

Reactions in Aqueous Solutions

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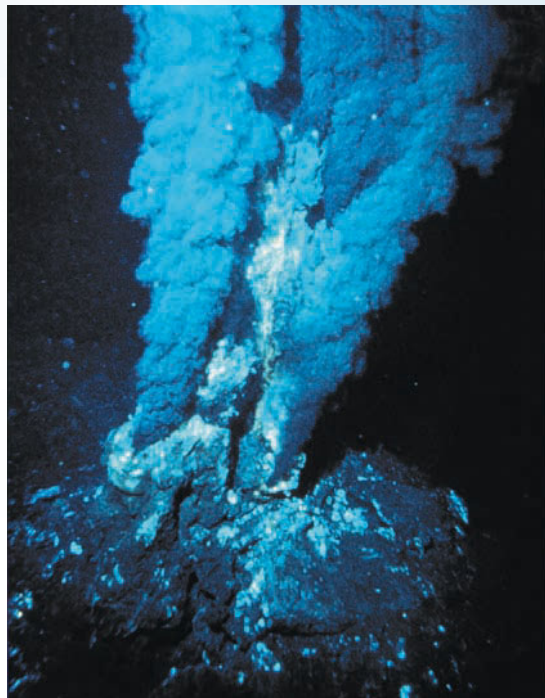
Essential Concepts

Reactions in Aqueous Solution Many chemical and almost all biological reactions occur in the aqueous medium. Substances (solutes) that dissolve in water (solvent) can be divided into two categories: electrolytes and nonelectrolytes, depending on their ability to conduct electricity.

Three Major Types of Reactions In a precipitation reaction, the product, an insoluble substance, separates from solution. Acid-base reactions involve the transfer of a proton (H^+) from an acid to a base. In an oxidation-reduction reaction, or redox reaction,

electrons are transferred from a reducing agent to an oxidizing agent. These three types of reactions represent the majority of reactions in chemical and biological systems.

Solution Stoichiometry Quantitative studies of reactions in solution require that we know the concentration of the solution, which is usually represented by the molarity unit. These studies include gravimetric analysis, which involves the measurement of mass, and titrations in which the unknown concentration of a solution is determined by reaction with a solution of known concentration.



"Black smoker," insoluble metal sulfides formed on the ocean floor through the lava on a mid-ocean-ridge volcano.

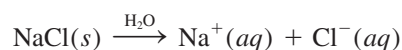
4.1 General Properties of Aqueous Solutions

Many chemical reactions and virtually all biological processes take place in an aqueous environment. Therefore, it is important to understand the properties of different substances in solution with water. To start with, what exactly is a solution? A **solution** is a homogeneous mixture of two or more substances. The substance present in a smaller amount is called the **solute**, whereas the substance present in a larger amount is called the **solvent**. A solution may be gaseous (such as air), solid (such as an alloy), or liquid (seawater, for example). In this section we will discuss only **aqueous solutions**, in which the solute initially is a liquid or a solid and the solvent is water.

Electrolytes versus Nonelectrolytes

All solutes that dissolve in water fit into one of two categories: electrolytes and nonelectrolytes. An **electrolyte** is a substance that, when dissolved in water, results in a solution that can conduct electricity. A **nonelectrolyte** does not conduct electricity when dissolved in water. Figure 4.1 shows an easy and straightforward method of distinguishing between electrolytes and nonelectrolytes. A pair of platinum electrodes is immersed in a beaker of water. To light the bulb, electric current must flow from one electrode to the other, thus completing the circuit. Pure water is a very poor conductor of electricity. However, if we add a small amount of sodium chloride (NaCl), the bulb will glow as soon as the salt dissolves in the water. Solid NaCl, an ionic compound, breaks up into Na^+ and Cl^- ions when it dissolves in water. The Na^+ ions are attracted to the negative electrode and the Cl^- ions to the positive electrode. This movement sets up an electrical current that is equivalent to the flow of electrons along a metal wire. Because the NaCl solution conducts electricity, we say that NaCl is an electrolyte. Pure water contains very few ions, so it cannot conduct electricity.

Comparing the lightbulb's brightness for the *same molar amounts* of dissolved substances helps us distinguish between strong and weak electrolytes. A characteristic of strong electrolytes is that the solute is assumed to be 100 percent dissociated into ions in solution. (By *dissociation* we mean the breaking up of the compound into cations and anions.) Thus, we can represent sodium chloride dissolving in water as



What this equation says is that all the sodium chloride that enters the aqueous solution ends up as Na^+ and Cl^- ions; there are no undissociated NaCl units in solution.

Tap water does conduct electricity because it contains many dissolved ions.

Animation
Strong Electrolytes, Weak Electrolytes,
and Nonelectrolytes

Figure 4.1 An arrangement for distinguishing between electrolytes and nonelectrolytes. A solution's ability to conduct electricity depends on the number of ions it contains. (a) A nonelectrolyte solution does not contain ions, and the lightbulb is not lit. (b) A weak electrolyte solution contains a small number of ions, and the lightbulb is dimly lit. (c) A strong electrolyte solution contains a large number of ions, and the lightbulb is brightly lit. The molar amounts of the dissolved solutes are equal in all three cases.

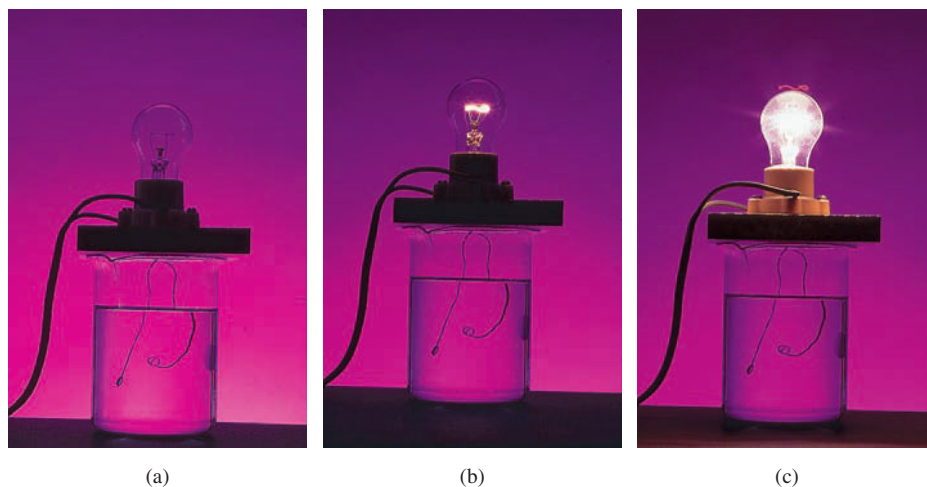


Table 4.1 Classification of Solutes in Aqueous Solution

Strong Electrolyte	Weak Electrolyte	Nonelectrolyte
HCl	CH ₃ COOH	(NH ₂) ₂ CO (urea)
HNO ₃	HF	CH ₃ OH (methanol)
HClO ₄	HNO ₂	C ₂ H ₅ OH (ethanol)
H ₂ SO ₄ *	NH ₃	C ₆ H ₁₂ O ₆ (glucose)
NaOH	H ₂ O [†]	C ₁₂ H ₂₂ O ₁₁ (sucrose)
Ba(OH) ₂		
Ionic compounds		

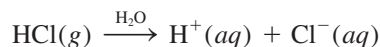
*H₂SO₄ has two ionizable H⁺ ions.

†Pure water is an extremely weak electrolyte.

Table 4.1 lists examples of strong electrolytes, weak electrolytes, and nonelectrolytes. Ionic compounds, such as sodium chloride, potassium iodide (KI), and calcium nitrate [Ca(NO₃)₂], are strong electrolytes. It is interesting to note that human body fluids contain many strong and weak electrolytes.

Water is a very effective solvent for ionic compounds. Although water is an electrically neutral molecule, it has a positive end (the H atoms) and a negative end (the O atom), or positive and negative “poles”; for this reason, it is often referred to as a *polar* solvent. When an ionic compound such as sodium chloride dissolves in water, the three-dimensional network of the ions in the solid is destroyed, and the Na⁺ and Cl⁻ ions are separated from each other. In solution, each Na⁺ ion is surrounded by a number of water molecules orienting their negative ends toward the cation. Similarly, each Cl⁻ ion is surrounded by water molecules with their positive ends oriented toward the anion (Figure 4.2). *The process in which an ion is surrounded by water molecules arranged in a specific manner is called hydration.* Hydration helps to stabilize ions in solution and prevents cations from combining with anions.

Acids and bases are also electrolytes. Some acids, including hydrochloric acid (HCl) and nitric acid (HNO₃), are strong electrolytes. These acids ionize completely in water; for example, when hydrogen chloride gas dissolves in water, it forms hydrated H⁺ and Cl⁻ ions:



In other words, *all* the dissolved HCl molecules separate into hydrated H⁺ and Cl⁻ ions in solution. Thus, when we write HCl(aq), it is understood that it is a solution of only H⁺(aq) and Cl⁻(aq) ions and there are no hydrated HCl molecules present. On the other hand, certain acids, such as acetic acid (CH₃COOH), which is found in vinegar, ionize to a much lesser extent. We represent the ionization of acetic acid as



 Animation
Hydration

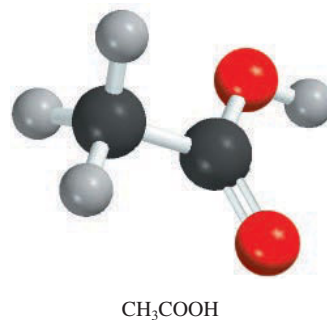


Figure 4.2 Hydration of Na⁺ and Cl⁻ ions.

in which CH_3COO^- is called the acetate ion. (In this book we will use the term *dissociation* for ionic compounds and *ionization* for acids and bases.) By writing the formula of acetic acid as CH_3COOH we indicate that the ionizable proton is in the COOH group.

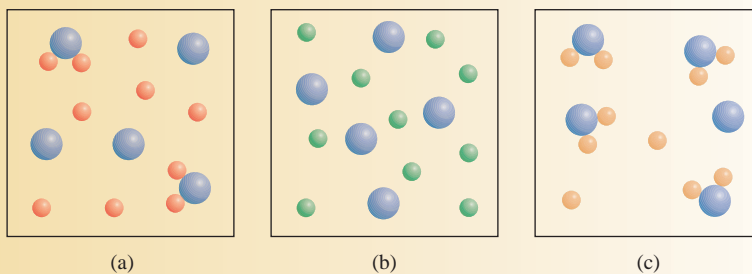
The double arrow \rightleftharpoons in an equation means that the reaction is *reversible*; that is, the *reaction can occur in both directions*. Initially, a number of CH_3COOH molecules break up to yield CH_3COO^- and H^+ ions. As time goes on, some of the CH_3COO^- and H^+ ions recombine to form CH_3COOH molecules. Eventually, a state is reached in which the acid molecules break up as fast as the ions recombine. Such a *chemical state, in which no net change can be observed* (although continuous activity is taking place on the molecular level), is called **chemical equilibrium**. Acetic acid, then, is a weak electrolyte because its ionization in water is incomplete. By contrast, in a hydrochloric acid solution, the H^+ and Cl^- ions have no tendency to recombine to form molecular HCl . We use the single arrow to represent complete ionizations.

In Sections 4.2–4.4 we will study three types of reactions in the aqueous medium (precipitation, acid-base, and oxidation-reduction) that are of great importance to industrial, environmental, and biological processes. They also play a role in our daily experience.

There are different types of chemical equilibrium. We will return to this very important topic in Chapter 15.

Review of Concepts

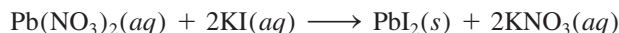
The diagrams show three compounds (a) AB_2 , (b) AC_2 , and (c) AD_2 dissolved in water. Which is the strongest electrolyte and which is the weakest? (For simplicity, water molecules are not shown.)



4.2 Precipitation Reactions

Animation
Precipitation Reactions

One common type of reaction that occurs in aqueous solution is the **precipitation reaction**, which results in the formation of an insoluble product, or *precipitate*. A **precipitate** is an insoluble solid that separates from the solution. Precipitation reactions usually involve ionic compounds. For example, when an aqueous solution of lead(II) nitrate [$\text{Pb}(\text{NO}_3)_2$] is added to an aqueous solution of potassium iodide (KI), a yellow precipitate of lead iodide (PbI_2) is formed:



Potassium nitrate remains in solution. Figure 4.3 shows this reaction in progress.

The preceding reaction is an example of a **metathesis reaction** (also called a double displacement reaction), a reaction that involves the exchange of parts between two compounds. (In this case, the compounds exchange the NO_3^- and I^- ions.) As we will see, the precipitation reactions discussed in this chapter are examples of metathesis reactions.

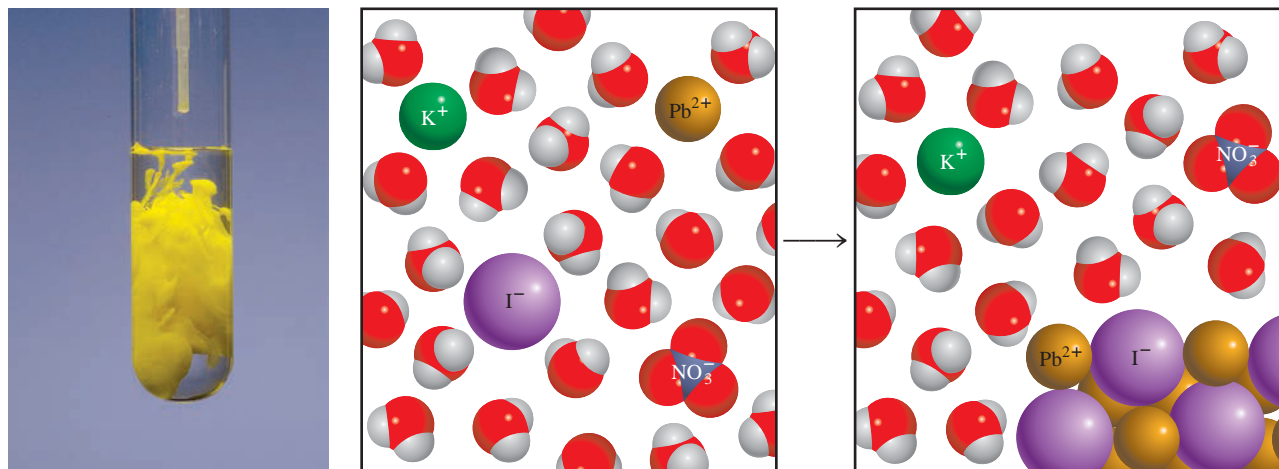


Figure 4.3 Formation of yellow PbI_2 precipitate as a solution of $\text{Pb}(\text{NO}_3)_2$ is added to a solution of KI .

Solubility

How can we predict whether a precipitate will form when a compound is added to a solution or when two solutions are mixed? It depends on the **solubility** of the solute, which is defined as *the maximum amount of solute that will dissolve in a given quantity of solvent at a specific temperature*. Chemists refer to substances as soluble, slightly soluble, or insoluble in a qualitative sense. A substance is said to be soluble if a fair amount of it visibly dissolves when added to water. If not, the substance is described as slightly soluble or insoluble. All ionic compounds are strong electrolytes, but they are not equally soluble.

Table 4.2 classifies a number of common ionic compounds as soluble or insoluble. Keep in mind, however, that even insoluble compounds dissolve to a certain extent. Figure 4.4 shows several precipitates.

Table 4.2 Solubility Rules for Common Ionic Compounds in Water at 25°C

Soluble Compounds	Insoluble Exceptions
Compounds containing alkali metal ions (Li^+ , Na^+ , K^+ , Rb^+ , Cs^+) and the ammonium ion (NH_4^+)	
Nitrates (NO_3^-), bicarbonates (HCO_3^-), and chlorates (ClO_3^-)	
Halides (Cl^- , Br^- , I^-)	Halides of Ag^+ , Hg_2^{2+} , and Pb^{2+}
Sulfates (SO_4^{2-})	Sulfates of Ag^+ , Ca^{2+} , Sr^{2+} , Ba^{2+} , Hg_2^{2+} , and Pb^{2+}
Insoluble Compounds	Soluble Exceptions
Carbonates (CO_3^{2-}), phosphates (PO_4^{3-}), chromates (CrO_4^{2-}), and sulfides (S^{2-})	Compounds containing alkali metal ions and the ammonium ion
Hydroxides (OH^-)	Compounds containing alkali metal ions and the Ba^{2+} ion



Figure 4.4 Appearance of several precipitates. From left to right: CdS , PbS , Ni(OH)_2 , Al(OH)_3 .

Example 4.1

Classify the following ionic compounds as soluble or insoluble: (a) lead sulfate (PbSO_4), (b) barium carbonate (BaCO_3), (c) lithium phosphate (Li_3PO_4).

Strategy Although it is not necessary to memorize the solubilities of compounds, you should keep in mind the following useful rules: all ionic compounds containing alkali metal cations; the ammonium ion; and the nitrate, bicarbonate, and chlorate ions are soluble. For other compounds we need to refer to Table 4.2.

Solution

- (a) According to Table 4.2, PbSO_4 is insoluble.
- (b) This is a carbonate and Ba is a Group 2A metal. Therefore, BaCO_3 is insoluble.
- (c) Lithium is an alkali metal (Group 1A) so Li_3PO_4 is soluble.

Practice Exercise Classify the following ionic compounds as soluble or insoluble: (a) FeS , (b) Ca(OH)_2 , (c) $\text{Co(NO}_3)_3$.

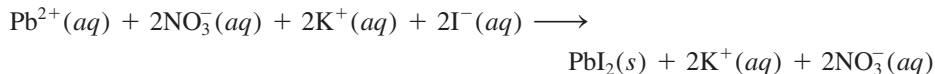
Similar problems: 4.19, 4.20.

