LINN-BENTON COMMUNITY COLLEGE

COLLEGE CHEMISTRY III (CH 123)

OPEN EDUCATION RESOURCES TEXTBOOK

(CHEMISTRY OER TEXTBOOK)

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- 19.1 Organic Compounds

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Chapter 14 Acids and Bases

Chapter Introduction

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

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

14.1 Definitions of Acid and Base

Learning Objectives

- Identify acids, bases, and conjugate acid-base pairs according to the Brønsted-Lowry definition
- Write equations for acid and base ionization reactions
- Describe the acid-base behavior of amphiprotic substances
- Extend previously introduced equilibrium concepts to acids and bases that may donate or accept more than one proton

Introduction

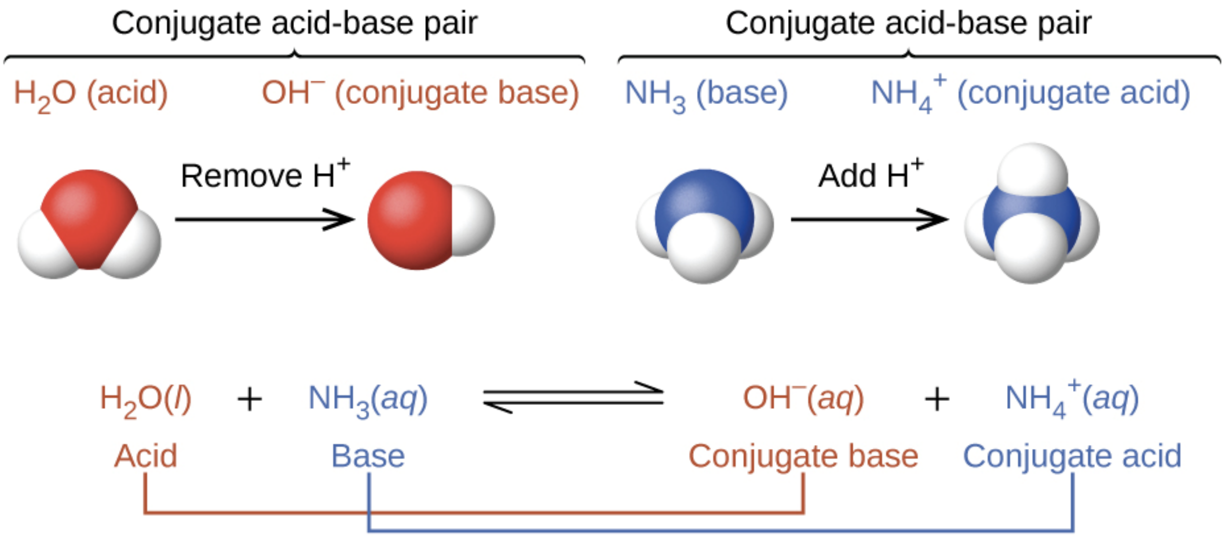
The acid-base reaction class has been studied for quite some time. In 1680, Robert Boyle reported traits of acid solutions that included their ability to dissolve many substances, to change the colors of certain natural dyes, and to lose these traits after coming in contact with alkali (base) solutions.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

Johannes Brønsted and Thomas Lowry proposed a more general description in 1923 in which acids and bases were defined in terms of the transfer of hydrogen ions, H^+. (Note that these hydrogen ions are often referred to simply as *protons*, since that subatomic particle is the only component of cations derived from the most abundant hydrogen isotope, ^1H.)

Brønsted-Lowry Acid and Base Definition

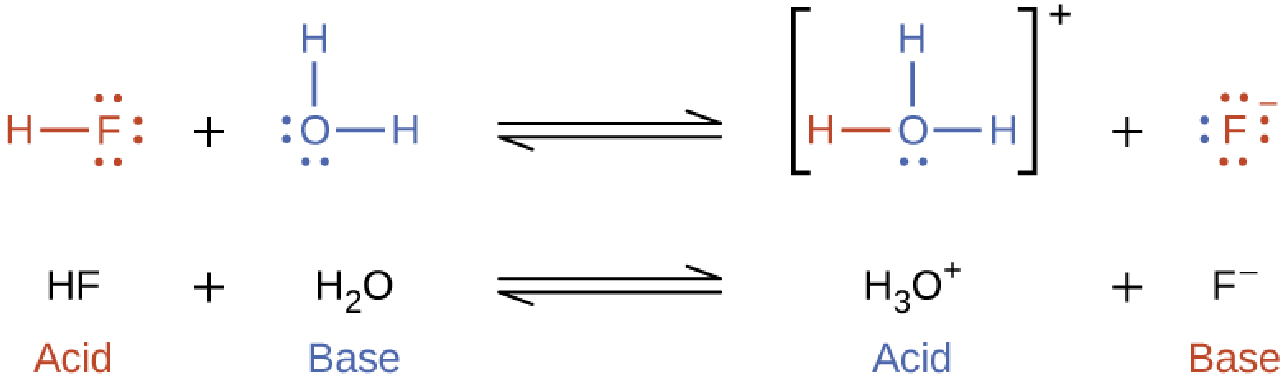
A compound that donates H^+ to another compound is called a **Brønsted-Lowry acid**, and a compound that accepts H^+ is called a **Brønsted-Lowry base**. An acid-base reaction is, thus, the transfer of a proton from a donor (acid) to an acceptor (base).

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



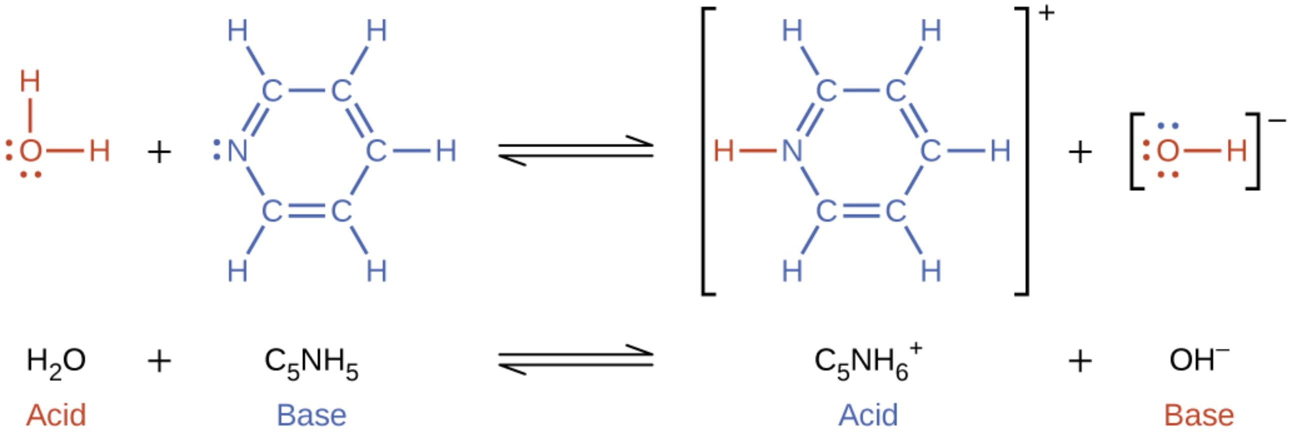
Acid Ionization

The reaction between a Brønsted-Lowry acid and water is called **acid ionization**. For example, when hydrogen fluoride dissolves in water and ionizes, protons (H^+) are transferred from hydrogen fluoride molecules to water molecules, yielding hydronium ions and fluoride ions:



Base Ionization

Base ionization of a species occurs when it accepts protons from water molecules. In the example below, pyridine molecules, C_5NH_5, undergo base ionization when dissolved in water, yielding hydroxide and pyridinium ions:



Amphoteric Substance

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

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

$$HCO_3^- (aq) + H_2O (l) \rightarrow H_2CO_3 (aq) + OH^- (aq)$$

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

Monoprotic and Polyprotic Acids

Monoprotic Acids

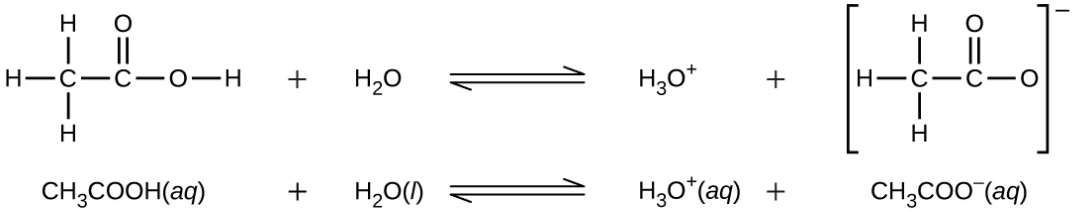
Acids are classified by the number of protons per molecule that they can give up in a reaction. Acids such as HCl, HNO_3, and HCN that contain one ionizable hydrogen atom in each molecule are called **monoprotic acids**. Their reactions with water are:

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

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

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

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



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

Diprotic acids

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: $H_2SO_4\ (aq)\ +\ H_2O\ (l)\ \rightleftharpoons\ H_3O^+\ (aq)\ +\ HSO_4^-\ (aq)$; complete dissociation

Second ionization: $HSO_4^-\ (aq) +\ H_2O\ (l)\ \rightleftharpoons\ H_3O^+\ (aq)\ +\ SO_4^{2-}\ (aq)$; partially dissociation

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

First ionization: $H_2CO_3\ (aq)\ +\ H_2O\ (l)\ \rightleftharpoons\ H_3O^+\ (aq)\ +\ HCO_3^-\ (aq)$; partially dissociation

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

Second ionization: $HCO_3^-\ (aq)\ +\ H_2O\ (l)\ \rightleftharpoons\ H_3O^+\ (aq) + CO_3^{2-}\ (aq)$; partially dissociation

If the first ionization constant of a weak diprotic acid is larger than the second by a factor of at least 20.

Triprotic Acids

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

First ionization: $H_3PO_4\,(aq) + H_2O\,(l) \rightleftharpoons H_3O^+\,(aq) + H_2PO_4^-\,(aq)$

Second ionization: $H_2PO_4^-\,(aq) + H_2O\,(l) \rightleftharpoons H_3O^+\,(aq) + HPO_4^{2-}\,(aq)$

Third ionization: $HPO_4^{2-}\,(aq) + H_2O\,(l) \rightleftharpoons H_3O^+\,(aq) + PO_4^{3-}\,(aq)$

As for the diprotic acid examples, each successive ionization reaction is less extensive than the former.

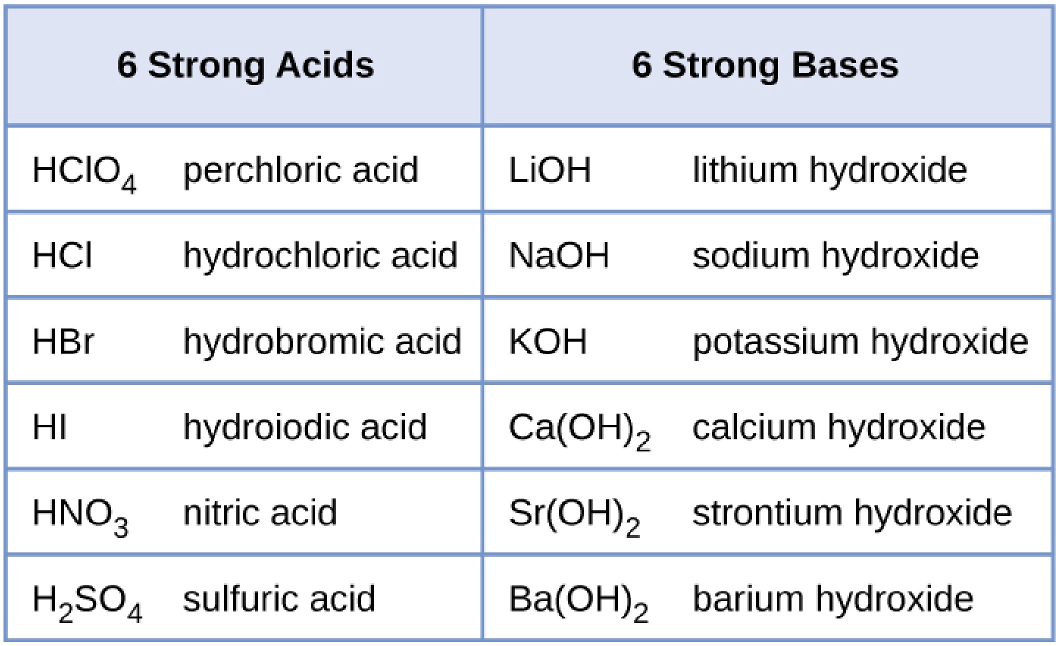
14.2 Acid and Base Strength and Their Molecular Structures

Learning Objectives

- Memorize the relative strengths of acids and bases according to their ionization constants
- Rationalize trends in acid–base strength in relation to molecular structure

Strong Acids and Strong Bases

The relative strength of an acid or base is the extent to which it ionizes when dissolved in water. If the ionization reaction is essentially complete, the acid or base is termed *strong*; if relatively little ionization occurs, the acid or base is *weak*. As will be evident throughout the remainder of this chapter, there are many more weak acids and bases than strong ones. The most common strong acids and bases are listed in Figure 14.2.



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

Figure 14.2 Some of the common strong acids and bases are listed here.

The ionization equations of strong acid and base are represented using the reaction arrow pointed in one direction, which indicating that these compounds ionize completely.

For example, the ionization equation for hydrochloric acid (HCl) in water is as the following:

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

The H^+ ions do not exist in water. They covalently react with water to form hydronium ions, H_3O^+ as described below:

$$H^+\ (aq) + H_2O\ (l) \rightarrow H_3O^+\ (aq)$$

Thus, the true representation for the hydrochloric acid ionization in water is:

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

For a strong polyprotic acid such as H_2SO_4, only the first dissociation is fully ionized.

$H_2SO_{4(aq)} \rightarrow H^+_{(aq)} + HSO_4^-{}_{(aq)}$ 1st dissociation is fully ionized.

$HSO_4^-{}_{(aq)} \rightleftharpoons H^+_{(aq)} + SO_4^{2-}{}_{(aq)}$ 2nd dissociation is partially ionized.

For the ionization of strong base, there is no need to include water in the equation.
For example, ionization of calcium hydroxide ($Ca(OH)_2$) in water:

$$Ca(OH)_2\ (aq) \rightarrow Ca^{2+}\ (aq) + 2OH^-\ (aq)$$

Weak Acids and Weak Bases

Acids and bases that partially ionize when dissolved in water are called weak acids and weak bases. All acids and bases that are not “strong” are considered “weak”.

Weak acids react with water to produce a small amount of H^+.

For example, look at the dissociation of acetic acid in water:

$$\mathbf{H}CH_3CO_2\text{ (aq)} + H_2O\text{ (l)} \rightleftarrows CH_3CO_2^-\text{ (aq)} + H_3O^+\text{ (aq)}$$

The reaction arrows points in both directions, indicating that acetic acid only partially ionizes with water to form H_3O^+ ions. Therefore, acetic acid is a weak acid.

Some Common Weak Acids	
Hydrofluoric Acid ($\mathbf{H}F$)	Sulfurous Acid ($\mathbf{H_2}SO_3$) *(diprotic)*
Acetic Acid ($\mathbf{H}CH_3CO_2$ or $\mathbf{H}C_2H_3O_2$)	Carbonic Acid ($\mathbf{H_2}CO_3$) *(diprotic)*
Formic Acid ($\mathbf{H}CHO_2$)	Phosphoric Acid (H_3PO_4) *(triprotic)*

Weak bases react with water to produce a small amount of OH^-.

For example, look at the reaction of ammonia with water.

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

Ammonia only partially reacts with water to form OH^- ions in solution. Therefore, ammonia is a weak base.

Some Common Weak Bases			
Carbonate ion	(CO_3^{2-})*	Methylamine	(CH_3NH_2)
Bicarbonate ion or hydrogen carbonate ion	(HCO_3^-)*	Ethylamine	($C_2H_5NH_2$)
Phosphate ion	(PO_4^{3-})*	Pyridine	(C_5H_5N)
Ammonia	(NH_3)	Aniline	($C_6H_5NH_2$)

*The carbonate, bicarbonate, and phosphate ions must occur with a positively charged ion such as Na^+ that serves to balance the charge but does not have any part in the ionization reaction. For example, it is the bicarbonate ion that makes sodium bicarbonate ($NaHCO_3$) basic.

Acid-Base Strength and Their Molecular Structures

Binary Acids

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

Across a row in the periodic table, the acid strength of binary hydrogen compounds increases with increasing electronegativity of the nonmetal atom because the polarity of the H-A bond increases. Thus, the order of increasing acidity (for removal of one proton) across the second row is $CH_4 < NH_3 < H_2O < HF$; across the third row, it is $SiH_4 < PH_3 < H_2S < HCl$ (see Figure 14.3).

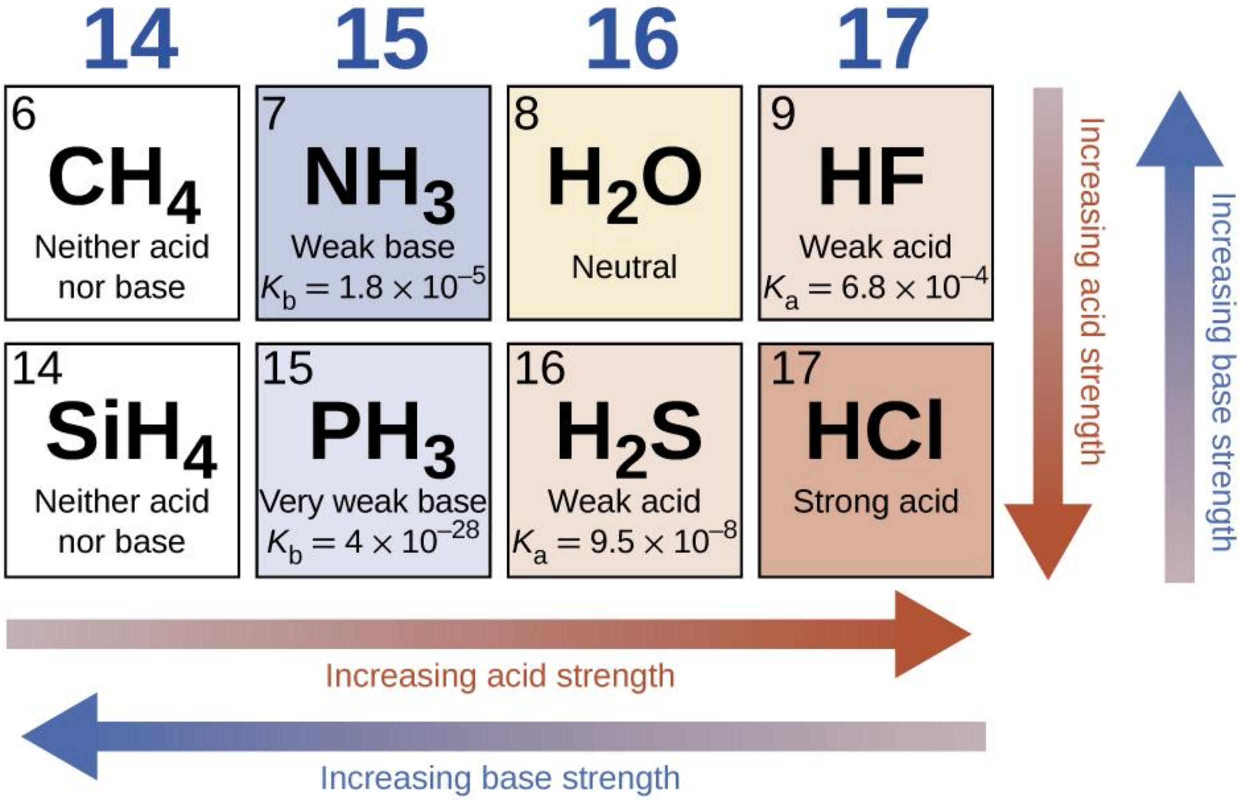
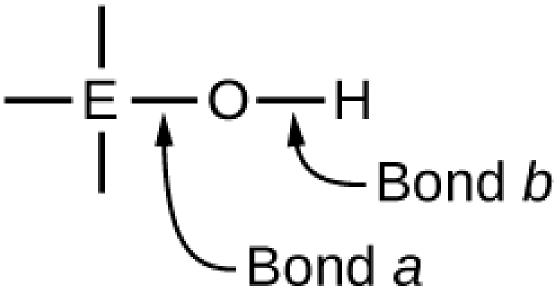


Figure 14.3 The figure shows trends in the strengths of binary acids and bases.

Ternary Molecules

Ternary compounds composed of hydrogen, oxygen, and some third element ("E") may be structured as depicted in the image below. In these compounds, the central E atom is bonded to one or more O atoms, and at least one of the O atoms is also bonded to an H atom, corresponding to the general molecular formula $O_mE(OH)_n$. These compounds may be acidic, basic, or amphoteric depending on the properties of the central E atom. Examples of such compounds include sulfuric acid, $O_2S(OH)_2$, sulfurous acid, $OS(OH)_2$, nitric acid, O_2NOH, perchloric acid, O_3ClOH, aluminum hydroxide, $Al(OH)_3$, calcium hydroxide, $Ca(OH)_2$, and potassium hydroxide, KOH:



Oxyacids

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

Bases

On the other hand, if the central atom, E has a low electronegativity, its attraction for electrons is low. Little tendency exists for the central atom to form a strong covalent bond with the oxygen atom, and bond *a* between the element and oxygen is more readily broken than bond *b* between oxygen and hydrogen. Hence bond *a* is ionic, hydroxide ions are released to the solution, and the material behaves as a base—this is the case with $Ca(OH)_2$ and KOH. Lower electronegativity is characteristic of the more metallic elements; hence, the metallic elements form ionic hydroxides that are by definition basic compounds.

14.3 Acid Ionization Constant

Learning Objectives

- Assess the relative strengths of acids according to their ionization constants
- Carry out simple equilibrium calculations for weak acid solutions
- Carry out percent ionization calculations for weak acid solutions

Acid-Ionization Constant, K_a

The relative strengths of acids may be quantified by measuring their equilibrium constants in aqueous solutions. In solutions of the same concentration, stronger acids ionize to a greater extent, and so yield higher concentrations of hydronium ions than do weaker acids. The equilibrium constant for an acid is called the **acid-ionization constant, K_a.**

For the reaction of an acid HA:

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

The acid ionization constant is written:

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

Where the concentrations are those at equilibrium.

Although water is a reactant in the reaction, it is the solvent as well, so we do not include $[H_2O]$ in the equation. The larger the K_a of an acid, the larger the concentration of H_3O^+ and A^- relative to the concentration of the nonionized acid, HA, in an equilibrium mixture, and the stronger the acid. An acid is classified as “strong” when it undergoes complete ionization, in which case the concentration of HA is zero and the acid ionization constant is immeasurably large ($K_a \approx \infty$). Acids that are partially ionized are called “weak,” and their acid ionization constants may be experimentally measured. A table of ionization constants for weak acids is provided in Appendix 14.3.

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

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

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

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

Another measure of the strength of an acid is its percent ionization.

The **percent ionization** of a weak acid is defined in terms of the composition of an equilibrium mixture:

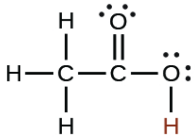
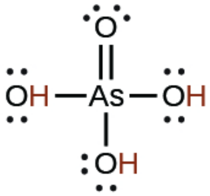
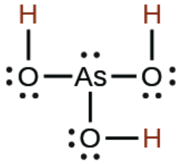
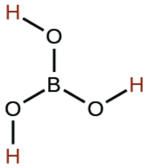
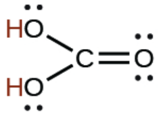
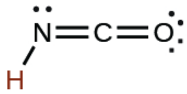
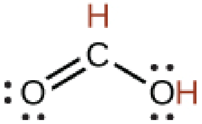
$$\%\ \text{ionization} = \frac{[H_3O^+]}{[HA]} \times 100$$

where the numerator is equivalent to the concentration of the acid's conjugate base (per stoichiometry, $[A^-] = [H_3O^+]$).

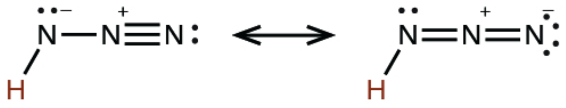
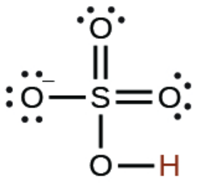
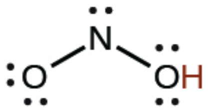
Unlike the K_a value, the percent ionization of a weak acid varies with the initial concentration of acid, typically decreasing as concentration increases. Equilibrium calculations of the sort described later in this chapter can be used to confirm this behavior.

Appendix 14.3

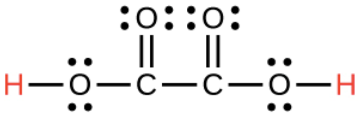
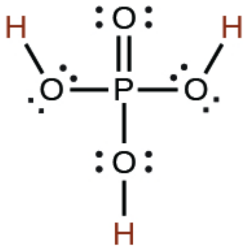
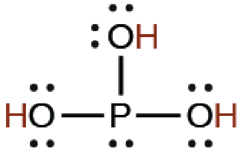
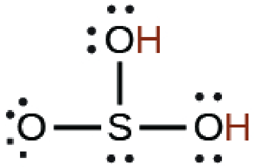
Ionization Constants of Weak Acids

Acid	Formula	K_a at 25 °C	Lewis Structure
acetic	CH_3CO_2H	1.8×10^{-5}	
arsenic	H_3AsO_4	5.5×10^{-3}	
	$H_2AsO_4^-$	1.7×10^{-7}	
	$HAsO_4^{2-}$	3.0×10^{-12}	
arsenous	H_3AsO_3	5.1×10^{-10}	
boric	H_3BO_3	5.4×10^{-10}	
carbonic	H_2CO_3	4.3×10^{-7}	
	HCO_3^-	4.7×10^{-11}	
cyanic	$HCNO$	2×10^{-4}	
formic	HCO_2H	1.8×10^{-4}	

Ionization Constants of Weak Acids

Acid	Formula	K_a at 25 °C	Lewis Structure
hydrazoic	HN_3	2.5×10^{-5}	
hydrocyanic	HCN	4.9×10^{-10}	
hydrofluoric	HF	6.4×10^{-4}	
hydrogen peroxide	H_2O_2	2.4×10^{-12}	
hydrogen selenide	H_2Se	1.29×10^{-4}	
	HSe^-	1×10^{-12}	
hydrogen sulfate ion		1.2×10^{-2}	
hydrogen sulfide	H_2S	8.9×10^{-8}	
	HS^-	1.0×10^{-19}	
hydrogen telluride	H_2Te	2.3×10^{-3}	
	HTe^-	1.6×10^{-11}	
hypobromous	HBrO	2.8×10^{-9}	
hypochlorous	HClO	2.9×10^{-8}	
nitrous	HNO_2	4.6×10^{-4}	

Ionization Constants of Weak Acids

Acid	Formula	K_a at 25 °C	Lewis Structure
oxalic	$H_2C_2O_4$	6.0×10^{-2}	
	$HC_2O_4^-$	6.1×10^{-5}	
phosphoric	H_3PO_4	7.5×10^{-3}	
	$H_2PO_4^-$	6.2×10^{-8}	
	HPO_4^{2-}	4.2×10^{-13}	
phosphorous	H_3PO_3	5×10^{-2}	
	$H_2PO_3^-$	2.0×10^{-7}	
sulfurous	H_2SO_3	1.6×10^{-2}	
	HSO_3^-	6.4×10^{-8}	

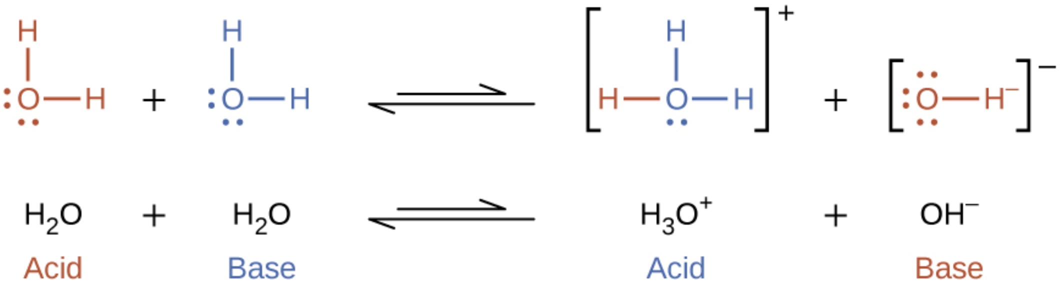
14.4 Autoionization of Water, pH, and pOH

Learning Objectives

- Use the ion-product constant for water to calculate [H_3O^+] and [HO^-]
- Explain the characterization of aqueous solutions as acidic, basic, or neutral
- Express hydronium and hydroxide ion concentrations on the pH and pOH scales

Autoionization of Water

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



The process in which like molecules react to yield ions is called **autoionization**. Liquid water undergoes autoionization to a very slight extent; at 25 °C, approximately two out of every billion water molecules are ionized.

The extent of the water autoionization process is reflected in the value of its equilibrium constant, the **ion-product constant for water, K_w**:

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

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.

pH and pOH Scales

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.
A solution is **acidic** if hydronium ion concentration is greater than hydroxide ions.
A solution is **basic** if hydronium ion concentration is less than hydroxide ions.

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

$$\text{pX} = -\log \text{X}$$

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

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

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

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

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

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

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

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

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

$$-\log K_w = -\log [H_3O^+] + -\log [OH^-]$$

$$pK_w = pH + pOH$$

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

$$14.00 = pH + pOH$$

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:

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

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

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 hydronium molarity of pure water at 80 °C is 4.9×10^{-7} *M*, which corresponds to pH and pOH values of:

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

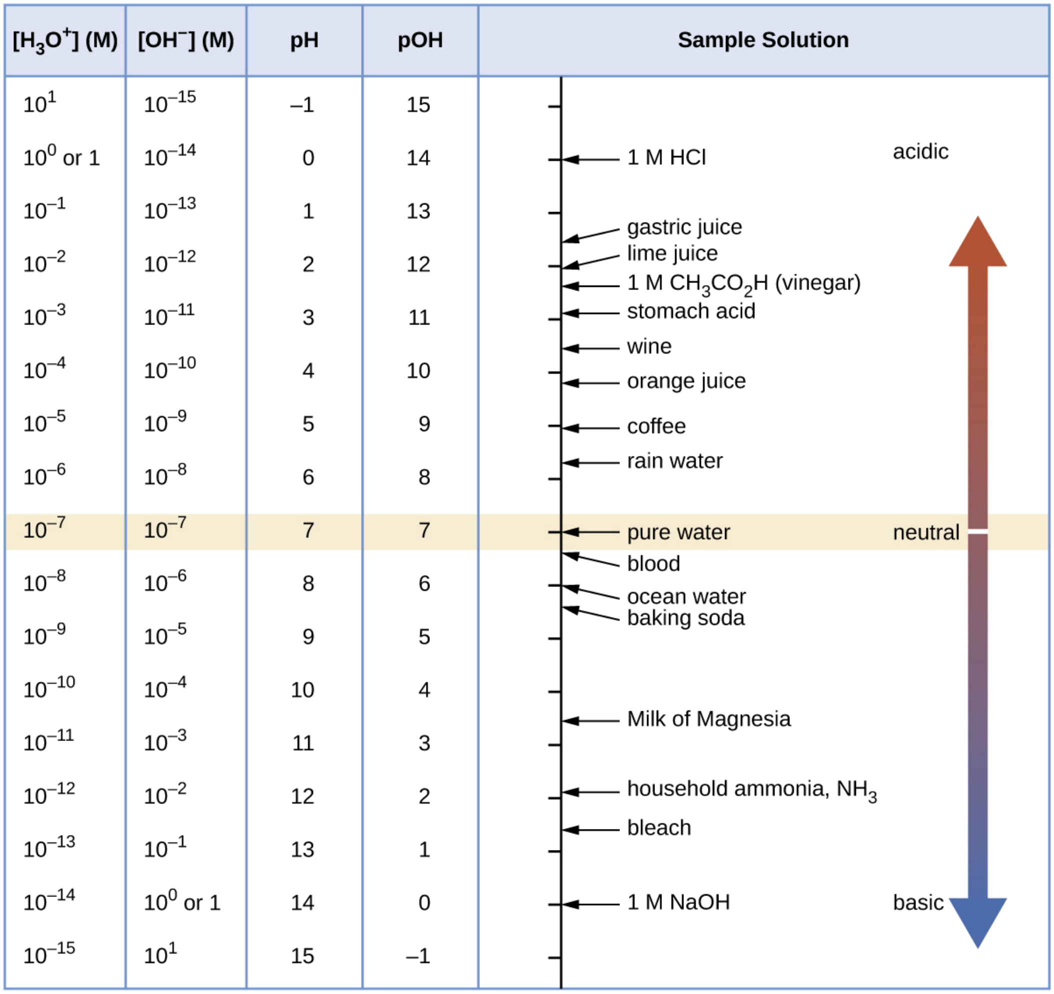
$$pOH = -\log [OH^-] = -\log (4.9 \times 10^{-7}) = 6.31$$

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

Table 14.1: Summary of Relations for Acidic, Basic and Neutral Solutions

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

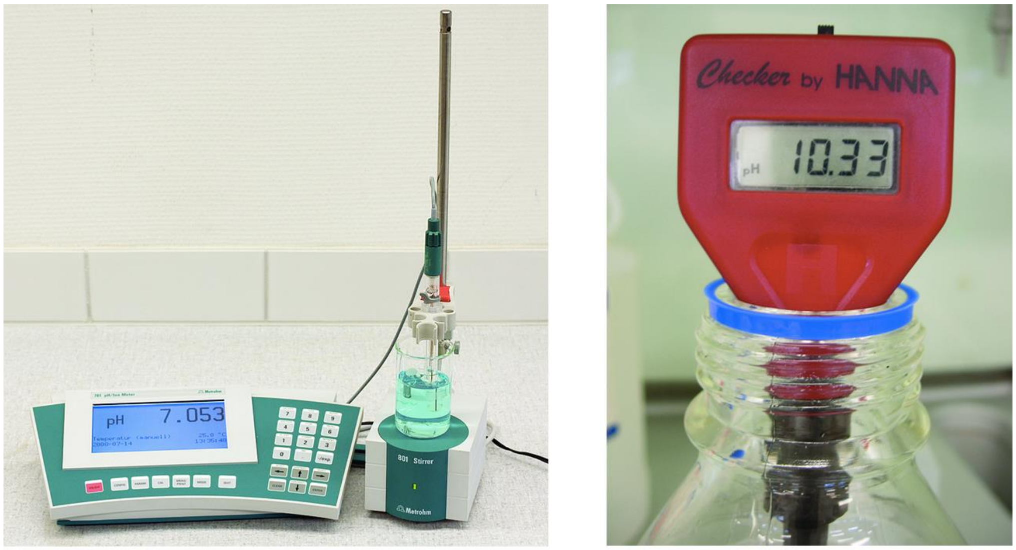
Below shows the relationships between $[H_3O^+]$, $[OH^-]$, pH, and pOH for different solutions.



$[H_3O^+]$ (M)	$[OH^-]$ (M)	pH	pOH
10^{1}	10^{-15}	–1	15
10^{0} or 1	10^{-14}	0	14
10^{-1}	10^{-13}	1	13
10^{-2}	10^{-12}	2	12
10^{-3}	10^{-11}	3	11
10^{-4}	10^{-10}	4	10
10^{-5}	10^{-9}	5	9
10^{-6}	10^{-8}	6	8
10^{-7}	10^{-7}	7	7
10^{-8}	10^{-6}	8	6
10^{-9}	10^{-5}	9	5
10^{-10}	10^{-4}	10	4
10^{-11}	10^{-3}	11	3
10^{-12}	10^{-2}	12	2
10^{-13}	10^{-1}	13	1
10^{-14}	10^{0} or 1	14	0
10^{-15}	10^{1}	15	–1

Figure 14.4 The pH and pOH scales represent concentrations of H_3O^+ and OH^-, respectively. The pH and pOH values of some common substances at 25 °C are shown in this chart.

The acidity of a solution is typically assessed experimentally by measurement of its pH. The pOH of a solution is not usually measured, as it is easily calculated from an experimentally determined pH value. The pH of a solution can be directly measured using a pH meter (Figure 14.5).

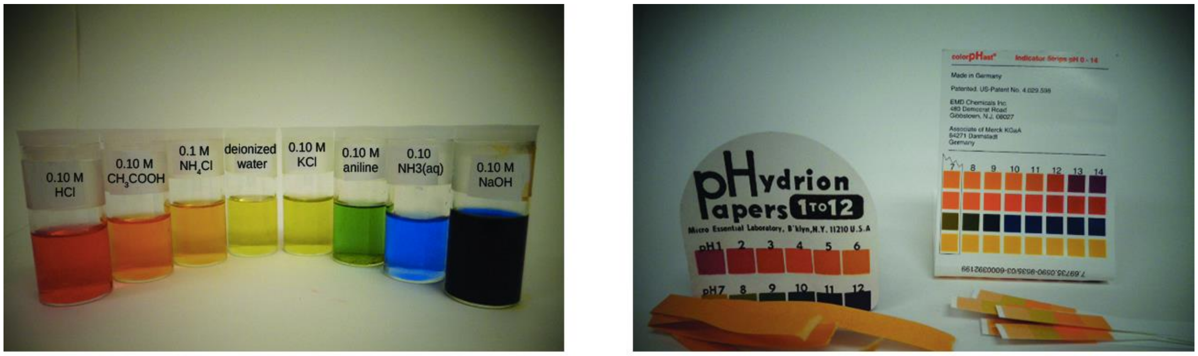


(a)

(b)

Figure 14.5 (a) A research-grade pH meter used in a laboratory can have a resolution of 0.001 pH units, an accuracy of ± 0.002 pH units, and may cost in excess of $1000. (b) A portable pH meter has lower resolution (0.01 pH units), lower accuracy (± 0.2 pH units), and a far lower price tag. (credit b: modification of work by Jacopo Werther)

The pH of a solution may also be visually estimated using colored indicators (Figure 14.6). The acid-base equilibria that enable use of these indicator dyes for pH measurements are described in a later section of this chapter.



(a)

(b)

Figure 14.6 (a) A solution containing a dye mixture, called universal indicator, takes on different colors depending upon its pH. (b) Convenient test strips, called pH paper, contain embedded indicator dyes that yield pH-dependent color changes on contact with aqueous solutions.(credit: modification of work by Sahar Atwa)

How Sciences Interconnect

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

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

Acid rain is rainwater that has a pH of less than 5, due to a variety of nonmetal oxides, including CO_2, SO_2, SO_3, NO, and NO_2being 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:

$$H_2O\,(l) + SO_3\,(g) \rightarrow H_2SO_4\,(aq)$$
$$H_2SO_4\,(aq) \rightarrow H^+\,(aq) + HSO_4^-\,(aq)$$

Carbon dioxide is naturally present in the atmosphere because most organisms produce it as a waste product of metabolism. Carbon dioxide is also formed when fires release carbon stored in vegetation or fossil fuels. Sulfur trioxide in the atmosphere is naturally produced by volcanic activity, but it also originates from burning fossil fuels, which have traces of sulfur, and from the process of “roasting” ores of metal sulfides in metal-refining processes. Oxides of nitrogen are formed in internal combustion engines where the high temperatures make it possible for the nitrogen and oxygen in air to chemically combine.

Acid rain is a particular problem in industrial areas where the products of combustion and smelting are released into the air without being stripped of sulfur and nitrogen oxides. In North America and Europe until the 1980s, it was responsible for the destruction of forests and freshwater lakes, when the acidity of the rain actually killed trees, damaged soil, and made lakes uninhabitable for all but the most acid-tolerant species. Acid rain also corrodes statuary and building facades that are made of marble and limestone (Figure 14.7). 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.

Figure 14.7 (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)

14.5 Base Ionization Constant

Learning Objectives

- Assess the relative strengths of bases according to their ionization constants
- Carry out simple equilibrium calculations for weak base solutions
- Carry out percent ionization calculations for weak base solutions

Base-Ionization Constant, K_b

The relative strengths of bases may be quantified by measuring their equilibrium constants in aqueous solutions. In solutions of the same concentration, stronger bases ionize to a greater extent, and so yield higher concentrations of hydroxide ions than do weaker bases. The equilibrium constant for a base is called the **base-ionization constant, K_b**.

For the reaction of a base B:

$$\text{B}\ (aq) + \text{H}_2\text{O}\ (l) \rightleftharpoons \text{BH}^+\ (aq) + \text{OH}^-\ (aq)$$

The base ionization constant is written:

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

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_b of a base (the larger the concentration of BH^+ and OH^- relative to the concentration of the nonionized base, B, in an equilibrium mixture), the stronger the base. A base is classified as “strong” when it undergoes complete ionization, in which case the concentration of B is zero and the base ionization constant is immeasurably large ($K_b \approx \infty$). Bases that are partially ionized are called “weak,” and their base ionization constants may be experimentally measured. A table of ionization constants for weak bases is provided in Appendix 14.5.

To illustrate this idea, three base ionization equations and K_b values are shown below. The ionization constants increase from first to last of the listed equations, indicating the relative acid strength increases in the order: $NO_2^- < CH_3CO_2^- < NH_3$.

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

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

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

Another measure of the strength of a base is its percent ionization.

The **percent ionization** of a weak base is defined in terms of the composition of an equilibrium mixture:

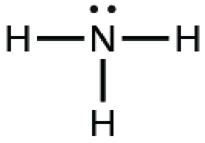
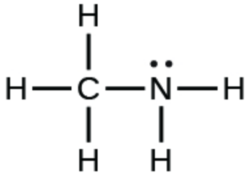
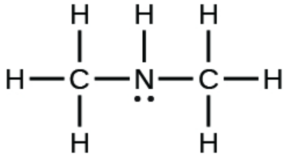
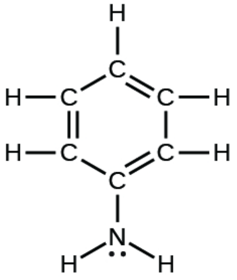
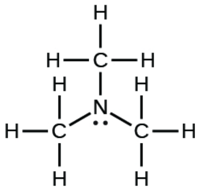
$$\%\ \text{ionization} = \frac{[OH^-]}{[B]} \text{ x } 100$$

where the numerator is equivalent to the concentration of the hydroxide ions, and the denominator is equivalent to the initial concentration of base.

Unlike the K_b value, the percent ionization of a weak base varies with the initial concentration of base, typically decreasing as concentration increases. Equilibrium calculations of the sort described later in this chapter can be used to confirm this behavior.

Appendix 14.5

Ionization Constants of Weak Bases

Acid	Formula	K_b at 25 °C	Lewis Structure
ammonia	NH_3	1.8×10^{-5}	
methylamine	CH_3NH_2	4.4×10^{-4}	
dimethylamine	$CH_3NH\ CH_3$	5.9×10^{-4}	
phenylamine (aniline)	$C_6H_5NH_2$	4.3×10^{-10}	
trimethylamine	$(CH_3)_3N$	6.3×10^{-5}	

14.6 pH and pOH Calculations for Strong Acids and Strong Bases

Learning Objectives

- Calculate pH, pOH, [H_3O^+] and [HO^-] for strong acids and strong bases

[H_3O^+] from Strong Acids and [OH^-] from Strong Bases

From previous sections, we learned that strong acids and strong bases dissociate completely in water. This means if there were hundred molecules of strong acid dissolving in water, it would yield hundred hydronium ions and hundred conjugate base. Likewise, when hundred molecules of strong base dissolving in water, it would yield hundred conjugate acid and hundred hydroxide ions. Thus, we can use the concentration of strong acid and strong base directly to calculate the pH of the solutions.

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:

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

(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

Calculation of Hydronium Ion Concentration from pH

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

Solution

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

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

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

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

(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*

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

$$\mathrm{pOH} = -\log [OH^-] = -\log 0.0125$$

$$= -(-1.903) = 1.903$$

The pH can be found from the pOH:

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

$$14.00 - \mathrm{pOH} = 14.00 - 1.903 = 12.10$$

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

14.7 pH and pOH Calculations for Weak Acids and Weak Bases

Learning Objectives

- Calculate pH, pOH, $[H_3O^+]$ and $[HO^-]$ for weak acids and weak bases

$[H_3O^+]$ from Weak Acids and $[OH^-]$ from Weak Bases

From previous sections, we learned that weak acids and weak bases dissociate partially in water. Only of those few hydronium ions and hydroxides ions that contributes to the acidity and basicity of solutions. To calculate pH and pOH of weak acids and weak bases, the concentration of hydronium ions and hydroxide ions at equilibrium must be determined.

Calculating the $[H_3O^+]$ and pH of Weak Acids

You can use the K_a and a R.I.C.E. table to calculate the pH of a weak acid solution.

Example: Calculate the pH of a 1.00 M acetic acid ($CH_3COO\mathbf{H}$) solution. The K_a for acetic acid is 1.77×10^{-5}.

Step 1: Write out the balanced reaction of the weak acid with water.

$$CH_3COO\mathbf{H}\ (aq) + H_2O\ (l) \rightleftarrows CH_3COO^-\ (aq) + H_3O^+\ (aq)$$

Step 2: Set up a RICE table and fill in the initial, change and equilibrium concentrations:

Reaction:	$CH_3COO\mathbf{H}$ (aq)	+	H_2O (l)	$\rightleftarrows$	CH_3COO^- (aq)	+	H_3O^+ (aq)
Initial:	1.00		doesn't matter		0		0
Change:	– 1x		doesn't matter		1x		1x
Equilibrium:	1.00 – 1x		doesn't matter		1x		1x

Initial: Before $CH_3COO\mathbf{H}$ reacts with water, it's at a concentration of 1.00 M with no ions formed in solution.

Change: After $CH_3COO\mathbf{H}$ reacts with water, it partially dissociates to form an ion concentration (represented by **x** multiplied by the stoichiometric coefficient). The 1**x** ion concentration is also the molar amount we subtract from our starting concentration since that's the amount of acetic acid that dissociated.

Equilibrium: At equilibrium, there is a 1**x** concentration ions and 1.00-1**x** concentration of $CH_3COO\mathbf{H}$. We will use these concentrations to solve for H_3O^+ concentration.

Step 3: Solve for **x** using K_a and the equilibrium concentrations from the RICE table
From the balanced equation:

$$CH_3COO\mathbf{H}\ (aq) + H_2O\ (l) \rightleftarrows CH_3COO^-\ (aq) + H_3O^+\ (aq)$$

We can write the K_a expression, which is:

$$K_a = \frac{[H_3O^+][CH_3COO^-]}{[CH_3COOH]}$$

We are given that $K_a = 1.77 \times 10^{-5}$ and we know the equilibrium concentrations from the R.I.C.E. table.

We can input these concentrations into the K_a expression and solve for **x** using algebra.

$$1.77 \times 10^{-5} = \frac{[x][x]}{[1.00 - x]}$$

Because the K_a is small, the amount of acetic acid that reacts with water is much smaller than the starting acetic acid concertation, and so we can neglect the (-x) in comparison to the initial concentration of the acid. Then we can solve for x:

$$1.77 \times 10^{-5} = \frac{[x^2]}{[1.00]} \xrightarrow{\text{Solve}} x = 4.21 \times 10^{-3}\ M$$

From the R.I.C.E. table, the $[H_3O^+] = x$. Therefore, $[H_3O^+] = 4.21 \times 10^{-3}$ M.

Using the pH equation ($pH = -\log[H_3O^+]$) we find the pH of the solution is **2.375**.

Calculating the $[OH^-]$ and pOH of Weak Bases

A weak base is analogous to a weak acid. You can use the K_b and a R.I.C.E. table to calculate the pOH and pH of a weak base solution.

Example: Calculate the $[OH]^-$ and pH of a 0.33 M methylamine (CH_3NH_2) solution. Methylamine has a K_b of 4.4×10^{-4}.

Step 1: Write out the balanced reaction of the weak base with water.

$$CH_3NH_2\,(aq) + H_2O\,(l) \rightleftarrows CH_3NH_3^+\,(aq) + OH^-\,(aq)$$

Step 2: Set up a RICE table and fill in the initial, change and equilibrium concentrations:

Reaction:	CH_3NH_2 (aq)	+	H_2O (l)	$\rightleftarrows$	$CH_3NH_3^+$ (aq)	+	OH^- (aq)
Initial:	0.33		doesn't matter		0		0
Change:	– 1x		doesn't matter		1x		1x
Equilibrium:	0.33 – 1x		doesn't matter		1x		1x

Initial: Before CH_3NH_2 reacts with water, it's at a concentration of 0.33 M with no ions formed in solution.

Change: After CH_3NH_2 reacts with water, it partially dissociates to form an ion concentration
(represented by **x** multiplied by the stoichiometric coefficient). The 1**x** ion concentration is also the molar amount we subtract from our starting concentration since that's the amount of acetic acid that dissociated.

Equilibrium: At equilibrium, there is a 1**x** concentration ions and 0.33 - 1**x** concentration of CH_3NH_2. We will use these concentrations to solve for OH^- concentration.

Step 3: Solve for **x** using K_b and the equilibrium concentrations from the RICE table
From the balanced equation:

$$CH_3NH_2\,(aq) + H_2O\,(l) \rightleftarrows CH_3NH_3^+\,(aq) + OH^-\,(aq)$$

We can write the K_b expression, which is:

$$K_b = \frac{[CH_3NH_3^+][OH^-]}{[CH_3NH_2]}$$

We are given that $K_b = 4.4 \times 10^{-4}$ and we know the equilibrium concentrations from the R.I.C.E. table.

We can input these concentrations into the K_b expression and solve for **x** using algebra.

$$4.4 \times 10^{-4} = \frac{[x][x]}{[0.33 - x]}$$

Because the K_b is small, the amount of methylamine that reacts with water is much smaller than the starting methylamine concertation, and so we can neglect the (-x) in comparison to the initial concentration of the base. Then we can solve for x:

$$4.4 \times 10^{-4} = \frac{[x]^2}{[0.33]} \xrightarrow{\text{Solve}} x = 0.012$$

From the R.I.C.E. table, the $[OH^-] = x$. Therefore, $[OH^-] = 0.012$ M.

Using the pOH equation ($pOH = -\log[OH^-]$) we find the pOH of the solution is 1.92.

The pH of the solution is 14.00 – pOH = 14.00 – 1.92 = **<u>12.08</u>**.

14.8 The Acid-Base Property of Salts

Learning Objectives

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

Relative Strengths of Conjugate Acid-Base Pairs

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

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

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

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

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

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

As discussed in another chapter on equilibrium, the equilibrium constant for a summed reaction is equal to the mathematical product of the equilibrium constants for the added reactions, and so

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

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

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

The inverse proportional relation between K_a and K_b means *the stronger the acid or base, the weaker its conjugate partner*. Figure 14.8 illustrates this relation for several conjugate acid-base pairs.

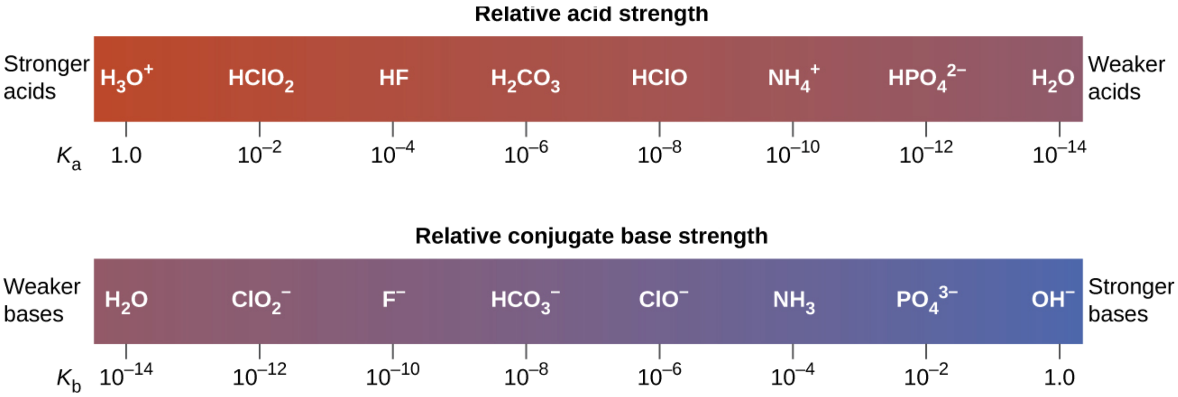
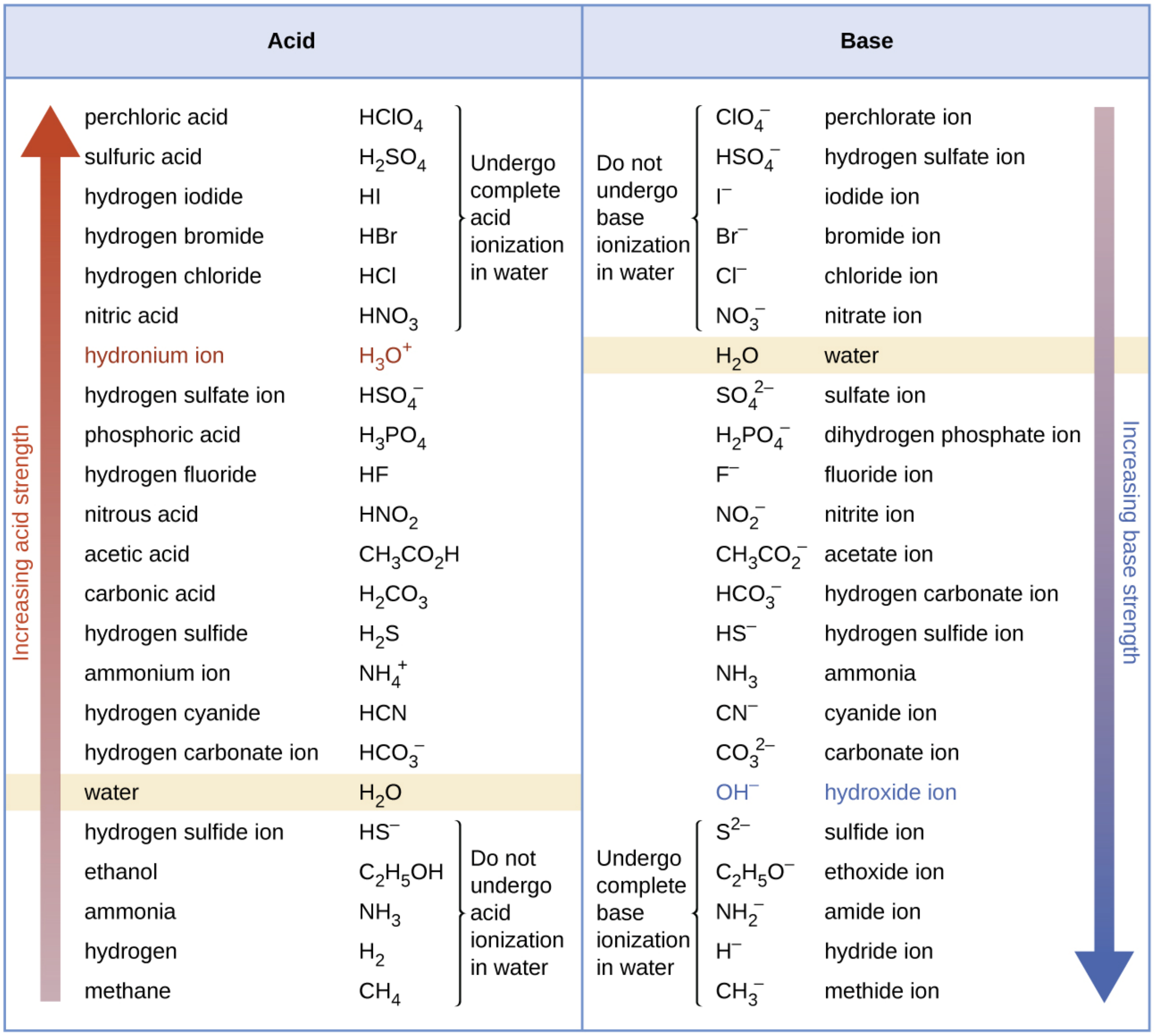


Figure 14.8 Relative strengths of several conjugate acid-base pairs are shown.



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

Figure 14.9 This figure shows strengths of conjugate acid-base pairs relative to the strength of water as the reference substance.

The listing of conjugate acid–base pairs shown in Figure 14.9 is arranged to show the relative strength of each species as compared with water, whose entries are highlighted in each of the table's columns. In the acid column, those species listed below water are weaker acids than water. These species do not undergo acid ionization in water; they are not Bronsted-Lowry acids. All the species listed above water are stronger acids, transferring protons to water to some extent when dissolved in an aqueous solution to generate hydronium ions. Species above water but below hydronium ion are *weak acids*, undergoing partial acid ionization, whereas those above hydronium ion are *strong acids* that are completely ionized in aqueous solution.

