# Chapter 14

# Acid-Base Equilibria



**Figure 14.1**   Sinkholes such as this are the result of reactions between acidic groundwaters and basic rock formations, like limestone. (credit: modification of work by Emil Kehnel)

## Chapter Outline

14.1 Brønsted-Lowry Acids and Bases

14.2 pH and pOH

14.3 Relative Strengths of Acids and Bases

14.4 Hydrolysis of Salts

14.5 Polyprotic Acids

14.6 Buffers

14.7 Acid-Base Titrations

# Introduction

Liquid water is essential to life on our planet, and chemistry involving the characteristic ions of water, $H^+$ and $OH^-$, is widely encountered in nature and society. As introduced in another chapter of this text, acid-base chemistry involves the transfer of hydrogen ions from donors (acids) to acceptors (bases). These H+ transfer reactions are reversible, and the equilibria established by acid-base systems are essential aspects of phenomena ranging from sinkhole formation (**Figure 14.1**) to oxygen transport in the human body. This chapter will further explore acid-base chemistry with an emphasis on the equilibrium aspects of this important reaction class.

# 14.1 Brønsted-Lowry Acids and Bases

By the end of this section, you will be able to:

• Identify acids, bases, and conjugate acid-base pairs according to the Brønsted-Lowry definition

• Write equations for acid and base ionization reactions

• Use the ion-product constant for water to calculate hydronium and hydroxide ion concentrations

• Describe the acid-base behavior of amphiprotic substances

The acid-base reaction class has been studied for quite some time. In 1680, Robert Boyle reported traits of acid solutions that included their ability to dissolve many substances, to change the colors of certain natural dyes, and to lose these traits after coming in contact with alkali (base) solutions. In the eighteenth century, it was recognized that acids have a sour taste, react with limestone to liberate a gaseous substance (now known to be $CO_2$), and interact with alkalis to form neutral substances. In 1815, Humphry Davy contributed greatly to the development of the modern acid-base concept by demonstrating that hydrogen is the essential constituent of acids. Around that same time, Joseph Louis Gay-Lussac concluded that acids are substances that can neutralize bases and that these two classes of substances can be defined only in terms of each other. The significance of hydrogen was reemphasized in 1884 when Svante Arrhenius defined an acid as a compound that dissolves in water to yield hydrogen cations (now recognized to be hydronium ions) and a base as a compound that dissolves in water to yield hydroxide anions.

Johannes Brønsted and Thomas Lowry proposed a more general description in 1923 in which acids and bases were defined in terms of the transfer of hydrogen ions, $H^+$. (Note that these hydrogen ions are often referred to simply as *protons*, since that subatomic particle is the only component of cations derived from the most abundant hydrogen isotope, $^1H$.) A compound that donates a proton to another compound is called a **Brønsted-Lowry acid**, and a compound that accepts a proton is called a **Brønsted-Lowry base**. An acid-base reaction is, thus, the transfer of a proton from a donor (acid) to an acceptor (base).

The concept of *conjugate pairs* is useful in describing Brønsted-Lowry acid-base reactions (and other reversible reactions, as well). When an acid donates $H^+$, the species that remains is called the **conjugate base** of the acid because it reacts as a proton acceptor in the reverse reaction. Likewise, when a base accepts $H^+$, it is converted to its **conjugate acid**. The reaction between water and ammonia illustrates this idea. In the forward direction, water acts as an acid by donating a proton to ammonia and subsequently becoming a hydroxide ion, $OH^-$, the conjugate base of water. The ammonia acts as a base in accepting this proton, becoming an ammonium ion, $NH_4^+$, the conjugate acid of ammonia. In the reverse direction, a hydroxide ion acts as a base in accepting a proton from ammonium ion, which acts as an acid.
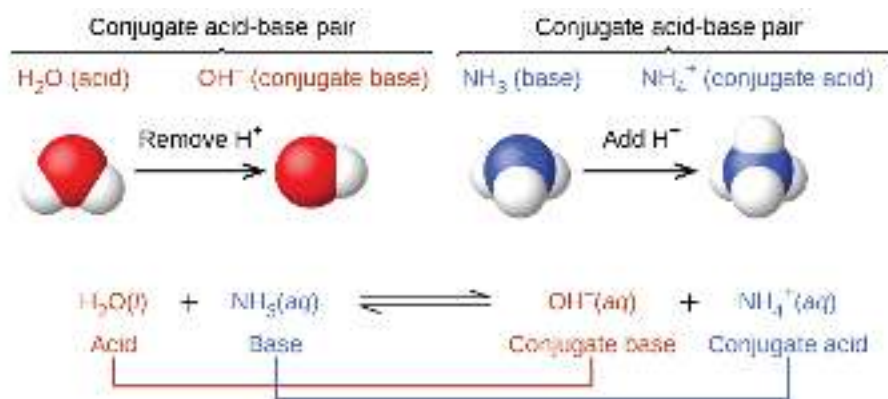


The reaction between a Brønsted-Lowry acid and water is called **acid ionization**. For example, when hydrogen fluoride dissolves in water and ionizes, protons are transferred from hydrogen fluoride molecules to water molecules, yielding hydronium ions and fluoride ions:
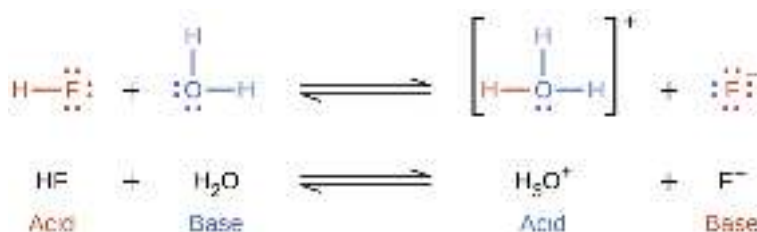
**Base ionization** of a species occurs when it accepts protons from water molecules. In the example below, pyridine molecules, $C_5NH_5$, undergo base ionization when dissolved in water, yielding hydroxide and pyridinium ions:
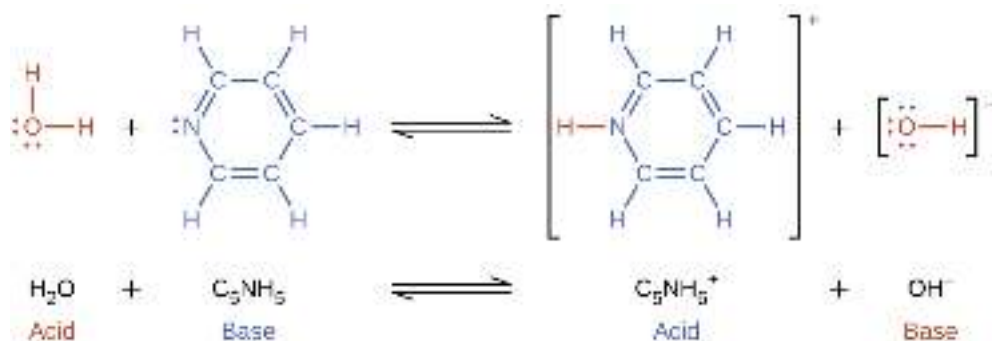


The preceding ionization reactions suggest that water may function as both a base (as in its reaction with hydrogen fluoride) and an acid (as in its reaction with ammonia). Species capable of either donating or accepting protons are called **amphiprotic**, or more generally, **amphoteric**, a term that may be used for acids and bases per definitions other than the Brønsted-Lowry one. The equations below show the two possible acid-base reactions for two amphiprotic species, bicarbonate ion and water:

$$HCO_3{}^-\left(aq\right) + H_2O(l) \qquad CO_3{}^{2-}\left(aq\right) + H_3O^+\left(aq\right)$$
$$HCO_3{}^-(aq) + H_2O(l) \qquad H_2CO_3(aq) + OH^-(aq)$$

The first equation represents the reaction of bicarbonate as an acid with water as a base, whereas the second represents reaction of bicarbonate as a base with water as an acid. When bicarbonate is added to water, both these equilibria are established simultaneously and the composition of the resulting solution may be determined through appropriate equilibrium calculations, as described later in this chapter.

In the liquid state, molecules of an amphiprotic substance can react with one another as illustrated for water in the equations below:
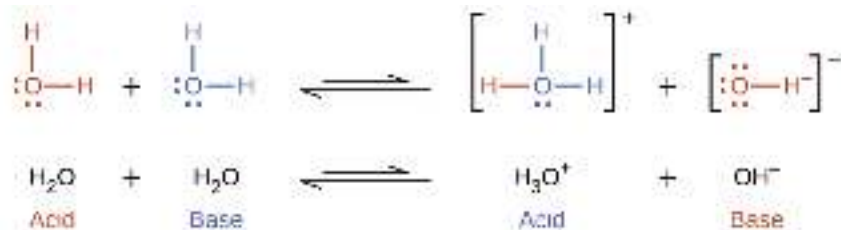


The process in which like molecules react to yield ions is called **autoionization**. Liquid water undergoes autoionization to a very slight extent; at 25 °C, approximately two out of every billion water molecules are ionized. The extent of the water autoionization process is reflected in the value of its equilibrium constant, the **ion-product constant for water, $K_w$**:

$$H_2O(l) + H_2O(l) \rightleftharpoons H_3O^+(aq) + OH^-(aq) \qquad\qquad K_w = [H_3O^+][OH^-]$$
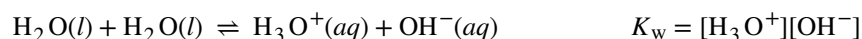
The slight ionization of pure water is reflected in the small value of the equilibrium constant; at 25 °C, $K_w$ has a value of $1.0 \times 10^{-14}$. The process is endothermic, and so the extent of ionization and the resulting concentrations of hydronium ion and hydroxide ion increase with temperature. For example, at 100 °C, the value for $K_w$ is about $5.6 \times$

$10^{-13}$, roughly 50 times larger than the value at 25 °C.

## Example 14.1

### Ion Concentrations in Pure Water

What are the hydronium ion concentration and the hydroxide ion concentration in pure water at 25 °C?

#### Solution

The autoionization of water yields the same number of hydronium and hydroxide ions. Therefore, in pure water, $[H_3O^+] = [OH^-] = x$. At 25 °C:

$$K_w = [H_3O^+][OH^-] = x = 1.0 \times 10^{-14}$$

So:

$$x = [H_3O^+] = [OH^-] = \sqrt{1.0 \times 10^{-14}} = 1.0 \times 10^{-7} \, M$$

The hydronium ion concentration and the hydroxide ion concentration are the same, $1.0 \times 10^{-7} \, M$.

#### Check Your Learning

The ion product of water at 80 °C is $2.4 \times 10^{-13}$. What are the concentrations of hydronium and hydroxide ions in pure water at 80 °C?
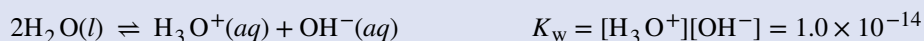
**Answer:** $[H_3O^+] = [OH^-] = 4.9 \times 10^{-7} \, M$

## Example 14.2

### The Inverse Relation between [H$_3$O$^+$] and [OH$^-$]

A solution of an acid in water has a hydronium ion concentration of $2.0 \times 10^{-6} \, M$. What is the concentration of hydroxide ion at 25 °C?

#### Solution

Use the value of the ion-product constant for water at 25 °C

$$2H_2O(l) \rightleftharpoons H_3O^+(aq) + OH^-(aq) \qquad K_w = [H_3O^+][OH^-] = 1.0 \times 10^{-14}$$

to calculate the missing equilibrium concentration.

Rearrangement of the $K_w$ expression shows that $[OH^-]$ is inversely proportional to $[H_3O^+]$:

$$[OH^-] = \frac{K_w}{[H_3O^+]} = \frac{1.0 \times 10^{-14}}{2.0 \times 10^{-6}} = 5.0 \times 10^{-9}$$

Compared with pure water, a solution of acid exhibits a higher concentration of hydronium ions (due to ionization of the acid) and a proportionally lower concentration of hydroxide ions. This may be explained via Le Châtelier's principle as a left shift in the water autoionization equilibrium resulting from the stress of increased hydronium ion concentration.

Substituting the ion concentrations into the $K_w$ expression confirms this calculation, resulting in the expected value:

$$K_w = [H_3O^+][OH^-] = (2.0 \times 10^{-6})(5.0 \times 10^{-9}) = 1.0 \times 10^{-14}$$
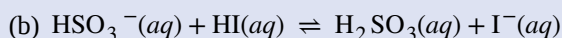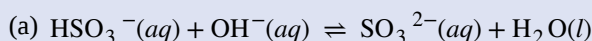
## Example 14.3

### Representing the Acid-Base Behavior of an Amphoteric Substance

Write separate equations representing the reaction of $HSO_3^-$

(a) as an acid with $OH^-$

(b) as a base with HI

**Solution**

(a) $HSO_3^-(aq) + OH^-(aq) \rightleftharpoons SO_3^{2-}(aq) + H_2O(l)$

(b) $HSO_3^-(aq) + HI(aq) \rightleftharpoons H_2SO_3(aq) + I^-(aq)$

**Check Your Learning**

Write separate equations representing the reaction of $H_2PO_4^-$

(a) as a base with HBr

(b) as an acid with $OH^-$

**Answer:**   (a) $H_2PO_4^-(aq) + HBr(aq) \rightleftharpoons H_3PO_4(aq) + Br^-(aq)$; (b)
$H_2PO_4^-(aq) + OH^-(aq) \rightleftharpoons HPO_4^{2-}(aq) + H_2O(l)$

# 14.2 pH and pOH

By the end of this section, you will be able to:

- Explain the characterization of aqueous solutions as acidic, basic, or neutral
- Express hydronium and hydroxide ion concentrations on the pH and pOH scales
- Perform calculations relating pH and pOH

As discussed earlier, hydronium and hydroxide ions are present both in pure water and in all aqueous solutions, and their concentrations are inversely proportional as determined by the ion product of water ($K_w$). The concentrations of these ions in a solution are often critical determinants of the solution's properties and the chemical behaviors of its other solutes, and specific vocabulary has been developed to describe these concentrations in relative terms. A solution is **neutral** if it contains equal concentrations of hydronium and hydroxide ions; **acidic** if it contains a greater concentration of hydronium ions than hydroxide ions; and **basic** if it contains a lesser concentration of hydronium ions than hydroxide ions.

A common means of expressing quantities that may span many orders of magnitude is to use a logarithmic scale. One such scale that is very popular for chemical concentrations and equilibrium constants is based on the p-function, defined as shown where "X" is the quantity of interest and "log" is the base-10 logarithm:

$$pX = -\log X$$

The **pH** of a solution is therefore defined as shown here, where $[H_3O^+]$ is the molar concentration of hydronium ion in the solution:

$$pH = -\log[H_3O^+]$$

Rearranging this equation to isolate the hydronium ion molarity yields the equivalent expression:

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

Likewise, the hydroxide ion molarity may be expressed as a p-function, or **pOH**:

$$pOH = -\log[OH^-]$$

or

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

Finally, the relation between these two ion concentration expressed as p-functions is easily derived from the $K_w$ expression:

$$K_w = [H_3O^+][OH^-]$$
$$-\log K_w = -\log([H_3O^+][OH^-]) = -\log[H_3O^+] + -\log[OH^-]$$
$$pK_w = pH + pOH$$

At 25 °C, the value of $K_w$ is $1.0 \times 10^{-14}$, and so:

$$14.00 = pH + pOH$$

As was shown in **Example 14.1**, the hydronium ion molarity in pure water (or any neutral solution) is $1.0 \times 10^{-7}$ $M$ at 25 °C. The pH and pOH of a neutral solution at this temperature are therefore:

$$pH = -\log[H_3O^+] = -\log(1.0 \times 10^{-7}) = 7.00$$
$$pOH = -\log[OH^-] = -\log(1.0 \times 10^{-7}) = 7.00$$

And so, *at this temperature*, acidic solutions are those with hydronium ion molarities greater than $1.0 \times 10^{-7}$ $M$ and hydroxide ion molarities less than $1.0 \times 10^{-7}$ $M$ (corresponding to pH values less than 7.00 and pOH values greater than 7.00). Basic solutions are those with hydronium ion molarities less than $1.0 \times 10^{-7}$ $M$ and hydroxide ion molarities greater than $1.0 \times 10^{-7}$ $M$ (corresponding to pH values greater than 7.00 and pOH values less than 7.00).

Since the autoionization constant $K_w$ is temperature dependent, these correlations between pH values and the acidic/neutral/basic adjectives will be different at temperatures other than 25 °C. For example, the "Check Your Learning" exercise accompanying **Example 14.1** showed the hydronium molarity of pure water at 80 °C is $4.9 \times 10^{-7}$ $M$, which corresponds to pH and pOH values of:

$$pH = -\log[H_3O^+] = -\log(4.9 \times 10^{-7}) = 6.31$$
$$pOH = -\log[OH^-] = -\log(4.9 \times 10^{-7}) = 6.31$$

At this temperature, then, neutral solutions exhibit pH = pOH = 6.31, acidic solutions exhibit pH less than 6.31 and pOH greater than 6.31, whereas basic solutions exhibit pH greater than 6.31 and pOH less than 6.31. This distinction can be important when studying certain processes that occur at other temperatures, such as enzyme reactions in warm-blooded organisms at a temperature around 36–40 °C. Unless otherwise noted, references to pH values are presumed to be those at 25 °C (**Table 14.1**).

### Summary of Relations for Acidic, Basic and Neutral Solutions

| Classification | Relative Ion Concentrations | pH at 25 °C |
|---|---|---|
| acidic | $[H_3O^+] > [OH^-]$ | pH < 7 |
| neutral | $[H_3O^+] = [OH^-]$ | pH = 7 |
| basic | $[H_3O^+] < [OH^-]$ | pH > 7 |

**Table 14.1**

**Figure 14.2** shows the relationships between $[H_3O^+]$, $[OH^-]$, pH, and pOH for solutions classified as acidic, basic, and neutral.