Molecular Equations, Ionic Equations, and Net Ionic Equations

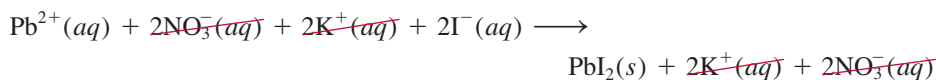
The equation describing the precipitation of lead iodide on page 100 is called a **molecular equation** because *the formulas of the compounds are written as though all species existed as molecules or whole units*. A molecular equation is useful because it identifies the reagents (that is, lead nitrate and potassium iodide). If we wanted to bring about this reaction in the laboratory, we would use the molecular equation. However, a molecular equation does not describe in detail what actually is happening in solution.

As pointed out earlier, when ionic compounds dissolve in water, they break apart into their component cations and anions. To be more realistic, the equations should

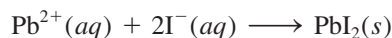
show the dissociation of dissolved ionic compounds into ions. Therefore, returning to the reaction between potassium iodide and lead nitrate, we would write



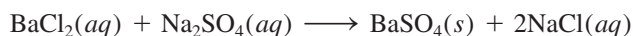
The preceding equation is an example of an **ionic equation**, which *shows dissolved species as free ions*. To see whether a precipitate might form from this solution, we first combine the cation and anion from different compounds; that is, PbI_2 and KNO_3 . Referring to Table 4.2, we see that PbI_2 is an insoluble compound and KNO_3 is soluble. Therefore, the dissolved KNO_3 remains in solution as separate K^{+} and NO_3^{-} ions, which are called **spectator ions**, or *ions that are not involved in the overall reaction*. Because spectator ions appear on both sides of an equation, they can be eliminated from the ionic equation



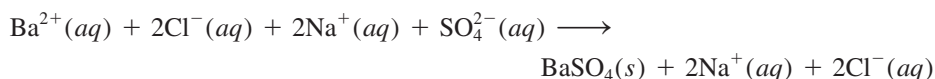
Finally, we end up with the **net ionic equation**, which *shows only the species that actually take part in the reaction*:



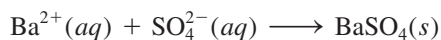
Looking at another example, we find that when an aqueous solution of barium chloride (BaCl_2) is added to an aqueous solution of sodium sulfate (Na_2SO_4), a white precipitate is formed (Figure 4.5). Treating this as a metathesis reaction, the products are BaSO_4 and NaCl . From Table 4.2 we see that only BaSO_4 is insoluble. Therefore, we write the molecular equation as



The ionic equation for the reaction is



Canceling the spectator ions (Na^{+} and Cl^{-}) on both sides of the equation gives us the net ionic equation



The following four steps summarize the procedure for writing ionic and net ionic equations:

1. Write a balanced molecular equation for the reaction, using the correct formulas for the reactant and product ionic compounds. Refer to Table 4.2 to decide which of the products is insoluble and therefore will appear as a precipitate.
2. Write the ionic equation for the reaction. The compound that does not appear as the precipitate should be shown as free ions.
3. Identify and cancel the spectator ions on both sides of the equation. Write the net ionic equation for the reaction.
4. Check that the charges and number of atoms balance in the net ionic equation.



Figure 4.5 Formation of BaSO_4 precipitate.

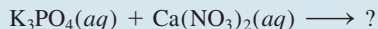


Precipitate formed by the reaction between $K_3PO_4(aq)$ and $Ca(NO_3)_2(aq)$.

Example 4.2

Predict what happens when a potassium phosphate (K_3PO_4) solution is mixed with a calcium nitrate [$Ca(NO_3)_2$] solution. Write a net ionic equation for the reaction.

Strategy From the given information, it is useful to first write the unbalanced equation



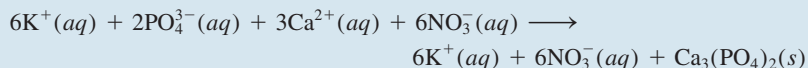
What happens when ionic compounds dissolve in water? What ions are formed from the dissociation of K_3PO_4 and $Ca(NO_3)_2$? What happens when the cations encounter the anions in solution?

Solution In solution, K_3PO_4 dissociates into K^+ and PO_4^{3-} ions and $Ca(NO_3)_2$ dissociates into Ca^{2+} and NO_3^- ions. According to Table 4.2, calcium ions (Ca^{2+}) and phosphate ions (PO_4^{3-}) will form an insoluble compound, calcium phosphate [$Ca_3(PO_4)_2$], while the other product, KNO_3 , is soluble and remains in solution. Therefore, this is a precipitation reaction. We follow the stepwise procedure just outlined.

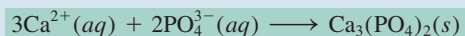
Step 1: The balanced molecular equation for this reaction is



Step 2: To write the ionic equation, the soluble compounds are shown as dissociated ions:



Step 3: Canceling the spectator ions (K^+ and NO_3^-) on each side of the equation, we obtain the net ionic equation:



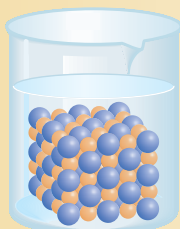
Step 4: Note that because we balanced the molecular equation first, the net ionic equation is balanced as to the number of atoms on each side and the number of positive (+6) and negative (-6) charges on the left-hand side is the same.

Practice Exercise Predict the precipitate produced by mixing an $Al(NO_3)_3$ solution with a $NaOH$ solution. Write the net ionic equation for the reaction.

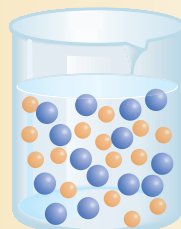
Similar problems: 4.21, 4.22.

Review of Concepts

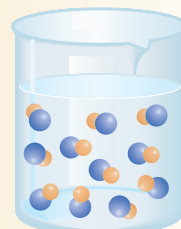
Which of the diagrams here accurately describes the reaction between $Ca(NO_3)_2(aq)$ and $Na_2CO_3(aq)$? For simplicity, only the Ca^{2+} (yellow) and CO_3^{2-} (blue) ions are shown.



(a)



(b)



(c)

4.3 Acid-Base Reactions

Acids and bases are as familiar as aspirin and milk of magnesia although many people do not know their chemical names—acetylsalicylic acid (aspirin) and magnesium hydroxide (milk of magnesia). In addition to being the basis of many medicinal and household products, acid-base chemistry is important in industrial processes and essential in sustaining biological systems. Before we can discuss acid-base reactions, we need to know more about acids and bases themselves.

General Properties of Acids and Bases

In Section 2.7 we defined acids as substances that ionize in water to produce H^+ ions and bases as substances that ionize in water to produce OH^- ions. These definitions were formulated in the late nineteenth century by the Swedish chemist Svante Arrhenius to classify substances whose properties in aqueous solutions were well known.

Acids

- Acids have a sour taste; for example, vinegar owes its sourness to acetic acid, and lemons and other citrus fruits contain citric acid.
- Acids cause color changes in plant dyes; for example, they change the color of litmus from blue to red.
- Acids react with certain metals, such as zinc, magnesium, and iron, to produce hydrogen gas. A typical reaction is that between hydrochloric acid and magnesium:



- Acids react with carbonates and bicarbonates, such as Na_2CO_3 , CaCO_3 , and NaHCO_3 , to produce carbon dioxide gas (Figure 4.6). For example,



- Aqueous acid solutions conduct electricity.

Bases

- Bases have a bitter taste.
- Bases feel slippery; for example, soaps, which contain bases, exhibit this property.
- Bases cause color changes in plant dyes; for example, they change the color of litmus from red to blue.
- Aqueous base solutions conduct electricity.

Brønsted Acids and Bases

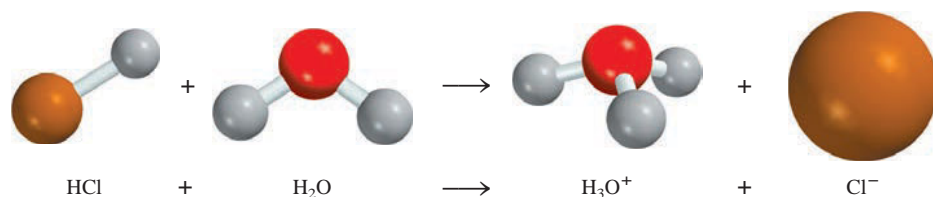
Arrhenius's definitions of acids and bases are limited in that they apply only to aqueous solutions. Broader definitions were proposed by the Danish chemist Johannes Brønsted in 1932; a **Brønsted acid** is a *proton donor*, and a **Brønsted base** is a *proton acceptor*. Note that Brønsted's definitions do not require acids and bases to be in aqueous solution.

Hydrochloric acid is a Brønsted acid because it donates a proton in water:

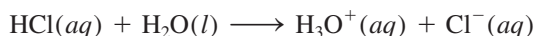


Figure 4.6 A piece of blackboard chalk, which is mostly CaCO_3 , reacts with hydrochloric acid to produce carbon dioxide gas.

Figure 4.7 Ionization of HCl in water to form the hydronium ion and the chloride ion.



Note that the H^+ ion is a hydrogen atom that has lost its electron; that is, it is just a bare proton. The size of a proton is about 10^{-15} m, compared to a diameter of 10^{-10} m for an average atom or ion. Such an exceedingly small charged particle cannot exist as a separate entity in aqueous solution owing to its strong attraction for the negative pole (the O atom) in H_2O . Consequently, the proton exists in the hydrated form, as shown in Figure 4.7. Therefore, the ionization of hydrochloric acid should be written as



The *hydrated proton*, H_3O^+ , is called the **hydronium ion**. This equation shows a reaction in which a Brønsted acid (HCl) donates a proton to a Brønsted base (H_2O).

Experiments show that the hydronium ion is further hydrated so that the proton may have several water molecules associated with it. Because the acidic properties of the proton are unaffected by the degree of hydration, in this text we will generally use $\text{H}^+(aq)$ to represent the hydrated proton. This notation is for convenience, but H_3O^+ is closer to reality. Keep in mind that both notations represent the same species in aqueous solution.

Acids commonly used in the laboratory include hydrochloric acid (HCl), nitric acid (HNO_3), acetic acid (CH_3COOH), sulfuric acid (H_2SO_4), and phosphoric acid (H_3PO_4). The first three are **monoprotic acids**; that is, *each unit of the acid yields one hydrogen ion upon ionization*:



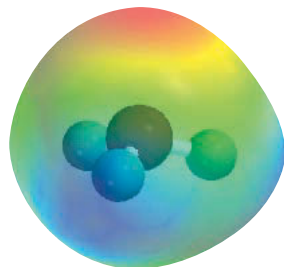
As mentioned earlier, because the ionization of acetic acid is incomplete (note the double arrows), it is a weak electrolyte. For this reason it is called a weak acid (see Table 4.1). On the other hand, HCl and HNO_3 are strong acids because they are strong electrolytes, so they are completely ionized in solution (note the use of single arrows).

Sulfuric acid (H_2SO_4) is a **diprotic acid** because *each unit of the acid gives up two H^+ ions*, in two separate steps:



H_2SO_4 is a strong electrolyte or strong acid (the first step of ionization is complete), but HSO_4^- is a weak acid or weak electrolyte, and we need a double arrow to represent its incomplete ionization.

Triprotic acids, which yield three H^+ ions, are relatively few in number. The best known triprotic acid is phosphoric acid, whose ionizations are



Electrostatic potential map of the H_3O^+ ion. In the rainbow color spectrum representation, the most electron-rich region is red and the most electron-poor region is blue.

In most cases, acids start with H in the formula or have a COOH group.

All three species (H_3PO_4 , H_2PO_4^- , and HPO_4^{2-}) in this case are weak acids, and we use the double arrows to represent each ionization step. Anions such as H_2PO_4^- and HPO_4^{2-} are found in aqueous solutions of phosphates such as NaH_2PO_4 and Na_2HPO_4 . Table 4.3 lists several common strong and weak acids.

Review of Concepts

Which of the following diagrams best represents a strong acid? Which represents a weak acid? Which represents a very weak acid? The proton exists in water as the hydronium ion. All of the acids are monoprotic. (For simplicity, water molecules are not shown.)

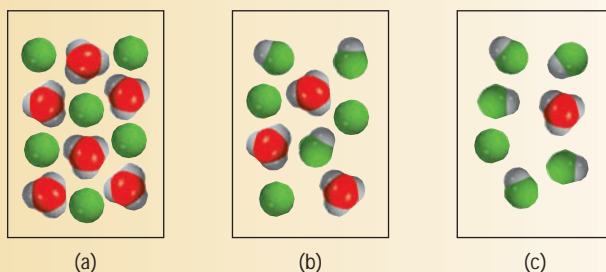


Table 4.3

Some Common Strong and Weak Acids

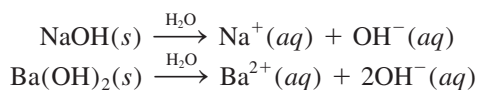
Strong Acids

Hydrochloric acid	HCl
Hydrobromic acid	HBr
Hydroiodic acid	HI
Nitric acid	HNO_3
Sulfuric acid	H_2SO_4
Perchloric acid	HClO_4

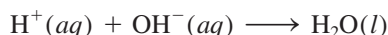
Weak Acids

Hydrofluoric acid	HF
Nitrous acid	HNO_2
Phosphoric acid	H_3PO_4
Acetic acid	CH_3COOH

Table 4.1 shows that sodium hydroxide (NaOH) and barium hydroxide [$\text{Ba}(\text{OH})_2$] are strong electrolytes. This means that they are completely ionized in solution:

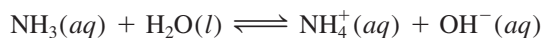


The OH^- ion can accept a proton as follows:



Thus, OH^- is a Brønsted base.

Ammonia (NH_3) is classified as a Brønsted base because it can accept a H^+ ion (Figure 4.8):



Ammonia is a weak electrolyte (and therefore a weak base) because only a small fraction of dissolved NH_3 molecules react with water to form NH_4^+ and OH^- ions.

The most commonly used strong base in the laboratory is sodium hydroxide. It is cheap and soluble. (In fact, all of the alkali metal hydroxides are soluble.) The most commonly used weak base is aqueous ammonia solution, which is sometimes erroneously

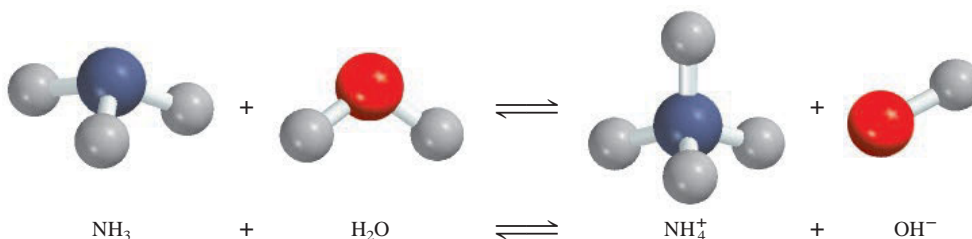


Figure 4.8 Ionization of ammonia in water to form the ammonium ion and the hydroxide ion.



A bottle of aqueous ammonia, which is sometimes erroneously called ammonium hydroxide.

called ammonium hydroxide; there is no evidence that the species NH_4OH actually exists other than the NH_4^+ and OH^- ions in solution. All of the Group 2A elements form hydroxides of the type $\text{M}(\text{OH})_2$, where M denotes an alkaline earth metal. Of these hydroxides, only $\text{Ba}(\text{OH})_2$ is soluble. Magnesium and calcium hydroxides are used in medicine and industry. Hydroxides of other metals, such as $\text{Al}(\text{OH})_3$ and $\text{Zn}(\text{OH})_2$ are insoluble and are not used as bases.

Example 4.3 classifies substances as Brønsted acids or Brønsted bases.

Example 4.3

Classify each of the following species in aqueous solution as a Brønsted acid or base:

(a) HBr , (b) NO_2^- , (c) HCO_3^- .

Strategy What are the characteristics of a Brønsted acid? Does it contain at least an H atom? With the exception of ammonia, most Brønsted bases that you will encounter at this stage are anions.

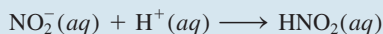
Solution

(a) We know that HCl is an acid. Because Br and Cl are both halogens (Group 7A), we expect HBr , like HCl , to ionize in water as follows:



Therefore, HBr is a Brønsted acid.

(b) In solution the nitrite ion can accept a proton from water to form nitrous acid:

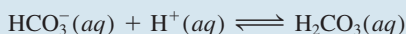


This property makes NO_2^- a Brønsted base.

(c) The bicarbonate ion is a Brønsted acid because it ionizes in solution as follows:



It is also a Brønsted base because it can accept a proton to form carbonic acid:



Comment The HCO_3^- species is said to be *amphoteric* because it possesses both acidic and basic properties. The double arrows show that this is a reversible reaction.

Practice Exercise Classify each of the following species as a Brønsted acid or base:

(a) SO_4^{2-} , (b) HI , (c) H_2PO_4^- .

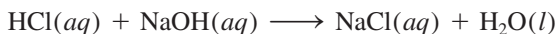
Similar problems: 4.31, 4.32.

Acid-Base Neutralization

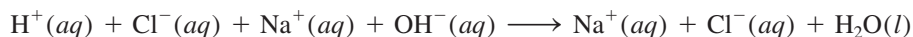
A **neutralization reaction** is a reaction between an acid and a base. Generally, aqueous acid-base reactions produce water and a **salt**, which is an ionic compound made up of a cation other than H^+ and an anion other than OH^- or O^{2-} :



For example, when a HCl solution is mixed with a NaOH solution, the following reaction occurs:



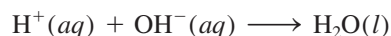
However, because both the acid and the base are strong electrolytes, they are completely ionized in solution. The ionic equation is



Animation
Neutralization Reactions

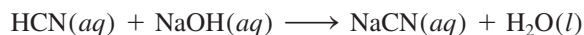
Acid-base reactions generally go to completion.

