Chapter 10

Acids and Bases

Figure 10.1 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

10.1 Brønsted-Lowry Acids and Bases

10.2 pH and pOH

10.3 Relative Strengths of Acids and Bases

10.4 Hydrolysis of Salt Solutions

10.5 Polyprotic Acids

10.6 Buffers

10.7 Acid-Base Titrations

Introduction

In our bodies, in our homes, and in our industrial society, acids and bases play key roles. Proteins, enzymes, blood, genetic material, and other components of living matter contain both acids and bases. We seem to like the sour taste of acids; we add them to soft drinks, salad dressings, and spices. Many foods, including citrus fruits and some vegetables, contain acids. Cleaners in our homes contain acids or bases. Acids and bases play important roles in the chemical industry. Currently, approximately 36 million metric tons of sulfuric acid are produced annually in the United States alone. Huge quantities of ammonia (8 million tons), urea (10 million tons), and phosphoric acid (10 million tons) are also produced annually. This chapter will illustrate the chemistry of acid-base reactions and equilibria, and provide you with tools for quantifying the concentrations of acids and bases in solutions.

10.1 Brønsted-Lowry Acids and Bases

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

- Identify acids, bases, name common acids and bases,
- Identify 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

Acids and bases have been known for a long time. When Robert Boyle characterized them in 1680, he noted that acids dissolve many substances, change the color of certain natural dyes (for example, they change litmus from blue to red), and lose these characteristic properties after coming into contact with alkalis (bases). 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.

We define acids and bases as Arrhenius did: We identify an acid as a compound that dissolves in water to yield hydronium ions (H_3O^+) and a base as a compound that dissolves in water to yield hydroxide ions (OH^-). This definition is not wrong; it is simply limited.

We can extend the definition of an acid or a base using the more general definition proposed in 1923 by the Danish chemist Johannes Brønsted and the English chemist Thomas Lowry. Their definition centers on the proton, H^+. A proton is what remains when the most common isotope of hydrogen, ^1H, loses an electron. 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 the transfer of a proton from a proton donor (acid) to a proton acceptor (base).

Acids are an important class of compounds containing hydrogen and having special nomenclature rules. Binary acids are named using the prefix *hydro-*, changing the *–ide* suffix to *–ic*, and adding "acid;" HCl is hydrochloric acid. Oxyacids are named by changing the ending of the anion (*–ate* to *–ic* and *–ite* to *–ous*), and adding "acid;" H_2CO_3 is carbonic acid.

Naming Binary Acids

Some compounds containing hydrogen are members of an important class of substances known as acids. The chemistry of these compounds is explored in more detail in later chapters of this text, but for now, it will suffice to note that many acids release hydrogen ions, H^+, when dissolved in water. To denote this distinct chemical property, a

mixture of water with an acid is given a name derived from the compound's name. If the compound is a **binary acid** (comprised of hydrogen and one other nonmetallic element):

1. The word "hydrogen" is changed to the prefix *hydro-*
2. The other nonmetallic element name is modified by adding the suffix *-ic*
3. The word "acid" is added as a second word

For example, when the gas HCl (hydrogen chloride) is dissolved in water, the solution is called *hydrochloric acid*. Several other examples of this nomenclature are shown in **Table 10.1**.

Name of Gas	Name of Acid
HF(*g*), hydrogen fluoride	HF(*aq*), hydrofluoric acid
HCl(*g*), hydrogen chloride	HCl(*aq*), hydrochloric acid
HBr(*g*), hydrogen bromide	HBr(*aq*), hydrobromic acid
HI(*g*), hydrogen iodide	HI(*aq*), hydroiodic acid
H_2S(*g*), hydrogen sulfide	H_2S(*aq*), hydrosulfuric acid

Table 10.1: Names of Some Simple Acids

Naming Oxyacids

Many compounds containing three or more elements (such as organic compounds or coordination compounds) are subject to specialized nomenclature rules that you will learn later. However, we will briefly discuss the important compounds known as oxyacids, compounds that contain hydrogen, oxygen, and at least one other element, and are bonded in such a way as to impart acidic properties to the compound. Typical oxyacids consist of hydrogen combined with a polyatomic, oxygen-containing ion. To name oxyacids:

1. Omit "hydrogen"
2. Start with the root name of the anion
3. Replace *–ate* with *–ic*, or *–ite* with *–ous*
4. Add "acid"

For example, consider H_2CO_3. To name this correctly, "hydrogen" is omitted; the *–ate* of carbonate is replace with *–ic*; and acid is added—so its name is carbonic acid. Other examples are given in **Table 10.2,** with some exceptions (e.g., H_2SO_4 is called sulfuric acid, not sulfic acid, and H_2SO_3 is sulfurous, not sulfous, acid).

Formula	Anion Name	Acid Name
HNO_3	nitrate	nitric acid
HNO_2	nitrite	nitrous acid
$HClO_4$	perchlorate	perchloric acid
H_2CO_3	carbonate	carbonic acid
H_2SO_4	sulfate	sulfuric acid
H_2SO_3	sulfite	sulfurous acid

H_3PO_4	phosphate	phosphoric acid
$HC_2H_3O_2$	acetate	acetic acid

Table 10.2: Names of Common Oxyacids

Acids may be compounds such as HCl or H_2SO_4, organic acids like acetic acid (CH_3COOH) or ascorbic acid (vitamin C), or H_2O. Anions (such as HSO_4^-, $H_2PO_4^-$, HS^-, and HCO_3^-) and cations (such as H_3O^+, NH_4^+, and $[Al(H_2O)_6]^{3+}$) may also act as acids. Bases fall into the same three categories. Bases may be neutral molecules (such as H_2O, NH_3, and CH_3NH_2), anions (such as OH^-, HS^-, HCO_3^-, CO_3^{2-}, F^-, and PO_4^{3-}), or cations (such as $[Al(H_2O)_5OH]^{2+}$). The most familiar bases are ionic compounds such as NaOH and $Ca(OH)_2$, which contain the hydroxide ion, OH^-. The hydroxide ion in these compounds accepts a proton from acids to form water:

$$H^+ + OH^- \longrightarrow H_2O$$

We call the product that remains after an acid donates a proton the **conjugate base** of the acid. This species is a base because it can accept a proton (to re-form the acid):

$$\textbf{acid} \rightleftharpoons \textbf{proton} + \textbf{conjugate base}$$

$$HF \rightleftharpoons H^+ + F^-$$

$$H_2SO_4 \rightleftharpoons H^+ + HSO_4^-$$

$$H_2O \rightleftharpoons H^+ + OH^-$$

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

$$NH_4^+ \rightleftharpoons H^+ + NH_3$$

We call the product that results when a base accepts a proton the base's conjugate acid. This species is an acid because it can give up a proton (and thus re-form the base):

$$\textbf{base} + \textbf{proton} \rightleftharpoons \textbf{conjugate acid}$$

$$OH^- + H^+ \rightleftharpoons H_2O$$

$$H_2O + H^+ \rightleftharpoons H_3O^+$$

$$NH_3 + H^+ \rightleftharpoons NH_4^+$$

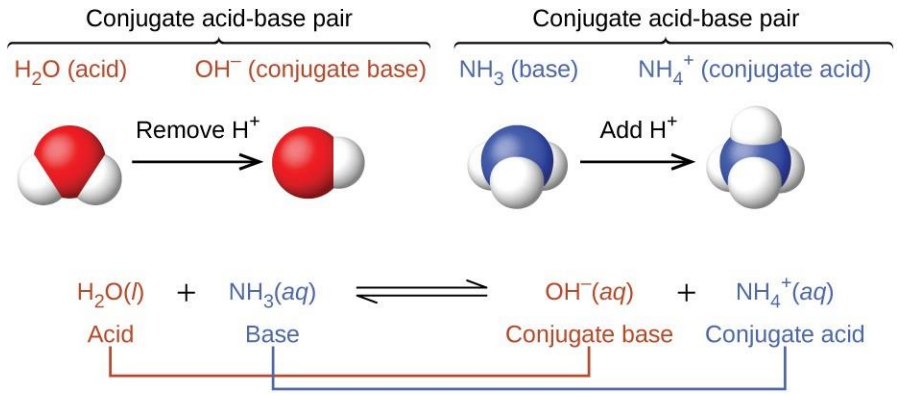
$$S^{2-} + H^+ \rightleftharpoons HS^-$$

$$CO_3^{2-} + H^+ \rightleftharpoons HCO_3^-$$

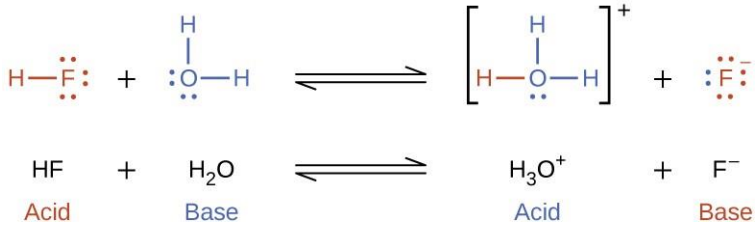
$$F^- + H^+ \rightleftharpoons HF$$

In these two sets of equations, the behaviors of acids as proton donors and bases as proton acceptors are represented in isolation. In reality, all acid-base reactions involve the *transfer* of protons between acids and bases. For example, consider the acid-base reaction that takes place when ammonia is dissolved in water. A water molecule (functioning as an acid) transfers a proton to an ammonia molecule (functioning as a base), yielding the conjugate base of water,

OH^-, and the conjugate acid of ammonia, NH_4^+:



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:



$$K = \frac{[H_3O^+][F^-]}{[HF]}$$

Notice that ionization reactions are represented as equilibrium processes.

Self-assessment 10.1:

Determine the conjugate acid or base for the following chemical species:

a) S^{2-}

b) O^{2-}

c) H_2CO_3

d) CH_3COOH

Answers:

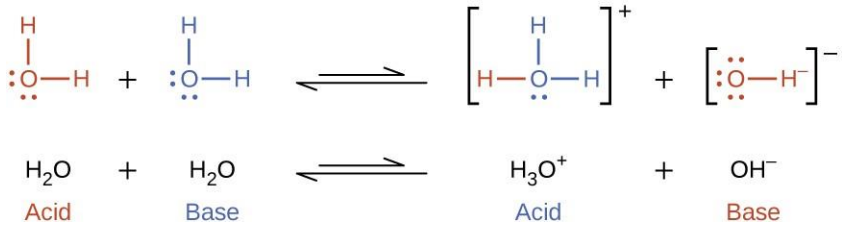
a) the conjugate acid is HS^-

b) the conjugate acid is OH^-

c) the conjugate base is HCO_3^-

d) the conjugate base is CH_3COO^-

In the preceding paragraph we saw that water can function as either an acid or a base, depending on the nature of the solute dissolved in it. In fact, in pure water or in any aqueous solution, water acts both as an acid and a base. A very



small fraction of water molecules donate protons to other water molecules to form hydronium ions and hydroxide ions:

This type of reaction, in which a substance ionizes when one molecule of the substance reacts with another molecule of the same substance, is referred to as **autoionization**.

Pure water undergoes autoionization to a very slight extent. Only about two out of every 10^9 molecules in a sample of pure water are ionized at 25 °C. The equilibrium constant for the ionization of water is called the **ion-product constant for water (K_w)**:

$$H_2O(l) + H_2O(l) \rightleftharpoons H_3O^+(aq) + OH^-(aq) \qquad K_w = [H_3O^+][OH^-]$$

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 1.0×10^{-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 5.6×10^{-13}, roughly 50 times larger than the value at 25 °C.

Example 10.1

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, $[H_3O^+] = [OH^-]$. At 25 °C:

$$K_w = [H_3O^+][OH^-] = [H_3O^+]^2 = [OH^-]^2 = 1.0 \times 10^{-14}$$

So: $$[H_3O^+] = [OH^-] = 1.0 \times 10^{-14} = 1.0 \times 10^{-7}\ M$$

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

Check Your Learning

The ion product of water at 80 °C is 2.4×10^{-13}. What are the concentrations of hydronium and hydroxide ions in pure water at 80 °C?

Answer: $[[H_3O^+] = [OH^-] = 4.9 \text{ x } 10^{-7}$ M

It is important to realize that the autoionization equilibrium for water is established in all aqueous solutions. Adding an acid or base to water will not change the position of the equilibrium. **Example 10.2** demonstrates the quantitative aspects of this relation between hydronium and hydroxide ion concentrations.

Example 10.2

Inverse Proportionality of $[H_3O^+]$ and $[OH^-]$: A solution of carbon dioxide 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:

We know the value of the ion-product constant for water at 25 °C:

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

Thus, we can calculate the missing equilibrium concentration. Rearrangement of the K_w expression yields that $[OH^-]$ is directly proportional to the inverse of $[H_3O^+]$:

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

The hydroxide ion concentration in water is reduced to 5.0×10^{-9} *M* as the hydronium ion concentration increases to 2.0×10^{-6} *M*. This is expected from Le Châtelier's principle; the autoionization reaction shifts to the left to reduce the stress of the increased hydronium ion concentration and the $[OH^-]$ is reduced relative to that in pure water.

A check of these concentrations confirms that our arithmetic is correct:

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

Check Your Learning

What is the hydronium ion concentration in an aqueous solution with a hydroxide ion concentration of 0.001 *M* at 25 °C?

Answer: $[H_3O^+] = 1 \times 10^{-11}\ M$

Self-assessment 10.2:

Most soft drinks are quite acidic and can erode tooth enamel. What is the hydronium ion concentration of a soda drink whose hydroxide concentration is 2.63×10^{-12} M?

Answer:

The ion product of water is constant: $K_W = [H_3O^+][OH^-] = 1.0 \times 10^{-14}$

$$[H_3O] = \frac{K_W}{[OH^-]} = \frac{1.0 \times 10^{-14}}{2.63 \times 10^{-13}} = 3.80 \times 10^{-3}\ M$$

The hydronium ion concentration of the soft drink is 3.80×10^{-3} *M*.

Amphiprotic Species

Like water, many molecules and ions may either gain or lose a proton under the appropriate conditions. Such species are said to be **amphiprotic**. Another term used to describe such species is **amphoteric**, which is a more general term for a species that may act either as an acid or a base by any definition (not just the Brønsted-Lowry one). Consider for example the bicarbonate ion, which may either donate or accept a proton as shown here:

$$HCO_3^-(aq) + H_2O(l) \rightleftharpoons CO_3^{2-}(aq) + H_3O^+(aq) \quad HCO_3^-(aq) + H_2O(l) \rightleftharpoons H_2CO_3(aq) + OH^-(aq)$$

Example 10.3

Representing the Acid-Base Behavior of an Amphoteric Substance: Write separate equations representing the reaction of HSO_3^- as an acid with OH^- and as a base with HI

Solution:

as an acid: $HSO_3^-(aq) + OH^-(aq) \rightleftharpoons SO_3^{2-}(aq) + H_2O(l)$

and as a base: $HSO_3^-(aq) + HI(aq) \rightleftharpoons H_2SO_3(aq) + I^-(aq)$

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

Self-assessment 10.3:

Ferrous sulfate, $FeSO_4$, is used to treat iron deficiency anemia, a lack of red blood cells due to lack of iron. The dosage has to be very precise as an overdose of iron can be fatal, especially in a young child. The anion portion of this dietary supplement is sulfate. The conjugate acid of sulfate, hydrogen sulfate, is amphoteric. Write the chemical equation for hydrogen sulfate reacting as a) a base and b) an acid.