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

The right column of Figure 14.9 lists a number of substances in order of increasing base strength from top to bottom. Following the same logic as for the left column, species listed above water are weaker bases and so they don't undergo base ionization when dissolved in water. Species listed between water and its conjugate base, hydroxide ion, are weak bases that partially ionize. Species listed below hydroxide ion are strong bases that completely ionize in water to yield hydroxide ions (i.e., they are *leveled* to hydroxide).

A comparison of the acid and base columns in this table supports the reciprocal relation between the strengths of conjugate acid-base pairs. For example, the conjugate bases of the strong acids (top of table) are all of negligible strength. A strong acid exhibits an immeasurably large K_a, and so its conjugate base will exhibit a K_b that is essentially zero:

$$\text{strong acid: } K_a \approx \infty \qquad \text{conjugate base: } K_b = \frac{K_W}{K_a} = \frac{K_W}{\infty} \approx 0$$

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

Salts with Acidic Ions

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

$$NH_4Cl\ (s) \rightleftharpoons NH_4^+\ (aq) + Cl^-\ (aq)$$

The ammonium ion, NH_4^+ is the conjugate acid of the base ammonia, NH_3; its acid ionization (or acid hydrolysis) reaction is represented by

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

Since NH_3 is a weak base, K_b is measurable, so $K_a > 0$ (NH_4^+ ion is a weak acid).

The Cl^- ion is the conjugate base of HCl, and so its base ionization (or *base hydrolysis*) reaction is represented by

$$Cl^-\ (aq) + H_2O\ (aq) \rightleftharpoons HCl\ (aq) + OH^-\ (aq) \qquad K_b = \frac{K_W}{K_a}$$

Since HCl is a strong acid, K_a is immeasurably large and $K_b \approx 0$ (chloride ions don’t undergo appreciable hydrolysis).

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

Calculating the pH of an Acidic Salt Solution

Aniline is an amine that is used to manufacture dyes. It is isolated as anilinium chloride, $[C_6H_5NH_3^+]Cl$, a salt prepared by the reaction of the weak base aniline and hydrochloric acid. What is the pH of a 0.233 *M* solution of anilinium chloride? K_b of aniline is 4.3×10^{-10}.

$$C_6H_5NH_3^+\ (aq) + H_2O\ (l) \rightleftharpoons H_3O^+\ (aq) + C_6H_5NH_2\ (aq)$$

Solution

The K_a for anilinium ion ($C_6H_5NH_3^+$) is derived from the K_b for its conjugate base, aniline:

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

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

Reaction:	$C_6H_5NH_3^+$ *(aq)* +	H_2O *(l)* ⇌	H_3O^+ *(aq)* +	$C_6H_5NH_2$ *(aq)*
Initial:	0.233	doesn't matter	0	0
Change:	– 1x	doesn't matter	1x	1x
Equilibrium:	0.233 – 1x	doesn't matter	1x	1x

Substituting these equilibrium concentration terms into the K_a expression gives

$$K_a = \frac{[C_6H_5NH_2][H_3O^+]}{[C_6H_5NH_3^+]}$$

$$2.3 \times 10^{-5} = \frac{[x][x]}{[0.233 - x]}$$

$$2.3 \times 10^{-5} = \frac{[x]^2}{[0.233]} \longrightarrow x = 0.0023$$

From the R.I.C.E. table, the $[H_3O^+] = x$. Therefore, $[H_3O^+] = 0.0023$ M.

The pH of the solution is $-\log [H_3O^+] = -\log [0.0023] =$ **<u>2.64</u>**

Check Your Learning

What is the hydronium ion concentration in a 0.100-*M* solution of ammonium nitrate, NH_4NO_3, a salt composed of the ions NH_4^+ and NO_3^-. K_b for NH_3 is 1.8×10^{-5}.
Which is the stronger acid $C_6H_5NH_3^+$ or NH_4^+?

Answer: $[H_3O^+] = 7.5 \times 10^{-6}$ *M ;* $C_6H_5NH_3^+$ is the stronger acid because from the previous example $C_6H_5NH_3^+$ produces more $[H_3O^+]$ (0.0023M).

Salts with Basic Ions

As another example, consider dissolving sodium acetate in water:

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

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

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

$$CH_3CO_2^-\ (aq)\ +\ H_2O\ (l)\ \rightleftharpoons\ CH_3CO_2H\ (aq)\ +\ OH^-\ (aq) \qquad K_b = \frac{K_W}{K_a}$$

Because CH_3CO_2H is a weak acid, its K_a is measurable, so $K_b > 0$ ($CH_3CO_2^-$ is a weak base).

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

Calculating the pH of an Basic Salt Solution

Determine the pH of a 2.50 M solution of sodium acetate ($NaCH_3CO_2$). K_a of acetic acid (CH_3CO_2H) is 1.8×10^{-5}.

Solution

The K_b for acetate ion ($CH_3CO_2^-$) is derived from the K_a for its conjugate acid, acetic acid:

$$K_b = \frac{K_W}{K_a} = \frac{1.0 \times 10^{-14}}{1.8 \times 10^{-5}} = 5.6 \times 10^{-10}$$

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

Reaction:	$CH_3CO_2^-$ (aq) +	H_2O (l) $\rightleftharpoons$	OH^- (aq) +	CH_3CO_2H (aq)
Initial:	2.50	doesn't matter	0	0
Change:	– 1x	doesn't matter	1x	1x
Equilibrium:	2.50 – 1x	doesn't matter	1x	1x

Substituting these equilibrium concentration terms into the K_b expression gives

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

$$5.6 \times 10^{-10} = \frac{[x][x]}{[2.50 - x]}$$

$$5.6 \times 10^{-10} = \frac{[x]^2}{[2.50]} \xrightarrow{\qquad} x = 3.7 \times 10^{-5}$$

From the R.I.C.E. table, the [OH$^-$] = x. Therefore, [OH$^-$] = 3.7×10^{-5} M.

The pOH of the solution is −log [OH$^-$] = −log [3.7×10^{-5}] = 4.43

The pH of the solution is 14.00 – pOH = 14.00 – 4.43 = **9.57**

Check Your Learning

What is the pH of a 0.083-*M* solution of NaCN? Ka for HCN is 6.2×10^{-10}.

Answer: 11.06

Salts with Acidic and Basic Ions

Some salts are composed of both acidic and basic ions, and so the pH of their solutions will depend on the relative strengths of these two species. For this type of salts, a comparison of the K_a and K_b values allows prediction of the solution's acid-base status, as illustrated in the following example exercise.

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_4Br (d) NH_4F

Solution

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

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

(b) The Na^+ cation is inert and will not affect the pH of the solution. The HCO_3^- anion is a conjugate base of a weak acid H_2CO_3. The HCO_3^- anion will react with water to form OH^- in the solution. Thus, this solution is basic.

(c) The NH_4^+ cation is a conjugate acid of a weak base NH_3. The NH_4^+ cation will react with water to form H_3O^+ in the solution. The Br^- ion is the conjugate base of a strong acid, and so it is of negligible base strength (no appreciable base ionization). Thus, based on NH_4^+ property, this solution is acidic.

(d) The NH_4^+ ion is acidic (see above discussion) and the F^- ion is basic (conjugate base of the weak acid HF). Comparing the two ionization constants: K_a of NH_4^+ is 5.6×10^{-10} and the K_b of F^- is 1.6×10^{-11}, so the solution is acidic, since $K_a > K_b$.

Check Your Learning

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

(a) K_2CO_3 (b) $CaCl_2$ (c) CH_3NH_3Br (d) $(NH_4)_2CO_3$

ANSWER: (a) basic; (b) neutral; (c) acidic; (d) basic

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15.1 Neutralization reactions

Create how to write equations for acid-base reactions.

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Chapter 15 Neutralization Reaction, Buffers, and Titrations

Chapter Introduction

[15.1 Neutralization Reaction](#)
[15.2 Buffers](#)
[15.3 Titrations and pH Curves](#)

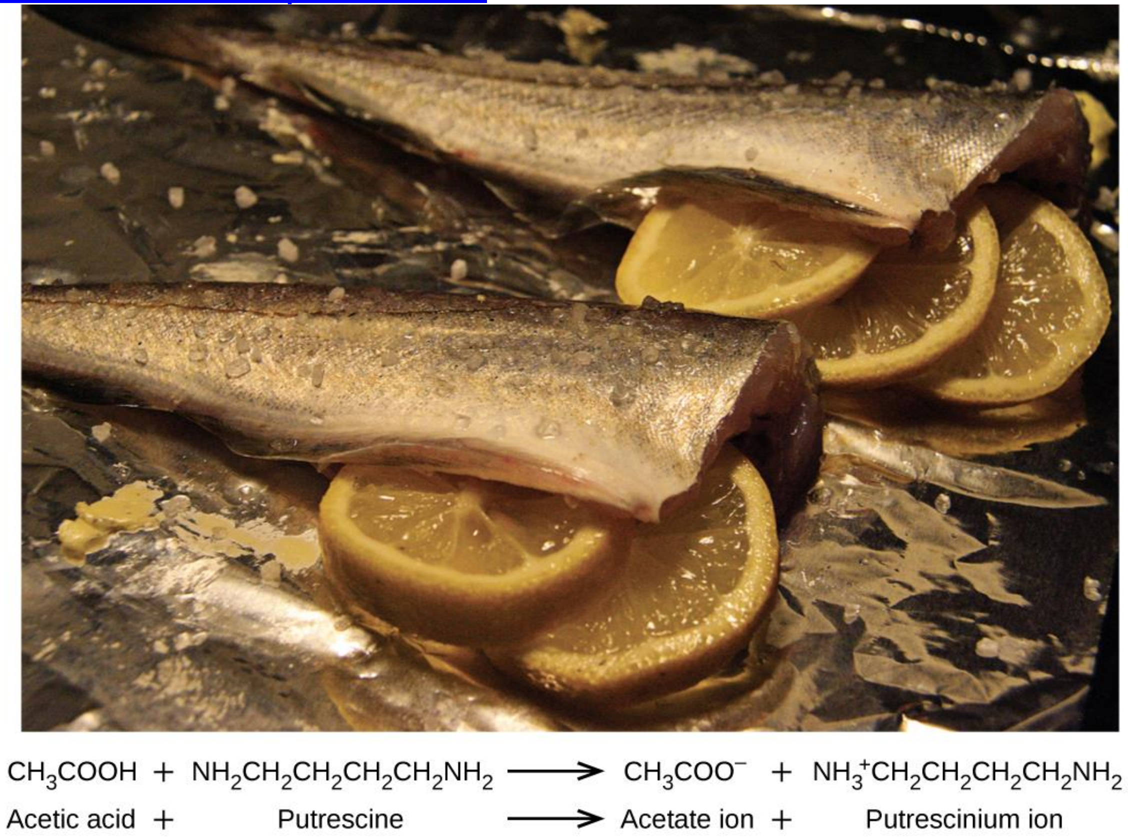


Figure 15.1 A neutralization reaction takes place between citric acid in lemons or acetic acid in vinegar, and the bases in the flesh of fish.

Examples of acid-base chemistry are abundant in the culinary world. One example is the use of baking soda, or sodium bicarbonate in baking. $NaHCO_3$ is a base. When it reacts with an acid such as lemon juice, buttermilk, or sour cream in a batter, bubbles of carbon dioxide gas are formed from decomposition of the resulting carbonic acid, and the batter “rises.” Baking powder is a combination of sodium bicarbonate, and one or more acid salts that react when the two chemicals come in contact with water in the batter.

Many people like to put lemon juice or vinegar, both of which are acids, on cooked fish (Figure 15.1). It turns out that fish have volatile amines (bases) in their systems, which are neutralized by the acids to yield nonvolatile ammonium salts. This reduces the odor of the fish, and also adds a “sour” taste that we seem to enjoy.

Pickling is a method used to preserve vegetables using a naturally produced acidic environment. The vegetable, such as a cucumber, is placed in a sealed jar submerged in a brine solution. The brine solution favors the growth of beneficial bacteria and suppresses the growth of harmful bacteria. The beneficial bacteria feed on starches in the cucumber and produce lactic acid as a waste product in a process called fermentation. The lactic acid eventually increases the acidity of the brine to a level that kills any harmful bacteria, which require a basic environment. Without the harmful bacteria consuming the cucumbers they are able to last much longer than if they were unprotected. A byproduct of the pickling process changes the flavor of the vegetables with the acid making them taste sour.

In this chapter, you will explore the acid-base neutralization reaction, buffers that can resist a large pH change, and titration that is an analytical technique.

15.1 Neutralization Reactions

Learning Objectives

- Write and balance chemical equations in molecular, total ionic, and net ionic formats for neutralization reaction
- Perform stoichiometric calculations involving solution molarity

Introduction

A **neutralization reaction** is a specific type of acid-base reaction in which the reactants are an acid and a base (but not water), and the products are often a **salt** and water

acid + base → salt + 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):

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

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

Writing Equations for Acid-Base Reactions

Strong Acid vs. Strong Base

Acids and bases dissociates in water in certain extent. When dissociated ions are involved in these reactions, the chemical equations may be written with various levels of detail appropriate to their intended use. For example, when aqueous solutions of strong acid HCl and strong base NaOH are mixed, a reaction takes place producing aqueous NaCl and liquid H_2O:

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

This balanced equation, representing the molecules involved, is called a **molecular equation** because it doesn’t explicitly represent the dissociated ions that are present in solution.

When strong acids, strong bases, and soluble ionic compounds (salts) dissolve in water, they *dissociate completely* into their constituent ions, which are subsequently dispersed homogenously throughout the resulting solution. The strong acid, strong base, and ionic compound dissolved in water are, therefore, more realistically represented as dissociated ions, in this case:

$$\mathrm{HCl\ (aq)} \rightarrow \mathrm{H^+\ (aq)} + \mathrm{Cl^-\ (aq)} \qquad \text{(strong acid)}$$

$$\mathrm{NaOH\ (aq)} \rightarrow \mathrm{Na^+\ (aq)} + \mathrm{OH^-\ (aq)} \qquad \text{(strong base)}$$

$$\mathrm{NaCl\ (aq)} \rightarrow \mathrm{Na^+\ (aq)} + \mathrm{Cl^-\ (aq)} \qquad \text{(soluble ionic compound, salt)}$$

Unlike the above, H_2O remains as a molecule, as signified by its physical state notation, *l*.

Explicitly representing all dissolved ions results in a **complete ionic equation**. In this particular case, the formulas for the dissolved ionic compounds are replaced by formulas for their dissociated ions:

$$\mathrm{H^+\ (aq)} + \mathrm{Cl^-\ (aq)} + \mathrm{Na^+\ (aq)} + \mathrm{OH^-\ (aq)} \rightarrow \mathrm{Na^+\ (aq)} + \mathrm{Cl^-\ (aq)} + \mathrm{H_2O\ (l)}$$

Examining this equation shows that two chemical species are present in identical form on both sides of the arrow, Na^+(*aq*) and Cl^-(aq). These **spectator ions**—ions whose presence is required to maintain charge neutrality—are neither chemically nor physically changed by the process, and so they may be eliminated from the equation to yield a more succinct representation called a **net ionic equation**:

$$\mathrm{H^+\ (aq)} + \mathrm{Cl^-\ (aq)} + \mathrm{Na^+\ (aq)} + \mathrm{OH^-\ (aq)} \rightarrow \mathrm{Na^+\ (aq)} + \mathrm{Cl^-\ (aq)} + \mathrm{H_2O\ (l)}$$

$$\mathrm{H^+\ (aq)} + \mathrm{OH^-\ (aq)} \rightarrow \mathrm{H_2O\ (l)}$$

This net ionic equation indicates that water is produced from acid (H^+) and base (OH^-), regardless of the source of these ions.

Strong Acid vs. Weak Base

For a reaction involving strong acids and weak bases, e.g. HCl and NH_4OH are mixed, **the molecular equation** can be written as:

$$HCl\ (aq)\ +\ NH_4OH\ (aq)\ \rightarrow\ NH_4Cl\ (aq)\ +\ H_2O\ (l)$$

While strong acids and soluble ionic compounds (salts) *dissociate completely* into their constituent ions in water, weak bases *only partially dissociate.* Thus, majority of weak base remain as molecules and do not represent as ions.

$HCl\ (aq)$ □ $H^+\ (aq)\ +\ Cl^-\ (aq)$ (strong acid)

$NH_4OH\ (aq)\ \rightleftharpoons\ NH_4OH\ (aq)$ (weak base)

$NH_4Cl\ (aq)$ □ $NH_4^+\ (aq)\ +\ Cl^-\ (aq)$ (soluble ionic compound, salt)

Explicitly representing all dissolved ions and molecules results in a **complete ionic equation** as follow:

$$H^+\ (aq)\ +\ Cl^-\ (aq)\ +\ NH_4OH\ (aq)\ \square\ NH_4^+\ (aq)\ +\ Cl^-\ (aq) + H_2O\ (l)$$

Examining this equation shows that the **spectator** ion for this reaction is the Cl^- (aq) ions. Thus, the net ionic equation can be written as:

$$H^+\ (aq)\ +\ NH_4OH\ (aq)\ \square\ NH_4^+\ (aq)\ +\ H_2O\ (l)$$

Weak Acid vs. Strong Base

For a reaction involving weak acids and strong bases, e.g. HF and NaOH are mixed, **the molecular equation** can be written as:

$$\mathrm{HF(aq)} + \mathrm{NaOH\,(aq)} \rightarrow \mathrm{NaF\,(aq)} + \mathrm{H_2O\,(l)}$$

While strong bases and soluble ionic compounds (salts) *dissociate completely* into their constituent ions in water, weak acids *only partially dissociate.* Thus, majority of weak acid remain as molecules and do not represent as ions.

$\mathrm{HF\,(aq)} \rightleftharpoons \mathrm{HF\,(aq)}$ (weak acid)

$\mathrm{NaOH\,(aq)}$ □ $\mathrm{Na^+\,(aq)} + \mathrm{OH^-\,(aq)}$ (strong base)

$\mathrm{NaF\,(aq)}$ □ $\mathrm{Na^+\,(aq)} + \mathrm{F^-\,(aq)}$ (soluble ionic compound, salt)

Explicitly representing all dissolved ions and molecules results in a **complete ionic equation** as follow:

$$\mathrm{HF\,(aq)} + \mathrm{Na^+\,(aq)} + \mathrm{OH^-\,(aq)}\ \square\ \mathrm{Na^+\,(aq)} + \mathrm{F^-\,(aq)} + \mathrm{H_2O\,(l)}$$

Examining this equation shows that the **spectator** ion for this reaction is the $\mathrm{Na^+\,(aq)}$ ions. Thus, the net ionic equation can be written as:

$$\mathrm{HF\,(aq)} + \mathrm{OH^-\,(aq)}\ \square\ \mathrm{F^-\,(aq)} + \mathrm{H_2O\,(l)}$$

EXAMPLE 15.1

Write balanced molecular, complete ionic, and net ionic 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.

Molecular equation: $HOCl\,(aq) + H_2O\,(l) \rightleftharpoons OCl^-\,(aq) + H_3O^+\,(aq)$

Complete ionic equation: $HOCl\,(aq) + H_2O\,(l) \rightleftharpoons OCl^-\,(aq) + H_3O^+\,(aq)$

Net ionic equation: $HOCl\,(aq) + H_2O\,(l) \rightleftharpoons OCl^-\,(aq) + H_3O^+\,(aq)$

** $\rightleftharpoons$ is used to indicate partially dissociation in water.

(b) The two reactants are provided, $Ba(OH)_2$ and HNO_3.

M.E.: $Ba(OH)_2\,(aq) + 2HNO_3\,(aq) \rightarrow Ba(NO_3)_2\,(aq) + 2H_2O\,(l)$

C.I.E: $Ba^{2+}(aq) + 2OH^-(aq) + 2H^+(aq) + 2NO_3^-(aq) \rightarrow Ba^{2+}(aq) + 2NO_3^-(aq) + 2H_2O(l)$

$2OH^-(aq) + 2H^+(aq) \rightarrow 2H_2O(l)$ (Ba^{2+} and NO_3^- are spectator ions)

N.I.E: $OH^-(aq) + H^+(aq) \rightarrow H_2O(l)$ (must reduce to the smallest coefficient)

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: $H_3O^+\,(aq) + OH^-\,(aq) \rightarrow 2H_2O\,(l)$

Acid-Base Stoichiometry

In the previous term, you learned about stoichiometry and various units of concentrations. In this module, the use of balanced acid-base chemical equations and molarity is explored.

Numerous variations on the beginning and ending computational steps are possible depending upon what particular quantities are provided and sought (volumes, solution concentrations, and so forth). Regardless of the details, all these calculations share a common essential component: the use of stoichiometric factors derived from balanced chemical equations. Figure 15.2 provides a general outline of the various computational steps associated with many reaction stoichiometry calculations.

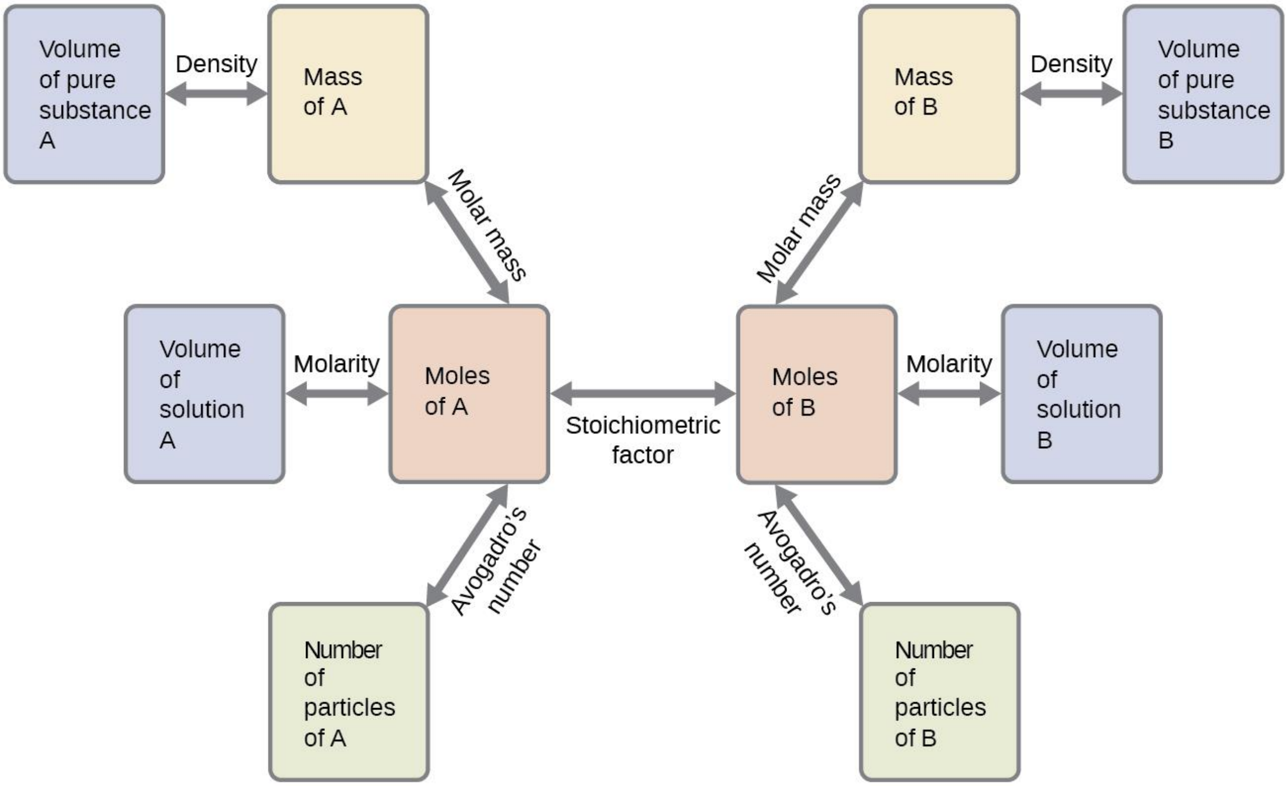


Figure 15.2 The flowchart depicts the various computational steps involved in most reaction stoichiometry calculations.

When studying reactions that occur in solution, the amounts of reactants and products are often expressed as concentrations instead of mass or moles. The units of molarity are then used as conversion factors that allow for the conversion between mol of solute and liter of solution.

EXAMPLE 15.1

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

Solution:

1. Write a balanced acid-base reaction:

$$Ca(OH)_2\ (aq)\ +\ 2HBr\ (aq)\ \rightarrow\ CaBr_2\ (aq)\ +\ 2H_2O\ (l)$$

2. Use the number with two units as conversion factors

$$\left(0.0105\text{-}M\ \text{HBr} = \frac{0.0105\ mol\ HBr}{1\ L\ HBr\ solution}\ \text{ and }\ 0.0100\text{-}M\ Ca(OH)_2 = \frac{0.0100\ mol\ Ca(OH)_2}{1\ L\ Ca(OH)_2\ solution}\right)$$

3. Start with number with one units (125 mL of $Ca(OH)_2$) and use stoichiometric ratio to solve problem:

$$125\ \text{mL}\ Ca(OH)_2 \times \frac{1\ L}{1000\ mL} \times \frac{0.0100\ mol\ Ca(OH)_2}{1\ L\ Ca(OH)_2} \times \frac{2\ mol\ HBr}{1\ mol\ Ca(OH)_2} \times \frac{1\ L\ HBr}{0.0105\ mol\ HBr}$$

= 0.238 L or 238 mL HBr solution

EXAMPLE 15.2

How many grams of $CaBr_2$ is produced when a 250.0 mL of 0.25 M HBr reacted with $Ca(OH)_2$ solution?

Solution:

1. Write a balanced acid-base reaction:

$$Ca(OH)_2\ (aq)\ +\ 2HBr\ (aq)\ \ \square\ \ CaBr_2\ (aq)\ +\ 2H_2O\ (l)$$

2. Use the number with two units as conversion factors

$$(0.25\ M\ \mathrm{HBr}\ =\ \frac{0.25\ mol\ HBr}{1\ L\ HBr\ solution}\ )$$

3. Start with number with one units (250.0 mL of HBr) and use stoichiometric ratio to solve problem:

$$250.0\ \mathrm{mL\ HBr} \times \frac{1\ L}{1000\ mL} \times \frac{0.25\ mol\ HBr}{1\ L\ HBr} \times \frac{1\ mol\ CaBr_2}{2\ mol\ HBr} \times \frac{199.88\ g\ CaBr_2}{1\ mol\ CaBr_2}$$

$$=\ 6.2\ \mathrm{g}\ CaBr_2$$

EXAMPLE 15.3

A 20.0-mL sample of acid rain required 1.7 mL of 0.0811 *M* NaOH to completely react. If we assume that the acidity of the rain is due to the presence of sulfuric acid, what was the molarity of sulfuric acid in this sample of rain?

Solution:

1. Write a balanced acid-base reaction:

$$H_2SO_4\ (aq)\ +\ 2NaOH\ (aq)\ \rightarrow\ Na_2SO_4\ (aq)\ +\ 2H_2O\ (l)$$

2. Use the number with two units as conversion factors

$$\left(0.0811\ M\ \text{NaOH}\ =\ \frac{0.0811\ mol\ NaOH}{1\ L\ NaOH\ solution}\right)$$

3. Start 1.7 mL of NaOH because we know its molarity and use stoichiometric ratio to solve problem:

$$1.7\ \text{mL NaOH} \times \frac{1\ L}{1000\ mL} \times \frac{0.0811\ mol\ NaOH}{1\ L\ NaOH} \times \frac{1\ mol\ H_2SO_4}{2\ mol\ NaOH}$$

$$=\ 0.0000689\ \text{mol}\ H_2SO_4$$

4. Find molarity of H_2SO_4 in 20.0 mL sample of acid

$$\text{Molarity}\ =\ \frac{mol\ H_2SO_4}{L\ \ solution}$$

$$\text{Molarity}\ =\ \frac{0.0000689\ \ mol\ H_2SO_4}{0.0200\ L\ \ solution}\ =\ 0.0034\ \text{mol/L}\ \ \text{or}\ \ 0.0034\ \text{M}$$

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, $CaCO_3$.

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

The reaction above, 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.

15.2 Buffers

Learning Objectives

- 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

Introduction

A solution containing appreciable amounts of a weak conjugate acid-base pair is called a buffer solution, or a **buffer**. Buffer solutions resist a change in pH when small amounts of a strong acid or a strong base are added (Figure 15.3).

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

How Buffers Work

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

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

Likewise, adding strong acid to this buffer solution will neutralize acetate ion, shifting the above ionization equilibrium right and returning $[H_3O^+]$ to near its original value.

Figure 15.4 provides a graphical illustration of the changes in conjugate-partner concentration that occur in this buffer solution when strong acid and base are added. The buffering action of the solution is essentially a result of the added strong acid and base being converted to the weak acid and base that make up the buffer's conjugate pair. The weaker acid and base undergo only slight ionization, as compared with the complete ionization of the strong acid and base, and the solution pH, therefore, changes much less drastically than it would in an unbuffered solution.

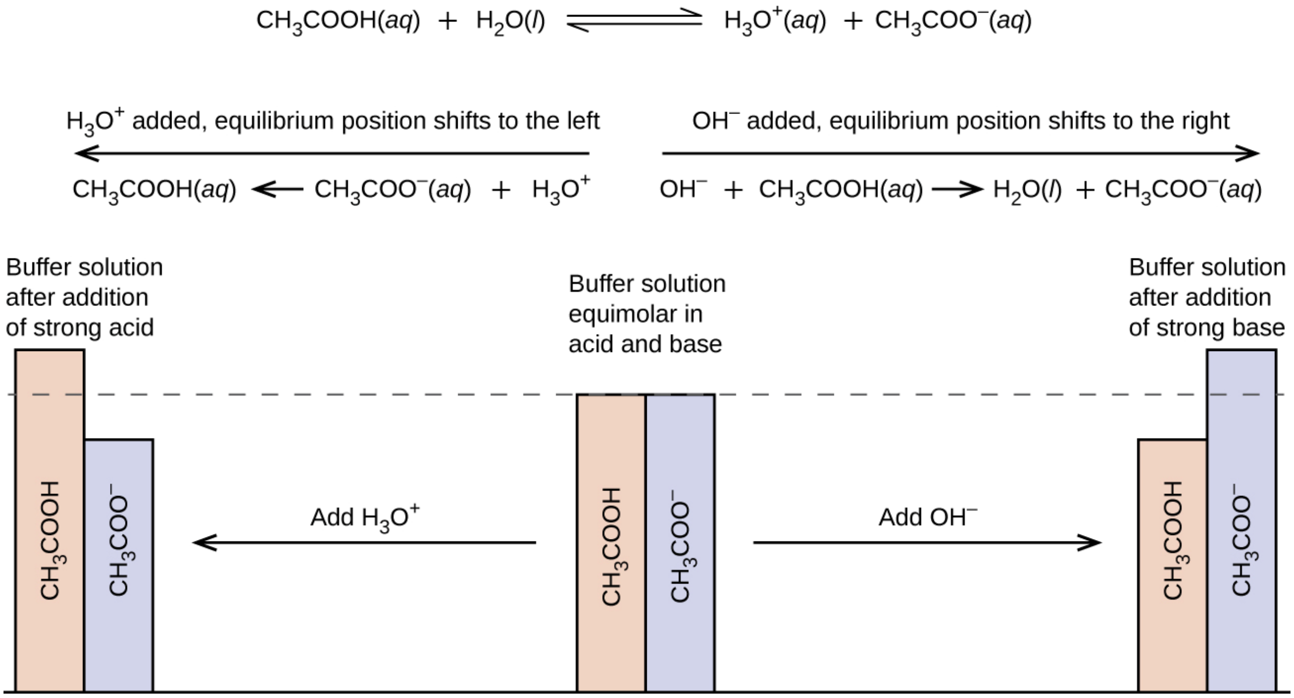


Figure 15.4 Buffering action in a mixture of acetic acid and acetate salt.

Buffer Capacity

Buffer solutions do not have an unlimited capacity to keep the pH relatively constant (Figure 15.5). Instead, the ability of a buffer solution to resist changes in pH relies on the presence of appreciable amounts of its conjugate weak acid-base pair. When enough strong acid or base is added to substantially lower the concentration of either member of the buffer pair, the buffering action within the solution is compromised.

Figure 15.5 The indicator color (methyl orange) shows that a small amount of acid added to a buffered solution of pH 8 (beaker on the left) has little affect on the buffered system (middle beaker). However, a large amount of acid exhausts the buffering capacity of the solution and the pH changes dramatically (beaker on the right). (credit: modification of work by Mark Ott)

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

Selection of Suitable Buffer Mixtures

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

1. A good buffer mixture should have about equal concentrations of both of its components. A buffer solution has generally lost its usefulness when one component of the buffer pair is less than about 10% of the other. Figure 15.6 shows how pH changes for an acetic acid-acetate ion buffer as base is added. The initial pH is 4.74. A change of 1 pH unit occurs when the acetic acid concentration is reduced to 11% of the acetate ion concentration.

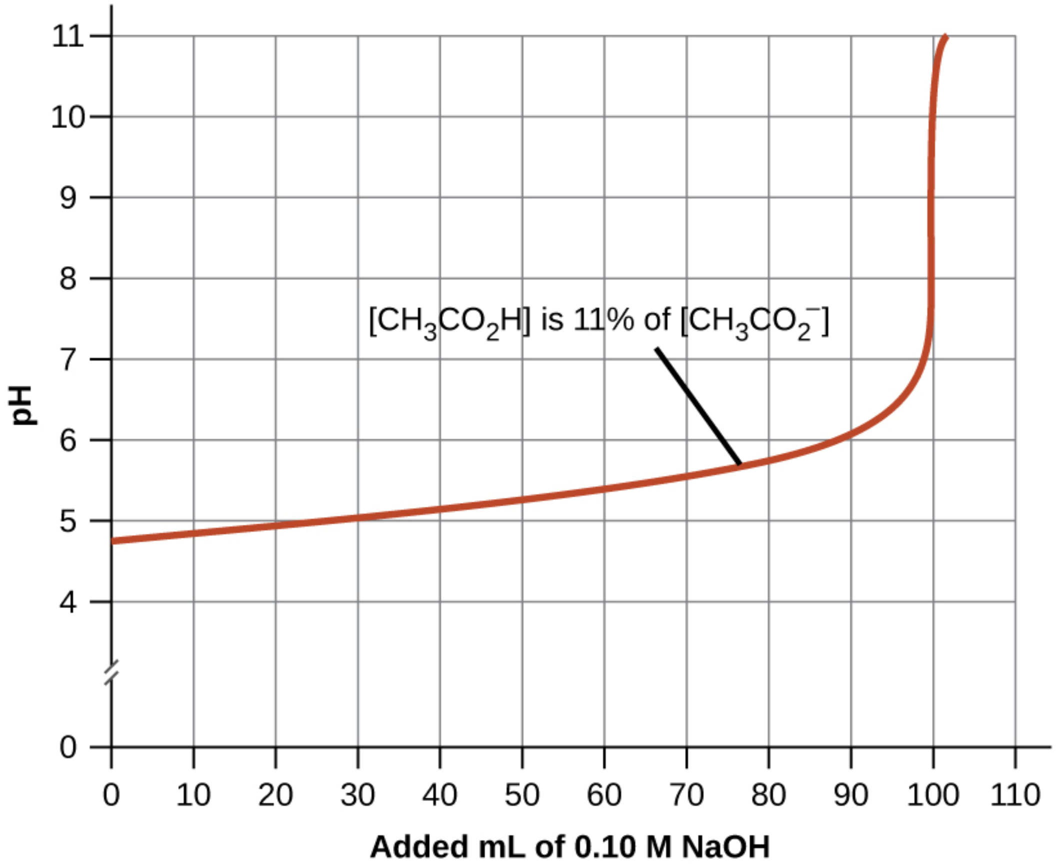


Figure 15.6 Change in pH as an increasing amount of a 0.10-*M* NaOH solution is added to 100 mL of a buffer solution in which, initially, $[CH_3CO_2H]$ = 0.10 *M* and [CH3CO2−]=0.10M. Note the greatly diminished buffering action occurring after the buffer capacity has been reached, resulting in drastic rises in pH on adding more strong base.

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

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

$$H_3O^+ (aq) + HCO_3^- (aq) \rightarrow H_2CO_3 (aq) + H_2O (l)$$

An added hydroxide ion is removed by the reaction:

$$OH^- (aq) + H_2CO_3 (aq) \rightarrow HCO_3^- (aq) + H_2O (l)$$

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:

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

Rearranging to solve for $[H_3O^+]$ yields:

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

Taking the negative logarithm of both sides of this equation gives

$$-\log [H_3O^+] = -\log \left(\frac{Ka \cdot [HA]}{[A^-]}\right)$$

$$-\log [H_3O^+] = -\log Ka + -\log\left(\frac{[HA]}{[A^-]}\right)$$

$$-\log [H_3O^+] = -\log Ka + \log\left(\frac{[A^-]}{[HA]}\right)$$

which can be written as

$$\boxed{pH = pKa + \log\left(\frac{[A^-]}{[HA]}\right)}$$

where pK_a is the negative of the 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 conjugate acid-base pair in a buffered solution. Scientists often use this expression, called the **Henderson-Hasselbalch equation**, to calculate the pH of buffer solutions. It is important to note that the “*x* is small” assumption must be valid to use this equation.

HOW SCIENCES INTERCONNECT

Medicine: The Buffer System in Blood

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

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

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 (pK_a = 6.4), we can calculate the pH of blood:

$$\begin{aligned} \text{pH} &= \text{pKa} + \log\left(\frac{[A^-]}{[HA]}\right) \\ &= 6.4 + \log\left(\frac{0.024}{0.0012}\right) = 7.7 \end{aligned}$$

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.

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.

15.3 Titrations

Learning Objectives

- Describe the fundamental aspects of titrations analysis.
- Perform stoichiometric calculations using typical titration data.
- Interpret titration curves for strong and weak acid-base systems
- Compute sample pH at important stages of a titration
- Explain the function of acid-base indicators

Introduction

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:

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

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 15.7) 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. Though any type of chemical reaction may serve as the basis for a titration analysis, the three described in this chapter (precipitation, acid-base, and redox) are most common. Additional details regarding titration analysis are provided in the chapter on acid-base equilibria.

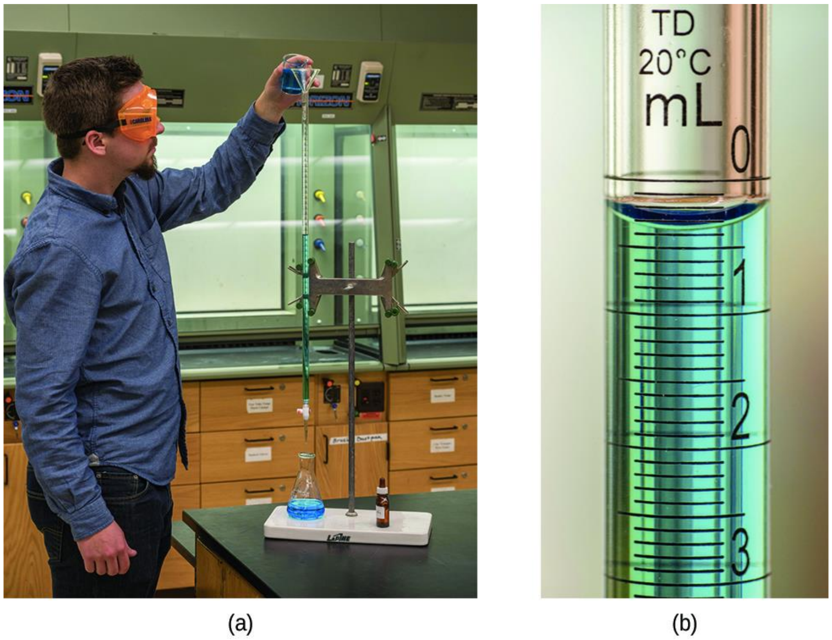


Figure 15.7 (a) A student fills a buret in preparation for a titration analysis.

(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)

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. What is the molarity of the HCl?

$$\text{HCl (aq)} + \text{NaOH (aq)} \rightarrow \text{NaCl (aq)} + H_2O\text{ (l)}$$

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.

The molar amount of HCl is calculated to be:

$$35.23\text{ mL NaOH} \times \frac{1\,L}{1000\,mL} \times \frac{0.250\,mol\,NaOH}{1\,L\,NaOH} \times \frac{1\,mol\,HCl}{1\,mol\,NaOH} = 8.81\times10^{-3}\text{ mol HCl}$$

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

$$\text{Molarity} = \frac{mol\,H_2SO_4}{L\ solution} = \frac{8.81\times10^{-3}\ mol\,HCl}{0.050\,L\ solution} = 0.176\text{ M}$$

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, $KMnO_4$.

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

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

ANSWER: 0.2648 *M*

Titration Curves

A **titration curve** is a plot of some solution property versus the amount of added titrant. For acid-base titrations, solution pH is a useful property to monitor because it varies predictably with the solution composition and, therefore, may be used to monitor the titration's progress and detect its end point.

A summary of pH/volume data pairs for the strong and weak acid titrations is provided in Table 15.1 and plotted as titration curves in Figure 15.8. A comparison of these two curves illustrates several important concepts that are best addressed by identifying the four stages of a titration:

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

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

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

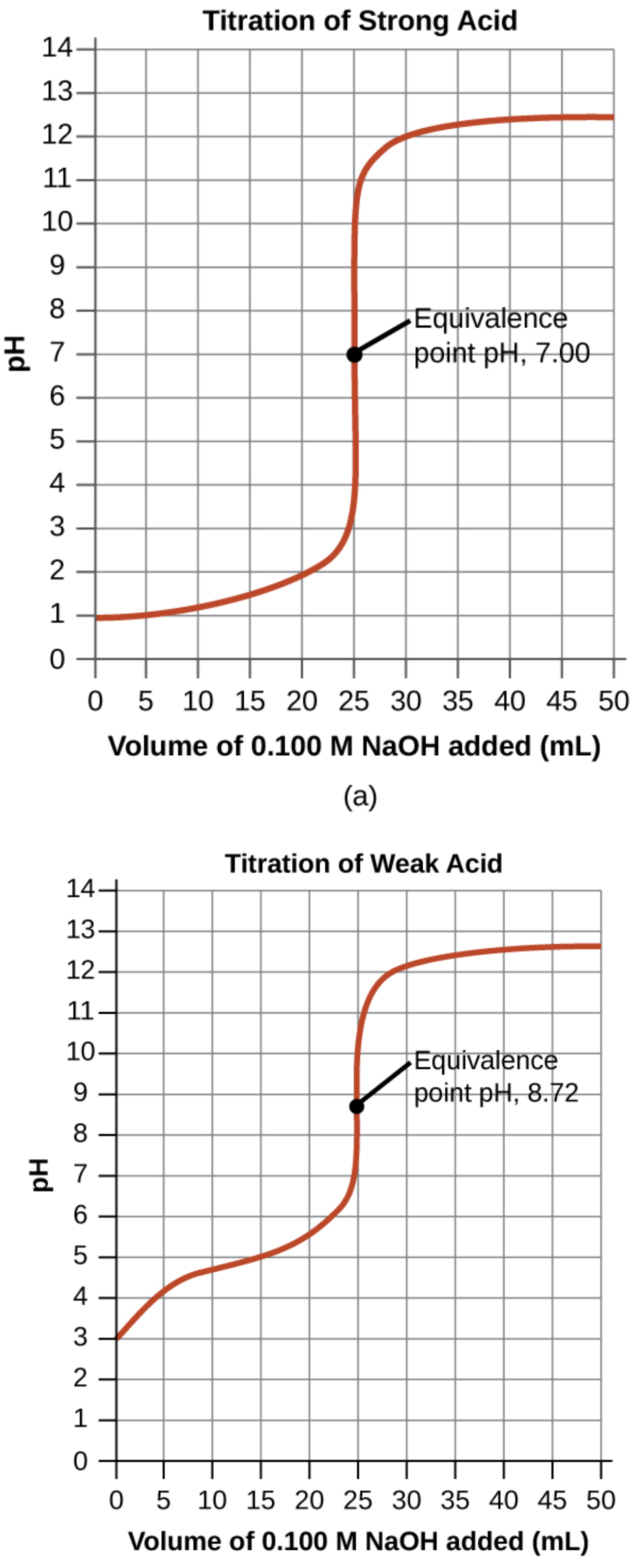
Postequivalence point (*V* > 25 mL): pH is determined by the amount of excess strong base titrant added; since both samples are titrated with the same titrant, both titration curves appear similar at this stage.

Table 15.1 pH Values in the Titrations of a Strong Acid and of a Weak Acid

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

Footnotes

- [1] Titration of 25.00 mL of 0.100 *M* HCl (0.00250 mol of HCl) with 0.100 *M* NaOH.
- [2] Titration of 25.00 mL of 0.100 *M* CH_3CO_2H (0.00250 mol of CH_3CO_2H) with 0.100 *M* NaOH.



(a)

(b)

Figure 15.8 (a) The titration curve for the titration of 25.00 mL of 0.100 *M* HCl (strong acid) with 0.100 *M* NaOH (strong base) has an equivalence point of 7.00 pH. (b) The titration curve for the titration of 25.00 mL of 0.100 *M* acetic acid (weak acid) with 0.100 *M* NaOH (strong base) has an equivalence point of 8.72 pH.

Calculating pH for Titration Solutions: Strong Acid/Strong Base

A titration is carried out for 25.00 mL of 0.100 *M* HCl (strong acid) with 0.100 *M* of a strong base NaOH (the titration curve is shown in Figure 15.8). Calculate the pH at these volumes of added base solution:

(a) 0.00 mL (b) 12.50 mL (c) 25.00 mL (d) 37.50 mL

Solution: $\text{HCl (aq)} + \text{NaOH (aq)} \rightarrow \text{NaCl (aq)} + \text{H}_2\text{O (l)}$

(a) Titrant volume = 0 mL. The solution pH is due to the acid ionization of HCl. Because this is a strong acid, the ionization is complete and the hydronium ion molarity is 0.100 *M*. The pH of the solution is then $\text{pH} = -\log(0.100) = 1.000$

(b) Titrant volume = 12.50 mL. Since the acid sample and the base titrant are both monoprotic and equally concentrated, this titrant addition involves less than a stoichiometric amount of base, and so it is completely consumed by reaction with the excess acid in the sample. The concentration of acid remaining and the pH can be calculated as follow:

Find total mol HCl: $25.00\text{ mL HCl} \times \frac{1\ L}{1000\ mL} \times \frac{0.100\ mol\ HCl}{1\ L\ HCl} = 2.50\times10^{-3}\text{ mol HCl}$

Find mol NaOH: $12.50\text{ mL NaOH} \times \frac{1\ L}{1000\ mL} \times \frac{0.100\ mol\ NaOH}{1\ L\ NaOH} = 1.25\times10^{-3}\text{ mol NaOH}$

Find reacted mol HCl: $1.25\times10^{-3}\text{ mol NaOH} \times \frac{1\ mol\ HCl}{1\ mol\ NaOH} = 1.25\times10^{-3}\text{ mol HCl reacted}$

Find unreacted mol HCl $= (2.50\times10^{-3}) - (1.25\times10^{-3}) = 1.25\times10^{-3}$ mol HCl unreacted

Find new molarity of unreacted HCl:

$$\text{Molarity} = \frac{mol\ HCl}{L\ solution} = \frac{1.25\times10^{-3}\ mol\ HCl}{(0.02500+0.0125)\ L\ solution} = 0.0333\ \text{M}$$

The pH of the solution is then $\text{pH} = -\log(0.0333) = 1.478$

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

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

Find total mol HCl: $25.00 \text{ mL HCl} \times \frac{1\, L}{1000\, mL} \times \frac{0.100\, mol\, HCl}{1\, L\, HCl} = 2.50\times10^{-3}$ mol HCl

Find mol NaOH: $37.50 \text{ mL NaOH} \times \frac{1\, L}{1000\, mL} \times \frac{0.100\, mol\, NaOH}{1\, L\, NaOH} = 3.75\times10^{-3}$ mol NaOH

Find reacted mol NaOH: 2.50×10^{-3} mol HCl $\times \frac{1\, mol\, NaOH}{1\, mol\, HCl} = 2.50\times10^{-3}$ mol NaOH reacted

Find unreacted mol NaOH = $(3.75\times10^{-3}) - (2.50\times10^{-3}) = 1.25\times10^{-3}$ mol NaOH unreacted

Find new molarity of unreacted NaOH:

$$\text{Molarity} = \frac{mol\, NaOH}{L\ solution} = \frac{1.25\times10^{-3}\ mol\, NaOH}{(0.02500+0.03750)\, L\ solution} = 0.0200\ \text{M}$$

The pOH of the solution is pOH = −log(0.0200) = 1.699
The pH of the solution is then pH = 14.00 – 1.699 = 12.30

Check Your Learning

Calculate the pH for the strong acid/strong base titration between 50.0 mL of 0.100 *M* $HNO_3(aq)$ and 0.200 *M* NaOH (titrant) at the listed volumes of added base: 0.00 mL, 15.0 mL, 25.0 mL, and 40.0 mL.

ANSWER:
0.00 mL → pH = 1.000;
15.0 mL → pH = 1.5111;
25.0 mL → pH = 7;
40.0 mL → pH = 12.523

Titration of a Weak Acid with a Strong Base

Consider the titration of 25.00 mL of 0.100 *M* CH_3CO_2H with 0.100 *M* NaOH. The reaction can be represented as:

$CH_3CO_2H + OH^- \rightarrow CH_3CO_2^- + H_2O$

Calculate the pH of the titration solution after the addition of the following volumes of NaOH titrant:

(a) 0.00 mL
(b) 25.00 mL
(c) 12.50 mL
(d) 37.50 mL

Solution

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

$Ka = \frac{[H_3O^+][CH_3CO_2^-]}{[CH_3CO_2H]} = \frac{x^2}{0.100} = 1.8 \times 10^{-5}$

$x = [H_3O^+] = 1.3 \times 10^{-3}$ M → pH = $-\log(1.3 \times 10^{-3}) = 2.87$

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

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

Base ionization of acetate is represented by the equation

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

Kb = $\frac{K_W}{K_a}$ = $\frac{1.0 \times 10^{-14}}{1.8 \times 10^{-5}}$ = 5.6 x 10^{-10}

Use the approximation, the pH may be calculated via the usual ICE approach:

Kb = $\frac{[OH^-][CH_3CO_2H]}{[CH_3CO_2^-]}$ = $\frac{x^2}{0.0500}$ = 5.6 x 10^{-10}

x = $[OH^-]$ = 5.3 x 10^{-6} M → pOH = −log (5.3 × 10^{-6}) = 5.28
→ pH = 14.00 – 5.28 = 8.72

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

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

pH = pKa + log$\frac{[Conj.Base]}{[Conj.Acid]}$
= −log(Ka) + log$\frac{[CH_3CO_2^-]}{[CH_3CO_2H]}$
= −log(1.8 × 10^{-5}) + log(1) = 4.74

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

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

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

Check Your Learning

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

ANSWER:
0.00 mL: 2.37; 15.0 mL: 3.92; 25.00 mL: 8.29; 30.0 mL: 12.097

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.

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

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

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

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

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

$$\text{pH} \quad = \text{pKa} + \log\frac{[In^-]}{[HIn]}$$

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

There are many different acid-base indicators that cover a wide range of pH values and can be used to determine the approximate pH of an unknown solution by a process of elimination. Universal indicators and pH paper contain a mixture of indicators and exhibit different colors at different pHs. Figure 15.9 presents several indicators, their colors, and their color-change intervals.

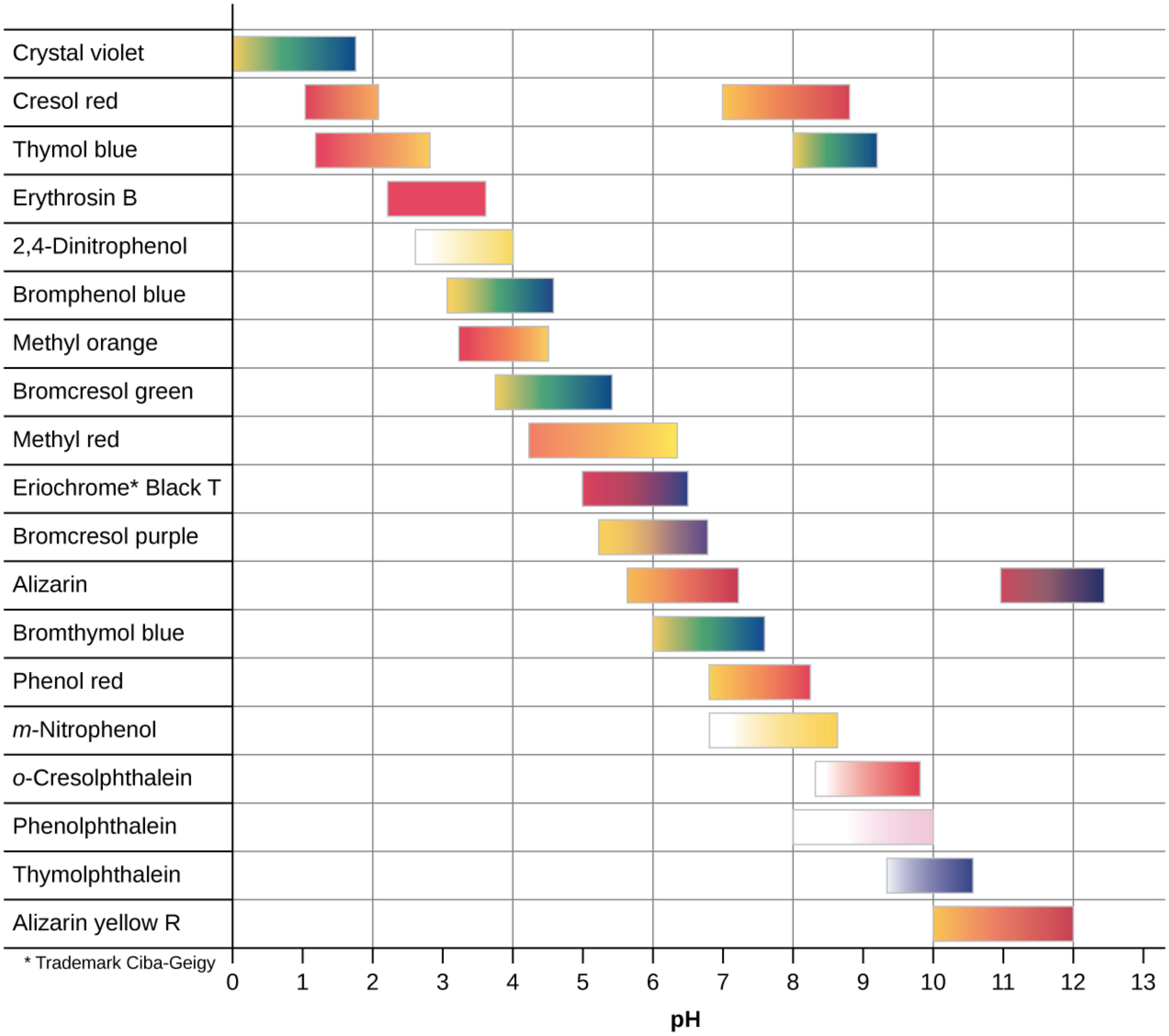


Figure 15.9 This chart illustrates the color change intervals for several acid-base indicators.