Therefore, the reaction can be represented by the net ionic equation

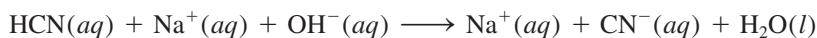


Both Na^+ and Cl^- are spectator ions.

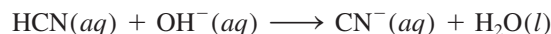
Now consider the reaction between NaOH with hydrocyanic acid (HCN), which is a weak acid:



In this case, the ionic equation is



and the net ionic equation is

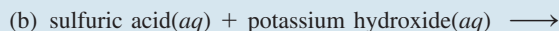
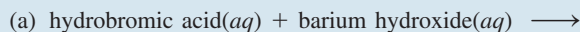


The following are also examples of acid-base neutralization reactions, represented by molecular equations:



Example 4.4

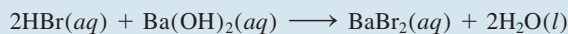
Write molecular, ionic, and net ionic equations for each of the following acid-base reactions:



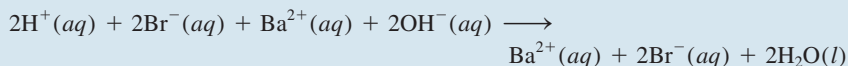
Strategy The first step is to identify the acids and bases as strong or weak. We see that HBr is a strong acid and H_2SO_4 is a strong acid for the first step ionization and a weak acid for the second step ionization. Both $\text{Ba}(\text{OH})_2$ and KOH are strong bases.

Solution

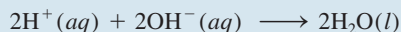
(a) Molecular equation:



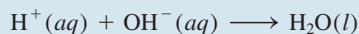
Ionic equation:



Net ionic equation:

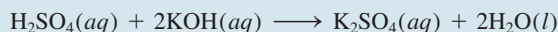


or

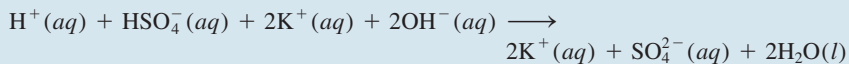


Both Ba^{2+} and Br^- are spectator ions.

(b) Molecular equation:

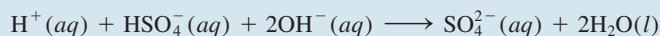


Ionic equation:



(Continued)

Net ionic equation:



Note that because HSO_4^- is a weak acid and does not ionize appreciably in water, the only spectator ion is K^+ .

Similar problem: 4.33(b).

Practice Exercise Write a molecular equation, an ionic equation, and a net ionic equation for the reaction between aqueous solutions of phosphoric acid and sodium hydroxide.

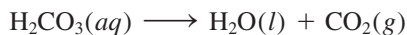
Acid-Base Reactions Leading to Gas Formation

Certain salts like carbonates (containing the CO_3^{2-} ion), bicarbonates (containing the HCO_3^- ion), sulfites (containing the SO_3^{2-} ion), and sulfides (containing the S^{2-} ion) react with acids to form gaseous products. For example, the molecular equation for the reaction between sodium carbonate (Na_2CO_3) and $\text{HCl}(aq)$ is

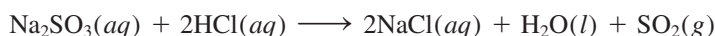
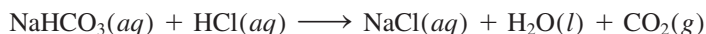


See Figure 4.6 on p. 105.

Carbonic acid is unstable and if present in solution in sufficient concentrations decomposes as follows:



Similar reactions involving other mentioned salts are

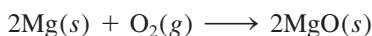


4.4 Oxidation-Reduction Reactions

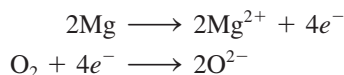
 **Animation**
Oxidation-Reduction Reactions

Whereas acid-base reactions can be characterized as proton-transfer processes, the class of reactions called *oxidation-reduction*, or *redox, reactions* are considered *electron-transfer reactions*. Oxidation-reduction reactions are very much a part of the world around us. They range from the burning of fossil fuels to the action of household bleach. Additionally, most metallic and nonmetallic elements are obtained from their ores by the process of oxidation or reduction.

Many important redox reactions take place in water, but not all redox reactions occur in aqueous solution. Nonaqueous redox reactions are less cumbersome to deal with, so we will begin our discussion with a reaction in which two elements combine to form a compound. Consider the formation of magnesium oxide (MgO) from magnesium and oxygen (Figure 4.9):



Magnesium oxide (MgO) is an ionic compound made up of Mg^{2+} and O^{2-} ions. In this reaction, two Mg atoms give up or transfer four electrons to two O atoms (in O_2). For convenience, we can think of this process as two separate steps, one involving the loss of four electrons by the two Mg atoms and the other being the gain of four electrons by an O_2 molecule:



In oxidation half-reaction, electrons appear as the product; in reduction half-reaction, electrons appear as the reactant.

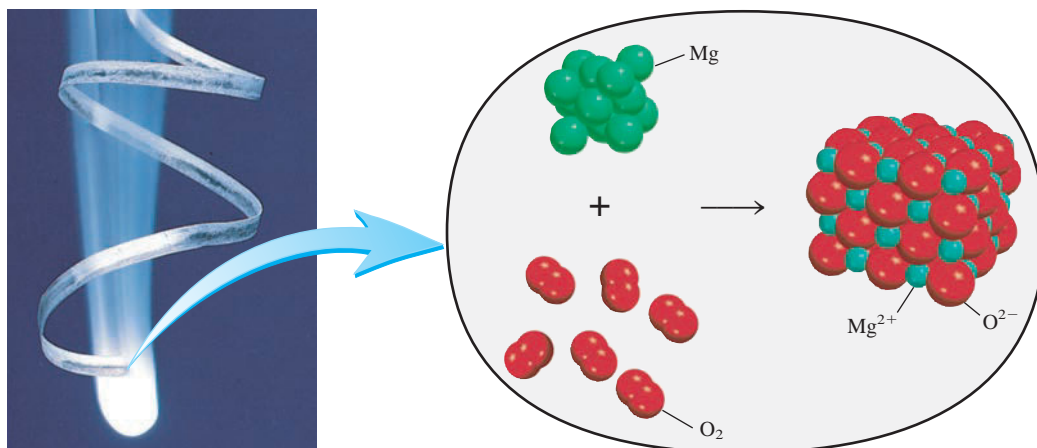
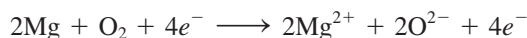
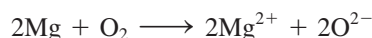


Figure 4.9 Magnesium burns in oxygen to form magnesium oxide.

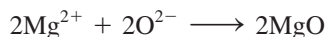
Each of these steps is called a **half-reaction**, which *explicitly shows the electrons involved in a redox reaction*. The sum of the half-reactions gives the overall reaction:



or, if we cancel the electrons that appear on both sides of the equation,



Finally, the Mg^{2+} and O^{2-} ions combine to form MgO :



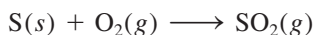
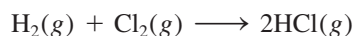
The term **oxidation reaction** refers to the *half-reaction that involves loss of electrons*. Chemists originally used “oxidation” to denote the combination of elements with oxygen. However, it now has a broader meaning that includes reactions not involving oxygen. A **reduction reaction** is a *half-reaction that involves gain of electrons*. In the formation of magnesium oxide, magnesium is oxidized. It is said to act as a **reducing agent** because it *donates electrons* to oxygen and causes oxygen to be reduced. Oxygen is reduced and acts as an **oxidizing agent** because it *accepts electrons* from magnesium, causing magnesium to be oxidized. Note that the extent of oxidation in a redox reaction must be equal to the extent of reduction; that is, the number of electrons lost by a reducing agent must be equal to the number of electrons gained by an oxidizing agent.

A useful mnemonic for redox is OILRIG: Oxidation Is Loss (of electrons) and Reduction Is Gain (of electrons).

Oxidizing agents are always reduced, and reducing agents are always oxidized. This statement may be somewhat confusing, but it is simply a consequence of the definitions of the two processes.

Oxidation Number

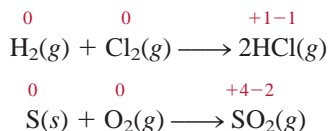
The definitions of oxidation and reduction in terms of loss and gain of electrons apply to the formation of ionic compounds such as MgO . However, these definitions do not accurately characterize the formation of hydrogen chloride (HCl) and sulfur dioxide (SO_2):



Because HCl and SO_2 are not ionic but molecular compounds, no electrons are actually transferred in the formation of these compounds, as they are in the case of MgO .

Nevertheless, chemists find it convenient to treat these reactions as redox reactions because experimental measurements show that there is a partial transfer of electrons (from H to Cl in HCl and from S to O in SO₂).

To keep track of electrons in redox reactions, it is useful to assign oxidation numbers to the reactants and products. An atom's **oxidation number**, also called **oxidation state**, signifies the *number of charges the atom would have in a molecule (or an ionic compound) if electrons were transferred completely*. For example, we can rewrite the preceding equations for the formation of HCl and SO₂ as follows:



The numbers above the element symbols are the oxidation numbers. In both of the reactions shown, there is no charge on the atoms in the reactant molecules. Thus, their oxidation number is zero. For the product molecules, however, it is assumed that complete electron transfer has taken place and that atoms have gained or lost electrons. The oxidation numbers reflect the number of electrons “transferred.”

Oxidation numbers enable us to identify elements that are oxidized and reduced at a glance. The elements that show an increase in oxidation number—hydrogen and sulfur in the preceding examples—are oxidized. Chlorine and oxygen are reduced, so their oxidation numbers show a decrease from their initial values. Note that the sum of the oxidation numbers of H and Cl in HCl (+1 and −1) is zero. Likewise, if we add the charges on S (+4) and two atoms of O [$2 \times (-2)$], the total is zero. The reason is that the HCl and SO₂ molecules are neutral, so the charges must cancel.

We use the following rules to assign oxidation numbers:

1. In free elements (that is, in the uncombined state), each atom has an oxidation number of zero. Thus, each atom in H₂, Br₂, Na, Be, K, O₂, and P₄ has the same oxidation number: zero.
2. For ions composed of only one atom (that is, monatomic ions), the oxidation number is equal to the charge on the ion. Thus, Li⁺ ion has an oxidation number of +1; Ba²⁺ ion, +2; Fe³⁺ ion, +3; I[−] ion, −1; O^{2−} ion, −2; and so on. All alkali metals have an oxidation number of +1 and all alkaline earth metals have an oxidation number of +2 in their compounds. Aluminum has an oxidation number of +3 in all its compounds.
3. The oxidation number of oxygen in most compounds (for example, MgO and H₂O) is −2, but in hydrogen peroxide (H₂O₂) and peroxide ion (O₂^{2−}), it is −1.
4. The oxidation number of hydrogen is +1, except when it is bonded to metals in binary compounds. In these cases (for example, LiH, NaH, CaH₂), its oxidation number is −1.
5. Fluorine has an oxidation number of −1 in *all* its compounds. Other halogens (Cl, Br, and I) have negative oxidation numbers when they occur as halide ions in their compounds. When combined with oxygen—for example in oxoacids and oxoanions (see Section 2.7)—they have positive oxidation numbers.
6. In a neutral molecule, the sum of the oxidation numbers of all the atoms must be zero. In a polyatomic ion, the sum of oxidation numbers of all the elements in the ion must be equal to the net charge of the ion. For example, in the ammonium ion, NH₄⁺, the oxidation number of N is −3 and that of H is +1. Thus,

the sum of the oxidation numbers is $-3 + 4(+1) = +1$, which is equal to the net charge of the ion.

7. Oxidation numbers do not have to be integers. For example, the oxidation number of O in the superoxide ion, O_2^- , is $-\frac{1}{2}$.

Example 4.5

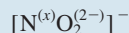
Assign oxidation numbers to all the elements in the following compounds and ion:

- (a) Na_2O , (b) HNO_2 , (c) $\text{Cr}_2\text{O}_7^{2-}$.

Strategy In general, we follow the rules just listed for assigning oxidation numbers. Remember that all alkali metals have an oxidation number of +1, and in most cases, hydrogen has an oxidation number of +1 and oxygen has an oxidation number of -2 in their compounds.

Solution

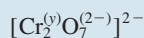
- (a) By rule 2, we see that sodium has an oxidation number of +1 (Na^+) and oxygen's oxidation number is -2 (O^{2-}).
- (b) This is the formula for nitrous acid, which yields a H^+ ion and a NO_2^- ion in solution. From rule 4, we see that H has an oxidation number of +1. Thus, the other group (the nitrite ion) must have a net oxidation number of -1 . Oxygen has an oxidation number of -2 , and if we use x to represent the oxidation number of nitrogen, then the nitrite ion can be written as



so that $x + 2(-2) = -1$

or $x = +3$

- (c) From rule 6, we see that the sum of the oxidation numbers in the dichromate ion $\text{Cr}_2\text{O}_7^{2-}$ must be -2 . We know that the oxidation number of O is -2 , so all that remains is to determine the oxidation number of Cr, which we call y . The dichromate ion can be written as



so that $2(y) + 7(-2) = -2$

or $y = +6$

Check In each case, does the sum of the oxidation numbers of all the atoms equal the net charge on the species?

Practice Exercise Assign oxidation numbers to all the elements in the following compound and ion: (a) PF_3 , (b) MnO_4^- .

Similar problems: 4.43, 4.45.

Figure 4.10 shows the known oxidation numbers of the familiar elements, arranged according to their positions in the periodic table. We can summarize the content of this figure as follows:

- Metallic elements have only positive oxidation numbers, whereas nonmetallic elements may have either positive or negative oxidation numbers.
- The highest oxidation number an element in Groups 1A–7A can have is its group number. For example, the halogens are in Group 7A, so their highest possible oxidation number is +7.
- The transition metals (Groups 1B, 3B–8B) usually have several possible oxidation numbers.

1 1A H +1 -1																	18 8A He				
2 2A												13 3A	14 4A	15 5A	16 6A	17 7A	18 8A				
3 Li +1	4 Be +2											5 B +3	6 C +4 -4	7 N +5 +4 +3 +2 +1 -3	8 O +2 -1 -2	9 F -1	10 Ne				
11 Na +1	12 Mg +2											13 Al +3	14 Si +4 -4	15 P +5 +3 -3	16 S +6 +4 +2 -2	17 Cl +7 +6 +5 +4 +3 +1 -1	18 Ar				
		3 3B	4 4B	5 5B	6 6B	7 7B	8	9	10	11 1B	12 2B					13 3A	14 4A	15 5A	16 6A	17 7A	18 8A
19 K +1	20 Ca +2	21 Sc +3	22 Ti +4 +3 +2	23 V +5 +4 +3 +2	24 Cr +6 +5 +4 +3 +2	25 Mn +7 +6 +4 +3 +2	26 Fe +3 +2	27 Co +3 +2	28 Ni +2	29 Cu +2 +1	30 Zn +2	31 Ga +3	32 Ge +4 -4	33 As +5 +3 -3	34 Se +6 +4 -2	35 Br +5 +3 +1 -1	36 Kr +4 +2				
37 Rb +1	38 Sr +2	39 Y +3	40 Zr +4	41 Nb +5 +4	42 Mo +6 +4 +3	43 Tc +7 +6 +4	44 Ru +8 +6 +4 +3	45 Rh +4 +3 +2	46 Pd +4 +2	47 Ag +1	48 Cd +2	49 In +3	50 Sn +4 +2	51 Sb +5 +3 -3	52 Te +6 +4 -2	53 I +7 +5 +1 -1	54 Xe +6 +4 +2				
55 Cs +1	56 Ba +2	57 La +3	72 Hf +4	73 Ta +5	74 W +6 +4	75 Re +7 +6 +4	76 Os +8 +4	77 Ir +4 +3	78 Pt +4 +2	79 Au +3 +1	80 Hg +2 +1	81 Tl +3 +1	82 Pb +4 +2	83 Bi +5 +3	84 Po +2	85 At -1	86 Rn				

Figure 4.10 The oxidation numbers of elements in their compounds. The more common oxidation numbers are in color.



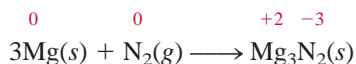
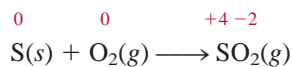
Sulfur burning in air to form sulfur dioxide.

Some Common Oxidation-Reduction Reactions

Among the most common oxidation-reduction reactions are combination, decomposition, combustion, and displacement reactions.

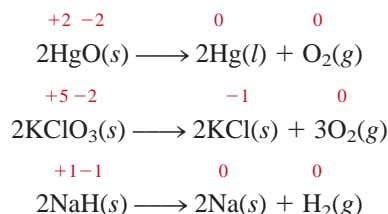
Combination Reactions

A *combination reaction* is a reaction in which two or more substances combine to form a single product. For example,



Decomposition Reactions

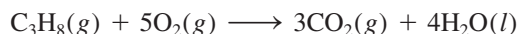
Decomposition reactions are the opposite of combination reactions. Specifically, a **decomposition reaction** is the breakdown of a compound into two or more components. For example,



Note that we show oxidation numbers only for elements that are oxidized or reduced.

