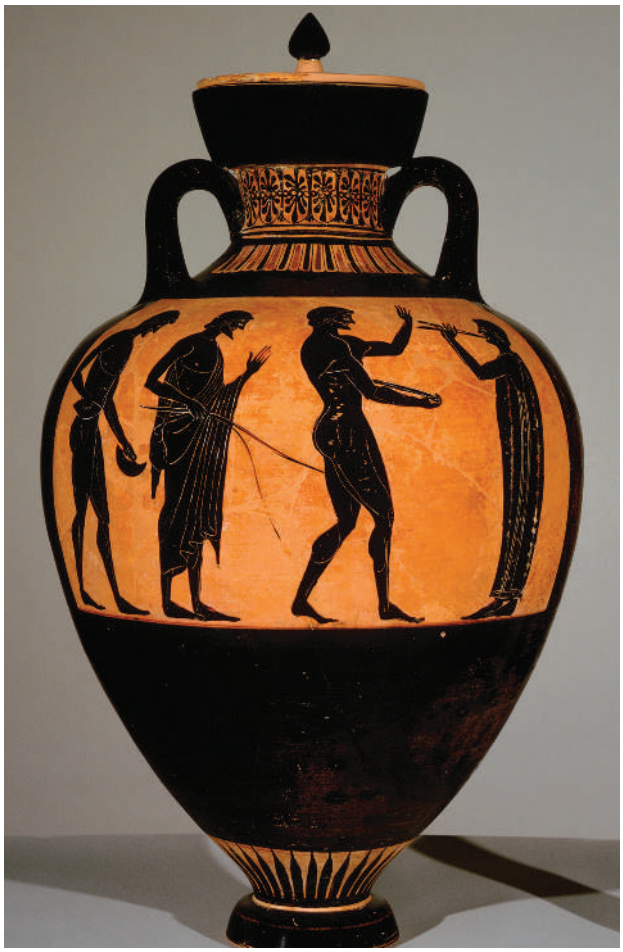
4 Reactions in Aqueous Solution

The three-phase firing process ancient Greek potters used to create this vase utilized both oxidation and reduction processes.



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He takes up the waters of the sea in his hand, leaving the salt;
He disperses it in mist through the skies;
He recollects and sprinkles it like grain in six-rayed snowy stars over the earth,
There to lie till he dissolves the bonds again.

—HENRY DAVID THOREAU
Journal (January 5, 1856)

Chapter Outline

4-1 Precipitation Reactions

4-2 Acid-Base Reactions

4-3 Oxidation-Reduction Reactions

Most of the reactions considered in Chapter 3 involved pure substances reacting with each other. However, most of the reactions you will carry out in the laboratory or hear about in lecture take place in water (aqueous) solution. Beyond that, most of the reactions that occur in the world around you involve ions or molecules dissolved in water. For these reasons, among others, you need to become familiar with some of the more important types of aqueous reactions. These include

- precipitation reactions (Section 4-1).
- acid-base reactions (Section 4-2).
- oxidation-reduction reactions (Section 4-3).

All of these reactions involve ions in solution. The corresponding equations are given a special name: net ionic equations. They can be used to do stoichiometric calculations similar to those discussed in Chapter 3.

To carry out these calculations for solution reactions, recall the concentration unit called molarity (Section 3-1), which tells you how many moles of a species are in a given volume of solution.

4-1 Precipitation Reactions

When water (aqueous) solutions of two different ionic compounds are mixed, we often find that an insoluble solid precipitates; this is called a **precipitation reaction**. To identify the solid, we must know which ionic compounds are soluble in water and which are not.

Solubility of Ionic Compounds

When an ionic solid dissolves in water two competing forces come into play:

- the attractive forces between the oppositely charged ions making up the solid
- the attractive forces between water and the ions.

For reasons discussed later in this text (Chapter 7), water has two partially positively charged (δ^+) hydrogen atoms (attractive to anions) and a partially negatively charged (δ^-) oxygen atom (attractive to cations). The extent to which solution occurs depends upon a balance between two forces, which are both electrical in nature:

1. The force of atraction between H_2O molecules and the ions of the solid, which tends to bring the solid into solution. If this factor predominates, we expect the compound to be very soluble in water, as in the case of KCl (Figure 4.1).
2. The force of attraction between oppositely charged ions, which tends to keep them in the solid state. If this is the major factor, we expect water solubility to be low. $SrSO_4$ is almost insoluble, which implies that the interionic forces between Sr^{2+} ions and SO_4^{2-} ions predominate.

Unfortunately, we cannot determine from first principles the relative strengths of these two forces for a given solid. For this reason, among others, we cannot predict in advance the water solubilities of ionic solids, which cover an enormous range of possibilities.

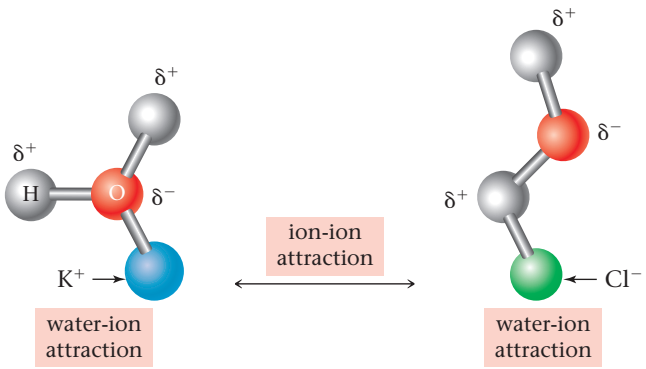

Figure 4.1 Competing forces when a solute is added to water. When KCl is added to water, the attraction between K^+ and Cl^- and the water molecules competes with the attraction of the ions for each other. In this case, the water to ion attraction is stronger than the ion to ion attraction, so KCl is soluble in water.

At one extreme, we have the white solid lithium chlorate, $LiClO_3$, which dissolves to the extent of 35 mol/L at room temperature. Mercury(II) sulfide, HgS, found in nature in the red mineral cinnabar, is at the other extreme. Its calculated solubility at 25°C is 10^{-26} mol/L. This means that, in principle at least, about 200 L of a solution of HgS would be required to contain a single pair of Hg^{2+} and S^{2-} ions.

Information on the solubility of common ionic solids in the form of a solubility diagram is given in Figure 4.2.

These rules are quite simple to interpret. For example, the following facts should be evident from Figure 4.2:

- $Ni(NO_3)_2$ is soluble. (All nitrates are soluble.)
- $CoCl_2$ is soluble. (It is not one of the three insoluble chlorides listed.)
- $PbCO_3$ is insoluble.

	NO_3^-	Cl^-	SO_4^{2-}	OH^-	CO_3^{2-}	PO_4^{3-}
Group 1 cations and NH_4^+						
Group 2 cations			$BaSO_4$	$Mg(OH)_2$		
Transition metal cations, Pb^{2+} and Hg_2^{2+}		$AgCl^*$ $PbCl_2^*$ $Hg_2Cl_2^*$	$PbSO_4$ Ag_2SO_4			

* The bromides and iodides of these cations are also insoluble.

Figure 4.2 Solubility chart for 0.1 *M* solutions of selected anions and cations. Choose the cation (row) and read across for the anion (column). If the block is white, no precipitate will form. If the block is shaded in green, a precipitate will form from dilute solution. Where a formula is shown, this is a cation-anion combination that will precipitate.

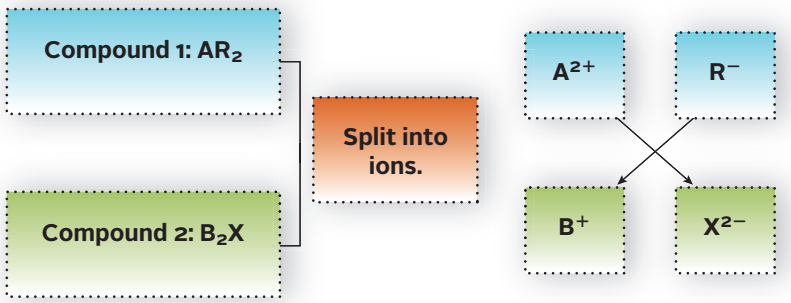

Figure 4.3 Partner-exchange reactions. The cation from a soluble compound joins with the anion from another soluble compound. The result may be no reaction, one precipitate, or two precipitates. In this figure, the possible precipitates are AX and/or BR.

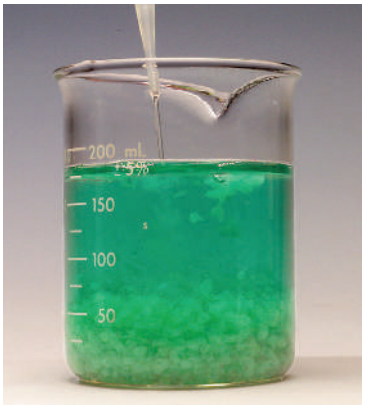

Figure 4.4 Precipitation of nickel hydroxide ($Ni(OH)_2$). The precipitate forms when solutions of nickel chloride ($NiCl_2$) and sodium hydroxide (NaOH) are mixed.

