[H^+]$
Asked for:	K_a

STRATEGY

1. Determine the original concentration, $[\ ]_o$, of aspirin.
2. $pH = [H^+]_{eq}$
3. Draw a table as illustrated in Example 12.4. Substitute $[\ ]_o$ for P_o, $\Delta[\ ]$ for ΔP, and $[\ ]_{eq}$ for P_{eq}. Since only one H atom ionizes at a time, $\Delta[\ ]$ for all species is the same. Recall that $[\ ]$ stands for the concentration in molarity.
4. Write the K expression for the ionization and calculate K_a.

SOLUTION

1. $[\ ]_o$ for aspirin

$$\frac{1.26\text{ g}}{0.3500\text{ L}} \times \frac{1\text{ mol}}{180.15\text{ g}} = 0.0200\ M$$

2. $[H^+]_{eq}$

$$2.60 = -\log_{10}[H^+];\ [H^+] = 10^{-2.60} = 2.5 \times 10^{-3}\ M$$

3. Table

	$HC_9H_7O_4(aq)$	$\rightleftharpoons$	$H^+(aq)$	+	$C_9H_7O_4^-(aq)$
$[\ ]_o$	0.0200		0.0000		0.0000
$\Delta[\ ]$	−0.0025		+0.0025		+0.0025
$[\ ]_{eq}$	0.0175		0.0025		0.0025

4. K expression

$$HC_9H_7O_4(aq) \rightleftharpoons H^+(aq) + C_9H_7O_4^-(aq)$$

K_a

$$K_a = \frac{[H^+][C_9H_7O_4^-]}{[HC_9H_7O_4]} = \frac{(0.0025)(0.0025)}{0.0175} = 3.6 \times 10^{-4}$$

END POINT

Aspirin is a relatively *strong* weak acid (Figure 13.9). It would be located near the top of Table 13.2.

For weak acids, it is always true that $\Delta[H^+] = \Delta[B^-] = -\Delta[HB]$.

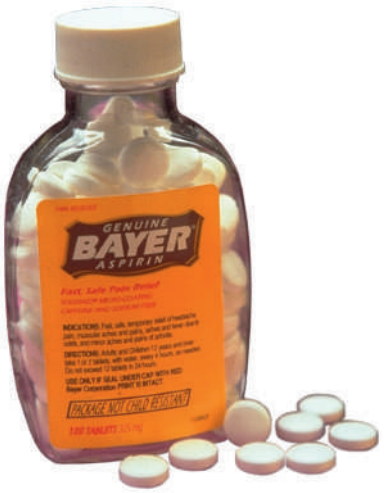


Figure 13.9 Aspirin is more acidic than vinegar.

In discussing the ionization of a weak acid,

$$HB(aq) \rightleftharpoons H^+(aq) + B^-(aq)$$

we often refer to the **percent ionization**:

$$\%\text{ ionization} = \frac{[H^+]_{eq}}{[HB]_o} \times 100\% \qquad (13.7)$$

For the aspirin solution referred to in Example 13.5,

$$\%\text{ ionization} = \frac{2.5 \times 10^{-3}}{2.0 \times 10^{-2}} \times 100\% = 12\%$$

As you might expect, percent ionization at a given concentration is directly related to K_a. Ibuprofen ($K_a = 2.5 \times 10^{-5}$), a weaker acid than aspirin ($K_a = 3.6 \times 10^{-4}$), should be only 3.6% ionized at 0.020 M compared with 12% for aspirin.

Percent ionization also depends on the concentration of weak acid, increasing as the acid is diluted (Figure 13.10).

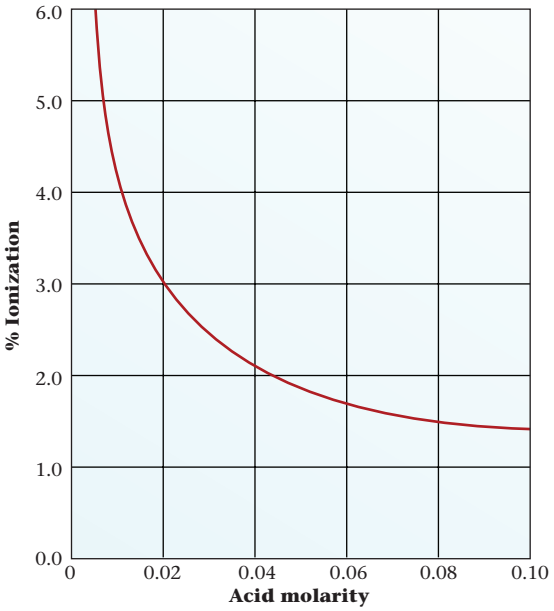


Figure 13.10 Percent ionization of acetic acid ($K_a = 1.8 \times 10^{-5}$). Like any weak acid, the percent ionization of acetic acid is inversely related to its molar concentration.

EXAMPLE 13.6 CONCEPTUAL

The box below shows a system at equilibrium. It has a volume of 0.50 L and the symbol ● represents 0.10 mol of a weak acid, HB. The symbol ● represents 0.10 mol of the conjugate base, B^-. Hydronium ions and water molecules are not shown. What is the percent ionization of the acid?

STRATEGY

1. Since there are 4 red circles (HB) and 1 blue circle (B^-) at equilibrium, there must have been 5 red circles to start with.
2. Substitute into Equation 13.7.

$$\% \text{ ionization} = \frac{[\ ]_{eq}}{[\ ]_o} \times 100$$

SOLUTION

% ionization

1 blue circle = $[B^-]_{eq}$; 5 red circles = $[HB]_o$

$$\% \text{ ionization} = \frac{1}{5} \times 100\% = 20\%$$

Calculation of $[H^+]$ in a Water Solution of a Weak Acid

Given the ionization constant of a weak acid and its original concentration, the H^+ concentration in solution is easy to calculate. The approach used is the inverse of that followed in Example 13.5, where K_a was calculated knowing $[H^+]$; here, K_a is known and $[H^+]$ must be calculated.

EXAMPLE 13.7

Nicotinic acid, $HC_6H_4O_2N$ ($K_a = 1.4 \times 10^{-5}$), is another name for niacin, an important member of the vitamin B group. Determine $[H^+]$ in a solution prepared by dissolving 3.0 g of nicotinic acid (MM = 123.11 g/mol), HNic, in enough water to form 245 mL of solution.

ANALYSIS

Information given:	molar mass for nicotinic acid, HNic (123.11 g/mol); mass of HNic (3.0 g) volume of solution (245 mL) K_a (1.4×10^{-5})
Information implied:	$[HNic]_o$
Asked for:	$[H^+]_{eq}$

STRATEGY

1. Determine the original concentration, $[\ ]_o$, of HNic.
2. Let $x = \Delta[H^+]$.

   Since all the coefficients in the reaction are one, $\Delta[HNic]$ and $\Delta[Nic^-]$ also equal x.
3. Draw a table as illustrated in Example 13.5.
4. Write the K expression for the ionization and subsitute the equilibrium concentrations for HNic, Nic^-, and H^+ obtained from the table.
5. To avoid the quadratic equation, assume $x << [HNic]_o$. Thus $[HNic]_{eq} = 0.10$. Then, substitute into the K_a expression and solve for x.

SOLUTION

1. $[\ ]_o$ for HNic

$$\frac{3.0\text{ g}}{0.245\text{ L}} \times \frac{1\text{ mol}}{123.11\text{ g}} = 0.10\ M$$

2. $\Delta[\ ]$

$$\Delta[HNic] = \Delta[Nic^-] = \Delta[H^+] = x$$

3. Table

	HNic(*aq*)	⇌	H^+(*aq*)	+	Nic^-(*aq*)
$[\ ]_o$	0.10		0.00		0.00
$\Delta[\ ]$	$-x$		$+x$		$+x$
$[\ ]_{eq}$	$0.10 - x$		x		x

4. K_a expression

$$1.4 \times 10^{-5} = \frac{[H^+][Nic^-]}{[HNic]} = \frac{(x)(x)}{0.10 - x}$$

5. x

$$1.4 \times 10^{-5} = \frac{(x)(x)}{0.10} \longrightarrow x = 0.0012\ M$$

END POINT

Note that the concentration of H^+, 0.0012 M, is

- much smaller than the original concentration of the weak acid, 0.10 M. In this case, then, the approximation $0.10 - x \approx 0.10$ is justified. This will usually, but not always, be the case (see Example 13.8).
- much larger than $[H^+]$ in pure water, 1×10^{-7} M, justifying the assumption that the ionization of water can be neglected. *This will always be the case, provided* $[H^+]$ *from the weak acid is* $\geq 10^{-6}$ M.

In general, the value of K_a is seldom known more accurately than ±5%. Hence in the expression

$$K_a = \frac{x^2}{a - x}$$

where $x = [H^+]$ and a = *original* concentration of weak acid, you can neglect the x in the denominator if doing so does not introduce an error of more than 5%. In

other words,

$$\text{if } \frac{x}{a} \leq 0.05$$

then

$$a - x \approx a$$

Note that $x = [H^+]_{eq}$ and $a = [HB]_o$. Hence,

$$\frac{x}{a} = \frac{[H^+]_{eq}}{[HB]_o}$$

If we multiply by 100%, then

$$\frac{x}{a}\% = \frac{[H^+]_{eq}}{[HB]_o} \times 100\%,$$

which is the equation for determining percent ionization (13.7). In other words, the approximation $x - a \approx a$ is valid if the % ionization is less than 5% (this is known as the **five percent rule**).

In most of the problems you will work, the approximation $a - x \approx a$ is valid, and you can solve for $[H^+]$ quite simply, as in Example 13.7, where $x = 0.012a$. Sometimes, though, you will find that the calculated $[H^+]$ is greater than 5% of the original concentration of weak acid. In that case, you can solve for x by using either the quadratic formula or the method of **successive approximations**.

EXAMPLE 13.8

Calculate $[H^+]$ in a 0.100 *M* solution of nitrous acid, HNO_2, for which $K_a = 6.0 \times 10^{-4}$.

ANALYSIS

Information given:	$[HNO_2]_o$ (0.100 *M*); K_a (6.0×10^{-4})
Asked for:	$[H^+] = [H^+]_{eq}$

STRATEGY

1. The table setup is identical to that of Example 13.7 giving the equilibrium expression

   Substitute values for equilibrium from the table. $$K_a = \frac{[H^+][NO_2^-]}{[HNO_2]} = \frac{(x)(x)}{0.100 - x}$$

2. Assume $x << 0.100$ and solve for x.
3. Check your assumption by calculating % ionization.
4. If the % ionization is less than 5%, your assumption is valid. If not, solve for x using the quadratic equation.