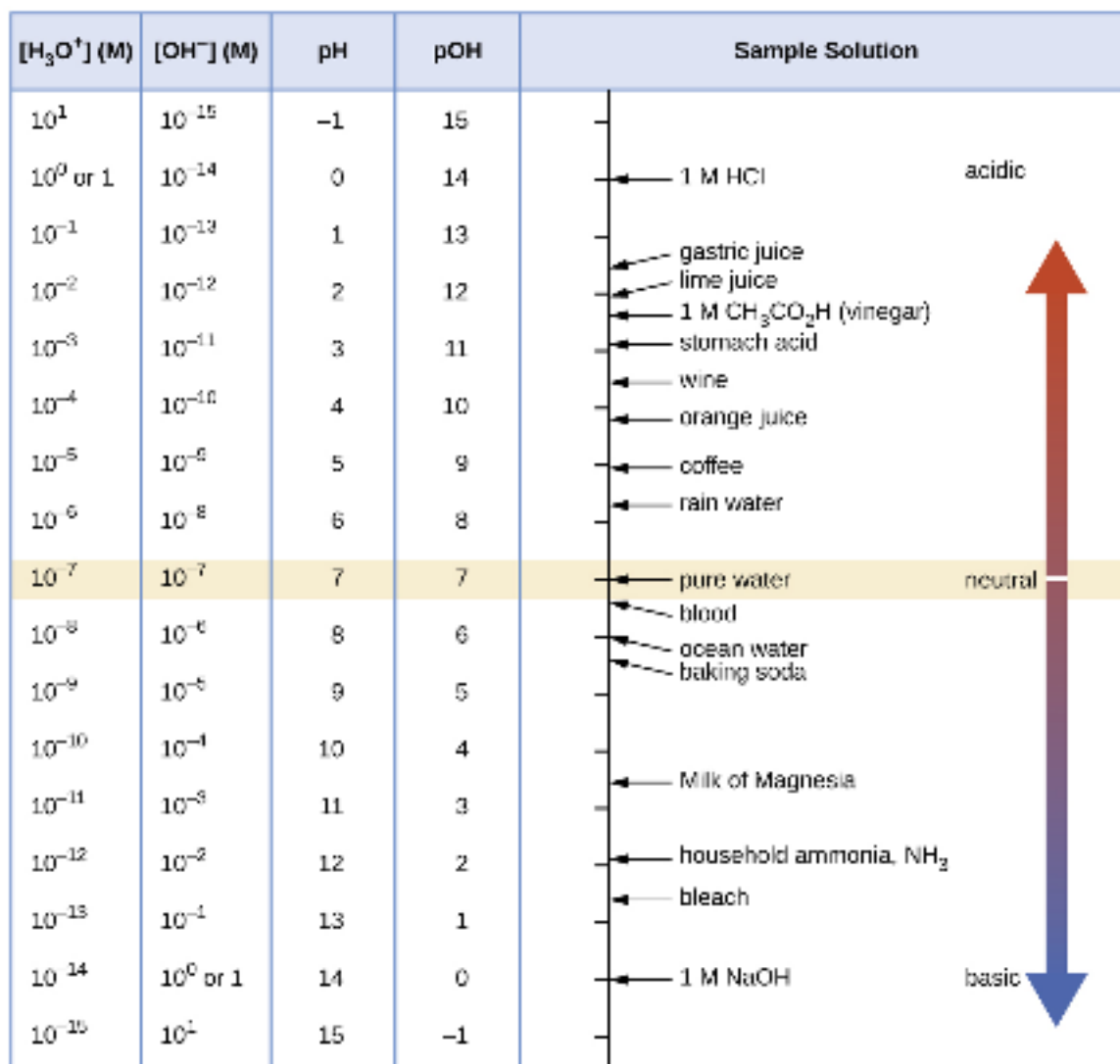| $[H_3O^+]$ (M) | $[OH^-]$ (M) | pH | pOH | Sample Solution |
|---|---|---|---|---|
| $10^1$ | $10^{-15}$ | −1 | 15 | |
| $10^0$ or 1 | $10^{-14}$ | 0 | 14 | 1 M HCl — acidic |
| $10^{-1}$ | $10^{-13}$ | 1 | 13 | gastric juice |
| $10^{-2}$ | $10^{-12}$ | 2 | 12 | lime juice; 1 M CH₃CO₂H (vinegar) |
| $10^{-3}$ | $10^{-11}$ | 3 | 11 | stomach acid |
| $10^{-4}$ | $10^{-10}$ | 4 | 10 | wine; orange juice |
| $10^{-5}$ | $10^{-9}$ | 5 | 9 | coffee |
| $10^{-6}$ | $10^{-8}$ | 6 | 8 | rain water |
| $10^{-7}$ | $10^{-7}$ | 7 | 7 | pure water — neutral |
| $10^{-8}$ | $10^{-6}$ | 8 | 6 | blood |
| $10^{-9}$ | $10^{-5}$ | 9 | 5 | ocean water; baking soda |
| $10^{-10}$ | $10^{-4}$ | 10 | 4 | |
| $10^{-11}$ | $10^{-3}$ | 11 | 3 | Milk of Magnesia |
| $10^{-12}$ | $10^{-2}$ | 12 | 2 | household ammonia, NH₃ |
| $10^{-13}$ | $10^{-1}$ | 13 | 1 | bleach |
| $10^{-14}$ | $10^0$ or 1 | 14 | 0 | 1 M NaOH — basic |
| $10^{-15}$ | $10^1$ | 15 | −1 | |

**Figure 14.2** The pH and pOH scales represent concentrations of $H_3O^+$ and $OH^-$, respectively. The pH and pOH values of some common substances at 25 °C are shown in this chart.

## Example 14.4

### Calculation of pH from $[H_3O^+]$

What is the pH of stomach acid, a solution of HCl with a hydronium ion concentration of $1.2 \times 10^{-3}$ M?

**Solution**

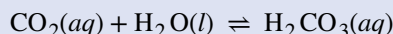$$pH = -\log[H_3O^+]$$
$$= -\log(1.2 \times 10^{-3})$$
$$= -(-2.92) = 2.92$$

(The use of logarithms is explained in **Appendix B**. When taking the log of a value, keep as many decimal places in the result as there are significant figures in the value.)

### Check Your Learning

Water exposed to air contains carbonic acid, $H_2CO_3$, due to the reaction between carbon dioxide and water:

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

Air-saturated water has a hydronium ion concentration caused by the dissolved $CO_2$ of $2.0 \times 10^{-6}\ M$, about 20-times larger than that of pure water. Calculate the pH of the solution at 25 °C.

**Answer:** 5.70

## Example 14.5

### Calculation of Hydronium Ion Concentration from pH

Calculate the hydronium ion concentration of blood, the pH of which is 7.3.

### Solution

$$pH = -\log[H_3O^+] = 7.3$$

$$\log[H_3O^+] = -7.3$$

$$[H_3O^+] = 10^{-7.3}\ \text{or}\ [H_3O^+] = \text{antilog of } -7.3$$

$$[H_3O^+] = 5 \times 10^{-8}\ M$$

(On a calculator take the antilog, or the "inverse" log, of −7.3, or calculate $10^{-7.3}$.)

### Check Your Learning

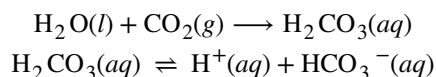Calculate the hydronium ion concentration of a solution with a pH of −1.07.

**Answer:** 12 $M$

## How Sciences Interconnect

### Environmental Science

Normal rainwater has a pH between 5 and 6 due to the presence of dissolved $CO_2$ which forms carbonic acid:

$$H_2O(l) + CO_2(g) \longrightarrow H_2CO_3(aq)$$
$$H_2CO_3(aq) \rightleftharpoons H^+(aq) + HCO_3{}^-(aq)$$

Acid rain is rainwater that has a pH of less than 5, due to a variety of nonmetal oxides, including $CO_2$, $SO_2$, $SO_3$, NO, and $NO_2$ being dissolved in the water and reacting with it to form not only carbonic acid, but sulfuric acid and nitric acid. The formation and subsequent ionization of sulfuric acid are shown here:

$$H_2O(l) + SO_3(g) \longrightarrow H_2SO_4(aq)$$
$$H_2SO_4(aq) \longrightarrow H^+(aq) + HSO_4{}^-(aq)$$
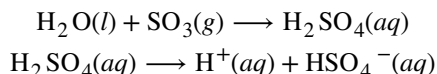
Carbon dioxide is naturally present in the atmosphere because most organisms produce it as a waste product of metabolism. Carbon dioxide is also formed when fires release carbon stored in vegetation or fossil fuels. Sulfur trioxide in the atmosphere is naturally produced by volcanic activity, but it also originates from burning fossil fuels, which have traces of sulfur, and from the process of "roasting" ores of metal sulfides in metal-

refining processes. Oxides of nitrogen are formed in internal combustion engines where the high temperatures make it possible for the nitrogen and oxygen in air to chemically combine.

Acid rain is a particular problem in industrial areas where the products of combustion and smelting are released into the air without being stripped of sulfur and nitrogen oxides. In North America and Europe until the 1980s, it was responsible for the destruction of forests and freshwater lakes, when the acidity of the rain actually killed trees, damaged soil, and made lakes uninhabitable for all but the most acid-tolerant species. Acid rain also corrodes statuary and building facades that are made of marble and limestone (**Figure 14.3**). Regulations limiting the amount of sulfur and nitrogen oxides that can be released into the atmosphere by industry and automobiles have reduced the severity of acid damage to both natural and manmade environments in North America and Europe. It is now a growing problem in industrial areas of China and India.

For further information on acid rain, visit this **website (http://openstaxcollege.org/l/16EPA)** hosted by the US Environmental Protection Agency.



**Figure 14.3**  (a) Acid rain makes trees more susceptible to drought and insect infestation, and depletes nutrients in the soil. (b) It also is corrodes statues that are carved from marble or limestone. (credit a: modification of work by Chris M Morris; credit b: modification of work by "Eden, Janine and Jim"/Flickr)

## Example 14.6

### Calculation of pOH

What are the pOH and the pH of a 0.0125-$M$ solution of potassium hydroxide, KOH?

**Solution**

Potassium hydroxide is a highly soluble ionic compound and completely dissociates when dissolved in dilute solution, yielding $[OH^-] = 0.0125\ M$:

$$pOH = -\log[OH^-] = -\log 0.0125$$
$$= -(-1.903) = 1.903$$

The pH can be found from the pOH:

$$pH + pOH = 14.00$$
$$pH = 14.00 - pOH = 14.00 - 1.903 = 12.10$$

> **Check Your Learning**
>
> The hydronium ion concentration of vinegar is approximately $4 \times 10^{-3}$ $M$. What are the corresponding values of pOH and pH?
>
> **Answer:**  pOH = 11.6, pH = 2.4

The acidity of a solution is typically assessed experimentally by measurement of its pH. The pOH of a solution is not usually measured, as it is easily calculated from an experimentally determined pH value. The pH of a solution can be directly measured using a pH meter (**Figure 14.4**).
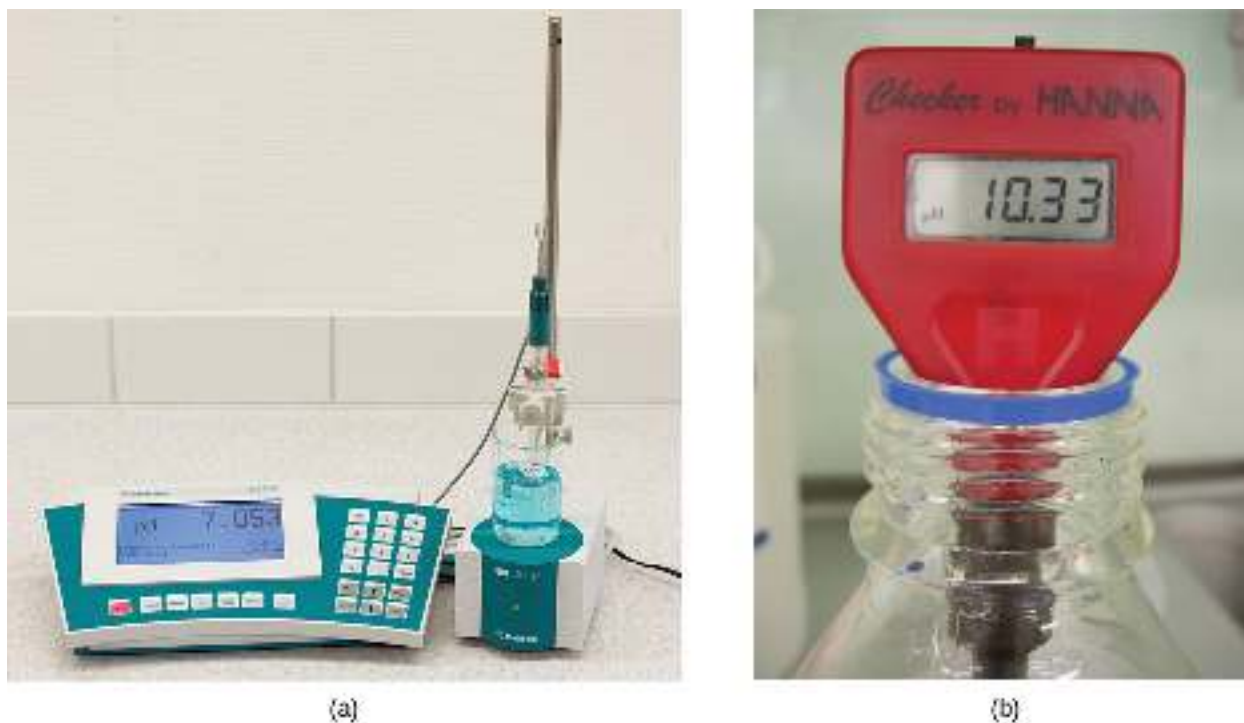


(a)                                                            (b)

**Figure 14.4**   (a) A research-grade pH meter used in a laboratory can have a resolution of 0.001 pH units, an accuracy of ± 0.002 pH units, and may cost in excess of $1000. (b) A portable pH meter has lower resolution (0.01 pH units), lower accuracy (± 0.2 pH units), and a far lower price tag. (credit b: modification of work by Jacopo Werther)

The pH of a solution may also be visually estimated using colored indicators (**Figure 14.5**). The acid-base equilibria that enable use of these indicator dyes for pH measurements are described in a later section of this chapter.

**Figure 14.5** (a) A solution containing a dye mixture, called universal indicator, takes on different colors depending upon its pH. (b) Convenient test strips, called pH paper, contain embedded indicator dyes that yield pH-dependent color changes on contact with aqueous solutions.(credit: modification of work by Sahar Atwa)

# 14.3 Relative Strengths of Acids and Bases

By the end of this section, you will be able to:

- Assess the relative strengths of acids and bases according to their ionization constants
- Rationalize trends in acid–base strength in relation to molecular structure
- Carry out equilibrium calculations for weak acid–base systems

## Acid and Base Ionization Constants

The relative strength of an acid or base is the extent to which it ionizes when dissolved in water. If the ionization reaction is essentially complete, the acid or base is termed *strong*; if relatively little ionization occurs, the acid or base is weak. As will be evident throughout the remainder of this chapter, there are many more weak acids and bases than strong ones. The most common strong acids and bases are listed in **Figure 14.6**.



| 6 Strong Acids | | 6 Strong Bases | |
|---|---|---|---|
| $HClO_4$ | perchloric acid | LiOH | lithium hydroxide |
| HCl | hydrochloric acid | NaOH | sodium hydroxide |
| HBr | hydrobromic acid | KOH | potassium hydroxide |
| HI | hydroiodic acid | $Ca(OH)_2$ | calcium hydroxide |
| $HNO_3$ | nitric acid | $Sr(OH)_2$ | strontium hydroxide |
| $H_2SO_4$ | sulfuric acid | $Ba(OH)_2$ | barium hydroxide |

**Figure 14.6** Some of the common strong acids and bases are listed here.

The relative strengths of acids may be quantified by measuring their equilibrium constants in aqueous solutions. In solutions of the same concentration, stronger acids ionize to a greater extent, and so yield higher concentrations of

hydronium ions than do weaker acids. The equilibrium constant for an acid is called the **acid-ionization constant,**
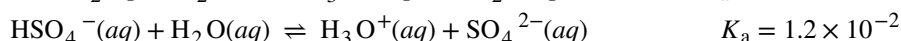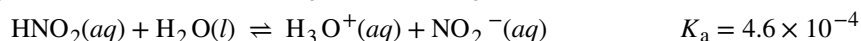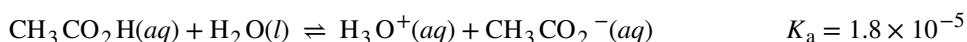$K_a$. For the reaction of an acid HA:

$$HA(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + A^-(aq),$$
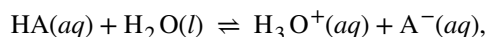
the acid ionization constant is written

$$K_a = \frac{[H_3O^+][A^-]}{[HA]}$$

where the concentrations are those at equilibrium. Although water is a reactant in the reaction, it is the solvent as well,
so we do not include $[H_2O]$ in the equation. The larger the $K_a$ of an acid, the larger the concentration of $H_3O^+$ and
$A^-$ relative to the concentration of the nonionized acid, HA, in an equilibrium mixture, and the stronger the acid. An
acid is classified as "strong" when it undergoes complete ionization, in which case the concentration of HA is zero
and the acid ionization constant is immeasurably large ($K_a \approx \infty$). Acids that are partially ionized are called "weak,"
and their acid ionization constants may be experimentally measured. A table of ionization constants for weak acids is
provided in **Appendix H**.

To illustrate this idea, three acid ionization equations and $K_a$ values are shown below. The ionization constants
increase from first to last of the listed equations, indicating the relative acid strength increases in the order $CH_3CO_2H$
$< HNO_2 < HSO_4^-$ :

$$CH_3CO_2H(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + CH_3CO_2^-(aq) \qquad K_a = 1.8 \times 10^{-5}$$
$$HNO_2(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + NO_2^-(aq) \qquad K_a = 4.6 \times 10^{-4}$$
$$HSO_4^-(aq) + H_2O(aq) \rightleftharpoons H_3O^+(aq) + SO_4^{2-}(aq) \qquad K_a = 1.2 \times 10^{-2}$$

Another measure of the strength of an acid is its percent ionization. The **percent ionization** of a weak acid is defined
in terms of the composition of an equilibrium mixture:

$$\% \text{ ionization} = \frac{[H_3O^+]_{eq}}{[HA]_0} \times 100$$

where the numerator is equivalent to the concentration of the acid's conjugate base (per stoichiometry, $[A^-] = [H_3O^+]$).
Unlike the $K_a$ value, the percent ionization of a weak acid varies with the initial concentration of acid, typically
decreasing as concentration increases. Equilibrium calculations of the sort described later in this chapter can be used
to confirm this behavior.

## Example 14.7

### Calculation of Percent Ionization from pH

Calculate the percent ionization of a 0.125-*M* solution of nitrous acid (a weak acid), with a pH of 2.09.

**Solution**

The percent ionization for an acid is:

$$\frac{[H_3O^+]_{eq}}{[HNO_2]_0} \times 100$$

Converting the provided pH to hydronium ion molarity yields

$$[H_3O^+] = 10^{-2.09} = 0.0081 \ M$$

Substituting this value and the provided initial acid concentration into the percent ionization equation gives

$$\frac{8.1 \times 10^{-3}}{0.125} \times 100 = 6.5\%$$

(Recall the provided pH value of 2.09 is logarithmic, and so it contains just two significant digits, limiting the certainty of the computed percent ionization.)

**Check Your Learning**

Calculate the percent ionization of a 0.10-$M$ solution of acetic acid with a pH of 2.89.