Answers:

a) $HSO_4^- + H_2O \rightleftharpoons H_2SO_4 + H_3O^+$, since HSO_4^- behaves as a base, it will capture a proton to become its conjugate acid.

b) $HSO_4^- + H_2O \rightleftharpoons SO_4^{2-} + OH^-$, since HSO_4^- behaves as an acid, it will lose a proton to become its conjugate base, sulfate, SO_4^{2-}. Public Health Service standards for drinking water set a maximum of 250 mg/L of $SO4^{2-}$ because of its cathartic action (it is a laxative).

Reaction of Metals with Acids

This is the most convenient laboratory method of producing hydrogen. Metals with lower reduction potentials reduce the hydrogen ion in dilute acids to produce hydrogen gas and metal salts. For example, as shown in **Figure 10.2**, iron in dilute hydrochloric acid produces hydrogen gas and iron(II) chloride:

$$Fe(s) + 2H_3O^+(aq) + 2Cl^-(aq) \longrightarrow Fe^{2+}(aq) + 2Cl^-(aq) + H_2(g) + 2H_2O(l)$$

Figure 10.2 The reaction of iron with an acid produces hydrogen. Here, iron reacts with hydrochloric acid. (credit: Mark Ott)

The chemistry of carbon is extensive; however, most of this chemistry is not relevant to this chapter. The other aspects of the chemistry of carbon will appear in the chapter covering organic chemistry. In this chapter, we will focus on the carbonate ion and related substances. The metals of groups 1 and 2, as well as zinc, cadmium, mercury, and lead(II),

form ionic **carbonates**—compounds that contain the carbonate anions, CO_3^{2-}. The metals of group 1, magnesium, calcium, strontium, and barium also form **hydrogen carbonates**—compounds that contain the hydrogen carbonate anion, HCO_3^-, also known as the **bicarbonate anion**.

Carbonates are moderately strong bases. Aqueous solutions are basic because the carbonate ion accepts hydrogen ion from water in this reversible reaction:

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

Carbonates react with acids to form salts of the metal, gaseous carbon dioxide, and water. The reaction of calcium carbonate, the active ingredient of the antacid Tums, with hydrochloric acid (stomach acid), as shown in **Figure 10.3**, illustrates the reaction:

$$CaCO_3(s) + 2HCl(aq) \longrightarrow CaCl_2(aq) + CO_2(g) + H_2O(l)$$

Figure 10.3 The reaction of calcium carbonate with hydrochloric acid is shown. (credit: Mark Ott)

Other applications of carbonates include glass making—where carbonate ions serve as a source of oxide ions—and synthesis of oxides.

Hydrogen carbonates are amphoteric because they act as both weak acids and weak bases. Hydrogen carbonate ions act as acids and react with solutions of soluble hydroxides to form a carbonate and water:

$$KHCO_3(aq) + KOH(aq) \longrightarrow K_2CO_3(aq) + H_2O(l)$$

With acids, hydrogen carbonates form a salt, carbon dioxide, and water. Baking soda (bicarbonate of soda or sodium bicarbonate) is sodium hydrogen carbonate. Baking powder contains baking soda and a solid acid such as potassium hydrogen tartrate (cream of tartar), $KHC_4H_4O_6$. As long as the powder is dry, no reaction occurs; immediately after the addition of water, the acid reacts with the hydrogen carbonate ions to form carbon dioxide:

$$HC_4H_4O_6^-(aq) + HCO_3^-(aq) \longrightarrow C_4H_4O_6^{2-}(aq) + CO_2(g) + H_2O(l)$$

Dough will trap the carbon dioxide, causing it to expand during baking, producing the characteristic texture of baked goods.

Occurrence, Preparation, and Properties of Carbonates: The usual method for the preparation of the carbonates of the alkali and alkaline earth metals is by reaction of an oxide or hydroxide with carbon dioxide. Other carbonates form by precipitation. Metal carbonates or hydrogen carbonates such as limestone ($CaCO_3$), the antacid Tums ($CaCO_3$), and baking soda ($NaHCO_3$) are common examples. Carbonates and hydrogen carbonates decompose in the presence of acids and most decompose on heating.

Figure 10.4 Calcium carbonate, $CaCO_3$, can be consumed in the form of an antacid to neutralize the effects of acid in your stomach. (credit: "Midnightcomm"/Wikimedia Commons)

10.2 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, the values of which 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:

$$K_W = [H_3O^+][OH^-] = 10^{-14}$$

$$-\log K_W = -\log([H_3O^+][OH^-]) = -\log 10^{-14}$$

$$K_W = pH + pOH = 14.00$$

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

14.00 = pH + pOH

As was shown in **Example 10.1**, the hydronium ion molarity in pure water (or any neutral solution) is 1.0×10^{-7} *M* at 25 °C. The pH and pOH of a neutral solution at this temperature are therefore:

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

And so, *at this temperature*, acidic solutions are those with hydronium ion molarities greater than 1.0×10^{-7} *M* and hydroxide ion molarities less than 1.0×10^{-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 1.0×10^{-7} *M* and hydroxide ion molarities greater than 1.0×10^{-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 10.1** showed the hydronium molarity of pure water at 80 °C is 4.9×10^{-7} *M*, which corresponds to pH and pOH values of:

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

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 nonstandard temperatures, such as enzyme reactions in warm-blooded organisms. Unless otherwise noted, references to pH values are presumed to be those at standard temperature (25 °C) (**Table 10.3**).

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 10.3: Summary of Relations for Acidic, Basic and Neutral Solutions

Figure 10.5 shows the relationships between $[H_3O^+]$, $[OH^-]$, pH, and pOH, and gives values for these properties at standard temperatures for some common substances.

$[H_3O^+]$ (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 CH_3CO_2H (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; ocean water; baking soda
10^{-9}	10^{-5}	9	5	
10^{-10}	10^{-4}	10	4	
10^{-11}	10^{-3}	11	3	Milk of Magnesia
10^{-12}	10^{-2}	12	2	household ammonia, NH_3
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 10.5 The pH and pOH scales represent concentrations of $[H_3O^+]$ and OH^-, respectively. The pH and pOH values of some common substances at standard temperature (25 °C) are shown in this chart.

Example 10.4

Calculation of pH from $[H_3O^+]$: What is the pH of stomach acid, a solution of HCl with a hydronium ion concentration of 1.2×10^{-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**. Recall that, as we have done here, 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 2.0×10^{-6} *M*, about 20-times larger than that of pure water. Calculate the pH of the solution at 25 °C.

Answer: 5.70

Example 10.5

Calculation of Hydronium Ion Concentration from pH: Calculate the hydronium ion concentration of blood, the pH of which is 7.3 (slightly alkaline).

Solution:

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

$$[H_3O^+] = 10^{-7.3} \text{ or } [H_3O^+] = \text{antilog of } -7.3 \; [H_3O^+] = 5 \times 10^{-8}\ M$$

(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*

Self-assessment 10.4:

The pH of normal urine is 6.30. What is the concentration of hydronium ions?

Answer:

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

$$[H_3O^+] = 10^{-6.30} = 5.01 \text{ x } 10^{-7}\ M$$

The concentration of hydronium ions is 5.01 x 10^{-7} 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:

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

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:

$$H_2O(l) + SO_3(g) \longrightarrow H_2SO_4(aq) \quad H_2SO_4(aq) \longrightarrow H^+(aq) + HSO_4^-(aq)$$

waste product of metabolism. Carbon dioxide is also formed when fires release carbon stored in vegetation or when we burn wood or fossil fuels. Sulfur trioxide in the atmosphere is naturally produced by volcanic activity, but it also stems 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 10.6**). 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 nvironmental Protection Agency

(a) (b)

Figure 10.6 (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 10.6

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 $[OH^-] = 0.0125\ M$:

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

The pH can be found from the pOH:

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

$$\text{pH} = 14.00 - \text{pOH} = 14.00 - 1.903 = 12.10$$

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

Self-assessment 10.5:

Sweat has a pOH of 8.8. What is the concentration of hydronium ions?

Answer:

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

$$[OH^-] = 10^{-8.8} = 1.58 \text{ x } 10^{-9}\ M$$

To find the hydronium ions concentration, we have to use the ion product of water, Kw.

$$[H_3O^+] = \frac{K_w}{[OH^-]}$$

$$[H_3O^+] = \frac{10^{-14}}{1.58 \text{ x } 10^{-9}\ M}$$

$$[H_3O^+] = 6.33\ x\ 10^{-6}\ M$$

The concentration of hydronium ions is 6.33 x 10^{-6} M.

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 10.7**).

Figure 10.7 (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 10.8**).

Figure 10.8 (a) A universal indicator assumes a different color in solutions of different pH values. Thus, it can be added to a solution to determine the pH of the solution. The eight vials each contain a universal indicator and 0.1-*M* solutions of progressively weaker acids: HCl (pH = l), CH_3CO_2H (pH = 3), and NH_4Cl (pH = 5), deionized water, a

neutral substance (pH = 7); and 0.1-*M* solutions of the progressively stronger bases: KCl (pH = 7), aniline, $C_6H_5NH_2$ (pH = 9), NH_3 (pH = 11), and NaOH (pH = 13). (b) pH paper contains a mixture of indicators that give different colors in solutions of differing pH values. (credit: modification of work by Sahar Atwa)

Acid-Base Reactions

An **acid-base reaction** is one in which a hydrogen ion, H^+, is transferred from one chemical species to another. Such reactions are of central importance to numerous natural and technological processes, ranging from the chemical transformations that take place within cells and the lakes and oceans, to the industrial-scale production of fertilizers, pharmaceuticals, and other substances essential to society. The subject of acid-base chemistry, therefore, is worthy of thorough discussion, and a full chapter is devoted to this topic later in the text.

For purposes of this brief introduction, we will consider only the more common types of acid-base reactions that take place in aqueous solutions. In this context, an **acid** is a substance that will dissolve in water to yield hydronium ions, H_3O^+. As an example, consider the equation shown here:

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

The process represented by this equation confirms that hydrogen chloride is an acid. When dissolved in water, H_3O^+ ions are produced by a chemical reaction in which H^+ ions are transferred from HCl molecules to H_2O molecules (**Figure 10.9**).

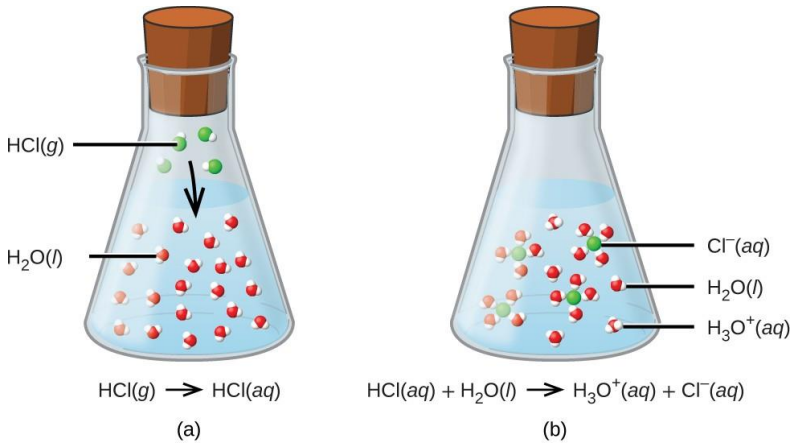


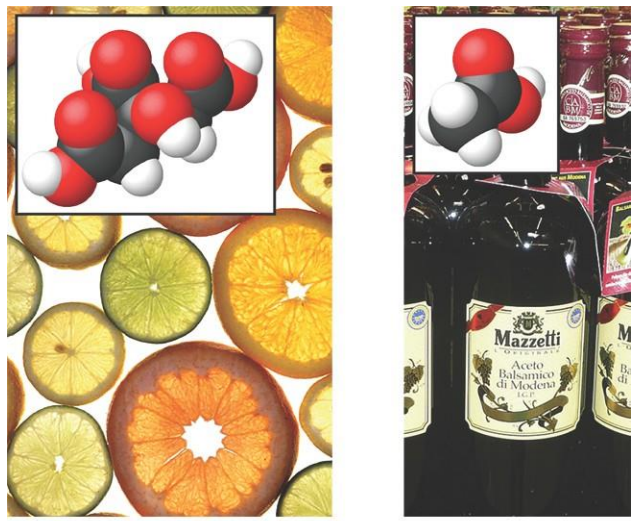
Figure 10.9 When hydrogen chloride gas dissolves in water, (a) it reacts as an acid, transferring protons to water molecules to yield (b) hydronium ions (and solvated chloride ions).

The nature of HCl is such that its reaction with water as just described is essentially 100% efficient: Virtually every HCl molecule that dissolves in water will undergo this reaction. Acids that completely react in this fashion are called **strong acids**, and HCl is one among just a handful of common acid compounds that are classified as strong (**Table 10.4**). A far greater number of compounds behave as **weak acids** and only partially react with water, leaving a large majority of dissolved molecules in their original form and generating a relatively small amount of hydronium ions. Weak acids are commonly encountered in nature, being the substances partly responsible for the tangy taste of citrus fruits, the stinging sensation of insect bites, and the unpleasant smells associated with body odor. A familiar example

of a weak acid is acetic acid, the main ingredient in food vinegars:

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

When dissolved in water under typical conditions, only about 1% of acetic acid molecules are present in the ionized form, $CH_3CO_2^-$ (**Figure 10.10**). (The use of a double-arrow in the equation above denotes the partial reaction aspect of this process, a concept addressed fully in the chapters on chemical equilibrium.)



(a) (b)

Figure 10.10 (a) Fruits such as oranges, lemons, and grapefruit contain the weak acid citric acid. (b) Vinegars contain the weak acid acetic acid. (credit a: modification of work by Scott Bauer; credit b: modification of work by Brücke-Osteuropa/Wikimedia Commons)

Compound Formula	Name in Aqueous Solution
HBr	hydrobromic acid
HCl	hydrochloric acid
HI	hydroiodic acid
HNO_3	nitric acid
$HClO_4$	perchloric acid
H_2SO_4	sulfuric acid

Table 10.4: Common Strong Acids

A **base** is a substance that will dissolve in water to yield hydroxide ions, OH^-. The most common bases are ionic compounds composed of alkali or alkaline earth metal cations (groups 1 and 2) combined with the hydroxide ion—for example, NaOH and $Ca(OH)_2$. When these compounds dissolve in water, hydroxide ions are released directly into the solution. For example, KOH and $Ba(OH)_2$ dissolve in water and dissociate completely to produce cations (K^+ and Ba^{2+}, respectively) and hydroxide ions, OH^-. These bases, along with other hydroxides that completely dissociate in

water, are considered **strong bases**.