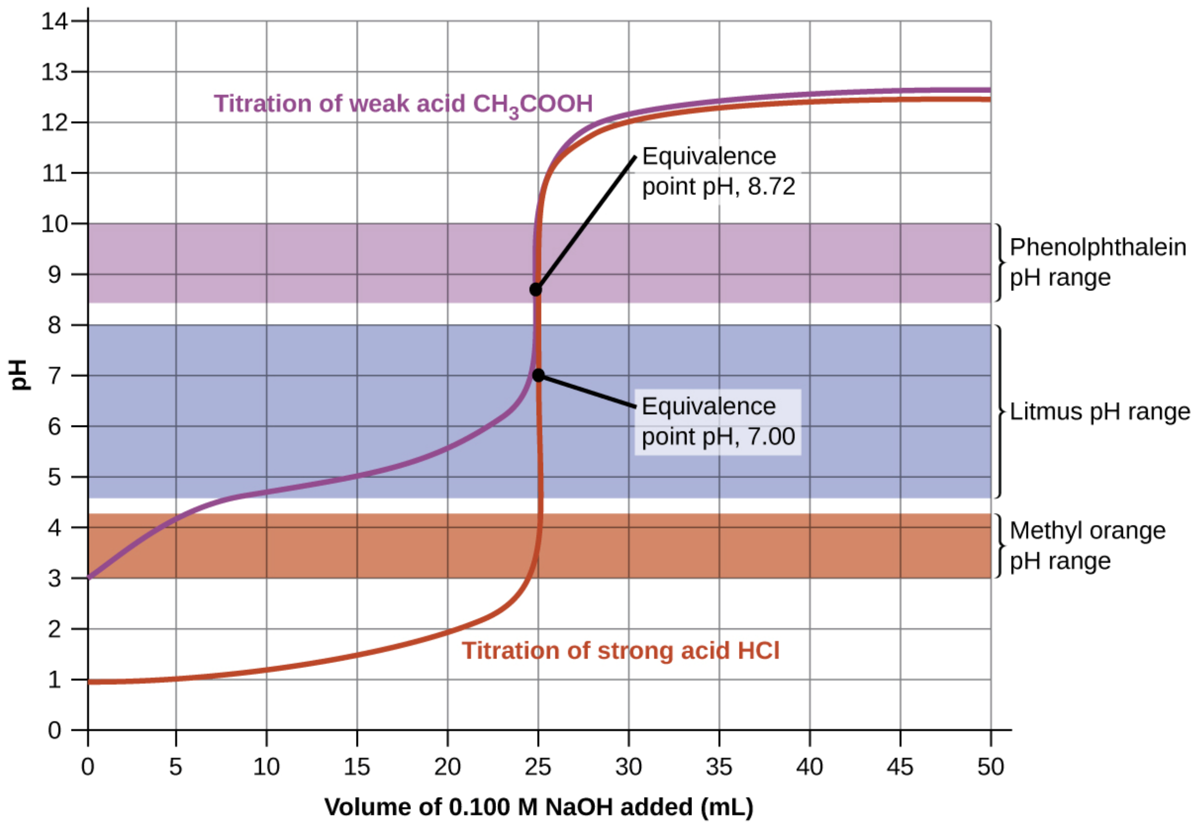


Figure 15.10 Titration curves for strong and weak acids illustrating the proper choice of acid-base indicator. Any of the three indicators will exhibit a reasonably sharp color change at the equivalence point of the strong acid titration, but only phenolphthalein is suitable for use in the weak acid titration.

The titration curves shown in Figure 15.10 illustrate the choice of a suitable indicator for specific titrations. In the strong acid titration, use of any of the three indicators should yield reasonably sharp color changes and accurate end point determinations. For this titration, the solution pH reaches the lower limit of the methyl orange color change interval after addition of ~24 mL of titrant, at which point the initially red solution would begin to appear orange. When 25 mL of titrant has been added (the equivalence point), the pH is well above the upper limit and the solution will appear yellow. The titration's end point may then be estimated as the volume of titrant that yields a distinct orange-to-yellow color change. This color change would be challenging for most human eyes to precisely discern. More-accurate estimates of the titration end point are possible using either litmus or phenolphthalein, both of which exhibit color change intervals that are encompassed by the steep rise in pH that occurs around the 25.00 mL equivalence point.

The weak acid titration curve in Figure 15.10 shows that only one of the three indicators is suitable for end point detection. If methyl orange is used in this titration, the solution will undergo a gradual red-to-orange-to-yellow color change over a relatively large volume interval (0–6 mL), completing the color change well before the equivalence point (25 mL) has been reached. Use of litmus would show a color change that begins after adding 7–8 mL of titrant and ends just before the equivalence point. Phenolphthalein, on the other hand, exhibits a color change interval that nicely brackets the abrupt change in pH occurring at the titration's equivalence point. A sharp color change from colorless to pink will be observed within a very small volume interval around the equivalence point.

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Chapter 16 Precipitation and Aqueous Ionic Equilibrium

Chapter Introduction

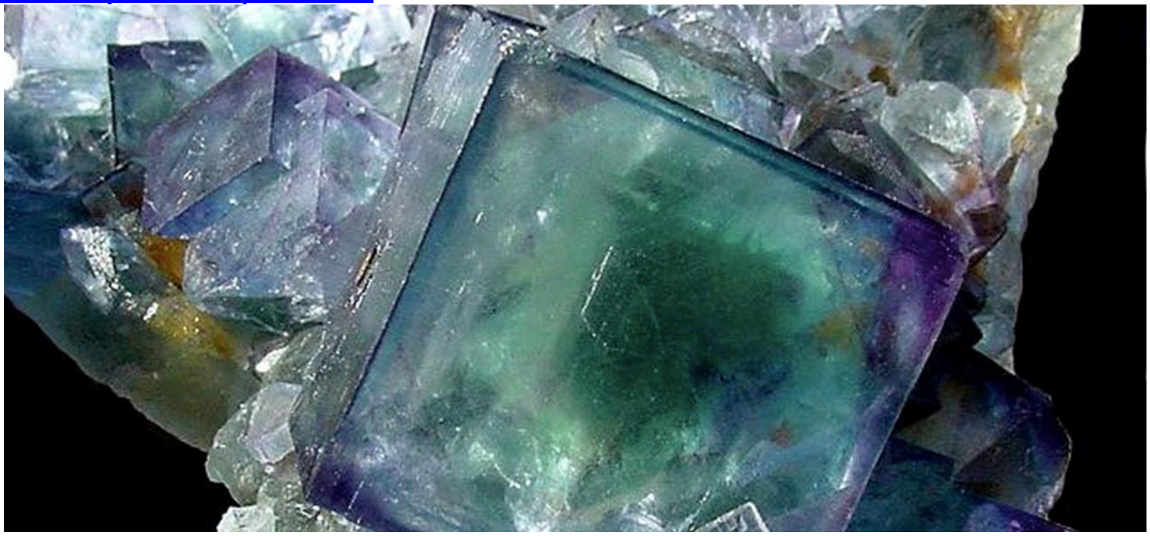

Figure 16.1 The mineral fluorite (CaF_2) is formed when dissolved calcium and fluoride ions precipitate from groundwater within the Earth's crust. Note that pure fluorite is colorless, and that the color in this sample is due to the presence of other metal ions in the crystal.

The mineral fluorite, CaF_2 Figure 16.1, is commonly used as a semiprecious stone in many types of jewelry because of its striking appearance. Deposits of fluorite are formed through a process called hydrothermal precipitation in which calcium and fluoride ions dissolved in groundwater combine to produce insoluble CaF_2 in response to some change in solution conditions. For example, a decrease in temperature may trigger fluorite precipitation if its solubility is exceeded at the lower temperature. Because fluoride ion is a weak base, its solubility is also affected by solution pH, and so geologic or other processes that change groundwater pH will also affect the precipitation of fluorite. This chapter extends the equilibrium discussion of other chapters by addressing some additional reaction classes (including precipitation) and systems involving coupled equilibrium reactions.

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16.1 Precipitation Reactions

Learning Objectives

- Define precipitation reactions
- Recognize precipitation reactions
- Write balanced equations for ionic reactions
- Predict the solubility of common ionic compounds by using solubility rules
- Solve precipitation stoichiometric problems

Precipitation Reactions and Solubility Rules

A **precipitation reaction** is one in which dissolved substances react to form one (or more) solid products. Many reactions of this type involve the exchange of ions between ionic compounds in aqueous solution and are sometimes referred to as *double displacement*, *double replacement*, or *metathesis* reactions. These reactions are common in nature and are responsible for the formation of coral reefs in ocean waters and kidney stones in animals. They are used widely in industry for production of a number of commodity and specialty chemicals. Precipitation reactions also play a central role in many chemical analysis techniques, including spot tests used to identify metal ions and *gravimetric methods* for determining the composition of matter.

The extent to which a substance may be dissolved in water, or any solvent, is quantitatively expressed as its **solubility**, defined as the maximum concentration of a substance that can be achieved under specified conditions. Substances with relatively large solubilities are said to be **soluble**. A substance will **precipitate** when solution conditions are such that its concentration exceeds its solubility. Substances with relatively low solubilities are said to be **insoluble**, and these are the substances that readily precipitate from solution. More information on these important concepts is provided in a later chapter on solutions. For purposes of predicting the identities of solids formed by precipitation reactions, one may simply refer to patterns of solubility that have been observed for many ionic compounds (Table 16.1).

Table 16.1 Solubility Rules for Ionic Compounds in Water

Soluble Ionic Compounds	
Contain these ions	**Exceptions**
NH_4^+ Group 1 cations: (Li^+, Na^+, K^+, Rb^+, Cs^+)	None
$C_2H_3O_2^-$ (same as $CH_3CO_2^-$) HCO_3^- NO_3^- ClO_3^-	None
Cl^-, Br^-, I^-	These ions combine with Ag^+, Hg_2^{2+}, or Pb^{2+}. Their compounds are insoluble.
F^-	This ion combines with Pb^{2+}, Fe^{3+}, or group 2 metal cations (Be^{2+}, Mg^{2+}, Ca^{2+}, Sr^{2+}, Ba^{2+}). Their compounds are insoluble.
SO_4^{2-}	This ion combines with Ag^+, Ba^{2+}, Ca^{2+}, Hg_2^{2+}, Pb^{2+} or Sr^{2+}. Their compounds are insoluble.
Insoluble Ionic Compounds	
Contain these ions	**Exceptions**
CO_3^{2-} CrO_4^{2-} PO_4^{3-} S^{2-}	These ions combine with group 1 metal cations, or NH_4^+ Their compounds are soluble.
OH^-	This ion combines with group 1 metal cations, or Ba^{2+} Their compounds are soluble.

Equations for Ionic Reactions

Given the abundance of water on earth, it stands to reason that a great many chemical reactions take place in aqueous media. When ions are involved in these reactions, the chemical equations may be written with various levels of detail appropriate to their intended use. To illustrate this, consider a reaction between ionic compounds taking place in an aqueous solution. When aqueous solutions of $CaCl_2$ and $AgNO_3$ are mixed, a reaction takes place producing aqueous $Ca(NO_3)_2$ and solid AgCl:

$$CaCl_2(aq) + 2AgNO_3(aq) \rightarrow Ca(NO_3)_2(aq) + 2AgCl(s)$$

This balanced equation, derived in the usual fashion, is called a **molecular equation** because it doesn't explicitly represent the ionic species that are present in solution. When ionic compounds dissolve in water, they may *dissociate* into their constituent ions, which are subsequently dispersed homogenously throughout the resulting solution (a thorough discussion of this important process is provided in the chapter on solutions). Ionic compounds dissolved in water are, therefore, more realistically represented as dissociated ions, in this case:

$$CaCl_2(aq) \rightarrow Ca^{2+}(aq) + 2Cl^-(aq)$$

$$2AgNO_3(aq) \rightarrow 2Ag^+(aq) + 2NO_3^-(aq)$$

$$Ca(NO_3)_2(aq) \rightarrow Ca^{2+}(aq) + 2NO_3^-(aq)$$

Unlike these three ionic compounds, AgCl does not dissolve in water to a significant extent, as signified by its physical state notation, *s*.

Explicitly representing all dissolved ions results in a **complete ionic equation**. In this particular case, the formulas for the dissolved ionic compounds are replaced by formulas for their dissociated ions:

$$Ca^{2+}(aq) + 2Cl^-(aq) + 2Ag^+(aq) + 2NO_3^-(aq) \rightarrow Ca^{2+}(aq) + 2NO_3^-(aq) + 2AgCl(s)$$

Examining this equation shows that two chemical species are present in identical form on both sides of the arrow, Ca^{2+}(*aq*) and NO_3^-(aq). These **spectator ions**—ions whose presence is required to maintain charge neutrality—are neither chemically nor physically changed by the process, and so they may be eliminated from the equation to yield a more succinct representation called a **net ionic equation**:

$$Ca^{2+}(aq) + 2Cl^-(aq) + 2Ag^+(aq) + 2NO_3^-(aq) \rightarrow Ca^{2+}(aq) + 2NO_3^-(aq) + 2AgCl(s)$$

$$2Cl^-(aq) + 2Ag^+(aq) \rightarrow 2AgCl(s)$$

Following the convention of using the smallest possible integers as coefficients, this equation is then written:

$$Cl^-(aq) + Ag^+(aq) \rightarrow AgCl(s)$$

This net ionic equation indicates that solid silver chloride may be produced from dissolved chloride and silver(I) ions, regardless of the source of these ions. These molecular and complete ionic equations provide additional information, namely, the ionic compounds used as sources of Cl^- and Ag^+.

A vivid example of precipitation is observed when solutions of potassium iodide and lead nitrate are mixed, resulting in the formation of solid lead iodide:

$$2KI(aq) + Pb(NO_3)_2(aq) \rightarrow PbI_2(s) + 2KNO_3(aq)$$

This observation is consistent with the solubility guidelines: The only insoluble compound among all those involved is lead iodide, one of the exceptions to the general solubility of iodide salts.

The net ionic equation representing this reaction is:

$$Pb^{2+}(aq) + 2I^-(aq) \rightarrow PbI_2(s)$$

Lead iodide is a bright yellow solid that was formerly used as an artist's pigment known as iodine yellow (Figure 16.2). The properties of pure PbI_2 crystals make them useful for fabrication of X-ray and gamma ray detectors.

Figure 16.2 A precipitate of PbI_2 forms when solutions containing Pb^{2+} and I^- are mixed. (credit: Der Kreole/Wikimedia Commons)

The solubility guidelines in Table 16.1 may be used to predict whether a precipitation reaction will occur when solutions of soluble ionic compounds are mixed together. One merely needs to identify all the ions present in the solution and then consider if possible cation/anion pairing could result in an insoluble compound. For example, mixing solutions of silver nitrate and sodium fluoride will yield a solution containing Ag^+, NO_3^-, Na^+, and F^- ions. Aside from the two ionic compounds originally present in the solutions, $AgNO_3$ and NaF, two additional ionic compounds may be derived from this collection of ions: $NaNO_3$ and AgF. The solubility guidelines indicate all nitrate salts are soluble but that AgF is one of the exceptions to the general solubility of fluoride salts. A precipitation reaction, therefore, is predicted to occur, as described by the following equations:

$NaF\ (aq) + AgNO_3\ (aq) \rightarrow AgF\ (s) + NaNO_3\ (aq)$ (molecular)

$Ag^+\ (aq) + F^-\ (aq) \rightarrow AgF\ (s)$ (net ionic)

EXAMPLE 16.1

Predict the result of mixing reasonably concentrated solutions of the following ionic compounds. If precipitation is expected, write a balanced net ionic equation for the reaction.

(a) potassium sulfate and barium nitrate
(b) lithium chloride and silver acetate
(c) lead nitrate and ammonium carbonate

Solution

(a) The two possible products for this combination are KNO_3 and $BaSO_4$. The solubility guidelines indicate $BaSO_4$ is insoluble, and so a precipitation reaction is expected. The net ionic equation for this reaction, derived in the manner detailed in the previous module, is

$$Ba^{2+}\,(aq) + SO_4^{2-}\,(aq) \rightarrow BaSO_4\,(s)$$

(b) The two possible products for this combination are $LiC_2H_3O_2$ and AgCl. The solubility guidelines indicate AgCl is insoluble, and so a precipitation reaction is expected. The net ionic equation for this reaction, derived in the manner detailed in the previous module, is

$$Ag^{+}\,(aq) + Cl^{-}\,(aq) \rightarrow AgCl\,(s)$$

(c) The two possible products for this combination are $PbCO_3$ and NH_4NO_3. The solubility guidelines indicate $PbCO_3$ is insoluble, and so a precipitation reaction is expected. The net ionic equation for this reaction, derived in the manner detailed in the previous module, is

$$Pb^{2+}\,(aq) + CO_3^{2-}\,(aq) \rightarrow PbCO_3\,(s)$$

Check Your Learning

Which solution could be used to precipitate the barium ion, Ba^{2+}, in a water sample: sodium chloride, sodium hydroxide, or sodium sulfate? What is the formula for the expected precipitate?

ANSWER: sodium sulfate, $BaSO_4$

Precipitation Stoichiometry

In the previous chapter, you learned about acid-base stoichiometry. In this module, similar idea will be used in precipitation stoichiometry.

The use of stoichiometric factors derived from balanced precipitation chemical equations can be used for several conversion (Figure 16.3).

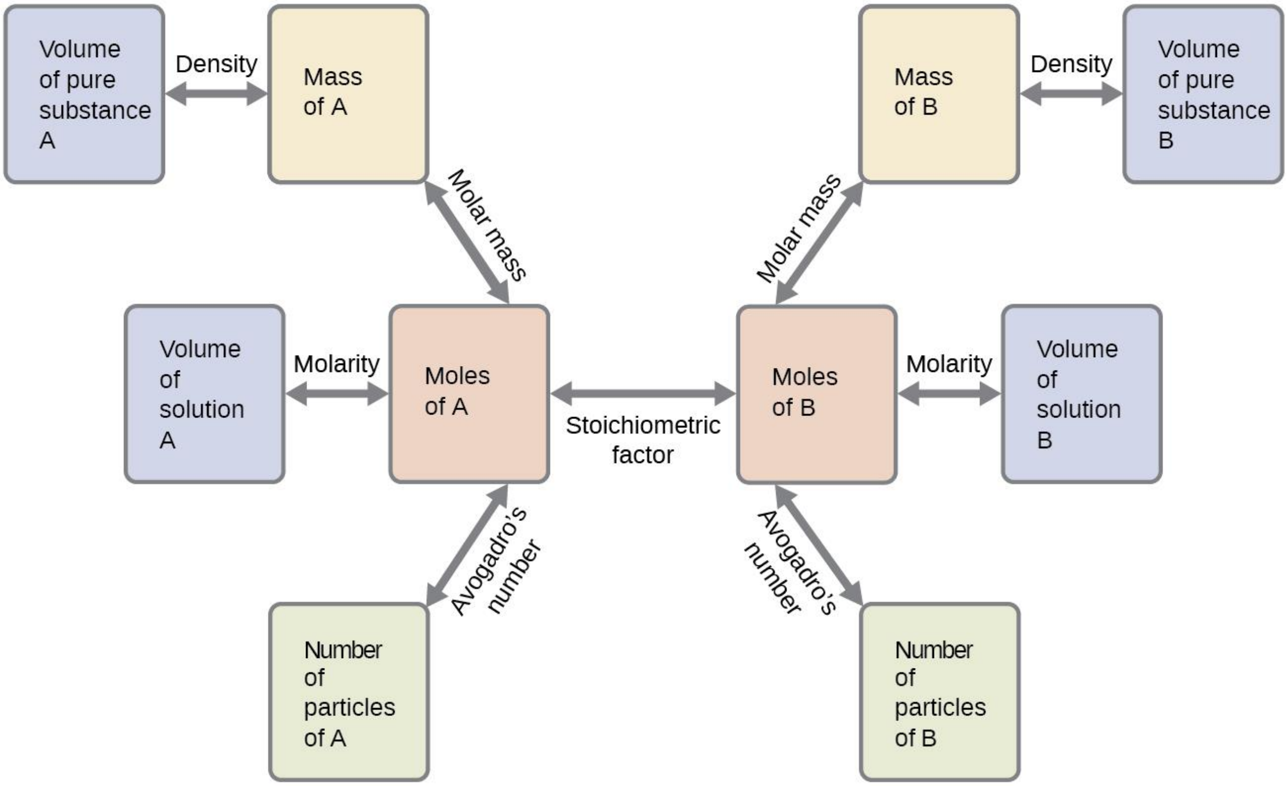


Figure 16.3 The flowchart depicts the various computational steps involved in most reaction stoichiometry calculations.

In the precipitation reactions, the amounts of reactants are often expressed as molarity, and the amounts of precipitate products are expressed as mass or moles.

EXAMPLE 16.2

How many grams of precipitate can be produced when 25.0 mL of 0.555 M lead (II) nitrate completely reacts with potassium iodide.

Solution:

1. Write a balanced precipitation reaction:

$$Pb(NO_3)_2\ (aq)\ +\ 2KI\ (aq)\ \rightarrow\ PbI_2\ (s)\ +\ 2KNO_3\ (aq)$$

2. Use the number with two units as conversion factors

$$(0.555\ M\ Pb(NO_3)_2\ =\ \frac{0.555\ mol\ Pb(NO_3)_2}{1\ L\ \ solution\ Pb(NO_3)_2})$$

3. Start with number with one units (25.0 mL of $Pb(NO_3)_2$) and use stoichiometric ratio to solve problem:

$$25.0\ mL\ Pb(NO_3)_2 \times \frac{1\ L}{1000\ mL} \times \frac{0.555\ mol\ Pb(NO_3)_2}{1\ L\ \ solution\ Pb(NO_3)_2} \times \frac{1\ mol\ PbI_2}{1\ mol\ Pb(NO_3)_2} \times \frac{461.01\ g\ PbI_2}{1\ mol\ PbI_2}$$

$$=\ 6.40\ g\ \ PbI_2$$

EXAMPLE 16.3

How many grams of precipitate can be produced when 15.0 mL of 0.733 M calcium chloride reacts with 20. mL of 0.653 M sodium carbonate.

Solution:

1. Write a balanced precipitation reaction:

$$CaCl_2\ (aq)\ +\ Na_2CO_3\ (aq)\ \rightarrow\ CaCO_3\ (s)\ +\ 2NaCl\ (aq)$$

2. Use the number with two units as conversion factors

$$(0.733\ M\ CaCl_2\ =\ \frac{0.733\ mol\ CaCl_2}{1\ L\ \ solution\ CaCl_2})$$

$$(0.653\ M\ Na_2CO_3\ =\ \frac{0.653\ mol\ Na_2CO_3}{1\ L\ \ solution\ \ Na_2CO_3})$$

3. This problem gives information for both reactants. In this case, you will need to find the limiting reactant and theoretical yield.

$$15.0\ mL\ CaCl_2 \times \frac{1\ L}{1000\ mL} \times \frac{0.733\ mol\ CaCl_2}{1\ L\ \ solution\ CaCl_2} \times \frac{1\ mol\ CaCO_3}{1\ mol\ CaCl_2} \times \frac{100.087\ g\ CaCO_3}{1\ mol\ CaCO_3}$$

= 1.10 g CaCO3

$$20.0\ mL\ Na_2CO_3 \times \frac{1\ L}{1000\ mL} \times \frac{0.653\ mol\ Na_2CO_3}{1\ L\ \ solution\ \ Na_2CO_3} \times \frac{1\ mol\ CaCO_3}{1\ mol\ Na_2CO_3} \times \frac{100.087\ g\ CaCO_3}{1\ mol\ CaCO_3}$$

= 1.31 g CaCO3

The available amount of $CaCl_2$ limits the amount of $CaCO_3$ that can be made.
Thus, $CaCl_2$ is the limiting reactant.
The amount of $CaCO_3$ that can be made (theoretical yield) is 1.10 g.

EXAMPLE 16.4

What is the volume (in mL) of 3.50 M $AgNO_3$ needed to completely react with $CaCl_2$ and produce 5.47 g AgCl?

Solution:

1. Write a balanced precipitation reaction:

$$2\ AgNO_3\ (aq)\ +\ CaCl_2\ (aq)\ \rightarrow\ 2AgCl\ (s)\ +\ Ca(NO_3)_2\ (aq)$$

2. Use the number with two units as conversion factors

$$\left(3.50\ M\ AgNO_3\ =\ \frac{3.50\ mol\ AgNO_3}{1\ L\ \ solution\ AgNO_3}\right)$$

3. Use given grams and stoichiometric ratio to solve problem:

$$5.47\ g\ AgCl\ \times \frac{1\ mol\ AgCl}{143.32\ g\ AgCl} \times \frac{2\ mol\ AgNO_3}{2\ mol\ AgCl} \times \frac{1\ L\ \ solution\ AgNO_3}{3.50\ mol\ AgNO_3} \times \frac{1000\ mL}{1\ L}$$

$$=\ 10.9\ mL\ AgNO_3$$

16.2 Solubility equilibria and the solubility product constant

Learning Objectives

- Write chemical equations and equilibrium expressions representing solubility equilibria
- Carry out equilibrium calculations involving solubility, equilibrium expressions, and solute concentrations

Introduction

Solubility equilibria are established when the dissolution and precipitation of a solute species occur at equal rates. These equilibria underlie many natural and technological processes, ranging from tooth decay to water purification. An understanding of the factors affecting compound solubility is, therefore, essential to the effective management of these processes. This section applies previously introduced equilibrium concepts and tools to systems involving dissolution and precipitation.

The Solubility Product

Recall from the chapter on solutions that the solubility of a substance can vary from essentially zero (*insoluble* or *sparingly soluble*) to infinity (*miscible*). A solute with finite solubility can yield a *saturated* solution when it is added to a solvent in an amount exceeding its solubility, resulting in a heterogeneous mixture of the saturated solution and the excess, undissolved solute.

For example, a saturated solution of silver chloride is one in which the equilibrium shown below has been established.

$$\mathrm{AgCl\ (s)} \rightleftharpoons \mathrm{Ag+\ (aq)} + \mathrm{Cl^{-}\ (aq)}$$

In this solution, an excess of solid AgCl dissolves and dissociates to produce aqueous Ag^+ and $Cl^–$ ions at the same rate that these aqueous ions combine and precipitate to form solid AgCl (Figure 16.4). Because silver chloride is a sparingly soluble salt, the equilibrium concentration of its dissolved ions in the solution is relatively low.

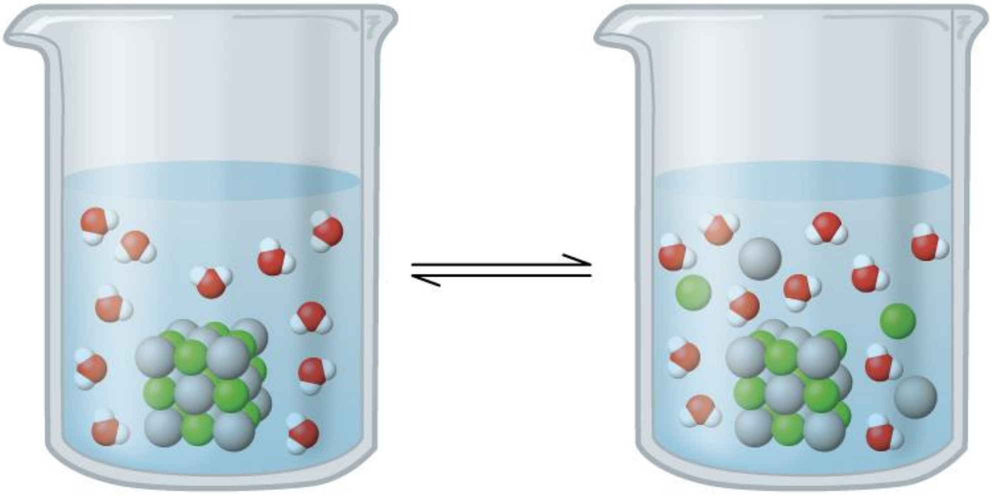


Figure 16.4 Silver chloride is a sparingly soluble ionic solid. When it is added to water, it dissolves slightly and produces a mixture consisting of a very dilute solution of Ag^+ and $Cl^–$ ions in equilibrium with undissolved silver chloride.

The equilibrium constant for solubility equilibria such as this one is called the **solubility product constant, K_{sp}**, in this case

$$\mathrm{AgCl\ (s)} \rightleftharpoons \mathrm{Ag+\ (aq)} + \mathrm{Cl^{-}\ (aq)} \qquad K_{sp} = [\mathrm{Ag^{+}(aq)}]\,[\mathrm{Cl^{-}(aq)}]$$

Recall that only gases and solutes are represented in equilibrium constant expressions, so the K_{sp} does not include a term for the undissolved AgCl. A listing of solubility product constants for several sparingly soluble compounds is provided in Appendix 16.2.

Writing Equations and Solubility Products

EXAMPLE 16.5

Write the dissolution equation and the solubility product expression for each of the following slightly soluble ionic compounds:

(a) AgI, a solid with antiseptic properties
(b) $CaCO_3$, the active ingredient in many over-the-counter chewable antacids
(c) $Mg(OH)_2$, the active ingredient in Milk of Magnesia
(d) $Mg(NH_4)PO_4$, an essentially insoluble substance used in tests for magnesium
(e) $Ca_5(PO_4)_3OH$, the mineral apatite, a source of phosphate for fertilizers

Solution

(a) $AgI\ (s) \rightleftharpoons Ag^+\ (aq) + I^-\ (aq)$ $K_{sp} = [Ag^+][I^-]$

(b) $CaCO_3\ (s) \rightleftharpoons Ca^{2+}\ (aq) + CO_3^{2-}\ (aq)$ $K_{sp} = [Ca^{2+}][CO_3^{2-}]$

(c) $Mg(OH)_2\ (s) \rightleftharpoons Mg^{2+}\ (aq) + 2OH^-\ (aq)$ $K_{sp} =[Mg^{2+}][OH^-]^2$

(d) $Mg(NH_4)PO_4\ (s) \rightleftharpoons Mg^{2+}\ (aq) + NH_4^+\ (aq) + PO_4^{3-}\ (aq)$ $K_{sp} = [Mg^{2+}][NH_4^+][PO_4^{3-}]$

(e) $Ca_5(PO_4)_3OH\ (s) \rightleftharpoons 5Ca^{2+}\ (aq) + 3PO_4^{3-}\ (aq) + OH^-\ (aq)$ $K_{sp} = [Ca^{2+}]^5[PO_4^{3-}]^3[OH^-]$

Check Your Learning

Write the dissolution equation and the solubility product for each of the following slightly soluble compounds:

(a) $BaSO_4$ (b) Ag_2SO_4 (c) $Al(OH)_3$

ANSWER:

(a) $BaSO_4\ (s) \rightleftharpoons Ba^{2+}\ (aq) + SO_4^{2-}\ (aq)$ $K_{sp} = [Ba^{2+}][SO_4^{2-}]$;

(b) $Ag_2SO_4\ (s) \rightleftharpoons 2Ag^+\ (aq) + SO_4^{2-}\ (aq)$ $K_{sp} = [Ag^+]^2[SO_4^{2-}]$;

(c) $Al(OH)_3\ (s) \rightleftharpoons Al^{3+}\ (aq) + 3OH^-\ (aq)$ $K_{sp} = [Al^{3+}][OH^-]^3$;

Calculation of K_{sp} from Equilibrium Concentrations

EXAMPLE 16.6

Fluorite, CaF_2, is a slightly soluble solid that dissolves according to the equation:

$$CaF_2\,(s) \rightleftharpoons Ca^{2+}\,(aq) + 2F^-\,(aq)$$

The concentration of Ca^{2+} in a saturated solution of CaF_2 is 2.15×10^{-4} *M*. What is the solubility product of fluorite?

Solution

According to the stoichiometry of the dissolution equation, the fluoride ion molarity of a CaF_2 solution is equal to twice its calcium ion molarity:

$$[\,F^-] = 2.15 \times 10^{-4}\ \frac{mol\ Ca^{2+}}{1\ L} \times \frac{2\ mol\ F^-}{1\ mol\ Ca^{2+}} = 4.30 \times 10^{-4}\ \frac{mol\ F^-}{1\ L} = 4.30 \times 10^{-4}\ \text{M}$$

Substituting the ion concentrations into the K_{sp} expression gives

$$K_{sp} = [Ca^{2+}][F^-]^2 = (2.15 \times 10^{-4})\,(4.30 \times 10^{-4})^2 = 3.98 \times 10^{-11}$$

Check Your Learning

In a saturated solution of $Mg(OH)_2$, the concentration of Mg^{2+} is 1.31×10^{-4} *M*.
What is the solubility product for $Mg(OH)_2$?

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

ANSWER: 8.99×10^{-12}

Determination of Molar Solubility from K_{sp}

EXAMPLE 16.7

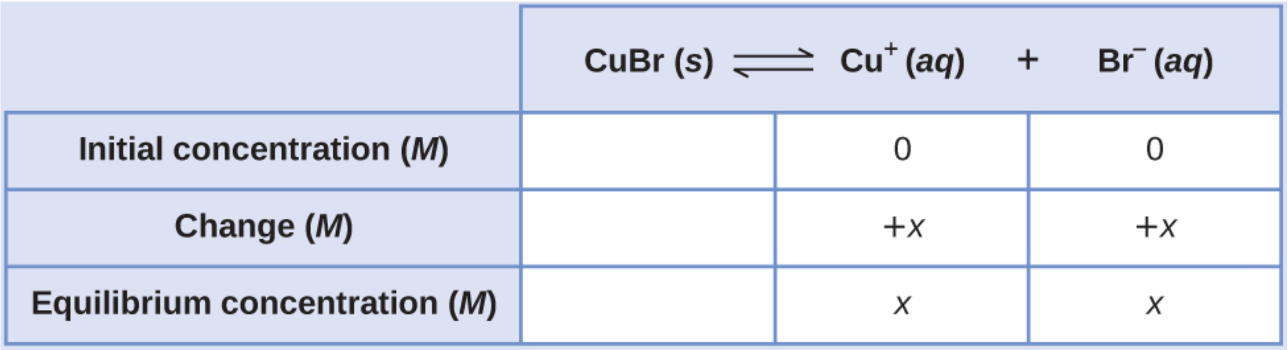
The K_{sp} of copper(I) bromide, CuBr, is 6.3×10^{-9}. Calculate the molar solubility of copper bromide.

Solution

The dissolution equation and solubility product expression are

$$CuBr\ (s) \rightleftharpoons Cu^{+}\ (aq) + Br^{-}\ (aq) \qquad K_{sp} = [Cu^{+}][Br^{-}]$$

Following the ICE approach to this calculation yields the table



	$CuBr\ (s)$ $\rightleftharpoons$	$Cu^{+}\ (aq)$ +	$Br^{-}\ (aq)$
Initial concentration (*M*)		0	0
Change (*M*)		$+x$	$+x$
Equilibrium concentration (*M*)		x	x

Substituting the equilibrium concentration terms into the solubility product expression and solving for *x* yields

$$K_{sp} = [Cu^{+}][Br^{-}]$$

$$6.3 \times 10^{-9} = (x)(x) = x^2$$

$$x = \sqrt{6.3 \times 10^{-9}} = 7.9 \times 10^{-5}\ M$$

Since the dissolution stoichiometry shows one mole of copper(I) ion and one mole of bromide ion are produced for each moles of Br dissolved, the molar solubility of CuBr is 7.9×10^{-5} *M*.

Check Your Learning

The K_{sp} of AgI is 1.5×10^{-16}. Calculate the molar solubility of silver iodide.

ANSWER: 1.2×10^{-8} *M*

EXAMPLE 16.8

The K_{sp} of calcium hydroxide, $Ca(OH)_2$, is 1.3×10^{-6}. Calculate the molar solubility of calcium hydroxide.

Solution

The dissolution equation and solubility product expression are

$$Ca(OH)_2\,(s) \rightleftharpoons Ca^{2+}\,(aq) + 2OH^-\,(aq) \qquad K_{sp} = [Ca^{2+}][OH^-]^2$$

The ICE table for this system is

	$Ca(OH)_2\,(s) \rightleftharpoons$	$Ca^{2+}\,(aq)$ +	$2OH^-\,(aq)$
Initial concentration (*M*)		0	0
Change (*M*)		$+x$	$+2x$
Equilibrium concentration (*M*)		x	$2x$

Substituting terms for the equilibrium concentrations into the solubility product expression and solving for *x* gives

$$K_{sp} = [Ca^{2+}][OH^-]^2$$

$$1.3 \times 10^{-6} = (x)(2x)^2 = (x)(4x^2) = 4x^3$$

$$x = \sqrt[3]{\frac{1.3 \times 10^{-6}}{4}} = 6.9 \times 10^{-3}\ M$$

As defined in the ICE table, *x* is the molarity of calcium ion in the saturated solution. The dissolution stoichiometry shows a 1:1 relation between moles of calcium ion in solution and moles of compound dissolved, and so, the molar solubility of $Ca(OH)_2$ is 6.9×10^{-3} *M*.

Check Your Learning

The K_{sp} of PbI_2 is 1.4×10^{-8}. Calculate the molar solubility of lead(II) iodide.

ANSWER: 1.5×10^{-3} *M*

Determination of K_{sp} from Gram Solubility

EXAMPLE 16.9

Many of the pigments used by artists in oil-based paints (Figure 15.3) are sparingly soluble in water. For example, the solubility of the artist's pigment chrome yellow, $PbCrO_4$, is 4.6×10^{-6} g/L. Determine the solubility product for $PbCrO_4$.

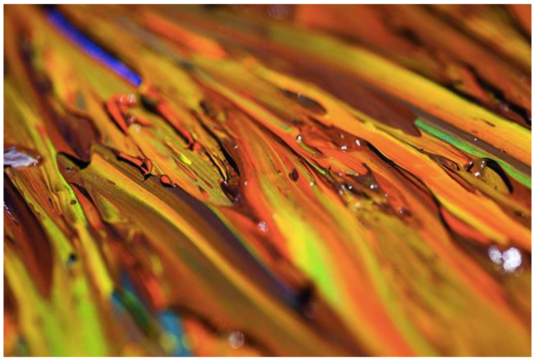


Figure 15.3 Oil paints contain pigments that are very slightly soluble in water. In addition to chrome yellow ($PbCrO_4$), examples include Prussian blue ($Fe_7(CN)_{18}$), the reddish-orange color vermilion (HgS), and green color veridian (Cr_2O_3). (credit: Sonny Abesamis)

Solution

Before calculating the solubility product, the provided solubility must be converted to molarity:

$$[\ PbCrO_4\ ] = \frac{4.6 \times 10^{-6}\ g\ PbCrO_4}{1\ L} \times \frac{1\ mol\ PbCrO_4}{323.2\ g\ PbCrO_4} = \frac{1.4 \times 10^{-8}\ mol\ PbCrO_4}{1\ L} = 1.4{\times}10^{-8}\ M$$

The dissolution equation for this compound is $PbCrO_4\ (s) \rightleftharpoons Pb^{2+}\ (aq) + CrO_4^{2-}\ (aq)$

The dissolution stoichiometry shows a 1:1 relation between the molar amounts of compound and its two ions, and so both $[Pb^{2+}]$ and $[CrO_4^{2-}]$ are equal to the molar solubility of $PbCrO_4$:

$$[Pb^{2+}] = [CrO_4^{2-}] = 1.4 \times 10^{-8}\ M$$

$$K_{sp} = [Pb^{2+}][CrO_4^{2-}] = (1.4 \times 10^{-8})(1.4 \times 10^{-8}) = 2.0 \times 10^{-16}$$

Check Your Learning

The solubility of TlCl [thallium(I) chloride], an intermediate formed when thallium is being isolated from ores, is 3.12 grams per liter at 20 °C. What is its solubility product?

ANSWER: 1.69×10^{-4}

EXAMPLE 16.10

Calculating the Solubility of Hg_2Cl_2

Calomel, Hg_2Cl_2, is a compound composed of the diatomic ion of mercury(I), Hg_2^{2+}, and chloride ions, $Cl^–$. Although most mercury compounds are now known to be poisonous, eighteenth-century physicians used calomel as a medication. Their patients rarely suffered any mercury poisoning from the treatments because calomel has a very low solubility, as suggested by its very small K_{sp}. Calculate the molar solubility of Hg_2Cl_2.

$$Hg_2Cl_2\,(s) \rightleftharpoons Hg_2^{2+}\,(aq) + 2Cl^-\,(aq) \quad K_{sp} = 1.1 \times 10^{-18}$$

Solution

The dissolution stoichiometry shows a 1:1 relation between the amount of compound dissolved and the amount of mercury(I) ions, and so the molar solubility of Hg_2Cl_2 is equal to the concentration of Hg_2^{2+} ions. Following the ICE approach results in

	$Hg_2Cl_2\,(s) \rightleftharpoons$	$Hg_2^{2+}\,(aq)$ +	$2Cl^-\,(aq)$
Initial concentration (*M*)		0	0
Change (*M*)		$+x$	$+2x$
Equilibrium concentration (*M*)		x	$2x$

Substituting the equilibrium concentration terms into the solubility product expression and solving for x gives

$$K_{sp} = [Hg_2^{2+}]\,[Cl^-]^2$$

$$1.1 \times 10^{-18} = (x)\,(2x)^2 = 4x^3$$

$$x = \sqrt[3]{\frac{1.1 \times 10^{-18}}{4}} = 6.5 \times 10^{-7}\ M$$

$$[Hg_2^{2+}] = x = 6.5 \times 10^{-7}\ M \qquad [Cl^-] = 2x = 2(6.5 \times 10^{-7}) = 1.3 \times 10^{-6}\ M$$

The dissolution stoichiometry shows the molar solubility of Hg_2Cl_2 is equal to $[Hg_2^{2+}]$, or 6.5×10^{-7} *M*.

Check Your Learning

Determine the molar solubility of MgF_2 from its solubility product: $K_{sp} = 6.4 \times 10^{-9}$.

ANSWER: 1.2×10^{-3} *M*

HOW SCIENCES INTERCONNECT

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. Since the K_{sp} of barium sulfate is 2.3×10^{-8}, very little of it dissolves as it coats the lining of the patient's intestinal tract. 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 15.4).

Figure 15.4 A suspension of barium sulfate coats the intestinal tract, permitting greater visual detail than a traditional X-ray. (credit modification of work by "glitzy queen00"/Wikimedia Commons)

Medical imaging using barium sulfate can be used to diagnose acid reflux disease, Crohn's disease, and ulcers in addition to other conditions.

Predicting Precipitation

The equation that describes the equilibrium between solid calcium carbonate and its solvated ions is:

$$CaCO_3(s) \rightleftharpoons Ca^{2+}(aq) + CO_3^{2-}(aq) \qquad K_{sp} = [Ca^{2+}][CO_3^{2-}] = 8.7 \times 10^{-9}$$

It is important to realize that this equilibrium is established in any aqueous solution containing Ca^{2+} and CO_3^{2-} ions, not just in a solution formed by saturating water with calcium carbonate. Consider, for example, mixing aqueous solutions of the soluble compounds sodium carbonate and calcium nitrate.

If the concentrations of calcium and carbonate ions in the mixture do not yield a reaction quotient, Q_{sp}, that exceeds the solubility product, K_{sp}, then no precipitation will occur.

If the ion concentrations yield a reaction quotient greater than the solubility product, then precipitation will occur, lowering those concentrations until equilibrium is established ($Q_{sp} = K_{\mathrm{sp}}$).

The comparison of Q_{sp} to K_{sp} to predict precipitation is an example of the general approach to predicting the direction of a reaction first introduced in the chapter on equilibrium. For the specific case of solubility equilibria:

$Q_{sp} < K_{\mathrm{sp}}$: the reaction proceeds in the forward direction (solution is not saturated; no precipitation observed)

$Q_{sp} > K_{\mathrm{sp}}$: the reaction proceeds in the reverse direction (solution is supersaturated; precipitation will occur)

This predictive strategy and related calculations are demonstrated in the next few example exercises.

EXAMPLE 16.11

Precipitation of $Mg(OH)_2$

The first step in the preparation of magnesium metal is the precipitation of $Mg(OH)_2$ from sea water by the addition of lime, $Ca(OH)_2$, a readily available inexpensive source of OH^- ion:

$$Mg(OH)_2\,(s) \rightleftharpoons Mg^{2+}\,(aq) + 2OH^-\,(aq) \qquad K_{sp} = 8.9 \times 10^{-12}$$

The concentration of $Mg^{2+}(aq)$ in sea water is 0.0537 *M*. Will $Mg(OH)_2$ precipitate when enough $Ca(OH)_2$ is added to give a $[OH^-]$ of 0.0010 *M*?

Solution

Calculation of the reaction quotient under these conditions is shown here:

$$Q = [Mg^{2+}]\,[OH^-]^2 = (0.0537)(0.0010)^2 = 5.4 \times 10^{-8}$$

Because Q is greater than K_{sp} ($Q = 5.4 \times 10^{-8}$ is larger than $K_{sp} = 8.9 \times 10^{-12}$), the reverse reaction will proceed, precipitating magnesium hydroxide until the dissolved ion concentrations have been sufficiently lowered, so that $Q_{sp} = K_{sp}$.

Check Your Learning

Predict whether $CaHPO_4$ will precipitate from a solution with $[Ca^{2+}] = 0.0001$ *M* and $[HPO_4^{2-}] = 0.001$ *M*.

ANSWER:

No precipitation of $CaHPO_4$; $Q = 1 \times 10^{-7}$, which is less than K_{sp} (7×10^{-7})

EXAMPLE 16.12

Precipitation of AgCl

Does silver chloride precipitate when equal volumes of a 2.0×10^{-4} M solution of $AgNO_3$ and a 2.0×10^{-4} M solution of NaCl are mixed?

Solution

The equation for the equilibrium between AgCl *(s)*, Ag^+ ion, and Cl^- ion is:

$$AgCl\,(s) \rightleftharpoons Ag^+\,(aq) + Cl^-\,(aq)$$

The solubility product is 1.6×10^{-10} (see Appendix 16.2). AgCl will precipitate if the reaction quotient calculated from the concentrations in the mixture of $AgNO_3$ and NaCl is greater than K_{sp}. Because the volume doubles when equal volumes of $AgNO_3$ and NaCl solutions are mixed, each concentration is reduced to half its initial value

$$\frac{1}{2}(2.0 \times 10^{-4})\text{ M} = 1.0 \times 10^{-4}\text{ M}$$

The Q, is greater than K_{sp} for AgCl, so a supersaturated solution is formed:

$$Q = [Ag^+][Cl^-] = (1.0 \times 10^{-4})(1.0 \times 10^{-4}) = 1.0 \times 10^{-8} > K_{sp}$$

AgCl will precipitate from the mixture until the dissolution equilibrium is established, with Q equal to K_{sp}.

Check Your Learning

Will $KClO_4$ precipitate when 20 mL of a 0.050-M solution of K^+ is added to 80 mL of a 0.50-M solution of ClO_4^-? (Hint: Use the dilution equation to calculate the concentrations of potassium and perchlorate ions in the mixture.)

ANSWER:

No, $Q = 4.0 \times 10^{-3}$, which is less than $K_{sp} = 1.05 \times 10^{-2}$

EXAMPLE 16.13

Precipitation of Calcium Oxalate

Blood will not clot if calcium ions are removed from its plasma. Some blood collection tubes contain salts of the oxalate ion, C2O42−, for this purpose (Figure 15.5). At sufficiently high concentrations, the calcium and oxalate ions form solid, $CaC_2O_4{\cdot}H_2O$ (calcium oxalate monohydrate). The concentration of Ca^{2+} in a sample of blood serum is 2.2×10^{-3} *M*. What concentration of C2O42− ion must be established before $CaC_2O_4{\cdot}H_2O$ begins to precipitate?

Figure 15.5 Anticoagulants can be added to blood that will combine with the Ca^{2+}ions in blood serum and prevent the blood from clotting.
(credit: modification of work by Neeta Lind)

Solution

The equilibrium expression is: $CaC_2O_4\ (s) \rightleftharpoons Ca^{2+}\ (aq) + C_2O_4^{2-}\ (aq)$

For this reaction: $K_{sp} = [Ca^{2+}][C_2O_4^{2-}] = 1.96 \times 10^{-8}$ (see Appendix 16.2)

Substitute the provided calcium ion concentration into the solubility product expression and solve for oxalate concentration:

$$K_{sp} = [Ca^{2+}][C_2O_4^{2-}] = 1.96 \times 10^{-8}$$

$$(2.2{\times}10{-}3)[C_2O_4^{2-}] = 1.96 \times 10^{-8}$$

$$[C_2O_4^{2-}] = \frac{1.96 \times 10^{-8}}{2.2 \times 10^{-3}} = 8.9 \times 10^{-6}\ \text{M}$$

A concentration of $[C_2O_4^{2-}] = 8.9 \times 10^{-6}$ *M* is necessary to initiate the precipitation of CaC_2O_4 under these conditions.

Check Your Learning

If a solution contains 0.0020 mol of CrO_4^{2-} per liter, what concentration of Ag^+ ion must be reached by adding solid $AgNO_3$ before Ag_2CrO_4 begins to precipitate? Neglect any increase in volume upon adding the solid silver nitrate.

ANSWER: 6.7×10^{-5} *M*

EXAMPLE 16.14

Concentrations Following Precipitation

Clothing washed in water that has a manganese [$Mn^{2+}(aq)$] concentration exceeding 0.1 mg/L (1.8×10^{-6} *M*) may be stained by the manganese upon oxidation, but the amount of Mn^{2+} in the water can be decreased by adding a base to precipitate $Mn(OH)_2$. What pH is required to keep [Mn^{2+}] equal to 1.8×10^{-6} *M*?

Solution

The dissolution of $Mn(OH)_2$ is described by the equation:

$$Mn(OH)_2\,(s) \rightleftharpoons Mn^{2+}\,(aq) + 2OH^-\,(aq) \qquad K_{sp} = 2 \times 10^{-13}$$

At equilibrium: $K_{sp} = [Mn^{2+}][OH^-]^2$ or $2 \times 10^{-13} = (1.8 \times 10^{-6})[OH^-]^2$

Thus, $[OH-] = \sqrt{\dfrac{2 \times 10^{-13}}{1.8 \times 10^{-6}}} = 3.3 \times 10^{-4}$ M

Calculate the pH from the pOH:

$pOH = -\log[OH-] = -\log(3.3 \times 10^{-4}) = 3.48$

$pH = 14.00 - pOH = 14.00 - 3.48 = 10.52$

(final result rounded to one significant digit, limited by the certainty of the K_{sp})

Check Your Learning

The first step in the preparation of magnesium metal is the precipitation of $Mg(OH)_2$ from sea water by the addition of $Ca(OH)_2$. The concentration of $Mg^{2+}(aq)$ in sea water is 5.37×10^{-2} *M*. Calculate the pH at which [Mg^{2+}] is decreased to 1.0×10^{-5} *M*

ANSWER: 10.97

CHEMISTRY IN EVERYDAY LIFE

The Role of Precipitation in Wastewater Treatment

Solubility equilibria are useful tools in the treatment of wastewater carried out in facilities that may treat the municipal water in your city or town (Figure 15.6). Specifically, selective precipitation is used to remove contaminants from wastewater before it is released back into natural bodies of water. For example, phosphate ions (PO_4^{3-}) are often present in the water discharged from manufacturing facilities. An abundance of phosphate causes excess algae to grow, which impacts the amount of oxygen available for marine life as well as making water unsuitable for human consumption.

Figure 15.6 Wastewater treatment facilities, such as this one, remove contaminants from wastewater before the water is released back into the natural environment. (credit: “eutrophication&hypoxia”/Wikimedia Commons)

One common way to remove phosphates from water is by the addition of calcium hydroxide, or lime, $Ca(OH)_2$. As the water is made more basic, the calcium ions react with phosphate ions to produce hydroxylapatite, $Ca_5(PO4)_3OH$, which then precipitates out of the solution:

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

Because the amount of calcium ion added does not result in exceeding the solubility products for other calcium salts, the anions of those salts remain behind in the wastewater. The precipitate is then removed by filtration and the water is brought back to a neutral pH by the addition of CO_2 in a recarbonation process. Other chemicals can also be used for the removal of phosphates by precipitation, including iron(III) chloride and aluminum sulfate.

Common Ion Effect

Compared with pure water, the solubility of an ionic compound is less in aqueous solutions containing a *common ion* (one also produced by dissolution of the ionic compound). This is an example of a phenomenon known as the **common ion effect**, which is a consequence of the law of mass action that may be explained using Le ChÂtelier's principle. Consider the dissolution of silver iodide:

$$\text{AgI (s)} \rightleftharpoons \text{Ag+ (aq)} + \text{I}^- \text{(aq)}$$

This solubility equilibrium may be shifted left by the addition of either silver(I) or iodide ions, resulting in the precipitation of AgI and lowered concentrations of dissolved Ag^+ and I^-. In solutions that already contain either of these ions, less AgI may be dissolved than in solutions without these ions.

This effect may also be explained in terms of mass action as represented in the solubility product expression:

$$K_{sp} = [\,Ag^+\,][\,I^-\,]$$

The mathematical product of silver(I) and iodide ion molarities is constant in an equilibrium mixture *regardless of the source of the ions*, and so an increase in one ion's concentration must be balanced by a proportional decrease in the other.

Common Ion Effect on Solubility

EXAMPLE 16.16

What is the effect on the amount of solid $Mg(OH)_2$ and the concentrations of Mg^{2+} and OH^- when each of the following are added to a saturated solution of $Mg(OH)_2$?

(a) $MgCl_2$ (b) KOH (c) $NaNO_3$ (d) $Mg(OH)_2$

Solution

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

(a) Adding a common ion, Mg^{2+}, will increase the concentration of this ion and shift the solubility equilibrium to the left, decreasing the concentration of hydroxide ion and increasing the amount of undissolved magnesium hydroxide.

(b) Adding a common ion, OH^-, will increase the concentration of this ion and shift the solubility equilibrium to the left, decreasing the concentration of magnesium ion and increasing the amount of undissolved magnesium hydroxide.

(c) The added compound does not contain a common ion, and no effect on the magnesium hydroxide solubility equilibrium is expected.

(d) Adding more solid magnesium hydroxide will increase the amount of undissolved compound in the mixture. The solution is already saturated, though, so the concentrations of dissolved magnesium and hydroxide ions will remain the same.

$$Q = [Mg^{2+}][OH^-]^2$$

Thus, changing the amount of solid magnesium hydroxide in the mixture has no effect on the value of *Q*, and no shift is required to restore *Q* to the value of the equilibrium constant.

Check Your Learning

What is the effect on the amount of solid $NiCO_3$ and the concentrations of Ni^{2+} and CO_3^{2-} when each of the following are added to a saturated solution of $NiCO_3$

(a) $Ni(NO_3)_2$ (b) $KClO_4$ (c) $NiCO_3$ (d) K_2CO_3

ANSWER:

(a) mass of $NiCO_3(s)$ increases, $[Ni^{2+}]$ increases, $[CO_3^{2-}]$ decreases;

(b) no appreciable effect;

(c) no effect except to increase the amount of solid $NiCO_3$;

(d) mass of $NiCO_3(s)$ increases, $[Ni^{2+}]$ decreases, $[CO_3^{2-}]$increases;

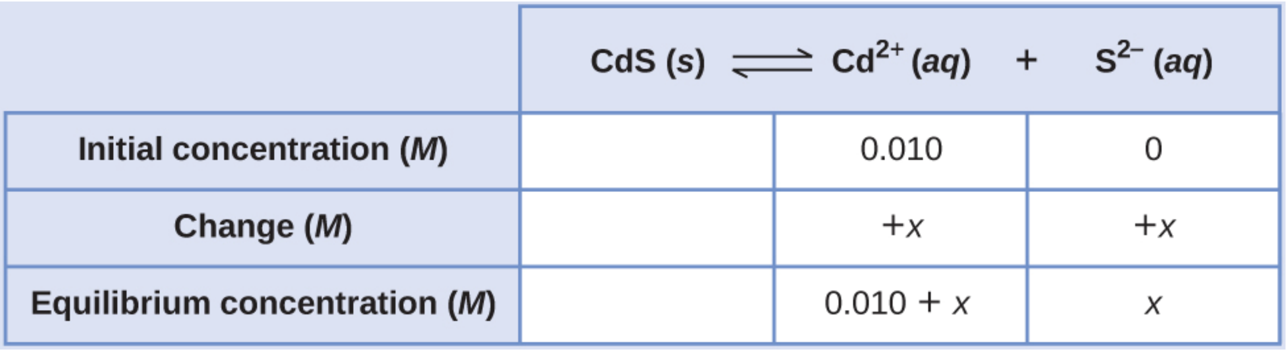
EXAMPLE 16.17

Calculate the molar solubility of cadmium sulfide (CdS) in a 0.010-*M* solution of cadmium bromide ($CdBr_2$). The K_{sp} of CdS is 1.0×10^{-28}.

Solution

This calculation can be performed using the ICE approach:

$$CdS\ (s) \rightleftharpoons Cd^{2+}\ (aq) + S^{2-}\ (aq)$$



	CdS (s) ⇌	Cd^{2+} (*aq*) +	S^{2-} (*aq*)
Initial concentration (*M*)		0.010	0
Change (*M*)		$+x$	$+x$
Equilibrium concentration (*M*)		$0.010 + x$	x

$$Ksp = [Cd^{2+}][S^{2-}] = 1.0 \times 10^{-28}$$

$$(0.010+x)(x) = 1.0 \times 10^{-28}$$

Because K_{sp} is very small, assume $x << 0.010$ and solve the simplified equation for x:

$$(0.010)(x) = 1.0 \times 10^{-28}$$

$$x = 1.0 \times 10^{-26}\ M$$

The molar solubility of CdS in this solution is 1.0×10^{-26} *M*.

Check Your Learning

Calculate the molar solubility of aluminum hydroxide, $Al(OH)_3$, in a 0.015 M solution of aluminum nitrate, $Al(NO_3)_3$. The $K_{sp}$of $Al(OH)_3$ is 2×10^{-32}.