Combustion Reactions

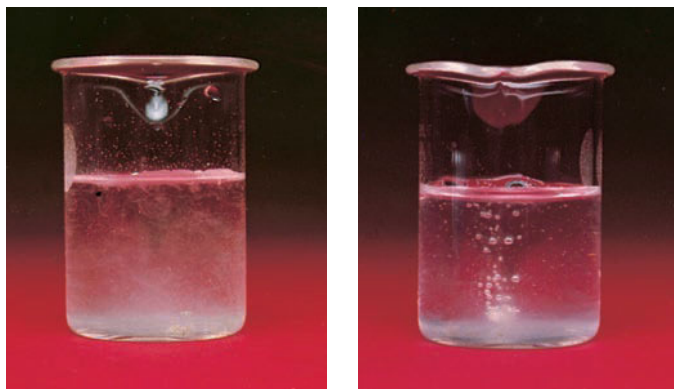
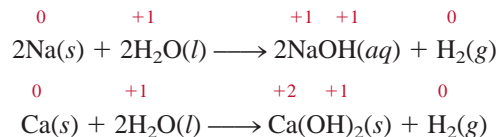
A **combustion reaction** is a reaction in which a substance reacts with oxygen, usually with the release of heat and light to produce a flame. The reactions between magnesium and sulfur with oxygen described earlier are combustion reactions. Another example is the burning of propane (C_3H_8), a component of natural gas that is used for domestic heating and cooking:



Displacement Reactions

In a **displacement reaction**, an ion (or atom) in a compound is replaced by an ion (or atom) of another element. Most displacement reactions fit into one of three subcategories: hydrogen displacement, metal displacement, or halogen displacement.

1. Hydrogen Displacement. All alkali metals and some alkaline earth metals (Ca, Sr, and Ba), which are the most reactive of the metallic elements, will displace hydrogen from cold water (Figure 4.11):



(a)

(b)



On heating, HgO decomposes to give Hg and O_2 .

All combustion reactions are redox processes.

Figure 4.11 Reactions of (a) sodium (Na) and (b) calcium (Ca) with cold water. Note that the reaction is more vigorous with Na than with Ca.

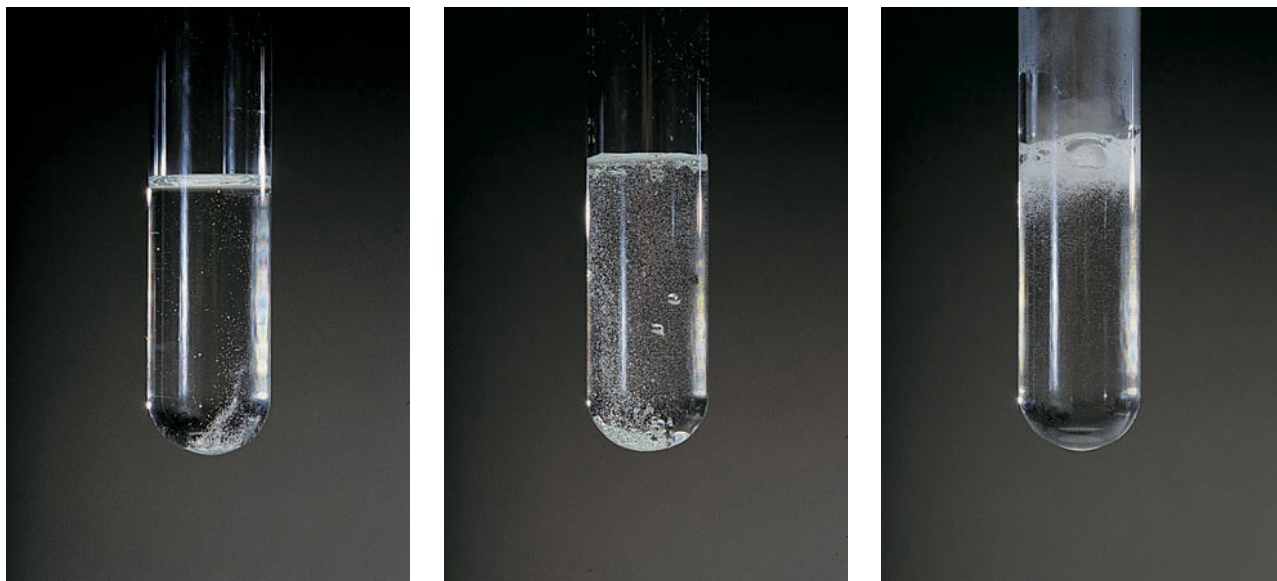


Figure 4.12 Left to right: Reactions of iron (Fe), zinc (Zn), and magnesium (Mg) with hydrochloric acid to form hydrogen gas and the metal chlorides (FeCl_2 , ZnCl_2 , MgCl_2). The reactivity of these metals is reflected in the rate of hydrogen gas evolution, which is slowest for the least reactive metal, Fe, and the fastest for the most reactive metal, Mg.

Many metals, including those that do not react with water, are capable of displacing hydrogen from acids. For example, zinc (Zn) and magnesium (Mg) do not react with cold water but do react with hydrochloric acid, as follows:

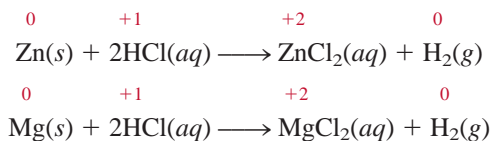
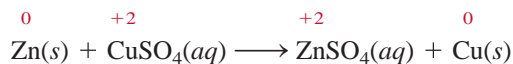
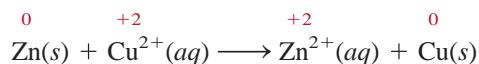


Figure 4.12 shows the reactions between hydrochloric acid (HCl) and iron (Fe), zinc (Zn), and magnesium (Mg). These reactions are used to prepare hydrogen gas in the laboratory.

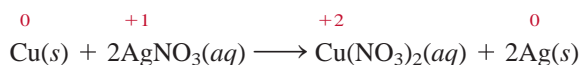
2. Metal Displacement. A metal in a compound can be displaced by another metal in the uncombined state. For example, when metallic zinc is added to a solution containing copper sulfate (CuSO_4), it displaces Cu^{2+} ions from the solution (Figure 4.13):



The net ionic equation is



Similarly, metallic copper displaces silver ions from a solution containing silver nitrate (AgNO_3) (also shown in Figure 4.13):



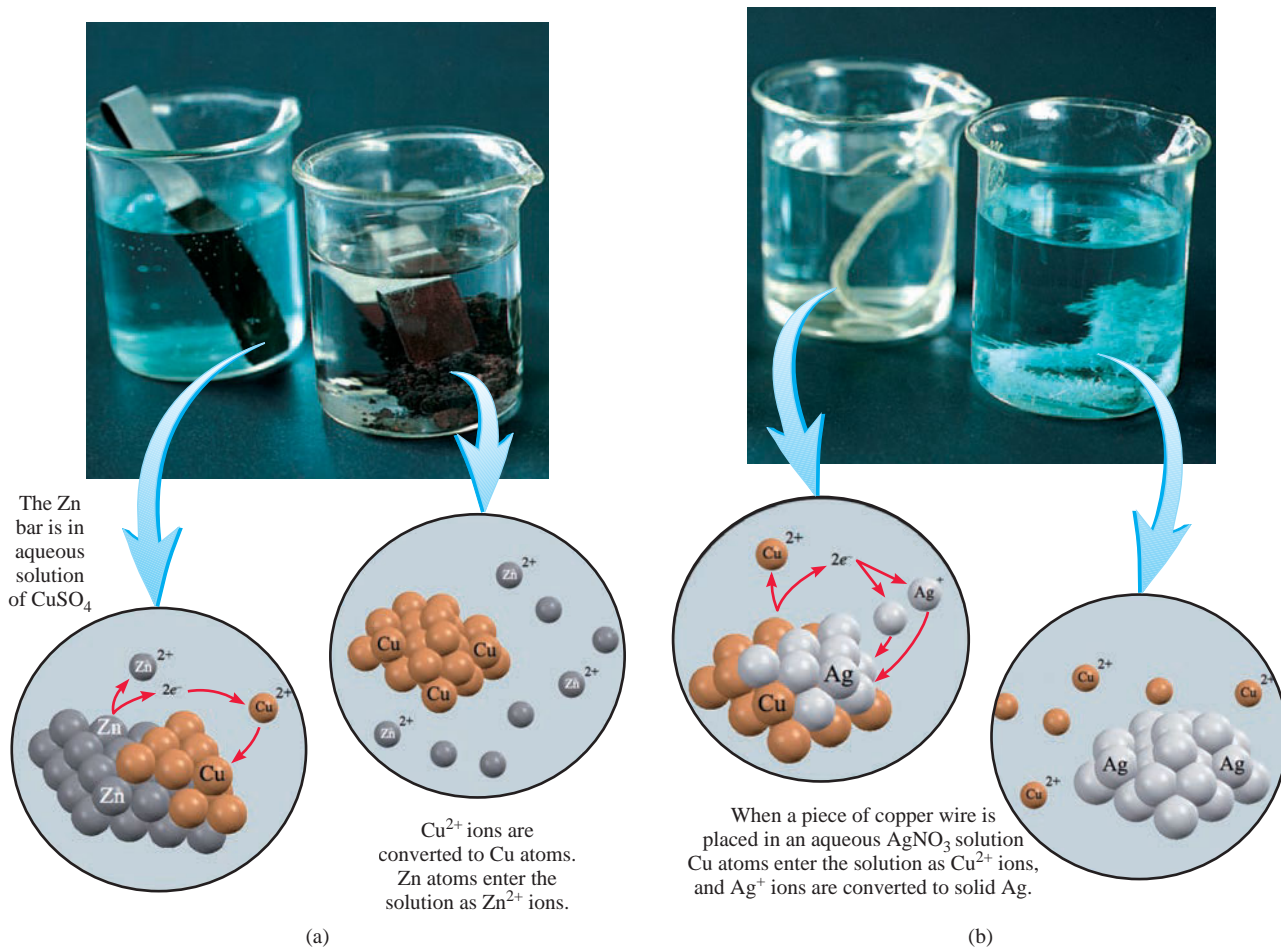
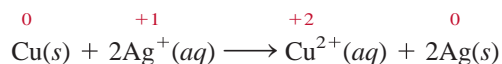


Figure 4.13 Metal displacement reactions in solution.

The net ionic equation is



Reversing the roles of the metals would result in no reaction. In other words, copper metal will not displace zinc ions from zinc sulfate, and silver metal will not displace copper ions from copper nitrate.

An easy way to predict whether a metal or hydrogen displacement reaction will actually occur is to refer to an **activity series** (sometimes called the *electrochemical series*), shown in Figure 4.14. Basically, an activity series is a *convenient summary of the results of many possible displacement reactions* similar to the ones already discussed. According to this series, any metal above hydrogen will displace it from water or from an acid, but metals below hydrogen will not react with either water or an acid. In fact, any metal listed in the series will react with any metal (in a compound) below it. For example, Zn is above Cu, so zinc metal will displace copper ions from copper sulfate.

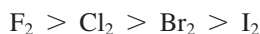
Figure 4.14 The activity series for metals. The metals are arranged according to their ability to displace hydrogen from an acid or water. Li (lithium) is the most reactive metal, and Au (gold) is the least reactive.

Reducing strength increases	$\text{Li} \rightarrow \text{Li}^+ + e^-$	
	$\text{K} \rightarrow \text{K}^+ + e^-$	
	$\text{Ba} \rightarrow \text{Ba}^{2+} + 2e^-$	React with cold water to produce H_2
	$\text{Ca} \rightarrow \text{Ca}^{2+} + 2e^-$	
	$\text{Na} \rightarrow \text{Na}^+ + e^-$	
	$\text{Mg} \rightarrow \text{Mg}^{2+} + 2e^-$	
	$\text{Al} \rightarrow \text{Al}^{3+} + 3e^-$	
	$\text{Zn} \rightarrow \text{Zn}^{2+} + 2e^-$	React with steam to produce H_2
	$\text{Cr} \rightarrow \text{Cr}^{3+} + 3e^-$	
	$\text{Fe} \rightarrow \text{Fe}^{2+} + 2e^-$	
	$\text{Cd} \rightarrow \text{Cd}^{2+} + 2e^-$	
	$\text{Co} \rightarrow \text{Co}^{2+} + 2e^-$	
	$\text{Ni} \rightarrow \text{Ni}^{2+} + 2e^-$	React with acids to produce H_2
	$\text{Sn} \rightarrow \text{Sn}^{2+} + 2e^-$	
$\text{Pb} \rightarrow \text{Pb}^{2+} + 2e^-$		
$\text{H}_2 \rightarrow 2\text{H}^+ + 2e^-$		
$\text{Cu} \rightarrow \text{Cu}^{2+} + 2e^-$		
$\text{Ag} \rightarrow \text{Ag}^+ + e^-$		
$\text{Hg} \rightarrow \text{Hg}^{2+} + 2e^-$	Do not react with water or acids to produce H_2	
$\text{Pt} \rightarrow \text{Pt}^{2+} + 2e^-$		
$\text{Au} \rightarrow \text{Au}^{3+} + 3e^-$		

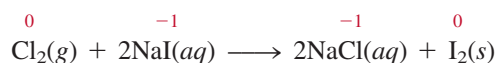
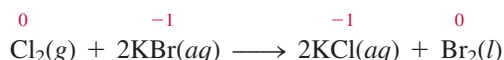
1A												8A
2A					3A	4A	5A	6A	7A			
									F			
									Cl			
									Br			
									I			

The halogens.

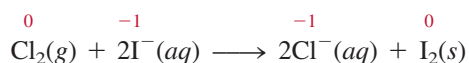
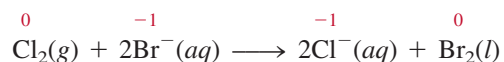
3. Halogen Displacement. Another activity series summarizes the halogens' behavior in halogen displacement reactions:



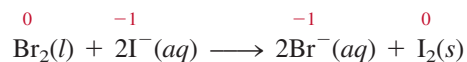
The power of these elements as oxidizing agents decreases as we move down Group 7A from fluorine to iodine, so molecular fluorine can replace chloride, bromide, and iodide ions in solution. In fact, molecular fluorine is so reactive that it also attacks water; thus, these reactions cannot be carried out in aqueous solutions. On the other hand, molecular chlorine can displace bromide and iodide ions in aqueous solution. The displacement equations are



The ionic equations are



Molecular bromine, in turn, can displace iodide ion in solution:



Reversing the roles of the halogens produces no reaction. Thus, bromine cannot displace chloride ions, and iodine cannot displace bromide and chloride ions.



Industrially, bromine (a fuming red liquid) is prepared by the action of chlorine on seawater, which is a rich source of Br^- ions.

Example 4.6

Classify the following redox reactions and indicate changes in the oxidation numbers of the elements:

- (a) $2\text{N}_2\text{O}(g) \longrightarrow 2\text{N}_2(g) + \text{O}_2(g)$
 (b) $6\text{Li}(s) + \text{N}_2(g) \longrightarrow 2\text{Li}_3\text{N}(s)$
 (c) $\text{Ni}(s) + \text{Pb}(\text{NO}_3)_2(aq) \longrightarrow \text{Pb}(s) + \text{Ni}(\text{NO}_3)_2(aq)$

Strategy Review the definitions of combination reactions, decomposition reactions, and displacement reactions.

Solution

- (a) This is a decomposition reaction because one reactant is converted to two different products. The oxidation number of N changes from +1 to 0, while that of O changes from -2 to 0.
 (b) This is a combination reaction (two reactants form a single product). The oxidation number of Li changes from 0 to +1 while that of N changes from 0 to -3 .
 (c) This is a metal displacement reaction. The Ni metal replaces (reduces) the Pb^{2+} ion. The oxidation number of Ni increases from 0 to +2 while that of Pb decreases from +2 to 0.

Similar problems: 4.81 (e), (g), (i).

Practice Exercise Identify the following redox reactions by type:

- (a) $\text{Fe} + \text{H}_2\text{SO}_4 \longrightarrow \text{FeSO}_4 + \text{H}_2$
 (b) $\text{S} + 3\text{F}_2 \longrightarrow \text{SF}_6$
 (c) $2\text{Ag} + \text{PtCl}_2 \longrightarrow 2\text{AgCl} + \text{Pt}$

Review of Concepts

Which of the following combination reactions is not a redox reaction?

- (a) $2\text{Mg}(s) + \text{O}_2(g) \longrightarrow 2\text{MgO}(s)$
 (b) $\text{H}_2(g) + \text{Cl}_2(g) \longrightarrow 2\text{HCl}(g)$
 (c) $\text{NH}_3(g) + \text{HCl}(g) \longrightarrow \text{NH}_4\text{Cl}(s)$
 (d) $2\text{Na}(s) + \text{S}(s) \longrightarrow \text{Na}_2\text{S}(s)$

4.5 Concentration of Solutions

To study solution stoichiometry, we must know how much of the reactants are present in a solution and also how to control the amounts of reactants used to bring about a reaction in aqueous solution.

The **concentration of a solution** is the amount of solute present in a given amount of solvent, or a given amount of solution. (For this discussion, we will assume the solute is a liquid or a solid and the solvent is a liquid.) The concentration of a solution can be expressed in many different ways, as we will see in Chapter 13. Here we will consider one of the most commonly used units in chemistry, **molarity** (M), or **molar concentration**, which is the number of moles of solute per liter of solution. Molarity is defined as

$$\text{molarity} = \frac{\text{moles of solute}}{\text{liters of soln}} \quad (4.1)$$

where “soln” denotes “solution.” Equation (4.1) can also be expressed algebraically as

$$M = \frac{n}{V} \quad (4.2)$$

Keep in mind that volume (V) is liters of solution, not liters of solvent. Also, the molarity of a solution depends on temperature.

where n denotes the number of moles of solute and V is the volume of the solution in liters. Thus, a 1.46 molar glucose ($\text{C}_6\text{H}_{12}\text{O}_6$) solution, written $1.46 \text{ M } \text{C}_6\text{H}_{12}\text{O}_6$, contains 1.46 moles of the solute ($\text{C}_6\text{H}_{12}\text{O}_6$) in 1 L of the solution; a 0.52 molar urea [$(\text{NH}_2)_2\text{CO}$] solution, written $0.52 \text{ M } (\text{NH}_2)_2\text{CO}$, contains 0.52 mole of $(\text{NH}_2)_2\text{CO}$ (the solute) in 1 L of solution; and so on.