Consider as an example the dissolution of lye (sodium hydroxide) in water:

$$NaOH(s) \longrightarrow Na^{+}(aq) + OH^{-}(aq)$$

This equation confirms that sodium hydroxide is a base. When dissolved in water, NaOH dissociates to yield Na^{+} and OH^{-} ions. This is also true for any other ionic compound containing hydroxide ions. Since the dissociation process is essentially complete when ionic compounds dissolve in water under typical conditions, NaOH and other ionic hydroxides are all classified as strong bases.

Unlike ionic hydroxides, some compounds produce hydroxide ions when dissolved by chemically reacting with water molecules. In all cases, these compounds react only partially and so are classified as **weak bases**. These types of compounds are also abundant in nature and important commodities in various technologies. For example, global production of the weak base ammonia is typically well over 100 metric tons annually, being widely used as an agricultural fertilizer, a raw material for chemical synthesis of other compounds, and an active ingredient in household cleaners (**Figure 10.11**). When dissolved in water, ammonia reacts partially to yield hydroxide ions, as shown here:

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

This is, by definition, an acid-base reaction, in this case involving the transfer of H^{+} ions from water molecules to ammonia molecules. Under typical conditions, only about 1% of the dissolved ammonia is present as NH_4^{+} ions.

(a) (b)

Figure 10.11 Ammonia is a weak base used in a variety of applications. (a) Pure ammonia is commonly applied as an agricultural fertilizer. (b) Dilute solutions of ammonia are effective household cleansers. (credit a: modification of work by National Resources Conservation Service; credit b: modification of work by pat00139)

The chemical reactions described in which acids and bases dissolved in water produce hydronium and hydroxide ions, respectively, are, by definition, acid-base reactions. In these reactions, water serves as both a solvent *and* a reactant. A **neutralization reaction** is a specific type of acid-base reaction in which the reactants are an acid and a base, the products are often a **salt** and water, and neither reactant is the water itself:

$$\text{acid} + \text{base} \longrightarrow \text{salt} + \text{water}$$

To illustrate a neutralization reaction, consider what happens when a typical antacid such as milk of magnesia (an aqueous suspension of solid $Mg(OH)_2$) is ingested to ease symptoms associated with excess stomach acid (HCl):

$$Mg(OH)_2(s) + 2HCl(aq) \longrightarrow MgCl_2(aq) + 2H_2O(l).$$

Note that in addition to water, this reaction produces a salt, magnesium chloride.

Example 10.7

Writing Equations for Acid-Base Reactions: Write balanced chemical equations for the acid-base reactions described here:

(a) the weak acid hydrogen hypochlorite reacts with water

(b) a solution of barium hydroxide is neutralized with a solution of nitric acid

Solution:

(a) The two reactants are provided, HOCl and H_2O. Since the substance is reported to be an acid, its reaction with water will involve the transfer of H^+ from HOCl to H_2O to generate hydronium ions, H_3O^+ and hypochlorite ions, OCl^-.

$$HOCl(aq) + H_2O(l) \rightleftharpoons OC^-(aq) + H_3O^+(aq)$$

A double-arrow is appropriate in this equation because it indicates the HOCl is a weak acid that has not reacted completely.

(b) The two reactants are provided, $Ba(OH)_2$ and HNO_3. Since this is a neutralization reaction, the two products will be water and a salt composed of the cation of the ionic hydroxide (Ba^{2+}) and the anion generated when the acid transfers its hydrogen ion (NO_3^-).

$$Ba(OH)_2(aq) + 2HNO_3(aq) \longrightarrow Ba(NO_3)_2(aq) + 2H_2O(l)$$

Check Your Learning

Write the net ionic equation representing the neutralization of any strong acid with an ionic hydroxide. (Hint: Consider the ions produced when a strong acid is dissolved in water.)

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

Link to Learning

Explore the microscopic **view (http://openstaxcollege.org/l/16AcidsBases)** of strong and weak acids and bases.

10.3 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

We can rank the strengths of acids by the extent to which they ionize in aqueous solution. The reaction of an acid with water is given by the general expression:

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

Water is the base that reacts with the acid HA, A^- is the conjugate base of the acid HA, and the hydronium ion is the conjugate acid of water. A strong acid yields 100% (or very nearly so) of H_3O^+ and A^- when the acid ionizes in water; **Figure 10.12** lists several strong acids. A weak acid gives small amounts of H_3O^+ and A^-.

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 10.12 Some of the common strong acids and bases are listed here. Soluble ionic hydroxides such as NaOH are considered strong bases because they dissociate completely when dissolved in water.

The relative strengths of acids may be determined 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:

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

we write the equation for the ionization constant as:

$$Ka = \frac{[H_3O^+]\,[[A^-]}{[AH]}$$

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. Thus a stronger acid has a larger ionization constant than does a weaker acid. The ionization constants increase as the strengths of the acids increase. (A table of ionization constants of weak acids appears in **Appendix H**, with a partial listing in **Table 10.5**.)

The following data on acid-ionization constants indicate the order of acid strength $CH_3CO_2H < HNO_2 < HSO_4^-$

$$CH_3CO_2H(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + CH_3CO_2^-(aq) \qquad K_a = 1.8 \times 10^{-5}$$

$$HNO_2(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + NO_2^-(aq) \qquad K_a = 4.6 \times 10^{-4}$$

$$HSO_4^-(aq) + H_2O(aq) \rightleftharpoons H_3O^+(aq) + SO_4^{2-}(aq) \qquad K_a = 1.2 \times 10^{-2}$$

Link to Learning

View the **simulation (http://openstaxcollege.org/l/16AcidBase)** of strong and weak acids and bases at the molecular level.

Strong acids form very weak conjugate bases, and weak acids form stronger conjugate bases (**Figure 10.13**).

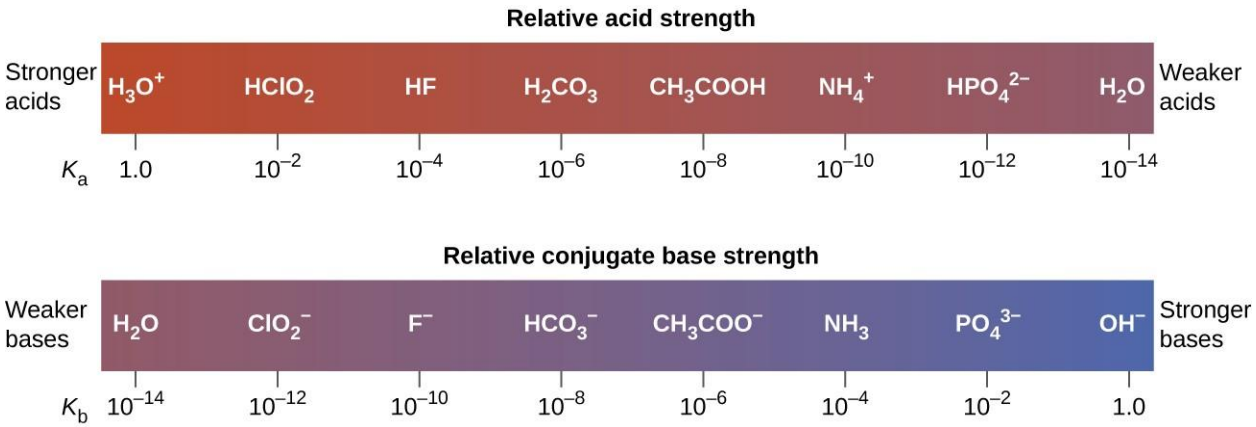


Figure 10.13 This diagram shows the relative strengths of conjugate acid-base pairs, as indicated by their ionization constants in aqueous solution.

Figure 10.14 lists a series of acids and bases in order of the decreasing strengths of the acids and the corresponding increasing strengths of the bases. The acid and base in a given row are conjugate to each other. The first six acids in **Table 10.4** are the most common strong acids. These acids are completely dissociated in aqueous solution. The conjugate bases of these acids are weaker bases than water. When one of these acids dissolves in water, their protons are completely transferred to water, the stronger base.

Those acids that lie between the hydronium ion and water in **Figure 10.14** form conjugate bases that can compete with water for possession of a proton. Both hydronium ions and nonionized acid molecules are present in equilibrium in a solution of one of these acids. Compounds that are weaker acids than water (those found below water in the column of acids) in **Figure 10.14** exhibit no observable acidic behavior when dissolved in water. Their conjugate bases are stronger than the hydroxide ion; if any conjugate base were formed, it would react with water to form the hydroxide ion. The extent to which a base forms hydroxide ion in aqueous solution depends on the strength of the base relative to that of the hydroxide ion, as shown in the last column in **Figure 10.14**. A strong base, such as one of those lying below hydroxide ion, accepts protons from water to yield 100% of the conjugate acid and hydroxide ion. Those bases lying between water and hydroxide ion accept protons from water, but a mixture of the hydroxide ion and the base results. Bases that are weaker than water (those that lie above water in the column of bases) show no observable basic behavior in aqueous solution.

Acid			Base		
perchloric acid	$HClO_4$	Undergo complete acid ionization in water	Do not undergo base ionization in water	ClO_4^-	perchlorate ion
sulfuric acid	H_2SO_4			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

Increasing base strength

Figure 10.14 The chart shows the relative strengths of conjugate acid-base pairs.

The Ionization of Weak Acids and Weak Bases

Many acids and bases are weak; that is, they do not ionize fully in aqueous solution. A solution of a weak acid in water is a mixture of the nonionized acid, hydronium ion, and the conjugate base of the acid, with the nonionized acid present in the greatest concentration. Thus, a weak acid increases the hydronium ion concentration in an aqueous solution (but not as much as the same amount of a strong acid).

Acetic acid, CH_3CO_2H, is a weak acid. When we add acetic acid to water, it ionizes to a small extent according to the equation:

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

giving an equilibrium mixture with most of the acid present in the nonionized (molecular) form. This equilibrium, like other equilibria, is dynamic; acetic acid molecules donate hydrogen ions to water molecules and form hydronium ions and acetate ions at the same rate that hydronium ions donate hydrogen ions to acetate ions to reform acetic acid

molecules and water molecules. We can tell by measuring the pH of an aqueous solution of known concentration that only a fraction of the weak acid is ionized at any moment (**Figure 10.18**). The remaining weak acid is present in the nonionized form.

Formic acid, HCO_2H, is also a weak acid, yet it is the irritant that causes the body's reaction to ant stings (**Figure 10.16**).

Figure 10.16 The pain of an ant's sting is caused by formic acid. (credit: John Tann)

Table 10.5 gives the ionization constants for several weak acids; additional ionization constants can be found in **Appendix H**

Ionization Reaction	K_a at 25 °C
$HSO_4^- + H_2O \rightleftharpoons H_3O^+ + SO_4^{2-}$	1.2×10^{-2}
$HF + H_2O \rightleftharpoons H_3O^+ + F^-$	3.5×10^{-4}
$HNO_2 + H_2O \rightleftharpoons H_3O^+ + NO_2^-$	4.6×10^{-4}
$HCNO + H_2O \rightleftharpoons H_3O^+ + NCO^-$	2×10^{-4}
$HCO_2H + H_2O \rightleftharpoons H_3O^+ + HCO_2^-$	1.8×10^{-4}
$CH_3CO_2H + H_2O \rightleftharpoons H_3O^+ + CH_3CO_2^-$	1.8×10^{-5}
$HClO + H_2O \rightleftharpoons H_3O^+ + ClO^-$	2.9×10^{-8}
$HBrO + H_2O \rightleftharpoons H_3O^+ + BrO^-$	2.8×10^{-9}
$HCN + H_2O \rightleftharpoons H_3O^+ + CN^-$	4.9×10^{-10}

Table 10.5: Ionization Constants of Some Weak Acids

Example 10.8

Determination of K_a from Equilibrium Concentrations: Acetic acid is the principal ingredient in vinegar (**Figure 10.17**); that's why it tastes sour. 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 10.17 Vinegar is a solution of acetic acid, a weak acid. (credit: modification of work by "HomeSpot HQ"/Flickr)

Solution:

We are asked to calculate an equilibrium constant from equilibrium concentrations.

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

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

Check Your Learning

What is the equilibrium constant for the ionization of the HSO_4^- ion, the weak acid used in some household cleansers:

$$HSO_4^-(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + SO_4^{2-}(aq)$$

In one mixture of $NaHSO_4$ and Na_2SO_4 at equilibrium, $[H_3O^+] = 0.027\ M$; $[HSO_4^-] = 0.29\ M$; and $[SO_4^{2-}] = 0.13\ M$.

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

Figure 10.18 pH paper indicates that a 0.l-*M* solution of HCl (beaker on left) has a pH of 1. The acid is fully ionized and $[H_3O^+] = 0.1\ M$. A 0.1-*M* solution of CH_3CO_2H (beaker on right) is a pH of 3 ($[H_3O^+] = 0.001\ M$) because the weak acid CH_3CO_2H is only partially ionized. In this solution, $[H_3O^+] < [CH_3CO_2H]$. (credit: modification of work by Sahar Atwa)

10.4 Hydrolysis of Salt Solutions

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

- Predict whether a salt solution will be acidic, basic, or neutral

As we have seen in the section on chemical reactions, when an acid and base are mixed, they undergo a neutralization reaction. The word "neutralization" seems to imply that a stoichiometrically equivalent solution of an acid and a base would be neutral. This is sometimes true, but the salts that are formed in these reactions may have acidic or basic properties of their own, as we shall now see.

Acid-Base Neutralization

A solution is neutral when it contains equal concentrations of hydronium and hydroxide ions. When we mix solutions of an acid and a base, an acid-base neutralization reaction occurs. However, even if we mix stoichiometrically equivalent quantities, we may find that the resulting solution is not neutral. It could contain either an excess of hydronium ions or an excess of hydroxide ions because the nature of the salt formed determines whether the solution is acidic, neutral, or basic. The following four situations illustrate how solutions with various pH values can arise following a neutralization reaction using stoichiometrically equivalent quantities:

1. A strong acid and a strong base, such as HCl(*aq*) and NaOH(*aq*) will react to form a neutral solution since the conjugate partners produced are of negligible strength (see **Figure 14.8**):

$$HCl(aq) + NaOH(aq) \rightleftharpoons NaCl(aq) + H_2O(l)$$

2. A strong acid and a weak base yield a weakly acidic solution. The products of this neutralization reaction are

the conjugate base of the strong acid (Kb ≈ 0, so it doesn't affect pH) and the conjugate acid of the weak base (Ka > 0, so it ionizes to make the solution acidic).