SOLUTION

1. Equilibrium expression
$$6.0 \times 10^{-4} = \frac{[H^+][NO_2^-]}{[HNO_2]} = \frac{(x)(x)}{0.100 - x}$$

2. Assume $x << 0.100$.
$$6.0 \times 10^{-4} = \frac{x^2}{0.100} \longrightarrow x = 0.0077\ M = [H^+]$$

3. Check the assumption.
$$\%\text{ ionization} = \frac{[H^+]_{eq}}{[HB]_o} \times 100\% = \frac{0.0077}{0.100} \times 100\% = 7.7\%$$
$$7.7\% > 5.0\% \longrightarrow \text{The assumption is not valid.}$$

continued

4. Use the quadratic equation.	$x^2 + (6.0 \times 10^{-4})x - (6.0 \times 10^{-5}) = 0$ $x = \dfrac{-b \pm \sqrt{b^2 - 4ac}}{2a} = \dfrac{-(6.0 \times 10^{-4}) \pm \sqrt{(6.0 \times 10^{-4})^2 - 4(-6.0 \times 10^{-5})}}{2}$ $x = 0.0074\ M$ or $-0.0080\ M$ $-0.0080\ M$ is physically impossible, so $x = [H^+] = 0.0074\ M$

Polyprotic Weak Acids

Certain weak acids are polyprotic; a **polyprotic acid** contains more than one ionizable hydrogen atom. Such acids ionize in steps, with a separate equilibrium constant for each step. Oxalic acid, a weak organic acid sometimes used to remove bloodstains, is *diprotic:*

$$H_2C_2O_4(aq) \rightleftharpoons H^+(aq) + HC_2O_4^-(aq) \qquad K_{a1} = 5.9 \times 10^{-2}$$
$$HC_2O_4^-(aq) \rightleftharpoons H^+(aq) + C_2O_4^{2-}(aq) \qquad K_{a2} = 5.2 \times 10^{-5}$$

Phosphoric acid, a common ingredient of cola drinks, is *triprotic:*

$$H_3PO_4(aq) \rightleftharpoons H^+(aq) + H_2PO_4^-(aq) \qquad K_{a1} = 7.1 \times 10^{-3}$$
$$H_2PO_4^-(aq) \rightleftharpoons H^+(aq) + HPO_4^{2-}(aq) \qquad K_{a2} = 6.2 \times 10^{-8}$$
$$HPO_4^{2-}(aq) \rightleftharpoons H^+(aq) + PO_4^{3-}(aq) \qquad K_{a3} = 4.5 \times 10^{-13}$$

The behavior of these acids is typical of all polyprotic acids in that

- ***the anion formed in one step*** (e.g., $HC_2O_4^-$, $H_2PO_4^-$) ***produces another H^+ ion in the next step.***
- ***the acid equilibrium constant becomes smaller with each successive step.***

$$K_{a1} > K_{a2} > K_{a3}$$

Putting it another way, ***the acids in successive steps become progressively weaker.*** This is reasonable; it should be more difficult to remove a positively charged proton, H^+, from a negatively charged species like $H_2PO_4^-$ than from a neutral molecule like H_3PO_4.

Ordinarily, successive values of K_a for polyprotic acids decrease by a factor of at least 100 (Table 13.3). In that case, essentially all the H^+ ions in the solution come from the first step. This makes it relatively easy to calculate the pH of a solution of a polyprotic acid.

Table 13.3 Equilibrium Constants for Some Weak Polyprotic Acids at 25°C

Acid	Formula	K_{a1}	K_{a2}	K_{a3}
Carbonic acid*	H_2CO_3	4.4×10^{-7}	4.7×10^{-11}	
Oxalic acid	$H_2C_2O_4$	5.9×10^{-2}	5.2×10^{-5}	
Phosphoric acid	H_3PO_4	7.1×10^{-3}	6.2×10^{-8}	4.5×10^{-13}
Sulfurous acid	H_2SO_3	1.7×10^{-2}	6.0×10^{-8}	

*Carbonic acid is a water solution of carbon dioxide:

$$CO_2(g) + H_2O \rightleftharpoons H_2CO_3(aq)$$

The ionization constants listed are calculated assuming that all the carbon dioxide that dissolves is in the form of H_2CO_3.

EXAMPLE 13.9

The distilled water you use in the laboratory is slightly acidic because of dissolved CO_2, which reacts to form carbonic acid, H_2CO_3. Calculate the pH of a 0.0010 *M* solution of H_2CO_3 and $[CO_3^{2-}]$ at equilibrium.

ANALYSIS

Information given:	$[H_2CO_3]_o$ (0.0010 *M*)
Information implied:	two-step ionization, K_a value for each ionization (Table 13.3)
Asked for:	pH, $[CO_3^{2-}]_{eq}$

STRATEGY

1. Write the ionization reaction for each ionization. Recall that ionization of polyprotic acids takes place one H^+ at a time.
2. Most of the H^+ is obtained from the first ionization. Find $[H^+]_{eq}$ for the first ionization and convert to pH.
3. Note $[H^+] = [HCO_3^-]$. Substitute into the expression for the second ionization to obtain $[CO_3^{2-}]_{eq}$.

SOLUTION

1. Ionization reactions

$$H_2CO_3(aq) \rightleftharpoons H^+(aq) + HCO_3^-(aq) \qquad K_{a1} = 4.4 \times 10^{-7}$$

$$HCO_3^-(aq) \rightleftharpoons H^+(aq) + CO_3^{2-}(aq) \qquad K_{a2} = 4.7 \times 10^{-11}$$

2. $[H^+]_{eq}$ from 1st ionization

$$4.4 \times 10^{-7} = \frac{[H^+][HCO_3^-]}{[H_2CO_3]} = \frac{x^2}{0.0010 - x}$$

Assume $x << 0.0010$

$$4.4 \times 10^{-7} = \frac{x^2}{0.0010} \longrightarrow x^2 = (0.0010)(4.4 \times 10^{-7})$$

$$x = 2.1 \times 10^{-5}\ M$$

Check assumption: % ionization = 2.1%; assumption is valid.

pH: $[H^+] = [HCO_3^-] = 2.1 \times 10^{-5}\ M$; pH = 4.68

3. $[CO_3^{2-}]_{eq}$

$$4.7 \times 10^{-11} = \frac{[H^+][CO_3^{2-}]}{[HCO_3^-]} \longrightarrow [H^+] = [HCO_3^-]$$

$$4.7 \times 10^{-11} = [CO_3^{2-}]$$

In a water solution of CO_2, there are very, very few CO_3^{2-} ions.

The conclusions in Example 13.9 are ordinarily valid for any weak diprotic acid, H_2B.

$$[H^+] \text{ is calculated from } K_{a1}\text{: } [H^+] = (K_{a1} \times [H_2B])^{1/2}$$

$$[HB^-] = [H^+]$$

$$[B^{2-}] = K_{a2}$$

Molecular Structure and Acid Strength

Equilibrium constants, K_a, are a measure of the strength of an acid. The values range from 0.010 to 1×10^{-13}. What is responsible for this variation?

As we saw earlier, a Brønsted-Lowry acid is a proton donor. The strength of the acid depends on how easily the bond between hydrogen and another atom is broken and how many of the H^+ ions are donated. So, as you might suspect, the stronger the bond, the weaker the acid because the more tightly the hydrogen atom is held, the less likely it is to come off.

For oxoacids—where hydrogen is bonded to oxygen, which in turn is bonded to some other atom—two other factors affect the strength of the acid. Those are the electronegativity of the nonmetal to which the oxygen atoms are bonded and the number of oxygen atoms bonded to the nonmetal. The more electronegative the nonmetal bonded to oxygen is, the more it polarizes and therefore weakens the O—H

Figure 13.11 Weak bases.

bond, resulting in a larger equilibrium constant. Increasing the number of oxygen atoms bonded to the nonmetal also weakens the O—H bond, resulting in a stronger acid. HClO is a much weaker acid than $HClO_2$, whereas $HClO_4$ is a strong acid. The acidity of oxoacids is discussed in more detail in Chapter 21.

13-5 Weak Bases and Their Equilibrium Constants

Like the weak acids, a large number of solutes act as weak bases (Figure 13.11). It is convenient to classify weak bases into two groups, molecules and anions.

1. ***Molecules.*** As pointed out in Chapter 4, there are many molecular weak bases, including the organic compounds known as amines. The simplest weak base is ammonia, whose reversible Brønsted-Lowry reaction with water is represented by the equation

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

This reaction proceeds to only a very small extent. In 0.10 *M* NH_3, the concentrations of NH_4^+ and OH^- are only about 0.0013 *M*.

2. ***Anions*** **(basic ion).** ***An anion derived from a weak acid is itself a weak base.*** A typical example is the fluoride ion, F^-, which is the conjugate base of the weak acid HF. The reaction of the F^- ion with water is

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

The OH^- ions formed make the solution basic. A 0.10 *M* solution of sodium fluoride, NaF, has a pH of about 8.1.

Notice the similarity between the equation just written and that for the NH_3 molecule cited above

- both weak bases (NH_3, F^-) accept protons to form the conjugate acid (NH_4^+, HF).
- water acts as a Brønsted-Lowry acid in each case, donating a proton to form the OH^- ion.

EXAMPLE 13.10

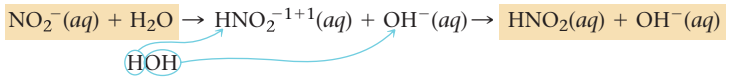
Write an equation to explain why NO_2^-, Na_2CO_3, and $KHCO_3$ produce basic water solutions.

STRATEGY

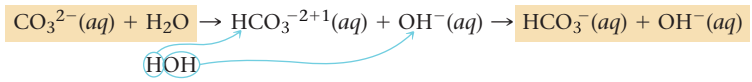
1. React each basic anion with a water molecule.
2. The weak base picks up the proton (H^+) and increases its charge by one unit to create its conjugate acid.
3. OH^- is the other product of the reaction.

SOLUTION

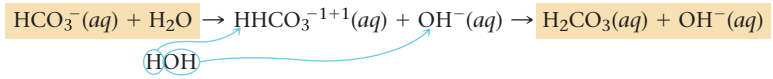
NO_2^-:



Na_2CO_3:



$KHCO_3$:



END POINT

The presence of OH^- as a product is the reason these anions in water are considered to be basic.