Of course, we do not always work with solution volumes of exactly 1 L. This is not a problem as long as we remember to convert the volume of the solution to liters. Thus, a 500-mL solution containing 0.730 mole of $\text{C}_6\text{H}_{12}\text{O}_6$ also has a concentration of 1.46 M :

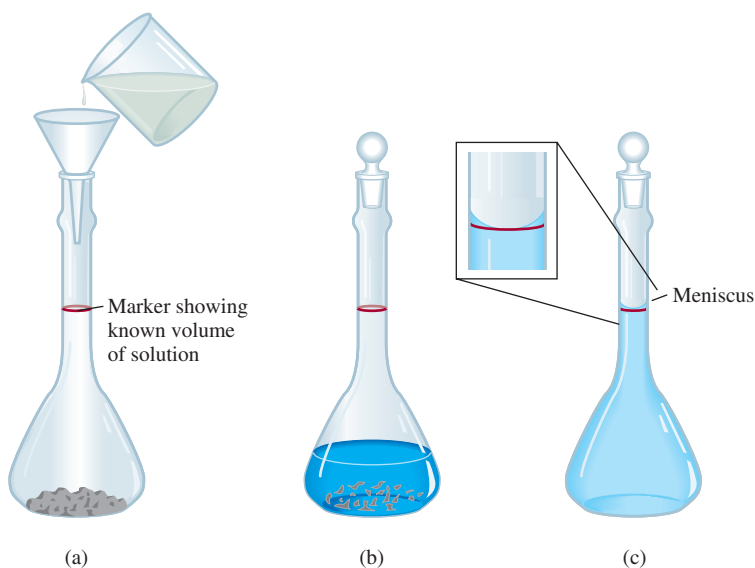
$$\begin{aligned} M = \text{molarity} &= \frac{0.730 \text{ mol}}{0.500 \text{ L}} \\ &= 1.46 \text{ mol/L} = 1.46 \text{ M} \end{aligned}$$

As you can see, the unit of molarity is moles per liter, so a 500-mL solution containing 0.730 mole of $\text{C}_6\text{H}_{12}\text{O}_6$ is equivalent to 1.46 mol/L or 1.46 M . Note that concentration, like density, is an intensive property, so its value does not depend on how much of the solution is present.

The procedure for preparing a solution of known molarity is as follows. First, the solute is accurately weighed and transferred to a volumetric flask through a funnel (Figure 4.15). Next, water is added to the flask, which is carefully swirled to dissolve the solid. After *all* the solid has dissolved, more water is added slowly to bring the level of solution exactly to the volume mark. Knowing the volume of the solution in the flask and the quantity of compound (the number of moles) dissolved, we can calculate the molarity of the solution using Equation (4.1). Note that this procedure does not require knowing the amount of water added, as long as the volume of the final solution is known.

Animation
Making a Solution

Figure 4.15 Preparing a solution of known molarity. (a) A known amount of a solid solute is transferred into the volumetric flask; then water is added through a funnel. (b) The solid is slowly dissolved by gently swirling the flask. (c) After the solid has completely dissolved, more water is added to bring the level of solution to the mark. Knowing the volume of solution and the amount of solute dissolved in it, we can calculate the molarity of the prepared solution.



Example 4.7

How many grams of potassium dichromate ($\text{K}_2\text{Cr}_2\text{O}_7$) are required to prepare a 125-mL solution whose concentration is 1.83 M ?

Strategy How many moles of $\text{K}_2\text{Cr}_2\text{O}_7$ does a 1-L (or 1000-mL) 1.83 M $\text{K}_2\text{Cr}_2\text{O}_7$ solution contain? A 125-mL solution? How would you convert moles to grams?

Solution The first step is to determine the number of moles of $\text{K}_2\text{Cr}_2\text{O}_7$ in 125 mL or 0.125 L of a 1.83 M solution:

$$\begin{aligned}\text{moles of } \text{K}_2\text{Cr}_2\text{O}_7 &= 0.125 \text{ L soln} \times \frac{1.83 \text{ mol } \text{K}_2\text{Cr}_2\text{O}_7}{1 \text{ L soln}} \\ &= 0.229 \text{ mol } \text{K}_2\text{Cr}_2\text{O}_7\end{aligned}$$

The molar mass of $\text{K}_2\text{Cr}_2\text{O}_7$ is 294.2 g, so we write

$$\begin{aligned}\text{grams of } \text{K}_2\text{Cr}_2\text{O}_7 \text{ needed} &= 0.229 \text{ mol } \text{K}_2\text{Cr}_2\text{O}_7 \times \frac{294.2 \text{ g } \text{K}_2\text{Cr}_2\text{O}_7}{1 \text{ mol } \text{K}_2\text{Cr}_2\text{O}_7} \\ &= 67.4 \text{ g } \text{K}_2\text{Cr}_2\text{O}_7\end{aligned}$$

Check As a ballpark estimate, the mass should be given by [molarity (mol/L) \times volume (L) \times molar mass (g/mol)] or [2 mol/L \times 0.125 L \times 300 g/mol] = 75 g. So the answer is reasonable.

Practice Exercise What is the molarity of a 85.0-mL ethanol ($\text{C}_2\text{H}_5\text{OH}$) solution containing 1.77 g of ethanol?



A $\text{K}_2\text{Cr}_2\text{O}_7$ solution.

Similar problems: 4.56, 4.57.

Example 4.8

In a biochemical assay, a chemist needs to add 4.07 g of glucose to a reaction mixture. Calculate the volume in milliliters of a 3.16 M glucose solution she should use for the addition.

Strategy We must first determine the number of moles contained in 4.07 g of glucose and then use Equation (4.2) to calculate the volume.

Solution From the molar mass of glucose, we write

$$4.07 \text{ g } \text{C}_6\text{H}_{12}\text{O}_6 \times \frac{1 \text{ mol } \text{C}_6\text{H}_{12}\text{O}_6}{180.2 \text{ g } \text{C}_6\text{H}_{12}\text{O}_6} = 2.259 \times 10^{-2} \text{ mol } \text{C}_6\text{H}_{12}\text{O}_6$$

Next, we calculate the volume of the solution that contains 2.259×10^{-2} mol of the solute. Rearranging Equation (4.2) gives

$$\begin{aligned}V &= \frac{n}{M} \\ &= \frac{2.259 \times 10^{-2} \text{ mol } \text{C}_6\text{H}_{12}\text{O}_6}{3.16 \text{ mol } \text{C}_6\text{H}_{12}\text{O}_6 / \text{L soln}} \times \frac{1000 \text{ mL soln}}{1 \text{ L soln}} \\ &= 7.15 \text{ mL soln}\end{aligned}$$

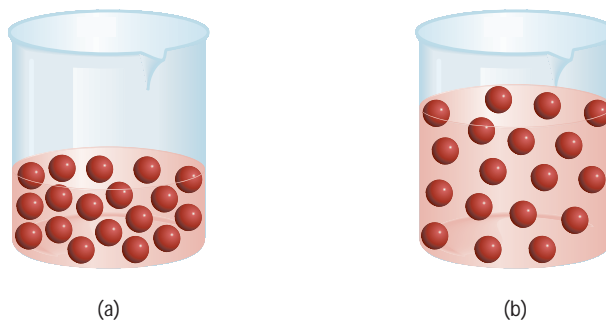
Check One liter of the solution contains 3.16 moles of $\text{C}_6\text{H}_{12}\text{O}_6$. Therefore, the number of moles in 7.15 mL or 7.15×10^{-3} L is $(3.16 \text{ mol} \times 7.15 \times 10^{-3})$ or 2.26×10^{-2} mol. The small difference is due to the different ways of rounding off.

Practice Exercise What volume (in milliliters) of a 0.315 M NaOH solution contains 6.22 g of NaOH?

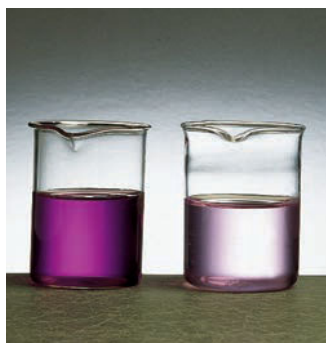
Note that we have carried an additional digit past the number of significant figures for the intermediate step.

Similar problem: 4.59.

Figure 4.16 The dilution of a more concentrated solution (a) to a less concentrated one (b) does not change the total number of solute particles (18).



Animation
Preparing a Solution by Dilution



Two KMnO_4 solutions of different concentrations.

Dilution of Solutions

Concentrated solutions are often stored in the laboratory stockroom for use as needed. Frequently we dilute these “stock” solutions before working with them. **Dilution** is the procedure for preparing a less concentrated solution from a more concentrated one.

Suppose that we want to prepare 1 L of a 0.400 M KMnO_4 solution from a solution of 1.00 M KMnO_4 . For this purpose, we need 0.400 mole of KMnO_4 . Because there is 1.00 mole of KMnO_4 in 1 L of a 1.00 M KMnO_4 solution, there is 0.400 mole of KMnO_4 in 0.400 L of the same solution:

$$\frac{1.00 \text{ mol}}{1 \text{ L soln}} = \frac{0.400 \text{ mol}}{0.400 \text{ L soln}}$$

Therefore, we must withdraw 400 mL from the 1.00 M KMnO_4 solution and dilute it to 1000 mL by adding water (in a 1-L volumetric flask). This method gives us 1 L of the desired solution of 0.400 M KMnO_4 .

In carrying out a dilution process, it is useful to remember that adding more solvent to a given amount of the stock solution changes (decreases) the concentration of the solution without changing the number of moles of solute present in the solution (Figure 4.16). In other words,

$$\text{moles of solute before dilution} = \text{moles of solute after dilution}$$

Because molarity is defined as moles of solute in one liter of solution, we see that the number of moles of solute is given by

$$\underbrace{\frac{\text{moles of solute}}{\text{liters of soln}}}_M \times \underbrace{\text{volume of soln (in liters)}}_V = \text{moles of solute}$$

or

$$MV = \text{moles of solute}$$

Because all the solute comes from the original stock solution, we can conclude that

$$\begin{array}{ccc} M_i V_i & = & M_f V_f \\ \text{moles of solute} & & \text{moles of solute} \\ \text{before dilution} & & \text{after dilution} \end{array} \quad (4.3)$$

where M_i and M_f are the initial and final concentrations of the solution in molarity and V_i and V_f are the initial and final volumes of the solution, respectively.

Of course, the units of V_i and V_f must be the same (mL or L) for the calculation to work. To check the reasonableness of your results, be sure that $M_i > M_f$ and $V_f > V_i$.

Example 4.9

Describe how you would prepare 2.50×10^2 mL of a $2.25 M$ H_2SO_4 solution, starting with a $7.41 M$ stock solution of H_2SO_4 .

Strategy Because the concentration of the final solution is less than that of the original one, this is a dilution process. Keep in mind that in dilution, the concentration of the solution decreases but the number of moles of the solute remains the same.

Solution We prepare for the calculation by tabulating our data:

$$\begin{array}{ll} M_i = 7.41 M & M_f = 2.25 M \\ V_i = ? & V_f = 2.50 \times 10^2 \text{ mL} \end{array}$$

Substituting in Equation (4.3),

$$\begin{aligned} (7.41 M)(V_i) &= (2.25 M)(2.50 \times 10^2 \text{ mL}) \\ V_i &= \frac{(2.25 M)(2.50 \times 10^2 \text{ mL})}{7.41 M} \\ V_i &= 75.9 \text{ mL} \end{aligned}$$

Thus, we must dilute 75.9 mL of the $7.41 M$ H_2SO_4 solution with sufficient water to give a final volume of 2.50×10^2 mL in a 250-mL volumetric flask to obtain the desired concentration.

Check The initial volume is less than the final volume, so the answer is reasonable.

Practice Exercise How would you prepare 2.00×10^2 mL of a $0.866 M$ KOH solution, starting with a $5.07 M$ stock solution?

Similar problems: 4.65, 4.66.

Review of Concepts

What is the final concentration of a $0.6 M$ NaCl solution if its volume is doubled and the number of moles of solute is tripled?

4.6 Solution Stoichiometry

In Chapter 3 we studied stoichiometric calculations in terms of the mole method, which treats the coefficients in a balanced equation as the number of moles of reactants and products. In working with solutions of known molarity, we have to use the relationship $MV = \text{moles of solute}$. We will examine two types of common solution stoichiometry here: gravimetric analysis and acid-base titration.

Gravimetric Analysis

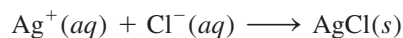
Gravimetric analysis is an analytical technique based on the measurement of mass. One type of gravimetric analysis experiment involves the formation, isolation, and mass determination of a precipitate. Generally, this procedure is applied to ionic compounds. A sample substance of unknown composition is dissolved in water and allowed to react with another substance to form a precipitate. The precipitate is filtered off, dried, and weighed. Knowing the mass and chemical formula of the precipitate formed, we can calculate the mass of a particular chemical component (that is, the

anion or cation) of the original sample. From the mass of the component and the mass of the original sample, we can determine the percent composition by mass of the component in the original compound.

A reaction that is often studied in gravimetric analysis, because the reactants can be obtained in pure form, is



The net ionic equation is



The precipitate is AgCl (see Table 4.2). As an example, let's say that we are interested in knowing the purity of a sample of NaCl obtained from seawater. To do so we need to determine *experimentally* the percent by mass of Cl in NaCl. First, we would accurately weigh out a sample of the NaCl and dissolve it in water. Next, we would add enough AgNO₃ solution to the NaCl solution to cause the precipitation of all the Cl⁻ ions present in solution as AgCl. In this procedure, NaCl is the limiting reagent and AgNO₃ the excess reagent. The AgCl precipitate is separated from the solution by filtration, dried, and weighed. From the measured mass of AgCl, we can calculate the mass of Cl using the percent by mass of Cl in AgCl. Because this same amount of Cl was present in the original NaCl sample, we can calculate the percent by mass of Cl in NaCl and hence deduce its purity. Figure 4.17 shows how this procedure is performed.

Gravimetric analysis is a highly accurate technique, because the mass of a sample can be measured accurately. However, this procedure is applicable only to reactions that go to completion, or have nearly 100 percent yield. Thus, if AgCl were slightly soluble instead of being insoluble, it would not be possible to remove all the Cl⁻ ions from the NaCl solution and the subsequent calculation would be in error.

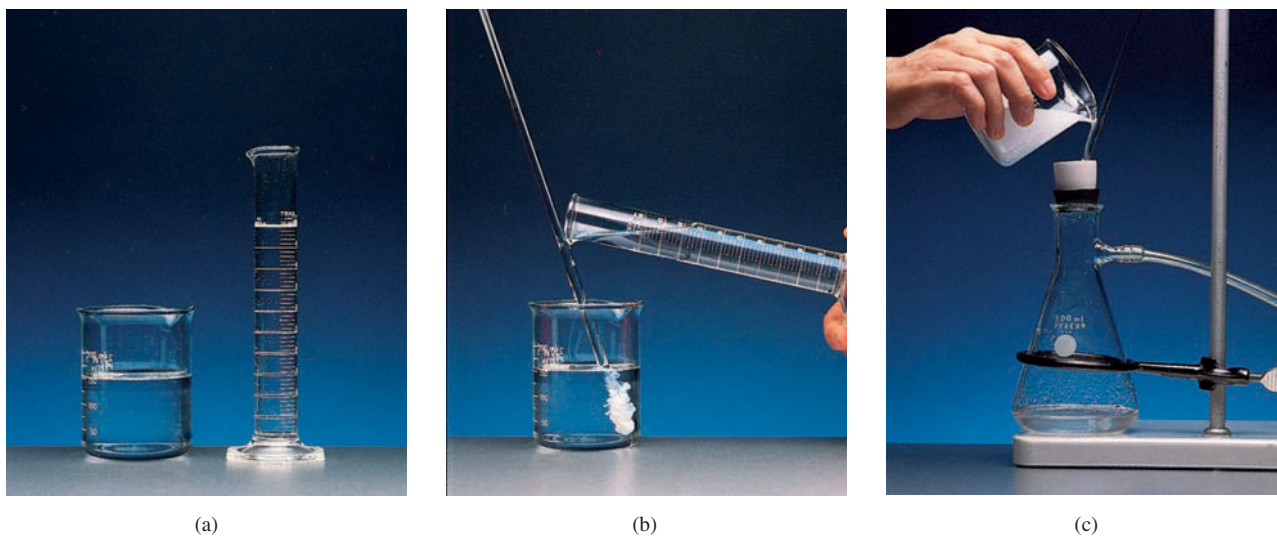


Figure 4.17 Basic steps for gravimetric analysis. (a) A solution containing a known amount of NaCl in a beaker. (b) The precipitation of AgCl upon the addition of AgNO₃ solution from a measuring cylinder. In this reaction, AgNO₃ is the excess reagent and NaCl is the limiting reagent. (c) The solution containing the AgCl precipitate is filtered through a preweighed sintered-disk crucible, which allows the liquid (but not the precipitate) to pass through. The crucible is then removed from the apparatus, dried in an oven, and weighed again. The difference between this mass and that of the empty crucible gives the mass of the AgCl precipitate.

Example 4.10

A 0.7077-g sample of an ionic compound containing chloride ions and an unknown metal is dissolved in water and treated with an excess of AgNO_3 . If 1.3602 g of AgCl precipitate forms, what is the percent by mass of Cl in the original compound?

Strategy We are asked to calculate the percent by mass of Cl in the unknown sample, which is

$$\% \text{Cl} = \frac{\text{mass of Cl}}{0.7077 \text{ g sample}} \times 100\%$$

The only source of Cl^- ions is the original compound. These chloride ions eventually end up in the AgCl precipitate. Can we calculate the mass of the Cl^- ions if we know the percent by mass of Cl in AgCl ?