Sometimes when water solutions of two different ionic compounds are mixed, an insoluble solid separates out of solution. The **precipitate** (abbreviation: ppt) that forms is itself ionic; the cation comes from one solution, the anion from the other. To predict the occurrence of reactions of this type, you must know which ionic substances are insoluble in water.

The precipitation diagram shown in Figure 4.2 and the schematic diagram (Figure 4.3) enable you to determine whether or not a precipitate will form when dilute solutions of two ionic solutes are mixed. If a cation in solution 1 mixes with an anion in solution 2 to form an insoluble compound (colored squares), that compound will precipitate. Cation-anion combinations that lead to the formation of a soluble compound (white squares) will not give a precipitate. For example, if solutions of $NiCl_2$ (Ni^{2+}, Cl^- ions) and NaOH (Na^+, OH^- ions) are mixed (Figure 4.4)

- a precipitate of $Ni(OH)_2$, an insoluble compound, will form.
- NaCl, a soluble compound, will not precipitate.

EXAMPLE 4.1

Predict what will happen when the following pairs of dilute aqueous solutions are mixed.

(a) $Cu(NO_3)_2$ and $(NH_4)_2SO_4$ (b) $FeCl_3$ and $AgNO_3$

STRATEGY

1. Follow the schematic diagram in Figure 4.3.
2. Use the precipitation diagram (Figure 4.2) to determine whether or not the possible precipitates are soluble.

SOLUTION

(a) Ions in solution	Cu^{2+} and NO_3^- from $Cu(NO_3)_2$; NH_4^+ and SO_4^{2-} from $(NH_4)_2SO_4$
Possible precipitates	$CuSO_4$ and NH_4NO_3
Solubility	Both are soluble, no precipitate forms
(b) Ions in solution	Fe^{3+} and Cl^- from $FeCl_3$; Ag^+ and NO_3^- from $AgNO_3$
Possible precipitates	AgCl and $Fe(NO_3)_3$
Solubility	$Fe(NO_3)_3$ is soluble, AgCl is insoluble. AgCl precipitates.

Net Ionic Equations

The precipitation reaction that occurs when solutions of Na_2CO_3 and $CaCl_2$ are mixed (Figure 4.5) can be represented by a simple equation. To obtain that equation, consider the identity of the reactants and products:

To write a net ionic equation, you first have to identify the ions.

Reactants: Na^+, CO_3^{2-}, Ca^{2+}, and Cl^- ions in water solution:

$$2Na^+(aq) + CO_3^{2-}(aq) + Ca^{2+}(aq) + 2Cl^-(aq)$$

Products: solid $CaCO_3$, Na^+ and Cl^- ions remaining in solution:

$$2Na^+(aq) + 2Cl^-(aq) + CaCO_3(s)$$

The total ionic equation for the reaction is

$$2Na^+(aq) + CO_3^{2-}(aq) + Ca^{2+}(aq) + 2Cl^-(aq) \longrightarrow$$
$$2Na^+(aq) + 2Cl^-(aq) + CaCO_3(s)$$

Canceling out the ions that appear on both sides of the equation ($2Na^+$, $2Cl^-$), we obtain the final equation:

$$Ca^{2+}(aq) + CO_3^{2-}(aq) \longrightarrow CaCO_3(s)$$

An equation such as this that excludes **spectator ions**, which take no part in the reaction, is referred to as a **net ionic equation**. We will use net ionic equations throughout this chapter and indeed the entire text to represent a wide variety of reactions in water solution. Like all equations, net ionic equations must show

- ***atom balance.*** There must be the same number of atoms of each element on both sides. In the preceding equation, the atoms present on both sides are one calcium atom, one carbon atom, and three oxygen atoms.
- ***charge balance.*** There must be the same total charge on both sides. In this equation, the total charge is zero on both sides.

$$Ca^{2+}(aq) + CO_3^{2-}(aq) \longrightarrow CaCO_3(s)$$

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Figure 4.5 Precipitation of calcium carbonate ($CaCO_3$). The precipitate forms when solutions of sodium carbonate (Na_2CO_3) and calcium chloride ($CaCl_2$) are mixed.

Spectator ions are in solution before, during, and after reaction.

EXAMPLE 4.2

Write a net ionic equation for any precipitation reaction that occurs when dilute solutions of the following ionic compounds are mixed.

(a) NaOH and $Cu(NO_3)_2$ (b) $Ba(OH)_2$ and $MgSO_4$ (c) $(NH_4)_3PO_4$ and K_2CO_3

STRATEGY

1. Follow the plan:

   Figure 4.3: compound → ions → possible precipitates

   possible precipitates → (Figure 4.2) → insoluble compound → net ionic equation

2. In writing the net ionic equation, start with the insoluble compound on the right, then write the component ions on the left. Do not forget the physical states: ions (*aq*), product (*s*).

SOLUTION

(a) Ions in solution	Na^+ and OH^- from NaOH; Cu^{2+} and NO_3^- from $Cu(NO_3)_2$
Possible precipitates	$NaNO_3$ and $Cu(OH)_2$
Solubility	$NaNO_3$ is soluble; $Cu(OH)_2$ is insoluble.
Net ionic equation	$Cu^{2+}(aq) + 2OH^-(aq) \rightarrow Cu(OH)_2(s)$.
(b) Ions in solution	Ba^{2+} and OH^- from $Ba(OH)_2$; Mg^{2+} and SO_4^{2-} from $MgSO_4$
Possible precipitates	$Mg(OH)_2$ and $BaSO_4$
Solubility	Both $BaSO_4$ and $Mg(OH)_2$ are insoluble.
Net ionic equation	$Mg^{2+}(aq) + 2OH^-(aq) \rightarrow Mg(OH)_2(s)$ $Ba^{2+}(aq) + SO_4^{2-}(aq) \rightarrow BaSO_4(s)$
(c) Ions in solution	NH_4^+ and PO_4^{3-} from $(NH_4)_3PO_4$; K^+ and CO_3^{2-} from K_2CO_3
Possible precipitates	$(NH_4)_2CO_3$ and K_3PO_4
Solubility	Both $(NH_4)_2CO_3$ and K_3PO_4 are soluble.
Net ionic equation	no reaction

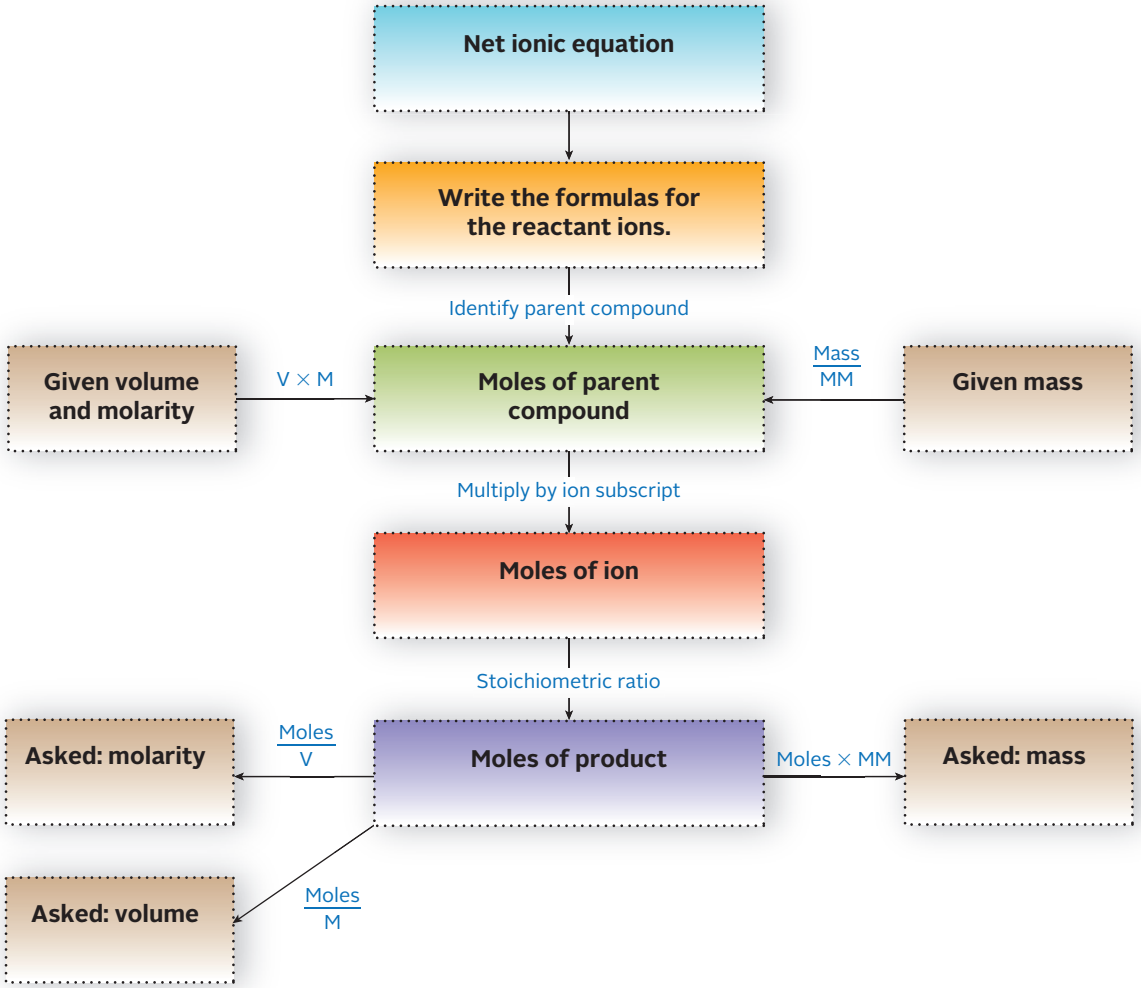

Figure 4.6 Flowchart for solution stoichiometry where the amount of product is asked. If the amount of reactant is needed, reverse the arrows and the operations. *V* is volume, *M* is molarity, and MM is molar mass.