The Equilibrium Constant for a Weak Base

For the weak base ammonia

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

the **base equilibrium constant** (K_b) is written in the usual way, omitting the term for solvent water.

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

For an anion B^- that acts as a weak base,

$$B^-(aq) + H_2O \rightleftharpoons HB(aq) + OH^-(aq)$$

a very similar expression can be written:

$$K_b = \frac{[HB] \times [OH^-]}{[B^-]} \qquad (13.8)$$

Values of K_b are listed at the right of Table 13.2 (page 340). The larger the value of K_b, the stronger the base. Because K_b for NH_3 (1.8×10^{-5}) is larger than K_b for $C_2H_3O_2^-$ (5.6×10^{-10}), ammonia is a stronger base than the acetate ion.

The quantity $\mathbf{pK_b}$ is defined as

$$pK_b = -\log_{10} K_b \qquad (13.9)$$

The pK_b of ammonia ($K_b = 1.8 \times 10^{-5}$) is 4.74.

Calculation of $[OH^-]$ in a Water Solution of a Weak Base

We showed in Section 13-4 how K_a of a weak acid can be used to calculate $[H^+]$ in a solution of that acid. In a very similar way, K_b can be used to find $[OH^-]$ in a solution of a weak base.

EXAMPLE 13.11 GRADED

Consider sodium hypochlorite, NaOCl, the main component in household bleach. The hypochlorite ion, OCl^-, has $K_b = 3.6 \times 10^{-7}$. A solution is prepared by dissolving 12.0 g of NaOCl (MM = 74.45 g/mol) in enough water to make 835 mL of solution.

a What is the pH of the solution?

ANALYSIS

Information given:	K_b for OCl^- (3.6×10^{-7}) mass of NaOCl (12.0 g); molar mass of NaOCl (74.45 g/mol) volume of solution (0.835 L)
Information implied:	K_w
Asked for:	pH of the solution

continued

STRATEGY

1. Determine the original concentration, $[\ ]_o$, of NaOCl.
2. Draw a table as illustrated in Example 13.5.
3. Write the K expression and find $[OH^-]$ assuming $[OH^-]_{eq} << [OCl^-]_o$. Check the validity of the assumption by finding % ionization.
4. Find $[H^+]$ using Equation 13.1 and pH using Equation 13.3.

SOLUTION

1. $[\ ]_o$ for NaOCl: $\dfrac{12.0\text{ g}}{0.835\text{ L}} \times \dfrac{1\text{ mol}}{74.45\text{ g}} = 0.193\ M$

2. Table

	$OCl^-(aq)$ + H_2O ⇌	$HOCl(aq)$ +	$OH^-(aq)$
$[\ ]_o$	0.193	0.00	0.00
$\Delta[\ ]$	$-x$	$+x$	$+x$
$[\ ]_{eq}$	$0.193 - x$	x	x

3. K expression: $K_b = \dfrac{[HOCl][OH^-]}{[OCl^-]} = 3.6 \times 10^{-7} = \dfrac{(x)(x)}{0.193 - x}$

   Assume $x << 0.193$: $x^2 = 0.193(3.6 \times 10^{-7}) \longrightarrow x = 2.6 \times 10^{-4}$

   Check assumption: % ionization = 0.14%; the assumption is justified. $[OH^-] = 2.6 \times 10^{-4}\ M$

4. $[H^+]$; pH: $1.0 \times 10^{-14} = [H^+](2.6 \times 10^{-4}) \longrightarrow [H^+] = 3.9 \times 10^{-11} \longrightarrow$ pH = 10.41

b Household bleach is 5.25% NaOCl by mass. Assuming that its density is 1.00 g/mL, is household bleach more alkaline than the prepared solution?

ANALYSIS

Information given: NaOCl content of household bleach (5.25% by mass); density of bleach (1.00 g/mL); pH of solution in part (a) (10.41)

Asked for: Compare pH of solution (a) and pH of bleach.

STRATEGY

1. Assume 100.0 g (= 100.0 mL) of bleach. Thus, there are 5.25 g of NaOCl in 100.0 mL of solution.
2. Find $[OH^-]$, $[H^+]$, and pH of bleach as in part (a).
3. Compare the pH of both solutions. The solution with a higher pH is more alkaline.

SOLUTION

$[NaOCl]_o = [OCl^-]_o$: $\dfrac{5.25\text{ g}}{0.100\text{ L}} \times \dfrac{1\text{ mol}}{74.45\text{ g}} = 0.705\ M$

K expression: (as in part (a)): $K_b = \dfrac{[HOCl][OH^-]}{[OCl^-]} = 3.6 \times 10^{-7} = \dfrac{(x)(x)}{0.705 - x}$

Assume $x << 0.705$: $x^2 = 0.705(3.6 \times 10^{-7}) \longrightarrow x = 5.0 \times 10^{-4} = [OH^-]$

Check assumption.: % ionization = 0.071%; the assumption is justified. $[OH^-] = 5.0 \times 10^{-4}\ M$

$[H^+]$; pH: $1.0 \times 10^{-14} = [H^+](5.0 \times 10^{-4}) \longrightarrow [H^+] = 2.0 \times 10^{-11} \longrightarrow$ pH = 10.70

Comparison: pH of the solution in part (a) = 10.41; pH of bleach = 10.70

10.70 > 10.41; bleach is more alkaline than the solution prepared in part (a).

Relation Between K_a and K_b

Equilibrium constants of weak bases can be measured in the laboratory by procedures very much like those used for weak acids. In practice, though, it is simpler to take advantage of a simple mathematical relationship between K_b for a weak base and K_a for its conjugate acid. This relationship can be derived by adding together the equations for the ionization of the weak acid HB and the reaction of the weak base B^- with water:

$$\begin{array}{lrll} (1) & HB(aq) \rightleftharpoons H^+(aq) + B^-(aq) & K_I = K_a \text{ of HB} \\ (2) & B^-(aq) + H_2O(aq) \rightleftharpoons HB(aq) + OH^-(aq) & K_{II} = K_b \text{ of } B^- \\ \hline (3) & H_2O \rightleftharpoons H^+(aq) + OH^-(aq) & K_{III} = K_w \end{array}$$

Because Equation (1) + Equation (2) = Equation (3), we have, according to the rule of multiple equilibria (Chapter 12),

$$K_I \times K_{II} = K_{III}$$

or

$$(K_a \text{ of HB})(K_b \text{ of } B^-) = K_w = 1.0 \times 10^{-14} \qquad \textbf{(13.10)}$$

Checking Table 13.2, you can see that this relation holds in each case. For example,

$$\begin{aligned} (K_aHNO_2)(K_bNO_2^-) &= (6.0 \times 10^{-4})(1.7 \times 10^{-11}) \\ &= 10 \times 10^{-15} = 1.0 \times 10^{-14} \end{aligned}$$

From the general relation between K_a of a weak acid and K_b of its conjugate weak base, it should be clear that these two quantities are inversely related to each other. *The larger the value of* K_a, *the smaller the value of* K_b *and vice versa*. Table 13.4 shows this effect and some other interesting features. In particular,

1. Brønsted-Lowry acids (left column) can be divided into three categories:
   (a) strong acids ($HClO_4$, . . .), which are stronger proton donors than the H_3O^+ ion.
   (b) weak acids (HF, . . .), which are weaker proton donors than the H_3O^+ ion, but stronger than the H_2O molecule.
   (c) species such as C_2H_5OH, which are weaker proton donors than the H_2O molecule and hence do not form acidic water solutions.
2. Brønsted-Lowry bases (right column) can be divided similarly:
   (a) strong bases (H^-, . . .) (Figure 13.12), which are stronger proton acceptors than the OH^- ion.
   (b) weak bases (F^-, . . .), which are weaker proton acceptors than the OH^- ion, but stronger than the H_2O molecule.
   (c) the anions of strong acids (ClO_4^-, . . .), which are weaker proton acceptors than the H_2O molecule and hence do not form basic water solutions.

We should point out that, just as the three strong acids at the top of Table 13.4 are completely converted to H_3O^+ ions in aqueous solution:

$$HClO_4(aq) + H_2O \longrightarrow H_3O^+(aq) + ClO_4^-(aq)$$
$$HCl(aq) + H_2O \longrightarrow H_3O^+(aq) + Cl^-(aq)$$
$$HNO_3(aq) + H_2O \longrightarrow H_3O^+(aq) + NO_3^-(aq)$$

Figure 13.12 Hydride ion–water reaction. As water is dropped onto solid calcium hydride, the hydride ion (H^-) reacts immediately and vigorously to form $H_2(g)$ (which is ignited by the heat of the reaction) and OH^-.

Table 13.4 Relative Strengths of Brønsted-Lowry Acids and Bases

K_a	Conjugate Acid	Conjugate Base	K_b
Very large	$HClO_4$	ClO_4^-	Very small
Very large	HCl	Cl^-	Very small
Very large	HNO_3	NO_3^-	Very small
	H_3O^+	**H_2O**	
6.9×10^{-4}	HF	F^-	1.4×10^{-11}
1.8×10^{-5}	$HC_2H_3O_2$	$C_2H_3O_2^-$	5.6×10^{-10}
1.2×10^{-5}	$Al(H_2O)_6^{3+}$	$Al(H_2O)_5(OH)^{2+}$	8.3×10^{-10}
4.4×10^{-7}	H_2CO_3	HCO_3^-	2.3×10^{-8}
2.8×10^{-8}	HClO	ClO^-	3.6×10^{-7}
5.6×10^{-10}	NH_4^+	NH_3	1.8×10^{-5}
4.7×10^{-11}	HCO_3^-	CO_3^{2-}	2.1×10^{-4}
	H_2O	**OH^-**	
Very small	C_2H_5OH	$C_2H_5O^-$	Very large
Very small	OH^-	O^{2-}	Very large
Very small	H_2	H^-	Very large

Species shown in deep pink or deep blue are unstable because they react with H_2O molecules.

The —OH group in C_2H_5OH does not act as an OH^- ion.

the three strong bases at the bottom of the table are completely converted to OH^- ions:

$$H^-(aq) + H_2O \longrightarrow OH^-(aq) + H_2(g)$$
$$O^{2-}(aq) + H_2O \longrightarrow OH^-(aq) + OH^-(aq)$$
$$C_2H_5O^-(aq) + H_2O \longrightarrow OH^-(aq) + C_2H_5OH(aq)$$

In other words, the species H^-, O^{2-}, and $C_2H_5O^-$ do not exist in water solution.

Figure 13.13 Sodium chloride solution. When the NaCl is completely dissolved, the solution will contain only Na^+, Cl^-, and H_2O, and it is neither acidic nor basic.