**Answer:** 1.3% ionized

**Link to Learning**

View the **simulation (http://openstaxcollege.org/l/16AcidBase)** of strong and weak acids and bases at the molecular level.
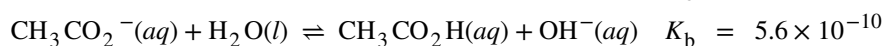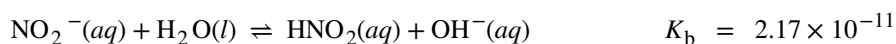
Just as for acids, the relative strength of a base is reflected in the magnitude of its **base-ionization constant ($K_b$)** in aqueous solutions. In solutions of the same concentration, stronger bases ionize to a greater extent, and so yield higher hydroxide ion concentrations than do weaker bases. A stronger base has a larger ionization constant than does a weaker base. For the reaction of a base, B:

$$B(aq) + H_2O(l) \rightleftharpoons HB^+(aq) + OH^-(aq),$$
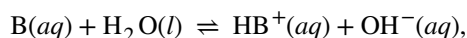
the ionization constant is written as

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

Inspection of the data for three weak bases presented below shows the base strength increases in the order $NO_2^- < CH_2CO_2^- < NH_3$.

$$NO_2^-(aq) + H_2O(l) \rightleftharpoons HNO_2(aq) + OH^-(aq) \qquad K_b = 2.17 \times 10^{-11}$$

$$CH_3CO_2^-(aq) + H_2O(l) \rightleftharpoons CH_3CO_2H(aq) + OH^-(aq) \quad K_b = 5.6 \times 10^{-10}$$

$$NH_3(aq) + H_2O(l) \rightleftharpoons NH_4^+(aq) + OH^-(aq) \qquad K_b = 1.8 \times 10^{-5}$$
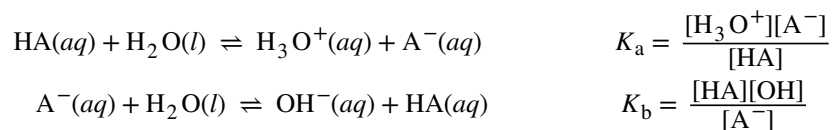
A table of ionization constants for weak bases appears in **Appendix I**. As for acids, the relative strength of a base is also reflected in its percent ionization, computed as

$$\% \text{ ionization} = [OH^-]_{eq}/[B]_0 \times 100\%$$

but will vary depending on the base ionization constant and the initial concentration of the solution.

## Relative Strengths of Conjugate Acid-Base Pairs

Brønsted-Lowry acid-base chemistry is the transfer of protons; thus, logic suggests a relation between the relative strengths of conjugate acid-base pairs. The strength of an acid or base is quantified in its ionization constant, $K_a$ or $K_b$, which represents the extent of the acid or base ionization reaction. For the conjugate acid-base pair HA / A$^-$, ionization equilibrium equations and ionization constant expressions are

$$HA(aq) + H_2O(l) \;\rightleftharpoons\; H_3O^+(aq) + A^-(aq) \qquad\qquad K_a = \frac{[H_3O^+][A^-]}{[HA]}$$

$$A^-(aq) + H_2O(l) \;\rightleftharpoons\; OH^-(aq) + HA(aq) \qquad\qquad K_b = \frac{[HA][OH]}{[A^-]}$$

Adding these two chemical equations yields the equation for the autoionization for water:

$$\cancel{HA(aq)} + H_2O(l) + \cancel{A^-(aq)} + H_2O(l) \;\rightleftharpoons\; H_3O^+(aq) + \cancel{A^-(aq)} + OH^-(aq) + \cancel{HA(aq)}$$

$$2H_2O(l) \;\rightleftharpoons\; H_3O^+(aq) + OH^-(aq)$$
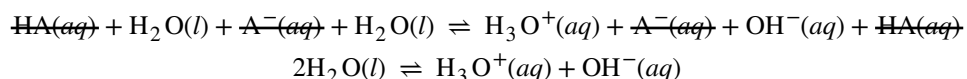
As discussed in another chapter on equilibrium, the equilibrium constant for a summed reaction is equal to the mathematical product of the equilibrium constants for the added reactions, and so

$$K_a \times K_b = \frac{[H_3O^+][A^-]}{[HA]} \times \frac{[HA][OH^-]}{[A^-]} = [H_3O^+][OH^-] = K_w$$

This equation states the relation between ionization constants for any conjugate acid-base pair, namely, their mathematical product is equal to the ion product of water, $K_w$. By rearranging this equation, a reciprocal relation between the strengths of a conjugate acid-base pair becomes evident:

$$K_a = K_w/K_b \text{ or } K_b = K_w/K_a$$

The inverse proportional relation between $K_a$ and $K_b$ means *the stronger the acid or base, the weaker its conjugate partner*. **Figure 14.7** illustrates this relation for several conjugate acid-base pairs.
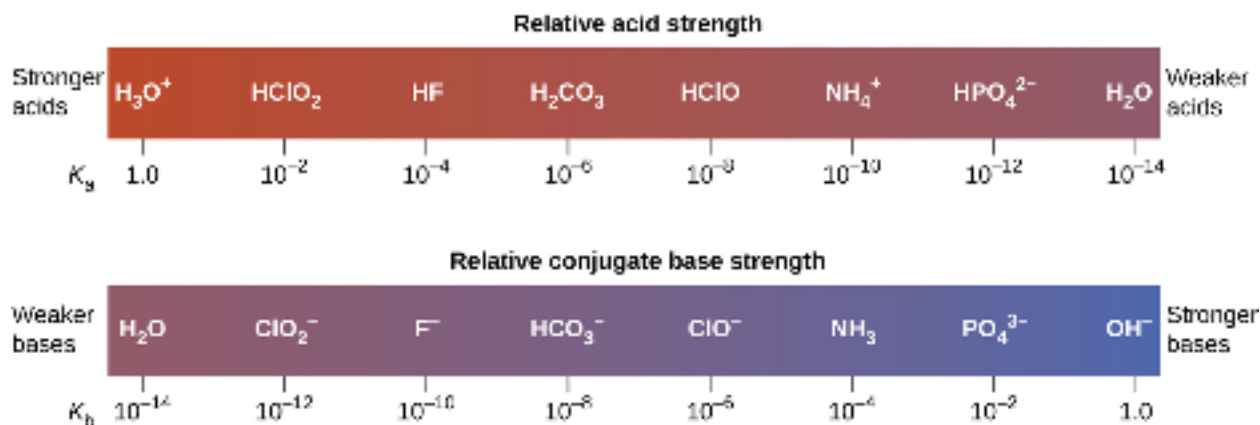


**Figure 14.7** Relative strengths of several conjugate acid-base pairs are shown.

| Acid | | | | | | Base | |
|---|---|---|---|---|---|---|---|
| perchloric acid | $HClO_4$ | | | | | $ClO_4^-$ | perchlorate ion |
| sulfuric acid | $H_2SO_4$ | Undergo complete acid ionization in water | Do not undergo base ionization in water | | | $HSO_4^-$ | hydrogen sulfate ion |
| hydrogen iodide | HI | | | | | $I^-$ | iodide ion |
| hydrogen bromide | HBr | | | | | $Br^-$ | bromide ion |
| hydrogen chloride | HCl | | | | | $Cl^-$ | chloride ion |
| nitric acid | $HNO_3$ | | | | | $NO_3^-$ | nitrate ion |
| hydronium ion | $H_3O^+$ | | | | | $H_2O$ | water |
| hydrogen sulfate ion | $HSO_4^-$ | | | | | $SO_4^{2-}$ | sulfate ion |
| phosphoric acid | $H_3PO_4$ | | | | | $H_2PO_4^-$ | dihydrogen phosphate ion |
| hydrogen fluoride | HF | | | | | $F^-$ | fluoride ion |
| nitrous acid | $HNO_2$ | | | | | $NO_2^-$ | nitrite ion |
| acetic acid | $CH_3CO_2H$ | | | | | $CH_3CO_2^-$ | acetate ion |
| carbonic acid | $H_2CO_3$ | | | | | $HCO_3^-$ | hydrogen carbonate ion |
| hydrogen sulfide | $H_2S$ | | | | | $HS^-$ | hydrogen sulfide ion |
| ammonium ion | $NH_4^+$ | | | | | $NH_3$ | ammonia |
| hydrogen cyanide | HCN | | | | | $CN^-$ | cyanide ion |
| hydrogen carbonate ion | $HCO_3^-$ | | | | | $CO_3^{2-}$ | carbonate ion |
| water | $H_2O$ | | | | | $OH^-$ | hydroxide ion |
| hydrogen sulfide ion | $HS^-$ | Do not undergo acid ionization in water | Undergo complete base ionization in water | | | $S^{2-}$ | sulfide ion |
| ethanol | $C_2H_5OH$ | | | | | $C_2H_5O^-$ | ethoxide ion |
| ammonia | $NH_3$ | | | | | $NH_2^-$ | amide ion |
| hydrogen | $H_2$ | | | | | $H^-$ | hydride ion |
| methane | $CH_4$ | | | | | $CH_3^-$ | methide ion |

*Increasing acid strength* (left column arrow upward) — *Increasing base strength* (right column arrow downward)

**Figure 14.8**   This figure shows strengths of conjugate acid-base pairs relative to the strength of water as the reference substance.

The listing of conjugate acid–base pairs shown in **Figure 14.8** is arranged to show the relative strength of each species as compared with water, whose entries are highlighted in each of the table's columns. In the acid column, those species listed below water are weaker acids than water. These species do not undergo acid ionization in water; they are not Bronsted-Lowry acids. All the species listed above water are stronger acids, transferring protons to water to some extent when dissolved in an aqueous solution to generate hydronium ions. Species above water but below hydronium ion are *weak acids*, undergoing partial acid ionization, wheres those above hydronium ion are *strong acids* that are completely ionized in aqueous solution.

If all these strong acids are completely ionized in water, why does the column indicate they vary in strength, with nitric acid being the weakest and perchloric acid the strongest? Notice that the sole acid species present in an aqueous solution of any strong acid is $H_3O^+(aq)$, meaning that hydronium ion is the strongest acid that may exist in water; any stronger acid will react completely with water to generate hydronium ions. This limit on the acid strength of solutes in a solution is called a **leveling effect**. To measure the differences in acid strength for "strong" acids, the acids must be dissolved in a solvent that is *less basic* than water. In such solvents, the acids will be "weak," and so any differences in the extent of their ionization can be determined. For example, the binary hydrogen halides HCl, HBr, and HI are

strong acids in water but weak acids in ethanol (strength increasing HCl < HBr < HI).

The right column of **Figure 14.8** lists a number of substances in order of increasing base strength from top to bottom. Following the same logic as for the left column, species listed above water are weaker bases and so they don't undergo base ionization when dissolved in water. Species listed between water and its conjugate base, hydroxide ion, are weak bases that partially ionize. Species listed below hydroxide ion are strong bases that completely ionize in water to yield hydroxide ions (i.e., they are *leveled* to hydroxide). A comparison of the acid and base columns in this table supports the reciprocal relation between the strengths of conjugate acid-base pairs. For example, the conjugate bases of the strong acids (top of table) are all of negligible strength. A strong acid exhibits an immeasurably large $K_a$, and so its conjugate base will exhibit a $K_b$ that is essentially zero:

strong acid :           $K_a \approx \infty$

conjugate base :  $K_b = K_w/K_a = K_w/\infty \approx 0$

A similar approach can be used to support the observation that conjugate acids of strong bases ($K_b \approx \infty$) are of negligible strength ($K_a \approx 0$).

## Example 14.8

### Calculating Ionization Constants for Conjugate Acid-Base Pairs

Use the $K_b$ for the nitrite ion, $NO_2^-$, to calculate the $K_a$ for its conjugate acid.

### Solution

$K_b$ for $NO_2^-$ is given in this section as $2.17 \times 10^{-11}$. The conjugate acid of $NO_2^-$ is $HNO_2$; $K_a$ for $HNO_2$ can be calculated using the relationship:

$$K_a \times K_b = 1.0 \times 10^{-14} = K_w$$

Solving for $K_a$ yields

$$K_a = \frac{K_w}{K_b} = \frac{1.0 \times 10^{-14}}{2.17 \times 10^{-11}} = 4.6 \times 10^{-4}$$

This answer can be verified by finding the $K_a$ for $HNO_2$ in **Appendix H**.

### Check Your Learning

Determine the relative acid strengths of $NH_4^+$ and HCN by comparing their ionization constants. The ionization constant of HCN is given in **Appendix H** as $4.9 \times 10^{-10}$. The ionization constant of $NH_4^+$ is not listed, but the ionization constant of its conjugate base, $NH_3$, is listed as $1.8 \times 10^{-5}$.

**Answer:**   $NH_4^+$ is the slightly stronger acid ($K_a$ for $NH_4^+ = 5.6 \times 10^{-10}$).

## Acid-Base Equilibrium Calculations

The chapter on chemical equilibria introduced several types of equilibrium calculations and the various mathematical strategies that are helpful in performing them. These strategies are generally useful for equilibrium systems regardless of chemical reaction class, and so they may be effectively applied to acid-base equilibrium problems. This section presents several example exercises involving equilibrium calculations for acid-base systems.

## Example 14.9

### Determination of $K_a$ from Equilibrium Concentrations

Acetic acid is the principal ingredient in vinegar (**Figure 14.9**) that provides its sour taste. At equilibrium, a solution contains $[CH_3CO_2H] = 0.0787 \ M$ and $[H_3O^+] = [CH_3CO_2^-] = 0.00118 \ M.$ What is the value of $K_a$ for acetic acid?

**Figure 14.9** Vinegar contains acetic acid, a weak acid. (credit: modification of work by "HomeSpot HQ"/Flickr)

**Solution**

The relevant equilibrium equation and its equilibrium constant expression are shown below. Substitution of the provided equilibrium concentrations permits a straightforward calculation of the $K_a$ for acetic acid.

$$CH_3CO_2H(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + CH_3CO_2^-(aq)$$

$$K_a = \frac{[H_3O^+][CH_3CO_2^-]}{[CH_3CO_2H]} = \frac{(0.00118)(0.00118)}{0.0787} = 1.77 \times 10^{-5}$$

**Check Your Learning**

The $HSO_4^-$ ion, weak acid used in some household cleansers:

$$HSO_4^-(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + SO_4^{2-}(aq)$$
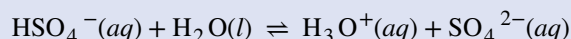
What is the acid ionization constant for this weak acid if an equilibrium mixture has the following composition: $[H_3O^+] = 0.027\ M$; $[HSO_4^-] = 0.29\ M$; and $[SO_4^{2-}] = 0.13\ M$?

**Answer:** $K_a$ for $HSO_4^- = 1.2 \times 10^{-2}$

## Example 14.10

### Determination of $K_b$ from Equilibrium Concentrations

Caffeine, $C_8H_{10}N_4O_2$ is a weak base. What is the value of $K_b$ for caffeine if a solution at equilibrium has $[C_8H_{10}N_4O_2] = 0.050\ M$, $[C_8H_{10}N_4O_2H^+] = 5.0 \times 10^{-3}\ M$, and $[OH^-] = 2.5 \times 10^{-3}\ M$?
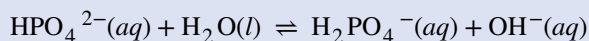
**Solution**

The relevant equilibrium equation and its equilibrium constant expression are shown below. Substitution of the provided equilibrium concentrations permits a straightforward calculation of the $K_b$ for caffeine.

$$C_8H_{10}N_4O_2(aq) + H_2O(l) \rightleftharpoons C_8H_{10}N_4O_2H^+(aq) + OH^-(aq)$$

$$K_b = \frac{[C_8H_{10}N_4O_2H^+][OH^-]}{[C_8H_{10}N_4O_2]} = \frac{(5.0 \times 10^{-3})(2.5 \times 10^{-3})}{0.050} = 2.5 \times 10^{-4}$$

**Check Your Learning**

What is the equilibrium constant for the ionization of the $HPO_4{}^{2-}$ ion, a weak base

$$HPO_4{}^{2-}(aq) + H_2O(l) \rightleftharpoons H_2PO_4{}^-(aq) + OH^-(aq)$$

if the composition of an equilibrium mixture is as follows: $[OH^-] = 1.3 \times 10^{-6}\ M$; $[H_2PO_4{}^-] = 0.042\ M$; and $[HPO_4{}^{2-}] = 0.341\ M$?

**Answer:** $K_b$ for $HPO_4{}^{2-} = 1.6 \times 10^{-7}$

## Example 14.11

## Determination of $K_a$ or $K_b$ from pH

The pH of a 0.0516-*M* solution of nitrous acid, $HNO_2$, is 2.34. What is its $K_a$?

$$HNO_2(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + NO_2{}^-(aq)$$
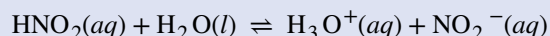
**Solution**

The nitrous acid concentration provided is a *formal* concentration, one that does not account for any chemical equilibria that may be established in solution. Such concentrations are treated as "initial" values for equilibrium calculations using the ICE table approach. Notice the initial value of hydronium ion is listed as *approximately* zero because a small concentration of $H_3O^+$ is present ($1 \times 10^{-7}\ M$) due to the autoprotolysis of water. In many cases, such as all the ones presented in this chapter, this concentration is much less than that generated by ionization of the acid (or base) in question and may be neglected.

The pH provided is a logarithmic measure of the hydronium ion concentration resulting from the acid ionization of the nitrous acid, and so it represents an "equilibrium" value for the ICE table:

$$[H_3O^+] = 10^{-2.34} = 0.0046\ M$$

The ICE table for this system is then

| | HNO₂ + | H₂O ⇌ H₃O⁺ | + NO₂⁻ |
|---|---|---|---|
| Initial concentration (M) | 0.0516 | ~0 | 0 |
| Change (M) | −0.0046 | +0.0046 | +0.0046 |
| Equilibrium concentration (M) | 0.0470 | 0.0046 | 0.0046 |

Finally, calculate the value of the equilibrium constant using the data in the table:

$$K_a = \frac{[H_3O^+][NO_2{}^-]}{[HNO_2]} = \frac{(0.0046)(0.0046)}{(0.0470)} = 4.6 \times 10^{-4}$$

**Check Your Learning.**

The pH of a solution of household ammonia, a 0.950-*M* solution of $NH_3$, is 11.612. What is $K_b$ for $NH_3$.

**Answer:** $K_b = 1.8 \times 10^{-5}$

## Example 14.12

### Calculating Equilibrium Concentrations in a Weak Acid Solution

Formic acid, $HCO_2H$, is one irritant that causes the body's reaction to some ant bites and stings (**Figure 14.10**).