3. A weak acid and a strong base yield a weakly basic solution. The products of this neutralization reaction are the conjugate acid of the strong base (Ka ≈ 0, so it doesn't affect pH) and the conjugate base of the weak acid (Kb > 0, so it ionizes to make the solution basic).

4. A weak acid plus a weak base can yield either an acidic or basic solution. This is the most complex of the four types of reactions. When the conjugate acid and the conjugate base are of unequal strengths, the solution can be either acidic or basic, depending on the relative strengths of the two conjugates. To predict whether a particular combination will be acidic or basic, tabulated K values of the conjugates must be compared. (Note: occasionally the weak acid and the weak base can have the same strength, so their respective conjugate base and acid will have the same strength, and the solution will be neutral.). This case is out of the scope of this textbook.

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) NH_4Cl

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 and the Br^- anion are both spectators, since they are the cation of a strong base (KOH) and the anion of a strong acid (HBr), respectively. The solution is neutral. Another way is to consider that KOH and HBr are both strong so their salt will be neutral.

(b) The Na^+ cation could come from a strong base, NaOH while the HCO_3^- anion comes from H_2CO_3 a weak acid, the resulting salt will thus be basic.

(c) The NH_4^+ ion comes from ammonia a weak base and and the Cl^- ion comes from HCl, a strong acid. The solution will be acidic

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) $(NH_4)_2CO_3$

(e) $AlBr_3$

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

Self-assessment 10.6:

About 50% of urinary calculi (kidney stones) consist of calcium phosphate, $Ca_3(PO_4)_2$. Its nature is (a) basic (b) acidic (c) neutral.

Answer:

(a) Calcium phosphate is basic salt, as it is a salt of weak acid (phosphoric acid) and slightly stronger base (calcium hydroxide) (though both are weak).

Self-assessment 10.7:

Magnesium hydroxide, also known as milk of magnesia, and magnesium citrate function as mild laxatives when they reach the small intestine. Is milk of magnesia basic, neutral of acidic? What about magnesium citrate?

Answer:

Milk of magnesia is a base as it is a hydroxide of an alkaline earth metal. Magnesium citrate is the salt obtained when combining magnesium hydroxide and citric acid. Citric acid is not one of the six strong acids so it is a weak acid, thus the resulting salt is basic.

10.5 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

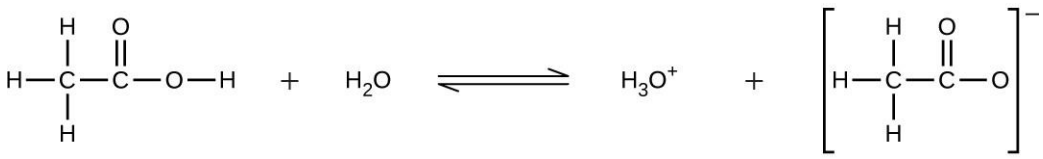
We can classify acids by the number of protons per molecule that they can give up in a reaction. Acids such as HCl,

HNO_3, and HCN that contain one ionizable hydrogen atom in each molecule are called **monoprotic acids**. Their reactions with water are:

$$HCl(aq)+H_2O(l)\longrightarrow H_3O^+(aq)+Cl^-(aq)\quad HNO_3(aq)+H_2O(l)\longrightarrow H_3O^+(aq)+NO_3^-(aq)$$

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

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:



$$CH_3COOH(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + CH_3COO^-(aq)$$

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

Second ionization: $HSO_4^-(aq)+H_2O(l)\rightleftharpoons H_3O^+(aq)+SO_4^{2-}(aq)$ $\quad K_{a2}=1.2\times10^{-2}$

A **triprotic acid** is an acid that has three dissociable protons that undergo stepwise ionization: Phosphoric acid is a typical example:

First ionization: $H_3PO_4(aq)+H_2O(l)\rightleftharpoons H_3O^+(aq)+H_2PO_4^-(aq)$ $\quad K_{a1}=7.5\times10^{-3}$

Second ionization: $H_2PO_4^-(aq)+H_2O(l)\rightleftharpoons H_3O^+(aq)+HPO_4^{2-}(aq)$ $\quad K_{a2}=6.2\times10^{-8}$

Third ionization: $HPO_4^{2-}(aq)+H_2O(l)\rightleftharpoons H_3O^+(aq)+PO_4^{3-}(aq)$ $\quad K_{a3}=4.2\times10^{-13}$

As with the diprotic acids, the differences in the ionization constants of these reactions tell us that in each successive step the degree of ionization is significantly weaker. 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, the calculations can be broken down into a series of parts similar to those for diprotic acids.

Polyprotic bases can accept more than one hydrogen ion in solution. The carbonate ion is an example of a **diprotic base**, since it can accept up to two protons. Solutions of alkali metal carbonates are quite alkaline, due to the reactions:

$$H_2O(l)+CO_3^{2-}(aq)\rightleftharpoons HCO_3^-(aq)+OH^-(aq)\quad\text{and}\quad H_2O(l)+HCO_3^-(aq)\rightleftharpoons H_2CO_3(aq)+OH^-(aq)$$

10.6 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 mixture of a weak acid and its conjugate base (or a mixture of a weak base and its conjugate acid) 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 10.19**). 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 ($NH_3(aq)$ + $NH_4Cl(aq)$).

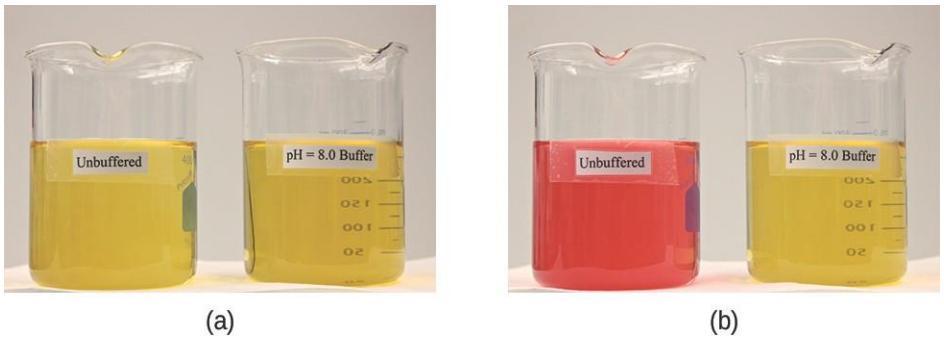


Figure 10.19 (a) The buffered solution on the left and the unbuffered solution on the right have the same pH (pH 8); they are basic, showing the yellow color of the indicator methyl orange at this pH. (b) After the addition of 1 mL of a 0.01-*M* HCl solution, the buffered solution has not detectably 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

A mixture of acetic acid and sodium acetate is acidic because the K_a of acetic acid is greater than the K_b of its conjugate base acetate. It is a buffer because it contains both the weak acid and its salt. Hence, it acts to keep the hydronium ion concentration (and the pH) almost constant by the addition of either a small amount of a strong acid or a strong base. If we add a base such as sodium hydroxide, the hydroxide ions react with the few hydronium ions present. The decrease in hydronium ion concentration causes the acetic acid hydrolysis equilibrium to shift to the right, restoring the hydronium ion concentration almost to its original value, and yielding a relatively modest increase in pH:

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

If we add an acid such as hydrochloric acid, the resultant increase in hydronium ion concentration shifts the equilibrium to the left. This effectively converts the added strong acid to a much weaker acid (acetic acid), and the buffer solution thus experiences only a slight decrease in pH.

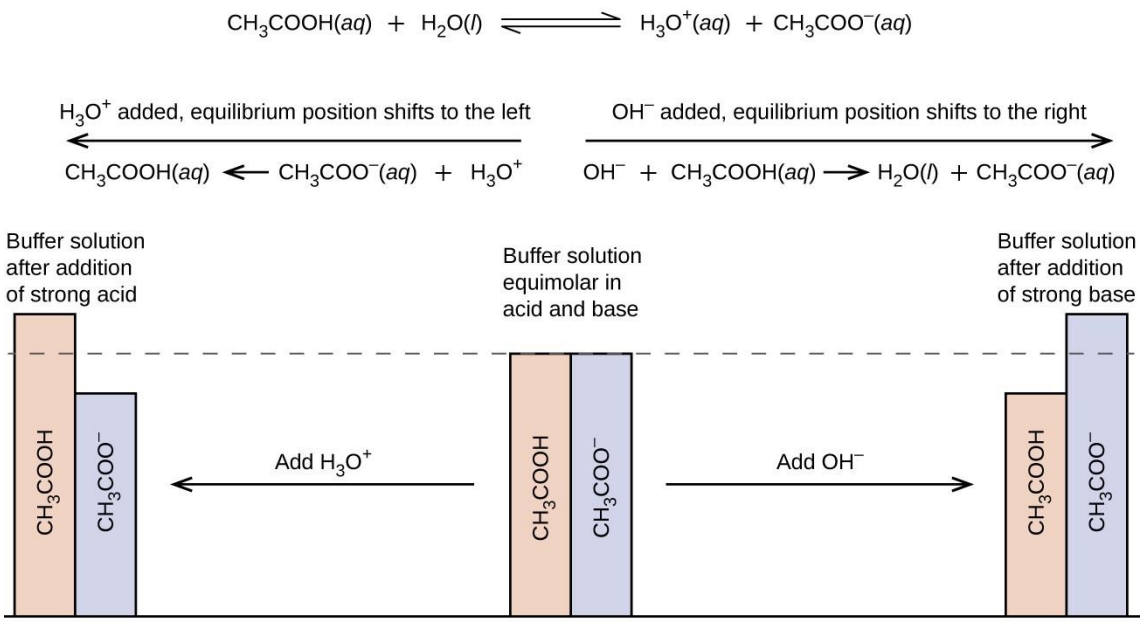


Figure 10.20 This diagram shows the buffer action of these reactions.

A mixture of ammonia and ammonium chloride is basic because the K_b for ammonia is greater than the K_a for the ammonium ion. It is a buffer because it also contains the salt of the weak base. If we add a base (hydroxide ions), ammonium ions in the buffer react with the hydroxide ions to form ammonia and water and reduce the hydroxide ion concentration almost to its original value:

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

If we add an acid (hydronium ions), ammonia molecules in the buffer mixture react with the hydronium ions to form ammonium ions and reduce the hydronium ion concentration almost to its original value:

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

Buffer Capacity

Buffer solutions do not have an unlimited capacity to keep the pH relatively constant (**Figure 10.21**). If we add so much base to a buffer that the weak acid is exhausted, no more buffering action toward the base is possible. On the other hand, if we add an excess of acid, the weak base would be exhausted, and no more buffering action toward any additional acid would be possible. In fact, we do not even need to exhaust all of the acid or base in a buffer to overwhelm it; its buffering action will diminish rapidly as a given component nears depletion.

Figure 10.21 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.

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:

$$Ka = \frac{[H_3O^+]\,[[A^-]}{[AH]}$$

Rearranging to solve for $[H_3O^+]$, we get:

$$[H_3O^+] = \frac{Ka\,[AH]}{[A^-]}$$

Taking the negative logarithm of both sides of this equation, we arrive at:

$$-\log[H_3O^+] = -\log Ka + \log\frac{[A^-]}{[AH]}$$

which can be written as:

$$pH = pKa + \log\frac{[A^-]}{[AH]}$$

where pK_a is the negative of the common logarithm of the ionization constant of the weak acid ($pK_a = -\log K_a$). This equation relates the pH, the ionization constant of a weak acid, and the concentrations of the weak acid and its salt 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.

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:

$$CO_2(g) + 2H_2O(l) \rightleftharpoons H_2CO_3(aq) \rightleftharpoons HCO_3^-(aq) + H_3O^+(aq)$$

The concentration of carbonic acid, H_2CO_3 is approximately 0.0012 *M*, and the concentration of the hydrogen carbonate ion, HCO_3^-, is around 0.024 *M*. Using the Henderson-Hasselbalch equation and the pK_a of carbonic acid at body temperature, we can calculate the pH of blood:

$$\text{pH} = \text{pKa} + \log\frac{[\text{base}]}{[\text{acid}]} = 6.4 + \log\frac{0.024}{0.001} = 7.7$$

The fact that the H_2CO_3 concentration is significantly lower than that of the 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.

Medicine: Lactic acid

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.

Self-assessment 10.8:

Barbituric acid is the parent compound of barbiturate drugs, that are used as hypnotics, sedatives, anticonvulsants and anesthetics and known as sleeping pills. Barbituric acid itself does not have any physiological activity. A buffer solution is prepared from equal volumes of 0.200 *M* barbituric acid and 0.600 *M* sodium barbiturate. ($K_a = 9.8 \times 10^{-5}$)

a) What is the pH of the solution? Is the solution acidic or basic?

Answers:

Since it is a buffer, the Henderson-Hasselbalch equation can be used to determine the pH as follows:

$$pH = pKa + \log\frac{[sodium\ barbiturate]}{[barbituric\ acid]}$$

$$pH = -\log(9.8x10^{-5}) + \log\frac{[0.600M]}{[0.200M]}$$

$$pH = 4.49$$

The pH of this buffer solution is 4.49, which is acidic.

Link to Learning

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

10.7 Acid-Base Titrations

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

- Describe the fundamental aspects of titrations.
- Perform stoichiometric calculations using typical titration.
- Explain the function of acid-base indicators

Titrations can be used to quantitatively analyze solutions for their acid or base concentrations. In this section, we will explore the different aspects of the process of a titration.

In the 18th century, the strength (actually the concentration) of vinegar samples was determined by noting the amount of potassium carbonate, K_2CO_3, which had to be added, a little at a time, before bubbling ceased. The greater the

weight of potassium carbonate added to reach the point where the bubbling ended, the more concentrated the vinegar. We now know that the effervescence that occurred during this process was due to reaction with acetic acid, CH_3CO_2H, the compound primarily responsible for the odor and taste of vinegar. Acetic acid reacts with potassium carbonate according to the following equation:

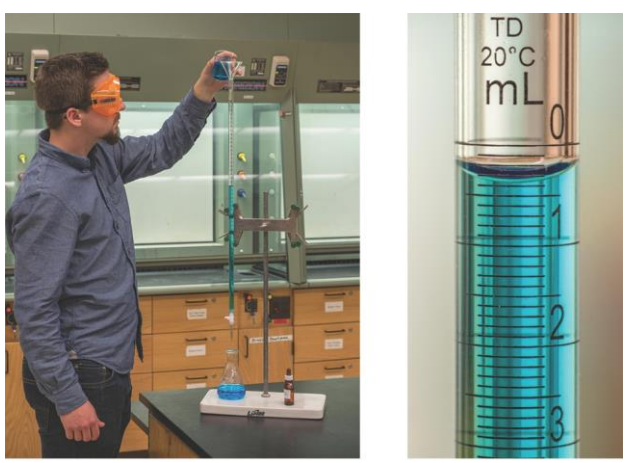
$$2CH_3CO_2H(aq) + K_2CO_3(s) \longrightarrow 2CH_3CO_2K(aq) + CO_2(g) + H_2O(l)$$

The bubbling was due to the production of CO_2.