13-6 Acid-Base Properties of Salt Solutions

A* salt *is an ionic solid containing a cation other than H^+ and an anion other than OH^- or O^{2-}. When a salt such as NaCl (Figure 13.13), K_2CO_3, or $Al(NO_3)_3$ dissolves in water, the cation and anion separate from one another.

$$NaCl(s) \longrightarrow Na^+(aq) + Cl^-(aq)$$
$$K_2CO_3(s) \longrightarrow 2K^+(aq) + CO_3^{2-}(aq)$$
$$Al(NO_3)_3(s) \longrightarrow Al^{3+}(aq) + 3NO_3^-(aq)$$

To predict whether a given salt solution will be acidic, basic, or neutral, you consider three factors in turn.

1. ***Decide what effect, if any, the cation has on the pH of water.***
2. ***Decide what effect, if any, the anion has on the pH of water.***
3. ***Combine the two effects to decide on the behavior of the salt.***

Table 13.5 Acid-Base Properties of Ions* in Water Solution

	Spectator	Basic	Acidic
Anion	Cl^- NO_3^- Br^- ClO_4^- I^-	$C_2H_3O_2^-$ CO_3^{2-} F^- PO_4^{3-} Many others	
Cation	Li^+ Ca^{2+} Na^+ Sr^{2+} K^+ Ba^{2+}		NH_4^+ Al^{3+} Mg^{2+} Transition metal ions

*For the acid-base properties of amphiprotic anions such as HCO_3^- or $H_2PO_4^-$, see the discussion at the end of this section.

Cations: Weak Acids or Spectator Ions?

As we pointed out in Section 13-4, certain cations act as weak acids in water solution because of reactions such as

$$NH_4^+(aq) + H_2O \rightleftharpoons H_3O^+(aq) + NH_3(aq)$$
$$Zn(H_2O)_4^{2+}(aq) + H_2O \rightleftharpoons H_3O^+(aq) + Zn(H_2O)_3(OH)^+(aq)$$

Essentially all transition metal ions behave like Zn^{2+}, forming a weakly acidic solution. Among the main-group cations, Al^{3+} and, to a lesser extent, Mg^{2+}, act as weak acids. In contrast the cations in Group 1 show little or no tendency to react with water.

If we say that *to classify an ion as acidic or basic in water solution, it must change the pH by more than 0.5 unit in 0.1 M solution,* then the cations derived from strong bases are:

- the alkali metal cations (Li^+, Na^+, K^+ . . .)
- the heavier alkaline earth cations (Ca^{2+}, Sr^{2+}, Ba^{2+})

are spectator ions as far as pH is concerned (Table 13.5).

Learn the spectator ions, not the players.

Anions: Weak Bases or Spectator Ions?

As pointed out in Section 13-5, anions that are the conjugate bases of weak acids act themselves as weak bases in water. They accept a proton from a water molecule, leaving an OH^- ion that makes the solution basic. The reactions of the fluoride and carbonate ions are typical:

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

Most anions behave this way, except those derived from strong acids (Cl^-, Br^-, I^-, NO_3^-, ClO_4^-), which show little or no tendency to react with water to form OH^- ions. Like the cations in the left column of Table 13.5, they act as spectator ions as far as pH is concerned. You can also use the flowchart shown in Figure 13.14.

Salts: Acidic, Basic, or Neutral?

If you know how the cation and anion of a salt affect the pH of water, it is a relatively simple matter to decide what the net effect will be (see the flowchart in Figure 13.14).

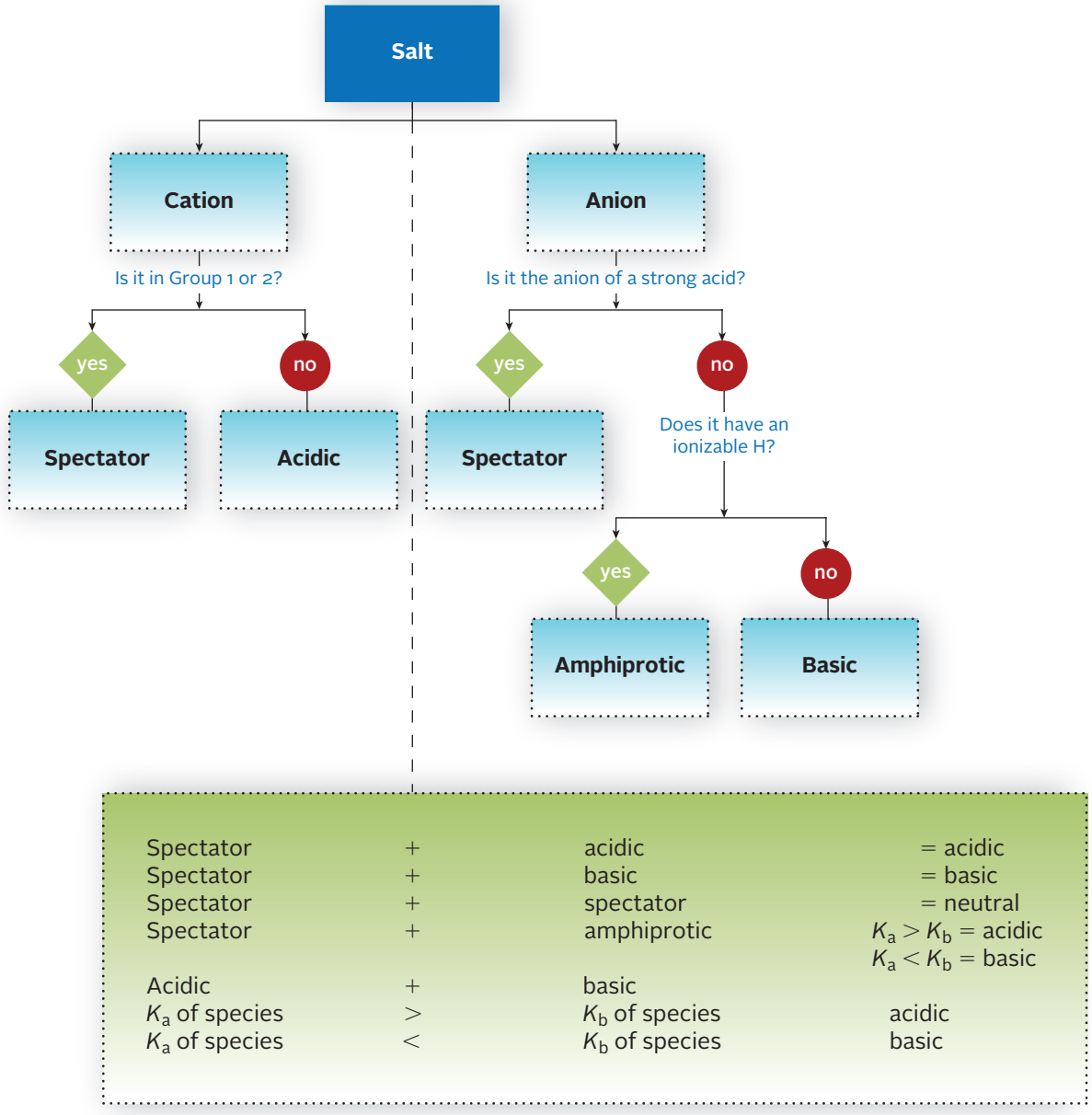


Figure 13.14 Flowchart for determining the acidity or basicity of a salt.

EXAMPLE 13.12

Consider aqueous solutions of the following salts:

$Zn(NO_3)_2$, $KClO_4$, Na_3PO_4, NH_4F, and $NaHCO_3$

Which of theses solutions are acidic? basic? neutral?

STRATEGY

Follow the flowchart in Figure 13.14.

SOLUTION

$Zn(NO_3)_2$:	
cation: Zn^{2+}	not in group 1 or 2 ⟶ acidic
anion: NO_3^-	anion of a strong acid ⟶ spectator
	$Zn(NO_3)_2$ is acidic

continued

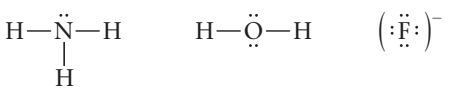
$KClO_4$:	
cation: K^+	group 1 ⟶ spectator
anion: ClO_4^-	anion of a strong acid ⟶ spectator
	$KClO_4$ is neutral
Na_3PO_4:	
cation: Na^+	group 1 ⟶ spectator
anion: PO_4^{3-}	not an anion of a strong acid; no ionizable H ⟶ basic
	Na_3PO_4 is basic
NH_4F:	
cation: NH_4^+	not in group 1 or 2 ⟶ acidic
anion: F^-	not an anion of a strong acid; no ionizable H ⟶ basic
	acidic + basic ⟶ Check K_a for NH_4^+ and K_b for F^-
	K_a for $NH_4^+ = 5.6 \times 10^{-10}$; K_b for $F^- = 1.4 \times 10^{-11}$ $K_a > K_b$
	NH_4F is acidic.
$NaHCO_3$:	
cation: Na^+	group 1 ⟶ spectator
anion: HCO_3^-	not an anion of a strong acid; has an ionizable H ⟶ amphiprotic
	spectator + amphiprotic ⟶ Check K_a and K_b for HCO_3^-
	K_a for $HCO_3^- = 4.7 \times 10^{-11}$; K_b for $HCO_3^- = 2.3 \times 10^{-8}$ $K_a < K_b$
	$NaHCO_3$ is basic.

13-7 Extending the Concept of Acids and Bases: The Lewis Model

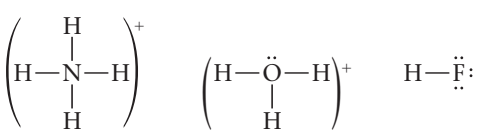
We have seen that the Brønsted-Lowry model extends the Arrhenius picture of acid-base reactions considerably. However, the Brønsted-Lowry model is restricted in one important respect. It can be applied only to reactions involving a proton transfer. For a species to act as a Brønsted-Lowry acid, it must contain an ionizable hydrogen atom.

The Lewis acid-base model removes that restriction. A **Lewis acid** is a species that in an acid-base reaction, ***accepts an electron pair.*** In this reaction, a **Lewis base** ***donates the electron pair.***

From a structural point of view, the Lewis model of a base does not differ in any essential way from the Brønsted-Lowry model. For a species to accept a proton and thereby act as a Brønsted-Lowry base, it must possess an unshared pair of electrons. Consider, for example, the NH_3 molecule, the H_2O molecule, and the F^- ion, all of which can act as Brønsted-Lowry bases:



Each of these species contains an unshared pair of electrons to form the NH_4^+ ion, the H_3O^+ ion, or the HF molecule:



Clearly, NH_3, H_2O, and F^- can also be Lewis bases because they possess an unshared electron pair that can be donated to an acid. We see then that the Lewis

model does not significantly change the number of species that can behave as bases.