Figure 4.7 Precipitation of iron(III) hydroxide ($Fe(OH)_3$). The red, gelatinous precipitate forms when aqueous solutions of sodium hydroxide (NaOH) and iron(III) nitrate ($Fe(NO_3)_3$) are mixed.

Although we have introduced net ionic equations to represent precipitation reactions, they have a much wider application. Indeed, we will use them for all kinds of reactions in water solution. In particular ***all of the chemical equations written throughout this chapter are net ionic equations.***

Stoichiometry

The approach followed in Chapter 3, with minor modifications, readily applies to the stoichiometry of solution reactions represented by net ionic equations.

An important consideration when solving these problems is that data are given about the parent compounds and not about the particular ions in the net ionic equation. After all, you do not have reagent bottles with labels that say 3*M* OH^- but rather 3*M* NaOH. Figure 4.6 shows how the modifications fit into the flowchart for the stoichiometry of solution reactions.

EXAMPLE 4.3 GRADED

When aqueous solutions of sodium hydroxide and iron(III) nitrate are mixed, a red precipitate forms (see Figure 4.7).

a Write a net ionic equation for the reaction.

ANALYSIS

Information given:	reactant compounds [NaOH and $Fe(NO_3)_3$]
Asked for:	net ionic equation

STRATEGY

1. Follow the schematic diagram in Figure 4.3 to determine possible precipitates.
2. Use the precipitation diagram (Figure 4.2) to determine whether the possible precipitates are soluble or insoluble.
3. Write the net ionic equation. Start with the product.

SOLUTION

1. Ions in solution	Na^+ and OH^- from NaOH; Fe^{3+} and NO_3^- from $Fe(NO_3)_3$
Possible precipitates	$Fe(OH)_3$ and $NaNO_3$
2. Solubility	$Fe(OH)_3$ is insoluble and forms a precipitate.
3. Net ionic equation	$Fe^{3+}(aq) + 3OH^-(aq) \rightarrow Fe(OH)_3(s)$

b What volume of 0.136 *M* iron(III) nitrate is required to produce 0.886 g of precipitate?

ANALYSIS

Information given:	net ionic equation from (a): [$Fe^{3+}(aq) + 3OH^-(aq) \rightarrow Fe(OH)_3(s)$] mass of precipitate (0.886 g); molarity of $Fe(NO_3)_3$ (0.136 *M*)
Information implied:	molarity of reacting ion, Fe^{3+} molar mass of precipitate
Asked for:	volume of $Fe(NO_3)_3$ used in the reaction

STRATEGY

Reverse the pathway shown in Figure 4.6.

mass $Fe(OH)_3 \rightarrow$ mol ppt $\rightarrow$ mol ion $\rightarrow$ mol of parent compound $\rightarrow$ *V* of parent compound

SOLUTION

mol $Fe(NO_3)_3$

$$0.886 \text{ g } Fe(OH)_3 \times \frac{1 \text{ mol } Fe(OH)_3}{106.87 \text{ g } Fe(OH)_3} \times \frac{1 \text{ mol } Fe^{3+}}{1 \text{ mol } Fe(OH)_3} \times \frac{1 \text{ mol } Fe(NO_3)_3}{1 \text{ mol } Fe^{3+}}$$

$$= 0.00829$$

$V_{Fe(NO_3)_3}$

$$V = \frac{\text{mol}}{M} = \frac{0.00829 \text{ mol}}{0.136 \text{ mol/L}} = 0.0610 \text{ L}$$

c How many grams of precipitate are formed when 50.00 mL of 0.200 *M* NaOH and 30.00 mL of 0.125 *M* $Fe(NO_3)_3$ are mixed?

ANALYSIS

Information given:	net ionic equation from (a): [$Fe^{3+}(aq) + 3OH^-(aq) \rightarrow Fe(OH)_3(s)$] volume (50.00 mL) and molarity (0.200 *M*) of NaOH volume (30.00 mL) and molarity (0.125 *M*) of $Fe(NO_3)_3$
Information implied:	number of moles of reacting ions, Fe^{3+} and OH^- Data for moles of both reactants is given, making this a limiting reactant problem.
Asked for:	mass of precipitate formed

continued

STRATEGY

1. Follow the pathway in Figure 4.6 for both NaOH and $Fe(NO_3)_3$ to obtain moles of precipitate formed.

   mol NaOH ($V \times M$) $\longrightarrow$ mol OH^- $\longrightarrow$ mol ppt mol $Fe(NO_3)_3$($V \times M$) $\longrightarrow$ mol Fe^{3+} $\longrightarrow$ mol ppt

2. Choose the smaller number of moles and convert moles to mass.

SOLUTION

1. mol ppt if NaOH limiting

$$0.0500\ \text{L} \times 0.200\ \frac{\text{mol NaOH}}{\text{L}} \times \frac{1\ \text{mol OH}^-}{1\ \text{mol NaOH}} \times \frac{1\ \text{mol Fe(OH)}_3}{3\ \text{mol OH}^-}$$
$$= 0.00333\ \text{mol Fe(OH)}_3$$

2. mol ppt if $Fe(NO_3)_3$ limiting

$$0.0300\ \text{L} \times 0.125\ \frac{\text{mol Fe(NO}_3)_3}{\text{L}} \times \frac{1\ \text{mol Fe}^{3+}}{1\ \text{mol Fe(NO}_3)_3} \times \frac{1\ \text{mol Fe(OH)}_3}{1\ \text{mol Fe}^{3+}}$$
$$= 0.00375\ \text{mol Fe(OH)}_3$$

3. Theoretical yield

   $0.00333 \text{ mol} < 0.00375 \text{ mol}$; 0.00333 mol $Fe(OH)_3$ is obtained

   $Fe(OH)_3$

$$0.00333\ \text{mol} \times \frac{106.87\ \text{g}}{1\ \text{mol}} = 0.356\ \text{g}$$

4-2 Acid-Base Reactions

You are probably familiar with a variety of aqueous solutions that are either acidic or basic (Figure 4.8). An **acidic solution** has a sour taste and affects the color of certain organic dyes known as acid-base indicators. For example, litmus turns from blue to red in acidic solution. A **basic solution** has a slippery feeling and changes the colors of indicators (e.g., red to blue for litmus).

The species that give these solutions their characteristic properties are called acids and bases. In this chapter, we use the definitions first proposed by Svante Arrhenius more than a century ago.

An* Arrhenius acid *is a species that produces H^+ ions in water solution.
An* Arrhenius base *is a species that produces OH^- ions in water solution.

We will consider more general definitions of acids and bases in Chapter 13.

Strong and Weak Acids and Bases

There are two types of acids, strong and weak, which differ in the extent of their ionization in water. A **strong acid** ionizes completely, forming H^+ ions and anions. A typical strong acid is HCl. It undergoes the following reaction on addition to water:

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

In a solution prepared by adding 0.1 mol of HCl to water, there is 0.1 mol of H^+ ions, 0.1 mol of Cl^- ions, and no HCl molecules. There are six common strong acids, whose names and formulas are listed in Table 4.1.

All acids other than those listed in Table 4.1 can be taken to be weak. A **weak acid** is only partially ionized to H^+ ions in water. All of the weak acids considered in this chapter are molecules containing an ionizable hydrogen atom. Their general formula can be represented as HB; the general ionization reaction in water is

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

Figure 4.8 Acidic and basic household solutions. Many common household items, including vinegar, orange juice, and cola drinks, are acidic. In contrast, baking soda and most detergents and cleaning agents are basic.

Table 4.1 Common Strong Acids and Bases

Acid	Name of Acid	Base	Name of Base
HCl	Hydrochloric acid	LiOH	Lithium hydroxide
HBr	Hydrobromic acid	NaOH	Sodium hydroxide
HI	Hydriodic acid	KOH	Potassium hydroxide
HNO_3	Nitric acid	$Ca(OH)_2$	Calcium hydroxide
$HClO_4$	Perchloric acid	$Sr(OH)_2$	Strontium hydroxide
H_2SO_4	Sulfuric acid	$Ba(OH)_2$	Barium hydroxide

Sulfuric acid ionization: $H_2SO_4(aq) \longrightarrow H^+(aq) + HSO_4^-(aq)$.