The test of vinegar with potassium carbonate is one type of **quantitative analysis**—the determination of the amount or concentration of a substance in a sample. In the analysis of vinegar, the concentration of the solute (acetic acid) was determined from the amount of reactant that combined with the solute present in a known volume of the solution. In other types of chemical analyses, the amount of a substance present in a sample is determined by measuring the amount of product that results.

Titration

The described approach to measuring vinegar strength was an early version of the analytical technique known as **titration analysis**. A typical titration analysis involves the use of a **buret** (**Figure 10.22**) to make incremental additions of a solution containing a known concentration of some substance (the **titrant**) to a sample solution containing the substance whose concentration is to be measured (the **analyte**). The titrant and analyte undergo a chemical reaction of known stoichiometry, and so measuring the volume of titrant solution required for complete reaction with the analyte (the **equivalence point** of the titration) allows calculation of the analyte concentration. The equivalence point of a titration may be detected visually if a distinct change in the appearance of the sample solution accompanies the completion of the reaction. The halt of bubble formation in the classic vinegar analysis is one such example, though, more commonly, special dyes called **indicators** are added to the sample solutions to impart a change in color at or very near the equivalence point of the titration. Equivalence points may also be detected by measuring some solution property that changes in a predictable way during the course of the titration. Regardless of the approach taken to detect a titration's equivalence point, the volume of titrant actually measured is called the **end point**. Properly designed titration methods typically ensure that the difference between the equivalence and end points is negligible.



(a) (b)

Figure 10.22 (a) A student fills a buret in preparation for a titration analysis. (b) A typical buret permits volume

measurements to the nearest 0.01 mL. (credit a: modification of work by Mark Blaser and Matt Evans; credit b: modification of work by Mark Blaser and Matt Evans)

The stoichiometry of chemical reactions may serve as the basis for quantitative chemical analysis methods. Titrations involve measuring the volume of a titrant solution required to completely react with a sample solution. This volume is then used to calculate the concentration of analyte in the sample using the stoichiometry of the titration reaction

Example 10.9

Titration Analysis: The end point in a titration of a 50.00-mL sample of aqueous HCl was reached by addition of 35.23 mL of 0.250 M NaOH titrant. The titration reaction is:

$$\mathrm{HCl}(aq) + \mathrm{NaOH}(aq) \longrightarrow \mathrm{NaCl}(aq) + \mathrm{H_2O}(l)$$

What is the molarity of the HCl?

Solution:

As for all reaction stoichiometry calculations, the key issue is the relation between the molar amounts of the chemical species of interest as depicted in the balanced chemical equation. The approach outlined in previous modules of this chapter is followed, with additional considerations required, since the amounts of reactants provided and requested are expressed as solution concentrations.

For this exercise, the calculation will follow the following outlined steps:

The molar amount of HCl is calculated to be:

$$35.23\ mL\ NaOH \times \frac{1\ L}{1000\ mL} \times \frac{.250\ mol\ NaOH}{1\ L\ NaOH} \times \frac{1\ mol\ HCl}{1\ mol\ NaOH} = 8.81 \times 10^{-3}\ mol\ HCl$$

Using the provided volume of HCl solution and the definition of molarity, the HCl concentration is:

$$50\ mL\ HCl\ \times \frac{1\ L}{1000\ mL} = 0.05\ L\ HCl$$

$$M = \frac{mol\ HCl}{L\ HCl} = \frac{8.81\ \times 10^{-3}\ mol\ HCl}{0.05\ L\ HCl} = 0.176\ M$$

Check Your Learning

A 20.00-mL sample of aqueous oxalic acid, $H_2C_2O_4$, was titrated with a 0.09113-*M* solution of potassium permanganate, $KMnO_4$.

$$2\mathrm{MnO_4^-}(aq) + 5\mathrm{H_2C_2O_4}(aq) + 6\mathrm{H^+}(aq) \longrightarrow 10\mathrm{CO_2}(g) + 2\mathrm{Mn^{2+}}(aq) + 8\mathrm{H_2O}(l)$$

A volume of 23.24 mL was required to reach the end point. What is the oxalic acid molarity?

Answer: 0.2648 *M*

Self-assessment 10.9:

Lactic acid, also known in the medical field as "*lactate" its conjugate base*, is a by-product of anaerobic carbohydrate metabolism, in other words it may be produced when energy is needed but there is insufficient oxygen for normal metabolic reactions. Those include strenuous exercise, heart failure, or sepsis to cite a few. Excess lactic can also occur from liver disease, since the liver helps regulates those levels. A normal blood lactate level is 0.5-1 mmol/L. If we use A^- as a symbol for lactate, what is the volume of HCl 1 M required to neutralize 1 Liter of blood whose lactate

concentration is 0.5 mmol/L?

Solution: First we write the balanced equation for this neutralization reaction:

$$A^- + HCl \rightarrow AH + Cl^-$$

We notice that the molar ratio is 1:1, so the number of mole of HCl is the same as the number of mole of lactate present in one liter: 0.5 mmol or 5 x 10^{-4} mol. The volume of HCl 1 M needed is thus:

$$V_{HCl} = \frac{mole_{HCl}}{[HCl]}$$

$$V_{HCl} = \frac{5\ x\ 10^{-4}\ mole_{HCl}}{1\ M}$$

$$V_{HCl} = 5\ x\ 10^{-4}\ L\ or\ 0.5\ mL$$

The volume of HCl needed is 0.5 mL.

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 5.0×10^{-9} *M* (pH < 8.3). In more basic solutions where the hydronium ion concentration is less than 5.0×10^{-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. 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. Titration curves help us pick an indicator that will provide a sharp color change at the equivalence point. The best selection would be an indicator that has a color change interval that brackets the pH at the equivalence point of the titration.

Tooth Decay

In some cases, we want to prevent dissolution from occurring. Tooth decay, for example, occurs when the calcium hydroxylapatite, which has the formula $Ca_5(PO_4)_3(OH)$, in our teeth dissolves. The dissolution process is aided when bacteria in our mouths feast on the sugars in our diets to produce lactic acid, which reacts with the hydroxide ions in the calcium hydroxylapatite. Preventing the dissolution prevents the decay. On the other hand, sometimes we want a substance to dissolve. We want the calcium carbonate in a chewable antacid to dissolve because the CO_3^{2-} ions produced in this process help soothe an upset stomach.

Link to Learning

Visit this **website (http://openstaxcollege.org/l/16barium)** for more information on how barium is used in medical diagnoses and which conditions it is used to diagnose.

Chemistry in Everyday Life: Stomach Antacids

Our stomachs contain a solution of roughly 0.03 *M* HCl, which helps us digest the food we eat. The burning sensation associated with heartburn is a result of the acid of the stomach leaking through the muscular valve at the top of the stomach into the lower reaches of the esophagus. The lining of the esophagus is not protected from the corrosive effects of stomach acid the way the lining of the stomach is, and the results can be very painful. When we have heartburn, it feels better if we reduce the excess acid in the esophagus by taking an antacid. As you may have guessed, antacids are bases. One of the most common antacids is calcium carbonate, $CaCO_3$. The reaction,

$$CaCO_3(s) + 2HCl(aq) \rightleftharpoons CaCl_2(aq) + H_2O(l) + CO_2(g)$$

not only neutralizes stomach acid, it also produces $CO_2(g)$, which may result in a satisfying belch.

Milk of Magnesia is a suspension of the sparingly soluble base magnesium hydroxide, $Mg(OH)_2$. It works according to the reaction:

$$Mg(OH)_2(s) \rightleftharpoons Mg^{2+}(aq) + 2OH^-(aq)$$

The hydroxide ions generated in this equilibrium then go on to react with the hydronium ions from the stomach acid, so that :

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

This reaction does not produce carbon dioxide, but magnesium-containing antacids can have a laxative effect.

Several antacids have aluminum hydroxide, $Al(OH)_3$, as an active ingredient. The aluminum hydroxide tends to cause constipation, and some antacids use aluminum hydroxide in concert with magnesium hydroxide to balance the side effects of the two substances.

How Sciences Interconnect: Acid Reflux Disease: Using Barium Sulfate for Medical Imaging

Various types of medical imaging techniques are used to aid diagnoses of illnesses in a noninvasive manner. One such technique utilizes the ingestion of a barium compound before taking an X-ray image. A suspension of barium sulfate, a chalky powder, is ingested by the patient. Most barium compounds are very poisonous; however, barium sulfate is often administered internally as an aid in the X-ray examination of the lower intestinal tract. This use of $BaSO_4$ is possible because of its low solubility. Barium-coated areas of the digestive tract then appear on an X-ray as white, allowing for greater visual detail than a traditional X-ray (**Figure 10.23**). Further diagnostic testing can be done using barium sulfate and fluoroscopy. In fluoroscopy, a continuous X- ray is passed through the body so the doctor can monitor, on a TV or computer screen, the barium sulfate's movement as it passes through the digestive tract. Medical imaging using barium sulfate can be used to diagnose acid reflux disease, Crohn's disease, and ulcers in addition to other conditions.

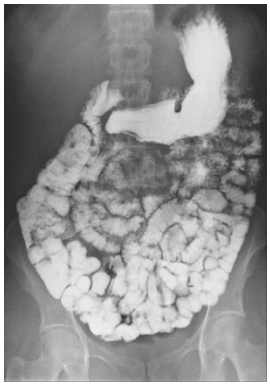


Figure 10.23 The suspension of barium sulfate coats the intestinal tract, which allows for greater visual detail than a traditional X-ray. (credit modification of work by "glitzy queen00"/Wikimedia Commons)

Role of Fluoride in Preventing Tooth Decay

Of particular relevance to us is the dissolution of hydroxylapatite, $Ca_5(PO_4)_3OH$, in acid. Apatites are a class of calcium phosphate minerals (**Figure 10.24**); a biological form of hydroxylapatite is found as the principal mineral in the enamel of our teeth. A mixture of hydroxylapatite and water (or saliva) contains an equilibrium mixture of solid $Ca_5(PO_4)_3OH$ and dissolved Ca^{2+}, PO_4^{3-}, and OH^- ions:

$$Ca_5(PO_4)_3\,OH(s) \rightleftharpoons 5Ca^{2+}(aq) + 3PO_4^{3-}(aq) + OH^-(aq)$$

Figure 10.24 Crystal of the mineral hydroxylapatite, $Ca_5(PO_4)_3OH$, is shown here. Pure apatite is white, but like many other minerals, this sample is colored because of the presence of impurities.

When exposed to acid, phosphate ions react with hydronium ions to form hydrogen phosphate ions and ultimately, phosphoric acid:

$$PO_4^{3-}(aq)+H_3O^+(aq)\longrightarrow H_2PO_4^{2-}(aq)+H_2O(l)$$

$$H_2PO_4^{2-}(aq)+H_3O^+(aq)\longrightarrow H_2PO_4^{-}(aq)+H_2O(l)$$

$$H_2PO_4^{-}(aq)+H_3O^+(aq)\longrightarrow H_3PO_4(aq)+H_2O(l)$$

Hydroxide ion reacts to form water:

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

These reactions decrease the phosphate and hydroxide ion concentrations, and additional hydroxylapatite dissolves in

an acidic solution in accord with Le Châtelier's principle. Our teeth develop cavities when acid waste produced by bacteria growing on them causes the hydroxylapatite of the enamel to dissolve. Fluoride toothpastes contain sodium fluoride, NaF, or stannous fluoride [more properly named tin(II) fluoride], SnF_2. They function by replacing the OH^- ion in hydroxylapatite with F^- ion, producing fluorapatite, $Ca_5(PO_4)_3F$:

$$NaF + Ca_5(PO_4)_3OH \rightleftharpoons Ca_5(PO_4)_3F + Na^+ + OH^-$$

The resulting $Ca_5(PO_4)_3F$ is slightly less soluble than $Ca_5(PO_4)_3OH$, and F^- is a weaker base than OH^-. Both of these factors make the fluorapatite more resistant to attack by acids than hydroxylapatite. Fluoride ions help protect our teeth by reacting with hydroxylapatite to form fluorapatite, $Ca_5(PO_4)_3F$. Since it lacks a hydroxide ion, fluorapatite is more resistant to attacks by acids in our mouths and is thus less soluble, protecting our teeth. Scientists discovered that naturally fluorinated water could be beneficial to your teeth, and so it became common practice to add fluoride to drinking water. Toothpastes and mouthwashes also contain amounts of fluoride (**Figure 10.25**)

Figure 10.25 Fluoride, found in many toothpastes, helps prevent tooth decay (credit: Kerry Ceszyk).

Unfortunately, excess fluoride can negate its advantages. Natural sources of drinking water in various parts of the world have varying concentrations of fluoride, and places where that concentration is high are prone to certain health risks when there is no other source of drinking water. The most serious side effect of excess fluoride is the bone disease, skeletal fluorosis. When excess fluoride is in the body, it can cause the joints to stiffen and the bones to thicken. It can severely impact mobility and can negatively affect the thyroid gland. Skeletal fluorosis is a condition that over 2.7 million people suffer from across the world. So while fluoride can protect our teeth from decay, the US Environmental Protection Agency sets a maximum level of 4 ppm (4 mg/
L) of fluoride in drinking water in the US. Fluoride levels in water are not regulated in all countries, so fluorosis is a problem in areas with high levels of fluoride in the groundwater

When acid rain attacks limestone or marble, which are calcium carbonates, a reaction occurs that is similar to the acid attack on hydroxylapatite. The hydronium ion from the acid rain combines with the carbonate ion from calcium carbonates and forms the hydrogen carbonate ion, a weak acid:

$$H_3O^+(aq) + CO_3^{2-}(aq) \longrightarrow HCO_3^-(aq) + H_2O(l)$$

Calcium hydrogen carbonate, $Ca(HCO_3)_2$, is soluble, so limestone and marble objects slowly dissolve in acid rain.

If we add calcium carbonate to a concentrated acid, hydronium ion reacts with the carbonate ion according to the equation:

$$2H_3O^+(aq) + CO_3^{2-}(aq) \longrightarrow H_2CO_3(aq) + 2H_2O(l)$$

(Acid rain is usually not sufficiently acidic to cause this reaction; however, laboratory acids are.) The solution may become saturated with the weak electrolyte carbonic acid, which is unstable, and carbon dioxide gas can be evolved:

$$H_2CO_3(aq) \longrightarrow CO_2(g) + H_2O(l)$$

These reactions decrease the carbonate ion concentration, and additional calcium carbonate dissolves. If enough acid is present, the concentration of carbonate ion is reduced to such a low level that the reaction quotient for the dissolution of calcium carbonate remains less than the solubility product of calcium carbonate, even after all of the calcium carbonate has dissolved.