On the other hand, the Lewis model greatly increases the number of species that can be considered to be acids. The substance that accepts an electron pair and therefore acts as a Lewis acid can be a proton:

$$\underset{\text{acid}}{H^+(aq)} + \underset{\text{base}}{H_2O} \longrightarrow H_3O^+(aq)$$

$$\underset{\text{acid}}{H^+(aq)} + \underset{\text{base}}{NH_3(aq)} \longrightarrow NH_4^+(aq)$$

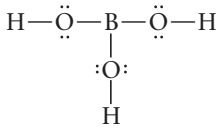
It can equally well be a cation such as Zn^{2+}, which can accept electron pairs from a Lewis base:

$$\underset{\text{acid}}{Zn^{2+}(aq)} + \underset{\text{base}}{4H_2O} \longrightarrow Zn(H_2O)_4^{2+}(aq)$$

$$\underset{\text{acid}}{Zn^{2+}(aq)} + \underset{\text{base}}{4NH_3(aq)} \longrightarrow Zn(NH_3)_4^{2+}(aq)$$

We will discuss reactions of this type in more detail in Chapters 15 and 19.

Another important class of Lewis acids are molecules containing an incomplete octet of electrons. A classic example is boric acid, an antiseptic sometimes found in eyewashes.



When boric acid is added to water, it acts as a Lewis acid, picking up an OH^- to complete the boron octet and at the same time liberating a proton.

$$\underset{\substack{\text{Lewis}\\\text{acid}}}{B(OH)_3(s)} + \underset{\substack{\text{Lewis}\\\text{base}}}{H_2O} \longrightarrow B(OH)_4^-(aq) + H^+(aq)$$

The Lewis model is commonly used in chemistry to consider the catalytic behavior of such Lewis acids as $ZnCl_2$ and BF_3. In general, when proton transfer reactions are involved, most chemists use the Arrhenius or Brønsted-Lowry models. Table 13.6 summarizes the acid-base models we have discussed.

Table 13.6 Alternative Definitions of Acids and Bases

Model	Acid	Base
Arrhenius	Supplies H^+ to water	Supplies OH^- to water
Brønsted-Lowry	H^+ donor	H^+ acceptor
Lewis	Electron pair acceptor	Electron pair donor

CHEMISTRY **BEYOND** THE CLASSROOM

Organic Acids and Bases

As pointed out earlier in this chapter, most molecular weak acids are organic in nature; they contain carbon as well as hydrogen atoms. By the same token, most molecular weak bases are organic compounds called amines, which were discussed briefly in Chapter 4.

Carboxylic Acids

Table A lists some of the organic acids found in foods. All of these compounds contain the carboxyl group

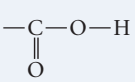
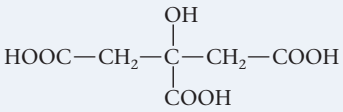
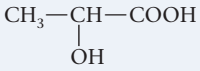
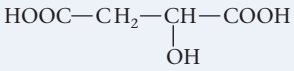
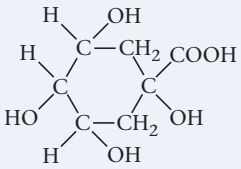
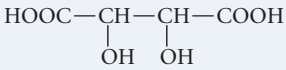


Table A Some Naturally Occurring Organic Acids

Name		Source
Acetic acid	$CH_3—COOH$	Vinegar
Citric acid		Citrus fruits
Lactic acid		Sour milk
Malic acid		Apples, watermelons, grape juice, wine
Oxalic acid	$HOOC—COOH$	Rhubarb, spinach, tomatoes
Quinic acid		Cranberries
Tartaric acid		Grape juice, wine

The general equation for the reversible dissociation of a carboxylic acid is

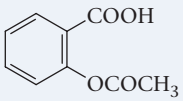
$$RCOOH(aq) \rightleftharpoons RCOO^-(aq) + H^+(aq)$$

where R is a hydrocarbon group such as CH_3, C_2H_5, ... The reaction of a carboxylic acid with a strong base can be represented by the equation

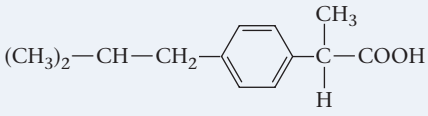
$$RCOOH(aq) + OH^-(aq) \longrightarrow RCOO^-(aq) + H_2O$$

This reaction, as is the case with all weak acids, goes essentially to completion.

Certain drugs, both prescription and over-the-counter, contain organic acids. Two of the most popular products of this type are the analgesics aspirin and ibuprofen (Advil®, Nuprin®, and so on).



aspirin



ibuprofen

Because these compounds are acidic, they can cause stomach irritation unless taken with food or water. Beyond that, aspirin inhibits blood clotting, which explains why it is often prescribed to reduce the likelihood of a stroke or heart attack. Indeed, it is now recommended for a person in the throes of a heart attack.

Amines

An **amine** is a derivative of ammonia, NH_3, in which one or more of the hydrogen atoms have been replaced by a hydrocarbon group (e.g., CH_3, C_2H_5). Amines can be classified according to the number (1, 2, or 3) of hydrocarbon groups bonded to nitrogen (Table B). Most amines of low molar mass are volatile with distinctly unpleasant odors. For example, $(CH_3)_3N$ is a gas at room temperature (bp = 3°C) with an odor somewhere between those of ammonia and spoiled fish.

Table B Types of Amines

Type	General Formula	Example
Primary	RNH_2	$CH_3—N(H)—H$
Secondary	R_2NH	$CH_3—N(H)—CH_3$
Tertiary	R_3N	$CH_3—N(CH_3)—CH_3$
	where R = CH_3, C_2H_5, . . .	

The general equation for the reaction of a primary amine with water is

$$RNH_2(aq) + H_2O \rightleftharpoons RNH_3^+(aq) + OH^-(aq)$$

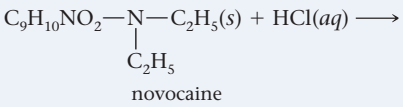
while its reaction with strong acid is

$$RNH_2(aq) + H^+(aq) \longrightarrow RNH_3^+(aq)$$

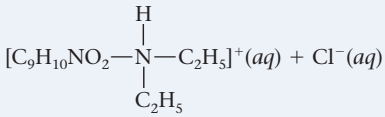
Secondary and tertiary amines react similarly, forming cations of general formula $R_2NH_2^+$ and R_3NH^+. In each case the added proton bonds to the unshared pair on the

nitrogen atom. (Compare RNH_3^+, $R_2NH_2^+$, and R_3NH^+ with the ammonium ion, NH_4^+.)

The reaction of amines with H^+ ions has an interesting practical application. Amines of high molar mass, frequently used as drugs, have very low water solubilities. They can be converted to a water-soluble form by treatment with strong acid. For example,



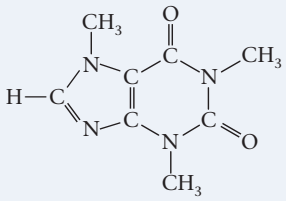
novocaine



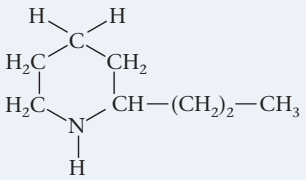
novocaine hydrochloride

Novocaine hydrochloride is about 200 times as soluble as novocaine itself. When your dentist injects "novocaine," the liquid in the syringe is a water solution of novocaine hydrochloride.

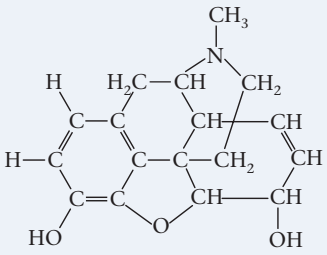
Alkaloids such as caffeine, coniine, and morphine (Figure A) are amines that are extracted from plants.



caffeine



coniine



morphine

Caffeine occurs in tea leaves, coffee beans, and cola nuts. Morphine is obtained from unripe opium poppy seed pods. Coniine, extracted from hemlock, is the alkaloid that killed Socrates. He was sentenced to death because of unconventional teaching methods; teacher evaluations had teeth in them in ancient Greece.

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Figure A Flowers and unripe seed capsules of the opium poppy. Within the capsule is a milky, gummy substance that contains the alkaloid morphine.

Key Concepts

1. Classify a species as a Brønsted-Lowry acid or base and explain by a net ionic equation.
   (Examples 13.1, 13.4, 13.10; Problems 1–12)
2. Given $[H^+]$, $[OH^-]$, pH, or pOH, calculate the other three quantities.
   (Examples 13.2, 13.3; Problems 13–32)
3. Given the pH and original concentration of a weak acid solution, calculate K_a.
   (Example 13.5; Problems 43–48)
4. Given K_a of a weak acid and its original concentration, calculate $[H^+]$.
   (Examples 13.7–13.9; Problems 49–56)
5. Given K_b of a weak base and its original concentration, calculate $[OH^-]$.
   (Example 13.11; Problems 71–76)
6. Given K_a for a weak acid, calculate K_b for its conjugate base (or vice versa).
   (Problems 69, 70, 73, 74)
7. Predict whether a salt solution is acidic, basic, or neutral.
   (Example 13.12; Problems 77–84)

Key Equations

Ionization of water	$K_w = [H^+][OH^-] = 1.0 \times 10^{-14}$ at 25°C
pH, pOH	$pH = -\log_{10}[H^+]$ $\quad pOH = -\log_{10}[OH^-]$
Expressions for K_a, K_b	$K_a = \dfrac{[H^+][B^-]}{[HB]}$ $\quad pK_a = -\log_{10}K_a$
	$K_b = \dfrac{[HB][OH^-]}{[B^-]}$ $\quad pK_b = -\log_{10}K_b$
	$(K_a)(K_b) = K_w$
% ionization (weak acid)	$\%\ \text{ionization} = \dfrac{[H^+]_{aq}}{[HB]_o} \times 100\%$

Key Terms

acid equilibrium constant
base equilibrium constant
Brønsted-Lowry acid
Brønsted-Lowry base
conjugate acid
conjugate base
ion product constant of water
Lewis acid
Lewis base
pH
pK_a
pK_b
pOH
polyprotic acid
salt

Summary Problem

Consider aqueous solutions of nitric acid, sodium hydroxide, ammonia, and hydrogen fluoride.