Solution The molar masses of Cl and AgCl are 35.45 g and 143.4 g, respectively. Therefore, the percent by mass of Cl in AgCl is given by

$$\begin{aligned} \% \text{Cl} &= \frac{35.45 \text{ g Cl}}{143.4 \text{ g AgCl}} \times 100\% \\ &= 24.72\% \end{aligned}$$

Next, we calculate the mass of Cl in 1.3602 g of AgCl . To do so we convert 24.72 percent to 0.2472 and write

$$\begin{aligned} \text{mass of Cl} &= 0.2472 \times 1.3602 \text{ g} \\ &= 0.3362 \text{ g} \end{aligned}$$

Because the original compound also contained this amount of Cl^- ions, the percent by mass of Cl in the compound is

$$\begin{aligned} \% \text{Cl} &= \frac{0.3362 \text{ g}}{0.7077 \text{ g}} \times 100\% \\ &= 47.51\% \end{aligned}$$

Check AgCl is about 25 percent chloride by mass, so the roughly 1 g of AgCl precipitate that formed corresponds to about 0.25 g of chloride, which is a little less than half of the mass of the original sample. Therefore, the calculated percent chloride of 47.51 percent is reasonable.

Practice Exercise A sample of 0.3220 g of an ionic compound containing the bromide ion (Br^-) is dissolved in water and treated with an excess of AgNO_3 . If the mass of the AgBr precipitate that forms is 0.6964 g, what is the percent by mass of Br in the original compound?

In general, gravimetric analysis does not establish the identity of the unknown, but it does narrow the possibilities.

Similar problem: 4.72.

Review of Concepts

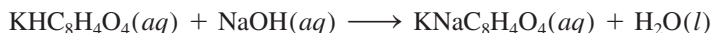
Calculate the mass of AgBr formed if a solution containing 6.00 g of KBr is treated with an excess of AgNO_3 .

Acid-Base Titrations

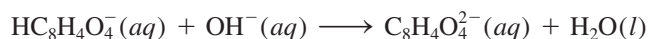
Quantitative studies of acid-base neutralization reactions are most conveniently carried out using a procedure known as **titration**. In a titration experiment, a solution of accurately known concentration, called a **standard solution**, is added gradually to another solution of unknown concentration, until the chemical reaction between the two solutions is complete. If we know the volumes of the standard and unknown

solutions used in the titration, along with the concentration of the standard solution, we can calculate the concentration of the unknown solution.

Sodium hydroxide is one of the bases commonly used in the laboratory. However, because it is difficult to obtain solid sodium hydroxide in a pure form, a solution of sodium hydroxide must be *standardized* before it can be used in accurate analytical work. We can standardize the sodium hydroxide solution by titrating it against an acid solution of accurately known concentration. The acid often chosen for this task is a monoprotic acid called potassium hydrogen phthalate (KHP), for which the molecular formula is $\text{KHC}_8\text{H}_4\text{O}_4$. KHP is a white, soluble solid that is commercially available in highly pure form. The reaction between KHP and sodium hydroxide is



The net ionic equation is



The procedure for the titration is shown in Figure 4.18. First, a known amount of KHP is transferred to an Erlenmeyer flask and some distilled water is added to make up a solution. Next, NaOH solution is carefully added to the KHP solution from a buret until we reach the **equivalence point**, that is, *the point at which the acid has completely reacted with or been neutralized by the base*. The equivalence point is usually signaled by a sharp change in the color of an indicator in the acid solution. In acid-base titrations, **indicators** are *substances that have distinctly different colors in acidic and basic media*. One commonly used indicator is phenolphthalein, which is colorless in acidic and neutral solutions but reddish pink in basic solutions. At the equivalence point, all the KHP present has been neutralized by the added NaOH and the solution is still colorless. However, if we add just one more drop of NaOH solution from the buret, the solution will immediately turn pink because the solution is now basic.

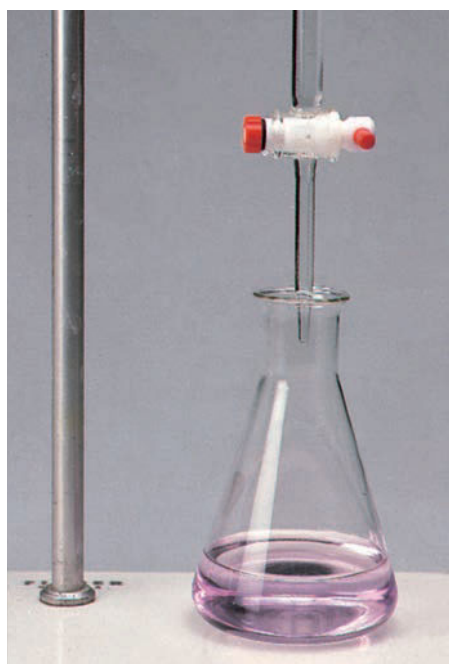


Potassium hydrogen phthalate is a weak acid.

Figure 4.18 (a) Apparatus for acid-base titration. A NaOH solution is added from the buret to a KHP solution in an Erlenmeyer flask. (b) A reddish-pink color appears when the equivalence point is reached. The color here has been intensified for visual display.



(a)



(b)

Example 4.11

In a titration experiment, a student finds that 25.46 mL of a NaOH solution are needed to neutralize 0.6092 g of KHP. What is the concentration (in molarity) of the NaOH solution?

Strategy We want to determine the molarity of the NaOH solution. What is the definition of molarity?

$$\text{molarity of NaOH} = \frac{\text{mol NaOH}}{\text{L soln}}$$

↑ want to calculate
↑ given
↑ need to find

The volume of NaOH is given in the problem. Therefore, we need to find the number of moles of NaOH to solve for molarity. From the preceding equation for the reaction between KHP and NaOH shown in the text, we see that 1 mole of KHP neutralizes 1 mole of NaOH. How many moles of KHP are contained in 0.6092 g of KHP?

Solution First, we calculate the number of moles of KHP consumed in the titration:

$$\begin{aligned} \text{moles of KHP} &= 0.6092 \text{ g KHP} \times \frac{1 \text{ mol KHP}}{204.2 \text{ g KHP}} \\ &= 2.983 \times 10^{-3} \text{ mol KHP} \end{aligned}$$

Recall that KHP is $\text{KHC}_8\text{H}_4\text{O}_4$.

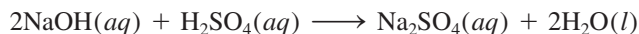
Because 1 mol KHP \approx 1 mol NaOH, there must be 2.983×10^{-3} mole of NaOH in 25.46 mL of NaOH solution. Finally, we calculate the number of moles of NaOH in 1 L of the solution or the molarity as follows:

$$\begin{aligned} \text{molarity of NaOH soln} &= \frac{2.983 \times 10^{-3} \text{ mol NaOH}}{25.46 \text{ mL soln}} \times \frac{1000 \text{ mL soln}}{\text{L soln}} \\ &= 0.1172 \text{ mol NaOH/L soln} = \mathbf{0.1172 \text{ M}} \end{aligned}$$

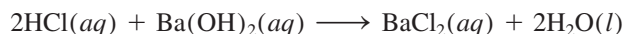
Similar problems: 4.77, 4.78.

Practice Exercise How many grams of KHP are needed to neutralize 18.64 mL of a 0.1004 M NaOH solution?

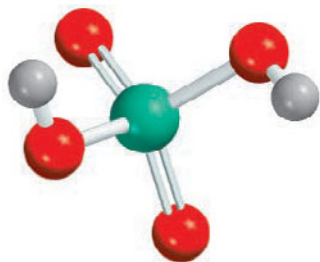
The neutralization reaction between NaOH and KHP is one of the simplest types of acid-base neutralization known. Suppose, though, that instead of KHP, we wanted to use a diprotic acid such as H_2SO_4 for the titration. The reaction is represented by



Because 2 mol NaOH \approx 1 mol H_2SO_4 , we need twice as much NaOH to react completely with a H_2SO_4 solution of the *same* molar concentration and volume as a monoprotic acid like HCl. On the other hand, we would need twice the amount of HCl to neutralize a $\text{Ba}(\text{OH})_2$ solution compared to a NaOH solution having the same concentration and volume because 1 mole of $\text{Ba}(\text{OH})_2$ yields 2 moles of OH^- ions:



In calculations involving acid-base titrations, regardless of the acid or base that takes place in the reaction, keep in mind that the total number of moles of H^+ ions that have reacted at the equivalence point must be equal to the total number of moles of OH^- ions that have reacted.



H_2SO_4 has two ionizable protons.

Example 4.12

The sodium hydroxide solution standardized in Example 4.11 is used to titrate 25.00 mL of a sulfuric acid solution. The titration requires 43.79 mL of the 0.1172 M NaOH solution to completely neutralize the acid. What is the concentration of the H_2SO_4 solution?

Strategy We want to calculate the concentration of the H_2SO_4 solution. Starting with the volume of NaOH solution required to neutralize the acid, we calculate the moles of NaOH.

$$\overset{\text{measured}}{\text{L soln}} \times \frac{\text{mol NaOH}}{\text{L soln}} = \overset{\text{want to find}}{\text{mol NaOH}}$$

(Note: 'measured' points to the first 'L soln', and 'want to find' points to 'mol NaOH'. 'given' points to the second 'L soln'.)

From the equation for the neutralization reaction just shown, we see that 2 moles of NaOH neutralize 1 mole of H_2SO_4 . How many moles of NaOH are contained in 43.79 mL of a 0.1172 M NaOH solution? How many moles of H_2SO_4 would this quantity of NaOH neutralize? What would be the concentration of the H_2SO_4 solution?

Solution First, we calculate the number of moles of NaOH contained in 43.79 mL of solution:

$$43.79 \text{ mL} \times \frac{1 \text{ L soln}}{1000 \text{ mL soln}} \times \frac{0.1172 \text{ mol NaOH}}{\text{L soln}} = 5.132 \times 10^{-3} \text{ mol NaOH}$$

From the stoichiometry we see that 1 mol $\text{H}_2\text{SO}_4 \approx 2 \text{ mol NaOH}$. Therefore, the number of moles of H_2SO_4 reacted must be

$$5.132 \times 10^{-3} \text{ mol NaOH} \times \frac{1 \text{ mol H}_2\text{SO}_4}{2 \text{ mol NaOH}} = 2.566 \times 10^{-3} \text{ mol H}_2\text{SO}_4$$

From the definition of molarity [see Equation (4.1)], we have

$$\text{molarity} = \frac{\text{moles of solute}}{\text{liters of soln}}$$

So the molarity of the H_2SO_4 solution is

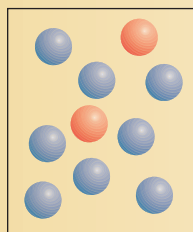
$$\frac{2.566 \times 10^{-3} \text{ mol H}_2\text{SO}_4}{25 \text{ mL} \times (1 \text{ L}/1000 \text{ mL})} = \mathbf{0.1026 \text{ M H}_2\text{SO}_4}$$

Similar problem: 4.79(b), (c).

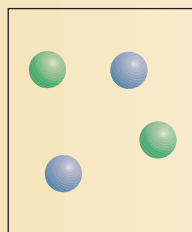
Practice Exercise If 60.2 mL of 0.427 M KOH solution are required to neutralize 10.1 mL of H_2SO_4 solution, what is the concentration of the H_2SO_4 solution in molarity?

Review of Concepts

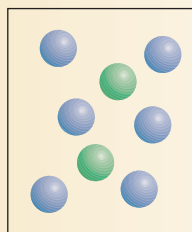
A NaOH solution is initially mixed with an acid solution shown in (a). Which of the diagrams shown in (b)–(d) corresponds to one of the following acids: HCl, H_2SO_4 , H_3PO_4 ? Color codes: Blue spheres (OH^- ions); red spheres (acid molecules); green spheres (anions of the acid). Assume all the acid-base neutralization reactions go to completion.



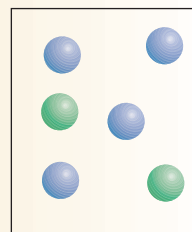
(a)



(b)



(c)



(d)

Key Equations

$$\text{molarity } (M) = \frac{\text{moles of solute}}{\text{liters of soln}} \quad (4.1)$$

$$M = \frac{n}{V} \quad (4.2)$$

$$M_i V_i = M_f V_f \quad (4.3)$$

Definition of molarity.

Definition of molarity.

Dilution of solution.

Summary of Facts and Concepts

1. Aqueous solutions are electrically conducting if the solutes are electrolytes. If the solutes are nonelectrolytes, the solutions do not conduct electricity.
2. Three major categories of chemical reactions that take place in aqueous solution are precipitation reactions, acid-base reactions, and oxidation-reduction reactions.
3. From general rules about solubilities of ionic compounds, we can predict whether a precipitate will form in a reaction.
4. Arrhenius acids ionize in water to give H^+ ions, and Arrhenius bases ionize in water to give OH^- ions. Brønsted acids donate protons, and Brønsted bases accept protons. The reaction of an acid and a base is called neutralization.
5. In redox reactions, oxidation and reduction always occur simultaneously. Oxidation is characterized by the loss of electrons, reduction by the gain of electrons. Oxidation numbers help us keep track of charge distribution and are assigned to all atoms in a compound or ion according to specific rules. Oxidation can be defined as an increase in oxidation number; reduction can be defined as a decrease in oxidation number.
6. The concentration of a solution is the amount of solute present in a given amount of solution. Molarity expresses concentration as the number of moles of solute in 1 L of solution. Adding a solvent to a solution, a process known as dilution, decreases the concentration (molarity) of the solution without changing the total number of moles of solute present in the solution.
7. Gravimetric analysis is a technique for determining the identity of a compound and/or the concentration of a solution by measuring mass. Gravimetric experiments often involve precipitation reactions.
8. In acid-base titration, a solution of known concentration (say, a base) is added gradually to a solution of unknown concentration (say, an acid) with the goal of determining the unknown concentration. The point at which the reaction in the titration is complete is called the equivalence point.

Key Words

- | | | | |
|-------------------------------------|-------------------------------|--------------------------------------|-----------------------------|
| Activity series, p. 117 | Displacement reaction, p. 115 | Monoprotic acid, p. 106 | Reducing agent, p. 111 |
| Aqueous solution, p. 98 | Electrolyte, p. 98 | Net ionic equation, p. 103 | Reduction reaction, p. 111 |
| Brønsted acid, p. 105 | Equivalence point, p. 126 | Neutralization reaction, p. 108 | Reversible reaction, p. 100 |
| Brønsted base, p. 105 | Gravimetric analysis, p. 123 | Nonelectrolyte, p. 98 | Salt, p. 108 |
| Chemical equilibrium, p. 100 | Half-reaction, p. 111 | Oxidation number, p. 112 | Solubility, p. 101 |
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| Combustion reaction, p. 115 | Hydronium ion, p. 106 | Oxidation reaction, p. 111 | Solution, p. 98 |
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| Decomposition reaction, p. 115 | Ionic equation, p. 103 | Oxidizing agent, p. 111 | Spectator ion, p. 103 |
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| Diprotic acid, p. 106 | Molar concentration, p. 119 | Precipitation reaction, p. 100 | Titration, p. 125 |
| | Molarity (M), p. 119 | Redox reaction, p. 110 | Triprotic acid, p. 106 |
| | Molecular equation, p. 102 | | |

Questions and Problems

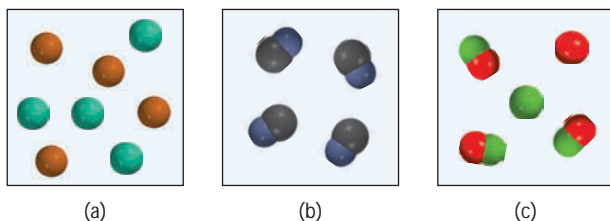
Properties of Aqueous Solutions

Review Questions

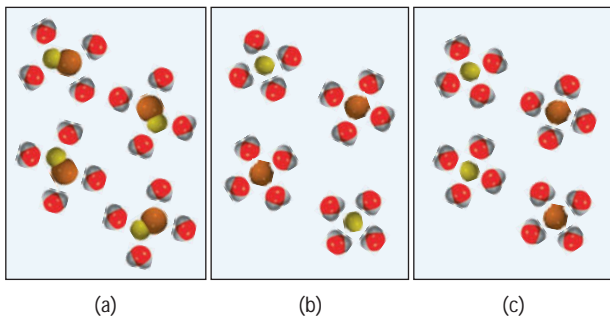
- 4.1 Define solute, solvent, and solution by describing the process of dissolving a solid in a liquid.
- 4.2 What is the difference between a nonelectrolyte and an electrolyte? Between a weak electrolyte and a strong electrolyte?
- 4.3 Describe hydration. What properties of water enable its molecules to interact with ions in solution?
- 4.4 What is the difference between the following symbols in chemical equations: \longrightarrow and \rightleftharpoons ?
- 4.5 Water is an extremely weak electrolyte and therefore cannot conduct electricity. Why are we often cautioned not to operate electrical appliances when our hands are wet?
- 4.6 Lithium fluoride (LiF) is a strong electrolyte. What species are present in LiF(aq)?

Problems

- 4.7 The aqueous solutions of three compounds are shown in the diagram. Identify each compound as a nonelectrolyte, a weak electrolyte, and a strong electrolyte.



- 4.8 Which of the following diagrams best represents the hydration of NaCl when dissolved in water? The Cl^- ion is larger in size than the Na^+ ion.



- 4.9 Identify each of the following substances as a strong electrolyte, weak electrolyte, or nonelectrolyte: (a) H_2O , (b) KCl, (c) HNO_3 , (d) CH_3COOH , (e) $\text{C}_{12}\text{H}_{22}\text{O}_{11}$.
- 4.10 Identify each of the following substances as a strong electrolyte, weak electrolyte, or nonelectrolyte: (a) $\text{Ba}(\text{NO}_3)_2$, (b) Ne, (c) NH_3 , (d) NaOH.