The double arrow implies that this reaction does not go to completion. Instead, a mixture is formed containing significant amounts of both products and reactants. With the weak acid hydrogen fluoride

$$HF(aq) \rightleftharpoons H^+(aq) + F^-(aq)$$

a solution prepared by adding 0.1 mol of HF to a liter of water contains about 0.01 mol of H^+ ions, 0.01 mol of F^- ions, and 0.09 mol of HF molecules.

Like HCl, HBr, and HI, HF has a halogen bonded to a hydrogen atom. Unlike the three other acids, HF is a weak acid. The others are strong acids.

Bases, like acids, are classified as strong or weak. A **strong base** in water solution is completely ionized to OH^- ions and cations. As you can see from Table 4.1, the strong bases are the hydroxides of the Group 1 and Group 2 metals. These are typical ionic solids, completely ionized both in the solid state and in water solution. The equations written to represent the processes by which NaOH and $Ca(OH)_2$ dissolve in water are

$$NaOH(s) \longrightarrow Na^+(aq) + OH^-(aq)$$
$$Ca(OH)_2(s) \longrightarrow Ca^{2+}(aq) + 2OH^-(aq)$$

In a solution prepared by adding 0.1 mol of NaOH to water, there is 0.1 mol of Na^+ ions, 0.1 mol of OH^- ions, and no NaOH molecules.

A **weak base** produces OH^- ions in a quite different manner. It reacts with H_2O molecules, acquiring H^+ ions and leaving OH^- ions behind. The reaction of ammonia, NH_3, is typical:

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

As with all weak bases, this reaction does not go to completion. In a solution prepared by adding 0.1 mol of ammonia to a liter of water, there is about 0.001 mol of NH_4^+, 0.001 mol of OH^-, and nearly 0.099 mol of NH_3.

Figure 4.9 Methylamine, CH_3NH_2

A common class of weak bases consists of the organic molecules known as *amines*. An **amine** can be considered to be a derivative of ammonia in which one or more hydrogen atoms have been replaced by hydrocarbon groups.

A hydrocarbon group has a string of C and H atoms.

In the simplest case, methylamine (Figure 4.9), a hydrogen atom is replaced by a $—CH_3$ group to give the CH_3NH_2 molecule, which reacts with water in a manner very similar to NH_3:

$$CH_3NH_2(aq) + H_2O \rightleftharpoons CH_3NH_3^+(aq) + OH^-(aq)$$

As we have pointed out, strong acids and bases are completely ionized in water. As a result, compounds such as HCl and NaOH are strong electrolytes like NaCl. In contrast, molecular weak acids and weak bases are poor conductors because their water solutions contain relatively few ions. Hydrofluoric acid and ammonia are commonly described as *weak electrolytes*.

Equations for Acid-Base Reactions

When an acidic water solution is mixed with a basic water solution, an acid-base reaction takes place. The nature of the reaction and hence the equation written for it depend on whether the acid and base involved are strong or weak.

You need to know the strong acids and bases to work with acid-base reactions.

1. ***Strong acid–strong base.*** Consider what happens when a solution of a strong acid such as HNO_3 is added to a solution of a strong base such as NaOH. Because HNO_3 is a strong acid, it is completely converted to H^+ and NO_3^- ions in solution. Similarly, with the strong base NaOH, the solution species are the Na^+ and OH^- ions. When the solutions are mixed, the H^+ and OH^- ions react with each other to form H_2O molecules. This reaction, referred to as **neutralization,** is represented by the net ionic equation

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

The Na^+ and NO_3^- ions take no part in the reaction and so do not appear in the equation. Here again, we are dealing with "spectator ions."

There is considerable evidence to indicate that the neutralization reaction occurs when any strong base reacts with any strong acid in water solution. It follows that the neutralization equation written above applies to any strong acid–strong base reaction.

When $HClO_4$ reacts with $Ca(OH)_2$, the equation is $H^+(aq) + OH^-(aq) \longrightarrow H_2O$.

2. ***Weak acid–strong base.*** When a strong base such as NaOH is added to a solution of a weak acid, HB, a two-step reaction occurs. The first step is the ionization of the HB molecule to H^+ and B^- ions; the second is the neutralization of the H^+ ions produced in the first step by the OH^- ions of the NaOH solution.

$$(1)\ HB(aq) \rightleftharpoons H^+(aq) + B^-(aq)$$
$$(2)\ H^+(aq) + OH^-(aq) \longrightarrow H_2O$$

The equation for the overall reaction is obtained by adding the two equations just written and canceling H^+ ions:

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

When an acid is weak, like HF, its formula appears in the equation.

For the reaction between solutions of sodium hydroxide and hydrogen fluoride, the net ionic equation is

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

Here, as always, spectator ions such as Na^+ are not included in the net ionic equation.

3. ***Strong acid–weak base.*** As an example of a reaction of a strong acid with a weak base, consider what happens when an aqueous solution of a strong acid like HCl is added to an aqueous solution of ammonia, NH_3. Again, we consider the reaction to take place in two steps. The first step is the reaction of NH_3 with H_2O to form NH_4^+ and OH^- ions. Then, in the second step, the H^+ ions of the strong acid neutralize the OH^- ions formed in the first step.

$$(1)\ NH_3(aq) + H_2O \rightleftharpoons NH_4^+(aq) + OH^-(aq)$$
$$(2)\ H^+(aq) + OH^-(aq) \longrightarrow H_2O$$

The overall equation is obtained by summing those for the individual steps. Canceling species (OH^-, H_2O) that appear on both sides, we obtain the net ionic equation

When a base is weak, like NH_3, its formula appears in the equation.

$$H^+(aq) + NH_3(aq) \longrightarrow NH_4^+(aq)$$

In another case, for the reaction of a strong acid such as HNO_3 with methylamine, CH_3NH_2, the net ionic equation is

$$H^+(aq) + CH_3NH_2(aq) \longrightarrow CH_3NH_3^+(aq)$$

Table 4.2 Types of Acid-Base Reactions

Reactants	Reacting Species	Net Ionic Equation
Strong acid–strong base	$H^+ - OH^-$	$H^+(aq) + OH^-(aq) \longrightarrow H_2O$
Weak acid–strong base	$HB - OH^-$	$HB(aq) + OH^-(aq) \longrightarrow H_2O + B^-(aq)$
Strong acid–weak base	$H^+ - B$	$H^+(aq) + B(aq) \longrightarrow BH^+(aq)$

Table 4.2 summarizes the equations written for the three types of acid-base reactions just discussed. Figure 4.10 visually illustrates the process of determining whether a compound is an acid (strong or weak) or a base (strong or weak) and the nature of the **reacting species**. You should find both Table 4.2 and Figure 4.10 useful in writing the equations called for in Example 4.4.

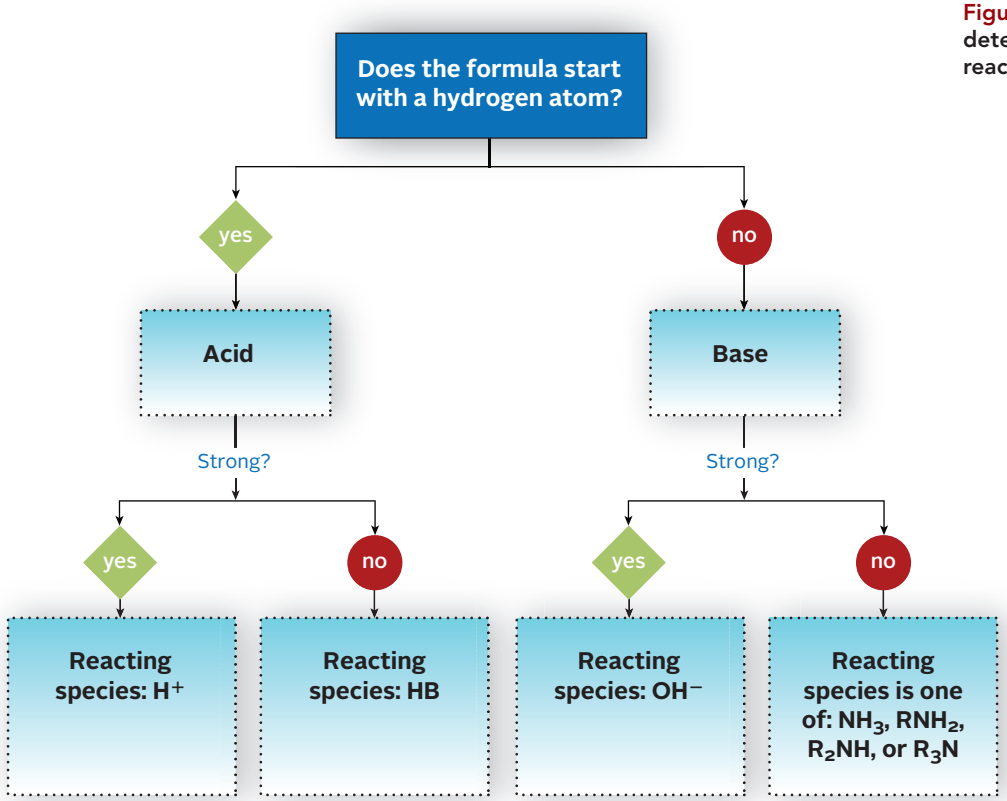

Figure 4.10 Flowchart for determining net ionic equations for reactions between acids and bases.