(a) When aqueous solutions of nitric acid and ammonia are combined, ammonium and nitrate ions are produced. When aqueous solutions of sodium hydroxide and hydrogen fluoride are combined, a solution containing sodium and fluoride ions is obtained. Classify each reactant as a strong or weak acid or base.

(b) Using the Brønsted-Lowry model, write equations to explain the acidity or basicity of HNO_3, NH_3, and HF.

(c) Calculate the pH of 0.45 *M* solutions of HNO_3, NaOH, NH_3, and HF.

(d) Consider NH_4^+.

1. What is its conjugate base?
2. What is the value of K_b for its conjugate base?

(e) Consider F^-.

1. What is its conjugate acid?
2. What is the value of K_a for its conjugate acid?

(f) Classify the salts NH_4NO_3 and NaF as acidic, basic, or neutral. Write net ionic equations to explain your answers.

(g) Would ammonium fluoride, NH_4F, be acidic or basic?

Answers

(a) **HNO_3, strong acid; NaOH, strong base; NH_3, weak base; HF, weak acid.**

(b) $HNO_3(aq) + H_2O \longrightarrow H_3O^+(aq) + NO_3^-(aq)$
$NH_3(aq) + H_2O \rightleftharpoons NH_4^+(aq) + OH^-(aq)$
$HF(aq) + H_2O \rightleftharpoons H_3O^+(aq) + F^-(aq)$

(c) **HNO_3: pH = 0.35; NaOH: pH = 13.65; HF: pH = 1.75; NH_3: pH = 11.45**

(d) **1. NH_3 2. $K_b = 1.8 \times 10^{-5}$**

(e) **1. HF 2. $K_a = 6.9 \times 10^{-4}$**

(f) **NH_4NO_3 is acidic;**
$NH_4^+(aq) + H_2O \rightleftharpoons NH_3(aq) + H_3O^+(aq)$
NaF is basic; $F^-(aq) + H_2O \rightleftharpoons HF(aq) + OH^-(aq)$

(g) **ammonium fluoride is acidic.**

Questions and Problems

Even-numbered questions and Challenge Problems have answers in Appendix 5 and fully worked solutions in the *Student Solutions Manual*.

13-1 Brønsted-Lowry Acid-Base Model

1. For each of the following reactions, indicate the Brønsted-Lowry acids and bases. What are the conjugate acid/base pairs?

(a) $H_3O^+(aq) + CN^-(aq) \rightleftharpoons HCN(aq) + H_2O$

(b) $HNO_2(aq) + OH^-(aq) \rightleftharpoons NO_2^-(aq) + H_2O$

(c) $HCHO_2(aq) + H_2O \rightleftharpoons CHO_2^-(aq) + H_3O^+(aq)$

2. Follow the directions for Question 1 for the following reactions.

(a) $CN^-(aq) + H_2O \rightleftharpoons HCN(aq) + OH^-(aq)$

(b) $HCO_3^-(aq) + H_3O^+(aq) \rightleftharpoons H_2CO_3(aq) + H_2O$

(c) $HC_2H_3O_2(aq) + HS^-(aq) \rightleftharpoons C_2H_3O_2^-(aq) + H_2S(aq)$

3. According to the Brønsted-Lowry theory, which of the following would you expect to act as an acid? Which as a base? Both acid and base?

(a) CHO_2^-

(b) NH_4^+

(c) HSO_3^-

4. According to the Brønsted-Lowry theory, which of the following would you expect to act as an acid? Which as a base?

(a) CH_3O^-

(b) CO_3^{2-}

(c) $HAsO_4^{2-}$

5. Give the formula of the conjugate acid of

(a) OH^- (b) HPO_4^{2-} (c) NH_3

(d) F^- (e) $Zn(H_2O)_2(OH)_2$

6. Give the formula for the conjugate base of

(a) $H_2AsO_4^-$ (b) $Fe(H_2O)_5(OH)^+$

(c) $HClO_3$ (d) NH_4^+ (e) $HC_2H_3O_2$

7. Write a balanced equation showing how the $H_2PO_4^-$ ion can be either a Brønsted-Lowry acid or a Brønsted-Lowry base.

8. Follow the instructions of Question 7 for the hydrogen carbonate ion, HCO_3^-.

9. Using the Brønsted-Lowry model, write equations to show why the following species behave as weak acids in water.

(a) $Ni(H_2O)_5OH^+$ (b) $Al(H_2O)_6^{3+}$

(c) H_2S (d) HPO_4^{2-}

(e) $HClO_2$ (f) $Cr(H_2O)_5(OH)^+$

10. Follow the directions of Question 9 for the following species.

(a) $Zn(H_2O)_3OH^+$ (b) HSO_4^- (c) HNO_2

(d) $Fe(H_2O)_6^{2+}$ (e) $HC_2H_3O_2$ (f) $H_2PO_4^-$

11. Using the Brønsted-Lowry model, write an equation to show why each of the following species produces a basic aqueous solution.

(a) NH_3 (b) NO_2^- (c) $C_6H_5NH_2$

(d) CO_3^{2-} (e) F^- (f) HCO_3^-

12. Follow the directions of Question 11 for the following

(a) $(CH_3)_3N$ (b) $HC_2O_4^-$ (c) CN^-

(d) S^{2-} (e) BrO_3^- (f) $H_2C_6O_5H_7^-$

13-2 The Ion Product of Water
13-3 pH and pOH

$[H^+]$, $[OH^-]$, pH, and pOH

13. Find the pH of solutions with the following $[H^+]$. Classify each as acidic or basic.

(a) 6.0 *M* (b) 0.33 *M*

(c) 4.6×10^{-8} *M* (d) 7.2×10^{-14} *M*

14. Find the pH of solutions with the following $[H^+]$. Classify each as acidic or basic.

(a) 2.7×10^{-3} *M* (b) 1.5 *M*

(c) 1.45×10^{-13} *M* (d) 6.4×10^{-9} *M*

15. Calculate H^+ and OH^- in solutions with the following pH.

(a) 9.0 (b) 3.20 (c) −1.05 (d) 7.46

16. Calculate $[H^+]$ and $[OH^-]$ in solutions with the following pH.

(a) −0.76 (b) 9.11 (c) 3.81 (d) 12.08

17. Complete the following table for solutions at 25°C.

	$[H^+]$	$[OH^-]$	pH	pOH	Acidic?
(a)	2.4×10^{-8}				
(b)		1.9×10^{-2}			
(c)			8.62		
(d)				12.22	

18. Complete the table below for solutions at 25°C.

	$[H^+]$	$[OH^-]$	pH	pOH	Basic?
(a)				8.14	
(b)			13.28		
(c)		4.3×10^{-3}			
(d)	2.75				

19. Solution 1 has $[H^+] = 1.7 \times 10^{-2}$ *M*. Solution 2 has $[H^+] = 4.3 \times 10^{-4}$ *M*. Which solution is more acidic? Which has the higher pH?

20. Solution R has pH 13.42. Solution Q has $[OH^-] = 0.16$ *M*. Which solution is more basic? Which has the lower pH?

21. Consider three solutions, R, Z, and Q.

- Solution R has $[H^+] = 0.0134$.
- Solution Z has a pH 6 times as large as solution R.
- Solution Q has $[OH^-]$ half as high as that of solution Z.

(a) Calculate the pH in solutions R, Q, and Z.

(b) What is the ratio of $[OH^-]$ in solutions R and Z and solutions R and Q?

(c) Classify each solution as acidic, basic, or neutral.

22. Solution A has a pH of 12.32. Solution B has $[H^+]$ three times as large as that of solution A. Solution C has a pH half that of solution A.

(a) What is $[H^+]$ for all three solutions?

(b) What is the pH of solutions B and C?

(c) Classify each solution as acidic, basic, or neutral.

23. Unpolluted rain water has a pH of about 5.5. Acid rain has been shown to have a pH as low as 3.0. Calculate the $[H^+]$ ratio of acid rain to unpolluted rain.

24. Most cola soft drinks have a pH of 3.1. Green tea has a pH of 5.8.

(**a**) Calculate $[H^+]$ for the cola soft drink and green tea.

(**b**) How much more acidic is a cola soft drink than green tea? Express your answer as a ratio of $[H^+]$ (cola) to $[H^+]$ (green tea).

25. Find $[OH^-]$ and the pH of the following solutions.

(**a**) 0.25 g of $Ba(OH)_2$ dissolved in enough water to make 0.655 L of solution.

(**b**) A 3.00-L solution of KOH is prepared by diluting 300.0 mL of 0.149 *M* KOH with water. What is the molarity of the diluted solution? What is the effect of a tenfold dilution on the pH?

26. Find $[H^+]$ and the pH of the following solutions.

(**a**) A 456-mL sample of a 12.0% (by mass) solution of HNO_3 (d = 1.00 g/mL). What is the pH of 10.0 mL of the same sample?

(**b**) A solution made up of 1.0 g of HCl dissolved in enough water to make 1.28 L of solution. What is the pH of the solution? If the same mass of HCl is dissolved in enough water to make 128 mL of solution, what would the pH be?

27. Find $[H^+]$, $[OH^-]$, and the pH of the following solutions.

(**a**) 30.0 mL of a 0.216 *M* solution of HCl diluted with enough water to make 125 mL of solution.

(**b**) A solution made by dissolving 275 mL of HBr gas at 25°C and 1.00 atm in enough water to make 475 mL of solution. Assume that all the HBr dissolves in water.

28. Find $[OH^-]$, $[H^+]$, and the pH of the following solutions.

(**a**) Thirty-eight mL of a 0.106 *M* solution of $Sr(OH)_2$, diluted with enough water to make 275 mL of solution.

(**b**) A solution prepared by dissolving 5.00 g of KOH in enough water to make 447 mL of solution.

29. How many grams of HI should be added to 265 mL of 0.215 *M* HCl so that the resulting solution has a pH of 0.38? Assume that the addition of HI does not change the volume of the resulting solution.

30. What is the pH of a solution obtained by adding 145 mL of 0.575 *M* HCl to 493 mL of a HNO_3 solution with a pH of 1.39? Assume that volumes are additive.

31. What is the pH of a solution obtained by adding 13.0 g of NaOH to 795 mL of a 0.200 *M* solution of $Sr(OH)_2$? Assume no volume change after NaOH is added.

32. What is the pH of a solution obtained by mixing 235 mL of NaOH with a pH of 11.57 and 316 mL of $Sr(OH)_2$ with a pH of 12.09? Assume that volumes are additive.