ANSWER: 4×10^{-11} *M*

Appendix 16.2: Solubility Products

Substance	**K_{sp} at 25 °C**	**Substance**	**K_{sp} at 25 °C**
$Al(OH)_3$	2×10^{-32}	CoS(*α*)	5×10^{-22}
$BaCO_3$	1.6×10^{-9}	CoS(*β*)	3×10^{-26}
$BaC_2O_4 \cdot 2H_2O$	1.1×10^{-7}	$CoCO_3$	1.4×10^{-13}
$BaSO_4$	2.3×10^{-8}	$Co(OH)_3$	2.5×10^{-43}
$BaCrO_4$	8.5×10^{-11}	CuCl	1.2×10^{-6}
BaF_2	2.4×10^{-5}	CuBr	6.27×10^{-9}
$Ba(OH)_2 \cdot 8H_2O$	5.0×10^{-3}	CuI	1.27×10^{-12}
$Ba_3(PO_4)_2$	6×10^{-39}	CuSCN	1.6×10^{-11}
$Ba_3(AsO_4)_2$	1.1×10^{-13}	Cu_2S	2.5×10^{-48}
BiO(OH)	4×10^{-10}	$Cu(OH)_2$	2.2×10^{-20}
BiOCl	1.8×10^{-31}	CuS	8.5×10^{-45}
Bi_2S_3	1×10^{-97}	$CuCO_3$	2.5×10^{-10}
$Cd(OH)_2$	5.9×10^{-15}	$Fe(OH)_2$	1.8×10^{-15}
CdS	1.0×10^{-28}	$FeCO_3$	2.1×10^{-11}
$CdCO_3$	5.2×10^{-12}	FeS	3.7×10^{-19}
$Ca(OH)_2$	1.3×10^{-6}	$Fe(OH)_3$	4×10^{-38}
$CaCO_3$	8.7×10^{-9}	$Pb(OH)_2$	1.2×10^{-15}
$CaSO_4 \cdot 2H_2O$	6.1×10^{-5}	PbF_2	4×10^{-8}
$CaC_2O_4 \cdot H_2O$	1.96×10^{-8}	$PbCl_2$	1.6×10^{-5}
$Ca_3(PO_4)_2$	1.3×10^{-32}	$PbBr_2$	4.6×10^{-6}
$CaHPO_4$	7×10^{-7}	PbI_2	1.4×10^{-8}
CaF_2	4.0×10^{-11}	$PbCO_3$	1.5×10^{-15}
$Co(OH)_2$	2.5×10^{-16}	PbS	7×10^{-29}
$Cr(OH)_3$	6.7×10^{-31}	$PbCrO_4$	2×10^{-16}

Substance	***K*$_{sp}$ at 25 °C**	**Substance**	***K*$_{sp}$ at 25 °C**
$PbSO_4$	1.3×10^{-8}	$KHC_4H_4O_6$	3×10^{-4}
$Pb_3(PO_4)_2$	1×10^{-54}	$AgCl$	1.6×10^{-10}
$Mg(OH)_2$	8.9×10^{-12}	$AgBr$	5.0×10^{-13}
$MgCO_3 \cdot 3H_2O$	*ca* 1×10^{-5}	AgI	1.5×10^{-16}
$MgNH_4PO_4$	3×10^{-13}	$AgCN$	1.2×10^{-16}
MgF_2	6.4×10^{-9}	$AgSCN$	1.0×10^{-12}
MgC_2O_4	7×10^{-7}	Ag_2S	1.6×10^{-49}
$Mn(OH)_2$	2×10^{-13}	Ag_2CO_3	8.1×10^{-12}
$MnCO_3$	8.8×10^{-11}	Ag_2CrO_4	9.0×10^{-12}
MnS	2.3×10^{-13}	$Ag_4Fe(CN)_6$	1.55×10^{-41}
$Hg_2O \cdot H_2O$	3.6×10^{-26}	Ag_2SO_4	1.2×10^{-5}
Hg_2Cl_2	1.1×10^{-18}	Ag_3PO_4	1.8×10^{-18}
Hg_2Br_2	1.3×10^{-22}	$Sr(OH)_2 \cdot 8H_2O$	3.2×10^{-4}
Hg_2I_2	4.5×10^{-29}	$SrCO_3$	7×10^{-10}
Hg_2CO_3	9×10^{-15}	$SrCrO_4$	3.6×10^{-5}
Hg_2SO_4	7.4×10^{-7}	$SrSO_4$	3.2×10^{-7}
Hg_2S	1.0×10^{-47}	$SrC_2O_4 \cdot H_2O$	4×10^{-7}
Hg_2CrO_4	2×10^{-9}	$TlCl$	1.7×10^{-4}
HgS	1.6×10^{-54}	$TlSCN$	1.6×10^{-4}
$Ni(OH)_2$	1.6×10^{-16}	Tl_2S	6×10^{-22}
$NiCO_3$	1.4×10^{-7}	$Tl(OH)_3$	6.3×10^{-46}
$NiS(\alpha)$	4×10^{-20}	$Sn(OH)_2$	3×10^{-27}
$NiS(\beta)$	1.3×10^{-25}	SnS	1×10^{-26}
$KClO_4$	1.05×10^{-2}	$Sn(OH)_4$	1.0×10^{-57}
K_2PtCl_6	7.48×10^{-6}	$ZnCO_3$	2×10^{-10}

16.3 Coupled Equilibria

Learning Objectives

- Describe examples of systems involving two (or more) coupled chemical equilibria
- Describe the effect of acidity and basicity on the solubility

Coupled Equilibria

Coupled equilibria involve two or more separate chemical reactions that share one or more reactants or products. This section of this chapter will address solubility equilibria coupled with acid-base and complex-formation reactions.

An environmentally relevant example illustrating the coupling of solubility and acid-base equilibria is the impact of ocean acidification on the health of the ocean's coral reefs. These reefs are built upon skeletons of sparingly soluble calcium carbonate excreted by colonies of corals (small marine invertebrates). The relevant dissolution equilibrium is

$$CaCO_3\ (s) \rightleftharpoons Ca^{2+}\ (aq) + CO_3^{2-}\ (aq) \qquad K_{sp} = 8.7 \times 10^{-9}$$

Rising concentrations of atmospheric carbon dioxide contribute to an increased acidity of ocean waters due to the dissolution, hydrolysis, and acid ionization of carbon dioxide:

$$CO_2\ (g) \rightleftharpoons CO_2\ (aq)$$

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

$$H_2CO_3\ (aq) + H_2O\ (l) \rightleftharpoons HCO_3^-\ (aq) + H_3O^+\ (aq) \qquad Ka_1 = 4.3 \times 10^{-7}$$

$$HCO_3^-\ (aq) + H_2O\ (l) \rightleftharpoons CO_3^{2-}\ (aq) + H_3O^+\ (aq) \qquad Ka_2 = 4.7 \times 10^{-11}$$

Inspection of these equilibria shows the carbonate ion is involved in the calcium carbonate dissolution and the acid hydrolysis of bicarbonate ion. Combining the dissolution equation with the reverse of the acid hydrolysis equation yields

$$CaCO_3\ (s) + H_3O^+\ (aq) \rightleftharpoons Ca^{2+}\ (aq) + HCO_3^-\ (aq) + H_2O(l) \qquad K = K_{sp}/Ka_2 = 180$$

The equilibrium constant for this net reaction is much greater than the K_{sp} for calcium carbonate, indicating its solubility is markedly increased in acidic solutions. As rising carbon dioxide levels in the atmosphere increase the acidity of ocean waters, the calcium carbonate skeletons of coral reefs become more prone to dissolution and subsequently less healthy (Figure 15.7).

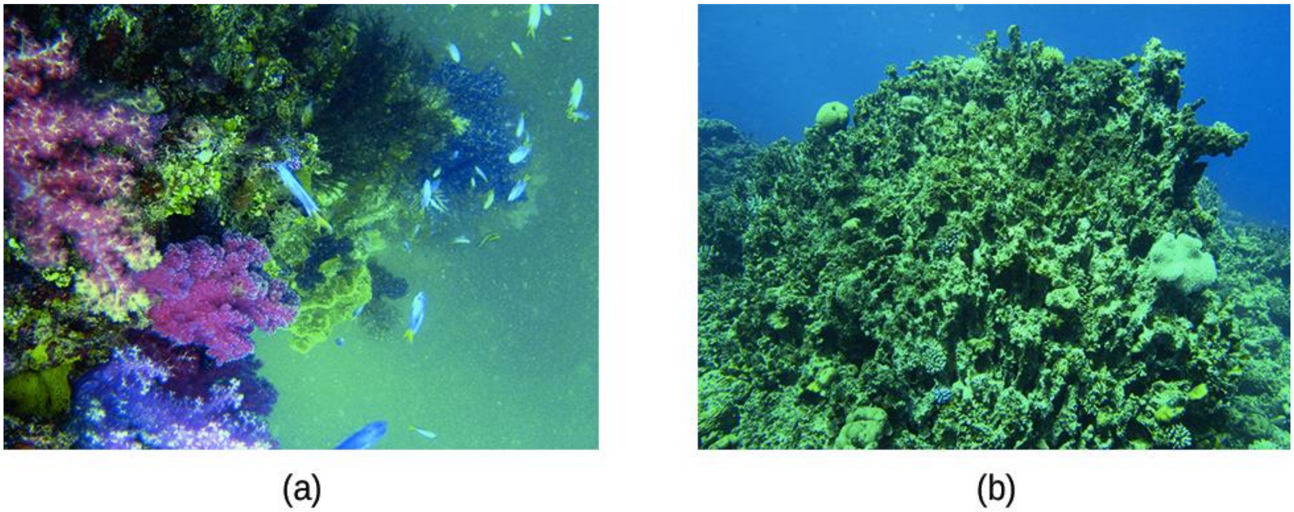


Figure 15.7 Healthy coral reefs (a) support a dense and diverse array of sea life across the ocean food chain. But when coral are unable to adequately build and maintain their calcium carbonate skeletons because of excess ocean acidification, the unhealthy reef (b) is only capable of hosting a small fraction of the species as before, and the local food chain starts to collapse. (credit a: modification of work by NOAA Photo Library; credit b: modification of work by “prilfish”/Flickr)

The dramatic increase in solubility with increasing acidity described above for calcium carbonate is typical of salts containing basic anions (e.g., carbonate, fluoride, hydroxide, sulfide). Another familiar example is the formation of dental cavities in tooth enamel. The major mineral component of enamel is calcium hydroxyapatite (Figure 15.8), a sparingly soluble ionic compound whose dissolution equilibrium is

$$Ca_5(PO_4)_3OH\ (s) \rightleftharpoons 5Ca^{2+}\ (aq) + 3PO_4^{3-}\ (aq) + OH^-\ (aq)$$

Figure 15.8 Crystal of the mineral hydroxyapatite, $Ca_5(PO_4)_3OH$, is shown here. The pure compound is white, but like many other minerals, this sample is colored because of the presence of impurities.

This compound dissolved to yield two different basic ions: triprotic phosphate ions

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

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

$$H_2PO_4^-(aq) + H_3O^+(aq) \rightleftharpoons H_3PO_4(aq) + H_2O(l)$$

and monoprotic hydroxide ions:

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

Of the two basic productions, the hydroxide is, of course, by far the stronger base (it’s the strongest base that can exist in aqueous solution), and so it is the dominant factor providing the compound an acid-dependent solubility. Dental cavities form when the acid waste of bacteria growing on the surface of teeth hastens the dissolution of tooth enamel by reacting completely with the strong base hydroxide, shifting the hydroxyapatite solubility equilibrium to the right. Some toothpastes and mouth rinses contain added NaF or SnF_2 that make enamel more acid resistant by replacing the strong base hydroxide with the weak base fluoride:

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

The weak base fluoride ion reacts only partially with the bacterial acid waste, resulting in a less extensive shift in the solubility equilibrium and an increased resistance to acid dissolution. See the Chemistry in Everyday Life feature on the role of fluoride in preventing tooth decay for more information.

CHEMISTRY IN EVERYDAY LIFE

Role of Fluoride in Preventing Tooth Decay

As we saw previously, 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 15.9).

Figure 15.9 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.

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Changed introduction and entropy and microstate

Modified change of entropy of surrounding and the prediction of the sign of $\Delta S_{surrounding}$

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Chapter 17 Thermodynamics

Chapter Introduction

Figure 17.1 Geysers are a dramatic display of thermodynamic principles in nature. Water deep within the underground channels of the geyser is under high pressure and heated to high temperature by magma. When a pocket of water near the surface reaches boiling point and is expelled, the resulting drop in pressure causes larger volumes of water to flash boil, forcefully ejecting steam and water in an impressive eruption. (credit: modification of work by Yellowstone National Park)

Among the many capabilities of chemistry is its ability to predict if a process will occur under specified conditions. Thermodynamics, the study of relationships between the energy and work associated with chemical and physical processes, provides this predictive ability. Previous chapters in this text have described various applications of thermochemistry, an important aspect of thermodynamics concerned with the heat flow accompanying chemical reactions and phase transitions. This chapter will introduce additional thermodynamic concepts, including those that enable the prediction of any chemical or physical changes under a given set of conditions.

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17.1 Spontaneous and Nonspontaneous Processes

Learning Objectives

- Distinguish between spontaneous and nonspontaneous processes
- Describe the dispersal of matter and energy that accompanies certain spontaneous processes

Spontaneity

Processes have a natural tendency to occur in one direction under a given set of conditions. Water will naturally flow downhill, but uphill flow requires outside intervention such as the use of a pump. Iron exposed to the earth’s atmosphere will corrode, but rust is not converted to iron without intentional chemical treatment. A **spontaneous process** is one that occurs naturally under certain conditions. A **nonspontaneous process**, on the other hand, will not take place unless it is “driven” by the continual input of energy from an external source. A process that is spontaneous in one direction under a particular set of conditions is nonspontaneous in the reverse direction. At room temperature and typical atmospheric pressure, for example, ice will spontaneously melt, but water will not spontaneously freeze.

Thermodynamics vs. Kinetics

The spontaneity of a process is *not* correlated to the speed of the process. A spontaneous change may be so rapid that it is essentially instantaneous or so slow that it cannot be observed over any practical period of time. To illustrate this concept, consider the decay of radioactive isotopes, a topic more thoroughly treated in the chapter on nuclear chemistry. Radioactive decay is by definition a spontaneous process in which the nuclei of unstable isotopes emit radiation as they are converted to more stable nuclei. All the decay processes occur spontaneously, but the rates at which different isotopes decay vary widely. Technetium-99m is a popular radioisotope for medical imaging studies that undergoes relatively rapid decay and exhibits a half-life of about six hours.

Uranium-238 is the most abundant isotope of uranium, and its decay occurs much more slowly, exhibiting a half-life of more than four billion years (Figure 17.2).

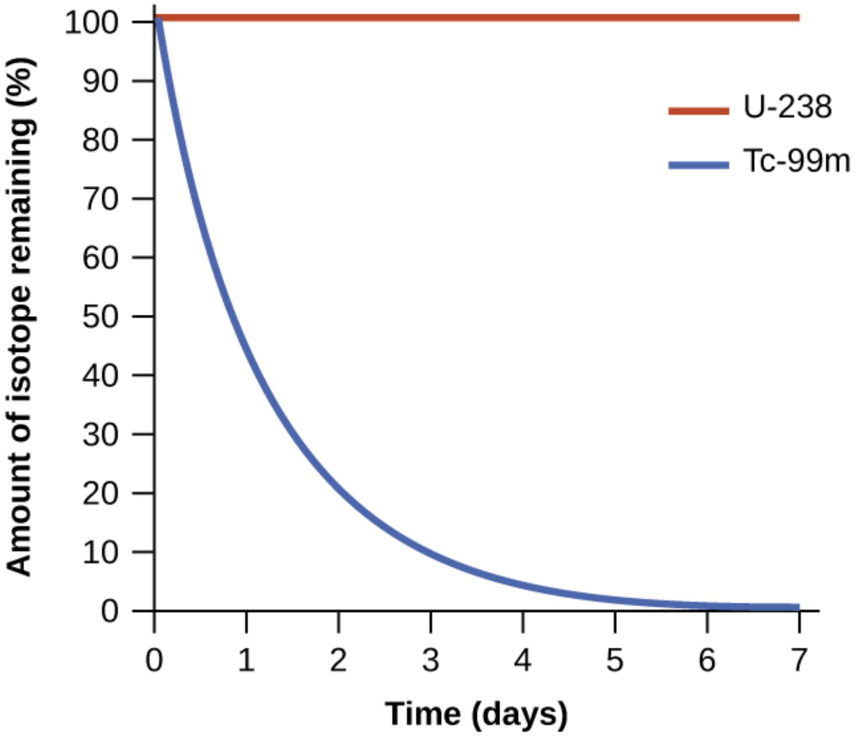


Figure 17.2 Both U-238 and Tc-99m undergo spontaneous radioactive decay, but at drastically different rates. Over the course of one week, essentially all of a Tc-99m sample and none of a U-238 sample will have decayed.

As another example, consider the conversion of diamond into graphite (Figure 17.3).

$$\text{C (s, diamond)} \longrightarrow \text{C (s, graphite)}$$

The phase diagram for carbon indicates that graphite is the stable form of this element under ambient atmospheric pressure, while diamond is the stable allotrope at very high pressures, such as those present during its geologic formation. Thermodynamic calculations of the sort described in the last section of this chapter indicate that the conversion of diamond to graphite at ambient pressure occurs spontaneously, yet diamonds are observed to exist, and persist, under these conditions. Though the process is spontaneous under typical ambient conditions, its rate is extremely slow; so, for all practical purposes diamonds are indeed “forever.” Situations such as these emphasize the important distinction between the thermodynamic and the kinetic aspects of a process. In this particular case, diamonds are said to be *thermodynamically unstable* but *kinetically stable* under ambient conditions.

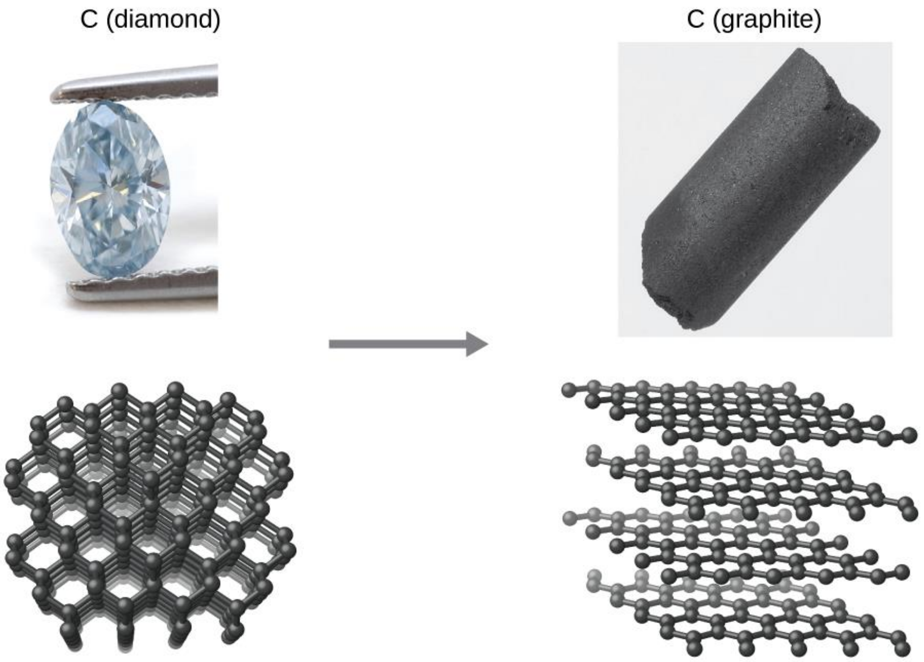


Figure 17.3 The conversion of carbon from the diamond allotrope to the graphite allotrope is spontaneous at ambient pressure, but its rate is immeasurably slow at low to moderate temperatures. This process is known as *graphitization*, and its rate can be increased to easily measurable values at temperatures in the 1000–2000 K range. (credit "diamond" photo: modification of work by "Fancy Diamonds"/Flickr; credit "graphite" photo: modificaton of work by images-of-elements.com/carbon.php)

Dispersal of Matter and Energy

Extending the discussion of thermodynamic concepts toward the objective of predicting spontaneity, consider now an isolated system consisting of two flasks connected with a closed valve. Initially there is an ideal gas in one flask and the other flask is empty (Figure 17.4). When the valve is opened, the gas spontaneously expands to fill both flasks equally.

The spontaneity of this process is not a consequence of any change in energy that accompanies the process. Instead, the driving force appears to be related to the *greater, more uniform dispersal of matter* that results when the gas is allowed to expand. Initially, the system was comprised of one flask containing matter and another flask containing nothing. After the spontaneous expansion took place, the matter was distributed both more widely (occupying twice its original volume) and more uniformly (present in equal amounts in each flask).

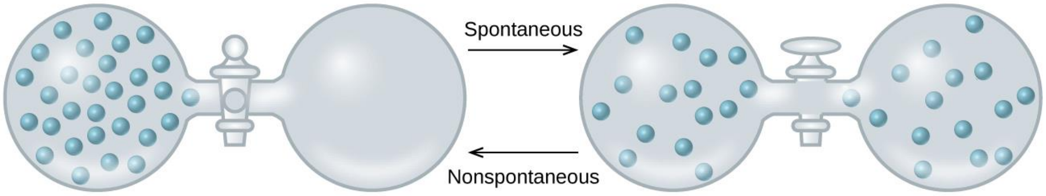


Figure 17.4 An isolated system consists of an ideal gas in one flask that is connected by a closed valve to a second flask containing a vacuum. Once the valve is opened, the gas spontaneously becomes evenly distributed between the flasks.

Now consider two objects at different temperatures: object X at temperature T_X and object Y at temperature T_Y, with $T_X > T_Y$ (Figure 17.5). When these objects come into contact, heat spontaneously flows from the hotter object (X) to the colder one (Y). This corresponds to a loss of thermal energy by X and a gain of thermal energy by Y.

From the perspective of this two-object system, there was no net gain or loss of thermal energy, rather the available thermal energy was redistributed among the two objects. This spontaneous process resulted in a *more uniform dispersal of energy*.

Figure 17.5 When two objects at different temperatures come in contact, heat spontaneously flows from the hotter to the colder object.

As illustrated by the two processes described, an important factor in determining the spontaneity of a process is the extent to which it changes the dispersal or distribution of matter and/or energy. In each case, a spontaneous process took place that resulted in a more uniform distribution of matter or energy.

Redistribution of Matter during a Spontaneous Process

EXAMPLE 17.1

Describe how matter is redistributed when the following spontaneous processes occur:

(a) A solid sublimes.

(b) A gas condenses.

(c) A drop of food coloring added to a glass of water forms a solution with uniform color.

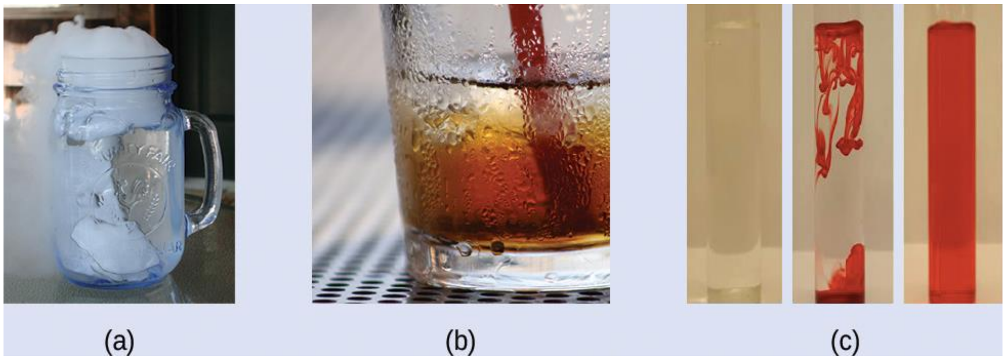


Figure 17.6 (credit a: modification of work by Jenny Downing; credit b: modification of work by "Fuzzy Gerdes"/Flickr; credit c: modification of work by Paul A. Flowers)

Solution

(a) Sublimation is the conversion of a solid (relatively high density) to a gas (much lesser density). This process yields a much greater dispersal of matter, since the molecules will occupy a much greater volume after the solid-to-gas transition.

(b) Condensation is the conversion of a gas (relatively low density) to a liquid (much greater density). This process yields a much lesser dispersal of matter, since the molecules will occupy a much lesser volume after the gas-to-liquid transition.

(c) The process in question is diffusion. This process yields a more uniform dispersal of matter, since the initial state of the system involves two regions of different dye concentrations (high in the drop of dye, zero in the water), and the final state of the system contains a single dye concentration throughout.

Check Your Learning

Describe how energy is redistributed when a spoon at room temperature is placed in a cup of hot coffee.

ANSWER: Heat will spontaneously flow from the hotter object (coffee) to the colder object (spoon), resulting in a more uniform distribution of thermal energy as the spoon warms and the coffee cools.

17.2 Entropy and the Second & Third Laws of Thermodynamics

Learning Objectives

- Define entropy
- State and explain the second and third laws of thermodynamics
- Predict the sign of the entropy change for the system including chemical and physical processes
- Predict the sign of the entropy change for the surrounding using enthalpy change for the system
- Calculate entropy changes for phase transitions and chemical reactions under standard conditions

Introduction

In 1824, a new thermodynamic property that relates the spontaneous heat flow accompanying the temperature at which the process takes place was introduced. This new thermodynamic property is called **entropy (*S*).** Similar to other thermodynamic properties, entropy is a state function, so its change depends only upon the initial and final states of a system. The entropy (*S*) was expressed as the ratio of the *reversible* heat (q_{rev}) and the kelvin temperature (*T*). In thermodynamics, a **reversible process** is one that takes place at such a slow rate that it is always at equilibrium and its direction can be changed (it can be "reversed") by an infinitesimally small change in some condition. Note that the idea of a reversible process is a formalism required to support the development of various thermodynamic concepts; no real processes are truly reversible, rather they are classified as *irreversible*.

Thus, we defined entropy change for any process as the following: $\Delta S = \frac{q_{rev}}{T}$

The entropy change for a real, irreversible process is then equal to that for the theoretical reversible process that involves the same initial and final states.

Entropy and Microstates

Later, a molecular-scale statistical model developed by Ludwig Boltzmann was developed to relate the entropy of a system to the *number of microstates* (*W*) possible for the system. A **microstate** is a specific configuration of all the locations and energies of the atoms or molecules that make up a system. The relation between a system's entropy and the number of possible microstates is

$$S = k \cdot \ln W$$

where *k* is the Boltzmann constant, 1.38×10^{-23} J/K.

As for other state functions, the change in entropy for a process is the difference between its final (S_f) and initial (S_i) values:

$$\Delta S = S_f - S_i = k \cdot \ln W_f - k \cdot \ln W_i = k \cdot \ln \frac{W_f}{W_i}$$

For processes involving an increase in the number of microstates, $W_f > W_i$, the entropy of the system increases and $\Delta S > 0$.

Conversely, processes that reduce the number of microstates, $W_f < W_i$, yield a decrease in system entropy, $\Delta S < 0$.

This molecular-scale interpretation of entropy provides a link to the probability that a process will occur as illustrated in the next paragraphs.

Consider the general case of a system comprised of *N* particles distributed among *n* boxes. The number of microstates possible for such a system is n^N.
For example, distributing four particles among two boxes will result in $2^4 = 16$ different microstates as illustrated in Figure 17.7. Microstates with equivalent particle arrangements (not considering individual particle identities) are grouped together and are called *distributions*. The probability that a system will exist with its components in a given distribution is proportional to the number of microstates within the distribution. Since entropy increases logarithmically with the number of microstates, *the most probable distribution is therefore the one of greatest entropy*.

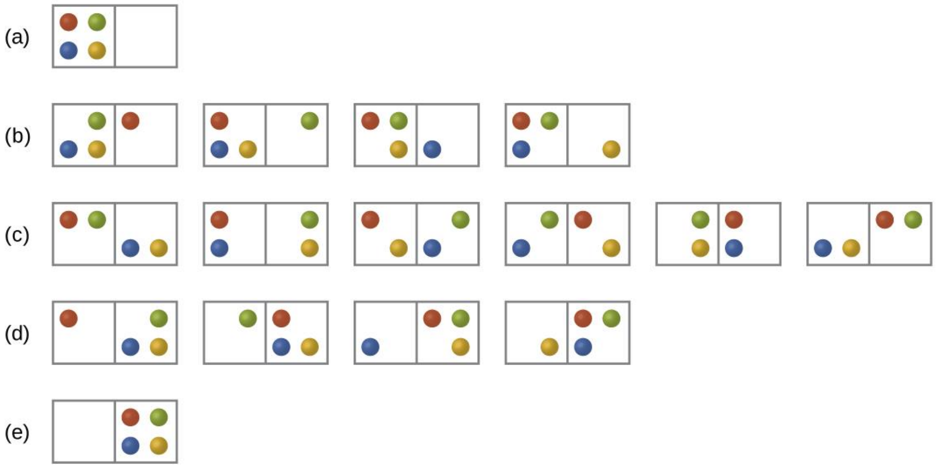


Figure 17.7 The sixteen microstates associated with placing four particles in two boxes are shown. The microstates are collected into five distributions—(a), (b), (c), (d), and (e)—based on the numbers of particles in each box.

For this system, the most probable configuration is one of the six microstates associated with distribution (c) where the particles are evenly distributed between the boxes, that is, a configuration of two particles in each box. The probability of finding the system in this configuration is $\frac{6}{16}$. The least probable configuration of the system is one in which all four particles are in one box, corresponding to distributions (a) and (e), each with a probability of $\frac{1}{16}$. The probability of finding all particles in only one box (either the left box or right box) is then $(\frac{1}{16} + \frac{1}{16}) = \frac{2}{16}$.

As you add more particles to the system, the number of possible microstates increases exponentially (2^N). A macroscopic (laboratory-sized) system would typically consist of moles of particles ($N \sim 10^{23}$), and the corresponding number of microstates would be staggeringly huge. Regardless of the number of particles in the system, however, the distributions in which roughly equal numbers of particles are found in each box are always the most probable configurations.

This matter dispersal model of entropy is often described qualitatively in terms of the *disorder* of the system. By this description, microstates in which all the particles are in a single box are the most ordered, thus possessing the least entropy. Microstates in which the particles are more evenly distributed among the boxes are more disordered, possessing greater entropy.

The previous description of an ideal gas expanding into a vacuum (Figure 17.4) is a macroscopic example of this particle-in-a-box model. For this system, the most probable distribution is confirmed to be the one in which the matter is most uniformly dispersed or distributed between the two flasks. Initially, the gas molecules are confined to just one of the two flasks. Opening the valve between the flasks increases the volume available to the gas molecules and, correspondingly, the number of microstates possible for the system. Since $W_f > W_i$, the expansion process involves an increase in entropy ($\Delta S > 0$) and is spontaneous.

A similar approach may be used to describe the spontaneous flow of heat and will support the common observation that placing hot and cold objects in contact results in spontaneous heat flow that ultimately equalizes the objects' temperatures.

The Second Law of Thermodynamics

In the quest to identify a property that may reliably predict the spontaneity of a process, a promising candidate has been identified: entropy. Processes that involve an increase in entropy *of the system* ($\Delta S > 0$) are very often spontaneous; however, examples to the contrary are plentiful. By expanding consideration of entropy changes to include *the surroundings*, we may reach a significant conclusion regarding the relation between this property and spontaneity. In thermodynamic models, the system and surroundings comprise everything, that is, the universe, and so the following is true:

$$\Delta S_{univ} = \Delta S_{sys} + \Delta S_{surr}$$

To illustrate this relation, consider again the process of heat flow between two objects, one identified as the system and the other as the surroundings. There are three possibilities for such a process:

1. The objects are at different temperatures, and heat flows from the hotter to the cooler object. *This is always observed to occur spontaneously.* Designating the hotter object as the system and invoking the definition of entropy yields the following:

$$\Delta S_{sys} = \frac{-q_{rev}}{T_{sys}} \quad \text{and} \quad \Delta S_{surr} = \frac{q_{rev}}{T_{surr}}$$

The magnitudes of $-q_{\text{rev}}$ and q_{rev} are equal, their opposite arithmetic signs denoting loss of heat by the system and gain of heat by the surroundings. Since $T_{\text{sys}} > T_{\text{surr}}$ in this scenario, the entropy *decrease* of the system will be less than the entropy *increase* of the surroundings, and so *the entropy of the universe will increase*:

$$\Delta S_{\text{univ}} = \Delta S_{\text{sys}} + \Delta S_{\text{surr}} > 0$$

2. The objects are at different temperatures, and heat flows from the cooler to the hotter object. *This is never observed to occur spontaneously.* Again designating the hotter object as the system and invoking the definition of entropy yields the following:

$$\Delta S_{\text{sys}} = \frac{q_{rev}}{T_{sys}} \quad \text{and} \quad \Delta S_{\text{surr}} = \frac{-q_{rev}}{T_{surr}}$$

The arithmetic signs of q_{rev} denote the gain of heat by the system and the loss of heat by the surroundings. Since $T_{\text{sys}} > T_{\text{surr}}$ in this scenario, the entropy *increase* of the system will be less than the entropy *decrease* of the surroundings, and so *the entropy of the universe will decrease,* yielding a negative value for ΔS_{univ}:

$$\Delta S_{\text{univ}} = \Delta S_{\text{sys}} + \Delta S_{\text{surr}} < 0$$

3. The objects are at essentially the same temperature, $T_{\text{sys}} \approx T_{\text{surr}}$, and so the magnitudes of the entropy changes are essentially the same for both the system and the surroundings. In this case, the entropy change of the universe is zero, and the system is *at equilibrium*.

$$\Delta S_{\text{univ}} = \Delta S_{\text{sys}} + \Delta S_{\text{surr}} = 0$$

These results lead to a profound statement regarding the relation between entropy and spontaneity known as the **second law of thermodynamics**: *all spontaneous changes cause an increase in the entropy of the universe.* A summary of these three relations is provided in Table 17.1.

Table 17.1 A Summary of The Entropy Change of The Universe and Spontaneity

$\Delta S_{\text{univ}} > 0$	spontaneous
$\Delta S_{\text{univ}} < 0$	nonspontaneous (spontaneous in opposite direction)
$\Delta S_{\text{univ}} = 0$	at equilibrium

Predicting the Sign of ΔS_{system}

The relationships between entropy, microstates, and matter/energy dispersal described previously allow us to make generalizations regarding the relative entropies of substances and to predict the sign of entropy changes for chemical and physical processes. Consider the phase changes illustrated in Figure 17.8. In the solid phase, the atoms or molecules are restricted to nearly fixed positions with respect to each other and are capable of only modest oscillations about these positions. With essentially fixed locations for the system's component particles, the number of microstates is relatively small. In the liquid phase, the atoms or molecules are free to move over and around each other, though they remain in relatively close proximity to one another. This increased freedom of motion results in a greater variation in possible particle locations, so the number of microstates is correspondingly greater than for the solid. As a result, $S_{\text{liquid}} > S_{\text{solid}}$ and the process of converting a substance from solid to liquid (melting) is characterized by an increase in entropy, $\Delta S > 0$. By the same logic, the reciprocal process (freezing) exhibits a decrease in entropy, $\Delta S < 0$.

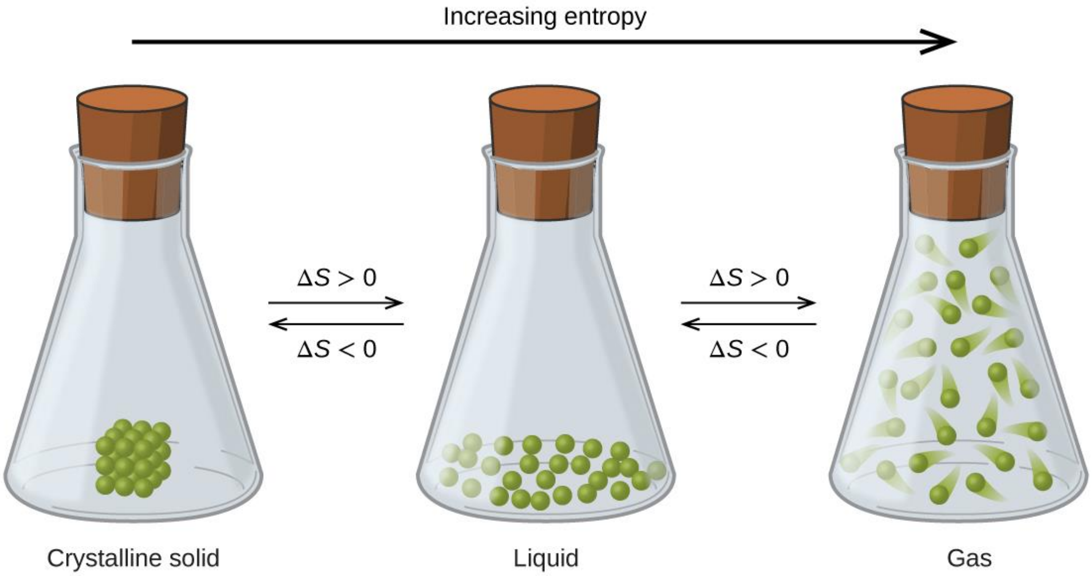


Figure 17.8 The entropy of a substance increases ($\Delta S > 0$) as it transforms from a relatively ordered solid, to a less-ordered liquid, and then to a still less-ordered gas. The entropy decreases ($\Delta S < 0$) as the substance transforms from a gas to a liquid and then to a solid.

Now consider the gaseous phase, in which a given number of atoms or molecules occupy a *much* greater volume than in the liquid phase. Each atom or molecule can be found in many more locations, corresponding to a much greater number of microstates. Consequently, for any substance, $S_{gas} > S_{liquid} > S_{solid}$, and the processes of vaporization and sublimation likewise involve increases in entropy, $\Delta S > 0$. Likewise, the reciprocal phase transitions, condensation and deposition, involve decreases in entropy, $\Delta S < 0$.

According to kinetic-molecular theory, the temperature of a substance is proportional to the average kinetic energy of its particles. Raising the temperature of a substance will result in more extensive vibrations of the particles in solids and more rapid translations of the particles in liquids and gases. At higher temperatures, the distribution of kinetic energies among the atoms or molecules of the substance is also broader (more dispersed) than at lower temperatures. Thus, the entropy for any substance increases with temperature (Figure 17.9).

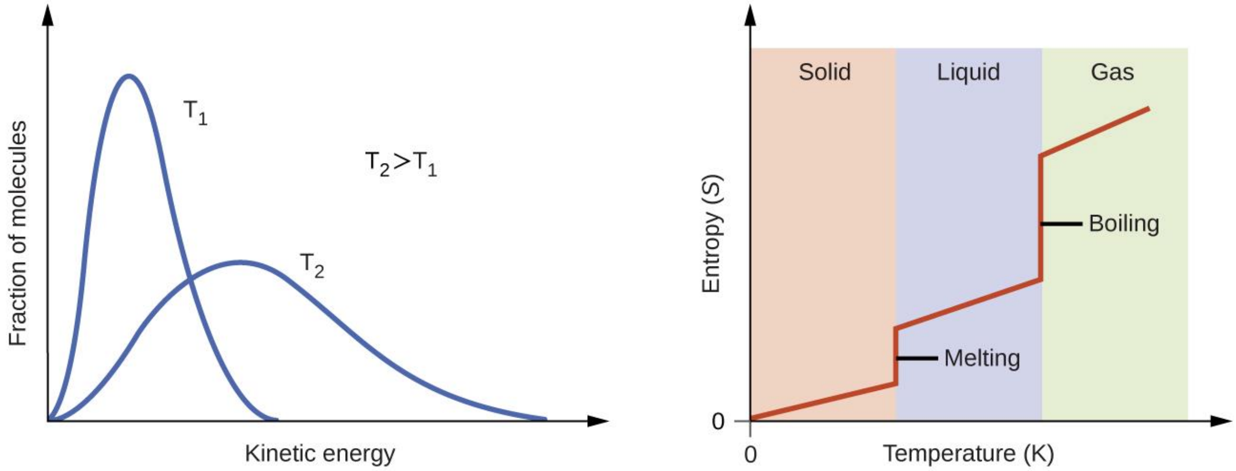


Figure 17.9 Entropy increases as the temperature of a substance is raised, which corresponds to the greater spread of kinetic energies. When a substance undergoes a phase transition, its entropy changes significantly.

The entropy of a substance is influenced by the structure of the particles (atoms or molecules) that comprise the substance. With regard to atomic substances, heavier atoms possess greater entropy at a given temperature than lighter atoms, which is a consequence of the relation between a particle’s mass and the spacing of quantized translational energy levels (a topic beyond the scope of this text). For molecules, greater numbers of atoms increase the number of ways in which the molecules can vibrate and thus the number of possible microstates and the entropy of the system.

Finally, variations in the types of particles affect the entropy of a system. Compared to a pure substance, the entropy of a mixture is greater. This is because of the additional orientations and interactions that are possible in a system comprised of nonidentical components. For example, when a solid dissolves in a liquid, the particles of the solid experience both a greater freedom of motion and additional interactions with the solvent particles. This corresponds to a more uniform dispersal of matter and energy and a greater number of microstates. The process of dissolution therefore involves an increase in entropy, $\Delta S > 0$. Considering the various factors that affect entropy allows us to make predictions of the sign of ΔS for various processes as illustrated in Example 17.2 .

EXAMPLE 17.2

Predict the sign of the entropy change for the following processes. Indicate the reason for each of your predictions.

(a) One mole liquid water at room temperature ⇌ one mole liquid water at 50 °C

(b) $Ag^+ (aq) + Cl^- (aq) \rightleftharpoons AgCl (s)$

(c) $2\ C_6H_6 (l) + 15\ O_2 (g) \rightleftharpoons 12\ CO_2 (g) + 6\ H_2O (l)$

(d) $NH_3 (s) \rightleftharpoons NH_3 (l)$

Solution

(a) positive, temperature increases
(b) negative, reduction in the number of ions in solution, decreased dispersal of matter
(c) negative, net decrease in the amount of gaseous species
(d) positive, phase transition from solid to liquid, net increase in dispersal of matter

Check Your Learning

Predict the sign of the entropy change for the following processes. Give a reason for your prediction.

(a) $NaNO_3 (s) \rightleftharpoons Na^+ (aq) + NO_3^- (aq)$

(b) the freezing of liquid water

(c) $CaCO (s) \rightleftharpoons CaO (s) + CO_2 (g)$

ANSWER:

(a) Positive; The solid dissolves to give an increase of mobile ions in solution.
(b) Negative; The liquid becomes a more ordered solid.
(c) Positive; There is a net increase in the amount of gaseous species.

Predicting the Sign of $\Delta S_{surrounding}$

The entropy change of surrounding (ΔS_{surr}) can be related to how heat transfer to/from surrounding (q_{surr}), in other word how much the surrounding energy become more/less disperse. The heat from the perspective of the surroundings is equal to the heat of the system but opposite in sign. Heat flowing out of the system is flowing into the surroundings vise versa.

Thus, the second law at constant temperature and pressure can be stated as the following:

$$\Delta S_{univ} = \Delta S_{sys} + \Delta S_{surr}$$

$$\Delta S_{univ} = \Delta S_{sys} + \frac{q_{surr}}{T}$$

The equation above may be used to predict the spontaneity of a process as illustrated in Example 17.3.

EXAMPLE 17.3

Will Ice Spontaneously Melt?

The entropy change for the process: H_2O (s) ⇌ H_2O (l) is 22.1 J/K and requires that the surroundings transfer 6.00 kJ of heat to the system.

Is the process spontaneous at −10.00 °C?
Is it spontaneous at +10.00 °C?

Solution
We can assess the spontaneity of the process by calculating the entropy change of the universe. If ΔS_{univ} is positive, then the process is spontaneous.

At both temperatures, ΔS_{sys} = 22.1 J/K and q_{surr} = −6.00 kJ (surrounding loses heat).

At −10.00 °C (263.15 K), the following is true:

$$\Delta S_{univ} = \Delta S_{sys} + \frac{q_{surr}}{T}$$

$$\Delta S_{univ} = 22.1 \text{ J/K} + \frac{-6.00 \times 10^3 J}{263.15\ K} = \text{-0.7 J/L}$$

$S_{univ} < 0$, so melting is nonspontaneous (*not* spontaneous) at −10.0 °C.

At 10.00 °C (283.15 K), the following is true:

$$\Delta S_{univ} = \Delta S_{sys} + \frac{q_{surr}}{T}$$

$$\Delta S_{univ} = 22.1 \text{ J/K} + \frac{-6.00 \times 10^3 J}{283.15\ K} = \text{+0.9 J/L}$$

$S_{univ} > 0$, so melting *is* spontaneous at 10.00 °C.

Check Your Learning

Using the above information, determine if liquid water will spontaneously freeze at the same temperatures. What can you say about the values of S_{univ}?

ANSWER:

Entropy is a state function, so $\Delta S_{freezing} = -\Delta S_{melting}$ = −22.1 J/K and q_{surr} = +6.00 kJ.
At −10.00 °C spontaneous, +0.7 J/K; at +10.00 °C nonspontaneous, −0.9 J/K.

The Third Law of Thermodynamics

The previous section described the various contributions of matter and energy dispersal that contribute to the entropy of a system. With these contributions in mind, consider the entropy of a pure, perfectly crystalline solid possessing no kinetic energy (that is, at a temperature of absolute zero, 0 K). This system may be described by a single microstate, as its purity, perfect crystallinity and complete lack of motion means there is but one possible location for each identical atom or molecule comprising the crystal ($W = 1$). According to the Boltzmann equation, the entropy of this system is zero.

$$S = k \cdot \ln W = k \cdot \ln(1) = 0$$

This condition represents the **third law of thermodynamics**:
the entropy of a pure, perfect crystalline substance at 0 K is zero.

Careful calorimetric measurements can be made to determine the temperature dependence of a substance's entropy and to derive absolute entropy values under specific conditions. **Standard entropies ($S°$)** are for one mole of substance under standard conditions (a pressure of 1 bar and a temperature of 298.15 K; see details regarding standard conditions in the thermochemistry chapter of this text). The **standard entropy change ($\Delta S°_{rxn}$)** for a reaction or system may be computed using standard entropies as shown below:

$$\Delta S°_{rxn} = \sum nS°(\text{products}) - \sum nS°(\text{reactants})$$

where n represents stoichiometric coefficients in the balanced equation representing the process. For example, $\Delta S°_{rxn}$ for the following reaction can be written as:

$$aA + bB \rightleftharpoons cC + dD,$$

$$\Delta S°_{rxn} = [c \cdot S°_{(C)} + d \cdot S°_{(D)}] - [a \cdot S°_{(A)} + b \cdot S°_{(B)}]$$

A partial listing of standard entropies is provided in Table 17.2 and additional values are provided in Appendix 17.2. The example exercises that follow demonstrate the use of *S*° values in calculating standard entropy changes for physical and chemical processes.

Table17.2 Standard entropies for selected substances measured at 1 atm and 298.15 K. (Values are approximately equal to those measured at 1 bar, the currently accepted standard state pressure.)

Substance	**S° (J mol⁻¹ K⁻¹)**
carbon	
C(*s*, graphite)	5.740
C(*s*, diamond)	2.38
$CO(g)$	197.7
$CO_2(g)$	213.8
$CH_4(g)$	186.3
$C_2H_4(g)$	219.5
$C_2H_6(g)$	229.5
$CH_3OH(l)$	126.8
$C_2H_5OH(l)$	160.7
hydrogen	
$H_2(g)$	130.57
$H(g)$	114.6
$H_2O(g)$	188.71
$H_2O(l)$	69.91
$HCl(g)$	186.8
$H_2S(g)$	205.7
oxygen	
$O_2(g)$	205.03

Determine $\Delta S°_{rxn}$ from the Standard Entropy (S^o)

EXAMPLE 17.4

Calculate the standard entropy change for the following process: $H_2O\ (g) \rightleftharpoons H_2O\ (l)$

Solution

Calculate the entropy change using standard entropies as shown above:

$$\Delta S°_{rxn} = \sum nS°(\text{products}) - \sum nS°(\text{reactants})$$

$$\Delta S°_{rxn} = (1)(70.0\ \text{Jmol}^{-1}\text{K}^{-1}) - (1)(188.8\ \text{Jmol}^{-1}\text{K}^{-1}) = -118.8\ \text{Jmol}^{-1}\text{K}^{-1}$$

The value for $\Delta S°_{rxn}$ is negative, as expected for this phase transition (condensation), which the previous section discussed.

Check Your Learning

Calculate the standard entropy change for the following process:

$H_2\ (g) + C_2H_4\ (g) \rightleftharpoons C_2H_6\ (g)$

ANSWER: $-120.6\ \text{J K}^{-1}\ \text{mol}^{-1}$

EXAMPLE 17.5

Calculate the standard entropy change for the combustion of methanol, CH_3OH:

$2\ CH_3OH\ (l) + 3O_2\ (g) \rightleftharpoons 2CO_2\ (g) + 4H_2O\ (l)$

Solution

Calculate the entropy change using standard entropies as shown above:

$$\Delta S°_{rxn} = \sum nS°(\text{products}) - \sum nS°(\text{reactants})$$

$$\Delta S°_{rxn} = [(2 \times S°(CO_{2(g)}) + 4 \times S°(H_2O_{(l)})] - [(2 \times S°(CH_3OH_{(l)}) + 3 \times S°(O_{2(g)})]$$

$$= [2 \cdot (213.8) + 4 \cdot (70.0)] - [2 \cdot (126.8) + 3(205.03)]$$

$$= -161.1 \text{ J K}^{-1} \text{ mol}^{-1}$$

Check Your Learning

Calculate the standard entropy change for the following reaction:

$Ca(OH)_2\ (s) \rightleftharpoons CaO\ (s) + H_2O\ (l)$

ANSWER:

24.7 J K^{-1} mol^{-1}

Appendix 17.2

Standard Thermodynamic Properties for Selected Substances

Substance	ΔHf° (kJ mol^{-1})	ΔGf° (kJ mol^{-1})	S° (J K^{-1} mol^{-1})
aluminum			
$Al(s)$	0	0	28.3
$Al(g)$	324.4	285.7	164.54
$Al^{3+}(aq)$	–531	–485	–321.7
$Al_2O_3(s)$	–1676	–1582	50.92
$AlF_3(s)$	–1510.4	–1425	66.5
$AlCl_3(s)$	–704.2	–628.8	110.67
$AlCl_3 \cdot 6H_2O(s)$	–2691.57	–2269.40	376.56
$Al_2S_3(s)$	–724.0	–492.4	116.9
$Al_2(SO_4)_3(s)$	–3445.06	–3506.61	239.32
antimony			
$Sb(s)$	0	0	45.69
$Sb(g)$	262.34	222.17	180.16
$Sb_4O_6(s)$	–1440.55	–1268.17	220.92
$SbCl_3(g)$	–313.8	–301.2	337.80
$SbCl_5(g)$	–394.34	–334.29	401.94
$Sb_2S_3(s)$	–174.89	–173.64	182.00
$SbCl_3(s)$	–382.17	–323.72	184.10
$SbOCl(s)$	–374.0	—	—
arsenic			

Standard Thermodynamic Properties for Selected Substances

Substance	ΔHf° (kJ mol^{-1})	ΔGf° (kJ mol^{-1})	S° (J K^{-1} mol^{-1})
As(*s*)	0	0	35.1
As(*g*)	302.5	261.0	174.21
As_4(*g*)	143.9	92.4	314
As_4O_6(*s*)	–1313.94	–1152.52	214.22
As_2O_5(*s*)	–924.87	–782.41	105.44
$AsCl_3$(*g*)	–261.50	–248.95	327.06
As_2S_3(*s*)	–169.03	–168.62	163.59
AsH_3(*g*)	66.44	68.93	222.78
H_3AsO_4(*s*)	–906.3	—	—
barium			
Ba(*s*)	0	0	62.5
Ba(*g*)	180	146	170.24
Ba^{2+}(*aq*)	–537.6	–560.8	9.6
BaO(*s*)	–548.0	–520.3	72.1
$BaCl_2$(*s*)	–855.0	–806.7	123.7
$BaSO_4$(*s*)	–1473.2	–1362.3	132.2
beryllium			
Be(*s*)	0	0	9.50
Be(*g*)	324.3	286.6	136.27
BeO(*s*)	–609.4	–580.1	13.8
bismuth			
Bi(*s*)	0	0	56.74

Standard Thermodynamic Properties for Selected Substances

Substance	ΔHf° (kJ mol^{-1})	ΔGf° (kJ mol^{-1})	S° (J K^{-1} mol^{-1})
Bi(*g*)	207.1	168.2	187.00
Bi_2O_3(*s*)	–573.88	–493.7	151.5
$BiCl_3$(*s*)	–379.07	–315.06	176.98
Bi_2S_3(*s*)	–143.1	–140.6	200.4
boron			
B(*s*)	0	0	5.86
B(*g*)	565.0	521.0	153.4
B_2O_3(*s*)	–1273.5	–1194.3	53.97
B_2H_6(*g*)	36.4	87.6	232.1
H_3BO_3(*s*)	–1094.33	–968.92	88.83
BF_3(*g*)	–1136.0	–1119.4	254.4
BCl_3(*g*)	–403.8	–388.7	290.1
$B_3N_3H_6$(*l*)	–540.99	–392.79	199.58
HBO_2(*s*)	–794.25	–723.41	37.66
bromine			
Br_2(*l*)	0	0	152.23
Br_2(*g*)	30.91	3.142	245.5
Br(*g*)	111.88	82.429	175.0
Br^-(*aq*)	–120.9	–102.82	80.71
BrF_3(*g*)	–255.60	–229.45	292.42
HBr(*g*)	–36.3	–53.43	198.7
cadmium			
Cd(*s*)	0	0	51.76

Standard Thermodynamic Properties for Selected Substances

Substance	ΔHf° (kJ mol^{-1})	ΔGf° (kJ mol^{-1})	S° (J K^{-1} mol^{-1})
Cd(*g*)	112.01	77.41	167.75
Cd^{2+}(*aq*)	–75.90	–77.61	–73.2
CdO(*s*)	–258.2	–228.4	54.8
$CdCl_2$(*s*)	–391.5	–343.9	115.3
$CdSO_4$(*s*)	–933.3	–822.7	123.0
CdS(*s*)	–161.9	–156.5	64.9
calcium			
Ca(*s*)	0	0	41.6
Ca(*g*)	178.2	144.3	154.88
Ca^{2+}(*aq*)	–542.96	–553.04	–55.2
CaO(*s*)	–634.9	–603.3	38.1
$Ca(OH)_2$(*s*)	–985.2	–897.5	83.4
$CaSO_4$(s)	–1434.5	–1322.0	106.5
$CaSO_4·2H_2O$(*s*)	–2022.63	–1797.45	194.14
$CaCO_3$(*s*) (calcite)	–1220.0	–1081.4	110.0
$CaSO_3·H_2O$(*s*)	–1752.68	–1555.19	184.10
carbon			
C(*s*) (graphite)	0	0	5.740
C(*s*) (diamond)	1.89	2.90	2.38
C(*g*)	716.681	671.2	158.1
CO(*g*)	–110.52	–137.15	197.7
CO_2(*g*)	–393.51	–394.36	213.8
$CO_3{}^{2-}$(*aq*)	–677.1	–527.8	–56.9

Standard Thermodynamic Properties for Selected Substances

Substance	ΔHf° (kJ mol^{-1})	ΔGf° (kJ mol^{-1})	S° (J K^{-1} mol^{-1})
$CH_4(g)$	–74.6	–50.5	186.3
$CH_3OH(l)$	–239.2	–166.6	126.8
$CH_3OH(g)$	–201.0	–162.3	239.9
$CCl_4(l)$	–128.2	–62.5	214.4
$CCl_4(g)$	–95.7	–58.2	309.7
$CHCl_3(l)$	–134.1	–73.7	201.7
$CHCl_3(g)$	–103.14	–70.34	295.71
$CS_2(l)$	89.70	65.27	151.34
$CS_2(g)$	116.9	66.8	238.0
$C_2H_2(g)$	227.4	209.2	200.9
$C_2H_4(g)$	52.4	68.4	219.3
$C_2H_6(g)$	–84.0	–32.0	229.2
$CH_3CO_2H(l)$	–484.3	–389.9	159.8
$CH_3CO_2H(g)$	–434.84	–376.69	282.50
$C_2H_5OH(l)$	–277.6	–174.8	160.7
$C_2H_5OH(g)$	–234.8	–167.9	281.6
$HCO_3{}^{-}(aq)$	–691.11	–587.06	95
$C_3H_8(g)$	–103.8	–23.4	270.3
$C_6H_6(g)$	82.927	129.66	269.2
$C_6H_6(l)$	49.1	124.50	173.4
$CH_2Cl_2(l)$	–124.2	–63.2	177.8
$CH_2Cl_2(g)$	–95.4	–65.90	270.2
$CH_3Cl(g)$	–81.9	–60.2	234.6