EXAMPLE 4.4

Write a net ionic equation for each of the following reactions in dilute water solution.

(a) Hypochlorous acid (HClO) and barium hydroxide.

(b) Ammonia with sulfuric acid (H_2SO_4).

(c) Hydrobromic acid (HBr) with potassium hydroxide.

STRATEGY

1. Determine the nature of the compound (acid or base; strong or weak) and its reacting species. (Table 4.1 and Figure 4.10 are helpful.)
2. Recall Table 4.2 and write a net ionic equation for the acid-base reaction.

continued

SOLUTION	
(a) Nature of the compounds	$HClO$: weak acid; $Ba(OH)_2$: strong base
reacting species	For $HClO$: $HClO$; for $Ca(OH)_2$: OH^-
net ionic equation	$HClO(aq) + OH^-(aq) \rightarrow ClO^-(aq) + H_2O$
(b) Nature of the compounds	$HClO_4$: strong acid; NH_3: weak base
reacting species	For $HClO_4$: H^+; for NH_3: NH_3
net ionic equation	$H^+(aq) + NH_3(aq) \rightarrow NH_4^+(aq)$
(c) Nature of the compounds	HBr: strong acid; KOH: strong base
reacting species	For HBr: H^+; for KOH: OH^-
net ionic equation	$H^+(aq) + OH^-(aq) \rightarrow H_2O$
END POINT	
Note that there are $2OH^-$ ions in $Ba(OH)_2$, and $2H^+$ ions in H_2SO_4. However, in the balanced equation, you use only one H^+ and one OH^- ion.	

Acid-Base Titrations

Acid-base reactions in water solution are commonly used to determine the concentration of a dissolved species or its percentage in a solid mixture. This is done by carrying out a **titration,** measuring the volume of a *standard solution* (a solution of known concentration) required to react with a measured amount of sample.

The experimental setup for a titration is shown in Figure 4.11. The flask contains vinegar, a water solution of a weak organic acid called acetic acid. A solution of sodium hydroxide of known concentration is added from a buret. The net ionic equation for the acid-base reaction that occurs is

$$HC_2H_3O_2(aq) + OH^-(aq) \longrightarrow C_2H_3O_2^-(aq) + H_2O$$

The objective of the titration is to determine the point at which reaction is complete, called the **equivalence point.** This is reached when the number of moles of

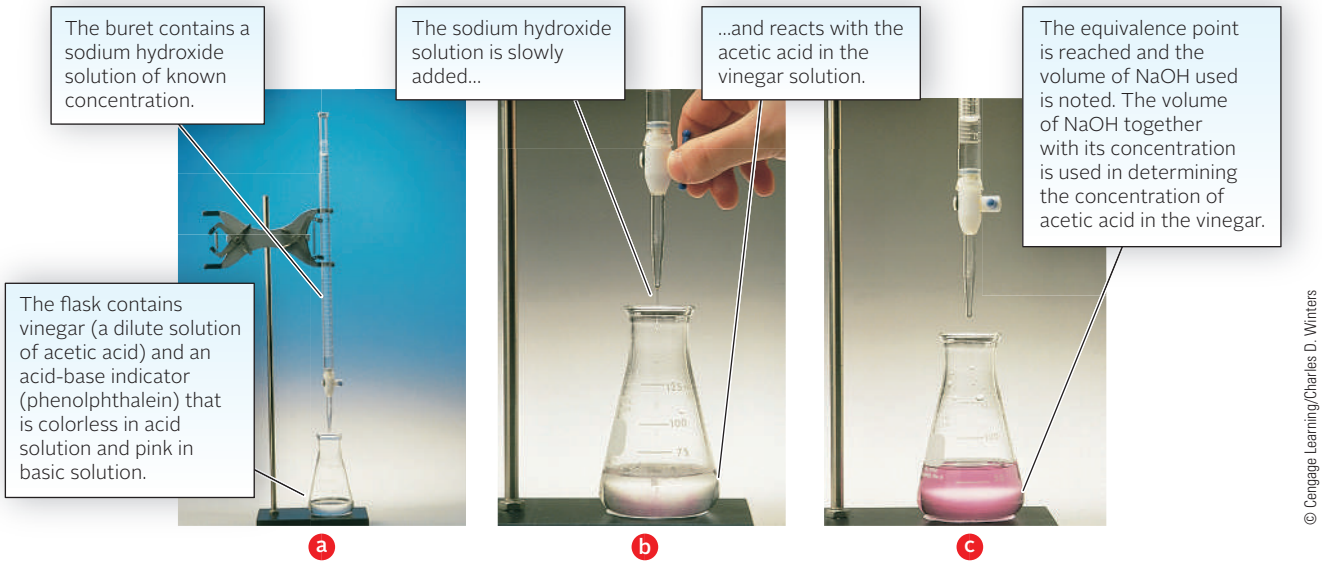

Figure 4.11 Titration of vinegar with sodium hydroxide (NaOH).

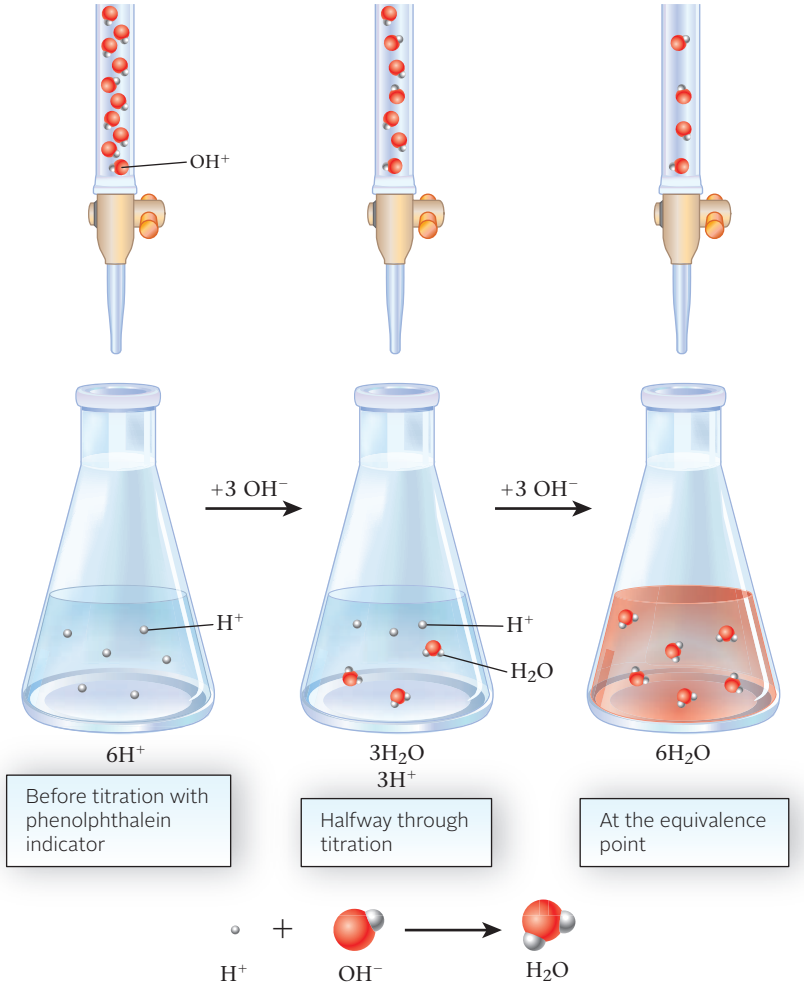

Figure 4.12 **A molecular view of an acid-base titration.**

OH^- added is exactly equal to the number of moles of acetic acid, $HC_2H_3O_2$, originally present. To determine this point, a single drop of an *acid-base indicator* such as phenolphthalein is used. It should change color (colorless to pink) at the equivalence point.

A molecular diagram for the titration of NaOH and HCl is shown in Figure 4.12. For simplicity, only the reacting species (H^+ and OH^-) are shown. The spectator ions (Na^+ and Cl^-) and water molecules in solution are not.

EXAMPLE 4.5 GRADED

Consider the weak acid H_2X. It is titrated with NaOH.

a Write a net ionic equation for the reaction.

STRATEGY

1. Determine the nature of the compound (acid or base; strong or weak) and its reacting species. (Table 4.1 and Figure 4.10 are helpful.)
2. Recall Table 4.2 and write a net ionic equation for the acid-base reaction.

SOLUTION

1. Nature of the compounds	H_2X—weak acid; NaOH—strong base
2. reacting species	For $H_2X - H_2X$; for $NaOH - OH^-$
3. net ionic equation	$H_2X(aq) + 2OH^-(aq) \rightarrow X^{2-}(aq) + 2H_2O$

continued

b What is the molarity of H_2X if 29.45 mL of 0.187 *M* NaOH are required to neutralize 15.00 mL of H_2X?