13-4 Weak Acids and Their Equilibrium Constants

Ionization Expressions, Weak Acids

33. Write the ionization equation and the K_a for each of the following acids.

(**a**) AsH_4^+ (**b**) $H_2C_3H_5O_7^-$ (c) H_2SO_3

34. Write the ionization equation and the K_a expression for each of the following acids.

(**a**) HSO_3^- (**b**) HPO_4^{2-} (**c**) HNO_2

35. Calculate K_a for the weak acids that have the following pK_a values.

(**a**) 3.9 (**b**) 10.12 (**c**) 13.07

36. Calculate pK_a for the weak acids that have the following K_a values:

(**a**) 1.8×10^{-4} (**b**) 6.8×10^{-8} (**c**) 4.0×10^{-11}

37. Consider these acids

Acid	A	B	C	D
pK_a	3.7	9.2	7.4	1.6

(**a**) Arrange the acids in order of decreasing acid strength from strongest to weakest.

(**b**) Which acid has the largest K_a value?

38. Consider these acids

Acid	A	B	C	D
K_a	1.6×10^{-3}	9×10^{-4}	2×10^{-6}	3×10^{-4}

(**a**) Arrange the acids in order of increasing acid strength from weakest to strongest.

(**b**) Which acid has the smallest pK_a value?

39. Rank the following solutions in order of increasing $[H^+]$. (Use Table 13.2.)

0.1 *M* HNO_3, 0.1 *M* HNO_2, 0.1 *M* $HC_7H_5O_2$, 0.1 *M* HClO

40. Rank the following acids (M = 0.10) in order of decreasing $[H^+]$:

HF HCl HCN HClO

41. Rank the solutions in Question 39 in order of increasing pH.

42. Rank the solutions in Question 40 in order of increasing pH.

Equilibrium Calculations, Weak Acids

43. The pH of a 0.129 *M* solution of a weak acid, HB, is 2.34. What is K_a for the weak acid?

44. The pH of a 2.642 *M* solution of a weak acid, HB, is 5.32. What is K_a for the weak acid?

45. Paraminobenzene (PABA), $HC_7H_6NO_2$, is used in some sunscreens. A solution is made up of 0.263 mol PABA in enough water to make 750.0 mL of solution. The solution has $[H^+] = 2.6 \times 10^{-3}$ *M*. What is K_a for PABA?

46. Acetaminophen, $HC_8H_8NO_2$ (MM = 151.17 g/mol), is the active ingredient in Tylenol®, a common pain reliever. A solution is made by dissolving 6.54 g of acetaminophen in enough water to make 250.0 mL of solution. The resulting solution has a pH of 5.24. What is K_a for acetaminophen?

47. Caproic acid, $HC_6H_{11}O_2$, is found in coconut oil and is used in making artificial flavors. A 2.00-L solution of caproic acid has a pH of 2.77 and contains 52.3 g of caproic acid. What is K_a for caproic acid?

48. Barbituric acid, $HC_4H_3N_2O_3$, is used to prepare barbiturates, a class of drugs used as sedatives. A 325-mL aqueous solution of barbituric acid has a pH of 2.34 and contains 9.00 g of the acid. What is K_a for barbituric acid?

49. When aluminum chloride dissolves in water, $Al(H_2O)_6^{3+}$ and Cl^- ions are obtained. Using the K_a in Table 13.2, calculate the pH of a 1.75 *M* solution of $AlCl_3$.

50. Using the K_a values in Table 13.2, calculate the pH of a 0.47 *M* solution of sodium hydrogen sulfite, $NaHSO_3$.

51. Barbituric acid, $HC_4H_3N_2O_3$, is used to prepare barbiturates, a class of drugs used as sedatives. Its K_a is 9.8×10^{-5}. Calculate $[H^+]$ in solutions prepared by adding enough water to the following to make 1.45 L.

(a) 0.344 mol

(b) 28.9 g

52. Penicillin (MM = 356 g/mol), an antibiotic often used to treat bacterial infections, is a weak acid. Its K_a is 1.7×10^{-3}. Calculate $[H^+]$ in solutions prepared by adding enough water to the following to make 725 mL.

(a) 0.187 mol (b) 127 g

53. Gallic acid, $HC_7H_5O_5$, is an ingredient in some ointments used to treat psoriasis. Its K_a is 3.9×10^{-5}. For a 0.168 *M* solution of gallic acid, calculate

(a) $[H^+]$ (b) $[OH^-]$

(c) pH (d) % ionization

54. Anisic acid ($K_a = 3.38 \times 10^{-5}$) is found in anise seeds and is used as a flavoring agent. For a 0.279 *M* solution of anisic acid, calculate

(a) $[H^+]$ (b) $[OH^-]$

(c) pH (d) % ionization

55. Phenol, once known as carbolic acid, HC_6H_5O, is a weak acid. It was one of the first antiseptics used by Lister. Its K_a is 1.1×10^{-10}. A solution of phenol is prepared by dissolving 14.5 g of phenol in enough water to make 892 mL of solution. For this solution, calculate

(a) pH (b) % ionization

56. Benzoic acid ($K_a = 6.6 \times 10^{-5}$) is present in many berries. Calculate the pH and % ionization of a 726-mL solution that contains 0.288 mol of benzoic acid.

Polyprotic Acids

Use the K_a values listed in Table 13.3 for polyprotic acids.

57. Chromic acid, H_2CrO_4, is commonly obtained by adding concentrated H_2SO_4 to a dichromate. It is used to clean glass. For chromic acid, K_a is 1.8×10^{-1} and 3.2×10^{-7} for its first and second dissociation, respectively. Write the overall equation and calculate *K* for the complete dissociation of chromic acid.

58. Consider citric acid, $H_3C_6H_5O_7$, added to many soft drinks. The equilibrium constants for its step-wise ionization are $K_{a1} = 7.5 \times 10^{-4}$, $K_{a2} = 1.7 \times 10^{-5}$, and $K_{a3} = 4.0 \times 10^{-7}$. Write the overall net ionic equation and calculate *K* for the complete ionization of citric acid.

59. Consider a 0.45 *M* solution of ascorbic acid, $H_2C_6H_6O_6$, one form of Vitamin C.

$$H_2C_6H_6O_6(aq) \rightleftharpoons HC_6H_6O_6^-(aq) + H^+(aq) \quad K_a = 7.9 \times 10^{-5}$$

$$HC_6H_6O_6^-(aq) \rightleftharpoons C_6H_6O_6^{2-}(aq) + H^+(aq) \quad K_a = 1.6 \times 10^{-12}$$

Calculate the pH of this solution and estimate $[HC_6H_6O_6^-]$ and $[C_6H_6O_6^{2-}]$.

60. Consider a 0.33 *M* solution of the diprotic acid H_2X.

$$H_2X \rightleftharpoons H^+(aq) + HX^-(aq) \qquad K_{a1} = 3.3 \times 10^{-4}$$

$$HX^- \rightleftharpoons H^+(aq) + X^{2-}(aq) \qquad K_{a2} = 9.7 \times 10^{-8}$$

Calculate the pH of the solution and estimate $[HX^-]$ and $[X^{2-}]$.

61. Phthalic acid, $H_2C_8H_4O_4$, is a diprotic acid. It is used to make phenolphthalein indicator. $K_{a1} = 0.0012$, and $K_{a2} = 3.9 \times 10^{-6}$. Calculate the pH of a 2.9 *M* solution of phthalic acid. Estimate $[HC_8H_4O_4^-]$ and $[C_8H_4O_4^{2-}]$.

62. Selenious acid, H_2SeO_3, is primarily used to chemically darken copper, brass, and bronze. It is a diprotic acid with the following K_a values: $K_{a1} = 2.7 \times 10^{-3}$ and $K_{a2} = 5.0 \times 10^{-8}$. What is the pH of a 2.89 *M* solution of selenious acid? Estimate $[HSeO_3^-]$ and $[SeO_3^{2-}]$.

13-5 Weak Bases and Their Equilibrium Constants

Ionization Expressions; Weak Bases

63. Write the ionization expression and the K_b expression for 0.1 *M* solutions of the following bases:

(a) $C_2H_3O_2^-$

(b) $C_2H_5NH_2$

(c) $HC_2O_4^-$

64. Follow the instructions for Question 63 for the following bases.

(a) NH_3 (b) HS^- (c) $(CH_3)_3N$

65. Using the equilibrium constants in Table 13.2, rank the following 0.1 *M* aqueous solutions in order of increasing K_b

(a) NO_2^- (b) $H_2PO_4^-$ (c) CO_3^{2-}

66. Follow the directions of Question 65 for the following bases:

(a) SO_3^{2-} (b) CHO_2^- (c) NO_2^-

67. Using the equilibrium constants listed in Table 13.2, arrange the following 0.1 *M* aqueous solutions in order of increasing pH (from lowest to highest).

(a) $NaNO_2$ (b) HCl

(c) NaF (d) $Zn(H_2O)_3(OH)(NO_3)$

68. Using the equilibrium constants listed in Table 13.2, arrange the following 0.1 *M* aqueous solutions in order of decreasing pH (from highest to lowest).

(a) KOH (b) NaCN (c) HCO_3^- (d) $Ba(OH)_2$

Equilibrium Calculations; Weak Bases

69. Find the value of K_b for the conjugate base of the following organic acids.

(a) picric acid used in the manufacture of explosives; $K_a = 0.16$

(b) trichloroacetic acid used in the treatment of warts; $K_a = 0.20$

70. Find the values of K_b for the conjugate bases of the following organic acids:

(a) glycolic acid, used by dermatologists as a chemical peel; $K_a = 1.5 \times 10^{-4}$

(b) butyric acid, responsible for the odor of rancid butter; $K_a = 1.5 \times 10^{-5}$

71. Determine $[OH^-]$, pOH and pH of a 0.28 *M* aqueous solution of Na_2CO_3.

72. Determine the $[OH^-]$ and pH of a 0.72 *M* solution of $NaHCO_3$.

73. Codeine (Cod), a powerful and addictive painkiller, is a weak base.

(a) Write a reaction to show its basic nature in water. Represent the codeine molecule as Cod.

(**b**) The K_a for its conjugate acid is 1.2×10^{-8}. What is K_b for the reaction written in (a)?

(**c**) What is the pH of a 0.0020 *M* solution of codeine?

74. Consider pyridine, C_5H_5N, a pesticide and deer repellent. Its conjugate acid, $C_5H_5NH^+$, has $K_a = 6.7 \times 10^{-6}$.