**Figure 14.10**   The pain of some ant bites and stings is caused by formic acid. (credit: John Tann)

What is the concentration of hydronium ion and the pH of a 0.534-$M$ solution of formic acid?

$$HCO_2H(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + HCO_2{}^-(aq) \qquad K_a = 1.8 \times 10^{-4}$$
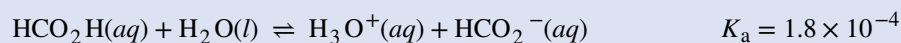
**Solution**

The ICE table for this system is

|  | $HCO_2H$ | + | $H_2O$ | $\rightleftharpoons$ | $H_3O^+$ | + | $HCO_2{}^-$ |
|---|---|---|---|---|---|---|---|
| Initial concentration ($M$) | 0.534 |  |  |  | ~0 |  | 0 |
| Change ($M$) |  |  |  |  | +$x$ |  | +$x$ |
| Equilibrium concentration ($M$) | 0.534 $-x$ |  |  |  | $x$ |  | $x$ |

Substituting the equilibrium concentration terms into the $K_a$ expression gives

$$K_a = 1.8 \times 10^{-4} = \frac{[H_3O^+][HCO_2{}^-]}{[HCO_2H]}$$

$$= \frac{(x)(x)}{0.534 - x} = 1.8 \times 10^{-4}$$

The relatively large initial concentration and small equilibrium constant permits the simplifying assumption that $x$ will be much lesser than 0.534, and so the equation becomes

$$K_a = 1.8 \times 10^{-4} = \frac{x^2}{0.534}$$

Solving the equation for $x$ yields

$$x^2 = 0.534 \times \left(1.8 \times 10^{-4}\right) = 9.6 \times 10^{-5}$$

$$x = \sqrt{9.6 \times 10^{-5}}$$

$$= 9.8 \times 10^{-3} \; M$$

To check the assumption that $x$ is small compared to 0.534, its relative magnitude can be estimated:

$$\frac{x}{0.534} = \frac{9.8 \times 10^{-3}}{0.534} = 1.8 \times 10^{-2} \; (1.8\% \text{ of } 0.534)$$

Because $x$ is less than 5% of the initial concentration, the assumption is valid.

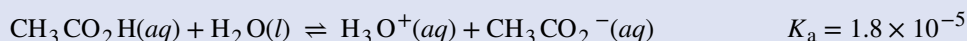As defined in the ICE table, $x$ is equal to the equilibrium concentration of hydronium ion:

$$x = [\text{H}_3\text{O}^+] = 0.0098 \; M$$

Finally, the pH is calculated to be

$$\text{pH} = -\log[\text{H}_3\text{O}^+] = -\log(0.0098) = 2.01$$

## Check Your Learning

Only a small fraction of a weak acid ionizes in aqueous solution. What is the percent ionization of a 0.100-$M$ solution of acetic acid, $\text{CH}_3\text{CO}_2\text{H}$?
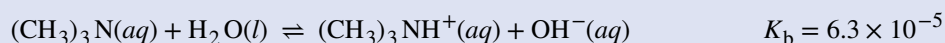
$$\text{CH}_3\text{CO}_2\text{H}(aq) + \text{H}_2\text{O}(l) \;\rightleftharpoons\; \text{H}_3\text{O}^+(aq) + \text{CH}_3\text{CO}_2{}^-(aq) \qquad K_a = 1.8 \times 10^{-5}$$

**Answer:**  percent ionization = 1.3%

## Example 14.13

## Calculating Equilibrium Concentrations in a Weak Base Solution

Find the concentration of hydroxide ion, the pOH, and the pH of a 0.25-$M$ solution of trimethylamine, a weak base:

$$(\text{CH}_3)_3\text{N}(aq) + \text{H}_2\text{O}(l) \;\rightleftharpoons\; (\text{CH}_3)_3\text{NH}^+(aq) + \text{OH}^-(aq) \qquad K_b = 6.3 \times 10^{-5}$$

## Solution

The ICE table for this system is

|  | $(\text{CH}_3)_3\text{N}$ + H$_2$O $\rightleftharpoons$ $(\text{CH}_3)_3\text{NH}^+$ | | + OH$^-$ |
|---|---|---|---|
| Initial concentration (M) | 0.25 | 0 | ~0 |
| Change (M) | −x | x | x |
| Equilibrium concentration (M) | 0.25 + (−x) | 0 + x | ~0 + x |

Substituting the equilibrium concentration terms into the $K_b$ expression gives

$$K_b = \frac{[(\text{CH}_3)_3\text{NH}^+][\text{OH}^-]}{[(\text{CH}_3)_3\text{N}]} = \frac{(x)(x)}{0.25 - x} = 6.3 \times 10^{-5}$$

Assuming $x \ll 0.25$ and solving for $x$ yields

$$x = 4.0 \times 10^{-3} \ M$$

This value is less than 5% of the initial concentration (0.25), so the assumption is justified. As defined in the ICE table, $x$ is equal to the equilibrium concentration of hydroxide ion:

$$[\text{OH}^-] = \sim 0 + x = x = 4.0 \times 10^{-3} \ M$$

$$= 4.0 \times 10^{-3} \ M$$

The pOH is calculated to be

$$\text{pOH} = -\log\!\left(4.0 \times 10^{-3}\right) = 2.40$$

Using the relation introduced in the previous section of this chapter:

$$\text{pH} + \text{pOH} = \text{p}K_{\text{w}} = 14.00$$

permits the computation of pH:

$$\text{pH} = 14.00 - \text{pOH} = 14.00 - 2.40 = 11.60$$

### Check Your Learning

Calculate the hydroxide ion concentration and the percent ionization of a 0.0325-$M$ solution of ammonia, a weak base with a $K_{\text{b}}$ of $1.76 \times 10^{-5}$.
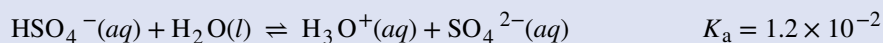
**Answer:** $7.56 \times 10^{-4} \ M$, 2.33%

In some cases, the strength of the weak acid or base and its formal (initial) concentration result in an appreciable ionization. Though the ICE strategy remains effective for these systems, the algebra is a bit more involved because the simplifying assumption that $x$ is negligible can not be made. Calculations of this sort are demonstrated in **Example 14.14** below.

### Example 14.14

### Calculating Equilibrium Concentrations without Simplifying Assumptions

Sodium bisulfate, $\text{NaHSO}_4$, is used in some household cleansers as a source of the $\text{HSO}_4{}^-$ ion, a weak acid. What is the pH of a 0.50-$M$ solution of $\text{HSO}_4{}^-$?

$$\text{HSO}_4{}^-(aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{H}_3\text{O}^+(aq) + \text{SO}_4{}^{2-}(aq) \qquad K_{\text{a}} = 1.2 \times 10^{-2}$$

### Solution

The ICE table for this system is

| | $HSO_4^-$ | + | $H_2O$ | $\rightleftharpoons$ | $H_3O^+$ | + | $SO_4^{2-}$ |
|---|---|---|---|---|---|---|---|
| Initial concentration (M) | 0.50 | | | | ~0 | | 0 |
| Change (M) | $-x$ | | | | $+x$ | | $+x$ |
| Equilibrium concentration (M) | $0.50 - x$ | | | | $x$ | | $x$ |

Substituting the equilibrium concentration terms into the $K_a$ expression gives

$$K_a = 1.2 \times 10^{-2} = \frac{[H_3O^+][SO_4{}^{2-}]}{[HSO_4{}^-]} = \frac{(x)(x)}{0.50 - x}$$

If the assumption that $x \ll 0.5$ is made, simplifying and solving the above equation yields

$$x = 0.077\ M$$

This value of $x$ is clearly not significantly less than 0.50 $M$; rather, it is approximately 15% of the initial concentration:

When we check the assumption, we calculate:

$$\frac{x}{[HSO_4{}^-]_i}$$

$$\frac{x}{0.50} = \frac{7.7 \times 10^{-2}}{0.50} = 0.15\ (15\%)$$

Because the simplifying assumption is not valid for this system, the equilibrium constant expression is solved as follows:

$$K_a = 1.2 \times 10^{-2} = \frac{(x)(x)}{0.50 - x}$$

Rearranging this equation yields

$$6.0 \times 10^{-3} - 1.2 \times 10^{-2} x = x^2$$

Writing the equation in quadratic form gives
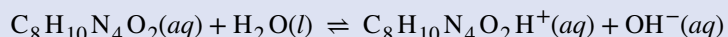
$$x^2 + 1.2 \times 10^{-2} x - 6.0 \times 10^{-3} = 0$$

Solving for the two roots of this quadratic equation results in a negative value that may be discarded as physically irrelevant and a positive value equal to $x$. As defined in the ICE table, $x$ is equal to the hydronium concentration.

$$x = [H_3O^+] = 0.072\ M$$

$$pH = -\log[H_3O^+] = -\log(0.072) = 1.14$$

> **Check Your Learning**
>
> Calculate the pH in a 0.010-*M* solution of caffeine, a weak base:
>
> $$C_8H_{10}N_4O_2(aq) + H_2O(l) \rightleftharpoons C_8H_{10}N_4O_2H^+(aq) + OH^-(aq) \qquad K_b = 2.5 \times 10^{-4}$$
>
> **Answer:** pH 11.16

## Effect of Molecular Structure on Acid-Base Strength
### Binary Acids and Bases

In the absence of any leveling effect, the acid strength of binary compounds of hydrogen with nonmetals (A) increases as the H-A bond strength decreases down a group in the periodic table. For group 17, the order of increasing acidity is HF < HCl < HBr < HI. Likewise, for group 16, the order of increasing acid strength is $H_2O$ < $H_2S$ < $H_2Se$ < $H_2Te$.

Across a row in the periodic table, the acid strength of binary hydrogen compounds increases with increasing electronegativity of the nonmetal atom because the polarity of the H-A bond increases. Thus, the order of increasing acidity (for removal of one proton) across the second row is $CH_4$ < $NH_3$ < $H_2O$ < HF; across the third row, it is $SiH_4$ < $PH_3$ < $H_2S$ < HCl (see **Figure 14.11**).
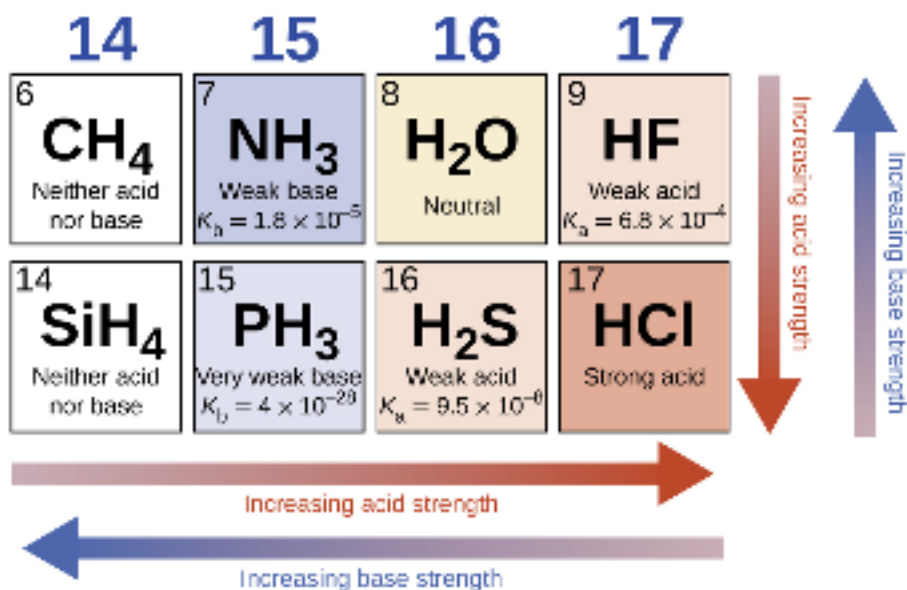


**Figure 14.11** The figure shows trends in the strengths of binary acids and bases.

### Ternary Acids and Bases

Ternary compounds composed of hydrogen, oxygen, and some third element ("E") may be structured as depicted in the image below. In these compounds, the central E atom is bonded to one or more O atoms, and at least one of the O atoms is also bonded to an H atom, corresponding to the general molecular formula $O_mE(OH)_n$. These compounds may be acidic, basic, or amphoteric depending on the properties of the central E atom. Examples of such compounds include sulfuric acid, $O_2S(OH)_2$, sulfurous acid, $OS(OH)_2$, nitric acid, $O_2NOH$, perchloric acid, $O_3ClOH$, aluminum hydroxide, $Al(OH)_3$, calcium hydroxide, $Ca(OH)_2$, and potassium hydroxide, KOH:
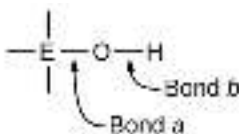
If the central atom, E, has a low electronegativity, its attraction for electrons is low. Little tendency exists for the central atom to form a strong covalent bond with the oxygen atom, and bond *a* between the element and oxygen is more readily broken than bond *b* between oxygen and hydrogen. Hence bond *a* is ionic, hydroxide ions are released to the solution, and the material behaves as a base—this is the case with $Ca(OH)_2$ and KOH. Lower electronegativity is characteristic of the more metallic elements; hence, the metallic elements form ionic hydroxides that are by definition basic compounds.

If, on the other hand, the atom E has a relatively high electronegativity, it strongly attracts the electrons it shares with the oxygen atom, making bond *a* relatively strongly covalent. The oxygen-hydrogen bond, bond *b*, is thereby weakened because electrons are displaced toward E. Bond *b* is polar and readily releases hydrogen ions to the solution, so the material behaves as an acid. High electronegativities are characteristic of the more nonmetallic elements. Thus, nonmetallic elements form covalent compounds containing acidic −OH groups that are called **oxyacids**.

Increasing the oxidation number of the central atom E also increases the acidity of an oxyacid because this increases the attraction of E for the electrons it shares with oxygen and thereby weakens the O-H bond. Sulfuric acid, $H_2SO_4$, or $O_2S(OH)_2$ (with a sulfur oxidation number of +6), is more acidic than sulfurous acid, $H_2SO_3$, or $OS(OH)_2$ (with a sulfur oxidation number of +4). Likewise nitric acid, $HNO_3$, or $O_2NOH$ (N oxidation number = +5), is more acidic than nitrous acid, $HNO_2$, or ONOH (N oxidation number = +3). In each of these pairs, the oxidation number of the central atom is larger for the stronger acid (**Figure 14.12**).
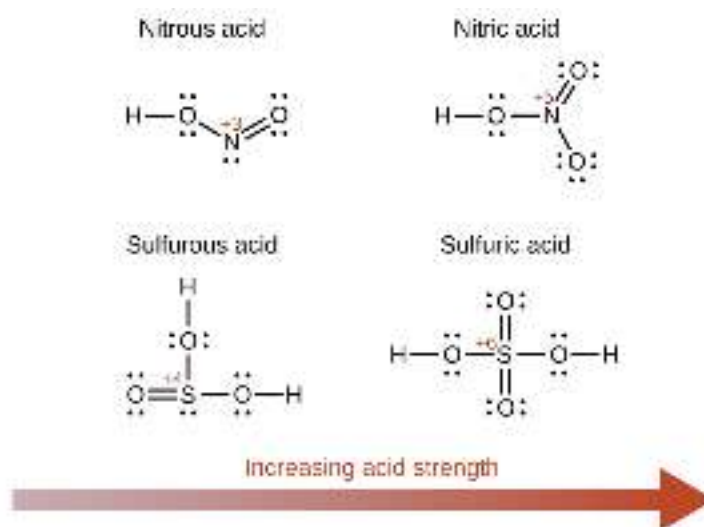


**Figure 14.12** As the oxidation number of the central atom E increases, the acidity also increases.

Hydroxy compounds of elements with intermediate electronegativities and relatively high oxidation numbers (for example, elements near the diagonal line separating the metals from the nonmetals in the periodic table) are usually amphoteric. This means that the hydroxy compounds act as acids when they react with strong bases and as bases when they react with strong acids. The amphoterism of aluminum hydroxide, which commonly exists as the hydrate $Al(H_2O)_3(OH)_3$, is reflected in its solubility in both strong acids and strong bases. In strong bases, the relatively insoluble hydrated aluminum hydroxide, $Al(H_2O)_3(OH)_3$, is converted into the soluble ion, $[Al(H_2O)_2(OH)_4]^-$, by reaction with hydroxide ion:

$$Al(H_2O)_3(OH)_3(aq) + OH^-(aq) \rightleftharpoons H_2O(l) + [Al(H_2O)_2(OH)_4]^-(aq)$$
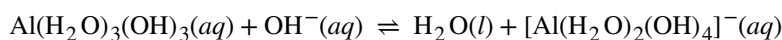
In this reaction, a proton is transferred from one of the aluminum-bound $H_2O$ molecules to a hydroxide ion in solution. The $Al(H_2O)_3(OH)_3$ compound thus acts as an acid under these conditions. On the other hand, when dissolved in strong acids, it is converted to the soluble ion $[Al(H_2O)_6]^{3+}$ by reaction with hydronium ion:

$$3H_3O^+(aq) + Al(H_2O)_3(OH)_3(aq) \rightleftharpoons Al(H_2O)_6{}^{3+}(aq) + 3H_2O(l)$$
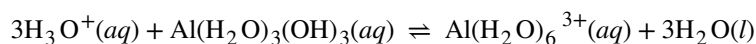
In this case, protons are transferred from hydronium ions in solution to $Al(H_2O)_3(OH)_3$, and the compound functions as a base.

# 14.4 Hydrolysis of Salts

By the end of this section, you will be able to:

- Predict whether a salt solution will be acidic, basic, or neutral
- Calculate the concentrations of the various species in a salt solution
- Describe the acid ionization of hydrated metal ions

## Salts with Acidic Ions

Salts are ionic compounds composed of cations and anions, either of which may be capable of undergoing an acid or base ionization reaction with water. Aqueous salt solutions, therefore, may be acidic, basic, or neutral, depending on the relative acid-base strengths of the salt's constituent ions. For example, dissolving ammonium chloride in water results in its dissociation, as described by the equation

$$NH_4Cl(s) \rightleftharpoons NH_4{}^+(aq) + Cl^-(aq)$$
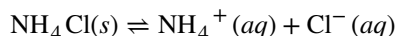
The ammonium ion is the conjugate acid of the weak base ammonia, $NH_3$, and so it will undergo acid ionization (or *acid hydrolysis*):
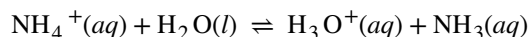
$$NH_4{}^+(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + NH_3(aq)$$

Salts are ionic compounds composed of cations and anions, either of which may be capable of undergoing an acid or base ionization reaction with water. Aqueous salt solutions, therefore, may be acidic, basic, or neutral, depending on the relative acid-base strengths of the salt's constituent ions. For example, dissolving the ammonium chloride in water results in its dissociation, as described by the equation
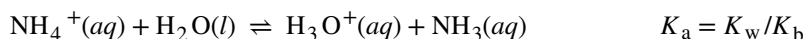
$$NH_4Cl(s) \rightleftharpoons NH_4{}^+(aq) + Cl^-(aq)$$

The ammonium ion is the conjugate acid of the base ammonia, NH3; its acid ionization (or acid hydrolysis) reaction is represented by

$$NH_4{}^+(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + NH_3(aq) \qquad\qquad K_a = K_w/K_b$$

Since ammonia is a weak base, $K_b$ is measurable and $K_a > 0$ (ammonium ion is a weak acid).