Key Terms

acid substance that produces H_3O^+ when dissolved in water

acid ionization constant (K_a) equilibrium constant for the ionization of a weak acid

acid ionization reaction involving the transfer of a proton from an acid to water, yielding hydronium ions and the conjugate base of the acid

acid-base indicator organic acid or base whose color changes depending on the pH of the solution it is in

acid-base reaction reaction involving the transfer of a hydrogen ion between reactant species

acidic describes a solution in which $[H_3O^+] > [OH^-]$

amphiprotic species that may either gain or lose a proton in a reaction

amphoteric species that can act as either an acid or a base

autoionization reaction between identical species yielding ionic products; for water, this reaction involves transfer of protons to yield hydronium and hydroxide ions

base substance that produces OH^- when dissolved in water

base ionization constant (K_b) equilibrium constant for the ionization of a weak base

base ionization reaction involving the transfer of a proton from water to a base, yielding hydroxide ions and the conjugate acid of the base

basic describes a solution in which $[H_3O^+] < [OH^-]$

Brønsted-Lowry acid Brønsted-Lowry base proton donor proton acceptor

buffer capacity amount of an acid or base that can be added to a volume of a buffer solution before its pH changes significantly (usually by one pH unit)

buffer mixture of a weak acid or a weak base and the salt of its conjugate; the pH of a buffer resists change when small amounts of acid or base are added

buret device used for the precise delivery of variable liquid volumes, such as in a titration analysis, required to completely react with the analyte in a sample

color-change interval range in pH over which the color change of an indicator takes place

conjugate acid substance formed when a base gains a proton

conjugate base substance formed when an acid loses a proton

diprotic acid acid containing two ionizable hydrogen atoms per molecule. A diprotic acid ionizes in two steps

diprotic base base capable of accepting two protons. The protons are accepted in two steps

end point measured volume of titrant solution that yields the change in sample solution appearance or other

property expected for stoichiometric equivalence (see *equivalence point*)

equivalence point volume of titrant solution required to react completely with the analyte in a titration analysis; provides a stoichiometric amount of titrant for the sample's analyte according to the titration reaction

Henderson-Hasselbalch equation equation used to calculate the pH of buffer solutions

indicator substance added to the sample in a titration analysis to permit visual detection of the end point

ion-product constant for water (K_w) equilibrium constant for the autoionization of water

leveling effect of water any acid stronger than H_3O^+, or any base stronger than OH^- will react with water to form H_3O^+, or OH^-, respectively; water acts as a base to make all strong acids appear equally strong, and it acts as an acid to make all strong bases appear equally strong

monoprotic acid acid containing one ionizable hydrogen atom per molecule

neutral describes a solution in which $[H_3O^+] = [OH^-]$

neutralization reaction reaction between an acid and a base to produce salt and water

oxyacid compound containing a nonmetal and one or more hydroxyl groups

percent ionization ratio of the concentration of the ionized acid to the initial acid concentration, times 100

pH logarithmic measure of the concentration of hydronium ions in a solution

pOH logarithmic measure of the concentration of hydroxide ions in a solution

salt ionic compound that can be formed by the reaction of an acid with a base that contains a cation and an anion other than hydroxide or oxide

stepwise ionization process in which an acid is ionized by losing protons sequentially

strong acid acid that reacts completely when dissolved in water to yield hydronium ions

strong base base that reacts completely when dissolved in water to yield hydroxide ions

titrant solution containing a known concentration of substance that will react with the analyte in a titration analysis

titration analysis quantitative chemical analysis method that involves measuring the volume of a reactant solution

titration curve plot of the pH of a solution of acid or base versus the volume of base or acid added during a titration

triprotic acid acid that contains three ionizable hydrogen atoms per molecule; ionization of triprotic acids occurs in three steps

weak acid acid that reacts only to a slight extent when dissolved in water to yield hydronium ions

weak base base that reacts only to a slight extent when dissolved in water to yield hydroxide ions

Key Equations

- $K_w = [H_3O^+][OH^-] = 1.0 \times 10^{-14}$ (at 25 °C)
- $pH = -\log[H_3O^+]$
- $pOH = -\log[OH^-]$
- $[H_3O^+] = 10^{-pH}$
- $[OH^-] = 10^{-pOH}$
- $pH + pOH = pK_w = 14.00$ at 25 °C

- $K_a = \frac{[H_3O^+][A^-]}{[HA]}$
- $K_b = \frac{[HB^+][OH^-]}{[B]}$
- $K_a \times K_b = 1.0 \times 10^{-14} = K_w$
- $pK_a = -\log K_a$
- $pK_b = -\log K_b$
- $PH = pKa + log\frac{[A^-]}{[HA]}$

Summary

10.1 Brønsted-Lowry Acids and Bases

A compound that can donate a proton (a hydrogen ion) to another compound is called a Brønsted-Lowry acid. The compound that accepts the proton is called a Brønsted-Lowry base. The species remaining after a Brønsted-Lowry acid has lost a proton is the conjugate base of the acid. The species formed when a Brønsted-Lowry base gains a proton is the conjugate acid of the base. Thus, an acid-base reaction occurs when a proton is transferred from an acid to a base, with formation of the conjugate base of the reactant acid and formation of the conjugate acid of the reactant base. Amphiprotic species can act as both proton donors and proton acceptors. Water is the most important amphiprotic species. It can form both the hydronium ion, H_3O^+, and the hydroxide ion, OH^- when it undergoes autoionization:

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

The ion product of water, K_w is the equilibrium constant for the autoionization reaction:

$$K_w = [H_3O^+][OH^-] = 1.0 \times 10^{-14} \text{ at } 25\,^\circ\text{C}$$

10.2 pH and pOH

The concentration of hydronium ion in a solution of an acid in water is greater than 1.0×10^{-7} *M* at 25 °C. The concentration of hydroxide ion in a solution of a base in water is greater than 1.0×10^{-7} *M* at 25 °C. The concentration of H_3O^+ in a solution can be expressed as the pH of the solution; $pH = -\log H_3O^+$. The concentration of OH^- can be expressed as the pOH of the solution: $pOH = -\log[OH^-]$. In pure water, pH = 7.00 and pOH = 7.00

10.3 Relative Strengths of Acids and Bases

The strengths of Brønsted-Lowry acids and bases in aqueous solutions can be determined by their acid or base ionization constants. Stronger acids form weaker conjugate bases, and weaker acids form stronger conjugate bases. Thus strong acids are completely ionized in aqueous solution because their conjugate bases are weaker bases than water. Weak acids are only partially ionized because their conjugate bases are strong enough to compete successfully with water for possession of protons. Strong bases react with water to quantitatively form hydroxide ions. Weak bases give only small amounts of hydroxide ion. The strengths of the binary acids increase from left to right across a period of the periodic table ($CH_4 < NH_3 < H_2O < HF$), and they increase down a group ($HF < HCl < HBr < HI$). The strengths of oxyacids that contain the same central element increase as the oxidation number of the element increases ($H_2SO_3 < H_2SO_4$). The strengths of oxyacids also increase as the electronegativity of the central element increases [H_2SeO_4

< H_2SO_4].

10.4 Hydrolysis of Salt Solutions

The characteristic properties of aqueous solutions of Brønsted-Lowry acids are due to the presence of hydronium ions; those of aqueous solutions of Brønsted-Lowry bases are due to the presence of hydroxide ions. The neutralization that occurs when aqueous solutions of acids and bases are combined results from the reaction of the hydronium and hydroxide ions to form water. Some salts formed in neutralization reactions may make the product solutions slightly acidic or slightly basic.

Solutions that contain salts or hydrated metal ions have a pH that is determined by the extent of the hydrolysis of the ions in the solution. The pH of the solutions may be calculated using familiar equilibrium techniques, or it may be qualitatively determined to be acidic, basic, or neutral depending on the relative K_a and K_b of the ions involved.

10.5 Polyprotic Acids

An acid that contains more than one ionizable proton is a polyprotic acid. The protons of these acids ionize in steps. The differences in the acid ionization constants for the successive ionizations of the protons in a polyprotic acid usually vary by roughly five orders of magnitude. As long as the difference between the successive values of K_a of the acid is greater than about a factor of 20, it is appropriate to break down the calculations of the concentrations of the ions in solution into a series of steps.

10.6 Buffers

A solution containing a mixture of a weak acid and its conjugate base, or of a weak base and its conjugate acid, is called a buffer solution. The presence of a weak conjugate acid-base pair provides reactants that may neutralize small additions of strong acid or base, yielding weaker conjugate partners. The hydronium ion concentration of a buffer solution therefore does not change significantly when a small amount of acid or base is added.

10.7 Acid-Base Titrations

A titration curve is a graph that relates the change in pH of an acidic or basic solution to the volume of added titrant. The characteristics of the titration curve are dependent on the specific solutions being titrated. The pH of the solution at the equivalence point may be greater than, equal to, or less than 7.00. The choice of an indicator for a given titration depends on the expected pH at the equivalence point of the titration, and the range of the color change of the indicator.

Exercises

10.1 Brønsted-Lowry Acids and Bases

1. Write equations that show NH_3 as both a conjugate acid and a conjugate base.

2. Write equations that show $H_2PO_4^-$ acting both as an acid and as a base.

3. Show by suitable net ionic equations that each of the following species can act as a Brønsted-Lowry acid:

(a) H_3O^+

(b) HCl

(c) NH_3

(d) CH_3CO_2H

(e) NH_4^+

(f) HSO_4^-

4. Show by suitable net ionic equations that each of the following species can act as a Brønsted-Lowry acid:

(a) HNO_3

(b) PH_4^+

(c) H_2S

(d) CH_3CH_2COOH

(e) $H_2PO_4^-$

(f) HS^-

5. Show by suitable net ionic equations that each of the following species can act as a Brønsted-Lowrybase:

(a) H_2O

(b) OH^-

(c) NH_3

(d) CN^-

(e) S^{2-}

(f) $H_2PO_4^-$

6. Show by suitable net ionic equations that each of the following species can act as a Brønsted-Lowrybase:

(a) HS^-

(b) PO_4^{3-}

(c) NH_2^-

(d) C_2H_5OH

(e) O^{2-}

(f) $H_2PO_4^-$

7. What is the conjugate acid of each of the following? What is the conjugate base of each?

(a) OH^-

(b) H_2O

(c) HCO_3^-

(d) NH_3

(e) HSO_4^-

(f) H_2O_2

(g) HS^-

(h) $H_5N_2^+$

8. What is the conjugate acid of each of the following? What is the conjugate base of each?

(a) H_2S

(b) $H_2PO_4^-$

(c) PH_3

(d) HS^-

(e) HSO_3^-

(f) $H_3O_2^+$

(g) H_4N_2

(h) CH_3OH

9. Identify and label the Brønsted-Lowry acid, its conjugate base, the Brønsted-Lowry base, and its conjugate acid in each of the following equations:

(a) $HNO_3 + H_2O \rightarrow H_3O^+ + NO_3^-$

(b) $CN^- + H_2O \rightarrow HCN + OH^-$

(c) $H_2SO_4 + Cl^- \rightarrow HCl + HSO_4^-$

(d) $HSO_4^- + OH^- \rightarrow SO_4^{2-} + H_2O$

(e) $O^{2-} + H_2O \rightarrow 2OH^-$

(f) $[Cu(H_2O)_3(OH)]^+ + [Al(H_2O)_6]^{3+} \rightarrow [Cu(H_2O)_4]^{2+} + [Al(H_2O)_5(OH)]^{2+}$

(g) $H_2S + NH_2^- \rightarrow HS^- + NH_3$

10. Identify and label the Brønsted-Lowry acid, its conjugate base, the Brønsted-Lowry base, and its conjugate acid in each of the following equations:

(a) $NO_2^- + H_2O \rightarrow HNO_2 + OH^-$

(b) $HBr + H_2O \rightarrow H_3O^+ + Br^-$

(c) $HS^- + H_2O \rightarrow H_2S + OH^-$

(d) $H_2PO_4^- + OH^- \rightarrow HPO_4^{2-} + H_2O$

(e) $H_2PO_4^- + HCl \rightarrow H_3PO_4 + Cl^-$

(f) $[Fe(H_2O)_5(OH)]^{2+} + [Al(H_2O)_6]^{3+} \rightarrow [Fe(H_2O)_6]^{3+} + [Al(H_2O)_5(OH)]^{2+}$

(g) $CH_3OH + H^- \rightarrow CH_3O^- + H_2$

11. What are amphiprotic species? Illustrate with suitable equations.

12. State which of the following species are amphiprotic and write chemical equations illustrating the

amphiprotic character of these species:

(a) H_2O

(b) $H_2PO_4^-$

(c) S^{2-}

(d) CO_3^{2-}

(e) HSO_4^-

13. State which of the following species are amphiprotic and write chemical equations illustrating the amphiprotic character of these species.

(a) NH_3

(b) HPO_4^-

(c) Br^-

(d) NH_4^+

(e) ASO_4^{3-}

14. Is the self ionization of water endothermic or exothermic? The ionization constant for water (K_w) is 2.9 $\times$ 10^{-14} at 40 °C and 9.3 $\times$ 10^{-14} at 60 °C.

10.2 pH and pOH

15. Explain why a sample of pure water at 40 °C is neutral even though $[H_3O^+] = 1.7 \times 10^{-7}$ *M*. K_w is 2.9 $\times$ 10^{-14} at 40 °C.

16. The ionization constant for water (K_w) is 2.9×10^{-14} at 40 °C. Calculate $[H_3O^+]$, $[OH^-]$, pH, and pOH for pure water at 40 °C.

17. The ionization constant for water (K_w) is 9.311×10^{-14} at 60 °C. Calculate $[H_3O^+]$, $[OH^-]$, pH, and pOH for pure water at 60 °C.

18. Calculate the pH and the pOH of each of the following solutions at 25 °C for which the substances ionize completely:

(a) 0.200 *M* HCl

(b) 0.0143 *M* NaOH

(c) 3.0 *M* HNO_3

(d) 0.0031 *M* $Ca(OH)_2$

19. Calculate the pH and the pOH of each of the following solutions at 25 °C for which the substances ionize completely:

(a) 0.000259 *M* $HClO_4$

(b) 0.21 *M* NaOH

(c) 0.000071 *M* $Ba(OH)_2$

(d) 2.5 *M* KOH

20. What are the pH and pOH of a solution of 2.0 M HCl, which ionizes completely?

21. What are the hydronium and hydroxide ion concentrations in a solution whose pH is 6.52?

22. Calculate the hydrogen ion concentration and the hydroxide ion concentration in wine from its pH. See **Figure 10.2** for useful information.

23. Calculate the hydronium ion concentration and the hydroxide ion concentration in lime juice from its pH. See **Figure 10.2** for useful information.

24. The hydronium ion concentration in a sample of rainwater is found to be 1.7×10^{-6} *M* at 25 °C. What is the concentration of hydroxide ions in the rainwater?

25. The hydroxide ion concentration in household ammonia is 3.2×10^{-3} *M* at 25 °C. What is the concentration of hydronium ions in the solution?