Standard Thermodynamic Properties for Selected Substances

Substance	ΔHf° (kJ mol^{-1})	ΔGf° (kJ mol^{-1})	S° (J K^{-1} mol^{-1})
$C_2H_5Cl(l)$	–136.52	–59.31	190.79
$C_2H_5Cl(g)$	–112.17	–60.39	276.00
$C_2N_2(g)$	308.98	297.36	241.90
$HCN(l)$	108.9	125.0	112.8
$HCN(g)$	135.5	124.7	201.8
cesium			
$Cs^+(aq)$	–248	–282.0	133
chlorine			
$Cl_2(g)$	0	0	223.1
$Cl(g)$	121.3	105.70	165.2
$Cl^-(aq)$	–167.2	–131.2	56.5
$ClF(g)$	–54.48	–55.94	217.78
$ClF_3(g)$	–158.99	–118.83	281.50
$Cl_2O(g)$	80.3	97.9	266.2
$Cl_2O_7(l)$	238.1	—	—
$Cl_2O_7(g)$	272.0	—	—
$HCl(g)$	–92.307	–95.299	186.9
$HClO_4(l)$	–40.58	—	—
chromium			
$Cr(s)$	0	0	23.77
$Cr(g)$	396.6	351.8	174.50
$CrO_4{}^{2-}(aq)$	–881.2	–727.8	50.21
$Cr_2O_7{}^{2-}(aq)$	–1490.3	–1301.1	261.9

Standard Thermodynamic Properties for Selected Substances

Substance	ΔHf° (kJ mol^{-1})	ΔGf° (kJ mol^{-1})	S° (J K^{-1} mol^{-1})
Cr_2O_3(*s*)	–1139.7	–1058.1	81.2
CrO_3(*s*)	–589.5	—	—
$(NH_4)_2Cr_2O_7$(*s*)	–1806.7	—	—
cobalt			
Co(*s*)	0	0	30.0
Co^{2+}(*aq*)	–67.4	–51.5	–155
Co^{3+}(*aq*)	92	134	–305.0
CoO(*s*)	–237.9	–214.2	52.97
Co_3O_4(*s*)	–910.02	–794.98	114.22
$Co(NO_3)_2$(*s*)	–420.5	—	—
copper			
Cu(*s*)	0	0	33.15
Cu(*g*)	338.32	298.58	166.38
Cu^{+}(*aq*)	51.9	50.2	–26
Cu^{2+}(*aq*)	64.77	65.49	–99.6
CuO(*s*)	–157.3	–129.7	42.63
Cu_2O(*s*)	–168.6	–146.0	93.14
CuS(*s*)	–53.1	–53.6	66.5
Cu_2S(*s*)	–79.5	–86.2	120.9
$CuSO_4$(*s*)	–771.36	–662.2	109.2
$Cu(NO_3)_2$(*s*)	–302.9	—	—
fluorine			
F_2(*g*)	0	0	202.8

Standard Thermodynamic Properties for Selected Substances

Substance	ΔHf° (kJ mol^{-1})	ΔGf° (kJ mol^{-1})	S° (J K^{-1} mol^{-1})
F(*g*)	79.4	62.3	158.8
F^-(*aq*)	–332.6	–278.8	–13.8
F_2O(*g*)	24.7	41.9	247.43
HF(*g*)	–273.3	–275.4	173.8
hydrogen			
H_2(*g*)	0	0	130.7
H(*g*)	217.97	203.26	114.7
H^+(*aq*)	0	0	0
OH^-(*aq*)	–230.0	–157.2	–10.75
H_3O^+(*aq*)	–285.8		69.91
H_2O(*l*)	–285.83	–237.1	70.0
H_2O(*g*)	–241.82	–228.59	188.8
H_2O_2(*l*)	–187.78	–120.35	109.6
H_2O_2(*g*)	–136.3	–105.6	232.7
HF(*g*)	–273.3	–275.4	173.8
HCl(*g*)	–92.307	–95.299	186.9
HBr(*g*)	–36.3	–53.43	198.7
HI(*g*)	26.48	1.70	206.59
H_2S(*g*)	–20.6	–33.4	205.8
H_2Se(*g*)	29.7	15.9	219.0
HNO_3	–206.64	—	—
iodine			
I_2(*s*)	0	0	116.14

Standard Thermodynamic Properties for Selected Substances

Substance	ΔHf° (kJ mol^{-1})	ΔGf° (kJ mol^{-1})	S° (J K^{-1} mol^{-1})
$I_2(g)$	62.438	19.3	260.7
$I(g)$	106.84	70.2	180.8
$I^-(aq)$	–55.19	–51.57	11.13
$IF(g)$	95.65	–118.49	236.06
$ICl(g)$	17.78	–5.44	247.44
$IBr(g)$	40.84	3.72	258.66
$IF_7(g)$	–943.91	–818.39	346.44
$HI(g)$	26.48	1.70	206.59
iron			
$Fe(s)$	0	0	27.3
$Fe(g)$	416.3	370.7	180.5
$Fe^{2+}(aq)$	–89.1	–78.90	–137.7
$Fe^{3+}(aq)$	–48.5	–4.7	–315.9
$Fe_2O_3(s)$	–824.2	–742.2	87.40
$Fe_3O_4(s)$	–1118.4	–1015.4	146.4
$Fe(CO)_5(l)$	–774.04	–705.42	338.07
$Fe(CO)_5(g)$	–733.87	–697.26	445.18
$FeCl_2(s)$	–341.79	–302.30	117.95
$FeCl_3(s)$	–399.49	–334.00	142.3
$FeO(s)$	–272.0	–255.2	60.75
$Fe(OH)_2(s)$	–569.0	–486.5	88.
$Fe(OH)_3(s)$	–823.0	–696.5	106.7
$FeS(s)$	–100.0	–100.4	60.29

Standard Thermodynamic Properties for Selected Substances

Substance	ΔHf° (kJ mol^{-1})	ΔGf° (kJ mol^{-1})	S° (J K^{-1} mol^{-1})
Fe_3C(*s*)	25.10	20.08	104.60
lead			
Pb(*s*)	0	0	64.81
Pb(*g*)	195.2	162.	175.4
Pb^{2+}(*aq*)	–1.7	–24.43	10.5
PbO(*s*) (yellow)	–217.32	–187.89	68.70
PbO(*s*) (red)	–218.99	–188.93	66.5
$Pb(OH)_2$(*s*)	–515.9	—	—
PbS(*s*)	–100.4	–98.7	91.2
$Pb(NO_3)_2$(*s*)	–451.9	—	—
PbO_2(*s*)	–277.4	–217.3	68.6
$PbCl_2$(*s*)	–359.4	–314.1	136.0
lithium			
Li(*s*)	0	0	29.1
Li(*g*)	159.3	126.6	138.8
Li^+(*aq*)	–278.5	–293.3	13.4
LiH(*s*)	–90.5	–68.3	20.0
Li(OH)(*s*)	–487.5	–441.5	42.8
LiF(*s*)	–616.0	–587.5	35.7
Li_2CO_3(*s*)	–1216.04	–1132.19	90.17
magnesium			
Mg^{2+}(*aq*)	–466.9	–454.8	–138.1

Standard Thermodynamic Properties for Selected Substances

Substance	ΔHf° (kJ mol^{-1})	ΔGf° (kJ mol^{-1})	S° (J K^{-1} mol^{-1})
manganese			
Mn(*s*)	0	0	32.0
Mn(*g*)	280.7	238.5	173.7
Mn^{2+}(*aq*)	–220.8	–228.1	–73.6
MnO(*s*)	–385.2	–362.9	59.71
MnO_2(*s*)	–520.03	–465.1	53.05
Mn_2O_3(*s*)	–958.97	–881.15	110.46
Mn_3O_4(*s*)	–1378.83	–1283.23	155.64
$MnO_4{}^{-}$(*aq*)	–541.4	–447.2	191.2
$MnO_4{}^{2-}$(*aq*)	–653.0	–500.7	59
mercury			
Hg(*l*)	0	0	75.9
Hg(*g*)	61.4	31.8	175.0
Hg^{2+}(*aq*)		164.8	
Hg^{2+}(*aq*)	172.4	153.9	84.5
HgO(*s*) (red)	–90.83	–58.5	70.29
HgO(*s*) (yellow)	–90.46	–58.43	71.13
$HgCl_2$(*s*)	–224.3	–178.6	146.0
Hg_2Cl_2(*s*)	–265.4	–210.7	191.6
HgS(*s*) (red)	–58.16	–50.6	82.4
HgS(*s*) (black)	–53.56	–47.70	88.28
$HgSO_4$(*s*)	–707.51	–594.13	0.00
nickel			

Standard Thermodynamic Properties for Selected Substances

Substance	ΔHf° (kJ mol^{-1})	ΔGf° (kJ mol^{-1})	S° (J K^{-1} mol^{-1})
Ni^{2+}(*aq*)	–64.0	–46.4	–159
nitrogen			
N_2(*g*)	0	0	191.6
N(*g*)	472.704	455.5	153.3
NO(*g*)	90.25	87.6	210.8
NO_2(*g*)	33.2	51.30	240.1
N_2O(*g*)	81.6	103.7	220.0
N_2O_3(*g*)	83.72	139.41	312.17
$NO_3{}^-$(*aq*)	–205.0	–108.7	146.4
N_2O_4(*g*)	11.1	99.8	304.4
N_2O_5(*g*)	11.3	115.1	355.7
NH_3(*g*)	–45.9	–16.5	192.8
$NH_4{}^+$(*aq*)	–132.5	–79.31	113.4
N_2H_4(*l*)	50.63	149.43	121.21
N_2H_4(*g*)	95.4	159.4	238.5
NH_4NO_3(*s*)	–365.56	–183.87	151.08
NH_4Cl(*s*)	–314.43	–202.87	94.6
NH_4Br(*s*)	–270.8	–175.2	113.0
NH_4I(*s*)	–201.4	–112.5	117.0
NH_4NO_2(*s*)	–256.5	—	—
HNO_3(*l*)	–174.1	–80.7	155.6
HNO_3(*g*)	–133.9	–73.5	266.9
oxygen			

Standard Thermodynamic Properties for Selected Substances

Substance	ΔHf° (kJ mol^{-1})	ΔGf° (kJ mol^{-1})	S° (J K^{-1} mol^{-1})
O_2(*g*)	0	0	205.2
O(*g*)	249.17	231.7	161.1
O_3(*g*)	142.7	163.2	238.9
phosphorus			
P_4(*s*)	0	0	164.4
P_4(*g*)	58.91	24.4	280.0
P(*g*)	314.64	278.25	163.19
PH_3(*g*)	5.4	13.5	210.2
PCl_3(*g*)	–287.0	–267.8	311.78
PCl_5(*g*)	–374.9	–305.0	364.4
P_4O_6(*s*)	–1640.1	—	—
P_4O_{10}(*s*)	–2984.0	–2697.0	228.86
$PO_4{}^{3-}$(*aq*)	–1277	–1019	–222
HPO_3(*s*)	–948.5	—	—
$HPO_4{}^{2-}$(*aq*)	–1292.1	–1089.3	–33
$H_2PO_4{}^{2-}$(*aq*)	–1296.3	–1130.4	90.4
H_3PO_2(*s*)	–604.6	—	—
H_3PO_3(*s*)	–964.4	—	—
H_3PO_4(*s*)	–1279.0	–1119.1	110.50
H_3PO_4(*l*)	–1266.9	–1124.3	110.5
$H_4P_2O_7$(*s*)	–2241.0	—	—
$POCl_3$(*l*)	–597.1	–520.8	222.5
$POCl_3$(*g*)	–558.5	–512.9	325.5

Standard Thermodynamic Properties for Selected Substances

Substance	ΔHf° (kJ mol^{-1})	ΔGf° (kJ mol^{-1})	S° (J K^{-1} mol^{-1})
potassium			
K(*s*)	0	0	64.7
K(*g*)	89.0	60.5	160.3
K^+(*aq*)	–252.4	–283.3	102.5
KF(*s*)	–576.27	–537.75	66.57
KCl(*s*)	–436.5	–408.5	82.6
rubidium			
Rb^+(*aq*)	–246	–282.2	124
silicon			
Si(*s*)	0	0	18.8
Si(*g*)	450.0	405.5	168.0
SiO_2(*s*)	–910.7	–856.3	41.5
SiH_4(*g*)	34.3	56.9	204.6
H_2SiO_3(*s*)	–1188.67	–1092.44	133.89
H_4SiO_4(*s*)	–1481.14	–1333.02	192.46
SiF_4(*g*)	–1615.0	–1572.8	282.8
$SiCl_4$(*l*)	–687.0	–619.8	239.7
$SiCl_4$(*g*)	–662.75	–622.58	330.62
SiC(*s, beta cubic*)	–73.22	–70.71	16.61
SiC(*s, alpha hexagonal*)	–71.55	–69.04	16.48
silver			
Ag(*s*)	0	0	42.55
Ag(*g*)	284.9	246.0	172.89

Standard Thermodynamic Properties for Selected Substances

Substance	ΔHf° (kJ mol^{-1})	ΔGf° (kJ mol^{-1})	S° (J K^{-1} mol^{-1})
Ag^+(*aq*)	105.6	77.11	72.68
Ag_2O(*s*)	–31.05	–11.20	121.3
AgCl(*s*)	–127.0	–109.8	96.3
Ag_2S(*s*)	–32.6	–40.7	144.0
sodium			
Na(*s*)	0	0	51.3
Na(*g*)	107.5	77.0	153.7
Na^+(*aq*)	–240.1	–261.9	59
Na_2O(*s*)	–414.2	–375.5	75.1
NaCl(*s*)	–411.2	–384.1	72.1
strontium			
Sr^{2+}(*aq*)	–545.8	–557.3	–32.6
sulfur			
S_8(*s*) (rhombic)	0	0	256.8
S(*g*)	278.81	238.25	167.82
S^{2-}(*aq*)	41.8	83.7	22
SO_2(*g*)	–296.83	–300.1	248.2
SO_3(*g*)	–395.72	–371.06	256.76
$SO_4{}^{2-}$(*aq*)	–909.3	–744.5	20.1
$S_2O_3{}^{2-}$(*aq*)	–648.5	–522.5	67
H_2S(*g*)	–20.6	–33.4	205.8
HS^-(*aq*)	–17.7	12.6	61.1
H_2SO_4(*l*)	–813.989	690.00	156.90

Standard Thermodynamic Properties for Selected Substances

Substance	ΔHf° (kJ mol^{-1})	ΔGf° (kJ mol^{-1})	S° (J K^{-1} mol^{-1})
$HSO_4{}^{2-}$(*aq*)	–885.75	–752.87	126.9
$H_2S_2O_7$(*s*)	–1273.6	—	—
SF_4(*g*)	–728.43	–684.84	291.12
SF_6(*g*)	–1220.5	–1116.5	291.5
SCl_2(*l*)	–50	—	—
SCl_2(*g*)	–19.7	—	—
S_2Cl_2(*l*)	–59.4	—	—
S_2Cl_2(*g*)	–19.50	–29.25	319.45
$SOCl_2$(*g*)	–212.55	–198.32	309.66
$SOCl_2$(*l*)	–245.6	—	—
SO_2Cl_2(*l*)	–394.1	—	—
SO_2Cl_2(g)	–354.80	–310.45	311.83
tin			
Sn(*s*)	0	0	51.2
Sn(*g*)	301.2	266.2	168.5
SnO(*s*)	–285.8	–256.9	56.5
SnO_2(*s*)	–577.6	–515.8	49.0
$SnCl_4$(*l*)	–511.3	–440.1	258.6
$SnCl_4$(*g*)	–471.5	–432.2	365.8
titanium			
Ti(*s*)	0	0	30.7
Ti(*g*)	473.0	428.4	180.3
TiO_2(*s*)	–944.0	–888.8	50.6

Standard Thermodynamic Properties for Selected Substances

Substance	ΔHf° (kJ mol^{-1})	ΔGf° (kJ mol^{-1})	S° (J K^{-1} mol^{-1})
$TiCl_4$(*l*)	–804.2	–737.2	252.4
$TiCl_4$(*g*)	–763.2	–726.3	353.2
tungsten			
W(*s*)	0	0	32.6
W(*g*)	849.4	807.1	174.0
WO_3(*s*)	–842.9	–764.0	75.9
zinc			
Zn(*s*)	0	0	41.6
Zn(*g*)	130.73	95.14	160.98
Zn^{2+}(*aq*)	–153.9	–147.1	–112.1
ZnO(*s*)	–350.5	–320.5	43.7
$ZnCl_2$(*s*)	–415.1	–369.43	111.5
ZnS(*s*)	–206.0	–201.3	57.7
$ZnSO_4$(*s*)	–982.8	–871.5	110.5
$ZnCO_3$(*s*)	–812.78	–731.57	82.42
complexes			
$[Co(NH_3)_4(NO_2)_2]NO_3$, *cis*	–898.7	—	—
$[Co(NH_3)_4(NO_2)_2]NO_3$, *trans*	–896.2	—	—
$NH_4[Co(NH_3)_2(NO_2)_4]$	–837.6	—	—
$[Co(NH_3)_6][Co(NH_3)_2(NO_2)_4]_3$	–2733.0	—	—

Standard Thermodynamic Properties for Selected Substances

Substance	ΔHf° (kJ mol^{-1})	ΔGf° (kJ mol^{-1})	S° (J K^{-1} mol^{-1})
$[Co(NH_3)_4Cl_2]Cl$, *cis*	–874.9	—	—
$[Co(NH_3)_4Cl_2]Cl$, *trans*	–877.4	—	—
$[Co(en)_2(NO_2)_2]NO_3$, *cis*	–689.5	—	—
$[Co(en)_2Cl_2]Cl$, *cis*	–681.2	—	—
$[Co(en)_2Cl_2]Cl$, *trans*	–677.4	—	—
$[Co(en)_3](ClO_4)_3$	–762.7	—	—
$[Co(en)_3]Br_2$	–595.8	—	—
$[Co(en)_3]I_2$	–475.3	—	—
$[Co(en)_3]I_3$	–519.2	—	—
$[Co(NH_3)_6](ClO_4)_3$	–1034.7	–221.1	615
$[Co(NH_3)_5NO_2](NO_3)_2$	–1088.7	–412.9	331
$[Co(NH_3)_6](NO_3)_3$	–1282.0	–524.5	448
$[Co(NH_3)_5Cl]Cl_2$	–1017.1	–582.5	366.1
$[Pt(NH_3)_4]Cl_2$	–725.5	—	—
$[Ni(NH_3)_6]Cl_2$	–994.1	—	—
$[Ni(NH_3)_6]Br_2$	–923.8	—	—
$[Ni(NH_3)_6]I_2$	–808.3	—	—

17.3 Gibbs Free Energy

Learning Objectives

- Define Gibbs free energy, and describe its relation to spontaneity

- Calculate free energy change for a process using free energies of formation for its reactants and products
- Calculate free energy change for a process using enthalpies of formation and the entropies for its reactants and products
- Explain how temperature affects the spontaneity of some processes
- Relate standard free energy changes to equilibrium constants

Gibbs Free Energy

One of the challenges of using the second law of thermodynamics to determine if a process is spontaneous is that it requires measurements of the entropy change for the system *and* the entropy change for the surroundings. An alternative approach involving a new thermodynamic property defined in terms of system properties only was introduced in the late nineteenth century by American mathematician Josiah Willard Gibbs. This new property is called the **Gibbs free energy (*G*)** (or simply the *free energy*), and it is defined in terms of a system's enthalpy and entropy as the following:

$$G_{sys} = H_{sys} - TS_{sys}$$

Free energy is a state function, and at constant temperature and pressure, the **free energy change (Δ*G*)** may be expressed as the following:

$$\Delta G_{sys} = \Delta H_{sys} - T\Delta S_{sys}$$

The relationship between this system property and the spontaneity of a process may be understood by recalling the previously derived second law expression:

$$\Delta S_{univ} = \Delta S_{sys} + \Delta S_{surr}$$

$$\Delta S_{univ} = \Delta S_{sys} + \frac{q_{surr}}{T}$$

Recall from chapter 8, the first law requires that $q_{surr} = -q_{sys}$, and at constant pressure $q_{sys} = \Delta H$, so this expression may be rewritten as:

$$\Delta S_{univ} = \Delta S_{sys} + \frac{-q_{sys}}{T}$$

$$\Delta S_{univ} = \Delta S_{sys} + \frac{-\Delta H_{sys}}{T}$$

$$\Delta S_{univ} = \Delta S_{sys} - \frac{\Delta H_{sys}}{T}$$

Multiplying both sides of this equation by $-T$, and rearranging yields the following:

$$-T\Delta S_{univ} = -T\Delta S_{sys} + \Delta H_{sys}$$

or $$-T\Delta S_{univ} = \Delta H_{sys} - T\Delta S_{sys}$$

Comparing this equation to the previous one for free energy change:

$$\Delta G_{sys} = \Delta H_{sys} - T\Delta S_{sys}$$
$$-T\Delta S_{univ} = \Delta H_{sys} - T\Delta S_{sys}$$

Shows the following relation: $\Delta G_{sys} = -T\Delta S_{univ}$

The free energy change is therefore a reliable indicator of the spontaneity of a process, being directly related to the previously identified spontaneity indicator, ΔS_{univ}.
Table 17.3 summarizes the relation between the spontaneity of a process and the arithmetic signs of these indicators.

For simplicity, the subscript “sys” will be omitted henceforth for the free energy equation:

$$\Delta G = \Delta H - T\Delta S$$

Table 17.3: Relation between Spontaneity and Signs of Thermodynamic Properties

$\Delta S_{univ} > 0$	$\Delta G < 0$	spontaneous
$\Delta S_{univ} < 0$	$\Delta G > 0$	nonspontaneous
$\Delta S_{univ} = 0$	$\Delta G = 0$	at equilibrium

What’s “Free” about Δ*G*?

In addition to indicating spontaneity, the free energy change also provides information regarding the amount of useful work (*w*) that may be accomplished by a spontaneous process. Although a rigorous treatment of this subject is beyond the scope of an introductory chemistry text, a brief discussion is helpful for gaining a better perspective on this important thermodynamic property.

For this purpose, consider a spontaneous, exothermic process that involves a decrease in entropy. The free energy, as defined by

$$\Delta G = \Delta H - T\Delta S$$

may be interpreted as representing the difference between the energy produced by the process, ΔH, and the energy lost to the surroundings, $T\Delta S$. The difference between the energy produced and the energy lost is the energy available (or "free") to do useful work by the process, ΔG.

If the process somehow could be made to take place under conditions of thermodynamic reversibility, the amount of work that could be done would be maximal. However, such conditions are not realistic. In addition, the technologies used to extract work from a spontaneous process (e.g., automobile engine, steam turbine) are never 100% efficient, and so the work done by these processes is always less than the theoretical maximum. Similar reasoning may be applied to a nonspontaneous process, for which the free energy change represents the *minimum* amount of work that must be done *on* the system to carry out the process.

Using Standard Enthalpy and Entropy Changes to Calculate $\Delta G°$

Free energy is a state function, so its value depends only on the conditions of the initial and final states of the system. A convenient and common approach to the calculation of free energy changes for physical and chemical reactions is by use of widely available compilations of standard state thermodynamic data. One method involves the use of standard enthalpies and entropies to compute **standard free energy changes, $\Delta G°$**, according to the following relation.

$$\Delta G^o = \Delta H^o - T\Delta S^o$$

EXAMPLE 17.6

Use standard enthalpy and entropy data from Appendix 17.2 to calculate the standard free energy change for the vaporization of water at room temperature (298 K). What does the computed value for $\Delta G°$ say about the spontaneity of this process?

Solution

The process of interest is the following: $H_2O\ (l) \rightleftharpoons H_2O\ (g)$

The standard change in free energy may be calculated using the following equation:

$$\Delta G° = \Delta H° - T\Delta S°$$

From Appendix 17.2:

Substance	**$\Delta H_f°$(kJ/mol)**	**S°(J/K·mol)**
$H_2O(l)$	−286.83	70.0
$H_2O(g)$	−241.82	188.8

Using the appendix data to calculate the standard enthalpy and entropy changes yields:

$$\begin{aligned}\Delta H° &= 1\times\Delta H_f°(H_2O_{(g)}) - 1\times\Delta H_f°(H_2O_{(l)}) \\ &= [(-241.82) - (-286.83)]\ \text{kJ/mol} \\ &= 45.01\ \text{kJ/mol}\end{aligned}$$

$$\begin{aligned}\Delta S° &= 1\times S°(H_2O_{(g)}) - 1\times S°(H_2O_{(l)}) \\ &= [(88.8J) - (70.0)]\ \text{J/molK} \\ &= 118.8\ \text{J/molK}\end{aligned}$$

Substitution into the standard free energy equation yields:

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ = 45.01 \text{ kJ/mol} - (298 \text{ K} \times 118.8 \text{ J/molK} \times \frac{1\ kJ}{1000\ J})$$

$$= 45.01 \text{ kJ/mol} - 35.4 \text{ kJ/mol}$$

$$= 9.6 \text{ kJ/mol}$$

At 298 K (25 °C) $\Delta G^\circ > 0$, so boiling is nonspontaneous (*not* spontaneous).

Check Your Learning

Use standard enthalpy and entropy data from Appendix 17.2to calculate the standard free energy change for the reaction shown here (298 K). What does the computed value for ΔG° say about the spontaneity of this process?

$$C_2H_6\ (g) \rightleftharpoons H_2\ (g) + C_2H_4\ (g)$$

ANSWER:

$\Delta G^\circ = 102.0$ kJ/mol; the reaction is nonspontaneous (*not* spontaneous) at 25 °C.

Using Standard Free Energies of Formation to Calculate ΔG°

The standard free energy change for a reaction may also be calculated from **standard free energy of formation ΔG_f°** values of the reactants and products involved in the reaction. The standard free energy of formation is the free energy change that accompanies the formation of one mole of a substance from its elements in their standard states. Similar to the standard enthalpy of formation, ΔG_f° is by definition zero for elemental substances under standard state conditions. The approach used to calculate ΔG° for a reaction from $\Delta G_f°$ values is the same as that demonstrated previously for enthalpy and entropy changes. For the following reaction, the standard free energy change at room temperature may be calculated as:

$$aA + bB \rightleftharpoons cC + dD,$$

$$\Delta G° = \sum n\Delta G_f°(\text{products}) - \sum n\Delta G_f°(\text{reactants})$$

$$\Delta G° = [c\cdot\Delta G_f°_{(C)} + d\cdot\Delta G_f°_{(D)}] - [a\cdot\Delta G_f°_{(A)} + b\cdot\Delta G_f°_{(B)}]$$

EXAMPLE 17.7

Consider the decomposition of yellow mercury(II) oxide.

$$\text{HgO (s, yellow)} \rightleftharpoons \text{Hg (l)} + \tfrac{1}{2}\,O_2(g)$$

Calculate the standard free energy change at room temperature, ΔG°, using (a) standard free energies of formation and (b) standard enthalpies of formation and standard entropies. Do the results indicate the reaction to be spontaneous or nonspontaneous under standard conditions?

Solution

The required data are available in Appendix 17.2 and are shown here.

Compound	**$\Delta G_f°$(kJ/mol)**	**$\Delta H_f°$(kJ/mol)**	**S°(J/K·mol)**
HgO (*s*, yellow)	−58.43	−90.46	71.13
Hg(*l*)	0	0	75.9
O_2(*g*)	0	0	205.2

(a) Using free energies of formation: $\Delta G° = \sum n\Delta G_f°(\text{products}) - \sum n\Delta G_f°(\text{reactants})$

$\Delta G° = [1\times\Delta G_f°(Hg_{(l)}) + ½ \times\Delta G_f°(O_{2(g)})] - 1\times\Delta G_f°(HgO_{(s,yellow)})$

$\Delta G° = [1\times(0) + ½ (0)] - 1\times(-58.43) \text{ kJ/mol} = 58.43 \text{ kJ/mol}$

(b) Using enthalpies and entropies of formation: ΔG° = ΔH°−TΔS°

$\Delta H° = \sum n\Delta H_f°(\text{products}) - \sum n\Delta H_f°(\text{reactants})$

$\Delta H° = [1\times\Delta H_f°(Hg_{(l)}) + ½ \times\Delta H_f°(O_{2(g)})] - 1\times\Delta H_f°(HgO_{(s,yellow)})$

$\Delta H° = [1\times(0) + ½ (0)] - 1\times(-90.46) \text{ kJ/mol} = 90.46 \text{ kJ/mol}$

$\Delta S° = \sum nS°(\text{products}) - \sum nS°(\text{reactants})$

$\Delta S° = [1\times S°(Hg_{(l)}) + ½ \times\Delta S°(O_{2(g)})] - 1\times S°(HgO_{(s,yellow)})$

$\Delta S° = [1\times(75.9) + ½ (205.2)] - 1\times(71.13) \text{ J/molK} = 107.4 \text{ J/molK}$

$$\Delta G° = \Delta H° - T\Delta S° = 90.46 \text{ kJ/mol} - (298.15 \text{ K} \times 107.4 \text{ J/molK} \times \frac{1\, kJ}{1000\, J})$$
$$= 90.46 \text{ kJ/mol} - 32.01 \text{ kJ/mol} = 58.45 \text{ kJ/mol}$$

Both ways to calculate the standard free energy change at 25 °C give the same numerical value (to three significant figures), and both predict that the process is nonspontaneous (*not* spontaneous) at room temperature.

Check Your Learning

Calculate Δ*G*° using (a) free energies of formation and (b) enthalpies of formation and entropies (Appendix 17.2). Do the results indicate the reaction to be spontaneous or nonspontaneous at 25 °C? $C_2H_4 (g) \rightleftharpoons H_2 (g) + C_2H_2 (g)$

ANSWER: (a) 140.8 kJ/mol, nonspontaneous (b) 141.5 kJ/mol, nonspontaneous

Using Hess's Law to Calculate Δ*G*°

The use of free energies of formation to compute free energy changes for reactions as described above is possible because Δ*G* is a state function, and the approach is analogous to the use of Hess' Law in computing enthalpy changes (see the chapter on thermochemistry). Consider the vaporization of water as an example:

$$H_2O\ (l) \rightarrow H_2O\ (g)$$

An equation representing this process may be derived by adding the formation reactions for the two phases of water (necessarily reversing the reaction for the liquid phase). The free energy change for the sum reaction is the sum of free energy changes for the two added reactions:

$$H_2\,(g) + \tfrac{1}{2}\,O_2\,(g) \rightarrow H_2O\,(g) \qquad \Delta G_f{}^\circ{}_{gas}$$

$$H_2O\,(l) \rightarrow H_2\,(g) + \tfrac{1}{2}\,O_2\,(g) \qquad -\Delta G_f{}^\circ{}_{liquid}$$

$$H_2O\,(l) \rightarrow H_2O\,(g) \qquad \Delta G^\circ = \Delta G_f{}^\circ{}_{gas} - \Delta G_f{}^\circ{}_{liquid}$$

This approach may also be used in cases where a nonspontaneous reaction is enabled by coupling it to a spontaneous reaction. For example, the production of elemental zinc from zinc sulfide is thermodynamically unfavorable, as indicated by a positive value for Δ*G*°:

$$ZnS\,(s) \rightarrow Zn\,(s) + S\,(s) \qquad \Delta G_1{}^\circ = 201.3\text{ kJ}$$

The industrial process for production of zinc from sulfidic ores involves coupling this decomposition reaction to the thermodynamically favorable oxidation of sulfur:

$$S\,(s) + O_2\,(g) \rightarrow SO_2\,(g) \qquad \Delta G_2{}^\circ = -300.1\text{ kJ}$$

The coupled reaction exhibits a negative free energy change and is spontaneous:

$$ZnS\,(s) + O_2\,(g) \rightarrow Zn\,(s) + SO_2\,(g) \qquad \Delta G^\circ = \Delta G_1{}^\circ + \Delta G_2{}^\circ$$

$$\Delta G^\circ = 201.3\text{ kJ} + -300.1\text{ kJ} = -98.8\text{ kJ}$$

This process is typically carried out at elevated temperatures, so this result obtained using standard free energy values is just an estimate. The gist of the calculation, however, holds true.

EXAMPLE 17.8

Is a reaction coupling the decomposition of ZnS to the formation of H_2S expected to be spontaneous under standard conditions?

Solution

Following the approach outlined above and using free energy values from Appendix 17.2:

Decomposition of zinc sulfide: $ZnS (s) \rightarrow Zn (s) + S (s)$ $\Delta G_1° = 201.3$ kJ

Formation of hydrogen sulfide: $S (s) + H2 (g) \rightarrow H2S (g)$ $\Delta G_2° = -33.4$ kJ

Coupled reaction: $ZnS (s) + H_2 (g) \rightarrow Zn (s) + H_2S (g)$ $\Delta G° = \Delta G_1° + \Delta G_2°$

$$\Delta G° = 201.3 \text{ kJ} + -33.4 \text{ kJ} = 167.9 \text{ kJ}$$

The coupled reaction exhibits a positive free energy change and is thus nonspontaneous.

Temperature Dependence of Spontaneity

As was previously demonstrated in this chapter's section on entropy, the spontaneity of a process may depend upon the temperature of the system. Phase transitions, for example, will proceed spontaneously in one direction or the other depending upon the temperature of the substance in question. Likewise, some chemical reactions can also exhibit temperature dependent spontaneities. To illustrate this concept, the equation relating free energy change to the enthalpy and entropy changes for the process is considered:

$$\Delta G = \Delta H - T\Delta S$$

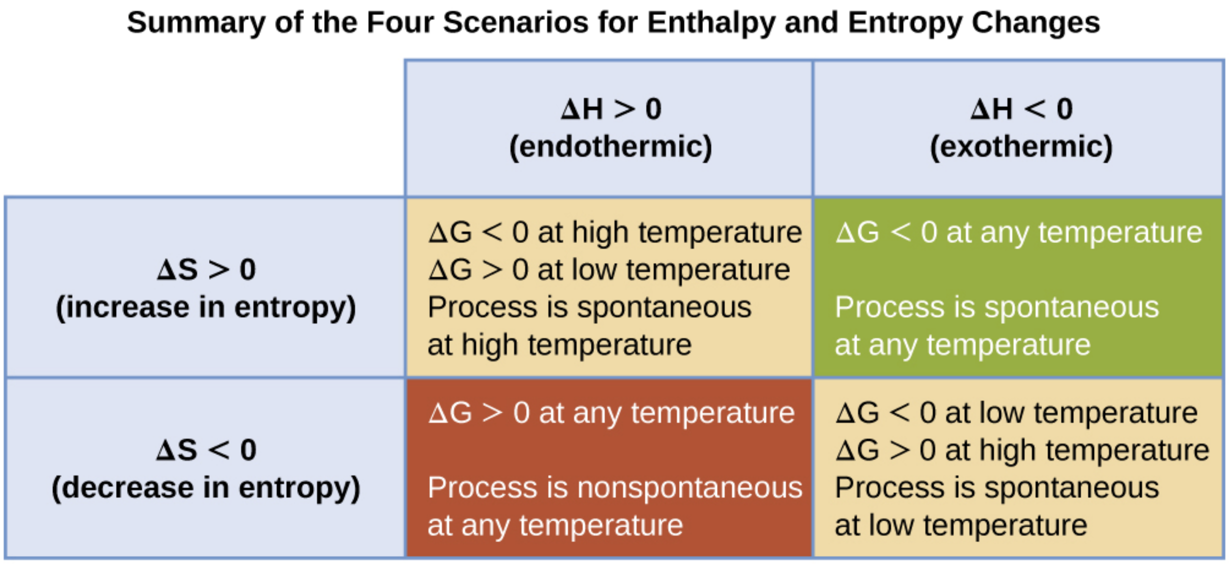
The spontaneity of a process, as reflected in the arithmetic sign of its free energy change, is then determined by the signs of the enthalpy and entropy changes and, in some cases, the absolute temperature. Since T is the absolute (kelvin) temperature, it can only have positive values. Four possibilities therefore exist with regard to the signs of the enthalpy and entropy changes:

1. **Both ΔH and ΔS are positive.** This condition describes an endothermic process that involves an increase in system entropy. In this case, ΔG will be negative if the magnitude of the $T\Delta S$ term is greater than ΔH. If the $T\Delta S$ term is less than ΔH, the free energy change will be positive. Such a process is *spontaneous at high temperatures and nonspontaneous at low temperatures.*
2. **Both ΔH and ΔS are negative.** This condition describes an exothermic process that involves a decrease in system entropy. In this case, ΔG will be negative if the magnitude of the $T\Delta S$ term is less than ΔH. If the $T\Delta S$ term's magnitude is greater

than Δ*H*, the free energy change will be positive. Such a process is *spontaneous at low temperatures and nonspontaneous at high temperatures.*

3. **Δ*H* is positive and Δ*S* is negative.** This condition describes an endothermic process that involves a decrease in system entropy. In this case, Δ*G* will be positive regardless of the temperature. Such a process is *nonspontaneous at all temperatures.*
4. **Δ*H* is negative and Δ*S* is positive.** This condition describes an exothermic process that involves an increase in system entropy. In this case, Δ*G* will be negative regardless of the temperature. Such a process is *spontaneous at all temperatures.*

These four scenarios are summarized in Figure 17.10.



Summary of the Four Scenarios for Enthalpy and Entropy Changes

	$\Delta H > 0$ **(endothermic)**	**$\Delta H < 0$** **(exothermic)**
$\Delta S > 0$ **(increase in entropy)**	$\Delta G < 0$ at high temperature $\Delta G > 0$ at low temperature Process is spontaneous at high temperature	$\Delta G < 0$ at any temperature Process is spontaneous at any temperature
$\Delta S < 0$ **(decrease in entropy)**	$\Delta G > 0$ at any temperature Process is nonspontaneous at any temperature	$\Delta G < 0$ at low temperature $\Delta G > 0$ at high temperature Process is spontaneous at low temperature

Figure 17.10 There are four possibilities regarding the signs of enthalpy and entropy changes.

Predicting the Temperature Dependence of Spontaneity

EXAMPLE 17.9

The incomplete combustion of carbon is described by the following equation:

$$2C\ (s) + O_2\ (g) \rightleftharpoons 2CO\ (g)$$

How does the spontaneity of this process depend upon temperature?

Solution

Combustion processes are exothermic ($\Delta H < 0$). This particular reaction involves an increase in entropy due to the accompanying increase in the amount of gaseous species (net gain of one mole of gas, $\Delta S > 0$). The reaction is therefore spontaneous ($\Delta G < 0$) at all temperatures.

Check Your Learning

Popular chemical hand warmers generate heat by the air-oxidation of iron:

$$4Fe\ (s) + 3O_2\ (g) \rightleftharpoons 2Fe_2O_3\ (s)$$

How does the spontaneity of this process depend upon temperature?

ANSWER:

ΔH and ΔS are negative; the reaction is spontaneous at low temperatures.

When considering the conclusions drawn regarding the temperature dependence of spontaneity, it is important to keep in mind what the terms “high” and “low” mean. Since these terms are adjectives, the temperatures in question are deemed high or low relative to some reference temperature. A process that is nonspontaneous at one temperature but spontaneous at another will necessarily undergo a change in “spontaneity” (as reflected by its ΔG) as temperature varies.

This is clearly illustrated by a graphical presentation (Figure 17.11) of the free energy change equation, in which ΔG is plotted on the *y* axis versus *T* on the *x* axis:

$$\Delta G = \Delta H - T\Delta S$$

Rearrange to get: $\Delta G = -(\Delta S)T + \Delta H$

Compare with liner equation: $y = mx + b$

A process whose enthalpy and entropy changes are of the same arithmetic sign will exhibit a temperature-dependent spontaneity as depicted by the two yellow lines in the plot. Each line crosses from one spontaneity domain (positive or negative ΔG) to the other at a temperature that is characteristic of the process in question. This temperature is represented by the *x*-intercept of the line, that is, the value of *T* for which Δ*G* is zero:

$$\Delta G = 0 \qquad T = \frac{\Delta H}{\Delta S}$$

So, saying a process is spontaneous at "high" or "low" temperatures means the temperature is above or below, respectively, that temperature at which Δ*G* for the process is zero. As noted earlier, the condition of ΔG = 0 describes a system at equilibrium.

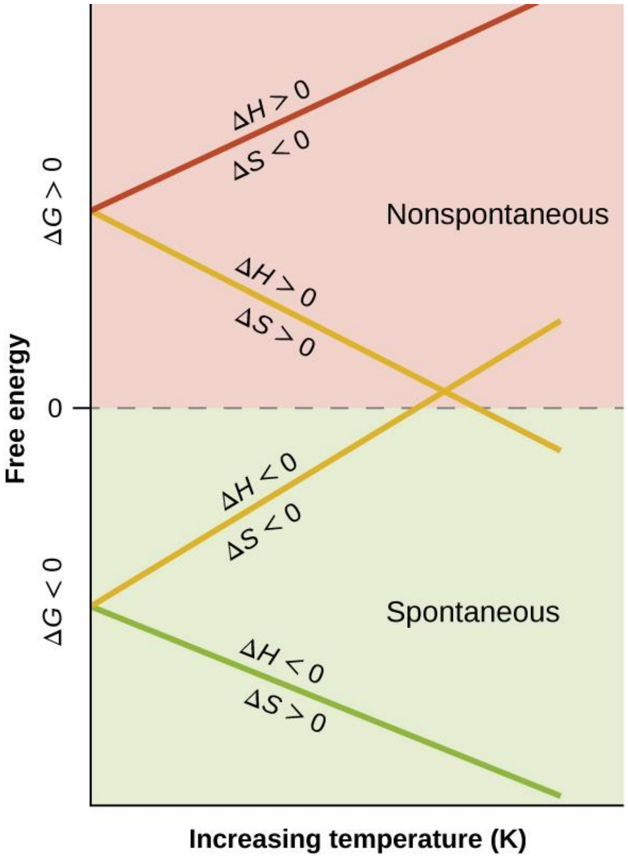


Figure 17.11 These plots show the variation in Δ*G* with temperature for the four possible combinations of arithmetic sign for Δ*H* and Δ*S*.

Equilibrium Temperature for a Phase Transition

EXAMPLE 17.10

As defined in the chapter on liquids and solids, the boiling point of a liquid is the temperature at which its liquid and gaseous phases are in equilibrium (that is, when vaporization and condensation occur at equal rates). Use the information in Appendix 17.2 to estimate the boiling point of water.

Solution

The process of interest is the following phase change: $H_2O\ (l) \rightleftharpoons H_2O\ (g)$

When this process is at equilibrium, Δ*G* = 0, so the following is true: $T = \frac{\Delta H}{\Delta S}$

Using the standard thermodynamic data from Appendix 17.2.

$$\Delta H^\circ = 1\times\Delta H_f^\circ(H_2O_{(g)}) - 1\times\Delta H_f^\circ(H_2O_{(l)})$$

$$= (-241.82) - (-286.83)\ \text{kJ/mol} = 44.01\ \text{kJ/mol}$$

$$\Delta S^\circ = 1\times S^\circ(H_2O_{(g)}) - 1\times S^\circ(H_2O_{(l)})$$

$$= (188.8) - (70.0)\ \text{J/K·mol} = 118.8\ \text{J/K·mol} = 0.1188\ \text{kJ/K·mol}$$

$$T = \frac{\Delta H^\circ}{\Delta S^\circ} = \frac{44.01\ \frac{kJ}{mol}}{0.1188\ \frac{kJ}{mol\cdot K}} = 370.5\ \text{K} = 97.3\ ^\circ\text{C}$$

The accepted value for water's normal boiling point is 373.2 K (100.0 °C), and so this calculation is in reasonable agreement. Note that the values for enthalpy and entropy changes data used were derived from standard data at 298 K (Appendix 7.2). If desired, you could obtain more accurate results by using enthalpy and entropy changes determined at (or at least closer to) the actual boiling point.

Check Your Learning

Use the information in Appendix 17.2 to estimate the boiling point of CS_2.

ANSWER: 313 K (accepted value 319 K)

Free Energy and Equilibrium

The free energy change for a process may be viewed as a measure of its driving force. A negative value for Δ*G* represents a driving force for the process in the forward direction, while a positive value represents a driving force for the process in the reverse direction. When Δ*G* is zero, the forward and reverse driving forces are equal, and the process occurs in both directions at the same rate (the system is at equilibrium).

In the chapter on equilibrium the *reaction quotient*, *Q*, was introduced as a convenient measure of the status of an equilibrium system. Recall that *Q* is the numerical value of the mass action expression for the system, and that you may use its value to identify the direction in which a reaction will proceed in order to achieve equilibrium. When *Q* is lesser than the equilibrium constant, *K*, the reaction will proceed in the forward direction until equilibrium is reached and $Q = K$. Conversely, if $Q > K$, the process will proceed in the reverse direction until equilibrium is achieved.

The free energy change for a process taking place with reactants and products present under *nonstandard conditions* (pressures other than 1 bar; concentrations other than 1 M) is related to the standard free energy change according to this equation:

$$\Delta G = \Delta G^\circ + RT\ln Q$$

R is the gas constant (8.314 J/K mol), *T* is the kelvin or absolute temperature, and *Q* is the reaction quotient.

For gas phase equilibria, the pressure-based reaction quotient, Q_P, is used. The concentration-based reaction quotient, Q_C, is used for condensed phase equilibria. This equation may be used to predict the spontaneity for a process under any given set of conditions as illustrated in Example 17.11

Calculating Δ*G* under Nonstandard Conditions

EXAMPLE 17.11

What is the free energy change for the process shown here under the specified conditions?

T = 25 °C, P_{N_2}=0 .870 atm, P_{H_2}= 0.250 atm, and P_{NH_3}= 12.9 atm

$$2NH_3\,(g) \rightleftharpoons 3H_2\,(g) + N_2\,(g) \qquad \Delta G^\circ = 33.0\text{ kJ/mol}$$

Solution

The equation relating free energy change to standard free energy change and reaction quotient may be used directly:

$$
\begin{aligned}
\Delta G &= \Delta G^\circ + RT\ln Q \\
&= 33.0 \times 10^3 \frac{J}{mol} + (8.314 \frac{J}{mol \cdot K} \times 298\ K \times \ln \left(\frac{0.250^3 \cdot 0.870}{12.9^2}\right) \\
&= 9.68 \times 10^3\ J/mol \\
&= 9.68\ kJ/mol
\end{aligned}
$$

Since the computed value for Δ*G* is positive, the reaction is nonspontaneous under these conditions.

Check Your Learning

Calculate the free energy change for this same reaction at 875 °C in a 5.00 L mixture containing 0.100 mol of each gas. Is the reaction spontaneous under these conditions?

ANSWER:

Δ*G* = +45.1 kJ/mol; no

Calculating an Equilibrium Constant using Standard Free Energy Change

For a system at equilibrium, *Q* = *K* and Δ*G* = 0, the previous equation may be written as

$$0 = \Delta G^\circ + RT\ln K_{\text{(at equilibrium)}}$$

Rearrange to get:

$$\Delta G^\circ = -RT\ln K \qquad \text{or} \qquad K = e^{\frac{-\Delta G^{º}}{RT}}$$

This form of the equation provides a useful link between these two essential thermodynamic properties, and it can be used to derive equilibrium constants from standard free energy changes and vice versa. The relations between standard free energy changes and equilibrium constants are summarized in Table 17.4.

Table17.4 Relations between Standard Free Energy Changes and Equilibrium Constants

K	**Δ*G*°**	**Composition of an Equilibrium Mixture**
> 1	< 0	Products are more abundant
< 1	> 0	Reactants are more abundant
= 1	= 0	Reactants and products are comparably abundant

EXAMPLE 17.12

Given that the standard free energies of formation of $Ag^+(aq)$, $Cl^-(aq)$, and $AgCl(s)$ are 77.1 kJ/mol, −131.2 kJ/mol, and −109.8 kJ/mol, respectively, calculate the solubility product, K_{sp}, for AgCl.

Solution

The reaction of interest is the following: $AgCl\ (s) \rightleftharpoons Ag^+\ (aq) + Cl^-\ (aq) \qquad K_{sp} = [Ag^+][Cl^-]$

The standard free energy change for this reaction is first computed using standard free energies of formation for its reactants and products:

$$\Delta G° = [\Delta G_f°(Ag^+_{(aq)}) + \Delta G_f°(Cl^-_{(aq)})] - [\Delta G_f°(AgCl_{(s)})]$$

$$= [(77.1) + (-131.2)] - (-109.8)\ \text{kJ/mol} = 55.7\ \text{kJ/mol}$$

The equilibrium constant for the reaction may then be derived from its standard free energy change:

$$K_{sp} = e^{\frac{-\Delta G^{\circ}}{RT}} = e^{\frac{-55.7 \times 10^{3}\,J/mol}{(8.314\frac{J}{molK})(298.15\,K)}} = e^{-22.470} = 1.74 \times 10^{-10}$$

This result is in reasonable agreement with the value provided in Appendix 16.2.

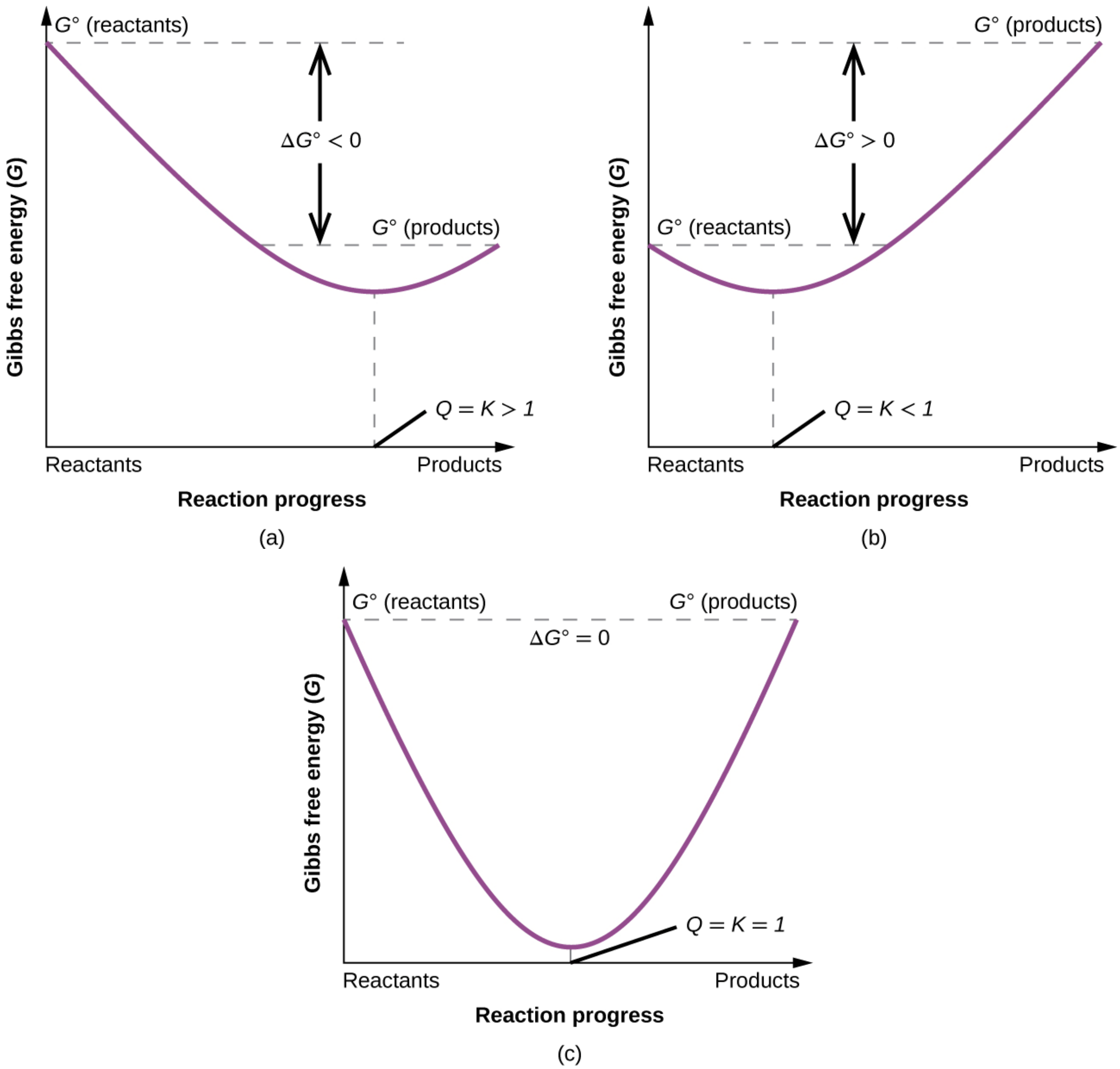
Check Your Learning

Use the thermodynamic data provided in Appendix 17.2 to calculate the equilibrium constant for the dissociation of dinitrogen tetroxide at 25 °C.

$$2NO_2\,(g) \rightleftharpoons N_2O_4\,(g)$$

ANSWER: $K = 6.9$

To further illustrate the relation between these two essential thermodynamic concepts, consider the observation that reactions spontaneously proceed in a direction that ultimately establishes equilibrium. As may be shown by plotting the free energy change versus the extent of the reaction (for example, as reflected in the value of *Q*), equilibrium is established when the system’s free energy is minimized (Figure 17.2). If a system consists of reactants and products in nonequilibrium amounts ($Q \neq K$), the reaction will proceed spontaneously in the direction necessary to establish equilibrium.



(a)

(b)

(c)

Figure 17.12 These plots show the free energy versus reaction progress for systems whose standard free energy changes are (a) negative, (b) positive, and (c) zero. Nonequilibrium systems will proceed spontaneously in whatever direction is necessary to minimize free energy and establish equilibrium.

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Modified the incorrect lithium ion battery equation

Modified the incorrect acid battery equation

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Chapter 18 Electrochemistry

Chapter Introduction

Figure 18.1 Electric vehicles are powered by batteries, devices that harness the energy of spontaneous redox reactions. (credit: modification of work by Robert Couse-Baker)

The important reduction-oxidation (redox) reaction class is defined by changes in oxidation states for one or more reactant elements, and it includes a subset of reactions involving the transfer of electrons between reactant species. Around the turn of the nineteenth century, chemists began exploring ways these electrons could be transferred *indirectly* via an external circuit rather than directly via intimate contact of redox reactants. In the two centuries since, the field of *electrochemistry* has evolved to yield significant insights on the fundamental aspects of redox chemistry as well as a wealth of technologies ranging from industrial-scale metallurgical processes to robust, rechargeable batteries for electric vehicles (Figure 18.1). In this chapter, the essential concepts of electrochemistry will be addressed.

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18.1 Redox Reactions

Learning Objectives

- Describe defining traits of redox chemistry
- Identify the oxidizing agent and reducing agent of a redox reaction
- Balance chemical equations for redox reactions using the half-reaction method

Oxidation-Reduction Reactions

Earth's atmosphere contains about 20% molecular oxygen, O_2, a chemically reactive gas that plays an essential role in the metabolism of aerobic organisms and in many environmental processes that shape the world. The term **oxidation** was originally used to describe chemical reactions involving O_2, but its meaning has evolved to refer to a broad and important reaction class known as *oxidation-reduction (redox) reactions*.

A few examples of such reactions will be used to develop a clear picture of this classification. Some redox reactions involve the transfer of electrons between reactant species to yield ionic products, such as the reaction between sodium and chlorine to yield sodium chloride:

$$2Na\ (s) + Cl_2\ (g) \longrightarrow 2NaCl\ (s)$$

It is helpful to view the process with regard to each individual reactant, that is, to represent the fate of each reactant in the form of an equation called a **half-reaction**:

$$2Na\ (s) \longrightarrow 2Na^+\ (s) + 2e^-$$

$$Cl_2\ (g) + 2e^- \longrightarrow 2Cl^-\ (s)$$

These equations show that Na atoms *lose electrons,* while Cl atoms (in the Cl_2 molecule) *gain electrons*. The "*s*" subscripts for the resulting ions signifying they are present in the form of a solid ionic compound.

For redox reactions of this sort, the loss and gain of electrons define the complementary processes that occur:

$$\text{oxidation} = \text{loss of electrons}$$

reduction = gain of electrons

In this reaction, sodium undergoes **oxidation**. In other words, sodium is **oxidized.** Chlorine undergoes **reduction**. In other words, chlorine is **reduced**.

Viewed from a more active perspective, sodium functions as a **reducing agent (reductant)**, since it provides electrons, causing chlorine to undergoes reduction.

Likewise, chlorine functions as an **oxidizing agent (oxidant)**, as it effectively removes electrons, causing sodium to undergoes oxidation.

reducing agent = species that is oxidized

oxidizing agent = species that is reduced

Several subclasses of redox reactions are recognized, including **combustion reactions** in which the reducing agent (also called a *fuel*) and oxidizing agent (often, but not necessarily, molecular oxygen) react vigorously and produce significant amounts of heat, and often light, in the form of a flame. Solid rocket-fuel reactions are combustion processes.

Some redox processes, however, do not involve the transfer of electrons. Consider, for example, a reaction similar to the one yielding NaCl:

$$H_2\,(g) + Cl_2\,(g) \longrightarrow 2HCl\,(g)$$

The product of this reaction is a covalent compound, so transfer of electrons in the explicit sense is not involved. To clarify the similarity of this reaction to the previous one and permit an unambiguous definition of redox reactions, a property called *oxidation number* has been defined.

Oxidation Numbers

The **oxidation number** (or **oxidation state**) of an element in a compound is the charge its atoms would possess *if the compound was ionic*. The following guidelines are used to assign oxidation numbers to each element in a molecule or ion.