The chloride ion is the conjugate base of hydrochloric acid, and so its base ionization (or *base hydrolysis*) reaction is represented by

$$Cl^-(aq) + H_2O(l) \rightleftharpoons HCl(aq) + OH^-(aq) \qquad\qquad K_b = K_w/K_a$$
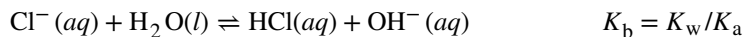
Since HCl is a strong acid, $K_a$ is immeasurably large and $K_b \approx 0$ (chloride ions don't undergo appreciable hydrolysis).

Thus, dissolving ammonium chloride in water yields a solution of weak acid cations ( $NH_4{}^+$ ) and inert anions ($Cl^-$), resulting in an acidic solution.

---

### Example 14.15

## Calculating the pH of an Acidic Salt Solution

Aniline is an amine that is used to manufacture dyes. It is isolated as anilinium chloride, $[C_6H_5NH_3{}^+]Cl$, a salt prepared by the reaction of the weak base aniline and hydrochloric acid. What is the pH of a 0.233 *M*

solution of anilinium chloride

$$C_6H_5NH_3{}^+(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + C_6H_5NH_2(aq)$$
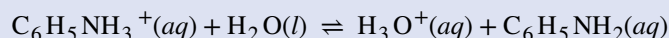
## Solution

The $K_a$ for anilinium ion is derived from the $K_b$ for its conjugate base, aniline (see **Appendix H**):

$$K_a = \frac{K_w}{K_b} = \frac{1.0 \times 10^{-14}}{4.3 \times 10^{-10}} = 2.3 \times 10^{-5}$$

Using the provided information, an ICE table for this system is prepared:

|  | $C_6H_5NH_3{}^+$ + | $H_2O$ $\rightleftharpoons$ | $C_6H_5NH_2$ + | $H_3O^+$ |
|---|---|---|---|---|
| Initial concentration (M) | 0.233 | | 0 | ~0 |
| Change (M) | $-x$ | | $+x$ | $+x$ |
| Equilibrium concentration (M) | $0.233 - x$ | | $x$ | $x$ |

Substituting these equilibrium concentration terms into the $K_a$ expression gives

$$K_a = [C_6H_5NH_2][H_3O^+]/[C_6H_5NH_3{}^+]$$
$$2.3 \times 10^{-5} = (x)(x)/0.233 - x$$

Assuming $x \ll 0.233$, the equation is simplified and solved for $x$:

$$2.3 \times 10^{-5} = x^2/0.233$$
$$x = 0.0023 \ M$$

The ICE table defines x as the hydronium ion molarity, and so the pH is computed as

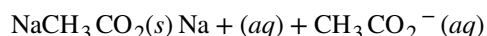$$pH = -\log[H_3O^+] = -\log(0.0023) = 2.64$$

## Check Your Learning

What is the hydronium ion concentration in a 0.100-*M* solution of ammonium nitrate, $NH_4NO_3$, a salt composed of the ions $NH_4{}^+$ and $NO_3{}^-$. Which is the stronger acid $C_6H_5NH_3{}^+$ or $NH_4{}^+$?

**Answer:** $[H_3O^+] = 7.5 \times 10^{-6} \ M$; $C_6H_5NH_3{}^+$ is the stronger acid.

## Salts with Basic Ions

As another example, consider dissolving sodium acetate in water:

$$NaCH_3CO_2(s) \ Na + (aq) + CH_3CO_2{}^-(aq)$$

The sodium ion does not undergo appreciable acid or base ionization and has no effect on the solution pH. This may seem obvious from the ion's formula, which indicates no hydrogen or oxygen atoms, but some dissolved metal ions function as weak acids, as addressed later in this section.

The acetate ion, $CH_3CO_2{}^-$, is the conjugate base of acetic acid, $CH_3CO_2H$, and so its base ionization (or *base hydrolysis*) reaction is represented by

$$CH_3CO_2{}^-(aq) + H_2O(l) \rightleftharpoons CH_3CO_2H(aq) + OH-(aq) \qquad K_b = K_w/K_a$$
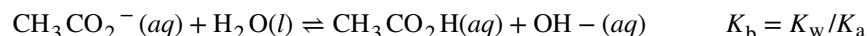
Because acetic acid is a weak acid, its $K_a$ is measurable and $K_b > 0$ (acetate ion is a weak base).

Dissolving sodium acetate in water yields a solution of inert cations ($Na^+$) and weak base anions ($CH_3CO_2{}^-$), resulting in a basic solution.
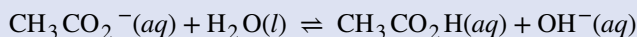
---

## Example 14.16

### Equilibrium in a Solution of a Salt of a Weak Acid and a Strong Base

Determine the acetic acid concentration in a solution with $[CH_3CO_2{}^-] = 0.050\ M$ and $[OH^-] = 2.5 \times 10^{-6}\ M$ at equilibrium. The reaction is:

$$CH_3CO_2{}^-(aq) + H_2O(l) \rightleftharpoons CH_3CO_2H(aq) + OH^-(aq)$$

**Solution**

The provided equilibrium concentrations and a value for the equilibrium constant will permit calculation of the missing equilibrium concentration. The process in question is the base ionization of acetate ion, for which

$$K_b \text{ (for } CH_3CO_2{}^-) = \frac{K_w}{K_a \text{ (for } CH_3CO_2H)} = \frac{1.0 \times 10^{-14}}{1.8 \times 10^{-5}} = 5.6 \times 10^{-10}$$

Substituting the available values into the $K_b$ expression gives

$$K_b = \frac{[CH_3CO_2H][OH^-]}{[CH_3CO_2{}^-]} = 5.6 \times 10^{-10}$$

$$= \frac{[CH_3CO_2H](2.5 \times 10^{-6})}{(0.050)} = 5.6 \times 10^{-10}$$

Solving the above equation for the acetic acid molarity yields $[CH_3CO_2H] = 1.1 \times 10^{-5}\ M$.

**Check Your Learning**

What is the pH of a 0.083-$M$ solution of NaCN?

**Answer:**   11.11

---

## Salts with Acidic and Basic Ions

Some salts are composed of both acidic and basic ions, and so the pH of their solutions will depend on the relative strengths of these two species. Likewise, some salts contain a single ion that is amphiprotic, and so the relative strengths of this ion's acid and base character will determine its effect on solution pH. For both types of salts, a comparison of the $K_a$ and $K_b$ values allows prediction of the solution's acid-base status, as illustrated in the following example exercise.

---

## Example 14.17

### Determining the Acidic or Basic Nature of Salts

Determine whether aqueous solutions of the following salts are acidic, basic, or neutral:

(a) KBr

(b) $NaHCO_3$

(c) $Na_2HPO_4$

(d) $NH_4F$

**Solution**

Consider each of the ions separately in terms of its effect on the pH of the solution, as shown here:

---

(a) The $K^+$ cation is inert and will not affect pH. The bromide ion is the conjugate base of a strong acid, and so it is of negligible base strength (no appreciable base ionization). The solution is neutral.

(b) The $Na^+$ cation is inert and will not affect the pH of the solution; while the $HCO_3^-$ anion is amphiprotic. The $K_a$ of $HCO_3^-$ is 4.7 × $10^{-11}$, and its $K_b$ is $\dfrac{1.0 \times 10^{-14}}{4.3 \times 10^{-7}} = 2.3 \times 10^{-8}$.

Since $K_b >> K_a$, the solution is basic.

(c) The $Na^+$ cation is inert and will not affect the pH of the solution, while the $HPO_4^{2-}$ anion is amphiprotic. The $K_a$ of $HPO_4^{2-}$ is 4.2 × $10^{-13}$,

and its $K_b$ is $\dfrac{1.0 \times 10^{-14}}{6.2 \times 10^{-8}} = 1.6 \times 10^{-7}$. Because $K_b >> K_a$, the solution is basic.

(d) The $NH_4^+$ ion is acidic (see above discussion) and the $F^-$ ion is basic (conjugate base of the weak acid HF). Comparing the two ionization constants: $K_a$ of $NH_4^+$ is 5.6 × $10^{-10}$ and the $K_b$ of $F^-$ is 1.4 × $10^{-11}$, so the solution is acidic, since $K_a > K_b$.

### Check Your Learning

Determine whether aqueous solutions of the following salts are acidic, basic, or neutral:

(a) $K_2CO_3$

(b) $CaCl_2$

(c) $KH_2PO_4$

(d) $(NH_4)_2CO_3$

**Answer:**   (a) basic; (b) neutral; (c) acidic; (d) basic

## The Ionization of Hydrated Metal Ions

Unlike the group 1 and 2 metal ions of the preceding examples ($Na^+$, $Ca^{2+}$, etc.), some metal ions function as acids in aqueous solutions. These ions are not just loosely solvated by water molecules when dissolved, instead they are covalently bonded to a fixed number of water molecules to yield a complex ion (see chapter on coordination chemistry). As an example, the dissolution of aluminum nitrate in water is typically represented as

$$Al(NO_3)(s) \rightleftharpoons Al^{3+}(aq) + 3NO_3^-(aq)$$
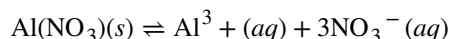
However, the aluminum(III) ion actually reacts with six water molecules to form a stable complex ion, and so the more explicit representation of the dissolution process is

$$Al(NO_3)_3(s) + 6H_2O(l) \rightleftharpoons Al(H_2O)_6^{3+}(aq) + 3NO_3^-(aq)$$

As shown in **Figure 14.13**, the $Al(H_2O)_6^{3+}$ ions involve bonds between a central Al atom and the O atoms of the six water molecules. Consequently, the bonded water molecules' O–H bonds are more polar than in nonbonded water molecules, making the bonded molecules more prone to donation of a hydrogen ion:

$$Al(H_2O)_6^{3+}(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + Al(H_2O)_5(OH)^{2+}(aq) \qquad K_a = 1.4 \times 10^{-5}$$

The conjugate base produced by this process contains five other bonded water molecules capable of acting as acids, and so the sequential or step-wise transfer of protons is possible as depicted in few equations below:

$$\text{Al}(\text{H}_2\text{O})_6{}^{3+}(aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{H}_3\text{O}^+(aq) + \text{Al}(\text{H}_2\text{O})_5(\text{OH})^{2+}(aq)$$
$$\text{Al}(\text{H}_2\text{O})_5(\text{OH})^{2+}(aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{H}_3\text{O}^+(aq) + \text{Al}(\text{H}_2\text{O})_4(\text{OH})_2{}^+(aq)$$
$$\text{Al}(\text{H}_2\text{O})_4(\text{OH})_2{}^+(aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{H}_3\text{O}^+(aq) + \text{Al}(\text{H}_2\text{O})_3(\text{OH})_3(aq)$$
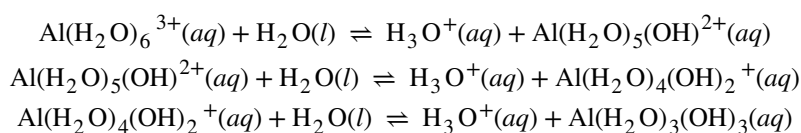
This is an example of a polyprotic acid, the topic of discussion in a later section of this chapter.
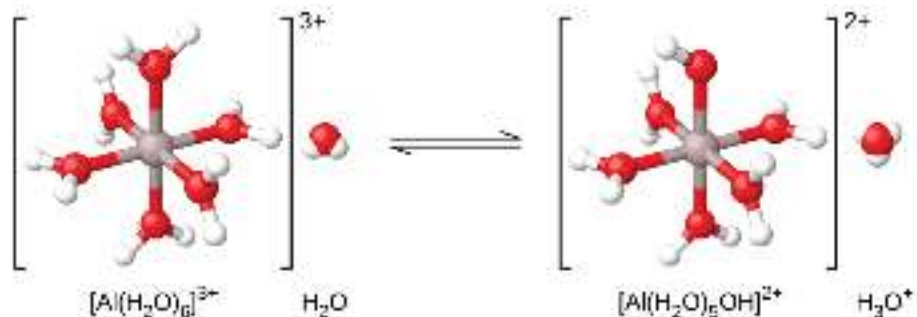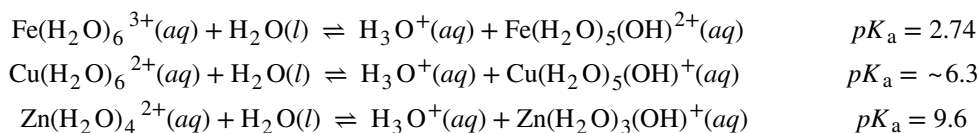


**Figure 14.13** When an aluminum ion reacts with water, the hydrated aluminum ion becomes a weak acid.

Aside from the alkali metals (group 1) and some alkaline earth metals (group 2), most other metal ions will undergo acid ionization to some extent when dissolved in water. The acid strength of these complex ions typically increases with increasing charge and decreasing size of the metal ions. The first-step acid ionization equations for a few other acidic metal ions are shown below:
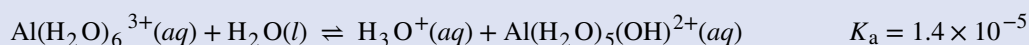
$$\text{Fe}(\text{H}_2\text{O})_6{}^{3+}(aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{H}_3\text{O}^+(aq) + \text{Fe}(\text{H}_2\text{O})_5(\text{OH})^{2+}(aq) \qquad pK_a = 2.74$$
$$\text{Cu}(\text{H}_2\text{O})_6{}^{2+}(aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{H}_3\text{O}^+(aq) + \text{Cu}(\text{H}_2\text{O})_5(\text{OH})^+(aq) \qquad pK_a = {\sim}6.3$$
$$\text{Zn}(\text{H}_2\text{O})_4{}^{2+}(aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{H}_3\text{O}^+(aq) + \text{Zn}(\text{H}_2\text{O})_3(\text{OH})^+(aq) \qquad pK_a = 9.6$$

## Example 14.18

### Hydrolysis of $[\text{Al}(\text{H}_2\text{O})_6]^{3+}$

Calculate the pH of a 0.10-$M$ solution of aluminum chloride, which dissolves completely to give the hydrated aluminum ion $[\text{Al}(\text{H}_2\text{O})_6]^{3+}$ in solution.

#### Solution

The equation for the reaction and $K_a$ are:

$$\text{Al}(\text{H}_2\text{O})_6{}^{3+}(aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{H}_3\text{O}^+(aq) + \text{Al}(\text{H}_2\text{O})_5(\text{OH})^{2+}(aq) \qquad K_a = 1.4 \times 10^{-5}$$

An ICE table with the provided information is

|  | $\text{Al}(\text{H}_2\text{O})_6{}^{3-} + \text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{O}^+ + \text{Al}(\text{H}_2\text{O})_5(\text{OH})^{2-}$ | | |
|---|---|---|---|
| Initial concentration ($M$) | 0.10 | ~0 | 0 |
| Change ($M$) | $-x$ | $+x$ | $+x$ |
| Equilibrium concentration ($M$) | $0.10 - x$ | $x$ | $x$ |

Substituting the expressions for the equilibrium concentrations into the equation for the ionization constant yields:

$$K_a = \frac{[H_3O^+][Al(H_2O)_5(OH)^{2+}]}{[Al(H_2O)_6{}^{3+}]}$$

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

Assuming $x \ll 0.10$ and solving the simplified equation gives:

$$x = 1.2 \times 10^{-3} \ M$$

The ICE table defined $x$ as equal to the hydronium ion concentration, and so the pH is calculated to be

$$[H_3O^+] = 0 + x = 1.2 \times 10^{-3} \ M$$

$$pH = -\log[H_3O^+] = 2.92 \text{ (an acidic solution)}$$

**Check Your Learning**

What is $[Al(H_2O)_5(OH)^{2+}]$ in a 0.15-$M$ solution of $Al(NO_3)_3$ that contains enough of the strong acid $HNO_3$ to bring $[H_3O^+]$ to 0.10 $M$?
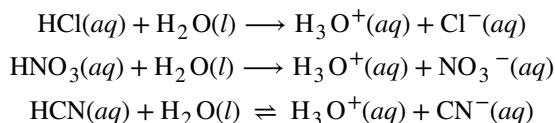
**Answer:**  $2.1 \times 10^{-5} \ M$

# 14.5 Polyprotic Acids

By the end of this section, you will be able to:

- Extend previously introduced equilibrium concepts to acids and bases that may donate or accept more than one proton

Acids are classified by the number of protons per molecule that they can give up in a reaction. Acids such as HCl, $HNO_3$, and HCN that contain one ionizable hydrogen atom in each molecule are called **monoprotic acids**. Their reactions with water are:
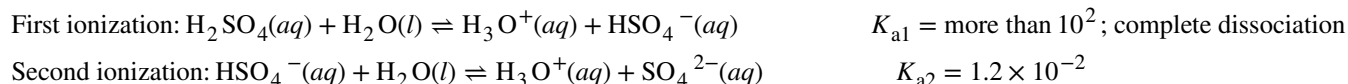
$$HCl(aq) + H_2O(l) \longrightarrow H_3O^+(aq) + Cl^-(aq)$$
$$HNO_3(aq) + H_2O(l) \longrightarrow H_3O^+(aq) + NO_3{}^-(aq)$$
$$HCN(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + CN^-(aq)$$

Even though it contains four hydrogen atoms, acetic acid, $CH_3CO_2H$, is also monoprotic because only the hydrogen atom from the carboxyl group (COOH) reacts with bases:
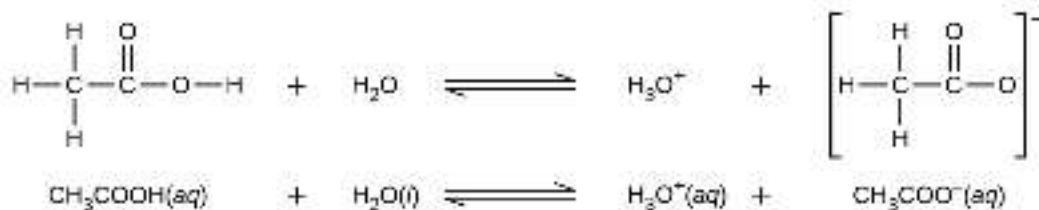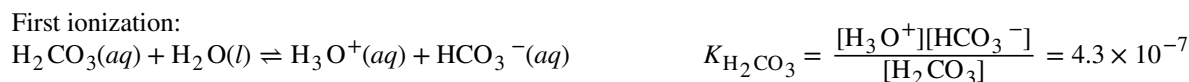


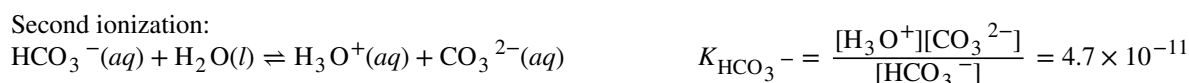Similarly, monoprotic bases are bases that will accept a single proton.