10.2 Relative Strengths of Acids and Bases

26. Explain why the neutralization reaction of a strong acid and a weak base gives a weakly acidic solution.

27. Explain why the neutralization reaction of a weak acid and a strong base gives a weakly basic solution.

28. Use this list of important industrial compounds (and **Figure 10.11**) to answer the following questions regarding: CaO, $Ca(OH)_2$, CH_3CO_2H, CO_2, HCl, H_2CO_3, HF, HNO_2, HNO_3, H_3PO_4, H_2SO_4, NH_3, NaOH, Na_2CO_3.

(a) Identify the strong Brønsted-Lowry acids and strong Brønsted-Lowry bases.

(b) List those compounds in (a) that can behave as Brønsted-Lowry acids with strengths lying between those of H_3O^+ and H_2O.

(c) List those compounds in (a) that can behave as Brønsted-Lowry bases with strengths lying between those of H_2O and OH^-.

29. The odor of vinegar is due to the presence of acetic acid, CH_3CO_2H, a weak acid. List, in order of descending concentration, all of the ionic and molecular species present in a 1-*M* aqueous solution of this acid.

30. Household ammonia is a solution of the weak base NH_3 in water. List, in order of descending concentration, all of the ionic and molecular species present in a 1-*M* aqueous solution of this base.

31. Explain why the ionization constant, K_a, for H_2SO_4 is larger than the ionization constant for H_2SO_3.

32. Explain why the ionization constant, K_a, for HI is larger than the ionization constant for HF.

33. Gastric juice, the digestive fluid produced in the stomach, contains hydrochloric acid, HCl. Milk of Magnesia, a suspension of solid $Mg(OH)_2$ in an aqueous medium, is sometimes used to neutralize excess stomach acid. Write a complete balanced equation for the neutralization reaction, and identify the conjugate acid-base pairs.

34. Nitric acid reacts with insoluble copper(II) oxide to form soluble copper(II) nitrate, $Cu(NO_3)_2$, a compound that has been used to prevent the growth of algae in swimming pools. Write the balanced chemical equation for the reaction of an aqueous solution of HNO_3 with CuO.

35. What is the ionization constant at 25 °C for the weak acid $CH_3NH_3^+$, the conjugate acid of the weak base CH_3NH_2, $K_b = 4.4 \times 10^{-4}$.

36. What is the ionization constant at 25 °C for the weak acid $(CH_3)_2NH_2^+$, the conjugate acid of the weak base $(CH_3)_2NH$, $K_b = 5.9 \times 10^{-4}$?

37. Which base, CH_3NH_2 or $(CH_3)_2NH$, is the stronger base? Which conjugate acid, $(CH_3)_2NH_2^+$ or $(CH_3)_2NH_3^+$, is the stronger acid?

38. Which is the stronger acid, NH_4^+ or HBrO?

39. Which is the stronger base, $(CH_3)_3N$ or $H_2BO_3^-$?

40. Predict which acid in each of the following pairs is the stronger and explain your reasoning for each.

(a) H_2O or HF

(b) $B(OH)_3$ or $Al(OH)_3$

(c) HSO_3^- or HSO_4^-

(d) NH_3 or H_2S

(e) H_2O or H_2Te

41. Predict which compound in each of the following pairs of compounds is more acidic and explain your reasoning for each.

(a) HSO_4^- or $HSeO_4^-$

(b) NH_3 or H_2O

(c) PH_3 or HI

(d) NH_3 or PH_3

(e) H_2S or HBr

42. Rank the compounds in each of the following groups in order of increasing acidity or basicity, as indicated, and explain the order you assign.

(a) acidity: HCl, HBr, HI

(b) basicity: H_2O, OH^-, H^-, Cl^-

(c) basicity: $Mg(OH)_2$, $Si(OH)_4$, $ClO_3(OH)$ (Hint: Formula could also be written as $HClO_4$).

(d) acidity: HF, H_2O, NH_3, CH_4

43. Rank the compounds in each of the following groups in order of increasing acidity or basicity, as indicated, and explain the order you assign.

(a) acidity: $NaHSO_3$, $NaHSeO_3$, $NaHSO_4$

(b) basicity: BrO_2^-, ClO_2^-, IO_2^-

(c) acidity: HOCl, HOBr, HOI

(d) acidity: HOCl, HOClO, $HOClO_2$, $HOClO_3$

(e) basicity: NH_2^-, HS^-, HTe^-, PH_2^-

(f) basicity: BrO^-, BrO_2^-, BrO_3^-, BrO_4^-

44. Both HF and HCN ionize in water to a limited extent. Which of the conjugate bases, F^- or CN^-, is the stronger base? See **Table 10.3**.

45. The active ingredient formed by aspirin in the body is salicylic acid, $C_6H_4OH(CO_2H)$. The carboxyl group ($-CO_2H$) acts as a weak acid. The phenol group (an OH group bonded to an aromatic ring) also acts as an acid but a much weaker acid. List, in order of descending concentration, all of the ionic and molecular species present in a 0.001-*M* aqueous solution of $C_6H_4OH(CO_2H)$.

46. What do we represent when we write:

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

47. Explain why equilibrium calculations are not necessary to determine ionic concentrations in solutions of certain strong electrolytes such as NaOH and HCl. Under what conditions are equilibrium calculations necessary as part of the determination of the concentrations of all ions of some other strong electrolytes in solution?

48. Are the concentrations of hydronium ion and hydroxide ion in a solution of an acid or a base in water directly proportional or inversely proportional? Explain your answer.

49. What two common assumptions can simplify calculation of equilibrium concentrations in a solution of a weak acid?

50. What two common assumptions can simplify calculation of equilibrium concentrations in a solution of a weak base?

51. Which of the following will increase the percent of NH_3 that is converted to the ammonium ion in water (Hint: Use LeChâtelier's principle.)?

(a) addition of NaOH

(b) addition of HCl

(c) addition of NH_4Cl

52. Which of the following will increase the percent of HF that is converted to the fluoride ion in water?

(a) addition of NaOH

(b) addition of HCl

(c) addition of NaF

53. What is the effect on the concentrations of NO_2^-, HNO_2, and OH^- when the following are added to a solution of KNO_2 in water:

(a) HCl

(b) HNO_2

(c) NaOH

(d) NaCl

(e) KNO

The equation for the equilibrium is:

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

54. What is the effect on the concentration of hydrofluoric acid, hydronium ion, and fluoride ion when the

following are added to separate solutions of hydrofluoric acid?

(a) HCl

(b) KF

(c) NaCl

(d) KOH

(e) HF

The equation for the equilibrium is:

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

55. Why is the hydronium ion concentration in a solution that is 0.10 *M* in HCl and 0.10 *M* in HCOOH determined by the concentration of HCl?

56. From the equilibrium concentrations given, calculate K_a for each of the weak acids and K_b for each of the weak bases.

(a) CH_3CO_2H: $[H_3O^+] = 1.34 \times 10^{-3}$ *M*;

$[CH_3CO_2^-] = 1.34 \times 10^{-3}$ *M*;

$[CH_3CO_2H] = 9.866 \times 10^{-2}$ *M*; (b) ClO^-: $[OH^-] = 4.0 \times 10^{-4}$ *M*; $[HClO] = 2.38 \times 10^{-5}$ *M*;

$[ClO^-] = 0.273$ *M*;

(c) HCO_2H: $[HCO_2H] = 0.524$ *M*; $[H_3O^+] = 9.8 \times 10^{-3}$ *M*; $[HCO_2^-] = 9.8 \times 10^{-3}$ *M*;

(d) $C_6H_5NH_3^+$: $[C_6H_5NH_3^+] = 0.233$ *M*; $[C_6H_5NH_2] = 2.3 \times 10^{-3}$ *M*;

$[H_3O^+] = 2.3 \times 10^{-3}$ *M*

57. From the equilibrium concentrations given, calculate K_a for each of the weak acids and K_b for each of the weak bases.

(a) NH_3: $[OH^-] = 3.1 \times 10^{-3}$ *M*;

$[NH_4^+] = 3.1 \times 10^{-3}$ *M*;

$[NH_3] = 0.533$ *M*;

(b) HNO_2: $[H_3O^+] = 0.011$ *M*;

$[NO_2^-] = 0.0438$ *M*;

$[HNO_2] = 1.07$ *M*;

(c) $(CH_3)_3N$: $[(CH_3)_3N] = 0.25$ *M*; $[(CH_3)_3NH^+] = 4.3 \times 10^{-3}$ *M*;

$[OH^-] = 4.3 \times 10^{-3}$ *M*;

(d) NH_4^+ : $[NH_4^+] = 0.100$ *M*; $[NH_3] = 7.5 \times 10^{-6}$ *M*;

$[H_3O^+] = 7.5 \times 10^{-6}$ *M*

58. Determine K_b for the nitrite ion, NO_2^-. In a 0.10-*M* solution this base is 0.0015% ionized.

59. Determine K_a for hydrogen sulfate ion, HSO_4^-. In a 0.10-*M* solution the acid is 29% ionized.

60. Calculate the ionization constant for each of the following acids or bases from the ionization constant of its conjugate base or conjugate acid:

(a) F^-

(b) NH_4^+

(c) AsO_4^{3-}

(d) $(CH_3)_2NH_2^+$

(e) NO_2^-

(f) $HC_2O_4^-$ (as a base)

61. Calculate the ionization constant for each of the following acids or bases from the ionization constant of its conjugate base or conjugate acid:

(a) HTe^- (as a base)

(b) $(CH_3)_3NH^+$

(c) $HAsO_4^{3-}$ (as a base)

(d) HO_2^- (as a base)

(e) $C_6H_5NH_3^+$

(f) HSO_3^- (as a base)

62. For which of the following solutions must we consider the ionization of water when calculating the pH or pOH?

(a) 3×10^{-8} *M* HNO_3

(b) 0.10 g HCl in 1.0 L of solution

(c) 0.00080 g NaOH in 0.50 L of solution (d) 1×10^{-7} *M* $Ca(OH)_2$

(e) 0.0245 *M* KNO_3

63. Even though both NH_3 and $C_6H_5NH_2$ are weak bases, NH_3 is a much stronger acid than $C_6H_5NH_2$. Which of the following is correct at equilibrium for a solution that is initially 0.10 *M* in NH_3 and 0.10 *M* in $C_6H_5NH_2$?

(a) $[OH^-] = [NH_4^+]$

(b) $[NH_4^+] = [C_6H_5NH_3^+]$

(c) $[OH^-] = [C_6H_5NH_3^+]$

(d) $[NH_3] = [C_6H_5NH_2]$

(e) both a and b are correct

64. Calculate the equilibrium concentration of the nonionized acids and all ions in a solution that is 0.25 *M* in HCO_2H and 0.10 *M* in HClO.

65. Calculate the equilibrium concentration of the nonionized acids and all ions in a solution that is 0.134 *M* in HNO_2 and 0.120 *M* in HBrO.

66. Calculate the equilibrium concentration of the nonionized bases and all ions in a solution that is 0.25 *M* in CH_3NH_2 and 0.10 *M* in C_5H_5N ($K_b = 1.7 \times 10^{-9}$).

67. Calculate the equilibrium concentration of the nonionized bases and all ions in a solution that is 0.115 *M* in NH_3 and 0.100 *M* in $C_6H_5NH_2$.

68. Using the K_a value of 1.4×10^{-5}, place $Al(H_2O)_6^{3+}$ in the correct location in **Figure 10.11**.

69. Calculate the concentration of all solute species in each of the following solutions of acids or bases. Assume that the ionization of water can be neglected, and show that the change in the initial concentrations can be neglected. Ionization constants can be found in **Appendix H** and **Appendix I**.

(a) 0.0092 *M* HClO, a weak acid

(b) 0.0784 *M* $C_6H_5NH_2$, a weak base

(c) 0.0810 *M* HCN, a weak acid

(d) 0.11 *M* $(CH_3)_3N$, a weak base

(e) 0.120 *M* $Fe(H_2O)_6^{2+}$ a weak acid, $K_a = 1.6 \times 10^{-7}$

70. Propionic acid, $C_2H_5CO_2H$ ($K_a = 1.34 \times 10^{-5}$), is used in the manufacture of calcium propionate, a food preservative. What is the hydronium ion concentration in a 0.698-*M* solution of $C_2H_5CO_2H$?

71. White vinegar is a 5.0% by mass solution of acetic acid in water. If the density of white vinegar is 1.007 g/cm^3, what is the pH?

72. The ionization constant of lactic acid, $CH_3CH(OH)CO_2H$, an acid found in the blood after strenuous exercise, is 1.36×10^{-4}. If 20.0 g of lactic acid is used to make a solution with a volume of 1.00 L, what is the concentration of hydronium ion in the solution?

73. Nicotine, $C_{10}H_{14}N_2$, is a base that will accept two protons ($K_1 = 7 \times 10^{-7}$, $K_2 = 1.4 \times 10^{-11}$). What is the concentration of each species present in a 0.050-*M* solution of nicotine?

74. The pH of a 0.20-*M* solution of HF is 1.92. Determine K_a for HF from these data.

75. The pH of a 0.15-*M* solution of HSO_4^- is 1.43. Determine K_a for HSO_4^- from these data.

76. The pH of a 0.10-*M* solution of caffeine is 11.16. Determine K_b for caffeine from these data:

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

77. The pH of a solution of household ammonia, a 0.950 M solution of NH_3, is 11.612. Determine K_b for NH_3 from these data.

10.3 Hydrolysis of Salt Solutions

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

(a) $Al(NO_3)_3$

(b) RbI

(c) $KHCO_2$

(d) CH_3NH_3Br

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

(a) $FeCl_3$

(b) K_2CO_3

(c) NH_4Br

(d) $KClO_4$

80. Novocaine, $C_{13}H_{21}O_2N_2Cl$, is the salt of the base procaine and hydrochloric acid. The ionization constant for procaine is 7×10^{-6}. Is a solution of novocaine acidic or basic? What are $[H_3O^+]$, $[OH^-]$, and pH of a 2.0% solution by mass of novocaine, assuming that the density of the solution is 1.0 g/mL.

10.4 Polyprotic Acids

81. Which of the following concentrations would be practically equal in a calculation of the equilibrium concentrations in a 0.134-*M* solution of H_2CO_3, a diprotic acid: $[H_3O^+]$, $[OH^-]$, $[H_2CO_3]$, $[HCO_3^-]$, $[CO_3^{2-}]$? No calculations are needed to answer this question.

82. Calculate the concentration of each species present in a 0.050-*M* solution of H_2S.

83. Calculate the concentration of each species present in a 0.010-*M* solution of phthalic acid, $C_6H_4(CO_2H)_2$.

$$C_6H_4(COH)_2(aq) + H_2O(l) \rightleftharpoons HO^+(aq) + C_6H_4(COH)(CO_2)^-(aq) \qquad K_{a2} = 1.1 \times 10^{-3}$$

$$C_6H_4(COH)(CO_2)^-(aq) + H_2O(l) \rightleftharpoons HO^+(aq) + C_6H_4(CO_2)_2^{2-}(aq) \qquad K_{a3} = 3.9 \times 10^{-6}$$

84. Salicylic acid, $HOC_6H_4CO_2H$, and its derivatives have been used as pain relievers for a long time. Salicylic acid occurs in small amounts in the leaves, bark, and roots of some vegetation (most notably historically in the bark of the willow tree). Extracts of these plants have been used as medications for centuries. The acid was first isolated in the laboratory in 1838.