- 4.11 The passage of electricity through an electrolyte solution is caused by the movement of (a) electrons only, (b) cations only, (c) anions only, (d) both cations and anions.
- 4.12 Predict and explain which of the following systems are electrically conducting: (a) solid NaCl, (b) molten NaCl, (c) an aqueous solution of NaCl.
- 4.13 You are given a water-soluble compound X. Describe how you would determine whether it is an electrolyte or a nonelectrolyte. If it is an electrolyte, how would you determine whether it is strong or weak?
- 4.14 Explain why a solution of HCl in benzene does not conduct electricity but in water it does.

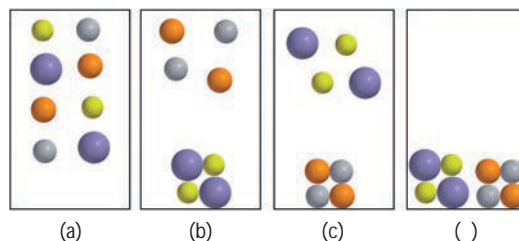
Precipitation Reactions

Review Questions

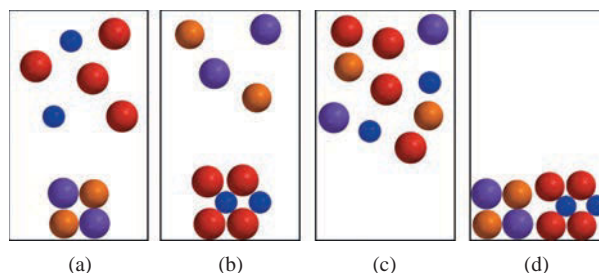
- 4.15 What is the difference between an ionic equation and a molecular equation?
- 4.16 What is the advantage of writing net ionic equations?

Problems

- 4.17 Two aqueous solutions of AgNO_3 and NaCl are mixed. Which of the following diagrams best represents the mixture? (Ag^+ = gray; Cl^- = orange; Na^+ = green; NO_3^- = blue) (For simplicity, water molecules are not shown.)



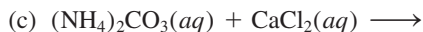
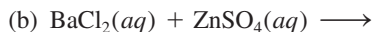
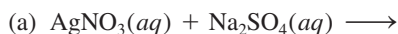
- 4.18 Two aqueous solutions of KOH and MgCl_2 are mixed. Which of the following diagrams best represents the mixture? (K^+ = purple; OH^- = red; Mg^{2+} = blue; Cl^- = orange) (For simplicity, water molecules are not shown.)



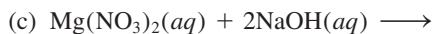
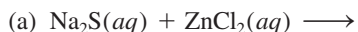
4.19 Characterize the following compounds as soluble or insoluble in water: (a) $\text{Ca}_3(\text{PO}_4)_2$, (b) $\text{Mn}(\text{OH})_2$, (c) AgClO_3 , (d) K_2S .

4.20 Characterize the following compounds as soluble or insoluble in water: (a) CaCO_3 , (b) ZnSO_4 , (c) $\text{Hg}(\text{NO}_3)_2$, (d) HgSO_4 , (e) NH_4ClO_4 .

4.21 Write ionic and net ionic equations for the following reactions:



4.22 Write ionic and net ionic equations for the following reactions:



4.23 Which of the following processes will likely result in a precipitation reaction? (a) Mixing a NaNO_3 solution with a CuSO_4 solution. (b) Mixing a BaCl_2 solution with a K_2SO_4 solution. Write a net ionic equation for the precipitation reaction.

4.24 With reference to Table 4.2, suggest one method by which you might separate (a) K^+ from Ag^+ , (b) Ba^{2+} from Pb^{2+} , (c) NH_4^+ from Ca^{2+} , (d) Ba^{2+} from Cu^{2+} . All cations are assumed to be in aqueous solution, and the common anion is the nitrate ion.

Acid-Base Reactions

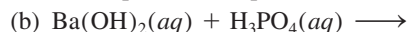
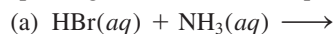
Review Questions

- 4.25 List the general properties of acids and bases.
- 4.26 Give Arrhenius's and Brønsted's definitions of an acid and a base. Why are Brønsted's definitions more useful in describing acid-base properties?
- 4.27 Give an example of a monoprotic acid, a diprotic acid, and a triprotic acid.
- 4.28 What are the characteristics of an acid-base neutralization reaction?
- 4.29 What factors qualify a compound as a salt? Specify which of the following compounds are salts: CH_4 , NaF , NaOH , CaO , BaSO_4 , HNO_3 , NH_3 , KBr ?
- 4.30 Identify the following as a weak or strong acid or base: (a) NH_3 , (b) H_3PO_4 , (c) LiOH , (d) HCOOH (formic acid), (e) H_2SO_4 , (f) HF , (g) $\text{Ba}(\text{OH})_2$.

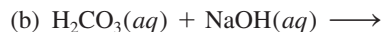
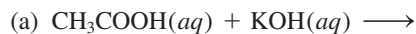
Problems

- 4.31 Identify each of the following species as a Brønsted acid, base, or both: (a) HI , (b) CH_3COO^- , (c) H_2PO_4^- , (d) HSO_4^- .
- 4.32** Identify each of the following species as a Brønsted acid, base, or both: (a) PO_4^{3-} , (b) ClO_2^- , (c) NH_4^+ , (d) HCO_3^- .

4.33 Balance the following equations and write the corresponding ionic and net ionic equations (if appropriate):



4.34 Balance the following equations and write the corresponding ionic and net ionic equations (if appropriate):



Oxidation-Reduction Reactions

Review Questions

- 4.35 Define the following terms: half-reaction, oxidation reaction, reduction reaction, reducing agent, oxidizing agent, redox reaction.
- 4.36 What is an oxidation number? How is it used to identify redox reactions? Explain why, except for ionic compounds, oxidation number does not have any physical significance.
- 4.37 (a) Without referring to Figure 4.10, give the oxidation numbers of the alkali and alkaline earth metals in their compounds. (b) Give the highest oxidation numbers that the Groups 3A–7A elements can have.
- 4.38 Is it possible to have a reaction in which oxidation occurs and reduction does not? Explain.

Problems

- 4.39 For the complete redox reactions given here, (i) break down each reaction into its half-reactions; (ii) identify the oxidizing agent; (iii) identify the reducing agent.
- (a) $2\text{Sr} + \text{O}_2 \longrightarrow 2\text{SrO}$
- (b) $2\text{Li} + \text{H}_2 \longrightarrow 2\text{LiH}$
- (c) $2\text{Cs} + \text{Br}_2 \longrightarrow 2\text{CsBr}$
- (d) $3\text{Mg} + \text{N}_2 \longrightarrow \text{Mg}_3\text{N}_2$
- 4.40** For the complete redox reactions given here, write the half-reactions and identify the oxidizing and reducing agents:
- (a) $4\text{Fe} + 3\text{O}_2 \longrightarrow 2\text{Fe}_2\text{O}_3$
- (b) $\text{Cl}_2 + 2\text{NaBr} \longrightarrow 2\text{NaCl} + \text{Br}_2$
- (c) $\text{Si} + 2\text{F}_2 \longrightarrow \text{SiF}_4$
- (d) $\text{H}_2 + \text{Cl}_2 \longrightarrow 2\text{HCl}$
- 4.41 Arrange the following species in order of increasing oxidation number of the sulfur atom: (a) H_2S , (b) S_8 , (c) H_2SO_4 , (d) S^{2-} , (e) HS^- , (f) SO_2 , (g) SO_3 .
- 4.42** Phosphorus forms many oxoacids. Indicate the oxidation number of phosphorus in each of the following acids: (a) HPO_3 , (b) H_3PO_2 , (c) H_3PO_3 , (d) H_3PO_4 , (e) $\text{H}_4\text{P}_2\text{O}_7$, (f) $\text{H}_5\text{P}_3\text{O}_{10}$.
- 4.43 Give the oxidation number of the underlined atoms in the following molecules and ions: (a) $\underline{\text{C}}\text{IF}$, (b) $\text{I}\underline{\text{F}}_7$, (c) $\underline{\text{C}}\text{H}_4$, (d) $\underline{\text{C}}_2\text{H}_2$, (e) $\underline{\text{C}}_2\text{H}_4$, (f) $\text{K}_2\underline{\text{C}}\text{rO}_4$, (g) $\text{K}_2\underline{\text{C}}\text{r}_2\text{O}_7$,

- (h) $\underline{\text{KMnO}}_4$, (i) $\text{NaH}\underline{\text{C}}\text{O}_3$, (j) $\underline{\text{Li}}_2$, (k) $\text{Na}\underline{\text{I}}\text{O}_3$, (l) $\text{K}\underline{\text{O}}_2$, (m) $\underline{\text{PF}}_6^-$, (n) $\text{K}\underline{\text{AuCl}}_4$.
- 4.44** Which of the following are redox processes?
 (a) $\text{CO}_2 \longrightarrow \text{CO}_3^{2-}$
 (b) $\text{VO}_3 \longrightarrow \text{VO}_2$
 (c) $\text{SO}_3 \longrightarrow \text{SO}_4^{2-}$
 (d) $\text{NO}_2^- \longrightarrow \text{NO}_3^-$
 (e) $\text{Cr}^{3+} \longrightarrow \text{CrO}_4^{2-}$
- 4.45 Give oxidation numbers for the underlined atoms in the following molecules and ions: (a) $\underline{\text{C}}\text{S}_2\text{O}$, (b) $\text{Ca}\underline{\text{I}}_2$, (c) $\underline{\text{Al}}_2\text{O}_3$, (d) $\text{H}_3\underline{\text{As}}\text{O}_3$, (e) $\underline{\text{Ti}}\text{O}_2$, (f) $\underline{\text{Mo}}\text{O}_4^{2-}$, (g) $\underline{\text{Pt}}\text{Cl}_4^{2-}$, (h) $\underline{\text{Pt}}\text{Cl}_6^{2-}$, (i) $\underline{\text{Sn}}\text{F}_2$, (j) $\underline{\text{Cl}}\text{F}_3$, (k) $\underline{\text{Sb}}\text{F}_6^-$.
- 4.46** Give the oxidation numbers of the underlined atoms in the following molecules and ions: (a) $\text{Mg}_3\underline{\text{N}}_2$, (b) $\text{Cs}\underline{\text{O}}_2$, (c) $\text{Ca}\underline{\text{C}}_2$, (d) $\underline{\text{C}}\text{O}_3^{2-}$, (e) $\underline{\text{C}}_2\text{O}_4^{2-}$, (f) $\text{Zn}\underline{\text{O}}_2^{2-}$, (g) $\text{Na}\underline{\text{B}}\text{H}_4$, (h) $\underline{\text{W}}\text{O}_4^{2-}$.
- 4.47 Nitric acid is a strong oxidizing agent. State which of the following species is *least* likely to be produced when nitric acid reacts with a strong reducing agent such as zinc metal, and explain why: N_2O , NO , NO_2 , N_2O_4 , N_2O_5 , NH_4^+ .
- 4.48** Which of the following metals can react with water?
 (a) Au, (b) Li, (c) Hg, (d) Ca, (e) Pt.
- 4.49 On the basis of oxidation number considerations, one of the following oxides would not react with molecular oxygen: NO , N_2O , SO_2 , SO_3 , P_4O_6 . Which one is it? Why?
- 4.50** Predict the outcome of the reactions represented by the following equations by using the activity series, and balance the equations.
 (a) $\text{Cu}(s) + \text{HCl}(aq) \longrightarrow$
 (b) $\text{I}_2(s) + \text{NaBr}(aq) \longrightarrow$
 (c) $\text{Mg}(s) + \text{CuSO}_4(aq) \longrightarrow$
 (d) $\text{Cl}_2(g) + \text{KBr}(aq) \longrightarrow$

Concentration of Solutions

Review Questions

- 4.51 Write the equation for calculating molarity. Why is molarity a convenient concentration unit in chemistry?
- 4.52 Describe the steps involved in preparing a solution of known molar concentration using a volumetric flask.

Problems

- 4.53 Barium hydroxide, often used to titrate weak organic acids, is obtained as the octahydrate, $\text{Ba}(\text{OH})_2 \cdot 8\text{H}_2\text{O}$. What mass of $\text{Ba}(\text{OH})_2 \cdot 8\text{H}_2\text{O}$ would be required to make 500.0 mL of a solution that is 0.1500 M in hydroxide ions?
- 4.54** Describe how you would prepare 250 mL of a 0.707 M NaNO_3 solution.
- 4.55 How many moles of MgCl_2 are present in 60.0 mL of 0.100 M MgCl_2 solution?
- 4.56** How many grams of KOH are present in 35.0 mL of a 5.50 M solution?

- 4.57 Calculate the molarity of each of the following solutions: (a) 29.0 g of ethanol ($\text{C}_2\text{H}_5\text{OH}$) in 545 mL of solution, (b) 15.4 g of sucrose ($\text{C}_{12}\text{H}_{22}\text{O}_{11}$) in 74.0 mL of solution, (c) 9.00 g of sodium chloride (NaCl) in 86.4 mL of solution.
- 4.58** Calculate the molarity of each of the following solutions: (a) 6.57 g of methanol (CH_3OH) in 1.50×10^2 mL of solution, (b) 10.4 g of calcium chloride (CaCl_2) in 2.20×10^2 mL of solution, (c) 7.82 g of naphthalene (C_{10}H_8) in 85.2 mL of benzene solution.
- 4.59 Calculate the volume in mL of a solution required to provide the following: (a) 2.14 g of sodium chloride from a 0.270 M solution, (b) 4.30 g of ethanol from a 1.50 M solution, (c) 0.85 g of acetic acid (CH_3COOH) from a 0.30 M solution.
- 4.60** Determine how many grams of each of the following solutes would be needed to make 2.50×10^2 mL of a 0.100 M solution: (a) cesium iodide (CsI), (b) sulfuric acid (H_2SO_4), (c) sodium carbonate (Na_2CO_3), (d) potassium dichromate ($\text{K}_2\text{Cr}_2\text{O}_7$), (e) potassium permanganate (KMnO_4).

Dilution of Solutions

Review Questions

- 4.61 Describe the basic steps involved in diluting a solution of known concentration.
- 4.62 Write the equation that enables us to calculate the concentration of a diluted solution. Give units for all the terms.

Problems

- 4.63 Describe how to prepare 1.00 L of 0.646 M HCl solution, starting with a 2.00 M HCl solution.
- 4.64** Water is added to 25.0 mL of a 0.866 M KNO_3 solution until the volume of the solution is exactly 500 mL. What is the concentration of the final solution?
- 4.65 How would you prepare 60.0 mL of 0.200 M HNO_3 from a stock solution of 4.00 M HNO_3 ?
- 4.66** You have 505 mL of a 0.125 M HCl solution and you want to dilute it to exactly 0.100 M. How much water should you add? Assume volumes are additive.
- 4.67 What volume of 0.416 M $\text{Mg}(\text{NO}_3)_2$ should be added to 255 mL of 0.102 M KNO_3 to produce a solution with a concentration of 0.278 M NO_3^- ions? Assume volumes are additive.
- 4.68** A 46.2-mL, 0.568 M calcium nitrate [$\text{Ca}(\text{NO}_3)_2$] solution is mixed with 80.5 mL of 1.396 M calcium nitrate solution. Calculate the concentration of the final solution.

Gravimetric Analysis

Review Questions

- 4.69 Describe the basic steps involved in gravimetric analysis. How does this procedure help us determine the

identity of a compound or the purity of a compound if its formula is known?

- 4.70 Distilled water must be used in the gravimetric analysis of chlorides. Why?

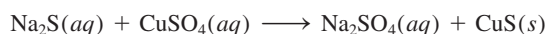
Problems

- 4.71 If 30.0 mL of 0.150 M CaCl_2 is added to 15.0 mL of 0.100 M AgNO_3 , what is the mass in grams of AgCl precipitate?

- 4.72** The concentration of sulfate in water can be determined by adding a solution of barium chloride to precipitate the sulfate ion. Write the net ionic equation for this reaction. Treating a 145-mL sample of water with excess $\text{BaCl}_2(aq)$ precipitated 0.330 g of BaSO_4 . Determine the concentration of sulfate in the original water sample.

- 4.73 How many grams of NaCl are required to precipitate most of the Ag^+ ions from 2.50×10^2 mL of 0.0113 M AgNO_3 solution? Write the net ionic equation for the reaction.

- 4.74** The concentration of Cu^{2+} ions in the water (which also contains sulfate ions) discharged from a certain industrial plant is determined by adding excess sodium sulfide (Na_2S) solution to 0.800 L of the water. The molecular equation is



Write the net ionic equation and calculate the molar concentration of Cu^{2+} in the water sample if 0.0177 g of solid CuS is formed.

Acid-Base Titrations

Review Questions

- 4.75 Describe the basic steps involved in an acid-base titration. Why is this technique of great practical value?
- 4.76 How does an acid-base indicator work?

Problems

- 4.77 A quantity of 18.68 mL of a KOH solution is needed to neutralize 0.4218 g of KHP. What is the concentration (in molarity) of the KOH solution?

- 4.78** Calculate the concentration (in molarity) of a NaOH solution if 25.0 mL of the solution are needed to neutralize 17.4 mL of a 0.312 M HCl solution.

- 4.79 Calculate the volume in mL of a 1.420 M NaOH solution required to titrate the following solutions:

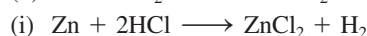
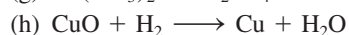
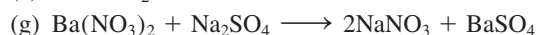
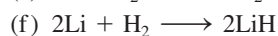
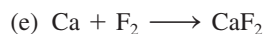
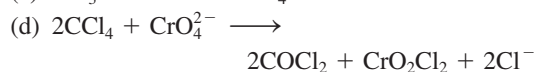
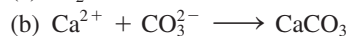
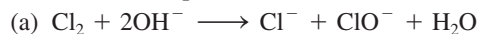
- (a) 25.00 mL of a 2.430 M HCl solution
 (b) 25.00 mL of a 4.500 M H_2SO_4 solution
 (c) 25.00 mL of a 1.500 M H_3PO_4 solution

- 4.80** What volume of a 0.500 M HCl solution is needed to neutralize each of the following:

- (a) 10.0 mL of a 0.300 M NaOH solution
 (b) 10.0 mL of a 0.200 M $\text{Ba}(\text{OH})_2$ solution

Additional Problems

- 4.81 Classify these reactions according to the types discussed in the chapter:

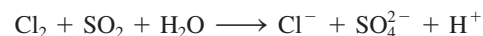


- 4.82** Using the apparatus shown in Figure 4.1, a student found that the lightbulb was brightly lit when the electrodes were immersed in a sulfuric acid solution. However, after the addition of a certain amount of barium hydroxide [$\text{Ba}(\text{OH})_2$] solution, the light began to dim even though $\text{Ba}(\text{OH})_2$ is also a strong electrolyte. Explain.