**Diprotic acids** contain two ionizable hydrogen atoms per molecule; ionization of such acids occurs in two steps. The first ionization always takes place to a greater extent than the second ionization. For example, sulfuric acid, a strong acid, ionizes as follows:

First ionization: $H_2SO_4(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + HSO_4{}^-(aq)$ $\qquad$ $K_{a1}$ = more than $10^2$; complete dissociation

Second ionization: $HSO_4{}^-(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + SO_4{}^{2-}(aq)$ $\qquad$ $K_{a2} = 1.2 \times 10^{-2}$

This **stepwise ionization** process occurs for all polyprotic acids. Carbonic acid, $H_2CO_3$, is an example of a weak diprotic acid. The first ionization of carbonic acid yields hydronium ions and bicarbonate ions in small amounts.

First ionization:
$H_2CO_3(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + HCO_3{}^-(aq)$ $\qquad$ $K_{H_2CO_3} = \dfrac{[H_3O^+][HCO_3{}^-]}{[H_2CO_3]} = 4.3 \times 10^{-7}$

The bicarbonate ion can also act as an acid. It ionizes and forms hydronium ions and carbonate ions in even smaller quantities.

Second ionization:
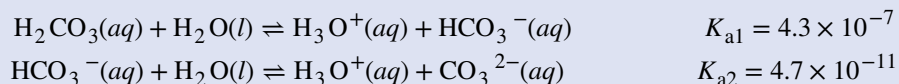$HCO_3{}^-(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + CO_3{}^{2-}(aq)$ $\qquad$ $K_{HCO_3{}^-} = \dfrac{[H_3O^+][CO_3{}^{2-}]}{[HCO_3{}^-]} = 4.7 \times 10^{-11}$

$K_{H_2CO_3}$ is larger than $K_{HCO_3{}^-}$ by a factor of $10^4$, so $H_2CO_3$ is the dominant producer of hydronium ion in the solution. This means that little of the $HCO_3{}^-$ formed by the ionization of $H_2CO_3$ ionizes to give hydronium ions (and carbonate ions), and the concentrations of $H_3O^+$ and $HCO_3{}^-$ are practically equal in a pure aqueous solution of $H_2CO_3$.

If the first ionization constant of a weak diprotic acid is larger than the second by a factor of at least 20, it is appropriate to treat the first ionization separately and calculate concentrations resulting from it before calculating concentrations of species resulting from subsequent ionization. This approach is demonstrated in the following example exercise.

## Example 14.19

### Ionization of a Diprotic Acid

"Carbonated water" contains a palatable amount of dissolved carbon dioxide. The solution is acidic because $CO_2$ reacts with water to form carbonic acid, $H_2CO_3$. What are $[H_3O^+]$, $[HCO_3{}^-]$, and $[CO_3{}^{2-}]$ in a saturated solution of $CO_2$ with an initial $[H_2CO_3] = 0.033\ M$?

$H_2CO_3(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + HCO_3{}^-(aq)$ $\qquad$ $K_{a1} = 4.3 \times 10^{-7}$

$HCO_3{}^-(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + CO_3{}^{2-}(aq)$ $\qquad$ $K_{a2} = 4.7 \times 10^{-11}$

**Solution**

As indicated by the ionization constants, $H_2CO_3$ is a much stronger acid than $HCO_3{}^-$, so the stepwise ionization reactions may be treated separately.

The first ionization reaction is

$H_2CO_3(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + HCO_3{}^-(aq)$ $\qquad$ $K_{a1} = 4.3 \times 10^{-7}$
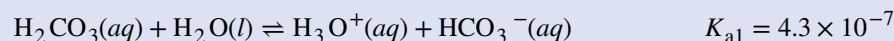
Using provided information, an ICE table for this first step is prepared:

| | $H_2CO_3$ | + | $H_2O$ | ⇌ | $H_3O^+$ | + | $HCO_3^-$ |
|---|---|---|---|---|---|---|---|
| Initial concentration (M) | 0.033 | | | | ~0 | | 0 |
| Change (M) | $-x$ | | | | $+x$ | | $+x$ |
| Equilibrium concentration (M) | $0.033 - x$ | | | | $x$ | | $x$ |

Substituting the equilibrium concentrations into the equilibrium equation gives

$$K_{H_2CO_3} = \frac{[H_3O^+][HCO_3^-]}{[H_2CO_3]} = \frac{(x)(x)}{0.033 - x} = 4.3 \times 10^{-7}$$

Assuming $x << 0.033$ and solving the simplified equation yields

$$x = 1.2 \times 10^{-4}$$

The ICE table defined $x$ as equal to the bicarbonate ion molarity and the hydronium ion molarity:

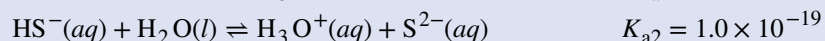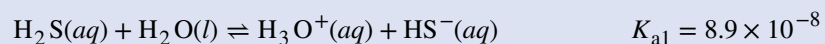$$[H_2CO_3] = 0.033 \, M$$

$$[H_3O^+] = [HCO_3^-] = 1.2 \times 10^{-4} \, M$$

Using the bicarbonate ion concentration computed above, the second ionization is subjected to a similar equilibrium calculation:

$$HCO_3^-(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + CO_3^{2-}(aq)$$
$$K_{HCO_3^-} = \frac{[H_3O^+][CO_3^{2-}]}{[HCO_3^-]} = \frac{(1.2 \times 10^{-4})[CO_3^{2-}]}{1.2 \times 10^{-4}}$$
$$[CO_3^{2-}] = \frac{(4.7 \times 10^{-11})(1.2 \times 10^{-4})}{1.2 \times 10^{-4}} = 4.7 \times 10^{-11} \, M$$

To summarize: at equilibrium $[H_2CO_3] = 0.033 \, M$; $[H_3O^+] = 1.2 \times 10^{-4}$; $[HCO_3^-] = 1.2 \times 10^{-4} \, M$; $[CO_3^{2-}] = 5.6 \times 10^{-11} \, M$.
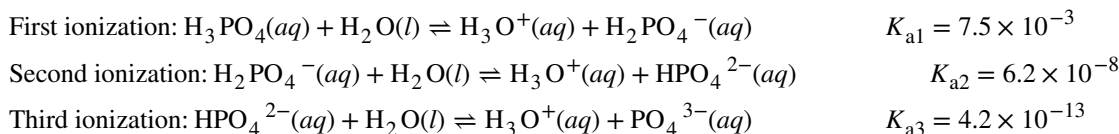
## Check Your Learning

The concentration of $H_2S$ in a saturated aqueous solution at room temperature is approximately 0.1 $M$. Calculate $[H_3O^+]$, $[HS^-]$, and $[S^{2-}]$ in the solution:

$$H_2S(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + HS^-(aq) \qquad K_{a1} = 8.9 \times 10^{-8}$$
$$HS^-(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + S^{2-}(aq) \qquad K_{a2} = 1.0 \times 10^{-19}$$

**Answer:** $[H_2S] = 0.1 \, M$; $[H_3O^+] = [HS^-] = 0.000094 \, M$; $[S^{2-}] = 1 \times 10^{-19} \, M$

A **triprotic acid** is an acid that has three ionizable H atoms. Phosphoric acid is one example:

First ionization: $H_3PO_4(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + H_2PO_4{}^-(aq)$ $\qquad K_{a1} = 7.5 \times 10^{-3}$

Second ionization: $H_2PO_4{}^-(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + HPO_4{}^{2-}(aq)$ $\qquad K_{a2} = 6.2 \times 10^{-8}$

Third ionization: $HPO_4{}^{2-}(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + PO_4{}^{3-}(aq)$ $\qquad K_{a3} = 4.2 \times 10^{-13}$

As for the diprotic acid examples, each successive ionization reaction is less extensive than the former, reflected in decreasing values for the stepwise acid ionization constants. This is a general characteristic of polyprotic acids and successive ionization constants often differ by a factor of about $10^5$ to $10^6$.

This set of three dissociation reactions may appear to make calculations of equilibrium concentrations in a solution of $H_3PO_4$ complicated. However, because the successive ionization constants differ by a factor of $10^5$ to $10^6$, large differences exist in the small changes in concentration accompanying the ionization reactions. This allows the use of math-simplifying assumptions and processes, as demonstrated in the examples above.

Polyprotic bases are capable of accepting more than one hydrogen ion. The carbonate ion is an example of a **diprotic base**, because it can accept two protons, as shown below. Similar to the case for polyprotic acids, note the ionization constants decrease with ionization step. Likewise, equilibrium calculations involving polyprotic bases follow the same approaches as those for polyprotic acids.

$$H_2O(l) + CO_3{}^{2-}(aq) \rightleftharpoons HCO_3{}^-(aq) + OH^-(aq) \qquad K_{b1} = 2.1 \times 10^{-4}$$

$$H_2O(l) + HCO_3{}^-(aq) \rightleftharpoons H_2CO_3(aq) + OH^-(aq) \qquad K_{b2} = 2.3 \times 10^{-8}$$
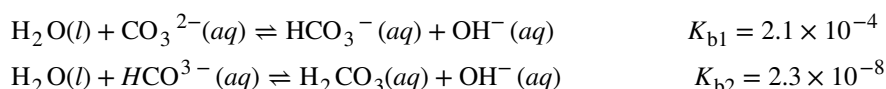
# 14.6 Buffers

By the end of this section, you will be able to:

- Describe the composition and function of acid–base buffers
- Calculate the pH of a buffer before and after the addition of added acid or base

A solution containing appreciable amounts of a weak conjugate acid-base pair is called a buffer solution, or a **buffer**. Buffer solutions resist a change in pH when small amounts of a strong acid or a strong base are added (**Figure 14.14**). A solution of acetic acid and sodium acetate ($CH_3COOH + CH_3COONa$) is an example of a buffer that consists of a weak acid and its salt. An example of a buffer that consists of a weak base and its salt is a solution of ammonia and ammonium chloride ($NH_3(aq) + NH_4Cl(aq)$).



**Figure 14.14**   (a) The buffered solution on the left and the unbuffered solution on the right have the same pH (pH 8); they are basic, showing the yellow color of the indicator methyl orange at this pH. (b) After the addition of 1 mL of a 0.01-*M* HCl solution, the buffered solution has not detectably changed its pH but the unbuffered solution has become acidic, as indicated by the change in color of the methyl orange, which turns red at a pH of about 4. (credit: modification of work by Mark Ott)

## How Buffers Work

To illustrate the function of a buffer solution, consider a mixture of roughly equal amounts of acetic acid and sodium acetate. The presence of a weak conjugate acid-base pair in the solution imparts the ability to neutralize modest amounts of added strong acid or base. For example, adding strong base to this solution will neutralize hydronium ion and shift the acetic acid ionization equilibrium to the right, partially restoring the decreased $H_3O^+$ concentration:

$$CH_3CO_2H(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + CH_3CO_2^-(aq)$$
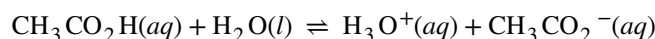
Likewise, adding strong acid to this buffer solution will neutralize acetate ion, shifting the above ionization equilibrium right and returning [H3O+] to near its original value. **Figure 14.15** provides a graphical illustration of the changes in conjugate-partner concentration that occur in this buffer solution when strong acid and base are added. The buffering action of the solution is essentially a result of the added strong acid and base being converted to the weak acid and base that make up the buffer's conjugate pair. The weaker acid and base undergo only slight ionization, as compared with the complete ionization of the strong acid and base, and the solution pH, therefore, changes much less drastically than it would in an unbuffered solution.
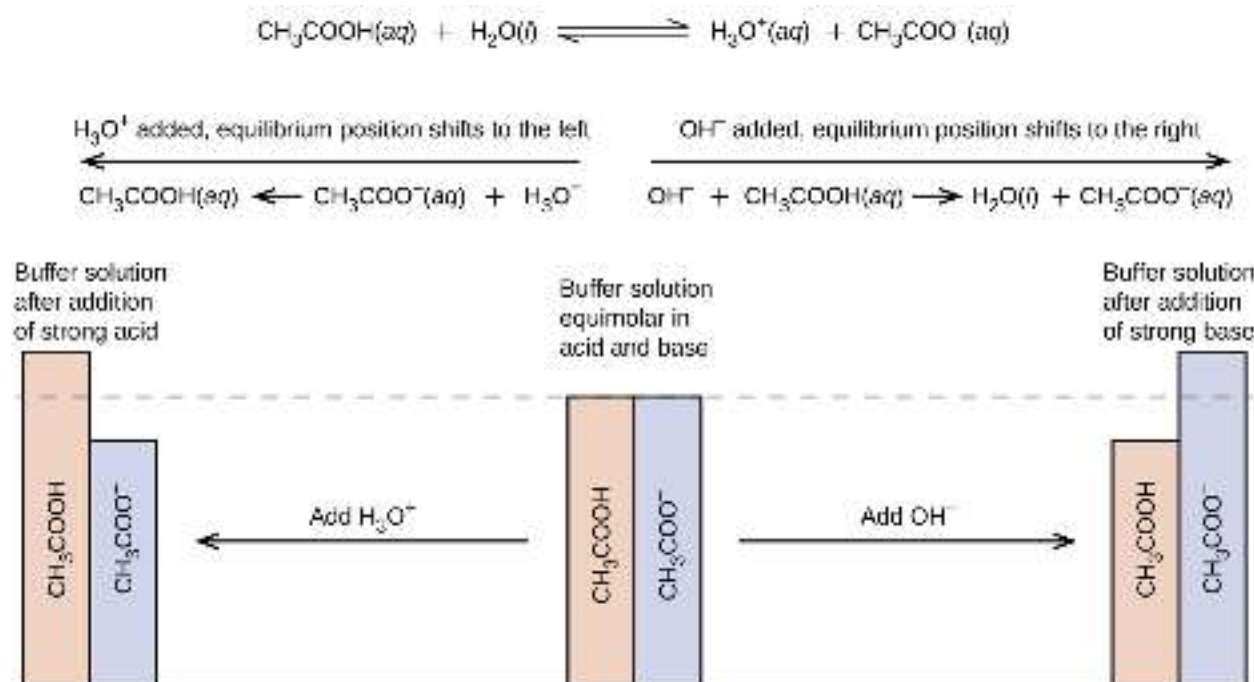


**Figure 14.15** Buffering action in a mixture of acetic acid and acetate salt.

## Example 14.20

### pH Changes in Buffered and Unbuffered Solutions

Acetate buffers are used in biochemical studies of enzymes and other chemical components of cells to prevent pH changes that might affect the biochemical activity of these compounds.

(a) Calculate the pH of an acetate buffer that is a mixture with 0.10 $M$ acetic acid and 0.10 $M$ sodium acetate.

(b) Calculate the pH after 1.0 mL of 0.10 NaOH is added to 100 mL of this buffer.

(c) For comparison, calculate the pH after 1.0 mL of 0.10 $M$ NaOH is added to 100 mL of a solution of an unbuffered solution with a pH of 4.74.

## Solution

(a) Following the ICE approach to this equilibrium calculation yields the following:

| | $CH_3CO_2H$ | $+$ | $H_2O$ | $\rightleftharpoons$ | $H_3O$ | $+$ | $CH_3CO_2^-$ |
|---|---|---|---|---|---|---|---|
| Initial concentration (M) | 0.10 | | | | ~0 | | 0.10 |
| Change (M) | $-x$ | | | | $+x$ | | $+x$ |
| Equilibrium concentration (M) | $0.10 - x$ | | | | $x$ | | $0.10 + x$ |

Substituting the equilibrium concentration terms into the $K_a$ expression, assuming $x << 0.10$, and solving the simplified equation for $x$ yields

$$x = 1.8 \times 10^{-5} M$$
$$[H_3O^+] = 0 + x = 1.8 \times 10^{-5} \ M$$
$$pH = -\log[H_3O^+] = -\log(1.8 \times 10^{-5})$$
$$= 4.74$$

(b) Calculate the pH after 1.0 mL of 0.10 $M$ NaOH is added to 100 mL of this buffer.

Adding strong acid will neutralize some of the acetic acid, yielding the conjugate base acetate ion. Compute the new concentrations of these two buffer components, then repeat the equilibrium calculation of part (a) using these new concentrations.

$$0.0010 \ \bcancel{L} \times \left( \frac{0.10 \text{ mol NaOH}}{1 \ \bcancel{L}} \right) = 1.0 \times 10^{-4} \text{ mol NaOH}$$

The initial molar amount of acetic acid is

$$0.100 \ \bcancel{L} \times \left( \frac{0.100 \text{ mol } CH_3CO_2H}{1 \ \bcancel{L}} \right) = 1.00 \times 10^{-2} \text{ mol } CH_3CO_2H$$

The amount of acetic acid remaining after some is neutralized by the added base is

$$(1.0 \times 10^{-2}) - (0.01 \times 10^{-2}) = 0.99 \times 10^{-2} \text{ mol } CH_3CO_2H$$

The newly formed acetate ion, along with the initially present acetate, gives a final acetate concentration of

$$(1.0 \times 10^{-2}) + (0.01 \times 10^{-2}) = 1.01 \times 10^{-2} \text{ mol } NaCH_3CO_2$$

Compute molar concentrations for the two buffer components:

$$[CH_3CO_2H] = \frac{9.9 \times 10^{-3} \text{ mol}}{0.101 \text{ L}} = 0.098 \ M$$
$$[NaCH_3CO_2] = \frac{1.01 \times 10^{-2} \text{ mol}}{0.101 \text{ L}} = 0.100 \ M$$

Using these concentrations, the pH of the solution may be computed as in part (a) above, yielding pH = 4.75 (only slightly different from that prior to adding the strong base).

(c) For comparison, calculate the pH after 1.0 mL of 0.10 $M$ NaOH is added to 100 mL of a solution of an unbuffered solution with a pH of 4.74.
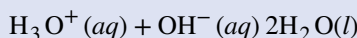
The amount of hydrogen ion initially present in the solution is

$$[H_3O^+] = 10^{-4.74} = 1.8 \times 10^{-5} \ M$$
$$\text{mol } H_3O^+ = (0.100 \ L)(1.8 \times 10^{-5} \ M) = 1.8 \times 10^{-6} \text{ mol } H_3O^+$$

The amount of hydroxide ion added to the solution is

$$\text{mol OH}^- = (0.0010\ L)(0.10\ M) = 1.0 \times 10^{-4}\ \text{mol OH}^-$$

The added hydroxide will neutralize hydronium ion via the reaction

$$\text{H}_3\text{O}^+(aq) + \text{OH}^-(aq)\ 2\text{H}_2\text{O}(l)$$

The 1:1 stoichiometry of this reaction shows that an excess of hydroxide has been added (greater molar amount than the initially present hydronium ion).