1. The oxidation number of an atom in an elemental substance is zero.
2. The oxidation number of a monatomic ion is equal to the ion's charge.
3. Oxidation numbers for common nonmetals are usually assigned as follows:
    - Hydrogen: +1 when combined with nonmetals, −1 when combined with metals
    - Oxygen: −2 in most compounds,

      sometimes −1 (so-called peroxides, O_2^{2-}),

      very rarely –½ (so-called superoxides, O_2^{-}),

      positive values when combined with F (values vary)
    - Halogens: −1 for F always,

      −1 for other halogens except when combined with oxygen or other halogens (positive oxidation numbers in these cases, varying values)
4. The sum of oxidation numbers for all atoms in a molecule or polyatomic ion equals the charge on the molecule or ion.

Note: The following convention aims to emphasize the distinction between charge and oxidation number.
Charge notation – The proper convention for reporting charge is to write the number first, followed by the sign (e.g., 2+).
Oxidation number notation – While oxidation number is written with the reversed sequence, sign followed by number (e.g., +2).

Assigning Oxidation Numbers

EXAMPLE 18.1

Follow the guidelines in this section of the text to assign oxidation numbers to all the elements in the following species: (a) H_2S (b) SO_3^{2-} (c) Na_2SO_4

Solution

(a) According to guideline 1, the oxidation number for H is +1.

Using this oxidation number and the compound's formula, guideline 4 may then be used to calculate the oxidation number for sulfur: charge on $H_2S = 0$

$$\begin{aligned} 0 &= 2(+1) + 1(x) \\ 0 &= 2 + x \\ x &= -2 \quad \rightarrow \text{ The oxidation number for S is } -2. \end{aligned}$$

(b) Guideline 3 suggests the oxidation number for oxygen is −2.

Using this oxidation number and the ion's formula, guideline 4 may then be used to calculate the oxidation number for sulfur: charge on $SO_3^{2-} = -2$

$$\begin{aligned} -2 &= 1(x) + 3(-2) \\ -2 &= x - 6 \\ x &= +4 \quad \rightarrow \text{ The oxidation number for S is } +4. \end{aligned}$$

(c) For ionic compounds, it's convenient to assign oxidation numbers for the cation and anion separately.

According to guideline 2, the oxidation number for sodium is +1.

Per guideline 3, the usual oxidation number for oxygen is −2.

Use guideline 4 to calculate the oxidation number for sulfur: charge on $SO_4^{2-} = -2$

$$\begin{aligned} -2 &= 1(x) + 4(-2) \\ -2 &= x - 8 \\ x &= +6 \quad \rightarrow \text{ The oxidation number for S is } +6. \end{aligned}$$

Check Your Learning

Assign oxidation states to the elements whose atoms are underlined in each of the following compounds or ions: (a) $K\underline{N}O_3$ (b) $\underline{Al}H_3$ (c) $\underline{N}H_4^+$ (d) $H_2\underline{P}O_4^-$

ANSWER: (a) N, +5; (b) Al, +3; (c) N, −3; (d) P, +5

Identify Redox Reactions

Using the oxidation number concept, an all-inclusive definition of redox reaction has been established. **Oxidation-reduction (redox) reactions** are those in which one or more elements involved undergo a change in oxidation number. (While the vast majority of redox reactions involve changes in oxidation number for two or more elements, a few interesting exceptions to this rule do exist Example 18.2) Definitions for the complementary processes of this reaction class are correspondingly revised as shown here:

$$\text{oxidation} = \text{increase in oxidation number}$$

$$\text{reduction} = \text{decrease in oxidation number}$$

Returning to the reactions used to introduce this topic, they may now both be identified as redox processes. In the reaction between sodium and chlorine to yield sodium chloride, sodium is oxidized (its oxidation number increases from 0 in Na to +1 in NaCl) and chlorine is reduced (its oxidation number decreases from 0 in Cl_2 to −1 in NaCl). In the reaction between molecular hydrogen and chlorine, hydrogen is oxidized (its oxidation number increases from 0 in H_2 to +1 in HCl) and chlorine is reduced (its oxidation number decreases from 0 in Cl_2 to −1 in HCl).

EXAMPLE 18.2

Identify which equations represent redox reactions, providing a name for the reaction if appropriate. For those reactions identified as redox, name the oxidizing agent and reducing agent.

(a) $ZnCO_3\,(s) \longrightarrow ZnO\,(s) + CO_2\,(g)$

(b) $2Ga\,(l) + 3Br_2\,(l) \longrightarrow 2GaBr_3\,(s)$

(c) $2H_2O_2\,(aq) \longrightarrow 2H_2O\,(l) + O_2\,(g)$

(d) $BaCl_2\,(aq) + K_2SO_4\,(aq) \longrightarrow BaSO_4\,(s) + 2KCl\,(aq)$

(e) $C_2H_4\,(g) + 3O_2\,(g) \longrightarrow 2CO_2\,(g) + 2H_2O\,(l)$

Solution

Redox reactions are identified per definition if one or more elements undergo a change in oxidation number.

(a) This is not a redox reaction, since oxidation numbers remain unchanged for all elements.

(b) This is a redox reaction. Gallium is oxidized, its oxidation number increasing from 0 in Ga(*l*) to +3 in $GaBr_3$(*s*). The reducing agent is Ga(*l*). Bromine is reduced, its oxidation number decreasing from 0 in Br_2(*l*) to −1 in $GaBr_3$(*s*). The oxidizing agent is Br_2(*l*).

(c) This is a redox reaction. It is a particularly interesting process, as it involves the same element, oxygen, undergoing both oxidation and reduction (a so-called *disproportionation reaction)*. Oxygen is oxidized, its oxidation number increasing from −1 in H_2O_2(*aq*) to 0 in O_2(*g*). Oxygen is also reduced, its oxidation number decreasing from −1 in H_2O_2(*aq*) to −2 in H_2O(*l*). For disproportionation reactions, the same substance functions as an oxidant and a reductant.

(d) This is not a redox reaction, since oxidation numbers remain unchanged for all elements.

(e) This is a redox reaction (combustion). Carbon is oxidized, its oxidation number increasing from −2 in C_2H_4(*g*) to +4 in CO_2(*g*). The reducing agent (fuel) is C_2H_4(*g*). Oxygen is reduced, its oxidation number decreasing from 0 in O_2(*g*) to −2 in H_2O(*l*). The oxidizing agent is O_2(*g*).

Check Your Learning

This equation describes the production of tin(II) chloride:

$$Sn\ (s) + 2HCl\ (g) \longrightarrow SnCl_2\ (s) + H_2\ (g)$$

Is this a redox reaction? If so, provide a more specific name for the reaction if appropriate, and identify the oxidant and reductant.

ANSWER: Yes, a single-replacement reaction. Sn(*s*) is the reductant, HCl(*g*) is the oxidant.

Balancing Redox Equations

The unbalanced equation below describes the decomposition of molten sodium chloride:

$$\text{NaCl (l)} \longrightarrow \text{Na (l)} + \text{Cl}_2\text{ (g)} \qquad \text{unbalanced}$$

This reaction satisfies the criterion for redox classification, since the oxidation number for Na is decreased from +1 to 0 (it undergoes *reduction*) and that for Cl is increased from −1 to 0 (it undergoes *oxidation*). The equation in this case is easily balanced by inspection, requiring stoichiometric coefficients of 2 for the NaCl and Na:

$$2\text{ NaCl (l)} \longrightarrow 2\text{ Na (l)} + \text{Cl}_2\text{ (g)} \qquad \text{balanced}$$

Redox reactions that take place in aqueous solutions are commonly encountered in electrochemistry, and many involve water or its characteristic ions, H^+(*aq*) and OH^-(*aq*), as reactants or products. In these cases, equations representing the redox reaction can be very challenging to balance by inspection, and the use of a systematic approach called the *half-reaction method* is helpful. This approach involves the following steps:

1. Write skeletal equations for the oxidation and reduction half-reactions.
2. Balance each half-reaction for all elements except H and O.
3. Balance each half-reaction for O by adding H_2O.
4. Balance each half-reaction for H by adding H^+.
5. Balance each half-reaction for charge by adding electrons.
6. If necessary, multiply one or both half-reactions so that the number of electrons consumed in one is equal to the number produced in the other.
7. Add the two half-reactions and simplify.
8. If the reaction takes place in a basic medium, add OH^- ions the equation obtained in step 7 to neutralize the H^+ ions (add in equal numbers to both sides of the equation) and simplify.

The next examples demonstrate the application of this method to balancing equations for aqueous redox reactions.

Balancing Equations for Redox Reactions in Acidic Solutions

EXAMPLE 18.3

Write the balanced equation representing reaction between solid copper and nitric acid to yield aqueous copper(II) ions and nitrogen monoxide gas.

Solution

Following the steps of the half-reaction method:

1. *Write skeletal equations for the oxidation and reduction half-reactions.*

   oxidation: $Cu\ (s) \longrightarrow Cu^{2+}\ (aq)$

   reduction: $HNO_3\ (aq) \longrightarrow NO\ (g)$

2. *Balance each half-reaction for all elements except H and O.*

   oxidation: $Cu\ (s) \longrightarrow Cu^{2+}\ (aq)$

   reduction: $HNO_3\ (aq) \longrightarrow NO\ (g)$

3. *Balance each half-reaction for O by adding H_2O.*

   oxidation: $Cu\ (s) \longrightarrow Cu^{2+}\ (aq)$

   reduction: $HNO_3\ (aq) \longrightarrow NO\ (g) + 2\ H_2O\ (l)$

4. *Balance each half-reaction for H by adding H^+.*

   oxidation: $Cu\ (s) \longrightarrow Cu^{2+}\ (aq)$

   reduction: $3\ H^+\ (aq) + HNO_3\ (aq) \longrightarrow NO\ (g) + 2\ H_2O\ (l)$

5. *Balance each half-reaction for charge by adding electrons.*

   oxidation: $Cu\ (s) \longrightarrow Cu^{2+}\ (aq) + 2\ e^-$

   reduction: $3\ e^- + 3\ H^+\ (aq) + HNO_3\ (aq) \longrightarrow NO\ (g) + 2\ H_2O\ (l)$

6. *If necessary, multiply one or both half-reactions so that the number of electrons consumed in one is equal to the number produced in the other.*

   oxidation (×3): $3\ Cu\ (s) \longrightarrow 3\ Cu^{2+}\ (aq) + 6\ e^-$

   reduction (×2): $6\ e^- + 6\ H^+\ (aq) + 2\ HNO_3\ (aq) \longrightarrow 2\ NO\ (g) + 4\ H_2O(l)$

7. *Add the two half-reactions and simplify.*

$$3Cu\ (s) + 6e^{-} + 6H^{+}\ (aq) + 2HNO_3\ (aq) \longrightarrow 3Cu^{2+}\ (aq) + 6e^{-} + 2NO\ (g) + 4H_2O(l)$$

$$3Cu\ (s) + 6H^{+}\ (aq) + 2HNO_3\ (aq) \longrightarrow 3Cu^{2+}\ (aq) + 2NO\ (g) + 4H_2O(l)$$

8. *If the reaction takes place in a basic medium, add OH^{-} ions the equation obtained in step 7 to neutralize the H^{+} ions (add in equal numbers to both sides of the equation) and simplify.*

   This step not necessary since the solution is stipulated to be acidic.

The balanced equation for the reaction in an acidic solution is then

$$3Cu\ (s) + 6H^{+}\ (aq) + 2HNO_3\ (aq) \longrightarrow 3Cu^{2+}\ (aq) + 2NO\ (g) + 4H_2O(l)$$

Check Your Learning

The reaction above results when using relatively diluted nitric acid. If concentrated nitric acid is used, nitrogen dioxide is produced instead of nitrogen monoxide. Write a balanced equation for this reaction.

ANSWER: $Cu\ (s) + 2H^{+}\ (aq) + 2HNO_3\ (aq) \longrightarrow Cu^{2+}\ (aq) + 2NO_2\ (g) + 2H_2O(l)$

Balancing Equations for Redox Reactions in Basic Solutions

EXAMPLE 18.4

Write the balanced equation representing reaction between aqueous permanganate ion, MnO_4^-, and solid chromium(III) hydroxide, $Cr(OH)_3$, to yield solid manganese(IV) oxide, MnO_2, and aqueous chromate ion, CrO_4^{2-} The reaction takes place in a basic solution.

Solution

Following the steps of the half-reaction method:

1. *Write skeletal equations for the oxidation and reduction half-reactions.*

   oxidation: $Cr(OH)_3\ (s) \longrightarrow CrO_4^{2-}\ (aq)$

   reduction: $MnO_4^-\ (aq) \longrightarrow MnO_2\ (s)$

2. *Balance each half-reaction for all elements except H and O.*

   oxidation: $Cr(OH)_3\ (s) \longrightarrow CrO_4^{2-}\ (aq)$

   reduction: $MnO_4^-\ (aq) \longrightarrow MnO_2\ (s)$

3. *Balance each half-reaction for O by adding H_2O.*

   oxidation: $H_2O\ (l) + Cr(OH)_3\ (s) \longrightarrow CrO_4^{2-}\ (aq)$

   reduction: $MnO_4^-\ (aq) \longrightarrow MnO_2\ (s) + 2H_2O\ (l)$

4. *Balance each half-reaction for H by adding H^+.*

   oxidation: $H_2O\ (l) + Cr(OH)_3\ (s) \longrightarrow CrO_4^{2-}\ (aq) + 5H^+\ (aq)$

   reduction: $4H^+\ (aq) + MnO_4^-\ (aq) \longrightarrow MnO_2\ (s) + 2H_2O\ (l)$

5. *Balance each half-reaction for charge by adding electrons.*

   oxidation: $H_2O\ (l) + Cr(OH)_3\ (s) \longrightarrow CrO_4^{2-}\ (aq) + 5H^+\ (aq) + 3e^-$

   reduction: $4H^+\ (aq) + MnO_4^-\ (aq) + 3e^- \longrightarrow MnO_2\ (s) + 2H_2O\ (l)$

6. *If necessary, multiply one or both half-reactions so that the number of electrons consumed in one is equal to the number produced in the other.*

   This step is not necessary since the number of electrons is already in balance.

7. *Add the two half-reactions and simplify.*

$H_2O\ (l) + Cr(OH)_3\ (s) + 4H^+\ (aq) + MnO_4^-\ (aq) + 3e^- \longrightarrow CrO_4^{2-}\ (aq) + 5H^+\ (aq) + 3e^- + MnO_2\ (s) + 2H_2O(l)$

$Cr(OH)_3\ (s) + MnO_4^-\ (aq) \longrightarrow CrO_4^{2-}\ (aq) + H^+\ (aq) + MnO_2\ (s) + H_2O(l)$

8. *If the reaction takes place in a basic medium, add OH^- ions the equation obtained in step 7 to neutralize the H^+ ions (add in equal numbers to both sides of the equation) and simplify.*

$OH^-\ (aq) + Cr(OH)_3\ (s) + MnO_4^-\ (aq) \longrightarrow CrO_4^{2-}\ (aq) + H^+\ (aq) + OH^-\ (aq) + MnO_2\ (s) + H_2O\ (l)$

$OH^-\ (aq) + Cr(OH)_3\ (s) + MnO_4^-\ (aq) \longrightarrow CrO_4^{2-}\ (aq) + MnO_2\ (s) + 2H_2O\ (l)$

Check Your Learning

Aqueous permanganate ion may also be reduced using aqueous bromide ion, Br^-, the products of this reaction being solid manganese(IV) oxide and aqueous bromate ion, BrO_3^-. Write the balanced equation for this reaction occurring in a basic medium.

ANSWER:

$H_2O\ (l) + 2MnO_4^-\ (aq) + Br^-\ (aq) \longrightarrow 2MnO_2\ (s) + BrO_3^-\ (aq) + 2OH^-\ (aq)$

18.2 Spontaneous Redox Reactions – Galvanic (or Voltaic) Cells

Learning Objectives

- Describe the function of a galvanic cell and its components

Introduction

As demonstration of spontaneous chemical change, Figure 18.2 shows the result of immersing a coiled wire of copper into an aqueous solution of silver nitrate. A gradual but visually impressive change spontaneously occurs as the initially colorless solution becomes increasingly blue, and the initially smooth copper wire becomes covered with a porous gray solid.

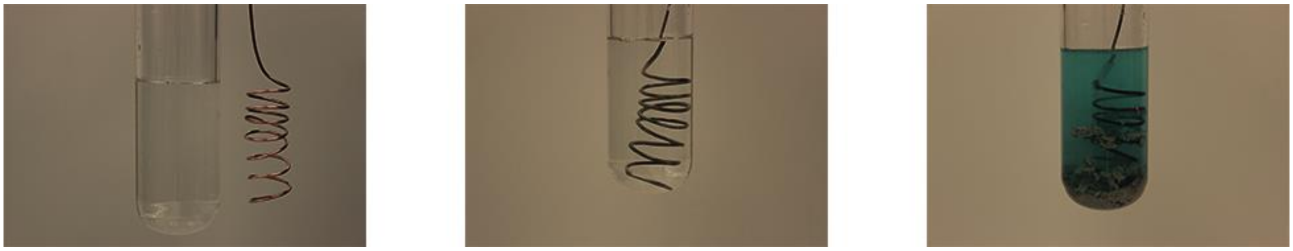

Figure 18.2 A copper wire and an aqueous solution of silver nitrate (left) are brought into contact (center) and a spontaneous transfer of electrons occurs, creating blue $Cu^{2+}(aq)$ and gray Ag(*s*) (right).

These observations are consistent with (i) the oxidation of elemental copper to yield copper(II) ions, $Cu^{2+}(aq)$, which impart a blue color to the solution, and (ii) the reduction of silver(I) ions to yield elemental silver, which deposits as a fluffy solid on the copper wire surface. And so, *the direct transfer of electrons from the copper wire to the aqueous silver ions is spontaneous* under the employed conditions. A summary of this redox system is provided by these equations:

Overall reaction: $Cu\ (s) + 2Ag^{+}\ (aq) \longrightarrow Cu^{2+}\ (aq) + 2Ag\ (s)$

Oxidation half-reaction: $Cu\ (s) \longrightarrow Cu^{2+}\ (aq) + 2e^{-}$

Reduction half-reaction: $2Ag^{+}\ (aq) + 2e^{-} \longrightarrow 2Ag\ (s)$

Galvaic Cells

Consider the construction of a device that contains all the reactants and products of a redox system like the one here, but prevents physical contact between the reactants. Direct transfer of electrons is, therefore, prevented; transfer, instead, takes place indirectly through an external circuit that contacts the separated reactants. Devices of this sort are generally referred to as *electrochemical cells*, and those in which a spontaneous redox reaction takes place are called **galvanic cells** (or **voltaic cells**).

Half-Cells

A galvanic cell based on the spontaneous reaction between copper and silver(I) is depicted in Figure 18.3. The cell is comprised of two **half-cells**, each containing the redox conjugate pair (“couple”) of a single reactant. The half-cell shown at the left contains the Cu(0)/Cu(II) couple in the form of a solid copper foil and an aqueous solution of copper nitrate. The right half-cell contains the Ag(I)/Ag(0) couple as solid silver foil and an aqueous silver nitrate solution.

Electrodes

An external circuit is connected to each half-cell at its solid foil, meaning the Cu and Ag foil each function as an *electrode*. By definition, the **anode** of an electrochemical cell is the electrode at which oxidation occurs (in this case, the Cu foil) and the **cathode** is the electrode where reduction occurs (the Ag foil).

Salt Bridge

The redox reactions in a galvanic cell occur only at the interface between each half-cell’s reaction mixture and its electrode. To keep the reactants separate while maintaining charge-balance, the two half-cell solutions are connected by a tube filled with inert electrolyte solution called a **salt bridge**.

The spontaneous reaction in this cell produces Cu^{2+} cations in the anode half-cell and consumes Ag^+ ions in the cathode half-cell, resulting in a compensatory flow of inert ions from the salt bridge that maintains charge balance. Increasing concentrations of Cu^{2+} in the anode half-cell are balanced by an influx of NO_3^- from the salt bridge, while a flow of Na^+ into the cathode half-cell compensates for the decreasing Ag^+ concentration.

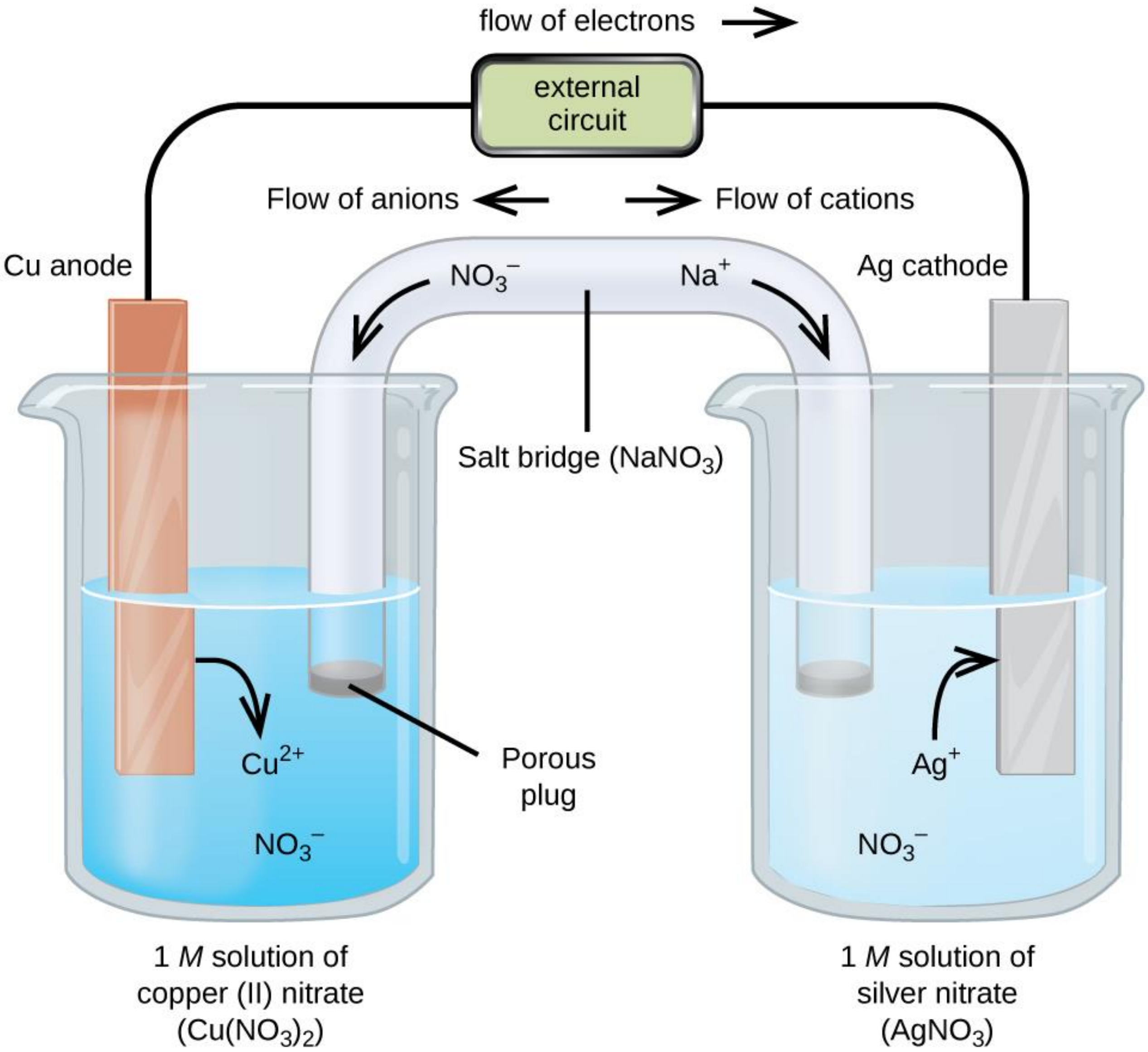

Figure 18.3 A galvanic cell based on the spontaneous reaction between copper and silver(I) ions.

18.3 Electrode and Cell Potentials

Learning Objectives

- Describe and relate the definitions of electrode and cell potentials
- Interpret electrode potentials in terms of relative oxidant and reductant strengths
- Calculate cell potentials and predict redox spontaneity using standard electrode potentials

Cell Potentials

Unlike the spontaneous oxidation of copper by aqueous silver(I) ions described in section 18.2, immersing a copper wire in an aqueous solution of lead(II) ions yields no reaction. The two species, $Ag^+(aq)$ and $Pb^{2+}(aq)$, thus show a distinct difference in their redox activity towards Cu(s): the $Ag^+(aq)$ spontaneously oxidized Cu(s), but the $Pb^{2+}(aq)$ did not.

Electrochemical cells permit this relative redox activity to be quantified by an easily measured property, ***potential***. This property is more commonly called ***voltage*** when referenced in regard to electrical applications, and it is a measure of energy accompanying the transfer of charge.

Potentials are measured in the volt unit, defined as one joule of energy per one coulomb of charge, V = J/C. When measured for purposes of electrochemistry, a potential reflects the driving force for a specific type of charge transfer process, namely, the transfer of electrons between redox reactants.

Considering the nature of potential in this context, it is clear that the potential of a single half-cell or a single electrode can't be measured; "transfer" of electrons requires both a donor and recipient, in this case a reductant and an oxidant, respectively. Instead, a half-cell potential may only be assessed relative to that of another half-cell. It is only the *difference in potential* between two half-cells that may be measured, and these measured potentials are called **cell potentials, E_{cell},** defined as:

$$E_{cell} = E_{cathode} - E_{anode}$$

where $E_{cathode}$ and E_{anode} are the potentials of two different half-cells functioning as specified in the subscripts.

As for other thermodynamic quantities, the **standard cell potential, E°cell,** is a cell potential measured when both half-cells are under standard-state conditions (1 *M* concentrations, 1 bar pressures, 298 K):

$$E°_{cell} = E°_{cathode} - E°_{anode}$$

To simplify the collection and sharing of potential data for half-reactions, the scientific community has designated one particular half-cell to serve as a universal reference for cell potential measurements, assigning it a potential of exactly 0 V. This half-cell is the **standard hydrogen electrode (SHE)** and it is based on half-reaction below: $2H+(aq)+2e^{-} \longrightarrow H2(g)$ A typical SHE contains an inert platinum electrode immersed in precisely 1 *M* aqueous $H+$ and a stream of bubbling $H2$ gas at 1 bar pressure, all maintained at a temperature of 298 K (see **Figure 18.4).**

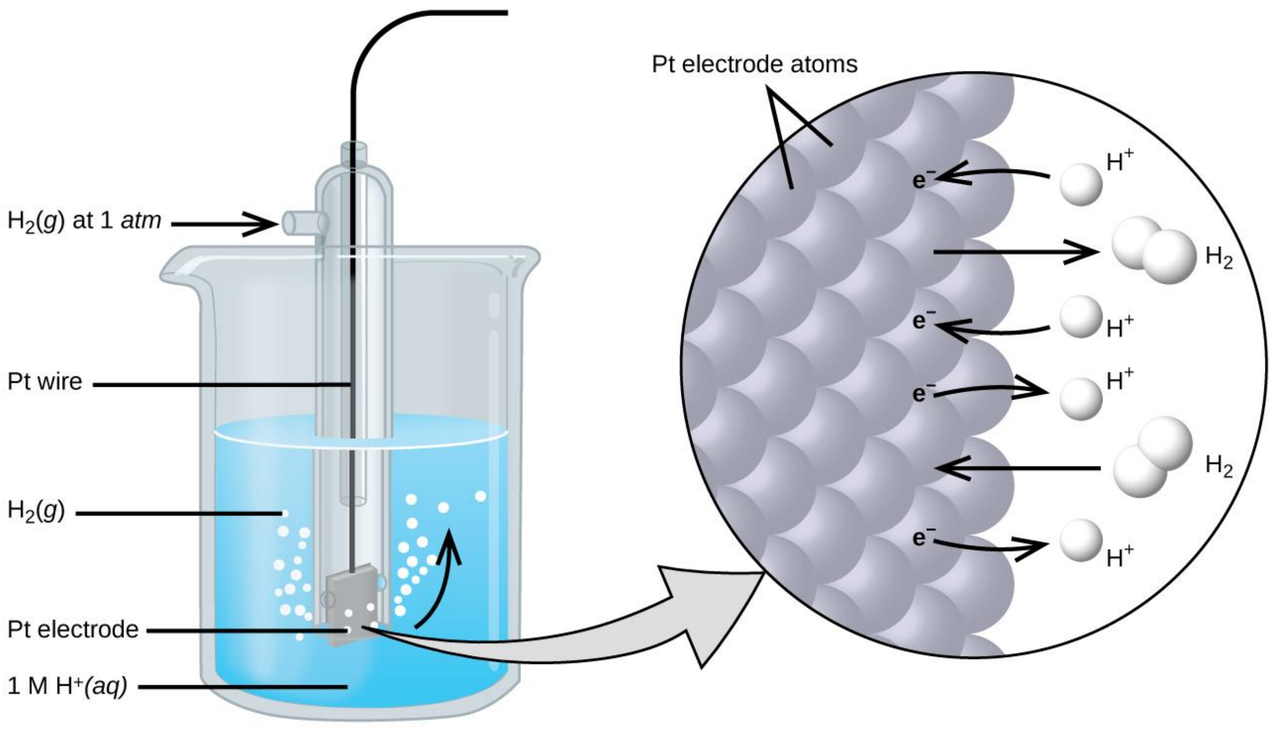

Figure 18.4 A standard hydrogen electrode (SHE).

The assigned potential of the SHE permits the definition of a conveniently measured potential for a single half-cell. The **electrode potential (E_X)** for a half-cell *X* is defined as *the potential measured for a cell comprised of X acting as cathode and the SHE acting as anode:*

$$E_{cell} = E_X - E_{SHE} \qquad E_{SHE} = 0 \text{ V (defined)}$$

$$E_{cell} = E_X$$

When the half-cell *X* is under standard-state conditions, its potential is the **standard electrode potential, $E°_X$.** Since the definition of cell potential requires the half-cells function as cathodes, these potentials are sometimes called *standard reduction potentials.*

This approach to measuring electrode potentials is illustrated in **Figure 18.5,** which depicts a cell comprised of an SHE connected to a copper(II)/copper(0) half-cell under standard-state conditions. A voltmeter in the external circuit allows measurement of the potential difference between the two half-cells. Since the Cu half-cell is designated as the cathode in the definition of cell potential, it is connected to the red (positive) input of the voltmeter, while the designated SHE anode is connected to the black (negative) input. These connections insure that the sign of the measured potential will be consistent with the sign conventions of electrochemistry per the various definitions discussed above. A cell potential of +0.337 V is measured, and so

$$E°_{cell} = E°_{Cu} = +0.337\ V$$

Tabulations of E° values for other half-cells measured in a similar fashion are available as reference literature to permit calculations of cell potentials and the prediction of the spontaneity of redox processes.

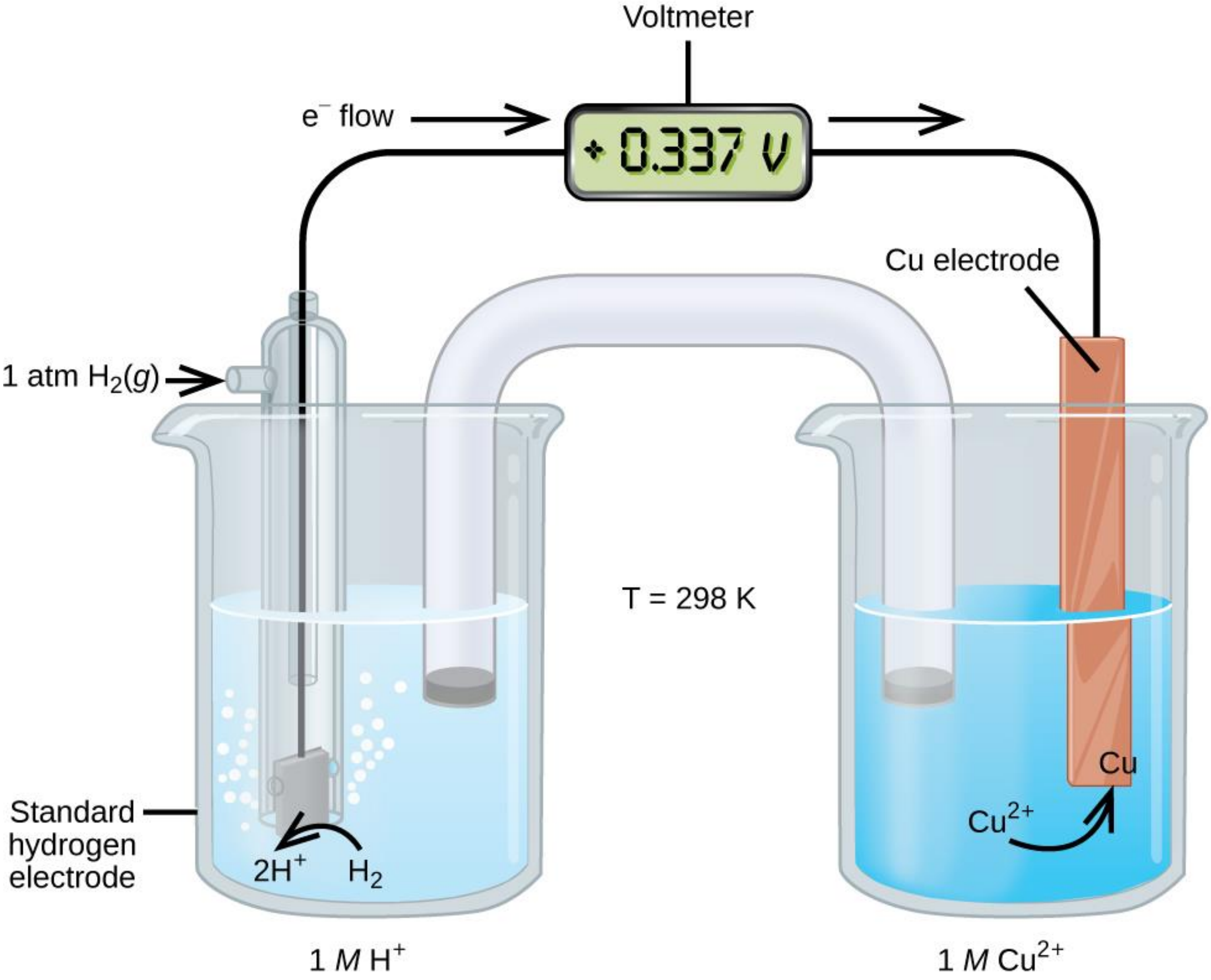

Figure 18.5 A cell permitting experimental measurement of the standard electrode potential for the half-reaction: $Cu^{2+}(aq) + 2e^- \longrightarrow Cu(s)$

Table 18.1 provides a listing of standard electrode potentials for a selection of half-reactions in numerical order, and a more extensive alphabetical listing is given in Appendix 18.3.

Table 18.1 Selected Standard Reduction Potentials at 25 °C

Half-Reaction	***E*° (V)**
F_2 (g) + $2e^-$ ⟶ $2F^-$ (aq)	+2.866
PbO_2 (s) + SO_4^{2-} (aq) + $4H^+$ (aq) + $2e^-$ ⟶ $PbSO_4$ (s) + $2H_2O$ (l)	+1.69
MnO_4^- (aq) + $8H^+$ (aq) + $5e^-$ ⟶ Mn^{2+} (aq) + $4H_2O$ (l)	+1.507
Au^{3+} (aq) + $3e^-$ ⟶ Au (s)	+1.498
Cl_2 (g) + $2e^-$ ⟶ $2Cl^-$ (aq)	+1.35827
O_2 (g) + $4H^+$ (aq) + $4e^-$ ⟶ $2H_2O$ (l)	+1.229
Pt^{2+} (aq) + $2e^-$ ⟶ Pt (s)	+1.20
Br_2 (l) + $2e^-$ ⟶ $2Br^-$ (aq)	+1.0873
Ag^+ (aq) + e^- ⟶ Ag (s)	+0.7996
Hg_2^{2+} (aq) + $2e^-$ ⟶ 2Hg (l)	+0.7973
Fe^{3+} (aq) + e^- ⟶ Fe^{2+} (aq)	+0.771
MnO_4^- (aq) + $2H_2O$ (l) + $3e^-$ ⟶ MnO_2 (s) + $4OH^-$(aq)	+0.558
I_2 (s) + $2e^-$ ⟶ $2I^-$ (aq)	+0.5355
NiO_2 (s) + $2H_2O$ (l) + $2e^-$ ⟶ $Ni(OH)_2$ (s) + $2OH^-$ (aq)	+0.49
Cu^{2+} (aq) + $2e^-$ ⟶ Cu (s)	+0.34
Hg_2Cl_2 (s) + $2e^-$ ⟶ 2Hg (l) + $2Cl^-$ (aq)	+0.26808
AgCl (s) + e^- ⟶ Ag (s) + Cl^- (aq)	+0.22233
Sn^{4+} (aq) + $2e^-$ ⟶ Sn^{2+} (aq)	+0.151
$2H^+$ (aq) + $2e^-$ ⟶ H_2 (g)	0.00
Pb^{2+} (aq) + $2e^-$ ⟶ Pb (s)	−0.1262
Sn^{2+} (aq) + $2e^-$ ⟶ Sn (s)	−0.1375
Ni^{2+} (aq) + $2e^-$ ⟶ Ni (s)	−0.257
Co^{2+} (aq) + $2e^-$ ⟶ Co (s)	−0.28

Half-Reaction	*E*° (V)
$PbSO_4 (s) + 2e^- \longrightarrow Pb (s) + SO_4^{2-} (aq)$	−0.3505
$Cd^{2+} (aq) + 2e^- \longrightarrow Cd (s)$	−0.4030
$Fe^{2+} (aq) + 2e^- \longrightarrow Fe (s)$	−0.447
$Cr^{3+} (aq) + 3e^- \longrightarrow Cr (s)$	−0.744
$Mn^{2+} (aq) + 2e^- \longrightarrow Mn (s)$	−1.185
$Zn(OH)_2 (s) + 2e^- \longrightarrow Zn (s) + 2OH^- (aq)$	−1.245
$Zn^{2+} (aq) + 2e^- \longrightarrow Zn (s)$	−0.7618
$Al^{3+} (aq) + 3e^- \longrightarrow Al (s)$	−1.662
$Mg^{2+} (aq) + 2e^- \longrightarrow Mg (s)$	−2.372
$Na^+ (aq) + e^- \longrightarrow Na (s)$	−2.71
$Ca^{2+} (aq) + 2e^- \longrightarrow Ca (s)$	−2.868
$Ba^{2+} (aq) + 2e^- \longrightarrow Ba (s)$	−2.912
$K^+ (aq) + e^- \longrightarrow K (s)$	−2.931
$Li^+ (aq) + e^- \longrightarrow Li (s)$	−3.04

Calculating Standard Cell Potentials

EXAMPLE 18.5

What is the standard potential of the galvanic cell shown in Figure 18.3?

Solution

The cell in Figure 18.3 is galvanic, the spontaneous cell reaction involving oxidation of its copper anode and reduction of silver(I) ions at its silver cathode:

Cell reaction: $Cu\ (s) + 2Ag^{+}\ (aq) \longrightarrow Cu^{2+}\ (aq) + 2Ag\ (s)$
Anode half-reaction: $Cu\ (s) \longrightarrow Cu^{2+}\ (aq) + 2e^{-}$
Cathode half-reaction: $2Ag^{+}\ (aq) + 2e^{-} \longrightarrow 2Ag\ (s)$

The standard cell potential computed as

$$E°_{cell} = E°_{cathode} - E°_{anode}$$
$$E°_{cell} = E°_{Ag} - E°_{Cu}$$
$$E°_{cell} = 0.7996\ V - 0.34\ V = +0.46\ V$$

Check Your Learning

What is the standard cell potential expected if the silver cathode half-cell in Figure 18.3 is replaced with a lead half-cell: $Pb^{2+}\ (aq) + 2e^{-} \longrightarrow Pb\ (s)$?

ANSWER: −0. 47 V

Interpreting Electrode and Cell Potentials

Thinking carefully about the definitions of cell and electrode potentials and the observations of spontaneous redox change presented thus far, a significant relation is noted. The previous section described the spontaneous oxidation of copper by aqueous silver(I) ions, but no observed reaction with aqueous lead(II) ions.

Results of the calculations in Example 18.5 have just shown ***the spontaneous process is described by a positive cell potential*** while ***the nonspontaneous process exhibits a negative cell potential***.

And so, with regard to the relative effectiveness ("strength") with which aqueous Ag^+ and Pb^{2+} ions oxidize Cu under standard conditions, ***the stronger oxidant is the one exhibiting the greater standard electrode potential, E°***. Since by convention electrode potentials are for reduction processes, an increased value of $E°$ corresponds to an increased driving force behind the reduction of the species (hence increased effectiveness of its action as an *oxidizing agent* on some other species).

Negative values for electrode potentials are simply a consequence of assigning a value of 0 V to the SHE, indicating the reactant of the half-reaction is a weaker oxidant than aqueous hydrogen ions.

Applying this logic to the numerically ordered listing of standard electrode potentials in Table 18.1 shows this listing to be likewise in order of the oxidizing strength of the half-reaction's reactant species, decreasing from strongest oxidant (most positive $E°$) to weakest oxidant (most negative $E°$). Predictions regarding the spontaneity of redox reactions under standard state conditions can then be easily made by simply comparing the relative positions of their table entries. By definition, $\boldsymbol{E°_{\text{cell}}}$ **is positive when** $\boldsymbol{E°_{\text{cathode}} > E°_{\text{anode}}}$**,** and so any redox reaction in which the oxidant's entry is above the reductant's entry is predicted to be spontaneous.

Reconsideration of the two redox reactions in Example 18.5 provides support for this fact. The entry for the silver(I)/silver(0) half-reaction is above that for the copper(II)/copper(0) half-reaction, and so the oxidation of Cu by Ag^+ is predicted to be spontaneous ($E°_{\text{cathode}} > E°_{\text{anode}}$ and so $E°_{\text{cell}} > 0$). Conversely, the entry for the lead(II)/lead(0) half-cell is beneath that for copper(II)/copper(0), and the oxidation of Cu by Pb^{2+} is nonspontaneous ($E°_{\text{cathode}} < E°_{\text{anode}}$ and so $E°_{\text{cell}} < 0$).

Recalling the chapter on thermodynamics, the spontaneities of the forward and reverse reactions of a reversible process show a reciprocal relationship: if a process is spontaneous in one direction, it is non-spontaneous in the opposite direction. As an indicator of spontaneity for redox reactions, the potential of a cell reaction shows a consequential relationship in its arithmetic sign. The spontaneous oxidation of copper by lead(II) ions is *not* observed,

$Cu\ (s) + Pb^{2+}\ (aq) \longrightarrow Cu^{2+}\ (aq) + Pb\ (s)$ $E°_{forward} = -0.47\ V$
(negative, non-spontaneous)

and so the reverse reaction, the oxidation of lead by copper(II) ions, is predicted to occur spontaneously:

$Pb\ (s) + Cu^{2+}\ (aq) \longrightarrow Pb^{2+}\ (aq) + Cu\ (s)$ $E°_{forward} = +0.47\ V$
(positive, spontaneous)

Note that reversing the direction of a redox reaction effectively interchanges the identities of the cathode and anode half-reactions, and so the cell potential is calculated from electrode potentials in the reverse subtraction order than that for the forward reaction. In practice, a voltmeter would report a potential of −0.47 V with its red and black inputs connected to the Pb and Cu electrodes, respectively. If the inputs were swapped, the reported voltage would be +0.47 V.

Predicting Redox Spontaneity

EXAMPLE 18.6

Are aqueous iron(II) ions predicted to spontaneously oxidize elemental chromium under standard state conditions? Assume the half-reactions to be those available in Table 18.1.

Solution

Referring to the tabulated half-reactions, the redox reaction in question can be represented by the equations below:

$$Cr\ (s) + Fe^{2+}\ (aq) \longrightarrow Cr^{3+}\ (aq) + Fe\ (s)$$

The entry for the putative oxidant, Fe^{2+}, appears *above* the entry for the reductant, Cr, and so a spontaneous reaction is predicted per the quick approach described above. Supporting this predication by calculating the standard cell potential for this reaction gives

$E°_{cell} = E°_{cathode} - E°_{anode}$
$E°_{cell} = E°_{Fe(II)} - E°_{Cr}$
$E°_{cell} = 0.447\ V - -0.774\ V = +0.297\ V$

The positive value for the standard cell potential indicates the process is spontaneous under standard state conditions.

Check Your Learning

Use the data in Table 18.1 to predict the spontaneity of the oxidation of bromide ion by molecular iodine under standard state conditions, supporting the prediction by calculating the standard cell potential for the reaction. Repeat for the oxidation of iodide ion by molecular bromine.

ANSWER:

$I_2\ (s) + 2Br^-\ (aq) \longrightarrow 2I^-\ (aq) + Br_2\ (l)$ $E°_{cell} = +0.5518\ V$ (spontaneous)
$Br_2\ (l) + 2I^-\ (aq) \longrightarrow 2Br^-\ (aq) + I_2\ (s)$ $E°_{cell} = -0.5518V$ (nonspontaneous)

Appendix 18.3

Standard Electrode (Half-Cell) Potentials	
Half-Reaction	***E*° (V)**
$Ag^+ + e^- \longrightarrow Ag$	+0.7996
$AgCl + e^- \longrightarrow Ag + Cl^-$	+0.22233
$[Ag(CN)_2]^- + e^- \longrightarrow Ag + 2CN^-$	−0.31
$Ag_2CrO_4 + 2e^- \longrightarrow 2Ag + CrO_4^{2-}$	+0.45
$[Ag(NH_3)_2]^+ + e^- \longrightarrow Ag + 2NH_3$	+0.373
$[Ag(S_2O_3)_2]^{3+} + e^- \longrightarrow Ag + 2S_2O_3^{2-}$	+0.017
$[AlF_6]^{3-} + 3e^- \longrightarrow Al + 6F^-$	−2.07
$Al^{3+} + 3e^- \longrightarrow Al$	−1.662
$Am^{3+} + 3e^- \longrightarrow Am$	−2.048
$Au^{3+} + 3e^- \longrightarrow Au$	+1.498
$Au^+ + e^- \longrightarrow Au$	+1.692
$Ba^{2+} + 2e^- \longrightarrow Ba$	−2.912
$Be^{2+} + 2e^- \longrightarrow Be$	−1.847
$Br_2 + 2e^- \longrightarrow 2Br^-$	+1.0873
$Ca^{2+} + 2e^- \longrightarrow Ca$	−2.868
$Ce^{3+} + 3e^- \longrightarrow Ce$	−2.483
$Ce^{4+} + e^- \longrightarrow Ce^{3+}$	+1.61
$Cd^{2+} + 2e^- \longrightarrow Cd$	−0.4030
$[Cd(CN)_4]^{2-} + 2e^- \longrightarrow Cd + 4CN^-$	−1.09
$[Cd(NH_3)_4]^{2+} + 2e^- \longrightarrow Cd + 4NH_3$	−0.61
$CdS + 2e^- \longrightarrow Cd + S^{2-}$	−1.17

Standard Electrode (Half-Cell) Potentials

Half-Reaction	***E*° (V)**
$Cl_2 + 2e^- \longrightarrow 2Cl^-$	+1.35827
$ClO_4^- + H_2O + 2e^- \longrightarrow ClO_3^- + 2OH^-$	+0.36
$ClO_3^- + H_2O + 2e^- \longrightarrow ClO_2^- + 2OH^-$	+0.33
$ClO_2^- + H_2O + 2e^- \longrightarrow ClO^- + 2OH^-$	+0.66
$ClO^- + H_2O + 2e^- \longrightarrow Cl^- + 2OH^-$	+0.89
$ClO_4^- + 2H_3O^+ + 2e^- \longrightarrow ClO_3^- + 3H_2O$	+1.189
$ClO_3^- + 3H_3O^+ + 2e^- \longrightarrow HClO_2 + 4H_2O$	+1.21
$HClO + H_3O^+ + 2e^- \longrightarrow Cl^- + 2H_2O$	+1.482
$HClO + H_3O^+ + e^- \longrightarrow 12Cl_2 + 2H_2O$	+1.611
$HClO_2 + 2H_3O^+ + 2e^- \longrightarrow HClO + 3H_2O$	+1.628
$Co^{3+} + e^- \longrightarrow Co^{2+}$ (2mol // H_2SO_4)	+1.83
$Co^{2+} + 2e^- \longrightarrow Co$	−0.28
$[Co(NH_3)_6]^{3+} + e^- \longrightarrow [Co(NH_3)_6]^{2+}$	+0.1
$Co(OH)_3 + e^- \longrightarrow Co(OH)_2 + OH^-$	+0.17
$Cr^{3+} + 3e^- \longrightarrow Cr$	−0.744
$Cr^{3+} + e^- \longrightarrow Cr^{2+}$	−0.407
$Cr^{2+} + 2e^- \longrightarrow Cr$	−0.913
$[Cu(CN)_2]^- + e^- \longrightarrow Cu + 2CN^-$	−0.43
$CrO_4^{2-} + 4H_2O + 3e^- \longrightarrow Cr(OH)_3 + 5OH^-$	−0.13
$Cr_2O_7^{2-} + 14H_3O^+ + 6e^- \longrightarrow 2Cr^{3+} + 21H_2O$	+1.232
$[Cr(OH)_4]^- + 3e^- \longrightarrow Cr + 4OH^-$	−1.2
$Cr(OH)_3 + 3e^- \longrightarrow Cr + 3OH^-$	−1.48
$Cu^{2+} + e^- \longrightarrow Cu^+$	+0.153

Standard Electrode (Half-Cell) Potentials

Half-Reaction	***E*° (V)**
$Cu^{2+} + 2e^- \longrightarrow Cu$	+0.34
$Cu^+ + e^- \longrightarrow Cu$	+0.521
$F_2 + 2e^- \longrightarrow 2F^-$	+2.866
$Fe^{2+} + 2e^- \longrightarrow Fe$	−0.447
$Fe^{3+} + e^- \longrightarrow Fe^{2+}$	+0.771
$[Fe(CN)_6]^{3-} + e^- \longrightarrow [Fe(CN)_6]^{4-}$	+0.36
$Fe(OH)_2 + 2e^- \longrightarrow Fe + 2OH^-$	−0.88
$FeS + 2e^- \longrightarrow Fe + S^{2-}$	−1.01
$Ga^{3+} + 3e^- \longrightarrow Ga$	−0.549
$Gd^{3+} + 3e^- \longrightarrow Gd$	−2.279
$12H_2 + e^- \longrightarrow H^-$	−2.23
$2H_2O + 2e^- \longrightarrow H_2 + 2OH^-$	−0.8277
$H_2O_2 + 2H_3O^+ + 2e^- \longrightarrow 4H_2O$	+1.776
$2H_3O^+ + 2e^- \longrightarrow H_2 + 2H_2O$	0.00
$HO_2^- + H_2O + 2e^- \longrightarrow 3OH^-$	+0.878
$Hf^{4+} + 4e^- \longrightarrow Hf$	−1.55
$Hg^{2+} + 2e^- \longrightarrow Hg$	+0.851
$2Hg^{2+} + 2e^- \longrightarrow Hg_2^{2+}$	+0.92
$Hg_2^{2+} + 2e^- \longrightarrow 2Hg$	+0.7973
$[HgBr_4]^{2-} + 2e^- \longrightarrow Hg + 4Br^-$	+0.21
$Hg_2Cl_2 + 2e^- \longrightarrow 2Hg + 2Cl^-$	+0.26808
$[Hg(CN)_4]^{2-} + 2e^- \longrightarrow Hg + 4CN^-$	−0.37
$[HgI_4]^{2-} + 2e^- \longrightarrow Hg + 4I^-$	−0.04

Standard Electrode (Half-Cell) Potentials	
Half-Reaction	***E*° (V)**
$HgS + 2e^- \longrightarrow Hg + S^{2-}$	−0.70
$I_2 + 2e^- \longrightarrow 2I^-$	+0.5355
$In^{3+} + 3e^- \longrightarrow In$	−0.3382
$K^+ + e^- \longrightarrow K$	−2.931
$La^{3+} + 3e^- \longrightarrow La$	−2.52
$Li^+ + e^- \longrightarrow Li$	−3.04
$Lu^{3+} + 3e^- \longrightarrow Lu$	−2.28
$Mg^{2+} + 2e^- \longrightarrow Mg$	−2.372
$Mn^{2+} + 2e^- \longrightarrow Mn$	−1.185
$MnO_2 + 2H_2O + 2e^- \longrightarrow Mn(OH)_2 + 2OH^-$	−0.05
$MnO_4^- + 2H_2O + 3e^- \longrightarrow MnO_2 + 4OH^-$	+0.558
$MnO_2 + 4H^+ + 2e^- \longrightarrow Mn^{2+} + 2H_2O$	+1.23
$MnO_4^- + 8H^+ + 5e^- \longrightarrow Mn^{2+} + 4H_2O$	+1.507
$Na^+ + e^- \longrightarrow Na$	−2.71
$Nd^{3+} + 3e^- \longrightarrow Nd$	−2.323
$Ni^{2+} + 2e^- \longrightarrow Ni$	−0.257
$[Ni(NH_3)_6]^{2+} + 2e^- \longrightarrow Ni + 6NH_3$	−0.49
$NiO_2 + 4H^+ + 2e^- \longrightarrow Ni^{2+} + 2H_2O$	+1.593
$NiO_2 + 2H_2O + 2e^- \longrightarrow Ni(OH)_2 + 2OH^-$	+0.49
$NiS + 2e^- \longrightarrow Ni + S^{2-}$	+0.76
$NO_3^- + 4H^+ + 3e^- \longrightarrow NO + 2H_2O$	+0.957
$NO_3^- + 3H^+ + 2e^- \longrightarrow HNO_2 + H_2O$	+0.92
$NO_3^- + H_2O + 2e^- \longrightarrow NO_2^- + 2OH^-$	+0.10

Standard Electrode (Half-Cell) Potentials	
Half-Reaction	***E*° (V)**
$Np^{3+} + 3e^- \longrightarrow Np$	−1.856
$O_2 + 2H_2O + 4e^- \longrightarrow 4OH^-$	+0.401
$O_2 + 2H^+ + 2e^- \longrightarrow H_2O_2$	+0.695
$O_2 + 4H^+ + 4e^- \longrightarrow 2H_2O$	+1.229
$Pb^{2+} + 2e^- \longrightarrow Pb$	−0.1262
$PbO_2 + SO_4^{2-} + 4H^+ + 2e^- \longrightarrow PbSO_4 + 2H_2O$	+1.69
$PbS + 2e^- \longrightarrow Pb + S^{2-}$	−0.95
$PbSO_4 + 2e^- \longrightarrow Pb + SO_4^{2-}$	−0.3505
$Pd^{2+} + 2e^- \longrightarrow Pd$	+0.987
$[PdCl_4]^{2-} + 2e^- \longrightarrow Pd + 4Cl^-$	+0.591
$Pt^{2+} + 2e^- \longrightarrow Pt$	+1.20
$[PtBr_4]^{2-} + 2e^- \longrightarrow Pt + 4Br^-$	+0.58
$[PtCl_4]^{2-} + 2e^- \longrightarrow Pt + 4Cl^-$	+0.755
$[PtCl_6]^{2-} + 2e^- \longrightarrow [PtCl_4]^{2-} + 2Cl^-$	+0.68
$Pu^{3+} + 3e^- \longrightarrow Pu$	−2.03
$Ra^{2+} + 2e^- \longrightarrow Ra$	−2.92
$Rb^+ + e^- \longrightarrow Rb$	−2.98
$[RhCl_6]^{3-} + 3e^- \longrightarrow Rh + 6Cl^-$	+0.44
$S + 2e^- \longrightarrow S^{2-}$	−0.47627
$S + 2H^+ + 2e^- \longrightarrow H_2S$	+0.142
$Sc^{3+} + 3e^- \longrightarrow Sc$	−2.09
$Se + 2H^+ + 2e^- \longrightarrow H_2Se$	−0.399
$[SiF_6]^{2-} + 4e^- \longrightarrow Si + 6F^-$	−1.2

Standard Electrode (Half-Cell) Potentials	
Half-Reaction	***E*° (V)**
$SiO_3^{2-} + 3H_2O + 4e^- \longrightarrow Si + 6OH^-$	−1.697
$SiO_2 + 4H^+ + 4e^- \longrightarrow Si + 2H_2O$	−0.86
$Sm^{3+} + 3e^- \longrightarrow Sm$	−2.304
$Sn^{4+} + 2e^- \longrightarrow Sn^{2+}$	+0.151
$Sn^{2+} + 2e^- \longrightarrow Sn$	−0.1375
$[SnF_6]^{2-} + 4e^- \longrightarrow Sn + 6F^-$	−0.25
$SnS + 2e^- \longrightarrow Sn + S^{2-}$	−0.94
$Sr^{2+} + 2e^- \longrightarrow Sr$	−2.89
$TeO_2 + 4H^+ + 4e^- \longrightarrow Te + 2H_2O$	+0.593
$Th^{4+} + 4e^- \longrightarrow Th$	−1.90
$Ti^{2+} + 2e^- \longrightarrow Ti$	−1.630
$U^{3+} + 3e^- \longrightarrow U$	−1.79
$V^{2+} + 2e^- \longrightarrow V$	−1.19
$Y^{3+} + 3e^- \longrightarrow Y$	−2.37
$Zn^{2+} + 2e^- \longrightarrow Zn$	−0.7618
$[Zn(CN)_4]^{2-} + 2e^- \longrightarrow Zn + 4CN^-$	−1.26
$[Zn(NH_3)_4]^{2+} + 2e^- \longrightarrow Zn + 4NH_3$	−1.04
$Zn(OH)_2 + 2e^- \longrightarrow Zn + 2OH^-$	−1.245
$[Zn(OH)_4]_2 + 2e^- \longrightarrow Zn + 4OH^-$	−1.199
$ZnS + 2e^- \longrightarrow Zn + S^{2-}$	−1.40
$Zr^{4+} + 4e^- \longrightarrow Zr$	−1.539

18.4 Batteries and Fuel Cells

Learning Objectives

- Describe the electrochemistry associated with several common batteries
- Distinguish the operation of a fuel cell from that of a battery

Batteries

There are many technological products associated with the past two centuries of electrochemistry research, none more immediately obvious than the battery. A **battery** is a galvanic cell that has been specially designed and constructed in a way that best suits its intended use a source of electrical power for specific applications. Among the first successful batteries was the *Daniell cell*, which relied on the spontaneous oxidation of zinc by copper(II) ions (Figure 18.6):

$$\text{Zn (s)} + \text{Cu}^{2+}\text{ (aq)} \longrightarrow \text{Zn}^{2+}\text{ (aq)} + \text{Cu (s)}$$

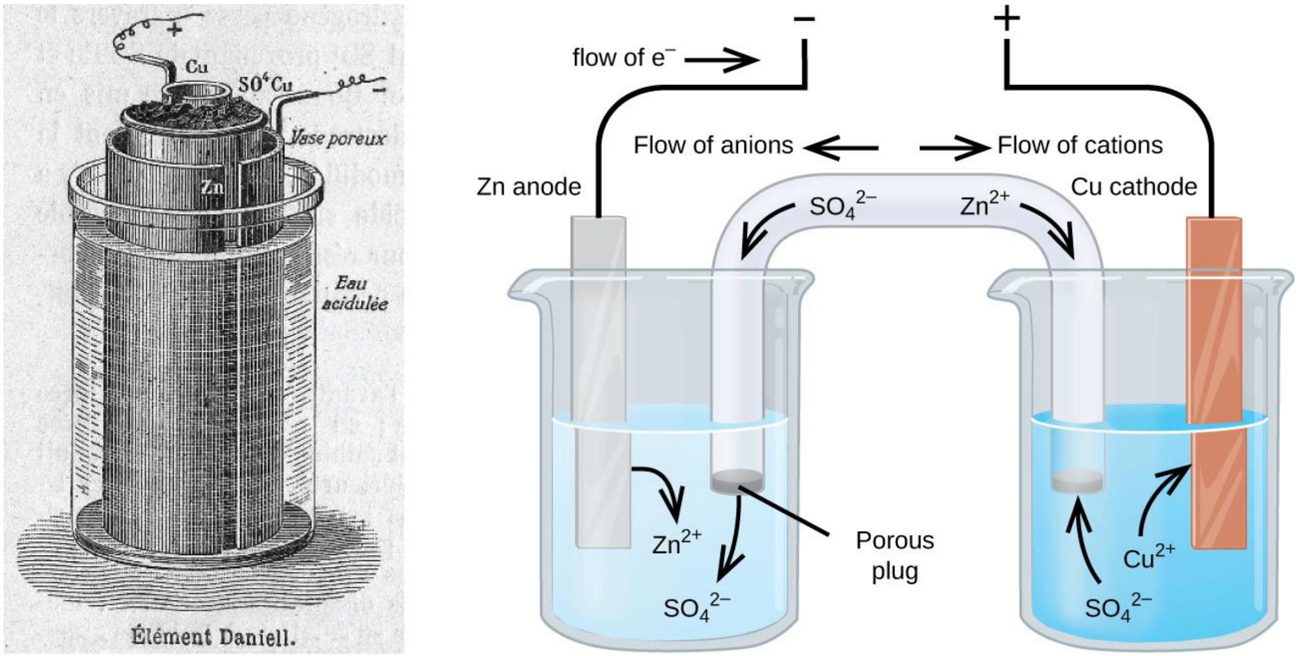

Figure 18.6 Illustration of a Daniell cell taken from a 1904 journal publication (left) along with a simplified illustration depicting the electrochemistry of the cell (right). The 1904 design used a porous clay pot to both contain one of the half-cell's content and to serve as a salt bridge to the other half-cell.