ANALYSIS

Information given:	Volume (29.45 mL) and molarity (0.187 *M*) of NaOH Volume (15.00 mL) of H_2X
Information implied:	stoichiometric ratio; reacting species Net ionic equation [$H_2X(aq) + 2OH^-(aq) \rightarrow 2H_2O + X^{2-}(aq)$]
Asked for:	Molarity of H_2X

STRATEGY

1. Use the stoichiometric ratio: 2 mol OH^-/1 mol H_2X
2. Follow the flowchart in Figure 4.6.

   H_2X does not break up into ions. Skip the moles parent compound → moles ion step for H_2X.

$$\text{mol NaOH} \xrightarrow{V \times M} \text{mol } OH^- \xrightarrow[\text{ratio}]{\text{stoichiometric}} \text{mol } H_2X \xrightarrow{n \div V} \text{molarity of } H_2X$$

SOLUTION

mol H_2X	$0.02945\ \text{L} \times 0.187 \dfrac{\text{mol NaOH}}{\text{L}} \times \dfrac{1\ \text{mol } OH^-}{1\ \text{mol NaOH}} \times \dfrac{1\ \text{mol } H_2X}{2\ \text{mol } OH^-} = 0.002754$
molarity of H_2X used	$M = n \div V = \dfrac{0.002754\ \text{mol}}{0.01500\ \text{L}} = 0.1836\ M$

c What is the molar mass of H_2X if 29.45 mL of 0.187 *M* NaOH are required to neutralize a solution prepared by adding 0.242 g of H_2X to enough water to make 25.00 mL of solution?

ANALYSIS

Information given:	Volume (29.45 mL) and molarity (0.187 *M*) of NaOH Mass (0.242 g) of H_2X Volume (25.00 mL) of water
Information implied:	stoichiometric ratio Net ionic equation [$H_2X(aq) + 2OH^-(aq) \rightarrow 2H_2O + X^{2-}(aq)$]
Asked for:	Molar mass of H_2X

STRATEGY

1. Use the stoichiometric ratio: 2 mol OH^-/1 mol H_2X
2. Follow the flowchart in Figure 4.6.

   H_2X does not break up into ions. Skip the moles parent compound → moles ion step for H_2X.

$$\text{mol NaOH} \xrightarrow{V \times M} \text{mol } OH^- \longrightarrow \text{mol NaOH} \xrightarrow[\text{ratio}]{\text{stoichiometric}} \text{mol } H_2X \xrightarrow{\text{mass} \div n} \text{MM of } H_2X$$

SOLUTION

mol H_2X	$0.02945\ \text{L} \times 0.187 \dfrac{\text{mol NaOH}}{\text{L}} \times \dfrac{1\ \text{mol } OH^-}{1\ \text{mol NaOH}} \times \dfrac{1\ \text{mol } H_2X}{2\ \text{mol } OH^-} = 0.002754$
molar mass of H_2X	$\text{MM} = \text{mass} \div n = \dfrac{0.242\ \text{g}}{0.002754\ \text{mol}} = 87.9\ \text{g/mol}$

END POINTS

1. You need to figure out the number of moles before you can calculate mass, molar mass, volume, or molarity.
2. The amount of water added to the solid H_2X is irrelevant to the solution of the problem.

CHEMISTRY THE **HUMAN** SIDE

For reasons that are by no means obvious, Sweden produced a disproportionate number of outstanding chemists in the eighteenth and nineteenth centuries. Jöns Jakob Berzelius (1779–1848) determined with amazing accuracy the atomic masses of virtually all the elements known in his time. In his spare time, he invented such modern laboratory tools as the beaker, the flask, the pipet, and the ringstand.

Svante Arrhenius, like Berzelius, was born in Sweden and spent his entire professional career there. According to Arrhenius, the concept of strong and weak acids and bases came to him on May 13, 1883, when he was 24 years old. He added, "I could not sleep that night until I had worked through the entire problem."

Almost exactly one year later, Arrhenius submitted his Ph.D. thesis at the University of Uppsala. He proposed that salts, strong acids, and strong bases are completely ionized in dilute water solution. Today, it seems quite reasonable that solutions of NaCl, HCl, and NaOH contain, respectively, Na^+ and Cl^- ions, H^+ and Cl^- ions, and Na^+ and OH^- ions. It did not seem nearly so obvious to the chemistry faculty at Uppsala in 1884. Arrhenius's dissertation received the lowest passing grade "approved without praise."

Arrhenius sent copies of his Ph.D. thesis to several well-known chemists in Europe and America. Most ignored his ideas; a few were openly hostile. A pair of young chemists gave positive responses: Jacobus van't Hoff (1852–1911) (age 32) at Amsterdam (Holland) and Wilhelm Ostwald (1853–1932) (also 32) at Riga (Latvia). For some years, these three young men were referred to, somewhat disparagingly, as "ionists" or "ionians." As time passed, the situation changed. The first Nobel Prize in chemistry was awarded to van't Hoff in 1901. Two years later, in 1903, Arrhenius became a Nobel laureate; Ostwald followed in 1909.

courtesy of the Nobel Foundation

Svante August Arrhenius
(1859–1927)

Among other contributions of Arrhenius, the most important were probably in chemical kinetics (Chapter 11). In 1889 he derived the relation for the temperature dependence of reaction rate. In quite a different area, in 1896 Arrhenius published an article, "On the Influence of Carbon Dioxide in the Air on the Temperature of the Ground." He presented the basic idea of the greenhouse effect, discussed in Chapter 16.

In his later years, Arrhenius turned his attention to popularizing chemistry. He wrote several different textbooks that were well received. In 1925, under pressure from his publisher to submit a manuscript (publishers are like that), Arrhenius started getting up at 4 A.M. to write. As might be expected, rising at such an early hour had an adverse effect on his health. Arrhenius suffered a physical breakdown in 1925, from which he never really recovered, dying two years later.

4-3 Oxidation-Reduction Reactions

Another common type of reaction in aqueous solution involves a transfer of electrons between two species. Such a reaction is called an oxidation-reduction or **redox reaction.** Many familiar reactions fit into this category, including the reaction of metals with acid.

In a redox reaction, one species *loses* (i.e., donates) electrons and is said to be *oxidized*. The other species, which *gains* (or receives) electrons, is *reduced*. To illustrate, consider the redox reaction that takes place when zinc pellets are added to hydrochloric acid (Figure 4.13). The net ionic equation for the reaction is

$$Zn(s) + 2H^+(aq) \longrightarrow Zn^{2+}(aq) + H_2(g)$$

This equation can be split into two **half-equations,** one of oxidation and the other of reduction. Zinc atoms are oxidized to Zn^{2+} ions by losing electrons. The oxidation half-equation is

$$\textit{oxidation:} \qquad Zn(s) \longrightarrow Zn^{2+}(aq) + 2e^-$$

At the same time, H^+ ions are reduced to H_2 molecules by gaining electrons; the reduction half-equation is

$$\textit{reduction:} \qquad 2H^+(aq) + 2e^- \longrightarrow H_2(g)$$

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Figure 4.13 Redox reaction of zinc with a strong acid. The zinc atoms are oxidized to Zn^{2+} ions in solution; the H^+ ions are reduced to H_2 molecules.

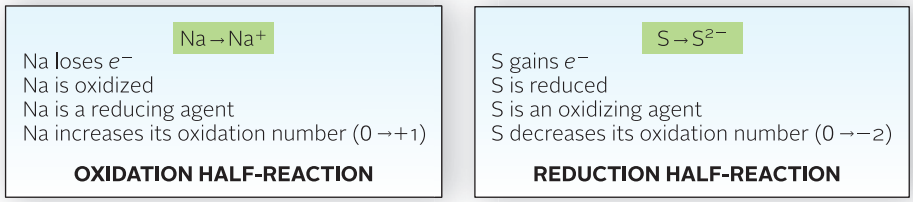

Figure 4.14 Summary of occurrences in oxidation and reduction half-reactions.

From this example, it should be clear that—

- ***oxidation and reduction occur together*** in the same reaction; you can't have one without the other.
- ***there is no net change in the number of electrons in a redox reaction.*** Those given off in the oxidation half-reaction are taken on by another species in the reduction half-reaction.

In earlier sections of this chapter, we showed how to write and balance equations for precipitation reactions (Section 4.1) and acid-base reactions (Section 4.2). We will show you how to balance redox reactions in Chapter 17. In this section we will identify the species oxidized or reduced, oxidizing or reducing agents, and oxidation and reduction half-reactions. Figure 4.14 summarizes this new terminology. To do that, it is convenient to introduce a new concept, oxidation number.

Oxidation Number

The concept of **oxidation number** is used to simplify the electron bookkeeping in redox reactions. For a monatomic ion (e.g., Na^+, S^{2-}), the oxidation number is, quite simply, the charge of the ion (+1, −2). In a molecule or polyatomic ion, the oxidation number of an element is a "pseudo-charge" obtained in a rather arbitrary way, assigning bonding electrons to the atom with the greater attraction for electrons.