(a) Both functional groups of salicylic acid ionize in water, with $K_a = 1.0 \times 10^{-3}$ for the—CO_2H group and 4.2×10^{-13} for the −OH group. What is the pH of a saturated solution of the acid (solubility = 1.8 g/L).

(b) Aspirin was discovered as a result of efforts to produce a derivative of salicylic acid that would not be irritating to the stomach lining. Aspirin is acetylsalicylic acid, $CH_3CO_2C_6H_4CO_2H$. The $-CO_2H$ functional group is still present, but its acidity is reduced, $K_a = 3.0 \times 10^{-4}$. What is the pH of a solution of aspirin with the same concentration as a saturated solution of salicylic acid (See Part a).

(c) Under some conditions, aspirin reacts with water and forms a solution of salicylic acid and acetic acid:

$$CH_3CO_2C_6H_4CO_2H(aq) + H_2O(l) \rightarrow HOC_6H_4CO_2H(aq) + CH_3CO_2H(aq)$$

i. Which of the acids, salicylic acid or acetic acid, produces more hydronium ions in such a solution?

ii. What are the concentrations of molecules and ions in a solution produced by the hydrolysis of 0.50 g of aspirin dissolved in enough water to give 75 mL of solution?

85. The ion HTe^- is an amphiprotic species; it can act as either an acid or a base.

(a) What is K_a for the acid reaction of HTe^- with H_2O?

(b) What is K_b for the reaction in which HTe^- functions as a base in water?

(c) Demonstrate whether or not the second ionization of H_2Te can be neglected in the calculation of $[HTe^-]$ in a 0.10 M solution of H_2Te.

10.5 Buffers

86. Explain why a buffer can be prepared from a mixture of NH_4Cl and NaOH but not from NH_3 and NaOH.

87. Explain why the pH does not change significantly when a small amount of an acid or a base is added to a solution that contains equal amounts of the acid H_3PO_4 and a salt of its conjugate base NaH_2PO_4.

88. Explain why the pH does not change significantly when a small amount of an acid or a base is added to a solution that contains equal amounts of the base NH_3 and a salt of its conjugate acid NH_4Cl.

89. What is $[H_3O^+]$ in a solution of 0.25 *M* CH_3CO_2H and 0.030 *M* $NaCH_3CO_2$?

$$CH_3CO_2H(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + CH_3CO_2^-(aq) \qquad K_a = 1.8 \times 10^{-5}$$

90. What is $[H_3O^+]$ in a solution of 0.075 *M* HNO_2 and 0.030 *M* $NaNO_2$?

$$HNO_2(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + NO_2^-(aq) \qquad K_a = 4.5 \times 10^{-5}$$

91. What is $[OH^-]$ in a solution of 0.125 *M* CH_3NH_2 and 0.130 *M* CH_3NH_3Cl?

$$CH_3NH_2(aq) + H_2O(l) \rightleftharpoons CH_3NH_3^+(aq) + OH^-(aq) \qquad K_b = 4.4 \times 10^{-4}$$

92. What is $[OH^-]$ in a solution of 1.25 *M* NH_3 and 0.78 *M* NH_4NO_3?

$$NH_3(aq) + H_2O(l) \rightleftharpoons NH_4^+(aq) + OH^-(aq) \qquad K_b = 1.8 \times 10^{-5}$$

93. What concentration of NH_4NO_3 is required to make $[OH^-] = 1.0 \times 10^{-5}$ in a 0.200-*M* solution of NH_3?

94. What concentration of NaF is required to make $[H_3O^+] = 2.3 \times 10^{-4}$ in a 0.300-*M* solution of HF?

95. What is the effect on the concentration of acetic acid, hydronium ion, and acetate ion when the following are added to an acidic buffer solution of equal concentrations of acetic acid and sodium acetate:

(a) HCl

(b) KCH_3CO_2

(c) NaCl

(d) KOH

(e) CH_3CO_2H

96. What is the effect on the concentration of ammonia, hydroxide ion, and ammonium ion when the following are added to a basic buffer solution of equal concentrations of ammonia and ammonium nitrate:

(a) KI

(b) NH_3

(c) HI

(d) NaOH

(e) NH_4Cl

97. What will be the pH of a buffer solution prepared from 0.20 mol NH_3, 0.40 mol NH_4NO_3, and just enough water to give 1.00 L of solution?

98. Calculate the pH of a buffer solution prepared from 0.155 mol of phosphoric acid, 0.250 mole of KH_2PO_4, and enough water to make 0.500 L of solution.

99. How much solid $NaCH_3CO_2 \cdot 3H_2O$ must be added to 0.300 L of a 0.50-*M* acetic acid solution to give a buffer with a pH of 5.00? (Hint: Assume a negligible change in volume as the solid is added.)

100. What mass of NH_4Cl must be added to 0.750 L of a 0.100-*M* solution of NH_3 to give a buffer solution with a pH of 9.26? (Hint: Assume a negligible change in volume as the solid is added.)

101. A buffer solution is prepared from equal volumes of 0.200 *M* acetic acid and 0.600 *M* sodium acetate. Use

1.80×10^{-5} as K_a for acetic acid.

(a) What is the pH of the solution?

(b) Is the solution acidic or basic?

10.7 Acid-Base Titrations

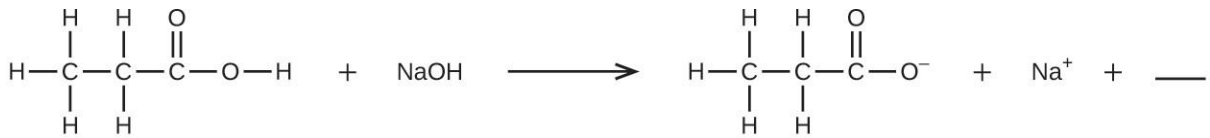
102. Calculate the pH at the following points in a titration of 40 mL (0.040 L) of 0.100 *M* barbituric acid () with 0.100 *M* KOH.

103. Write a balanced equation describing each of the following chemical reactions.

104. When solid sodium chloride is added to aqueous sulfuric acid, hydrogen chloride gas and aqueous sodium sulfate are produced.

105. Aqueous solutions of phosphoric acid and potassium hydroxide react to produce aqueous potassium dihydrogen phosphate and liquid water.

106. Fill in the blank with a single chemical formula for a covalent compound that will balance the equation:



107. Aqueous hydrogen fluoride (hydrofluoric acid) is used to etch glass and to analyze minerals for their silicon content. Hydrogen fluoride will also react with sand (silicon dioxide).

108. Write an equation for the reaction of solid silicon dioxide with hydrofluoric acid to yield gaseous silicon tetrafluoride and liquid water.

109. The mineral fluorite (calcium fluoride) occurs extensively in Illinois. Solid calcium fluoride can also be prepared

by the reaction of aqueous solutions of calcium chloride and sodium fluoride, yielding aqueous sodium chloride as the other product. Write complete and net ionic equations for this reaction.

110. Complete and balance the following acid-base equations:
    (a) HCl gas reacts with solid $Ca(OH)_2(s)$.
    (b) A solution of $Sr(OH)_2$ is added to a solution of HNO_3.
    (c) A solution of $HClO_4$ is added to a solution of LiOH.
    (d) Aqueous H_2SO_4 reacts with NaOH.
    (e) $Ba(OH)_2$ reacts with HF gas.

111. Complete and balance the equations for the following acid-base neutralization reactions. If water is used as a solvent, write the reactants and products as aqueous ions. In some cases, there may be more than one correct answer, depending on the amounts of reactants used.
    (a) $Mg(OH)_2(s) + HClO_4(aq) \rightarrow$
    (b) $SO_3(g) + H_2O(l) \rightarrow$ (assume an excess of water and that the product dissolves)
    (c) $SrO(s) + H_2SO_4(l) \rightarrow$

112. Lithium hydroxide may be used to absorb carbon dioxide in enclosed environments, such as manned spacecraft and submarines. Write an equation for the reaction that involves 2 mol of LiOH per 1 mol of CO_2. (Hint: Water is one of the products.)

113. Calcium propionate is sometimes added to bread to retard spoilage. This compound can be prepared by the reaction of calcium carbonate, $CaCO_3$, with propionic acid, $C_2H_5CO_2H$, which has properties similar to those of acetic acid. Write the balanced equation for the formation of calcium propionate.

114. Complete and balance the equations of the following reactions, each of which could be used to remove hydrogen sulfide from natural gas:
    (a) $Ca(OH)_2(s) + H_2S(g) \rightarrow$
    (b) $Na_2CO_3(aq) + H_2S(g) \rightarrow$

115. H_2 is produced by the reaction of 118.5 mL of a 0.8775-M solution of H_3PO_4 according to the following equation: $2Cr + 2H_3PO_4 \rightarrow 3H_2 + 2CrPO_4$.
    (a) Outline the steps necessary to determine the number of moles and mass of H_2.
    (b) Perform the calculations outlined.

116. Gallium chloride is formed by the reaction of 2.6 L of a 1.44 M solution of HCl according to the following equation: $2Ga + 6HCl \rightarrow 2GaCl_3 + 3H_2$.
    (a) Outline the steps necessary to determine the number of moles and mass of gallium chloride.
    (b) Perform the calculations outlined.

117. In an accident, a solution containing 2.5 kg of nitric acid was spilled. Two kilograms of Na_2CO_3 was quickly spread on the area and CO_2 was released by the reaction. Was sufficient Na_2CO_3 used to neutralize all of the acid?

118. A mordant is a substance that combines with a dye to produce a stable fixed color in a dyed fabric. Calcium acetate is used as a mordant. It is prepared by the reaction of acetic acid with calcium hydroxide.

(a) $2CH_3CO_2H + Ca(OH)_2 \longrightarrow Ca(CH_3CO_2)_2 + 2H_2O$

(b) What mass of $Ca(OH)_2$ is required to react with the acetic acid in 25.0 mL of a solution having a density of 1.065 g/ mL and containing 58.0% acetic acid by mass?

119. What volume of 0.600 *M* HCl is required to react completely with 2.50 g of sodium hydrogen carbonate?

$$NaHCO_3(aq) + HCl(aq) \longrightarrow NaCl(aq) + CO_2(g) + H_2O(l)$$

120. What volume of 0.08892 *M* HNO_3 is required to react completely with 0.2352 g of potassium hydrogen phosphate?

$$2HNO3(aq) + K2\ HPO4(aq) \longrightarrow H2\ PO4(aq) + 2KNO3(aq)$$

121. What volume of a 0.3300-*M* solution of sodium hydroxide would be required to titrate 15.00 mL of 0.1500 *M* oxalic acid?

$$C2\ O4\ H2(aq) + 2NaOH(aq) \longrightarrow Na2\ C2\ O4(aq) + 2H2\ O(l)$$

122. What volume of a 0.00945-*M* solution of potassium hydroxide would be required to titrate 50.00 mL of a sample of acid rain with a H_2SO_4 concentration of 1.23×10^{-4} *M*.

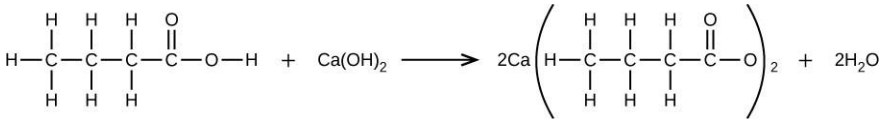
$$H2\ SO4(aq) + 2KOH(aq) \longrightarrow K2\ SO4(aq) + 2H2\ O(l)$$

123. A sample of solid calcium hydroxide, $Ca(OH)_2$, is allowed to stand in water until a saturated solution is formed. A titration of 75.00 mL of this solution with 5.00×10^{-2} *M* HCl requires 36.6 mL of the acid to reach the end point.

$$Ca(OH)2(aq) + 2HCl(aq) \longrightarrow CaCl2(aq) + 2H2\ O(l)$$

124. What is the molarity?

125. What mass of $Ca(OH)_2$ will react with 25.0 g of butanoic to form the preservative calcium butanoate according to the equation?



126. How many milliliters of a 0.1500-*M* solution of KOH will be required to titrate 40.00 mL of a 0.0656-*M* solution of H_3PO_4?

$$H3\ PO4(aq) + 2KOH(aq) \longrightarrow K2\ HPO4(aq) + 2H2\ O(l)$$

127. Potassium acid phthalate, $KNaC_8H_4O_4$, or KHP, is used in many laboratories, including general chemistry laboratories, to standardize solutions of base. KHP is one of only a few stable solid acids that can be dried by warming and weighed. A 0.3420-g sample of $KNaC_8H_4O_4$ reacts with 35.73 mL of a NaOH solution in a titration. What is the molar concentration of the NaOH?

$$KNaC8\ H4\ O4(aq) + NaOH(aq) \longrightarrow KNaC8\ H4\ O4(aq) + H2\ O(aq)$$

128. What volume of 0.0105-M HBr solution is required to titrate 125 mL of a 0.0100-*M* $Ca(OH)_2$ solution?

$$Ca(OH)2(aq) + 2HBr(aq) \longrightarrow CaBr2(aq) + 2H2\ O(l)$$

129. Titration of a 20.0-mL sample of acid rain required 1.7 mL of 0.0811 *M* NaOH to reach the end point. If we assume that the acidity of the rain is due to the presence of sulfuric acid, what was the concentration of sulfuric acid in this sample of rain?

130. What is the concentration of NaCl in a solution if titration of 15.00 mL of the solution with 0.2503 *M* $AgNO_3$ requires 20.22 mL of the $AgNO_3$ solution to reach the end point?

$$AgNO3(aq) + NaCl(aq) \longrightarrow AgCl(s) + NaNO\ 3(aq)$$

131. In a common medical laboratory determination of the concentration of free chloride ion in blood serum, a serum sample is titrated with a $Hg(NO_3)_2$ solution.

$$2Cl—(aq) + Hg(NO3)2(aq) \longrightarrow 2NO3\ —(aq) + HgCl2(s)$$

What is the Cl^- concentration in a 0.25-mL sample of normal serum that requires 1.46 mL of 8.25×10^{-4} *M* $Hg(NO_3)_2(aq)$ to reach the end point?

132. Potatoes can be peeled commercially by soaking them in a 3-M to 6-M solution of sodium hydroxide, then removing the loosened skins by spraying them with water. Does a sodium hydroxide solution have a suitable concentration if titration of 12.00 mL of the solution requires 30.6 mL of 1.65 M HCI to reach the end point?