- 4.83 Someone gave you a colorless liquid. Describe three chemical tests you would perform on the liquid to show that it is water.

- 4.84** You are given two colorless solutions, one containing NaCl and the other sucrose ($\text{C}_{12}\text{H}_{22}\text{O}_{11}$). Suggest a chemical and a physical test that would distinguish between these two solutions.

- 4.85 Chlorine (Cl_2) is used to purify drinking water. Too much chlorine is harmful to humans. The excess chlorine is often removed by treatment with sulfur dioxide (SO_2). Balance the following equation that represents this procedure:

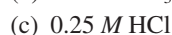
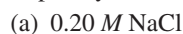


- 4.86** Before aluminum was obtained by electrolytic reduction from its ore (Al_2O_3), the metal was produced by chemical reduction of AlCl_3 . Which metals would you use to reduce Al^{3+} to Al ?

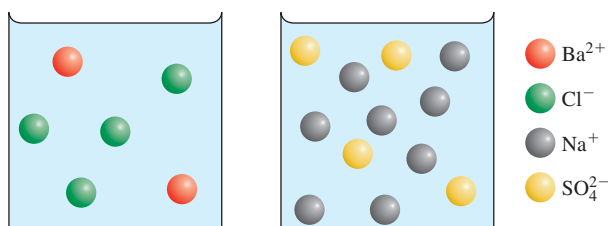
- 4.87 Oxygen (O_2) and carbon dioxide (CO_2) are colorless and odorless gases. Suggest two chemical tests that would enable you to distinguish between them.

- 4.88** Based on oxidation number, explain why carbon monoxide (CO) is flammable but carbon dioxide (CO_2) is not.

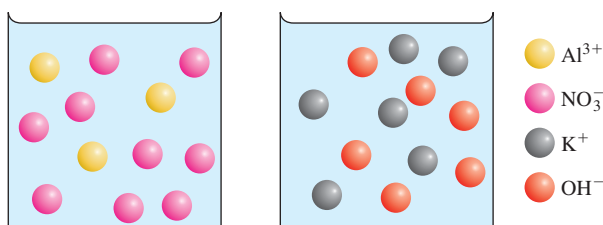
- 4.89 Which of these aqueous solutions would you expect to be the best conductor of electricity at 25°C? Explain your answer.



- 4.90** A 5.00×10^2 -mL sample of $2.00 M$ HCl solution is treated with 4.47 g of magnesium. Calculate the concentration of the acid solution after all the metal has reacted. Assume that the volume remains unchanged.
- 4.91** Calculate the volume (in liters) of a $0.156 M$ CuSO_4 solution that would react with 7.89 g of zinc.
- 4.92** The molar mass of a certain metal carbonate, MCO_3 , can be determined by adding an excess of HCl acid to react with all the carbonate and then “back titrating” the remaining acid with a NaOH solution. (a) Write an equation for these reactions. (b) In a certain experiment, 20.00 mL of $0.0800 M$ HCl were added to a 0.1022 -g sample of MCO_3 . The excess HCl required 5.64 mL of $0.1000 M$ NaOH for neutralization. Calculate the molar mass of the carbonate and identify M.
- 4.93** A 0.3664 -g sample of a monoprotic acid was dissolved in water and required 20.27 mL of a $0.1578 M$ NaOH solution for neutralization. Calculate the molar mass of the acid.
- 4.94** The molecular formula of malonic acid is $\text{C}_3\text{H}_4\text{O}_4$. If a solution containing 0.762 g of the acid requires 12.44 mL of $1.174 M$ NaOH for neutralization, how many ionizable H atoms are present in the molecule?
- 4.95** Shown here are two aqueous solutions containing various ions. The volume of each solution is 200 mL. (a) Calculate the mass of the precipitate (in g) after the solutions are mixed. (b) What are the concentrations (in M) of the ions in the final solution? Treat each sphere as 0.100 mol. Assume the volumes are additive.



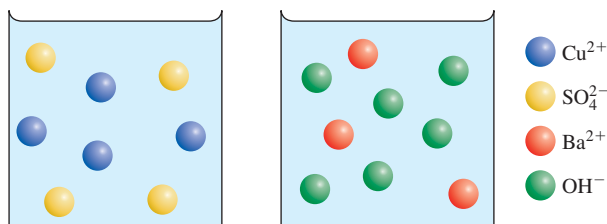
- 4.96** Shown here are two aqueous solutions containing various ions. The volume of each solution is 200 mL. (a) Calculate the mass of the precipitate (in g) after the solutions are mixed. (b) What are the concentrations (in M) of the ions in the final solution? Treat each sphere as 0.100 mol. Assume the volumes are additive.



- 4.97** Calculate the mass of precipitate formed when 2.27 L of $0.0820 M$ $\text{Ba}(\text{OH})_2$ are mixed with 3.06 L of $0.0664 M$ Na_2SO_4 .
- 4.98** Milk of magnesia is an aqueous suspension of magnesium hydroxide [$\text{Mg}(\text{OH})_2$] used to treat acid indigestion. Calculate the volume of a $0.035 M$ HCl solution (a typical acid concentration in an upset stomach) needed to react with two spoonfuls of milk of magnesia [approximately 10.0 mL of 0.080 g $\text{Mg}(\text{OH})_2/\text{mL}$].
- 4.99** A 1.00 -g sample of a metal X (that is known to form X^{2+} ions) was added to 0.100 L of $0.500 M$ H_2SO_4 . After all the metal had reacted, the remaining acid required 0.0334 L of $0.500 M$ NaOH solution for neutralization. Calculate the molar mass of the metal and identify the element.
- 4.100** A 60.0 -mL $0.513 M$ glucose ($\text{C}_6\text{H}_{12}\text{O}_6$) solution is mixed with 120.0 mL of $2.33 M$ glucose solution. What is the concentration of the final solution? Assume the volumes are additive.
- 4.101** You are given a soluble compound of unknown molecular formula. (a) Describe three tests that would show that the compound is an acid. (b) Once you have established that the compound is an acid, describe how you would determine its molar mass using an NaOH solution of known concentration. (Assume the acid is monoprotic.) (c) How would you find out whether the acid is weak or strong? You are provided with a sample of NaCl and an apparatus like that shown in Figure 4.1 for comparison.
- 4.102** Someone spilled concentrated sulfuric acid on the floor of a chemistry laboratory. To neutralize the acid, would it be preferable to pour concentrated sodium hydroxide solution or spray solid sodium bicarbonate over the acid? Explain your choice and the chemical basis for the action.
- 4.103** These are common household compounds: table salt (NaCl), table sugar (sucrose), vinegar (contains acetic acid), baking soda (NaHCO_3), washing soda ($\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$), boric acid (H_3BO_3 , used in eye-wash), epsom salt ($\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$), sodium hydroxide (used in drain openers), ammonia, milk of magnesia [$\text{Mg}(\text{OH})_2$], and calcium carbonate. Based on what you have learned in this chapter, describe test(s) that would enable you to identify each of these compounds.
- 4.104** A 0.8870 -g sample of a mixture of NaCl and KCl is dissolved in water, and the solution is then treated with an excess of AgNO_3 to yield 1.913 g of AgCl. Calculate the percent by mass of each compound in the mixture.
- 4.105** Phosphoric acid (H_3PO_4) is an important industrial chemical used in fertilizers, detergents, and in the food industry. It is produced by two different methods. In the *electric furnace method* elemental phosphorus (P_4) is burned in air to form P_4O_{10} , which is then reacted with water to give H_3PO_4 . In the *wet process* the mineral phosphate rock [$\text{Ca}_5(\text{PO}_4)_3\text{F}$] is

reacted with sulfuric acid to give H_3PO_4 (and HF and CaSO_4). Write equations for these processes and classify each step as precipitation, acid-base, or redox reaction.

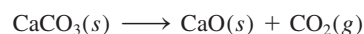
- 4.106** Give a chemical explanation for each of these: (a) When calcium metal is added to a sulfuric acid solution, hydrogen gas is generated. After a few minutes, the reaction slows down and eventually stops even though none of the reactants is used up. Explain. (b) In the activity series aluminum is above hydrogen, yet the metal appears to be unreactive toward steam and hydrochloric acid. Why? (c) Sodium and potassium lie above copper in the activity series. Explain why Cu^{2+} ions in a CuSO_4 solution are not converted to metallic copper upon the addition of these metals. (d) A metal M reacts slowly with steam. There is no visible change when it is placed in a pale green iron(II) sulfate solution. Where should we place M in the activity series?
- 4.107 A number of metals are involved in redox reactions in biological systems in which the oxidation state of the metals changes. Which of these metals are most likely to take part in such reactions: Na, K, Mg, Ca, Mn, Fe, Co, Cu, Zn? Explain.
- 4.108** The recommended procedure for preparing a very dilute solution is not to weigh out a very small mass or measure a very small volume of a stock solution. Instead, it is done by a series of dilutions. A sample of 0.8214 g of KMnO_4 was dissolved in water and made up to the volume in a 500-mL volumetric flask. A 2.000-mL sample of this solution was transferred to a 1000-mL volumetric flask and diluted to the mark with water. Next, 10.00 mL of the diluted solution were transferred to a 250-mL flask and diluted to the mark with water. (a) Calculate the concentration (in molarity) of the final solution. (b) Calculate the mass of KMnO_4 needed to directly prepare the final solution.
- 4.109 A 325-mL sample of solution contains 25.3 g of CaCl_2 . (a) Calculate the molar concentration of Cl^- in this solution. (b) How many grams of Cl^- are in 0.100 L of this solution?
- 4.110** Acetylsalicylic acid ($\text{C}_9\text{H}_8\text{O}_4$) is a monoprotic acid commonly known as “aspirin.” A typical aspirin tablet, however, contains only a small amount of the acid. In an experiment to determine its composition, an aspirin tablet was crushed and dissolved in water. It took 12.25 mL of 0.1466 M NaOH to neutralize the solution. Calculate the number of grains of aspirin in the tablet. (One grain = 0.0648 g.)
- 4.111 Referring to Figure 4.15, explain why one must first dissolve the solid completely before making up the solution to the correct volume.
- 4.112** Ammonium nitrate (NH_4NO_3) is one of the most important nitrogen-containing fertilizers. Its purity can be analyzed by titrating a solution of NH_4NO_3 with a standard NaOH solution. In one experiment a 0.2041-g sample of industrially prepared NH_4NO_3 required 24.42 mL of 0.1023 M NaOH for neutralization. (a) Write a net ionic equation for the reaction. (b) What is the percent purity of the sample?
- 4.113 Shown here are two aqueous solutions containing various ions. The volume of each solution is 600 mL. (a) Write a net ionic equation for the reaction after the solutions are mixed. (b) Calculate the mass of the precipitates formed and the concentrations of the ions in the mixed solution. Treat each sphere as 0.0500 mol.



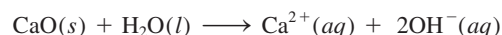
Special Problems

- 4.114** Many proteins contain metal ions for structural and/or redox functions. Which of the following metals fit into one or both categories: Ca, Cu, Fe, Mg, Mn, Ni, Zn?
- 4.115 Magnesium is a valuable, lightweight metal. It is used as a structural metal and in alloys, in batteries, and in chemical synthesis. Although magnesium is plentiful in Earth’s crust, it is cheaper to “mine” the metal from seawater. Magnesium forms the second most abundant cation in the sea (after sodium); there are about 1.3 g of magnesium in 1 kg of seawater. The method of obtaining magnesium from seawater

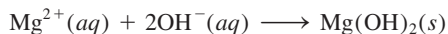
employs all three types of reactions discussed in this chapter: precipitation, acid-base, and redox reactions. In the first stage in the recovery of magnesium, limestone (CaCO_3) is heated at high temperatures to produce quicklime, or calcium oxide (CaO):



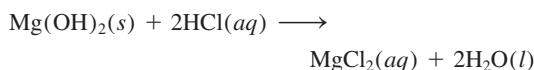
When calcium oxide is treated with seawater, it forms calcium hydroxide [$\text{Ca}(\text{OH})_2$], which is slightly soluble and ionizes to give Ca^{2+} and OH^- ions:



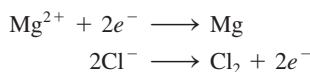
The surplus hydroxide ions cause the much less soluble magnesium hydroxide to precipitate:



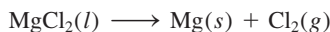
The solid magnesium hydroxide is filtered and reacted with hydrochloric acid to form magnesium chloride (MgCl_2):



After the water is evaporated, the solid magnesium chloride is melted in a steel cell. The molten magnesium chloride contains both Mg^{2+} and Cl^{-} ions. In a process called electrolysis, an electric current is passed through the cell to reduce the Mg^{2+} ions and oxidize the Cl^{-} ions. The half-reactions are



The overall reaction is



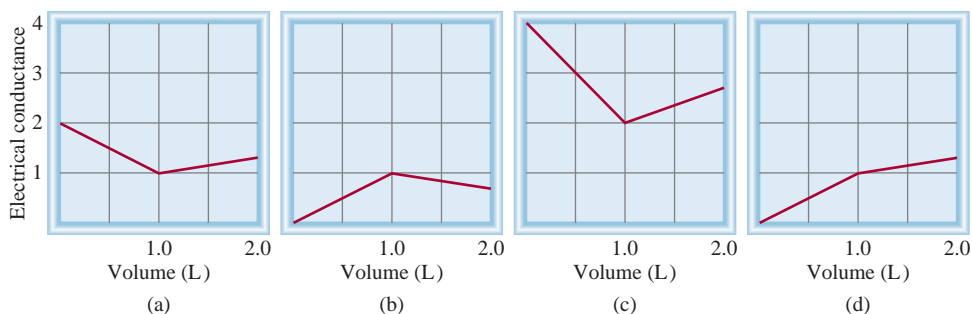
This is how magnesium metal is produced. The chlorine gas generated can be converted to hydrochloric acid and recycled through the process.

- Identify the precipitation, acid-base, and redox processes.
- Instead of calcium oxide, why don't we simply add sodium hydroxide to precipitate magnesium hydroxide?
- Sometimes a mineral called dolomite (a combination of CaCO_3 and MgCO_3) is substituted for limestone (CaCO_3) to bring about the precipitation

of magnesium hydroxide. What is the advantage of using dolomite?

- What are the advantages of mining magnesium from the ocean rather than from Earth's crust?

- 4.116** A 5.012-g sample of an iron chloride hydrate was dried in an oven. The mass of the anhydrous compound was 3.195 g. The compound was dissolved in water and reacted with an excess of AgNO_3 . The precipitate of AgCl formed weighed 7.225 g. What is the formula of the original compound?
- 4.117 A 22.02-mL solution containing 1.615 g $\text{Mg}(\text{NO}_3)_2$ is mixed with a 28.64-mL solution containing 1.073 g NaOH . Calculate the concentrations of the ions remaining in solution after the reaction is complete. Assume volumes are additive.
- 4.118** Because acid-base and precipitation reactions discussed in this chapter all involve ionic species, their progress can be monitored by measuring the electrical conductance of the solution. Match the following reactions with the diagrams shown here. The electrical conductance is shown in arbitrary units.
- A 1.0 M KOH solution is added to 1.0 L of 1.0 M CH_3COOH .
 - A 1.0 M NaOH solution is added to 1.0 L of 1.0 M HCl .
 - A 1.0 M BaCl_2 solution is added to 1.0 L of 1.0 M K_2SO_4 .
 - A 1.0 M NaCl solution is added to 1.0 L of 1.0 M AgNO_3 .
 - A 1.0 M CH_3COOH solution is added to 1.0 L of 1.0 M NH_3 .



Answers to Practice Exercises

4.1 (a) Insoluble, (b) insoluble, (c) soluble.

4.2 $\text{Al}^{3+}(aq) + 3\text{OH}^{-}(aq) \longrightarrow \text{Al}(\text{OH})_3(s)$.

4.3 (a) Brønsted base, (b) Brønsted acid, (c) Brønsted acid and Brønsted base. **4.4** Molecular equation: $\text{H}_3\text{PO}_4(aq) + 3\text{NaOH}(aq) \longrightarrow \text{Na}_3\text{PO}_4(aq) + 3\text{H}_2\text{O}(l)$; ionic equation: $\text{H}_3\text{PO}_4(aq) + 3\text{Na}^{+}(aq) + 3\text{OH}^{-}(aq) \longrightarrow 3\text{Na}^{+}(aq) + \text{PO}_4^{3-}(aq) + 3\text{H}_2\text{O}(l)$; net ionic equation: $\text{H}_3\text{PO}_4(aq) + 3\text{OH}^{-}(aq) \longrightarrow \text{PO}_4^{3-}(aq) + 3\text{H}_2\text{O}(l)$.

4.5 (a) P: +3, F: -1; (b) Mn: +7, O: -2.

4.6 (a) Hydrogen displacement reaction, (b) combination reaction, (c) metal displacement reaction.

4.7 0.452 M. **4.8** 494 mL. **4.9** Dilute 34.2 mL of the stock solution to 200 mL. **4.10** 92.02%.

4.11 0.3822 g. **4.12** 1.27 M.