The amount of hydroxide ion remaining is

$$1.0 \times 10^{-4}\ \text{mol} - 1.8 \times 10^{-6}\ \text{mol} = 9.8 \times 10^{-5}\ \text{mol OH}^-$$

corresponding to a hydroxide molarity of

$$9.8 \times 10^{-5}\ \text{mol OH}^- / 0.101\ L = 9.7 \times 10^{-4}\ M$$

The pH of the solution is then calculated to be

$$\text{pH} = 14.00 - \text{pOH} = 14.00 - -\log(9.7 \times 10^{-4}) = 10.99$$

In this unbuffered solution, addition of the base results in a significant rise in pH (from 4.74 to 10.99) compared with the very slight increase observed for the buffer solution in part (b) (from 4.74 to 4.75).

### Check Your Learning

Show that adding 1.0 mL of 0.10 $M$ HCl changes the pH of 100 mL of a $1.8 \times 10^{-5}\ M$ HCl solution from 4.74 to 3.00.

**Answer:** Initial pH of $1.8 \times 10^{-5}\ M$ HCl; pH = $-\log[\text{H}_3\text{O}^+] = -\log[1.8 \times 10^{-5}] = 4.74$

Moles of $\text{H}_3\text{O}^+$ in 100 mL $1.8 \times 10^{-5}\ M$ HCl; $1.8 \times 10^{-5}$ moles/L $\times$ 0.100 L = $1.8 \times 10^{-6}$

Moles of $\text{H}_3\text{O}^+$ added by addition of 1.0 mL of 0.10 $M$ HCl: 0.10 moles/L $\times$ 0.0010 L = $1.0 \times 10^{-4}$ moles; final pH after addition of 1.0 mL of 0.10 $M$ HCl:

$$\text{pH} = -\log[\text{H}_3\text{O}^+] = -\log\left(\frac{\text{total moles H}_3\text{O}^+}{\text{total volume}}\right) = -\log\left(\frac{1.0 \times 10^{-4}\ \text{mol} + 1.8 \times 10^{-6}\ \text{mol}}{101\ \text{mL}\left(\frac{1\ \text{L}}{1000\ \text{mL}}\right)}\right) = 3.00$$

## Buffer Capacity

Buffer solutions do not have an unlimited capacity to keep the pH relatively constant (**Figure 14.16**). Instead, the ability of a buffer solution to resist changes in pH relies on the presence of appreciable amounts of its conjugate weak acid-base pair. When enough strong acid or base is added to substantially lower the concentration of either member of the buffer pair, the buffering action within the solution is compromised.

**Figure 14.16**   The indicator color (methyl orange) shows that a small amount of acid added to a buffered solution of pH 8 (beaker on the left) has little affect on the buffered system (middle beaker). However, a large amount of acid exhausts the buffering capacity of the solution and the pH changes dramatically (beaker on the right). (credit: modification of work by Mark Ott)

The **buffer capacity** is the amount of acid or base that can be added to a given volume of a buffer solution before the pH changes significantly, usually by one unit. Buffer capacity depends on the amounts of the weak acid and its conjugate base that are in a buffer mixture. For example, 1 L of a solution that is 1.0 $M$ in acetic acid and 1.0 $M$ in sodium acetate has a greater buffer capacity than 1 L of a solution that is 0.10 $M$ in acetic acid and 0.10 $M$ in sodium acetate even though both solutions have the same pH. The first solution has more buffer capacity because it contains more acetic acid and acetate ion.

## Selection of Suitable Buffer Mixtures

There are two useful rules of thumb for selecting buffer mixtures:

1.   A good buffer mixture should have about equal concentrations of both of its components. A buffer solution has generally lost its usefulness when one component of the buffer pair is less than about 10% of the other. **Figure 14.17** shows how pH changes for an acetic acid-acetate ion buffer as base is added. The initial pH is 4.74. A change of 1 pH unit occurs when the acetic acid concentration is reduced to 11% of the acetate ion concentration.
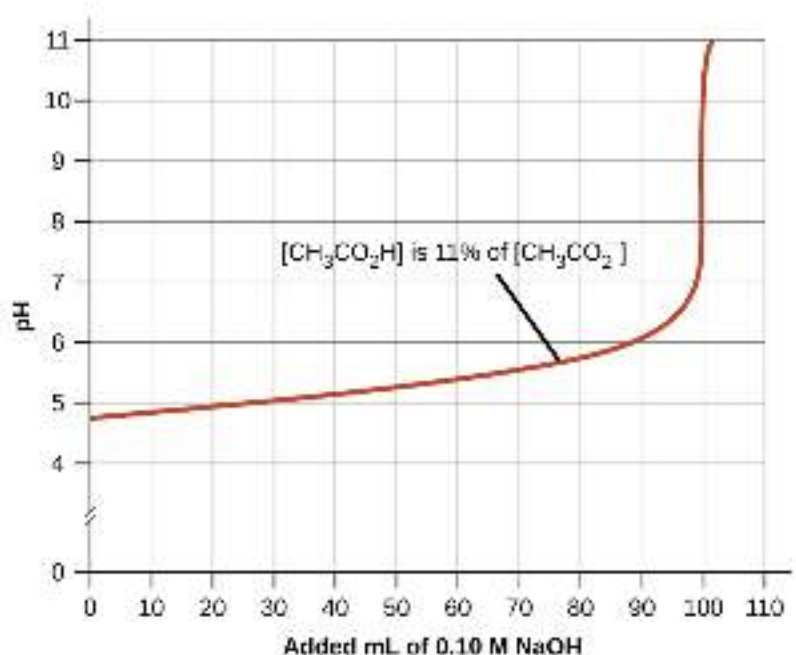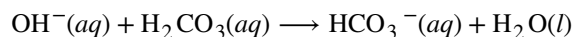
**Figure 14.17** Change in pH as an increasing amount of a 0.10-*M* NaOH solution is added to 100 mL of a buffer solution in which, initially, [CH₃CO₂H] = 0.10 *M* and $[CH_3CO_2{}^-]$ = 0.10 *M*. Note the greatly diminished buffering action occurring after the buffer capacity has been reached, resulting in drastic rises in pH on adding more strong base.

2. Weak acids and their salts are better as buffers for pHs less than 7; weak bases and their salts are better as buffers for pHs greater than 7.

Blood is an important example of a buffered solution, with the principal acid and ion responsible for the buffering action being carbonic acid, $H_2CO_3$, and the bicarbonate ion, $HCO_3{}^-$. When a hydronium ion is introduced to the blood stream, it is removed primarily by the reaction:

$$H_3O^+(aq) + HCO_3{}^-(aq) \longrightarrow H_2CO_3(aq) + H_2O(l)$$
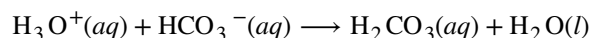
An added hydroxide ion is removed by the reaction:

$$OH^-(aq) + H_2CO_3(aq) \longrightarrow HCO_3{}^-(aq) + H_2O(l)$$

The added strong acid or base is thus effectively converted to the much weaker acid or base of the buffer pair ($H_3O^+$ is converted to $H_2CO_3$ and OH⁻ is converted to $HCO_3^-$). The pH of human blood thus remains very near the value determined by the buffer pairs pKa, in this case, 7.35. Normal variations in blood pH are usually less than 0.1, and pH changes of 0.4 or greater are likely to be fatal.

## The Henderson-Hasselbalch Equation

The ionization-constant expression for a solution of a weak acid can be written as:

$$K_a = \frac{[H_3O^+][A^-]}{[HA]}$$

Rearranging to solve for [H₃O⁺] yields:

$$[H_3O^+] = K_a \times \frac{[HA]}{[A^-]}$$

Taking the negative logarithm of both sides of this equation gives

$$-\log[\text{H}_3\text{O}^+] \;=\; -\log K_\text{a} - \log\frac{[\text{HA}]}{[\text{A}^-]},$$

which can be written as

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

where $\text{p}K_\text{a}$ is the negative of the logarithm of the ionization constant of the weak acid ($\text{p}K_\text{a} = -\log K_\text{a}$). This equation relates the pH, the ionization constant of a weak acid, and the concentrations of the weak conjugate acid-base pair in a buffered solution. Scientists often use this expression, called the **Henderson-Hasselbalch equation**, to calculate the pH of buffer solutions. It is important to note that the "$x$ is small" assumption must be valid to use this equation.

## Portrait of a Chemist

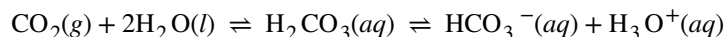### Lawrence Joseph Henderson and Karl Albert Hasselbalch

Lawrence Joseph Henderson (1878–1942) was an American physician, biochemist and physiologist, to name only a few of his many pursuits. He obtained a medical degree from Harvard and then spent 2 years studying in Strasbourg, then a part of Germany, before returning to take a lecturer position at Harvard. He eventually became a professor at Harvard and worked there his entire life. He discovered that the acid-base balance in human blood is regulated by a buffer system formed by the dissolved carbon dioxide in blood. He wrote an equation in 1908 to describe the carbonic acid-carbonate buffer system in blood. Henderson was broadly knowledgeable; in addition to his important research on the physiology of blood, he also wrote on the adaptations of organisms and their fit with their environments, on sociology and on university education. He also founded the Fatigue Laboratory, at the Harvard Business School, which examined human physiology with specific focus on work in industry, exercise, and nutrition.

In 1916, Karl Albert Hasselbalch (1874–1962), a Danish physician and chemist, shared authorship in a paper with Christian Bohr in 1904 that described the Bohr effect, which showed that the ability of hemoglobin in the blood to bind with oxygen was inversely related to the acidity of the blood and the concentration of carbon dioxide. The pH scale was introduced in 1909 by another Dane, Sørensen, and in 1912, Hasselbalch published measurements of the pH of blood. In 1916, Hasselbalch expressed Henderson's equation in logarithmic terms, consistent with the logarithmic scale of pH, and thus the Henderson-Hasselbalch equation was born.

## How Sciences Interconnect

### Medicine: The Buffer System in Blood

The normal pH of human blood is about 7.4. The carbonate buffer system in the blood uses the following equilibrium reaction:

$$\text{CO}_2(g) + 2\text{H}_2\text{O}(l) \;\rightleftharpoons\; \text{H}_2\text{CO}_3(aq) \;\rightleftharpoons\; \text{HCO}_3{}^-(aq) + \text{H}_3\text{O}^+(aq)$$

The concentration of carbonic acid, $\text{H}_2\text{CO}_3$ is approximately 0.0012 *M*, and the concentration of the hydrogen carbonate ion, $\text{HCO}_3{}^-$, is around 0.024 *M*. Using the Henderson-Hasselbalch equation and the $\text{p}K_\text{a}$ of carbonic acid at body temperature, we can calculate the pH of blood:

$$\text{pH} = \text{p}K_\text{a} + \log\frac{[\text{base}]}{[\text{acid}]} = 6.4 + \log\frac{0.024}{0.0012} = 7.7$$

The fact that the $\text{H}_2\text{CO}_3$ concentration is significantly lower than that of the $\text{HCO}_3{}^-$ ion may seem unusual, but this imbalance is due to the fact that most of the by-products of our metabolism that enter our bloodstream are acidic. Therefore, there must be a larger proportion of base than acid, so that the capacity of the buffer will not be exceeded.

Lactic acid is produced in our muscles when we exercise. As the lactic acid enters the bloodstream, it is neutralized by the $HCO_3^-$ ion, producing $H_2CO_3$. An enzyme then accelerates the breakdown of the excess carbonic acid to carbon dioxide and water, which can be eliminated by breathing. In fact, in addition to the regulating effects of the carbonate buffering system on the pH of blood, the body uses breathing to regulate blood pH. If the pH of the blood decreases too far, an increase in breathing removes $CO_2$ from the blood through the lungs driving the equilibrium reaction such that $[H_3O^+]$ is lowered. If the blood is too alkaline, a lower breath rate increases $CO_2$ concentration in the blood, driving the equilibrium reaction the other way, increasing $[H^+]$ and restoring an appropriate pH.

### Link to Learning

View **information (http://openstaxcollege.org/l/16BufferSystem)** on the buffer system encountered in natural waters.

# 14.7 Acid-Base Titrations

By the end of this section, you will be able to:

- Interpret titration curves for strong and weak acid-base systems
- Compute sample pH at important stages of a titration
- Explain the function of acid-base indicators

As seen in the chapter on the stoichiometry of chemical reactions, titrations can be used to quantitatively analyze solutions for their acid or base concentrations. In this section, we will explore the underlying chemical equilibria that make acid-base titrimetry a useful analytical technique.

## Titration Curves

A **titration curve** is a plot of some solution property versus the amount of added titrant. For acid-base titrations, solution pH is a useful property to monitor because it varies predictably with the solution composition and, therefore, may be used to monitor the titration's progress and detect its end point. The following example exercise demonstrates the computation of pH for a titration solution after additions of several specified titrant volumes. The first example involves a strong acid titration that requires only stoichiometric calculations to derive the solution pH. The second example addresses a weak acid titration requiring equilibrium calculations.

### Example 14.21

#### Calculating pH for Titration Solutions: Strong Acid/Strong Base

A titration is carried out for 25.00 mL of 0.100 $M$ HCl (strong acid) with 0.100 $M$ of a strong base NaOH (the titration curve is shown in **Figure 14.18**). Calculate the pH at these volumes of added base solution:

(a) 0.00 mL

(b) 12.50 mL

(c) 25.00 mL

(d) 37.50 mL

**Solution**

(a) Titrant volume = 0 mL. The solution pH is due to the acid ionization of HCl. Because this is a strong acid, the ionization is complete and the hydronium ion molarity is 0.100 $M$. The pH of the solution is then

$$\text{pH} = -\log(0.100) = 1.000$$

(b) Titrant volume = 12.50 mL. Since the acid sample and the base titrant are both monoprotic and equally concentrated, this titrant addition involves less than a stoichiometric amount of base, and so it is completely consumed by reaction with the excess acid in the sample. The concentration of acid remaining is computed by subtracting the consumed amount from the intial amount and then dividing by the solution volume:

$$[H_3O^+] = \frac{n(H^+)}{V} = \frac{0.002500 \text{ mol} \times \left(\frac{1000 \text{ mL}}{1 \text{ L}}\right) - 0.100 \ M \times 12.50 \text{ mL}}{25.00 \text{ mL} + 12.50 \text{ mL}} = 0.0333 \ M$$

(c) Titrant volume = 25.00 mL. This titrant addition involves a stoichiometric amount of base (the *equivalence point*), and so only products of the neutralization reaction are in solution (water and NaCl). Neither the cation nor the anion of this salt undergo acid-base ionization; the only process generating hydronium ions is the autoprotolysis of water. The solution is neutral, having a pH = 7.00.

(d) Titrant volume = 37.50 mL. This involves the addition of titrant in excess of the equivalence point. The solution pH is then calculated using the concentration of hydroxide ion:

$$n(OH^-)_0 > n(H^+)_0$$

$$[OH^-] = \frac{n(OH^-)}{V} = \frac{0.100 \ M \times 35.70 \text{ mL} - 0.002500 \text{ mol} \times \left(\frac{1000 \text{ mL}}{1 \text{ L}}\right)}{25.00 \text{ mL} + 37.50 \text{ mL}} = 0.0200 \ M$$

pH = 14 − pOH = 14 + log([OH⁻]) = 14 + log(0.0200) = 12.30

**Check Your Learning**

Calculate the pH for the strong acid/strong base titration between 50.0 mL of 0.100 $M$ HNO₃($aq$) and 0.200 $M$ NaOH (titrant) at the listed volumes of added base: 0.00 mL, 15.0 mL, 25.0 mL, and 40.0 mL.

**Answer:**   0.00: 1.000; 15.0: 1.5111; 25.0: 7; 40.0: 12.523

## Example 14.22

### Titration of a Weak Acid with a Strong Base

Consider the titration of 25.00 mL of 0.100 $M$ CH₃CO₂H with 0.100 $M$ NaOH. The reaction can be represented as:

$$CH_3CO_2H + OH^- \longrightarrow CH_3CO_2^- + H_2O$$
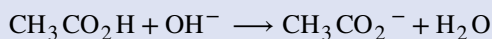
Calculate the pH of the titration solution after the addition of the following volumes of NaOH titrant:

(a) 0.00 mL

(b) 25.00 mL

(c) 12.50 mL

(d) 37.50 mL

**Solution**

(a) The initial pH is computed for the acetic acid solution in the usual ICE approach:

$$K_a = \frac{[H_3O^+][CH_3CO_2{}^-]}{[CH_3CO_2H]} \approx \frac{[H_3O^+]^2}{[CH_3CO_2H]_0},$$  and

$$[H_3O^+] = \sqrt{K_a \times [CH_3CO_2H]} = \sqrt{1.8 \times 10^{-5} \times 0.100} = 1.3 \times 10^{-3}$$

$$pH = -\log(1.3 \times 10^{-3}) = 2.87$$

(b) The acid and titrant are both monoprotic and the sample and titrant solutions are equally concentrated; thus, this volume of titrant represents the equivalence point. Unlike the strong-acid example above, however, the reaction mixture in this case contains a weak conjugate base (acetate ion). The solution pH is computed considering the base ionization of acetate, which is present at a concentration of

$$\frac{0.00250 \text{ mol}}{0.0500 \text{ L}} = 0.0500 \text{ M} CH_3CO_2{}^-$$

Base ionization of acetate is represented by the equation

$$CH_3CO_2{}^-(aq) + H_2O(l) \rightleftharpoons CH_3CO_2H(aq) + OH^-(aq)$$
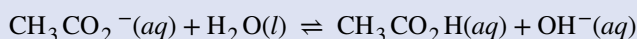
$$K_b = \frac{[H^+][OH^-]}{K_a} = \frac{K_w}{K_a} = \frac{1.0 \times 10^{-14}}{1.8 \times 10^{-5}} = 5.6 \times 10^{-10}$$

Assuming $x \ll 0.0500$, the pH may be calculated via the usual ICE approach: $K_b = \dfrac{x^2}{0.0500 \text{ } M}$

$$x = [OH^-] = 5.3 \times 10^{-6}$$
$$pOH = -\log(5.3 \times 10^{-6}) = 5.28$$
$$pH = 14.00 - 5.28 = 8.72$$

Note that the pH at the equivalence point of this titration is significantly greater than 7, as expected when titrating a weak acid with a strong base.