(**a**) Write a balanced net ionic equation for the reaction that shows the basicity of aqueous solutions of pyridine.

(**b**) Calculate K_b for the reaction in (a).

(**c**) Find the pH of a solution prepared by mixing 2.74 g of pyridine in enough water to make 685 mL of solution.

75. A solution of baking soda, $NaHCO_3$, has a pH of 10.08. What is the percent (by mass) of $NaHCO_3$ in a 235-mL solution? (Assume a density of 1.00 g/mL.)

76. A solution of sodium cyanide, NaCN, has a pH of 12.10. How many grams of NaCN are in 425 mL of a solution with the same pH?

13-6 Acid-Base Properties of Salt Solutions

77. Write formulas for two salts that

(**a**) contain Ni^{3+} and are acidic.

(**b**) contain Na^+ and are basic.

(**c**) contain ClO_4^- and are neutral.

(**d**) contain NH_4^+ and are acidic.

78. Write formulas for two salts that

(**a**) contain NH_4^+ and are basic.

(**b**) contain CO_3^{2-} and are basic.

(**c**) contain Br^- and are neutral.

(**d**) contain CrO_4^{2-} and are acidic.

79. State whether 1 *M* solutions of the following salts in water are acidic, basic, or neutral.

(**a**) K_2CO_3 (**b**) NH_4F (**c**) LiH_2PO_4

(**d**) $NaNO_2$ (**e**) $Ba(ClO_4)_2$

80. State whether 1 *M* solutions of the following salts in water would be acidic, basic, or neutral.

(**a**) $FeCl_3$ (**b**) BaI_2 (**c**) NH_4NO_2

(**d**) Na_2HPO_4 (**e**) K_3PO_4

81. Write net ionic equations to explain the acidity or basicity of the various salts listed in Question 79.

82. Write net ionic equations to explain the acidity or basicity of the various salts listed in Question 80.

83. Arrange the following aqueous 0.1 *M* solutions in order of decreasing pH (highest to lowest).

$Ca(NO_3)_2$ HCl H_2SO_4 NaClO KOH

84. Arrange the following aqueous 0.1 *M* solutions in order of increasing pH (lowest to highest).

$ZnBr_2$ NaOH LiF $Sr(OH)_2$ $KClO_4$

Unclassified

85. At 25°C, a 0.20 *M* solution of methylamine, CH_3NH_2, is 5.0% ionized. What is K_b for methylamine?

86. Ammonium chloride is mixed with sodium nitrite. An acid-base reaction could take place. Write a balanced equation and calculate *K* for the reaction. How likely is the reaction taking place?

87. There are 324 mg of acetylsalicylic acid (MM = 180.15 g/mol) per aspirin tablet. If two tablets are dissolved in water to give two ounces ($\frac{1}{16}$ quart) of solution, estimate the pH. K_a of acetylsalicylic acid is 3.6×10^{-4}.

88. A student is asked to bubble enough ammonia gas through water to make 4.00 L of an aqueous ammonia solution with a pH of 11.55. What volume of ammonia gas at 25°C and 1.00 atm pressure is necessary?

89. Consider an acid HY (MM = 100 g/mol [3 significant figures]). What is the pH of a 33.0% by mass solution of HY (d = 1.10 g/mL)? The K_a of HY is 2.0×10^{-8}.

90. A student prepares 455 mL of a KOH solution, but neglects to write down the mass of KOH added. His TA suggests that he take the pH of the solution. The pH is 13.33. How many grams of KOH were added?

91. Consider the process

$$H_2O \rightleftharpoons H^+(aq) + OH^-(aq) \qquad \Delta H^\circ = 55.8 \text{ kJ}$$

(**a**) Will the pH of pure water at body temperature (37°C) be 7.0?

(**b**) If not, calculate the pH of pure water at 37°C.

92. Household bleach is prepared by dissolving chlorine in water.

$$Cl_2(g) + H_2O \rightleftharpoons H^+(aq) + Cl^-(aq) + HOCl(aq)$$

K_a for HOCl is 3.2×10^{-8}. How much chlorine must be dissolved in one liter of water so that the pH of the solution is 1.19?

93. A tablet with a mass of 4.08 g contains 71.2% $NaHCO_3$. It is recommended for heartburn relief. If the stomach can hold 2.0×10^2 mL, will four tablets neutralize an "acid stomach" with a pH of 1.5?

94. Consider a weak organic base (nonelectrolyte) with molar mass 281 g/mol. An aqueous solution of the base has a pH of 8.73 and an osmotic pressure of 55 mm Hg at 25°C. What is K_b for the weak base?

95. Is a saline (NaCl) solution at 80°C acidic, basic, or neutral?

Conceptual Problems

96. Which of the following is/are true regarding a 0.1 *M* solution of $Ba(OH)_2$?

(**a**) $[OH^-] = 0.1\ M$ (**b**) $[OH^-] = [Ba^{2+}]$

(**c**) pH = 13.30 (**d**) $[H^+] = 1 \times 10^{-7}\ M$

97. Which of the following is/are true about a 0.10 *M* solution of a strong acid, HY?

(**a**) $[Y^-] = 0.10\ M$ (**b**) $[HY] = 0.10\ M$

(**c**) $[H^+] = 0.10\ M$ (**d**) pH = 1.0

(**e**) $[H^+] + [Y^-] = 0.20\ M$

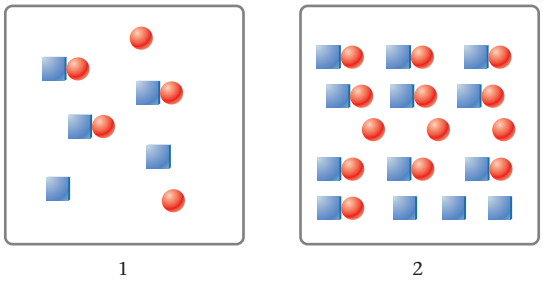
98. Consider the following six beakers. All have 100 mL of aqueous 0.1 *M* solutions of the following compounds:

beaker A has HI
beaker B has HNO_2
beaker C has NaOH
beaker D has $Ba(OH)_2$
beaker E has NH_4Cl
beaker F has $C_2H_5NH_2$

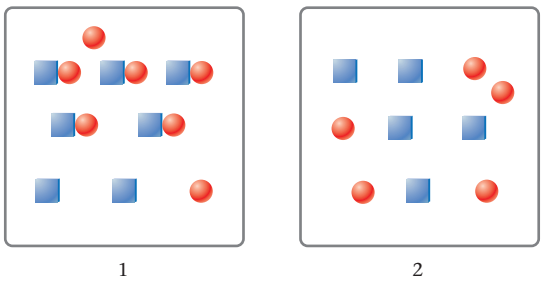
Answer the questions below, using **LT** (for *is less than*), **GT** (for *is greater than*), **EQ** (for *is equal to*), or **MI** (for *more information required*).

(a) The pH in beaker A _____ the pH in beaker B.
(b) The pH in beaker C _____ the pH in beaker D.
(c) The % ionization in beaker A _____ the % ionization in beaker C.
(d) The pH in beaker B _____ the pH in beaker E.
(e) The pH in beaker E _____ the pH in beaker F.
(f) The pH in beaker C _____ the pH in beaker F.

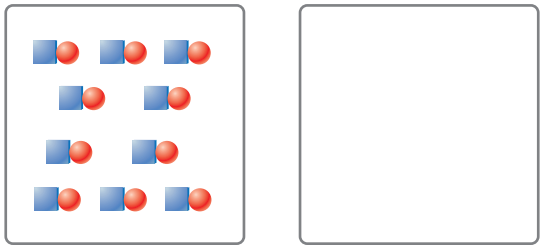
99. Each box represents an acid solution at equilibrium. Squares represent H^+ ions. Circles represent anions. (Although the anions have different identities in each figure, they are all represented as circles.) Water molecules are not shown. Assume that all solutions have the same volume.
(a) Which figure represents the strongest acid?
(b) Which figure represents the acid with the smallest K_a?
(c) Which figure represents the acid with the lowest pH?



100. Each box represents an acid solution at equilibrium. Squares represent H^+ ions, and circles represent the anion. Water molecules are not shown. Which figure represents a strong acid? Which figure is a weak acid?



101. If □○ represents the weak acid HA (□ = H^+, ○ = A^-) in Figure (a), fill in Figure (b) with □○, □, and/or ○ to represent HA as being 10% ionized. (Water molecules are omitted.)



102. You are asked to determine whether an unknown white solid is acidic or basic. You also need to say whether the acid or base is weak or strong. You are given the molar mass of the solid and told that it is soluble in water. Describe an experiment that you can perform to obtain the desired characteristics of the white solid.

Challenge Problems

103. What is the pH of a 0.020 *M* solution of H_2SO_4? You may assume that the first ionization is complete. The second ionization constant is 0.010.

104. Using the Tables in Appendix 1, calculate ΔH for the reaction of the following.
(a) 1.00 L of 0.100 *M* NaOH with 1.00 L of 0.100 *M* HCl
(b) 1.00 L of 0.100 *M* NaOH with 1.00 L of 0.100 *M* HF, taking the heat of formation of HF(*aq*) to be −320.1 kJ/mol

105. What is the pH of a solution obtained by mixing 0.30 L of 0.233 *M* $Ba(OH)_2$ and 0.45 L of 0.12 *M* HCl? Assume that volumes are additive.

106. A solution is made up of 273 mL of 0.164 *M* HNO_3 and 0.800 *M* HCl. The resulting pH of the solution is 0.39. How many mL of HCl are used to make up the solution? Assume volumes are additive.

107. What is the freezing point of vinegar, which is an aqueous solution of 5.00% acetic acid, $HC_2H_3O_2$, by mass (d = 1.006 g/cm^3)?

108. The solubility of $Ca(OH)_2$ at 25°C is 0.153 g/100 g H_2O. Assuming that the density of a saturated solution is 1.00 g/mL, calculate the maximum pH one can obtain when $Ca(OH)_2$ is dissolved in water.

109. Consider two weak acids, HA (MM = 138 g/mol) and HB (MM = 72.0 g/mol). A solution consisting of 11.0 g of HA in 745 mL has the same pH as a solution made up of 5.00 g of HB in 525 mL. Which of the two acids is stronger? Justify your answer by an appropriate calculation.

110. Consider an aqueous solution of a weak base, NaB (MM = 233 g/mol). It has a pH of 10.54. The freezing point of the solution is −0.89°C and its density is 1.00 g/mol. Find K_b for the weak base B^-.