Modern batteries exist in a multitude of forms to accommodate various applications, from tiny button batteries that provide the modest power needs of a wristwatch to the very large batteries used to supply backup energy to municipal power grids. Some batteries are designed for single-use applications and cannot be recharged (**primary cells**), while others are based on conveniently reversible cell reactions that allow recharging by an external power source (**secondary cells**). This section will provide a summary of the basic electrochemical aspects of several batteries familiar to most consumers, and will introduce a related electrochemical device called a *fuel cell* that can offer improved performance in certain applications.

Single-Use Batteries

A common primary battery is the **dry cell**, which uses a zinc can as both container and anode ("–" terminal) and a graphite rod as the cathode ("+" terminal). The Zn can is filled with an electrolyte paste containing manganese(IV) oxide, zinc(II) chloride, ammonium chloride, and water. A graphite rod is immersed in the electrolyte paste to complete the cell. The spontaneous cell reaction involves the oxidation of zinc and the reduction of manganese(IV).

Anode Reaction: $Zn\ (s) \longrightarrow Zn^{2+}\ (aq) + 2e^-$

Reduction Reaction: $2MnO_{2(s)} + 2NH_4Cl_{(aq)} + 2e^- \longrightarrow Mn_2O_{3(s)} + 2NH_{3(aq)} + H_2O_{(l)} + 2Cl^-_{(aq)}$

which together yield the cell reaction:

$$2MnO_2\ (s) + 2NH_4Cl\ (aq) + Zn\ (s) \longrightarrow Zn^{2+}\ (aq) + Mn_2O_3\ (s) + 2NH_3\ (aq) + H_2O\ (l) + 2Cl^-$$

$$E_{cell} = 1.5V$$

The voltage (*cell potential*) of a dry cell is approximately 1.5 V. Dry cells are available in various sizes (e.g., D, C, AA, AAA). All sizes of dry cells comprise the same components, and so they exhibit the same voltage, but larger cells contain greater amounts of the redox reactants and therefore are capable of transferring correspondingly greater amounts of charge. Like other galvanic cells, dry cells may be connected in series to yield batteries with greater voltage outputs, if needed.

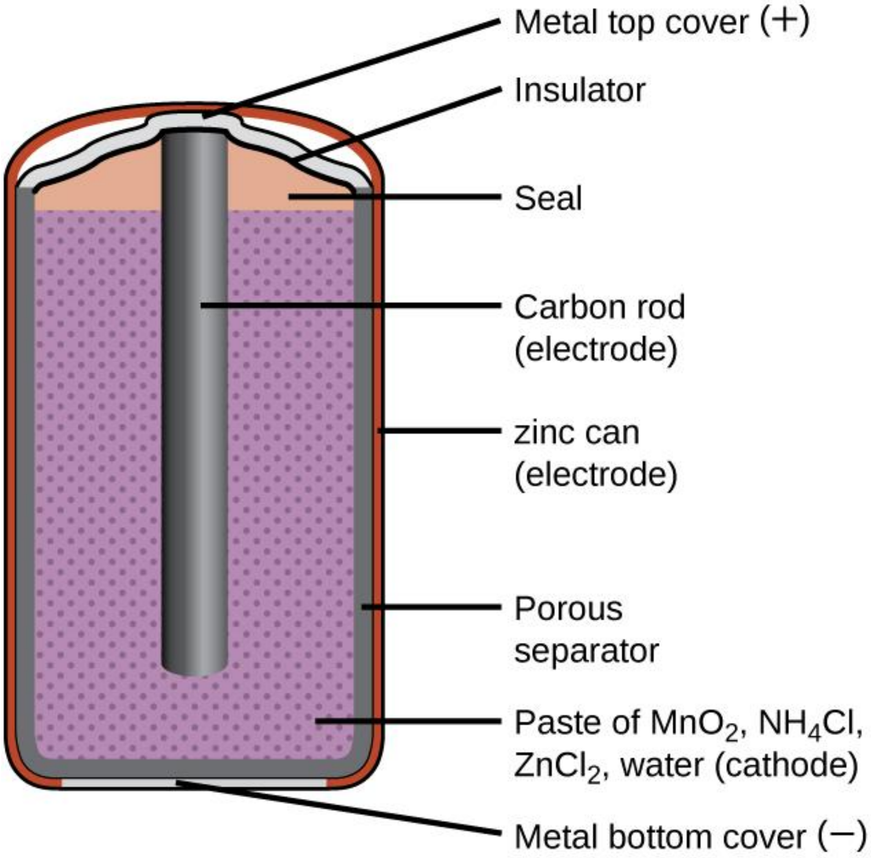

Figure 18.7 A schematic diagram shows a typical dry cell.

Alkaline Batteries

Alkaline batteries (Figure 18.8) were developed in the 1950s to improve on the performance of the dry cell, and they were designed around the same redox couples. As their name suggests, these types of batteries use alkaline electrolytes, often potassium hydroxide. The reactions are

Anode: $\text{Zn (s)} + 2\text{OH}^- \text{(aq)} \longrightarrow \text{ZnO (s)} + \text{H}_2\text{O (l)} + 2\text{e}^-$

Cathode: $2\text{MnO}_2 \text{(s)} + \text{H}_2\text{O (l)} + 2\text{e}^- \longrightarrow \text{Mn}_2\text{O}_3 \text{(s)} + 2\text{OH}^- \text{(aq)}$

Cell: $\text{Zn (s)} + 2\text{MnO}_2 \text{(s)} \longrightarrow \text{ZnO (s)} + \text{Mn}_2\text{O}_3 \text{(s)} \qquad E_{\text{cell}} = +1.43\text{ V}$

An alkaline battery can deliver about three to five times the energy of a zinc-carbon dry cell of similar size. Alkaline batteries are prone to leaking potassium hydroxide, so they should be removed from devices for long-term storage. While some alkaline batteries are rechargeable, most are not. Attempts to recharge an alkaline battery that is not rechargeable often leads to rupture of the battery and leakage of the potassium hydroxide electrolyte.

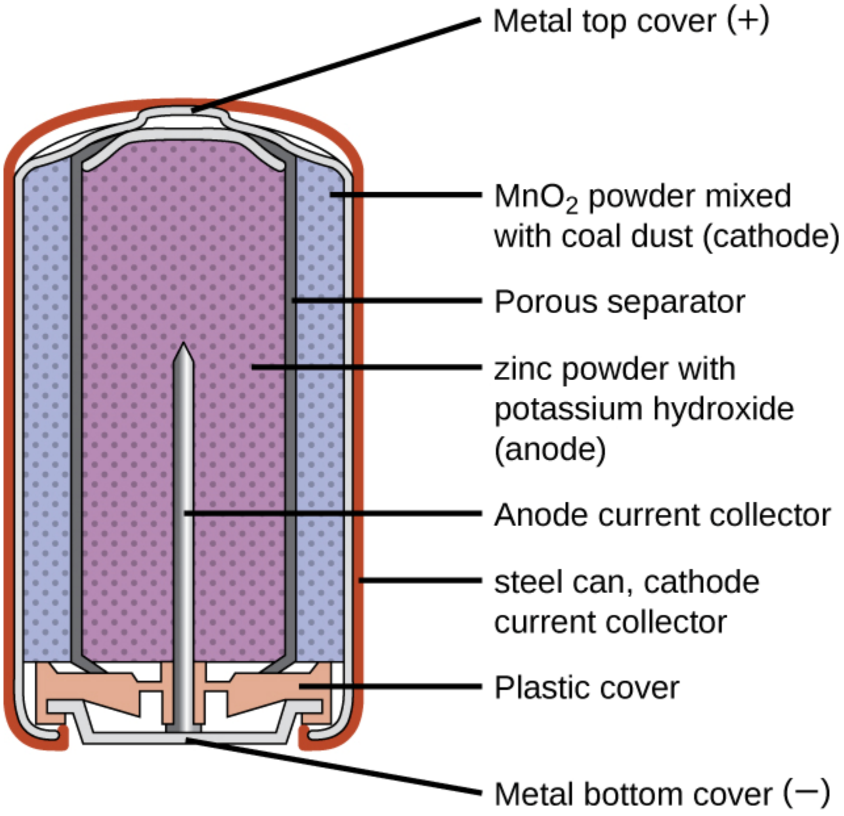

Figure 18.8 Alkaline batteries were designed as improved replacements for zinc-carbon (dry cell) batteries.

Rechargeable (Secondary) Batteries

Nickel-Cadmium

Nickel-cadmium, or NiCd, batteries (Figure 18.9) consist of a nickel-plated cathode, cadmium-plated anode, and a potassium hydroxide electrode. The positive and negative plates, which are prevented from shorting by the separator, are rolled together and put into the case. This is a “jelly-roll” design and allows the NiCd cell to deliver much more current than a similar-sized alkaline battery. The reactions are

Anode: $\mathrm{Cd}\ (s) + 2\mathrm{OH}^-\ (aq) \longrightarrow \mathrm{Cd(OH)_2}\ (s) + 2e^-$

Cathode: $\mathrm{NiO_2}\ (s) + 2\mathrm{H_2O}\ (l) + 2e^- \longrightarrow \mathrm{Ni(OH)_2}\ (s) + 2\mathrm{OH}^-\ (aq)$

Cell: $\mathrm{Cd}\ (s) + \mathrm{NiO_2}\ (s) + 2\mathrm{H_2O}\ (l) \longrightarrow \mathrm{Cd(OH)_2}\ (s) + \mathrm{Ni(OH)_2}\ (s) \qquad E_{\mathrm{cell}} = 1.2\mathrm{V}$

When properly treated, a NiCd battery can be recharged about 1000 times. Cadmium is a toxic heavy metal so NiCd batteries should never be ruptured or incinerated, and they should be disposed of in accordance with relevant toxic waste guidelines.

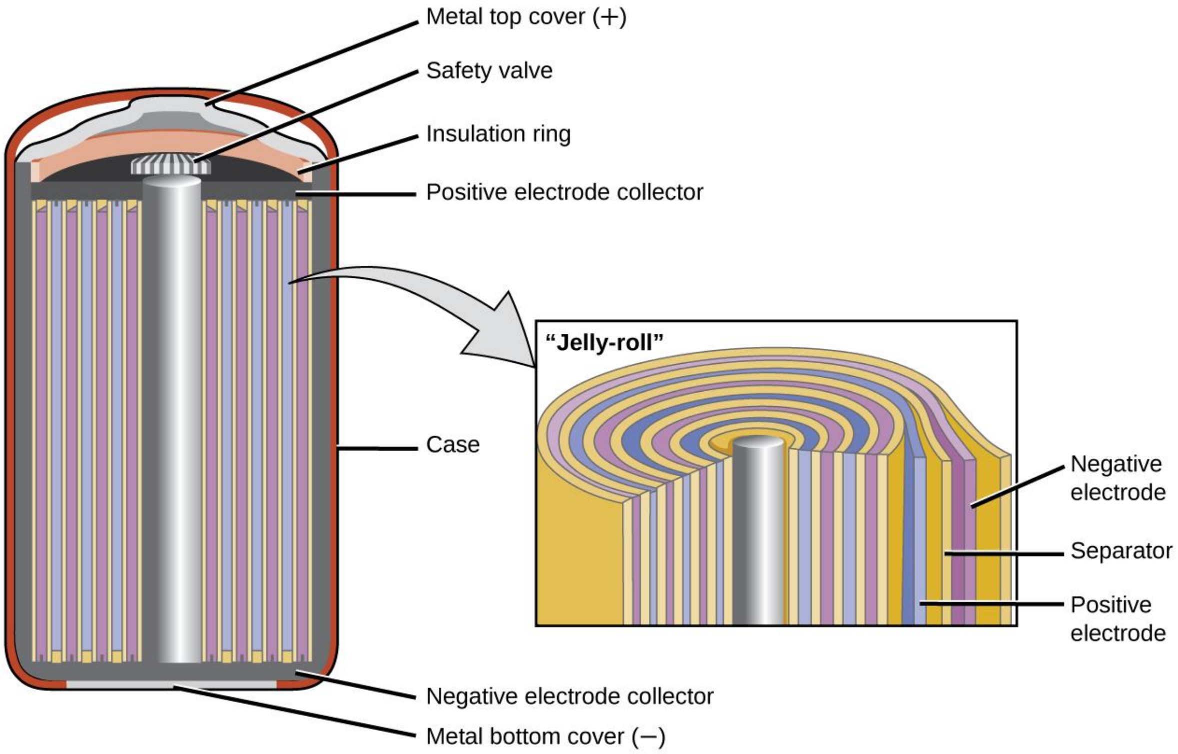

Figure 18.9 NiCd batteries use a “jelly-roll” design that significantly increases the amount of current the battery can deliver as compared to a similar-sized alkaline battery.

Lithium Ion Batteries

Lithium ion batteries (Figure 18.10) are among the most popular rechargeable batteries and are used in many portable electronic devices. The reactions are

Anode: $\text{xLiC}_6 \rightleftharpoons \text{xLi}^+ + \text{xe}^- + \text{xC}_6$

Cathode: $\text{Li}_{1-\text{x}}\text{CoO}_2 + \text{xLi}^+ + \text{xe}^- \rightleftharpoons \text{LiCoO}_2$

Cell: $\text{Li}_{1-\text{x}}\text{CoO}_2 + \text{xLiC}_6 \rightleftharpoons \text{LiCoO}_2 + \text{xC}_6$ $E_{\text{cell}} = 3.7\text{ V}$

The variable stoichiometry of the cell reaction leads to variation in cell voltages, but for typical conditions, *x* is usually no more than 0.5 and the cell voltage is approximately 3.7 V. Lithium batteries are popular because they can provide a large amount current, are lighter than comparable batteries of other types, produce a nearly constant voltage as they discharge, and only slowly lose their charge when stored.

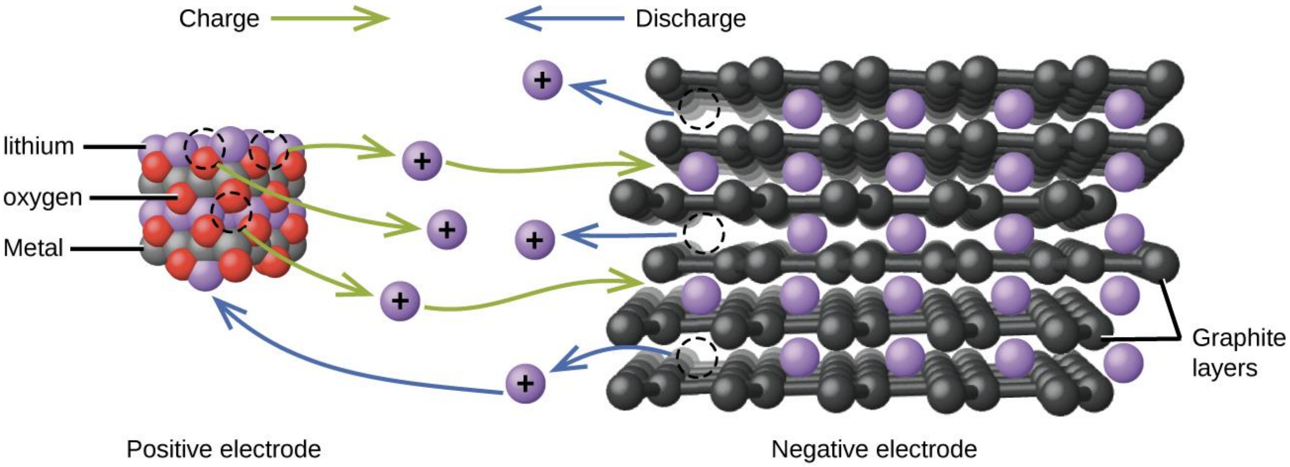

Figure 18.10 In a lithium ion battery, charge flows as the lithium ions are transferred between the anode and cathode.

Lead Acid Battery

The **lead acid battery** (Figure 18.11) is the type of secondary battery commonly used in automobiles. It is inexpensive and capable of producing the high current required by automobile starter motors. The reactions for a lead acid battery are

Anode: $Pb\ (s) + SO_4^{2-}\ (aq) \longrightarrow PbSO_4\ (s) + 2e^-$

Cathode: $PbO_2\ (s) + SO_4^{2-}\ (aq) + 4H^+\ (aq) + 2e^- \longrightarrow PbSO_4\ (s) + 2H_2O\ (l)$

Cell: $Pb\ (s) + PbO_2\ (s) + 2H_2SO_4\ (aq) \longrightarrow 2PbSO_4\ (s) + 2H_2O\ (l)$ $E_{cell} = 2\ V$

Each cell produces 2 V, so six cells are connected in series to produce a 12-V car battery. Lead acid batteries are heavy and contain a caustic liquid electrolyte, H_2SO_4(*aq*), but are often still the battery of choice because of their high current density. Since these batteries contain a significant amount of lead, they must always be disposed of properly.

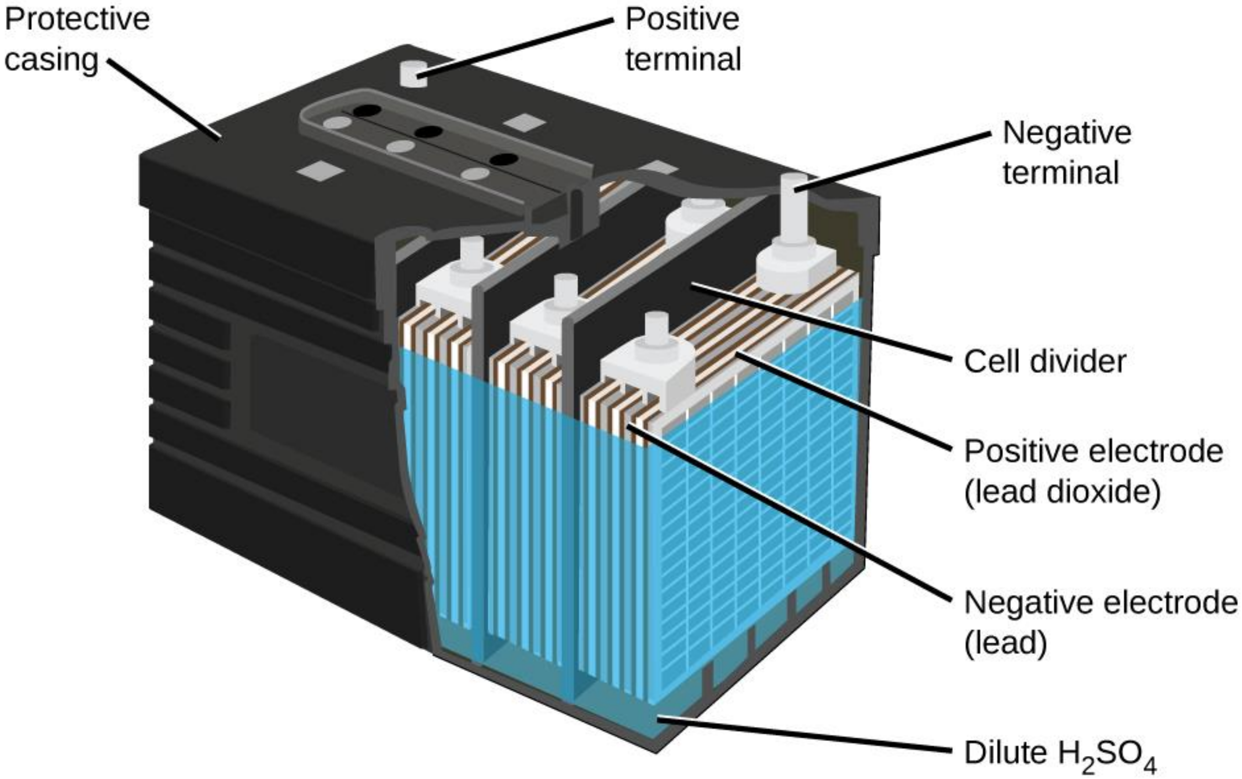

Figure 18.11 The lead acid battery in your automobile consists of six cells connected in series to give 12 V.

Fuel Cells

A **fuel cell** is a galvanic cell that uses traditional combustive fuels, most often hydrogen or methane, that are continuously fed into the cell along with an oxidant. (An alternative, but not very popular, name for a fuel cell is a *flow battery*.) Within the cell, fuel and oxidant undergo the same redox chemistry as when they are combusted, but via a catalyzed electrochemical that is significantly more efficient. For example, a typical hydrogen fuel cell uses graphite electrodes embedded with platinum-based catalysts to accelerate the two half-cell reactions:

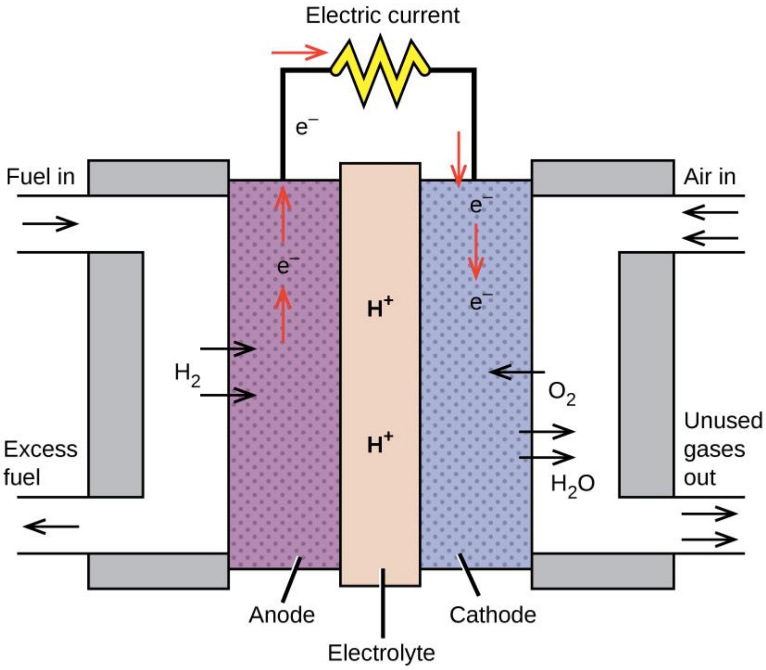

Figure 18.12 In this hydrogen fuel cell, oxygen from the air reacts with hydrogen, producing water and electricity.

Anode: $2H_2\ (g) \longrightarrow 4H^+\ (aq) + 4e^-$

Cathode: $O_2\ (g) + 4H^+\ (aq) + 4e^- \longrightarrow 2H_2O\ (g)$

Cell: $2H_2\ (g) + O_2\ (g) \longrightarrow 2H_2O\ (g)$ E_{cell} ~1.2 V

These types of fuel cells generally produce voltages of approximately 1.2 V. Compared to an internal combustion engine, the energy efficiency of a fuel cell using the same redox reaction is typically more than double (~20%–25% for an engine versus ~50%–75% for a fuel cell). Hydrogen fuel cells are commonly used on extended space missions, and prototypes for personal vehicles have been developed, though the technology remains relatively immature.

18.5 Nonspontaneous Redox Reactions - Electrolysis

Learning Objectives

- Describe the process of electrolysis
- Compare the operation of electrolytic cells with that of galvanic cells
- Perform stoichiometric calculations for electrolytic processes

Electrolysis

Electrochemical cells in which spontaneous redox reactions take place (*galvanic cells*) have been the topic of discussion so far in this chapter. In these cells, *electrical work is done by a redox system on its surroundings* as electrons produced by the redox reaction are transferred through an external circuit. This final section of the chapter will address an alternative scenario in which *an external circuit does work on a redox system* by imposing a voltage sufficient to drive an otherwise nonspontaneous reaction, a process known as **electrolysis**. A familiar example of electrolysis is recharging a battery, which involves use of an external power source to drive the spontaneous (discharge) cell reaction in the reverse direction, restoring to some extent the composition of the half-cells and the voltage of the battery. Perhaps less familiar is the use of electrolysis in the refinement of metallic ores, the manufacture of commodity chemicals, and the *electroplating* of metallic coatings on various products (e.g., jewelry, utensils, auto parts). To illustrate the essential concepts of electrolysis, a few specific processes will be considered.

The Electrolysis of Molten Sodium Chloride

Metallic sodium, Na, and chlorine gas, Cl_2, are used in numerous applications, and their industrial production relies on the large-scale electrolysis of molten sodium chloride, NaCl(*l*). The industrial process typically uses a *Downs cell* similar to the simplified illustration shown in Figure 18.13. The reactions associated with this process are:

Anode: $2Cl^- (l) \longrightarrow Cl_2 (g) + 2e^-$

Cathode: $Na^+ (l) + e^- \longrightarrow Na (l)$

Cell: $2Na^+ (l) + 2Cl^- (l) \longrightarrow 2Na (l) + Cl_2 (g)$

The cell potential for the above process is negative, indicating the reaction as written (decomposition of liquid NaCl) is not spontaneous. To force this reaction, *a positive potential of magnitude greater than the negative cell potential* must be applied to the cell.

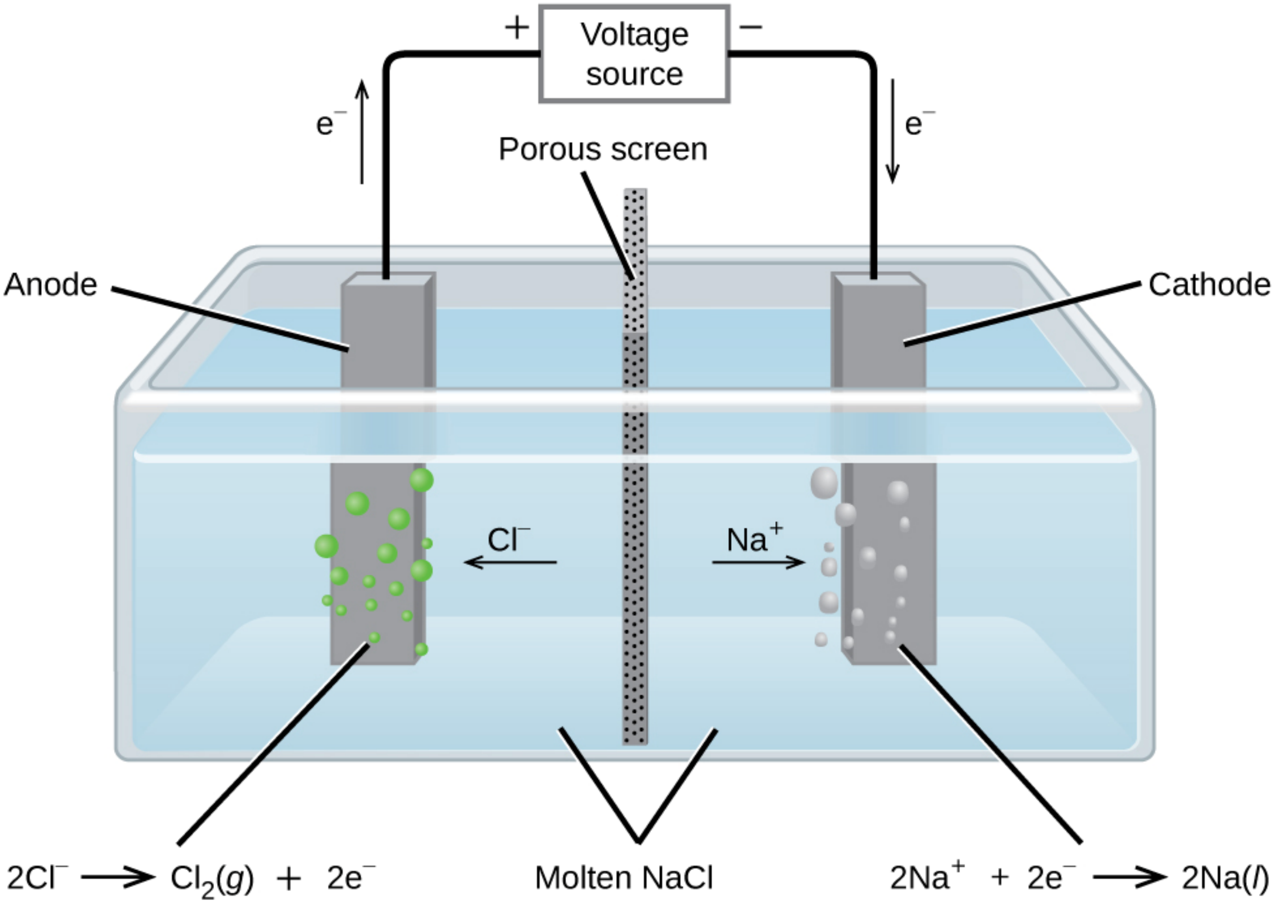

Figure 18.13 Cells of this sort (a cell for the electrolysis of molten sodium chloride) are used in the *Downs process* for production of sodium and chlorine, and they typically use iron cathodes and carbon anodes.

The Electrolysis of Water

Water may be electrolytically decomposed in a cell similar to the one illustrated in Figure 18.14. To improve electrical conductivity without introducing a different redox species, the hydrogen ion concentration of the water is typically increased by addition of a strong acid. The redox processes associated with this cell are

Anode: $2H_2O\ (l) \longrightarrow O_2\ (g) + 4H^+\ (aq) + 4e^-$ $E_{anode}° = +1.229\ V$

Cathode: $2H^+\ (aq) + 2e^- \longrightarrow H_2\ (g)$ $E_{cathode}° = 0\ V$

Cell: $2H_2O\ (l) \longrightarrow 2H_2\ (g) + O_2\ (g)$ $E_{cell}° = -1.229\ V$

Again, the cell potential as written is negative, indicating a nonspontaneous cell reaction that must be driven by imposing a cell voltage greater than +1.229 V. Keep in mind that *standard* electrode potentials are used to inform thermodynamic predictions here, though the cell is *not* operating under standard state conditions. Therefore, at best, calculated cell potentials should be considered ballpark estimates.

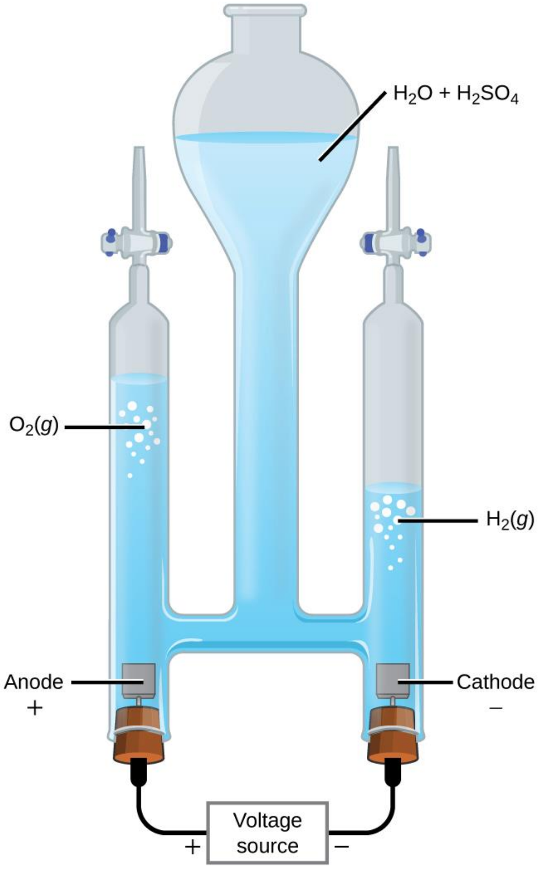

Figure 18.14 The electrolysis of water produces stoichiometric amounts of oxygen gas at the anode and hydrogen at the anode.

The Electrolysis of Aqueous Sodium Chloride

When aqueous solutions of ionic compounds are electrolyzed, the anode and cathode half-reactions may involve the electrolysis of either water species (H_2O, H^+, OH^-) or solute species (the cations and anions of the compound). As an example, the electrolysis of aqueous sodium chloride could involve either of these two anode reactions:

(i) $2Cl^- (aq) \longrightarrow Cl_2 (g) + 2e^-$ $E_{anode}° = +1.35827$ V

(ii) $2H_2O (l) \longrightarrow O_2 (g) + 4H^+ (aq) + 4e^-$ $E_{anode}° = +1.229$ V

The standard electrode (*reduction*) potentials of these two half-reactions indicate water may be *oxidized* at a less negative/more positive potential (–1.229 V) than chloride ion (–1.358 V). Thermodynamics thus predicts that water would be more readily oxidized, though in practice it is observed that both water and chloride ion are oxidized under typical conditions, producing a mixture of oxygen and chlorine gas.

Turning attention to the cathode, the possibilities for reduction are:

(iii) $2H^+ (aq) + 2e^- \longrightarrow H_2 (g)$ $E_{cathode}° = 0$ V

(iv) $2H_2O (l) + 2e^- \longrightarrow H_2 (g) + 2OH^- (aq)$ $E_{cathode}° = -0.8277$ V

(v) $Na^+ (aq) + e^- \longrightarrow Na (s)$ $E_{cathode}° = -2.71$ V

Comparison of these *standard* half-reaction potentials suggests the reduction of hydrogen ion is thermodynamically favored. However, in a neutral aqueous sodium chloride solution, the concentration of hydrogen ion is far below the standard state value of 1*M* (approximately 10^{-7} *M*), and so the observed cathode reaction is actually reduction of water. The net cell reaction in this case is then

Cell: $2H_2O (l) + 2Cl^- (aq) \longrightarrow H_2 (g) + Cl_2 (g) + 2OH^- (aq)$ $E_{cell}° = -2.186$ V

This electrolysis reaction is part of the *chlor-alkali process* used by industry to produce chlorine and sodium hydroxide (lye).

CHEMISTRY IN EVERYDAY LIFE

Electroplating

An important use for electrolytic cells is in **electroplating**. Electroplating results in a thin coating of one metal on top of a conducting surface. Reasons for electroplating include making the object more corrosion resistant, strengthening the surface, producing a more attractive finish, or for purifying metal. The metals commonly used in electroplating include cadmium, chromium, copper, gold, nickel, silver, and tin. Common consumer products include silver-plated or gold-plated tableware, chrome-plated automobile parts, and jewelry. The silver plating of eating utensils is used here to illustrate the process. (Figure 18.15).

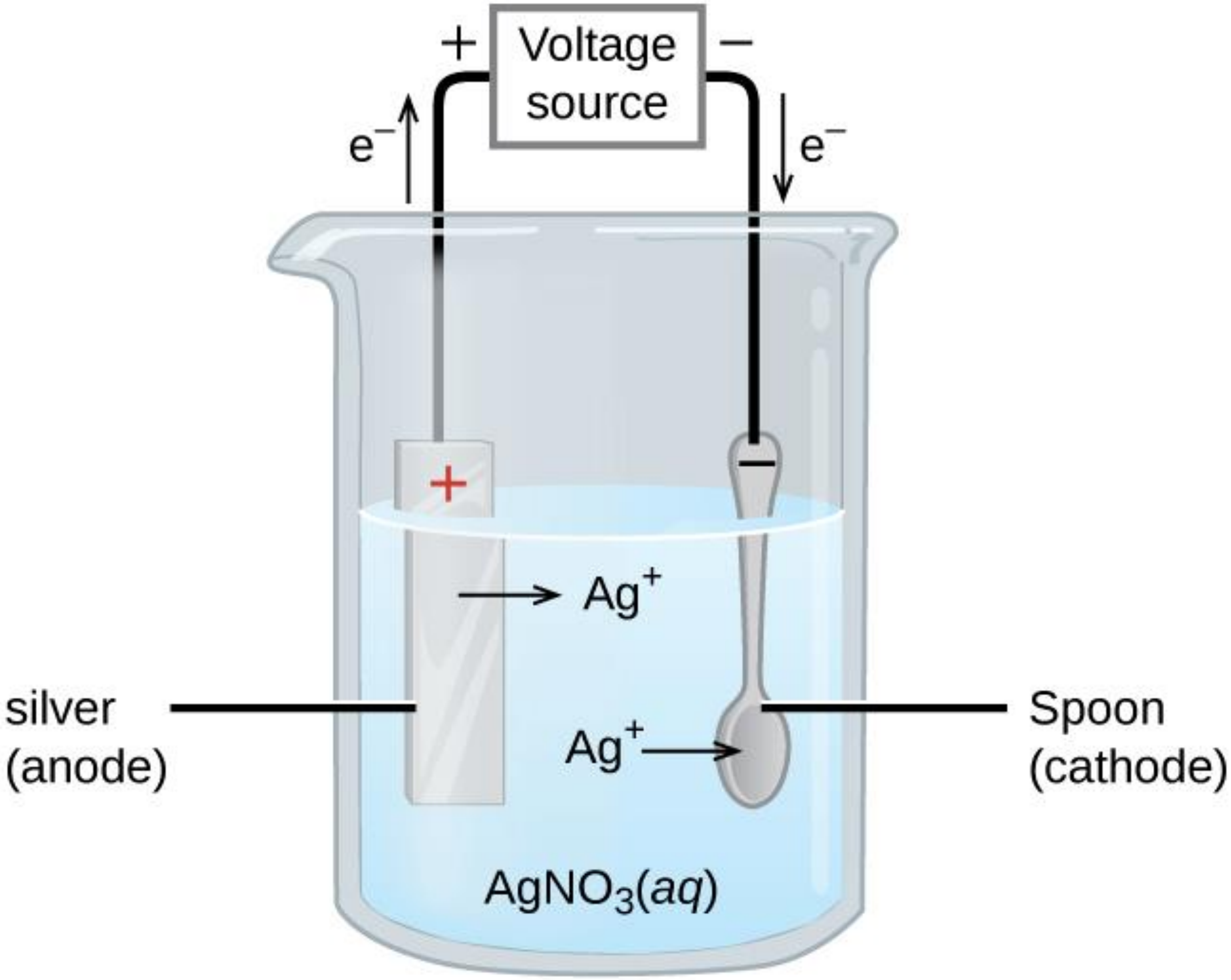

Figure 18.15 This schematic shows an electrolytic cell for silver plating eating utensils.

In the figure, the anode consists of a silver electrode, shown on the left. The cathode is located on the right and is the spoon, which is made from inexpensive metal. Both electrodes are immersed in a solution of silver nitrate. Applying a sufficient potential results in the oxidation of the silver anode

Anode: $Ag\ (s) \longrightarrow Ag^{+}\ (aq) + e^{-}$

and reduction of silver ion at the (spoon) cathode:

Cathode: $Ag^{+}\ (aq) + e^{-} \longrightarrow Ag\ (s)$

The net result is the transfer of silver metal from the anode to the cathode. Several experimental factors must be carefully controlled to obtain high-quality silver coatings, including the exact composition of the electrolyte solution, the cell voltage applied, and the rate of the electrolysis reaction (electrical current).

18.6 Potential, Free Energy, and Equilibrium

Learning Objectives

- Explain the relations between potential, free energy change, and equilibrium constants
- Perform calculations involving the relations between cell potentials, free energy changes, and equilibrium
- Use the Nernst equation to determine cell potentials under nonstandard conditions

Introduction

So far in this chapter, the relationship between the cell potential and reaction *spontaneity* has been described, suggesting a link to the free energy change for the reaction and equilibrium. This section provides a summary of the relationships between potential and the related thermodynamic properties ΔG and K.

E° and ΔG°

The standard free energy change of a process, $\Delta G°$, was defined in a previous chapter as the maximum work that could be performed by a system. In the case of a redox reaction taking place within a galvanic cell under standard state conditions, essentially all the work is associated with transferring the electrons from reductant-to-oxidant. The work associated with transferring electrons is determined by the total amount of charge (coulombs) transferred and the cell potential:

$$\Delta G° = -nFE_{cell}°$$

where n is the number of moles of electrons transferred, F is **Faraday's constant**, and $E°_{cell}$ is the standard cell potential. The relation between free energy change and standard cell potential confirms the sign conventions and spontaneity criteria previously discussed for both of these properties: spontaneous redox reactions exhibit positive potentials and negative free energy changes.

E° and K

Combining a previously derived relation between ΔG° and K (see the chapter on thermodynamics) and the equation above relating ΔG° and $E°_{cell}$ yields the following:

$$\Delta G° = -RT\ln K = -nFE_{cell}°$$

$E_{cell}° = \frac{RT}{nF}\ln K$ At 25 ºC, we can obtain: $E_{cell}° = \frac{0.0592\ V}{n}\log K$

This equation indicates redox reactions with large (positive) standard cell potentials will proceed far towards completion, reaching equilibrium when the majority of reactant has been converted to product. A summary of the relations between *E*°, Δ*G*° and *K* is depicted in Figure 18.16, and a table correlating reaction spontaneity to values of these properties is provided in Table 18.2.

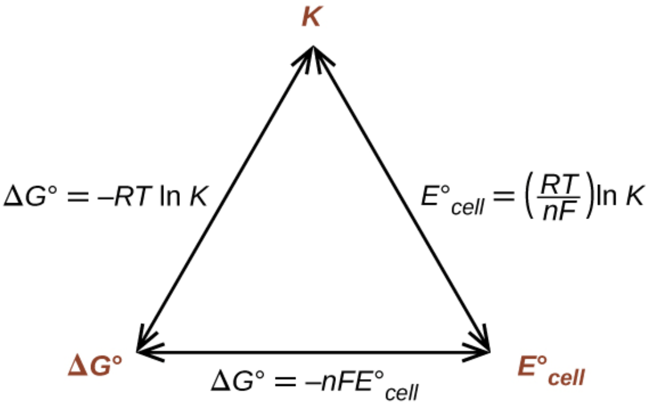

Figure 18.16 Graphic depicting the relation between three important thermodynamic properties.

Table 18.2 Correlation between K, ΔGº, E^o_{cell}, and reaction spontaneity.

K	Δ*G*°	$E°_{cell}$	Spontaneity
> 1	< 0	> 0	Reaction is spontaneous under standard conditions Products more abundant at equilibrium
< 1	> 0	< 0	Reaction is non-spontaneous under standard conditions Reactants more abundant at equilibrium
= 1	= 0	= 0	Reaction is at equilibrium under standard conditions Reactants and products equally abundant

EXAMPLE 17.6

Use data from Appendix 18.3 to calculate the standard cell potential, standard free energy change, and equilibrium constant for the following reaction at 25 °C. Comment on the spontaneity of the forward reaction and the composition of an equilibrium mixture of reactants and products. $2Ag^{+}\,(aq) + Fe\,(s) \rightleftharpoons 2Ag\,(s) + Fe^{2+}\,(aq)$

Solution

The reaction involves an oxidation-reduction reaction, so the standard cell potential can be calculated using the data in Appendix 18.3.

Anode (oxidation): $Fe\,(s) \longrightarrow Fe^{2+}\,(aq) + 2e^{-}$ $E^{\circ}_{Fe^{2+}/Fe} = -0.447\text{ V}$

Cathode (reduction): $2\times(Ag^{+}\,(aq) + e^{-} \longrightarrow Ag\,(s))$ $E^{\circ}_{Ag^{+}/Ag} = 0.7996\text{ V}$

$$E^{\circ}_{cell} = E^{\circ}_{cathode} - E^{\circ}_{anode} = E^{\circ}_{Ag^{+}/Ag} - E^{\circ}_{Fe^{2+}/Fe} = +1.247\text{ V}$$

With $n = 2$, the equilibrium constant is then

$$E_{cell}^{\circ} = \frac{0.0592\ V}{n}\log K \quad \rightarrow \quad 1.247\text{ V} = \frac{0.0592\ V}{2}\log K$$

$$\log K = 42.128 \quad \rightarrow \quad K = 10^{42.128} = 1.3 \times 10^{42}$$

The standard free energy is then $\Delta G^{\circ} = -nFE^{\circ}_{cell}$

$$\Delta G^{\circ} = -2 \times 96{,}485\text{ C/mol} \times 1.247\text{ J/C} = -240.6\text{ kJ/mol}$$

The reaction is spontaneous, as indicated by a negative free energy change and a positive cell potential. The *K* value is very large, indicating the reaction proceeds to near completion to yield an equilibrium mixture containing mostly products.

Check Your Learning

What is the standard free energy change and the equilibrium constant for the following reaction at room temperature? Is the reaction spontaneous?

$$Sn\,(s) + 2Cu^{2+}\,(aq) \rightleftharpoons Sn^{2+}\,(aq) + 2Cu^{+}\,(aq)$$

ANSWER: Spontaneous; $n = 2$; $E^{\circ}_{cell} = +0.291$ V; $\Delta G^{\circ} = -56.2$ kJ/mol; $K = 6.8 \times 10^{9}$.

Potentials at Nonstandard Conditions: The Nernst Equation

Most of the redox processes that interest science and society do not occur under standard state conditions, and so the potentials of these systems under nonstandard conditions are a property worthy of attention. Having established the relationship between potential and free energy change in this section, the previously discussed relation between free energy change and reaction mixture composition can be used for this purpose.

$$\Delta G = \Delta G° + RT\ln Q$$

Notice the reaction quotient, *Q*, appears in this equation, making the free energy change dependent upon the composition of the reaction mixture. Substituting the equation relating free energy change to cell potential yields the **Nernst equation**:

$$-nFE_{cell} = -nFE°_{cell} + RT\ln Q$$

$$E_{cell} = E°_{cell} - \frac{RT}{nF}\ln Q$$

This equation describes how the potential of a redox system (such as a galvanic cell) varies from its standard state value, specifically, showing it to be a function of the number of electrons transferred, *n*, the temperature, *T*, and the reaction mixture composition as reflected in *Q*. A convenient form of the Nernst equation for most work is one in which values for the fundamental constants (R and F) and a factor converting from natural to base-10 logarithms have been included:

$$E_{cell} = E°_{cell} - \frac{0.0592\ V}{n}\log Q$$

EXAMPLE 17.7

Use the Nernst equation to predict the spontaneity of the redox reaction shown below.

$$\text{Co (s)} + \text{Fe}^{2+}\text{(aq, 1.94 M)} \longrightarrow \text{Co}^{2+}\text{(aq, 0.15 M)} + \text{Fe (s)}$$

Solution

Collecting information from Appendix 18.3 and the problem,

Anode (oxidation): $\text{Co (s)} \longrightarrow \text{Co}^{2+}\text{(aq)} + 2e^-$ $E°_{Co^{2+}/Co} = -0.28\text{ V}$

Cathode (reduction): $\text{Fe}^{2+}\text{(aq)} + 2e^- \longrightarrow \text{Fe (s)}$ $E°_{Fe^{2+}/Fe} = -0.447\text{ V}$

$$E°_{cell} = E°_{cathode} - E°_{anode} = -0.447\text{ V} - (-0.28\text{ V}) = -0.17\text{ V}$$

Notice the negative value of the standard cell potential indicates the process is not spontaneous under standard conditions. Substitution of the Nernst equation terms for the nonstandard conditions yields:

$$Q = \frac{[Co^{2+}]}{[Fe^{2+}]} = \frac{[0.15\ M]}{[1.94\ M]} = 0.077$$

$$E_{cell} = E°_{cell} - \frac{0.0592\ V}{n}\log Q$$

$$E_{cell} = -0.17\text{ V} - \frac{0.0592\ V}{2}\log 0.077$$

$$E_{cell} = -0.17\text{ V} + 0.033\text{ V} = -0.014\text{ V}$$

The cell potential remains negative (slightly) under the specified conditions, and so the reaction remains nonspontaneous.

Check Your Learning

For the cell schematic below, identify values for *n* and *Q*, and calculate the cell potential, E_{cell}.

$$2\text{Al (s)} + 3\text{Cu}^{2+}\text{(aq, 0.025 M)} \rightleftharpoons 2\text{Al}^{3+}\text{(aq, 0.15 M)} + 3\text{Cu (s)}$$

ANSWER: $n = 6$; $Q = 1440$; $E_{cell} = +1.97\text{ V}$, spontaneous.

A **concentration cell** is constructed by connecting two nearly identical half-cells, each based on the same half-reaction and using the same electrode, varying only in the concentration of one redox species. The potential of a concentration cell, therefore, is determined only by the difference in concentration of the chosen redox species. The example problem below illustrates the use of the Nernst equation in calculations involving concentration cells.

EXAMPLE 17.8

Concentration Cells

What is the cell potential of the concentration cell described by

$$\text{Zn (s)} + \text{Zn}^{2+}\text{ (aq, 0.50 M)} \rightleftharpoons \text{Zn}^{2+}\text{ (aq, 0.10 M)} + \text{Zn (s)}$$

Solution: From the information given:

Anode: $\text{Zn (s)} \longrightarrow \text{Zn2+ (aq, 0.10M)} + 2\text{e}^-$ $\quad E°_{\text{anode}} = -0.7618\text{ V}$

Cathode: $\text{Zn}^{2+}\text{ (aq, 0.50M)} + 2\text{e}^- \longrightarrow \text{Zn (s)}$ $\quad E°_{\text{cathode}} = -0.7618\text{ V}$

Overall: $\text{Zn}^{2+}\text{ (aq, 0.50M)} \longrightarrow \text{Zn}^{2+}\text{ (aq, 0.10M)}$ $\quad E°_{\text{cell}} = 0.000\text{ V}$

Substituting into the Nernst equation,

$$E_{\text{cell}} = E°_{\text{cell}} - \frac{0.0592\,V}{n}\log Q$$

$$E_{\text{cell}} = 0.000\text{ V} - \frac{0.0592\,V}{2}\log\left(\frac{0.10}{0.50}\right) = +0.021\text{ V}$$

The positive value for cell potential indicates the overall cell reaction (see above) is spontaneous. This spontaneous reaction is one in which the zinc ion concentration in the cathode falls (it is reduced to elemental zinc) while that in the anode rises (it is produced by oxidation of the zinc anode). A greater driving force for zinc reduction is present in the cathode, where the zinc(II) ion concentration is greater ($E_{\text{cathode}} > E_{\text{anode}}$).

Check Your Learning

The concentration cell above was allowed to operate until the cell reaction reached equilibrium. What are the cell potential and the concentrations of zinc(II) in each half-cell for the cell now? **ANSWER:** $E_{\text{cell}} = 0.000$ V; $[\text{Zn}^{2+}]_{\text{cathode}} = [\text{Zn}^{2+}]_{\text{anode}} = 0.30\ M$

Chapter 19 – Attributions

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19.2 Structural Representations

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19.3 Isomerism (Conformational isomer, Structural isomers, Stereoisomers)

Modified isomerism chart

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19.4 Hydrocarbons (alkane, alkene, alkyne, not aromatic)

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19.5 Nomenclature of hydrocarbons

Created cyclic alkanes

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19.6 Functional Groups

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Chapter 19 Organic Compounds

Chapter Introduction

Figure 19.1 All organic compounds contain carbon and most are formed by living things, although they are also formed by geological and artificial processes. (credit left: modification of work by Jon Sullivan; credit left middle: modification of work by Deb Tremper; credit right middle: modification of work by “annszyp”/Wikimedia Commons; credit right: modification of work by George Shuklin)

All living things on earth are formed mostly of carbon compounds. The prevalence of carbon compounds in living things has led to the epithet “carbon-based” life. The truth is we know of no other kind of life. Early chemists regarded substances isolated from *organisms* (plants and animals) as a different type of matter that could not be synthesized artificially, and these substances were thus known as *organic compounds*. The widespread belief called vitalism held that organic compounds were formed by a vital force present only in living organisms. The German chemist Friedrich Wohler was one of the early chemists to refute this aspect of vitalism, when, in 1828, he reported the synthesis of urea, a component of many body fluids, from nonliving materials. Since then, it has been recognized that organic molecules obey the same natural laws as inorganic substances, and the category of organic compounds has evolved to include both natural and synthetic compounds that contain carbon. Some carbon-containing compounds are *not* classified as organic, for example, carbonates and cyanides, and simple oxides, such as CO and CO_2. Although a single, precise definition has yet to be identified by the chemistry community, most agree that a defining trait of organic molecules is the presence of carbon as the principal element, bonded to hydrogen and other carbon atoms.

Today, organic compounds are key components of plastics, soaps, perfumes, sweeteners, fabrics, pharmaceuticals, and many other substances that we use every day. The value to us of organic compounds ensures that organic chemistry is an important discipline within the general field of chemistry. In this chapter, we discuss why the element carbon gives rise to a vast number and variety of compounds, how those compounds are classified, and the role of organic compounds in representative biological and industrial settings.

19.1 Organic Compounds

Content Statement

The content of this chapter section (from page 241 – 242) has been removed from public sharing version due to an incompatibile license.

19.2 Structural Representations

Learning Objectives

- Represent organic molecules using Lewis structure, condensed structure, line-angle structure, and dashed-wedge line-angle structure.