In practice, oxidation numbers in all kinds of species are assigned according to a set of arbitrary rules:

1. ***The oxidation number of an element in an elementary substance is 0*** *(*Figure 4.15*).*
   Example: The oxidation number for chlorine in Cl_2 and for phosphorus in P_4 is 0.
2. ***The oxidation number of an element in a monoatomic ion is equal to the charge of that ion.***
   Example: The oxidation number for chlorine in Cl^- is −1; for sodium in Na^+ it is +1.
3. ***Certain elements (we will call them "leading elements") have the same oxidation number in all their compounds.***
   Group 1 elements always have an oxidation number of +1.
   Group 2 elements always have an oxidation number of +2.
   Fluorine (F) always has an oxidation number of −1.
4. ***Hydrogen in a compound has an oxidation number of +1, unless it is combined with a metal, in which case it is −1.***
   Example: The oxidation number for hydrogen in HCl is +1; for hydrogen in NaH it is −1.
5. ***The sum of the oxidation numbers in a neutral species is 0 and in a polyatomic ion is equal to the charge of the ion.***
   Examples:
   (a) To determine the oxidation number of P in PH_3, use the fact that H has an oxidation number of +1 (since it is combined with P, a nonmetal) and solve algebraically using the above rule. Note that there are 3 H atoms, each with an oxidation number of +1. We will call the oxidation number of P, x.
   $3(+1) + x = 0$; $x = -3$. The oxidation number for P in PH_3 is −3.

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Figure 4.15 Rusting and oxidation number. As iron rusts, its oxidation number changes from 0 in Fe(s) to +3 in Fe^{3+}.

(b) To determine the oxidation number of N in NH_4^+, use the fact that H has an oxidation number of +1 (since it is combined with N, a nonmetal) and solve algebraically using the above rule. Note that there are 4 H atoms, each with an oxidation number of +1. We will call the oxidation number of N, *y*.

$4(+1) + y = -1$; $y = -3$. The oxidation number for N in NH_4^+ is −3.

6. ***Oxygen in a compound has an oxidation number of −2, unless it is combined with a Group 1 metal (always +1) or Group 2 metal (always +2). Solve algebraically*** ***for the oxidation number of oxygen.***

Examples:

(a) The oxidation number (O.N.) for oxygen in Na_2O is

$$2(+1) + \text{O.N. O} = 0;\ \text{O.N. O} = -2$$

(b) The oxidation number (O.N.) for oxygen in Na_2O_2 is

$$2(+1) + 2(\text{O.N. O}) = 0;\ \text{O.N. O} = -1$$

(c) The oxidation number (O.N.) for oxygen in NaO_2 is

$$+1 + 2(\text{O.N. O}) = 0;\ \text{O.N. O} = -1/2$$

Oxidation numbers are calculated, not determined experimentally.

Figure 4.16 (page 90) shows you how to use these rules in the form of a flowchart. The application of these rules is illustrated in Example 4.6.

EXAMPLE 4.6

Assign an oxidation number (O.N.) to each element in the following species:

(a) N_2 (b) N^{3-} (c) NO_3^- (d) BaO (e) K_2O_2

SOLUTION

(a) N_2 is in its elementary state. (Rule 1)	O.N. N = 0
(b) N^{3-} is a monoatomic ion. (Rule 2)	O.N. N = −3
(c) There are no Group 1 or Group 2 metals. (Rule 6)	O.N. O = −2
NO_3^- is a polyatomic ion. (Rule 5)	$3(-2) + x = -1$; O.N. N = +5
(d) Ba is a Group 2 metal. (Rule 3)	O.N. Ba = +2
The sum of the oxidation numbers is 0. (Rule 5)	$+2 + x = 0$; O.N. O = −2
(e) K is a Group 1 metal. (Rule 3)	O.N. K = +1
The sum of the oxidation numbers is 0. (Rule 5)	$2(1) + 2x = 0$; O.N. O = −1

END POINT

Always look for the "leading elements" (Group 1 and Group 2 metals and F) in a compound when you start. These elements will lead you to the oxidation numbers of the other elements in the compound. If these leading elements are not present, then look for H and O (+1 and −2, respectively, when not combined with Group 1 or 2 metals).

The concept of oxidation number leads directly to a working definition of the terms oxidation and reduction. **Oxidation** is defined as ***an increase in oxidation number and*** **reduction** ***as a decrease in oxidation number.*** Consider once again the reaction of zinc with a strong acid:

$$Zn(s) + 2H^+(aq) \longrightarrow Zn^{2+}(aq) + H_2(g)$$

Zn is oxidized (O.N.: $0 \longrightarrow +2$)
H^+ is reduced (O.N.: $+1 \longrightarrow 0$)

These definitions are of course compatible with the interpretation of oxidation and reduction in terms of loss and gain of electrons. An element that loses electrons

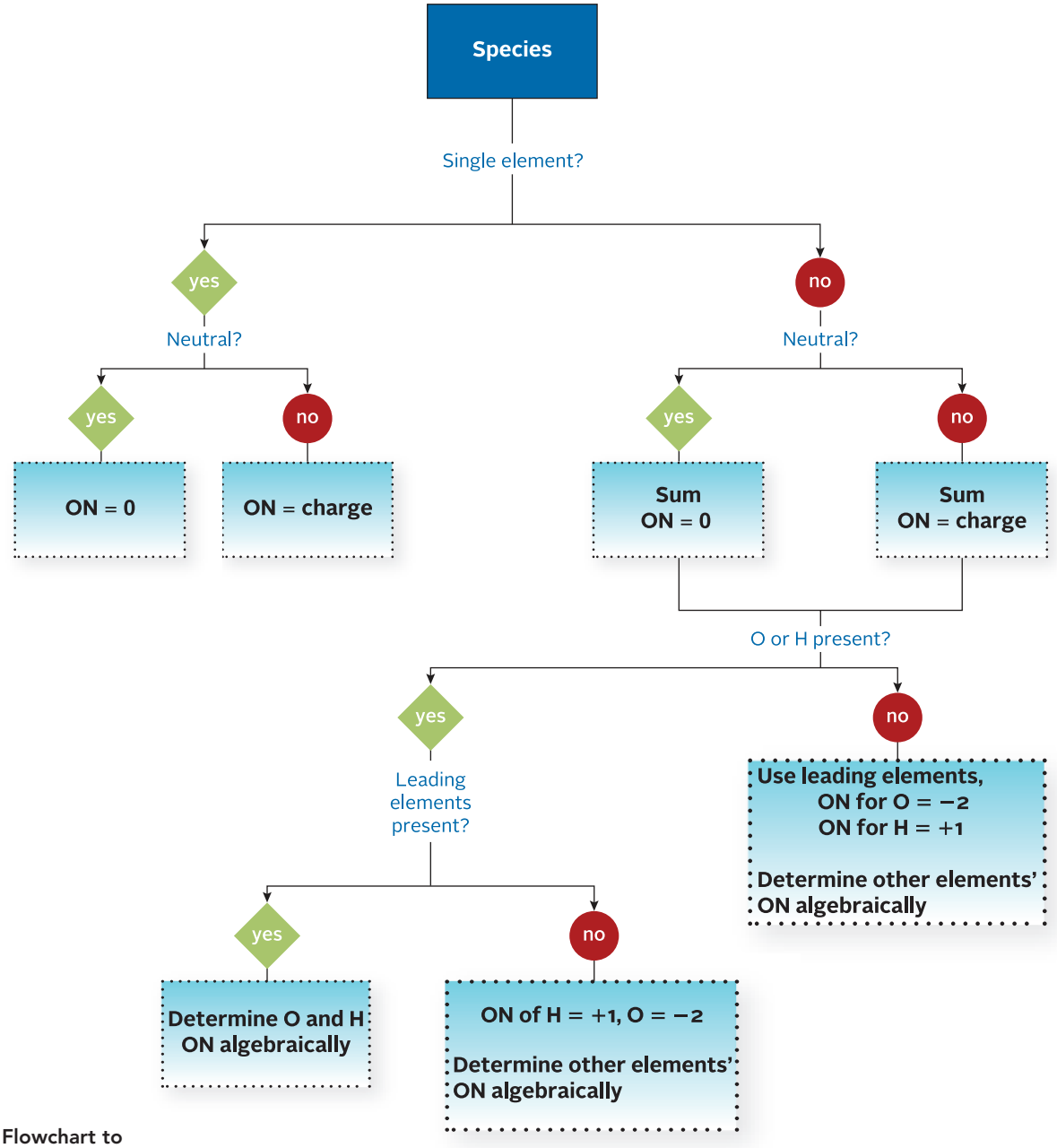

Figure 4.16 Flowchart to determine oxidation number. Leading elements ON are Group 1 = +1, Group 2 = +2, F = −1. (ON in the figure stands for oxidation number.)

must increase in oxidation number. The gain of electrons always results in a decrease in oxidation number.