(c) Titrant volume = 12.50 mL. This volume represents one-half of the stoichiometric amount of titrant, and so one-half of the acetic acid has been neutralized to yield an equivalent amount of acetate ion. The concentrations of these conjugate acid-base partners, therefore, are equal. A convenient approach to computing the pH is use of the Henderson-Hasselbalch equation:

$$pH = pK_a + \log \frac{[Base]}{[Acid]} = -\log(K_a) + \log \frac{[CH_3CO_2{}^-]}{[CH_3CO_2H]} = -\log(1.8 \times 10^{-5}) + \log(1)$$

$$pH = -\log(1.8 \times 10^{-5}) = 4.74$$

(pH = $pK_a$ at the half-equivalence point in a titration of a weak acid)

(d) Titrant volume = 37.50 mL. This volume represents a stoichiometric excess of titrant, and a reaction solution containing both the titration product, acetate ion, and the excess strong titrant. In such solutions, the solution pH is determined primarily by the amount of excess strong base:

$$[OH^-] = \frac{(0.003750 \text{ mol} - 0.00250 \text{ mol})}{0.06250 \text{ L}} = 2.00 \times 10^{-2} \text{ } M$$
$$pOH = -\log(2.00 \times 10^{-2}) = 1.70, \text{ and } pH = 14.00 - 1.70 = 12.30$$

### Check Your Learning

Calculate the pH for the weak acid/strong base titration between 50.0 mL of 0.100 $M$ HCOOH(aq) (formic acid) and 0.200 $M$ NaOH (titrant) at the listed volumes of added base: 0.00 mL, 15.0 mL, 25.0 mL, and 30.0 mL.

**Answer:**  0.00 mL: 2.37; 15.0 mL: 3.92; 25.00 mL: 8.29; 30.0 mL: 12.097

Performing additional calculations similar to those in the preceding example permits a more full assessment of titration curves. A summary of pH/volume data pairs for the strong and weak acid titrations is provided in **Table**

**14.2** and plotted as titration curves in **Figure 14.18**. A comparison of these two curves illustrates several important concepts that are best addressed by identifying the four stages of a titration:

initial state (added titrant volume = 0 mL): pH is determined by the acid being titrated; because the two acid samples are equally concentrated, the weak acid will exhibit a greater initial pH

pre-equivalence point (0 mL < V < 25 mL): solution pH increases gradually and the acid is consumed by reaction with added titrant; composition includes unreacted acid and the reaction product, its conjugate base

equivalence point (V = 25 mL): a drastic rise in pH is observed as the solution composition transitions from acidic to either neutral (for the strong acid sample) or basic (for the weak acid sample), with pH determined by ionization of the conjugate base of the acid

postequivalence point (V > 25 mL): pH is determined by the amount of excess strong base titrant added; since both samples are titrated with the same titrant, both titration curves appear similar at this stage.

**pH Values in the Titrations of a Strong Acid and of a Weak Acid**

| Volume of 0.100 $M$ NaOH Added (mL) | Moles of NaOH Added | pH Values 0.100 $M$ HCl[1] | pH Values 0.100 $M$ $CH_3CO_2H$[2] |
|---|---|---|---|
| 0.0 | 0.0 | 1.00 | 2.87 |
| 5.0 | 0.00050 | 1.18 | 4.14 |
| 10.0 | 0.00100 | 1.37 | 4.57 |
| 15.0 | 0.00150 | 1.60 | 4.92 |
| 20.0 | 0.00200 | 1.95 | 5.35 |
| 22.0 | 0.00220 | 2.20 | 5.61 |
| 24.0 | 0.00240 | 2.69 | 6.13 |
| 24.5 | 0.00245 | 3.00 | 6.44 |
| 24.9 | 0.00249 | 3.70 | 7.14 |
| 25.0 | 0.00250 | 7.00 | 8.72 |
| 25.1 | 0.00251 | 10.30 | 10.30 |
| 25.5 | 0.00255 | 11.00 | 11.00 |
| 26.0 | 0.00260 | 11.29 | 11.29 |
| 28.0 | 0.00280 | 11.75 | 11.75 |
| 30.0 | 0.00300 | 11.96 | 11.96 |
| 35.0 | 0.00350 | 12.22 | 12.22 |
| 40.0 | 0.00400 | 12.36 | 12.36 |
| 45.0 | 0.00450 | 12.46 | 12.46 |
| 50.0 | 0.00500 | 12.52 | 12.52 |

**Table 14.2**

1. Titration of 25.00 mL of 0.100 $M$ HCl (0.00250 mol of HCl) with 0.100 $M$ NaOH.
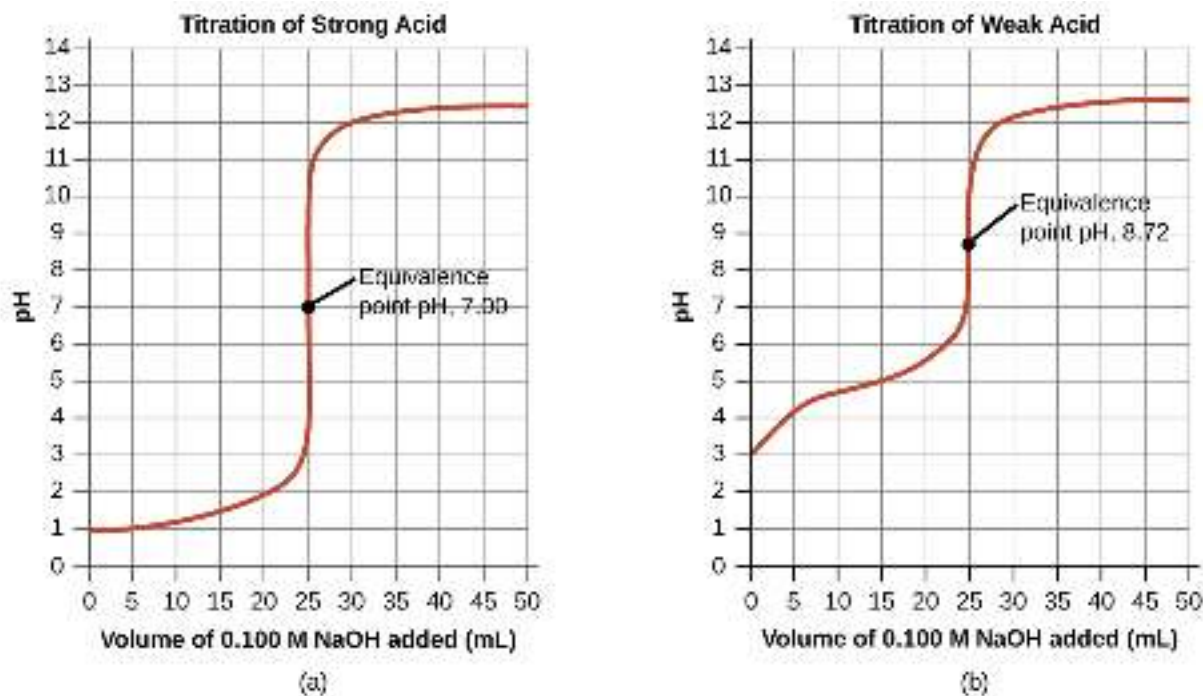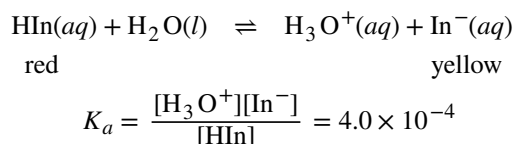2. Titration of 25.00 mL of 0.100 $M$ $CH_3CO_2H$ (0.00250 mol of $CH_3CO_2H$) with 0.100 $M$ NaOH.

**Figure 14.18** (a) The titration curve for the titration of 25.00 mL of 0.100 *M* HCl (strong acid) with 0.100 *M* NaOH (strong base) has an equivalence point of 7.00 pH. (b) The titration curve for the titration of 25.00 mL of 0.100 *M* acetic acid (weak acid) with 0.100 *M* NaOH (strong base) has an equivalence point of 8.72 pH.

## Acid-Base Indicators

Certain organic substances change color in dilute solution when the hydronium ion concentration reaches a particular value. For example, phenolphthalein is a colorless substance in any aqueous solution with a hydronium ion concentration greater than $5.0 \times 10^{-9}$ *M* (pH < 8.3). In more basic solutions where the hydronium ion concentration is less than $5.0 \times 10^{-9}$ *M* (pH > 8.3), it is red or pink. Substances such as phenolphthalein, which can be used to determine the pH of a solution, are called **acid-base indicators**. Acid-base indicators are either weak organic acids or weak organic bases.

The equilibrium in a solution of the acid-base indicator methyl orange, a weak acid, can be represented by an equation in which we use HIn as a simple representation for the complex methyl orange molecule:

$$HIn(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + In^-(aq)$$
$$\text{red} \qquad\qquad\qquad\qquad \text{yellow}$$

$$K_a = \frac{[H_3O^+][In^-]}{[HIn]} = 4.0 \times 10^{-4}$$

The anion of methyl orange, In$^-$, is yellow, and the nonionized form, HIn, is red. When we add acid to a solution of methyl orange, the increased hydronium ion concentration shifts the equilibrium toward the nonionized red form, in accordance with Le Châtelier's principle. If we add base, we shift the equilibrium towards the yellow form. This behavior is completely analogous to the action of buffers.

The perceived color of an indicator solution is determined by the ratio of the concentrations of the two species In$^-$ and HIn. If most of the indicator (typically about 60−90% or more) is present as In$^-$, the perceived color of the solution is yellow. If most is present as HIn, then the solution color appears red. The Henderson-Hasselbalch equation is useful for understanding the relationship between the pH of an indicator solution and its composition (thus, perceived color):

$$\text{pH} = \text{p}K\text{a} + \log\left(\frac{[\text{In}^-]}{[\text{HIn}]}\right)$$

In solutions where pH > $\text{p}K_a$, the logarithmic term must be positive, indicating an excess of the conjugate base form of the indicator (yellow solution). When pH > $\text{p}K_a$, the log term must be negative, indicating an excess of the conjugate acid (red solution). When the solution pH is close to the indicator pKa, appreciable amounts of both conjugate partners are present, and the solution color is that of an additive combination of each (yellow and red, yielding orange). The **color change interval** (or *pH interval*) for an acid-base indicator is defined as the range of pH values over which a change in color is observed, and for most indicators this range is approximately $\text{p}K_a \pm 1$.

There are many different acid-base indicators that cover a wide range of pH values and can be used to determine the approximate pH of an unknown solution by a process of elimination. Universal indicators and pH paper contain a mixture of indicators and exhibit different colors at different pHs. **Figure 14.19** presents several indicators, their colors, and their color-change intervals.
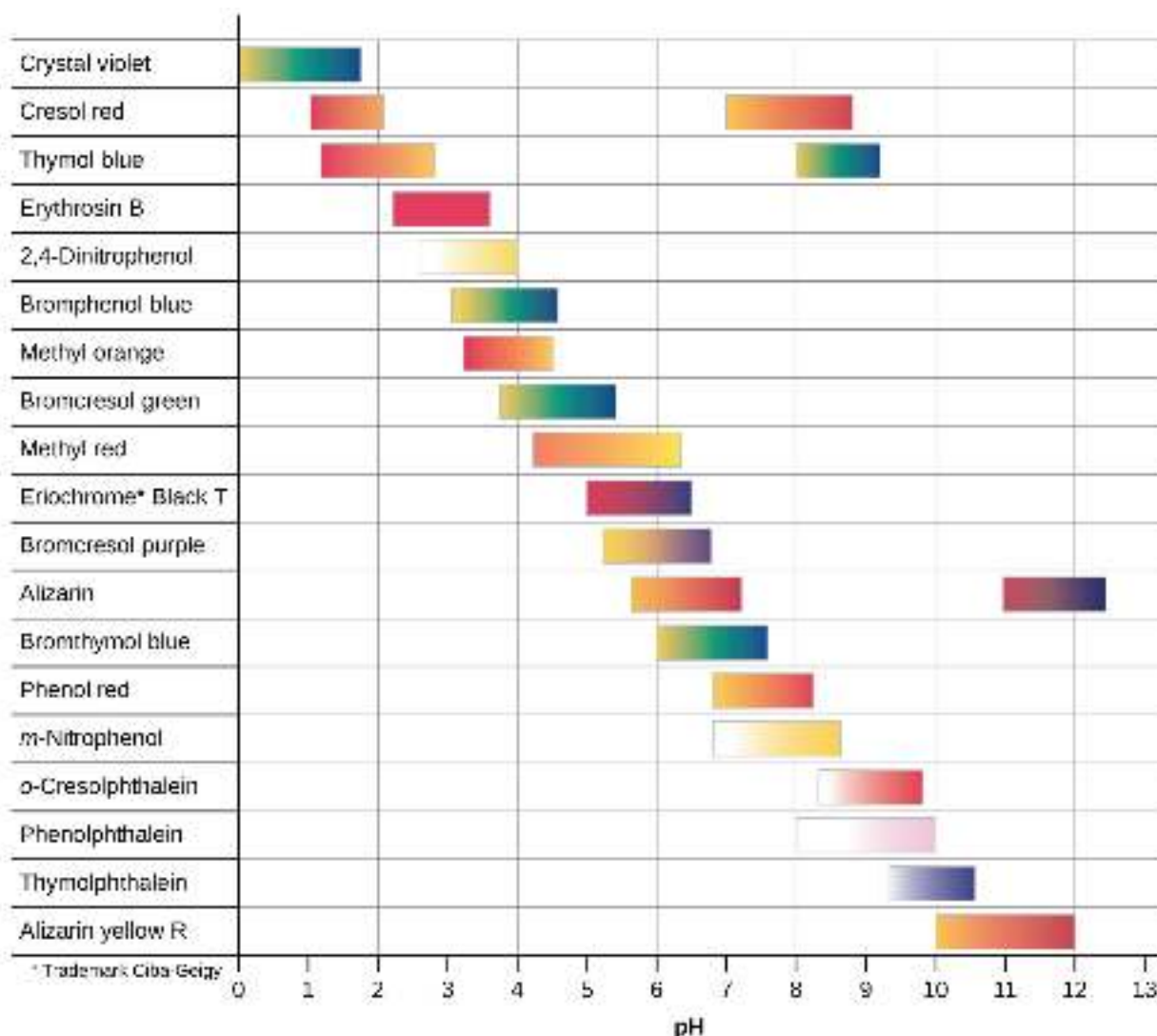


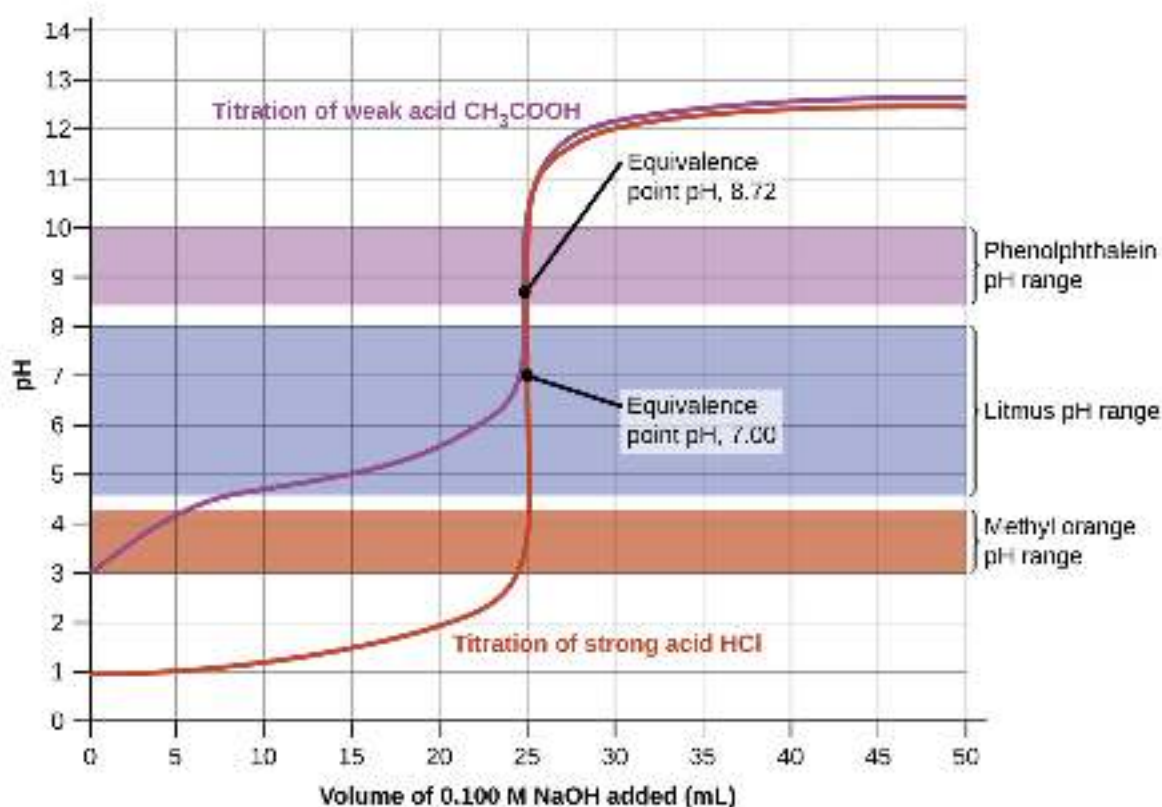**Figure 14.19**   This chart illustrates the color change intervals for several acid-base indicators.

**Figure 14.20**   Titration curves for strong and weak acids illustrating the proper choice of acid-base indicator. Any of the three indicators will exhibit a reasonably sharp color change at the equivalence point of the strong acid titration, but only phenolphthalein is suitable for use in the weak acid titration.

The titration curves shown in **Figure 14.20** illustrate the choice of a suitable indicator for specific titrations. In the strong acid titration, use of any of the three indicators should yield reasonably sharp color changes and accurate end point determinations. For this titration, the solution pH reaches the lower limit of the methyl orange color change interval after addition of ~24 mL of titrant, at which point the initially red solution would begin to appear orange. When 25 mL of titrant has been added (the equivalence point), the pH is well above the upper limit and the solution will appear yellow. The titration's end point may then be estimated as the volume of titrant that yields a distinct orange-to-yellow color change. This color change would be challenging for most human eyes to precisely discern. More-accurate estimates of the titration end point are possible using either litmus or phenolphthalein, both of which exhibit color change intervals that are encompassed by the steep rise in pH that occurs around the 25.00 mL equivalence point.

The weak acid titration curve in **Figure 14.20** shows that only one of the three indicators is suitable for end point detection. If methyl orange is used in this titration, the solution will undergo a gradual red-to-orange-to-yellow color change over a relatively large volume interval (0–6 mL), completing the color change well before the equivalence point (25 mL) has been reached. Use of litmus would show a color change that begins after adding 7–8 mL of titrant and ends just before the equivalence point. Phenolphthalein, on the other hand, exhibits a color change interval that nicely brackets the abrupt change in pH occurring at the titration's equivalence point. A sharp color change from colorless to pink will be observed within a very small volume interval around the equivalence point.