Lewis Structure

A common way to display how atoms within molecule connect is to use Lewis structure. For ionic compounds, the Lewis structures show how electrons transferred, which atoms lose electrons and which atoms gain electrons. For molecular compounds such as organic compounds, the Lewis structures shows how electrons are shared between two atoms (single, double, or triple bonds).

Keep in mind that Lewis structures are not intended to indicate the geometry of molecules. Notice that the carbon atoms in the structural models (the ball-and-stick and space-filling models) do not lie in a straight line. This is because carbon atoms can undergoes three different types of hybridization: *sp*^{3} (single bond), *sp*^{2} (double bond), and *sp* (triple bond), resulting in different bond angles: 109.5º in single bonds, 120º in double bonds, and 180º in triple bonds. Thus, the carbon chains in organic compounds are in a zigzag shape.

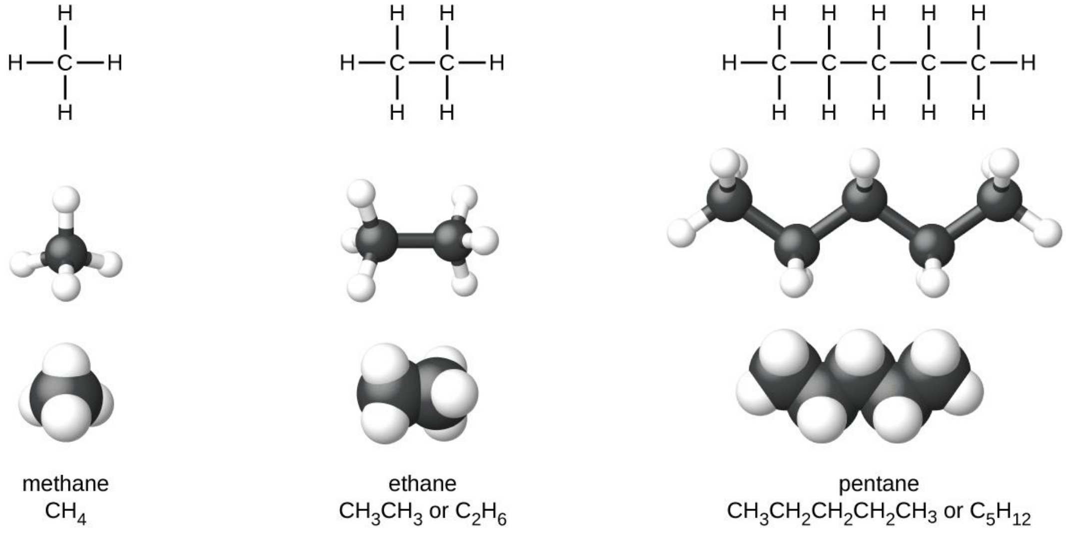


Figure 19.2 Pictured are the Lewis structures, ball-and-stick models, and space-filling models for molecules of methane, ethane, and pentane.

Condensed Structure

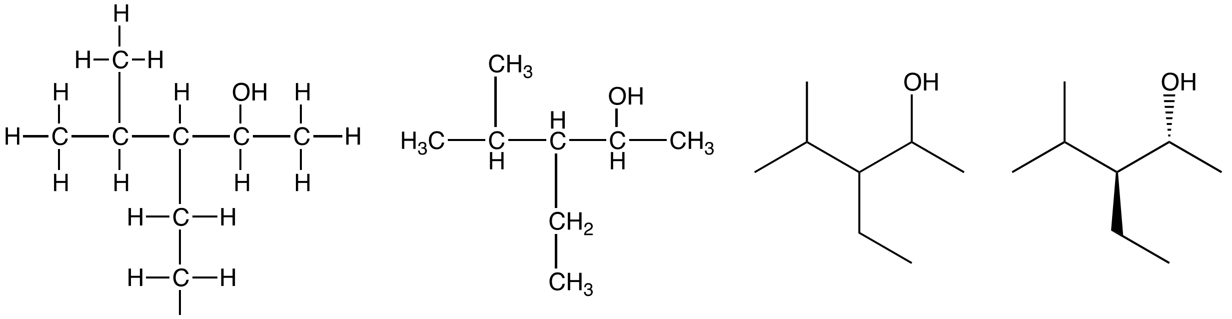
The structures of organic molecules may also be represented in a less detailed manner by **condensed structural formulas** (or simply, ***condensed sturcture***). Instead of the usual format for chemical formulas in which each element symbol appears just once, a condensed formula is written to suggest the bonding in the molecule. These formulas have the appearance of a Lewis structure from which most or all of the bond symbols have been removed.

Line-Angle Structure

A common method used by organic chemists to simplify the drawings of larger molecules is to use a **skeletal structure** (also called a **line-angle structure**). In this type of structure, carbon atoms are not symbolized with a C, but represented by each end of a line or bend in a line. Hydrogen atoms are not drawn if they are attached to a carbon. Other atoms besides carbon and hydrogen are represented by their elemental symbols

Dashed-Wedge Line-Angle Structure

Another method used to display the arrangement of atoms in 3-dimensional space is a **dashed-wedge line-angle structure**. The dashed-wedge line-angle structure is only used on the atoms with sp^3 hybridization that connect to four different groups as it exhibits tetrahedral geometry that is not flat. The dashed line (┅) represents atoms/groups that are pointing away from the observer. On the contrary, the solid wedge (◀) represents atoms/groups that are sticking out toward the observer.



Lewis Structure Condensed Structure Line-Angle Structure Dashed-Wedge Line-Angle Structure

Figure 19.3 The same structure can be represented three different ways: an expanded formula, a condensed formula, and a skeletal structure.

19.3 Isomerism

Learning Objectives

- Define isomer.
- Determine the isomeric relationship between a pair of molecules.
- Identify the chiral centers in a molecule.
- Describe different types of isomers.

Isomerism

One of the interesting aspects of organic chemistry is that it is three-dimensional. A molecule can have a shape in space that may contribute to its properties. Molecules can differ in the way the atoms are arranged - the same combination of atoms can be assembled in more than one way. These compounds are known as **isomers**.

Isomers are molecules with the same molecular formulas, but different arrangements of atoms. There are several different types of isomers which will be described and a flowchart (Figure 19.4) can help you determine which type of isomers are present.

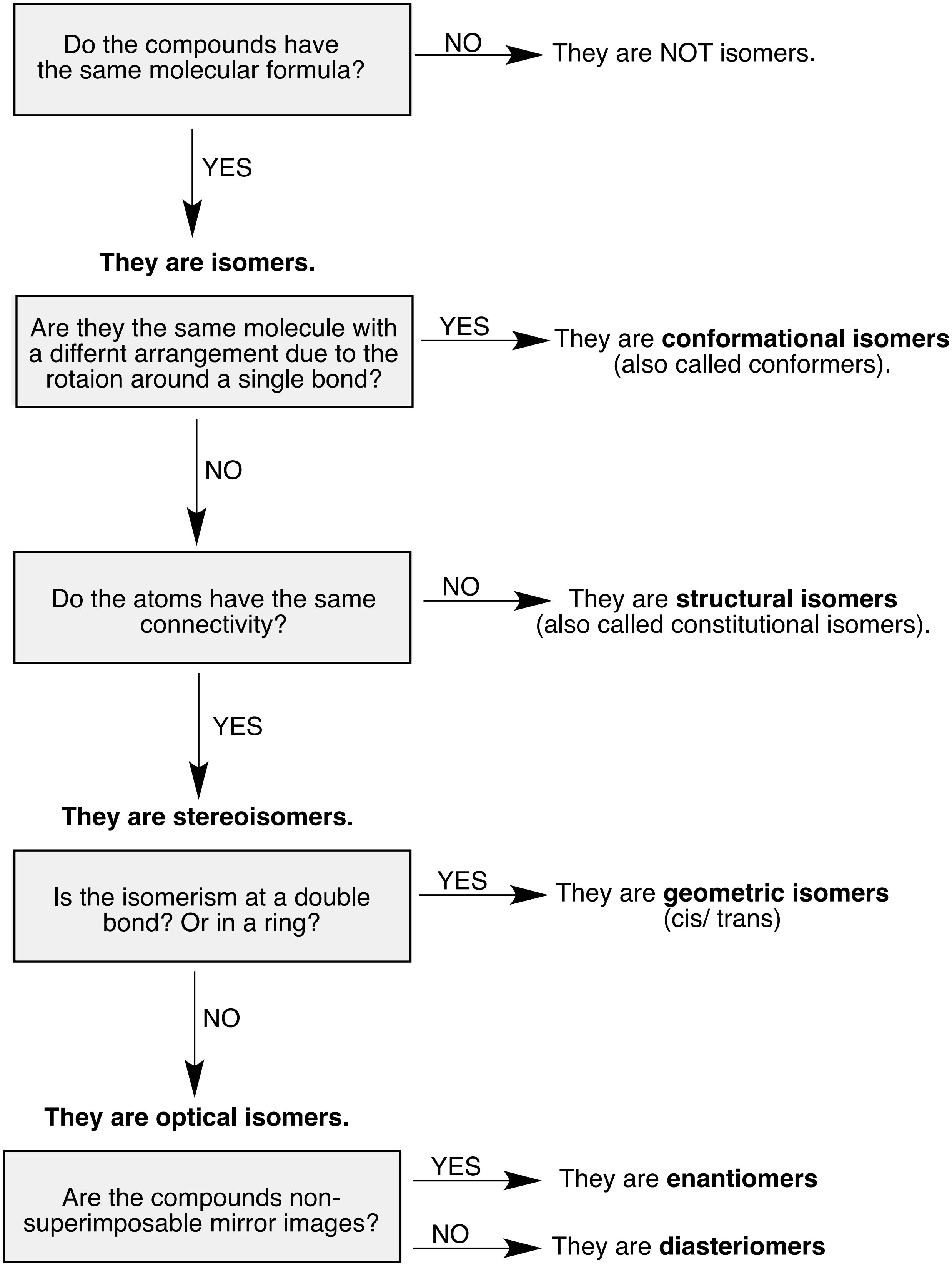


Figure 19.4 This flowchart is used to determine types of isomerism.

Conformational Isomers

Conformational isomers, also known as conformers, differ from one another by their rotation around a single bond. Rotations occur freely around single carbon-carbon bonds. Unlike double and triple bonds, which are "locked" in their orientation, single bonds have no such restrictions.

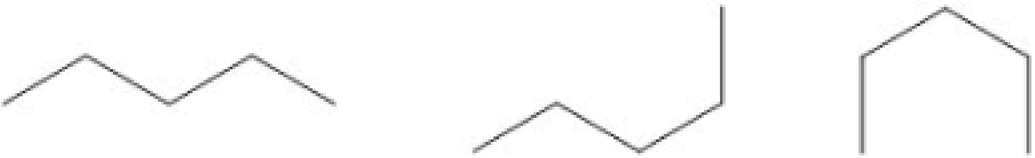
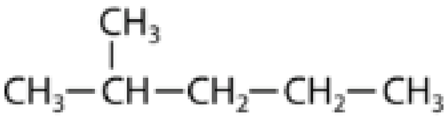


Figure 19.5 Conformational isomers of pentane (C_5H_{12}).

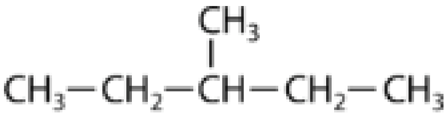
Structural Isomers

A **structural isomer**, also known as a constitutional isomer, is one in which two or more organic compounds have the same molecular formulas but different structures. The two molecules below have the same chemical formula, but are different molecules because they differ in the location of the methyl group.



$$CH_3-\overset{\overset{\displaystyle CH_3}{|}}{C}H-CH_2-CH_2-CH_3$$

2-methylpentane



$$CH_3-CH_2-\overset{\overset{\displaystyle CH_3}{|}}{C}H-CH_2-CH_3$$

3-methylpentane

Organic molecules with double bonds can also demonstrate structural isomerism. There are multiple structural isomers based on where in the chain the double bond occurs. The condensed structural formulas of 1-butene and 2-butene show this.

$CH_2{=}CH-CH_2-CH_3$

1-butene

$CH_3-CH{=}CH-CH_3$

2-butene

The number in the name of the alkene (organic molecules containing C and H with double bonds) refers to the lowest numbered carbon in the chain that is part of the double bond.

Stereoisomers

Stereoisomers have the same connectivity in their atoms but a different arrangement in three-dimensional space. There are different classifications of stereoisomers depending on how the arrangements differ from one another. Notice that in the structural isomers, there was some difference in the connection of atoms. For example, 1-butene has a double bond followed by two single bonds while 2-butene has a single bond, then a double bond, then a single bond. A stereoisomer will have the same connectivity among all atoms in the molecule.

Geometric Isomers

Geometric isomers are isomers in which the order of atom bonding is the same but the arrangement of atoms in space is different. Physical and chemical properties of geometric isomers are generally different. The double bond is not free to rotate because of the nature of the bond. Therefore, there are two different ways to construct the 2-butene molecule (see figure below). The image below shows the two geometric isomers, called *cis*-2-butene and *trans*-2-butene.

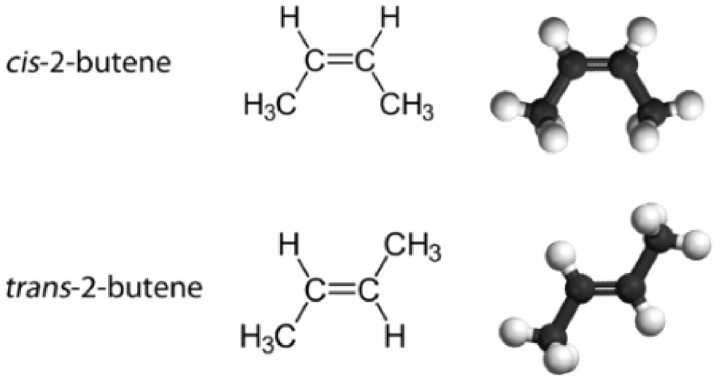


Figure 19.6: cis and trans of *2-butene*

The *cis* isomer has the two single hydrogen atoms on the same side of the molecule, while the *trans* isomer has them on opposite sides of the molecule. In both molecules, the bonding order of the atoms is the same. In order for geometric isomers to exist, there must be a rigid structure in the molecule to prevent free rotation around a bond. This occurs with a double bond or a ring. In addition, the two carbon atoms must each have two different groups attached in order for there to be geometric isomers. Propene (see figure below) has no geometric isomers because one of the carbon atoms (the one on the far left) involved in the double bond has two single hydrogens bonded to it.

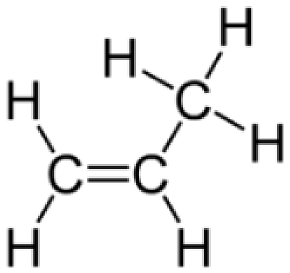
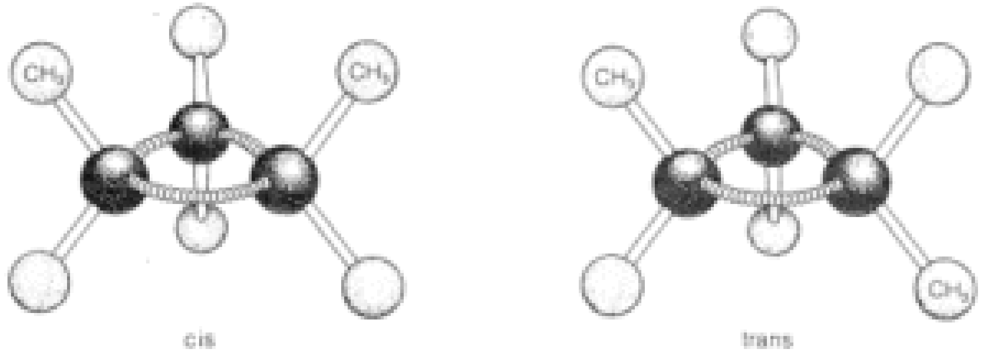


Figure 19.7 Propene does not have a geometric isomer.

Ring formation also confers rigidity on molecular structure such that rotation about the ring bonds is prevented. As a result, stereoisomerism of the cis-trans type is possible. For example, 1,2-dimethylcyclopropane exists in two forms that differ in the arrangement of the two methyl groups with respect to the ring.



Ball-and-stick models of cis and trans isomers of 1,2-dimethylcyclopropane

In the *cis* isomer, the methyl groups both are situated above (or below) the plane of the ring and in the *trans* isomer they are situated one above and one below, as shown in the figure. Interconversion of these isomers does not occur without breaking one or more chemical bonds.

Note that geometric isomers present in structure with ring and with double bonds that have two different groups on the double bonded carbon. For the compounds with triple bonds, there are no geometric isomers because there is only one other group bonded to the carbon atoms that are involved in the triple bond.

Optical Isomers

Stereoisomers that are not geometric isomers are known as optical isomers. Optical isomers differ in the placement of substituted groups around one or more atoms of the molecule. They were given their name because of their interactions with plane-polarized light. Optical isomers are labeled enantiomers or diastereomers.

Enantiomers

Enantiomers are non-superimposable mirror images. A common example of a pair of enantiomers is your hands. Your hands are mirror images of one another but no matter how you turn, twist, or rotate your hands, they are not superimposable.

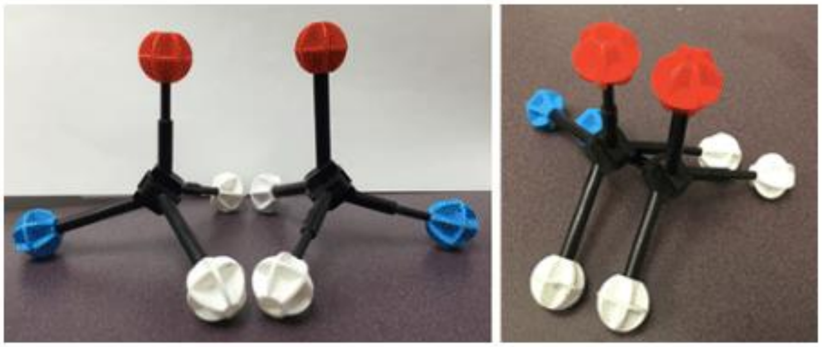


Figure 19.8 Two models that are mirror images and superimposable. Since they are superimposable, they are the same molecule and are not isomers.

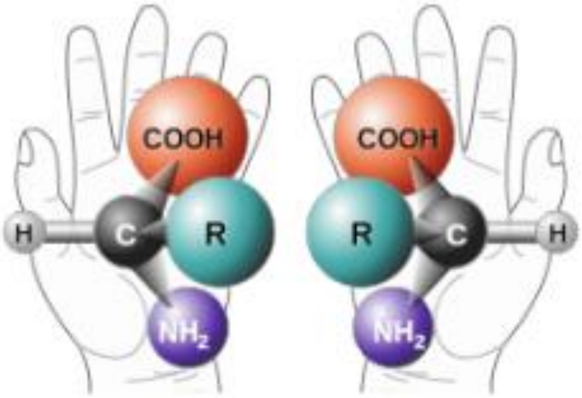


Figure 19.9 Your hands and some molecules are mirror images but are not superimposable. These pairs of molecules are called enantiomers.

Objects that have non-superimposable mirror images are called **chiral**. When examining a molecule, carbon atoms with four unique groups attached are considered chiral. Look at the figure below to see an example of a chiral molecule. Note that we have to look beyond the first atom attached to the central carbon atom. The four circles indicate the four unique groups attached to the central carbon atom, which is chiral.

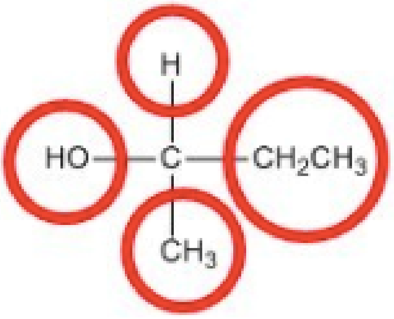


Figure 19.10 A chiral carbon has four unique groups attached to it.

Diastereomers

Another type of optical isomer are **diastereomers**, which are non-mirror image optical isomers. Diastereomers have a different arrangement around one or more atoms while some of the atoms have the same arrangement. As shown in the figure below, note that the orientation of groups on the first and third carbons are different but the second one remains the same so they are not the same molecule. The solid wedge indicates a group coming out of the page/screen towards you and the dashed line indicates that a group is going away from you "behind" the page/screen.

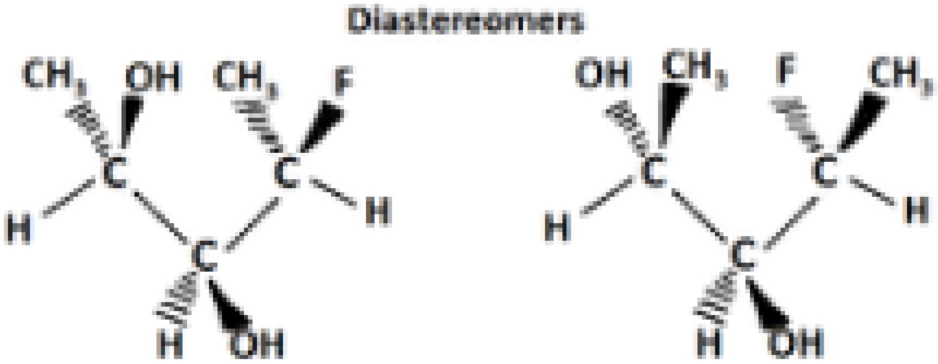


Figure 19.11 Diastereomers differ at one or more atom. These molecules are not mirror images and they are not superimposable. They are optical isomers because they have the same connectivity between atoms but a different arrangement of substituent groups.

19.4 Hydrocarbons

Learning Objectives

- Differentiate alkane, alkene, alkyne, and aromatic hydrocarbons

Hydrocarbons

The simplest organic compounds contain only the elements carbon and hydrogen, and are called **hydrocarbons**. Even though they are composed of only two types of atoms, there is a wide variety of hydrocarbons because they may consist of varying lengths of chains, branched chains, and rings of carbon atoms, or combinations of these structures. In addition, hydrocarbons may differ in the types of carbon-carbon bonds present in their molecules. Many hydrocarbons are found in plants, animals, and their fossils; other hydrocarbons have been prepared in the laboratory. We use hydrocarbons every day, mainly as fuels, such as natural gas, acetylene, propane, butane, and the principal components of gasoline, diesel fuel, and heating oil. The familiar plastics polyethylene, polypropylene, and polystyrene are also hydrocarbons. We can distinguish several types of hydrocarbons by differences in the bonding between carbon atoms. This leads to differences in geometries and in the hybridization of the carbon orbitals.

Alkanes

Alkanes, or **saturated hydrocarbons**, contain only single covalent bonds between carbon atoms. Each of the carbon atoms in an alkane has *sp*^{3} hybrid orbitals and is bonded to four other atoms, each of which is either carbon or hydrogen. All alkanes are composed of carbon and hydrogen atoms, and have similar bonds, structures, and formulas; noncyclic alkanes all have a formula of C_nH_{2n+2}. The number of carbon atoms present in an alkane has no limit. Greater numbers of atoms in the molecules will lead to stronger intermolecular attractions (dispersion forces) and correspondingly different physical properties of the molecules. Properties such as melting point and boiling point (Table 19.2) usually change smoothly and predictably as the number of carbon and hydrogen atoms in the molecules change.

Table 19.2 Properties of Some Alkanes[1]

Alkane	Molecular Formula	Melting Point (°C)	Boiling Point (°C)	Phase at STP[2]	Number of Structural Isomers
methane	CH_4	–182.5	–161.5	gas	1
ethane	C_2H_6	–183.3	–88.6	gas	1
propane	C_3H_8	–187.7	–42.1	gas	1
butane	C_4H_{10}	–138.3	–0.5	gas	2
pentane	C_5H_{12}	–129.7	36.1	liquid	3
hexane	C_6H_{14}	–95.3	68.7	liquid	5
heptane	C_7H_{16}	–90.6	98.4	liquid	9
octane	C_8H_{18}	–56.8	125.7	liquid	18
nonane	C_9H_{20}	–53.6	150.8	liquid	35
decane	$C_{10}H_{22}$	–29.7	174.0	liquid	75
tetradecane	$C_{14}H_{30}$	5.9	253.5	solid	1858
octadecane	$C_{18}H_{38}$	28.2	316.1	solid	60,523

Footnotes

- 1 Physical properties for C_4H_{10} and heavier molecules are those of the *normal isomer*, *n*-butane, *n*-pentane, etc.
- 2 STP indicates a temperature of 0 °C and a pressure of 1 atm.

Alkanes are relatively stable molecules, but heat or light will activate reactions that involve the breaking of C–H or C–C single bonds. Combustion is one such reaction:

$$CH_4\,(g) + 2O_2\,(g) \longrightarrow CO_2\,(g) + 2H_2O\,(g)$$

Alkanes burn in the presence of oxygen, a highly exothermic oxidation-reduction reaction that produces carbon dioxide and water. As a consequence, alkanes are excellent fuels. For example, methane, CH_4, is the principal component of natural gas. Butane, C_4H_{10}, used in camping stoves and lighters is an alkane. Gasoline is a liquid mixture of continuous- and branched-chain alkanes, each containing from five to nine carbon atoms, plus various additives to improve its performance as a fuel. Kerosene, diesel oil, and fuel oil are primarily mixtures of alkanes with higher molecular masses. The main source of these liquid alkane fuels is crude oil, a complex mixture that is separated by fractional distillation. Fractional distillation takes advantage of differences in the boiling points of the components of the mixture. You may recall that boiling point is a function of intermolecular interactions, which was discussed in the chapter on solutions and colloids.

Alkenes

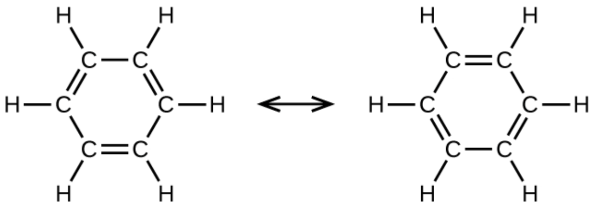
Organic compounds that contain one or more double or triple bonds between carbon atoms are described as unsaturated. You have likely heard of unsaturated fats. These are complex organic molecules with long chains of carbon atoms, which contain at least one double bond between carbon atoms. Unsaturated hydrocarbon molecules that contain one or more double bonds are called **alkenes**. Carbon atoms linked by a double bond are bound together by two bonds, one σ bond and one π bond. Double and triple bonds give rise to a different geometry around the carbon atom that participates in them, leading to important differences in molecular shape and properties. The differing geometries are responsible for the different properties of unsaturated versus saturated fats.

Alkynes

Hydrocarbon molecules with one or more triple bonds are called **alkynes**; they make up another series of unsaturated hydrocarbons. Two carbon atoms joined by a triple bond are bound together by one σ bond and two π bonds. The *sp*-hybridized carbons involved in the triple bond have bond angles of 180°, giving these types of bonds a linear, rod-like shape.

Aromatic Hydrocarbons

Benzene, C_6H_6, is the simplest member of a large family of hydrocarbons, called **aromatic hydrocarbons**. These compounds contain ring structures and exhibit bonding that must be described using the resonance hybrid concept of valence bond theory or the delocalization concept of molecular orbital theory. The resonance structures for benzene, C_6H_6, are:



Valence bond t e and other planar aromatic hydrocarbon molecules as hexagonal rings of sp^2-hybridized carbon atoms with the unhybridized *p* orbital of each carbon atom perpendicular to the plane of the ring. Three valence electrons in the sp^2 hybrid orbitals of each carbon atom and the valence electron of each hydrogen atom form the framework of σ bonds in the benzene molecule. The fourth valence electron of each carbon atom is shared with an adjacent carbon atom in their unhybridized *p* orbitals to yield the π bonds. Benzene does not, however, exhibit the characteristics typical of an alkene. Each of the six bonds between its carbon atoms is equivalent and exhibits properties that are intermediate between those of a C–C single bond and a C=C double bond. To represent this unique bonding, structural formulas for benzene and its derivatives are typically drawn with single bonds between the carbon atoms and a circle within the ring as shown in Figure 19.12.

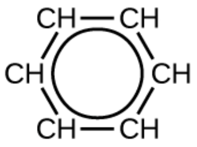
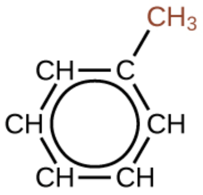
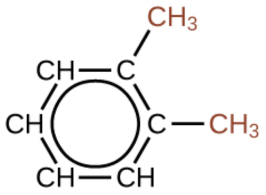


Figure 19.12 This condensed formula shows the unique bonding structure of benzene.

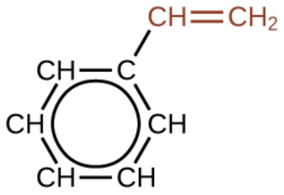
There are many derivatives of benzene. The hydrogen atoms can be replaced by many different substituents. The following are typical examples of substituted benzene derivatives:



toluene



xylene



styrene

19.5 Nomenclature of Hydrocarbons

Learning Objectives

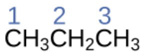
- Name saturated and unsaturated hydrocarbons, and molecules derived from them

Naming Alkane

The International Union of Pure and Applied Chemistry (IUPAC) has devised a system of nomenclature that begins with the names of the alkanes and can be adjusted from there to account for more complicated structures. The nomenclature for alkanes is based on two rules:

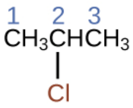
1. To name an alkane, first identify the longest chain of carbon atoms in its structure. A two-carbon chain is called ethane; a three-carbon chain, propane; and a four-carbon chain, butane. Longer chains are named as follows: pentane (five-carbon chain), hexane (6), heptane (7), octane (8), nonane (9), and decane (10). These prefixes can be seen in the names of the alkanes described in Table 19.2.

2. Add prefixes to the name of the longest chain to indicate the positions and names of **substituents**. Substituents are branches or functional groups that replace hydrogen atoms on a chain. The position of a substituent or branch is identified by the number of the carbon atom it is bonded to in the chain. We number the carbon atoms in the chain by counting from the end of the chain nearest the substituents. Multiple substituents are named individually and placed in alphabetical order at the front of the name.



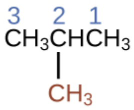
$CH_3CH_2CH_3$

propane



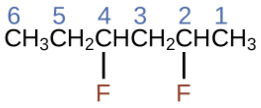
$CH_3\underset{\underset{Cl}{|}}{C}HCH_3$

2-chloropropane



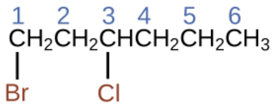
$CH_3\underset{\underset{CH_3}{|}}{C}HCH_3$

2-methylpropane



$CH_3CH_2\underset{\underset{F}{|}}{C}HCH_2\underset{\underset{F}{|}}{C}HCH_3$

2,4-difluorohexane

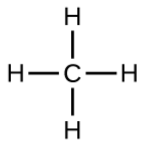


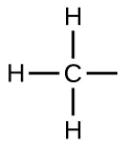
$\underset{\underset{Br}{|}}{CH_2}CH_2\underset{\underset{Cl}{|}}{C}HCH_2CH_2CH_3$

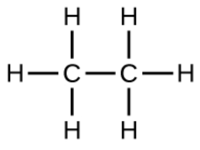
1-bromo-3-chlorohexane

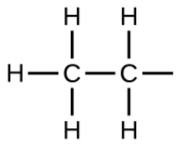
When more than one substituent is present, either on the same carbon atom or on different carbon atoms, the substituents are listed alphabetically. Because the carbon atom numbering begins at the end closest to a substituent, the longest chain of carbon atoms is numbered in such a way as to produce the lowest number for the substituents. The ending -*o* replaces -*ide* at the end of the name of an electronegative substituent (in ionic compounds, the negatively charged ion ends with -*ide* like chloride; in organic compounds, such atoms are treated as substituents and the *-o* ending is used). The number of substituents of the same type is indicated by the prefixes *di-* (two), *tri-* (three), *tetra-* (four), and so on (for example, *difluoro-* indicates two fluoride substituents).

We call a substituent that contains one less hydrogen than the corresponding alkane an alkyl group. The name of an **alkyl group** is obtained by dropping the suffix *-ane* of the alkane name and adding *-yl*:


methane


methyl group


ethane

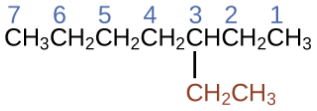

ethyl group

The open bonds in the methyl and ethyl groups indicate that these alkyl groups are bonded to another atom.

Alkyl Group	Structure
methyl	CH_3-
ethyl	CH_3CH_2-
n-propyl	$CH_3CH_2CH_2-$
isopropyl	$CH_3\overset{\vert}{C}HCH_3$
n-butyl	$CH_3CH_2CH_2CH_2-$
sec-butyl	$CH_3CH_2\overset{\vert}{C}HCH_3$
isobutyl	$CH_3\underset{\underset{CH_3}{\vert}}{C}HCH_2-$
tert-butyl	$CH_3\overset{\vert}{\underset{\underset{CH_3}{\vert}}{C}}CH_3$

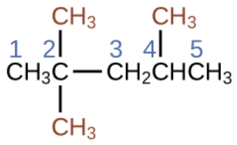
Figure 19.13 This listing gives the names and formulas for various alkyl groups formed by the removal of hydrogen atoms from different locations.

Note that alkyl groups do not exist as stable independent entities. They are always a part of some larger molecule. The location of an alkyl group on a hydrocarbon chain is indicated in the same way as any other substituent:



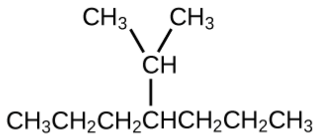
$CH_3CH_2CH_2CH_2CH(CH_2CH_3)CH_2CH_3$

3-ethylheptane



$CH_3C(CH_3)_2-CH_2CH(CH_3)CH_3$

2,2,4-trimethylpentane

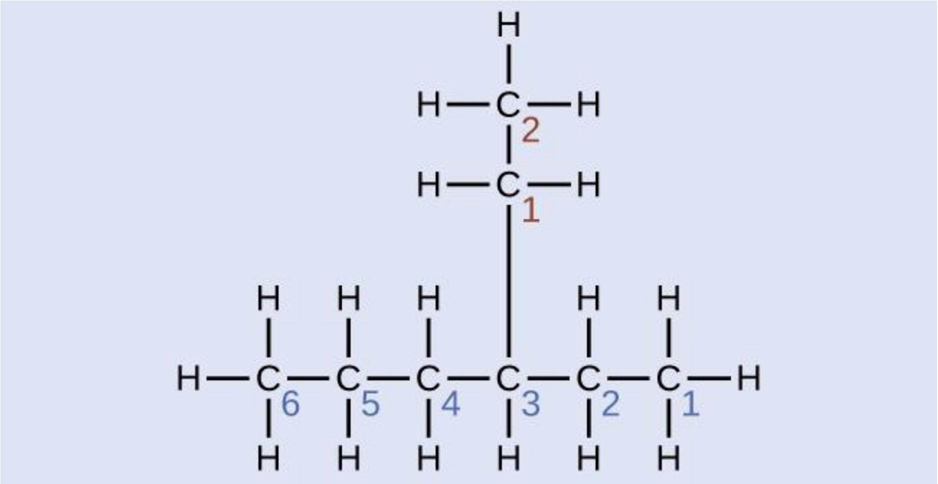


4-isopropylheptane

EXAMPLE 20.4

Naming Substituted Alkanes

Name the molecule whose structure is shown here:

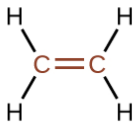


Solution

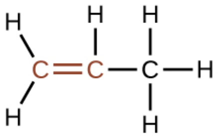
The longest carbon chain runs horizontally across the page and contains six carbon atoms (this makes the base of the name hexane, but we will also need to incorporate the name of the branch). In this case, we want to number from right to left (as shown by the blue numbers) so the branch is connected to carbon 3 (imagine the numbers from left to right—this would put the branch on carbon 4, violating our rules). The branch attached to position 3 of our chain contains two carbon atoms (numbered in red)—so we take our name for two carbons *eth-* and attach *-yl* at the end to signify we are describing a branch. Putting all the pieces together, this molecule is 3-ethylhexane.

Naming Alkene and Alkyne

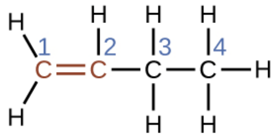
The name of an alkene is derived from the name of the alkane with the same number of carbon atoms. The presence of the double bond is signified by replacing the suffix *-ane* with the suffix *-ene*. The location of the double bond is identified by naming the smaller of the numbers of the carbon atoms participating in the double bond:



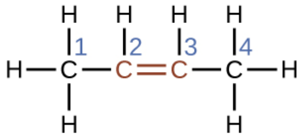
ethene
(ethylene)



propene
(propylene)



1-butene

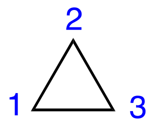


2-butene

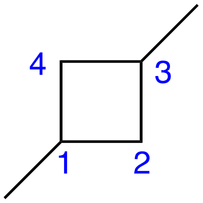
The IUPAC nomenclature for alkynes is similar to that for alkenes except that the suffix -*yne* is used to indicate a triple bond in the chain. For example, $CH_3CH_2C\equiv CH$ is called 1-butyne.

Naming Cyclic Alkane

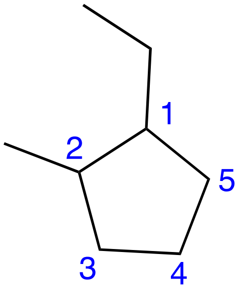
The IUPAC nomenclature for cyclic alkane is similar to that for alkanes, except the pre-fix “cyclo” will be used in front of the name of an alkane.



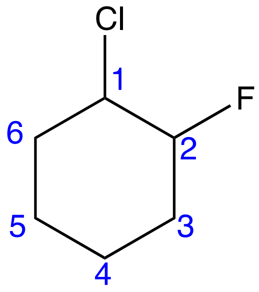
cyclopentane



1,3-dimethyl
cyclobutane



1-ethyl-2-methyl
cyclopentane



1-chloro-2-fluoro
cyclohexane

19.6 Functional Groups

Learning Objectives

- Describe the importance and purpose of functional groups in organic reactions.
- Identify and name functional groups in compounds.

Introduction

With over twenty million known organic compounds in existence, it would be very challenging to memorize chemical reactions for each one. Fortunately, molecules with similar functional groups tend to undergo similar reactions. A **functional group** is defined as an atom or group of atoms within a molecule that has similar chemical properties whenever it appears in various compounds. Even if other parts of the molecule are quite different, certain functional groups tend to react in certain ways.

We've already looked at alkanes, but they are generally unreactive. We primarily use alkanes as a source of energy when they are combusted. While the majority of functional groups involve atoms other than carbon and hydrogen, we will also look at some that include only carbon and hydrogen. Some of the most common functional groups are presented in the following sections.

Organic molecules vary greatly in size and when focusing on functional groups, we want to direct our attention to the atoms involved in the functional group. As a result, the abbreviation R is used in some examples. The letter R is used in molecular structures to represent the "**R**est of the molecule". It consists of a group of carbon and hydrogen atoms of any size. It is used as an abbreviation since a group of carbon and hydrogen atoms does not affect the functionality of the compound. In some molecules, you will see R, R', or R'' which indicates that the R groups in the molecule can be different from one another. For example, R might be $–CH_2CH_3$ while R' is $–CH_2CH_2CH_2CH_3$.

Alkenes and Alkynes

Alkenes are hydrocarbons that contain one or more double bonds between neighboring carbon atoms. Alkynes contain one or more triple bonds between neighboring carbon atoms. The presence of a double or triple bond results in reactivity not present in alkane and alkynes (see figure below) undergo characteristic reactions which will be covered later.

Figure 19.14 Alkenes (left) contain one or more double bonds while alkynes (right) contain one or more triple bonds.

Aromatics

The additional functional group that contains only carbon and hydrogen is an aromatic ring which is a six-carbon ring with alternative double bonds. The aromatic ring is also shown as a ring with a circle in the middle representing the double bonds. Aromatic rings (see figure below) are found in many compounds including steroids and medications.

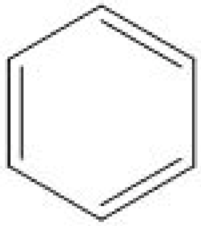


Figure 19.15 Aromatic rings contain alternating double bonds.

Alcohols

The **alcohol** functional group involves an oxygen atom that is bonded to one hydrogen atom and one carbon atom. The carbon atom will be part of a larger organic structure. One way to indicate a generic alcohol would be with the formula $R-OH$. R represents any organic fragment in which a carbon atom is directly bonded to the explicitly indicated functional group (in this case, OH). The R group is typically a chain of carbon atoms.

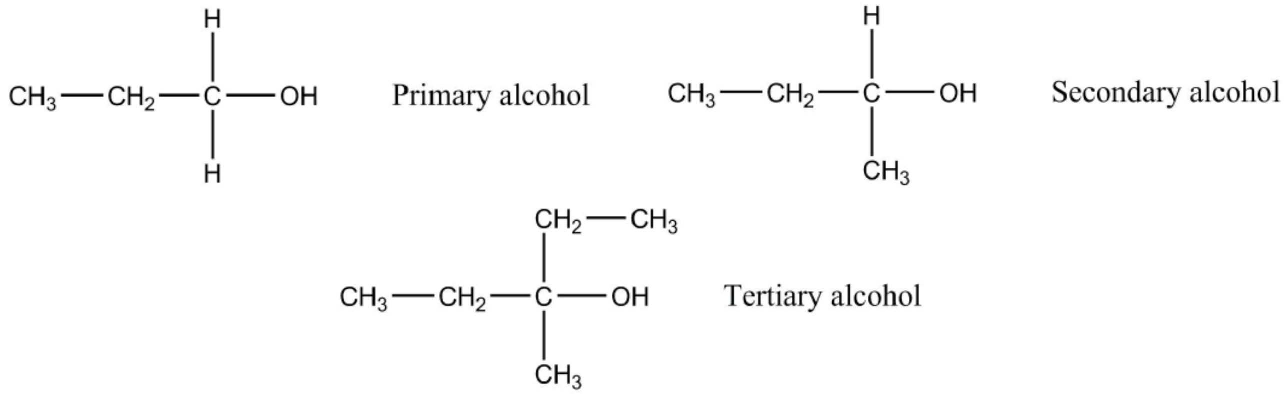


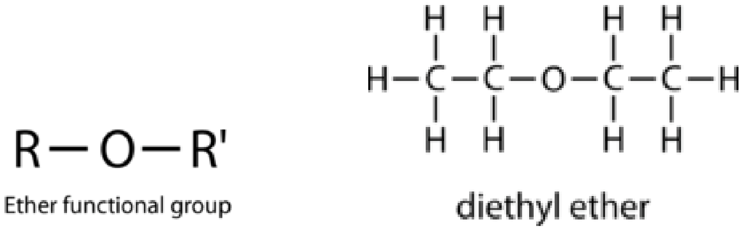
Figure 19.16 Primary, secondary, and tertiary alcohols.

Alcohols can be classified as primary, secondary, or tertiary based on the characteristics of the carbon to which it is attached. In a primary alcohol, the carbon bonded directly to the oxygen atom is also bonded to exactly one carbon atom, with the other bonds generally going to hydrogen atoms. In a secondary alcohol, the carbon is attached to two other carbon atoms, and in a tertiary alcohol, the carbon is bonded to three other carbon atoms. The type of alcohol being used will determine the product of certain reactions. Note the naming of alcohols as illustrated in the figure above. The location of the $-OH$ group is indicated with the number of the carbon to which it is attached.

We are already familiar with several common alcohols. For example, ethanol (CH_3CH_2OH) is the alcohol present in alcoholic beverages. It is also widely used in the industrial manufacture of other chemicals. Methanol (CH_3OH) is used as a gasoline additive or alternative. Additionally, methanol can be used to manufacture formaldehyde, which is employed in the production of plastics, paints, and other useful substances. Isopropanol is commonly known as rubbing alcohol. In addition to its industrial uses, isopropanol is used to clean various surfaces, including computer monitors, whiteboards, and even skin (e.g., before getting blood drawn).

Ethers

The **ether** functional group consists of an oxygen atom that forms single bonds with two carbon atoms.


Ether functional group

diethyl ether

Figure 19.17 *Ethers*

Ethers are good solvents for other organic compounds because of their low reactivity. They readily dissolve nonpolar molecules. Diethyl ether is perhaps the best known ether. It is widely used as a solvent and has been used as an inhalable anesthetic.

Although ethers themselves are relatively unreactive, they can be converted to peroxides after prolonged exposure to oxygen. Peroxides are very reactive and are often explosive at elevated temperatures. Many commercially available ethers come with a small amount of a peroxide scavenger dissolved in them to help prevent this type of safety hazard.

Thiol

The **thiol** functional group contains a sulfur atom bonded to a hydrogen atom. It is very similar to an alcohol functional group with the sulfur replacing the O.

$$R\text{——}SH$$

Figure 19.18 Thiol

Thiols are also called mercaptans which is derived from the Latin phrase for "capturing mercury" because of the strong bonds it forms with mercury-containing compounds. Some thiol compounds have a distinctive smell similar to rotten eggs. They are often added to natural gas, which itself has no odor, as a way to detect leaks since its odor can be detected by humans in very small amounts. A thiol group is also present in the amino acid cysteine which will be discussed later.

Amines

An **amine** consists of a nitrogen atom bonded to some combination of carbons and hydrogens.

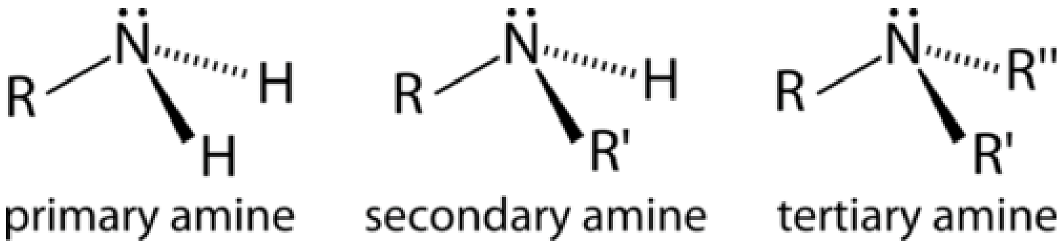


Figure 19.19 Amines

Like alcohols, amines can be classified as primary, secondary, or tertiary. However, the rules for assigning these categories are slightly different. In an alcohol, the oxygen atom is always bonded to exactly one carbon atom, so we look at the branching on the adjacent carbon, not the oxygen atom itself. In a neutral amine, the nitrogen can be bonded to one, two, or three carbon atoms, and this is how we decide whether it is called a primary, secondary, or tertiary amine.

Neutral amines are weak bases, because the lone pair on nitrogen can act as a proton acceptor. Many smaller amines have very strong and offensive odors. For example, the aptly-named compounds cadaverine and putrescine are foul-smelling amines, formed as a part of the decay process after death.

Amines serve a wide variety of uses. Diphenylamine acts as a stabilizer for certain types of explosives. Amines are found as components in some lubricating materials, in developers, and are a part of waterproofing textiles. Some amines, such as novocaine, are used as anesthetics. Many pharmaceutical compounds contain amines, including 8 of the 10 most prescribed medications in 2012.

Aldehydes

A very common structural component of organic structures is the **carbonyl**, which is simply a carbon atom and an oxygen atom connected by a double bond. The reactivity of carbonyls is primarily dictated by the polarization of the C=O bond, but the surrounding atoms also play a role in its specific reaction pathways. While carbonyl is a component of many functional groups, it is not itself a functional group.

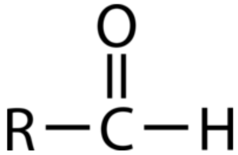


Figure 19.20 *Aldehyde*

An **aldehyde** is a carbonyl in which the carbon atom is bonded to at least one hydrogen atom. The other group attached to the carbonyl may be an RR-group or a hydrogen atom. Because the hydrogen atom is so small, the partial positive charge on the carbonyl carbon is very easy for other molecules to approach, making aldehydes a particularly reactive type of carbonyl. Aldehydes are versatile reactants for a wide variety of organic syntheses. Many aldehydes also have distinctive flavors and aromas. For example, the flavor of cinnamon is primarily due to the molecule cinnamaldehyde, and vanillin is the aldehyde most responsible for the smell and taste of vanilla extract.

A special aldehyde is the molecule in which the carbonyl is bonded to two hydrogen atoms. This molecule, called formaldehyde, has a wide variety of uses. By itself, it can be used as a tissue preservative or as a very harsh disinfectant. It is also used as a precursor to various materials, including plastics, resins, and other polymers.

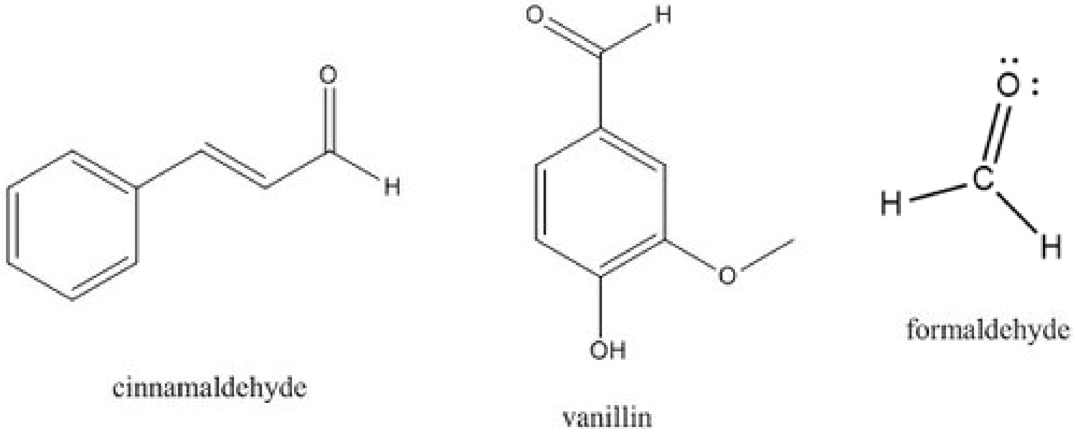
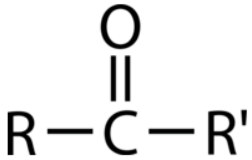


Figure 19.21 Examples of molecules with aldehyde functional groups.

Ketones

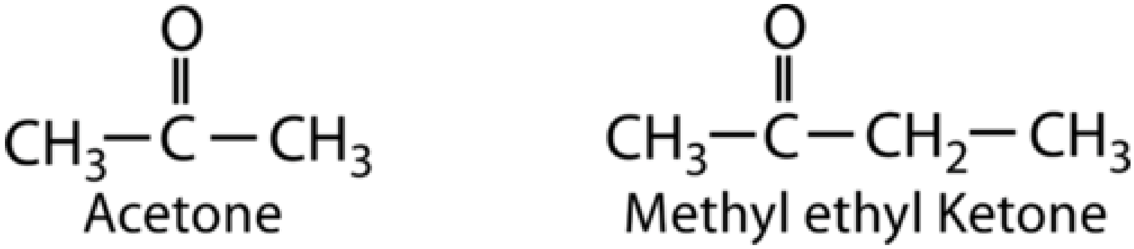
A **ketone** involves a carbonyl (C=O) in which the carbon atom makes single bonds with two R-groups.



$$R-\overset{\overset{\displaystyle O}{\|}}{C}-R'$$

Figure 19.22 Ketone

Ketones undergo most of the same reactions as aldehydes, but they tend to be slightly less reactive. The simplest ketone is acetone, in which the carbonyl carbon is bonded to two CH_3 groups. This ketone is commonly used to remove fingernail polish and serves as an industrial solvent. Methyl ethyl ketone is used as a paint stripper and a solvent. Ketones are also used in the production of various polymers, either as a building block or as a solvent. The RR-group in a ketone can be the same or different as seen in the example.



$$CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-CH_3$$

Acetone

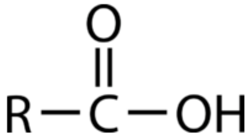
$$CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-CH_2-CH_3$$

Methyl ethyl Ketone

Figure 19.23 Two examples of ketones.

Carboxylic Acids

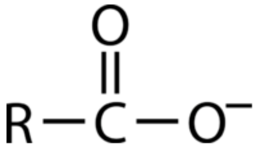
Carboxylic acids are another carbonyl-containing functional group, in which the carbon atom is bonded to an OH group on one side and either a carbon or hydrogen atom on the other.



$R-\overset{\overset{\displaystyle O}{\|}}{C}-OH$

Figure 19.24 *Carboxylic acid*

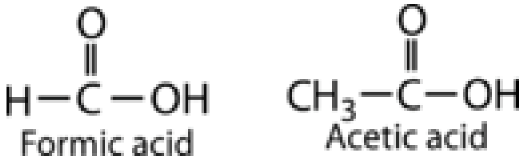
As the name implies, carboxylic acids are weak acids. An OH group that is directly connected to a carbonyl will ionize to a small extent when dissolved in water. The reason for this is the relative stability of the resulting anion. A carboxylate ion (see figure below), in which the negative charge is spread over two different oxygen atoms through resonance structures, is more stable than an isolated oxygen-centered anion. The carboxylic acid and carboxylate ion are interchangeable. Carboxylate ions are often present in amino acids.



$R-\overset{\overset{\displaystyle O}{\|}}{C}-O^-$

Figure 19.25 Carboxylate ion

Carboxylic acids are used in a variety of environments. Formic acid acts as a protective chemical for many stinging insects and plants. Acetic acid gives vinegar its characteristic smell and flavor and is a fundamental biological and industrial building block. Carboxylic acids with longer carbon chains (fatty acids) are used by animals as a way of storing energy and are widely used in the manufacture of soaps. Some compounds contain multiple carboxylic acids within a single molecule. For example, citric acid (three carboxyl groups) is especially abundant in citrus fruits and it used as a flavoring and preservative in many foods and beverages.



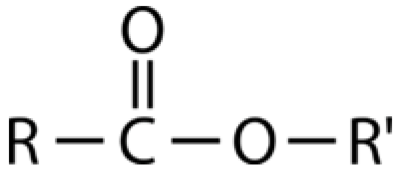
$H-\overset{\overset{\displaystyle O}{\|}}{C}-OH$ Formic acid

$CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-OH$ Acetic acid

Figure 19.26 Carboxylic acids

Esters

An **ester** is similar to a carboxylic acid, in that it contains a carbonyl where the carbon is bonded to one additional oxygen atom and one carbon or hydrogen atom. However, the second oxygen atom is bonded to another carbon instead of to an acidic hydrogen atom. Structurally, carboxylic acids and esters are related to one another in the same way as alcohols and ethers.



$$R-\overset{\overset{\displaystyle O}{\|}}{C}-O-R'$$

Figure 19.27 Ester

Esters can be formed by heating carboxylic acids and alcohols in the presence of an acid catalyst. This process is reversible, and the starting materials can be regenerated by reacting an ester with water in the presence of a weak base.

Some esters have very pleasant odors, so they are used in the manufacture of many perfumes. Propyl acetate contributes to the odor of pears, while isoamyl acetate gives bananas their smell. This ester also serves as an alarm signal for honeybees. Esters are employed in the manufacture of fabrics (polyesters) and Plexiglass. Anesthetics such as procaine and benzocaine also contain esters.

Amides

An **amide** is a carbonyl in which the carbon is attached to one nitrogen atom and one carbon or hydrogen atom. Alternatively, we could define an amide as an amine in which one of the carbon atoms attached to the nitrogen is part of a carbonyl.

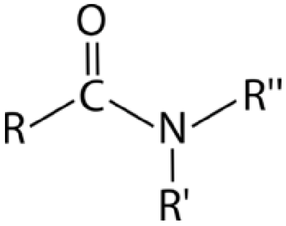


Figure 19.28 Amide

An amide can be formed by combining a carboxylic acid and an amine. Only primary and secondary amines can be sued to form amides, since they have a hydrogen that can be replaced with the carbonyl carbon; tertiary amines will not form amides. The amide shown in the figure above was formed from a carboxylic acid and a primary amine.

Amides are used as coloring agents in crayons, pencils, and ink. They are employed in the paper, plastic, and rubber industries. Polyacrylamide is a very widely used amide; it is involved in t he treatment of drinking water and sewage, and in plastics manufacture. The amide Kevlar is widely employed for the production of body armor, and nylon is another type of amide-based polymer.

Haloalkanes

The haloalkanes, also known as alkyl halides, are a group of chemical compounds comprised of an alkane with one or more hydrogens replaced by a halogen atom (Group 17 atom). There is a fairly large distinction between the structural and physical properties of haloalkanes and the structural and physical properties of alkanes.

Figure 19.29 Amide

Haloalkanes are found in fire extinguishers, refrigerants, propellants, solvents, and medications. They are also a significant source of pollution and their use has been reduced or eliminated in some products. Chlorofluorocarbons (CFCs) were used as refrigerants in air-conditioners but were found to be a major cause of the depletion of the ozone layer. Research and development of alternatives began in the 1970s. Hydrochlorofluorocarbons (HCFCs) have been used for many years since they cause less damage to the ozone layer, but many countries agreed to eliminate HCFCs by 2020.