An easy way to recognize a redox equation is to note changes in oxidation number of two different elements. The net ionic equation

$$2Al(s) + 3Cu^{2+}(aq) \longrightarrow 2Al^{3+}(aq) + 3Cu(s)$$

must represent a redox reaction because aluminum increases in oxidation number, from 0 to +3, and copper decreases from +2 to 0. In contrast, the reaction

$$CO_3^{2-}(aq) + 2H^+(aq) \longrightarrow CO_2(g) + H_2O$$

is not of the redox type because each element has the same oxidation number in both reactants and products: for O it is −2, for H it is +1, and for C it is +4.

The two species that exchange electrons in a redox reaction are given special names. The ion or molecule that accepts electrons is called the **oxidizing agent;** by

accepting electrons it brings about the oxidation of another species. Conversely, the species that donates electrons is called the **reducing agent;** when reaction occurs it reduces the other species.

The oxidizing agent is reduced; the reducing agent is oxidized.

To illustrate these concepts consider the reaction

$$Zn(s) + 2H^+(aq) \longrightarrow Zn^{2+}(aq) + H_2(g)$$

The H^+ ion is the oxidizing agent; it brings about the oxidation of zinc. By the same token, zinc acts as a reducing agent; it furnishes the electrons required to reduce H^+ ions.

Metallic elements taking part in redox reactions, such as zinc in the reaction above, commonly act as reducing agents; they are oxidized to cations such as Zn^{2+}. Other reducing agents include hydrogen gas, which can be oxidized to H^+ ions:

$$H_2(g) \longrightarrow 2H^+(aq) + 2e^-$$

and a few cations such as Fe^{2+} that can be oxidized to a higher state:

$$Fe^{2+}(aq) \longrightarrow Fe^{3+}(aq) + e^-$$

Nonmetallic elements frequently act as oxidizing agents, being reduced to the corresponding anions:

$$Cl_2(g) + 2e^- \longrightarrow 2Cl^-(aq)$$
$$S(s) + 2e^- \longrightarrow S^{2-}(aq)$$

The equations shown above are called half-reactions. They are *not* complete redox reactions.

EXAMPLE 4.7

Consider the following redox equation:

$$Cr^{3+}(aq) + H_2O_2(aq) \rightarrow 2H_2O + Cr_2O_7^{2-}(aq)$$

(a) Identify the element oxidized and the element reduced.

(b) What are the oxidizing and reducing agents?

STRATEGY

1. Determine the oxidation number of each element.
2. Find elements whose oxidation numbers change.

SOLUTION

Oxidation numbers	Cr: +3; H: +1; O: −1 → H: +1; O: −2; Cr: +6
Change	Cr: +3 → +6 (increase)
	O: −1 → −2 (decrease)
Element reduced	O (decrease in oxidation number)
Element oxidized	Cr (increase in oxidation number)
Oxidizing agent	H_2O_2 (It is the species that contains the element that is reduced.)
Reducing agent	$Cr_2O_7^{2-}$ (It is the species that contains the element that is oxidized.)

Stoichiometric calculations for redox reactions in water solution are carried out in much the same way as those for precipitation reactions (Example 4.3) or acid-base reactions (Example 4.5).

EXAMPLE 4.8

Consider the balanced equation for the reaction between iron(II) and permanganate ions in acidic solution:

$$MnO_4^-(aq) + 5Fe^{2+}(aq) + 8H^+(aq) \rightarrow 5Fe^{3+}(aq) + Mn^{2+}(aq) + 4H_2O$$

What volume of 0.684 *M* $KMnO_4$ solution is required to completely react with 27.50 mL of 0.250 *M* $Fe(NO_3)_2$ (Figure 4.17)?

ANALYSIS

Information given:	*V* (27.50 mL) and *M* (0.250) of $Fe(NO_3)_2$ *M* (0.684) of $KMnO_4$
Information implied:	reacting species; stoichiometric ratios
Asked for:	volume of $KMnO_4$

STRATEGY

Follow the flowchart shown in Figure 4.6.

$V \times M \rightarrow$ mol parent $\rightarrow$ mol ion $\rightarrow$ mol ion $\rightarrow$ mol parent $\rightarrow V \times M$

SOLUTION

1. Parent $\rightarrow$ ion

$Fe(NO_3)_2$ (parent) $\rightarrow Fe^{2+}$ (ion)
$KMnO_4$ (parent) $\rightarrow MnO_4^-$ (ion)

2. mol $Fe(NO_3)_2$

$$V \times M = (0.02750\ \text{L})(0.250\ \text{mol/L}) = 0.00688$$

3. mol Fe^{2+}

$$0.00688\ \text{mol } Fe(NO_3)_2 \times \frac{1\ \text{mol } Fe^{2+}}{1\ \text{mol } Fe(NO_3)_2} = 0.00688$$

4. mol MnO_4^-

$$0.00688\ \text{mol } Fe^{2+} \times \frac{1\ \text{mol } MnO_4^-}{5\ \text{mol } Fe^{2+}} = 0.00138$$

5. mol $KMnO_4$

$$0.00138\ \text{mol } MnO_4^- \times \frac{1\ \text{mol } KMnO_4}{1\ \text{mol } MnO_4^-} = 0.00138$$

6. *V* $KMnO_4$

$$\text{moles} = V \times M;\ V = \frac{0.00138\ \text{mol}}{0.684\ \text{mol/L}} = 0.00202\ \text{L} = 2.02\ \text{mL}$$

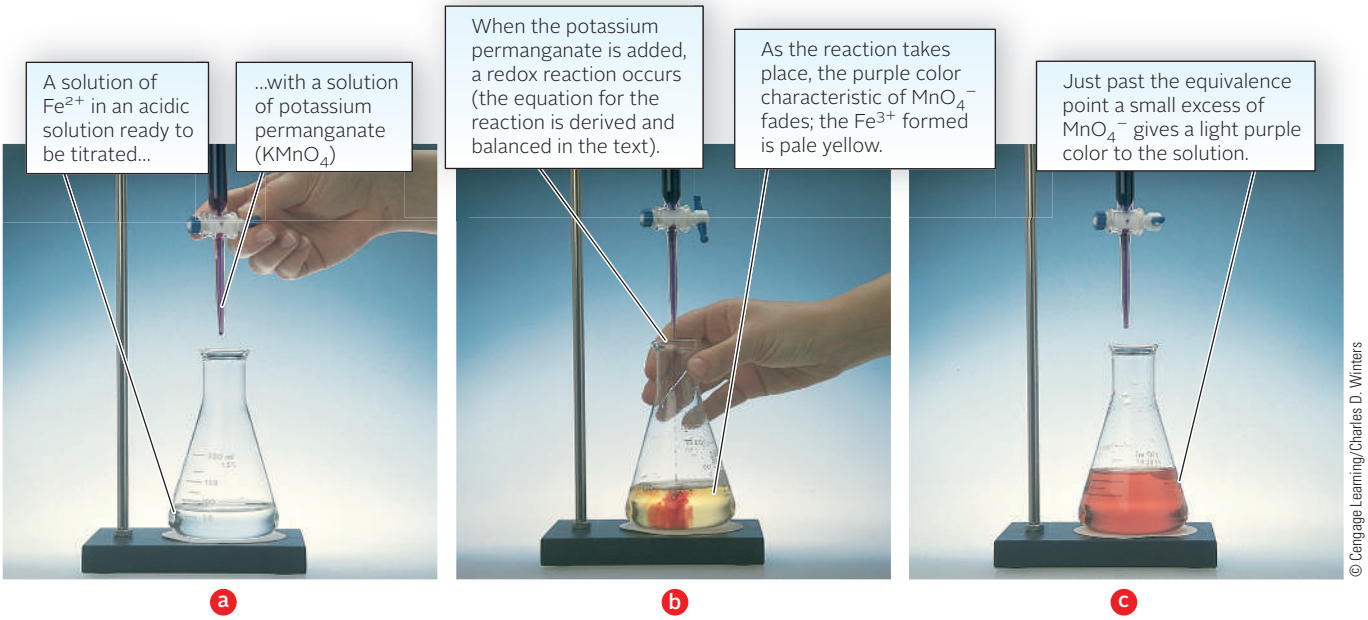

Figure 4.17 A redox titration.

Antacids

As you eat your evening meal, tiny glands in the mucous lining of your stomach discharge hydrochloric acid (HCl) to help you digest your food. If all goes well, the concentration of HCl in your stomach builds up to about 0.1 *M*, digestion takes place smoothly, and you're ready for a long night of studying chemistry (or whatever). Sometimes, though, too much acid is released and you suffer from a condition called "acid indigestion," "sour stomach," or "heartburn." This is particularly likely to happen if you eat too much spicy or high-fat food.

One way to relieve this discomfort is to take an *antacid*, which may be in the form of solid tablets or a water solution (Figure A). The antacid reduces stomach acidity by a chemical reaction that consumes excess H^+ ions. Several antacids are listed in Table A, along with the brand names of the commercial product that contains them.

Notice that in almost every case, the antacid is an *insoluble carbonate or hydroxide*. Typical reactions of these species with excess H^+ ions can be represented by the following equations:

$$CaCO_3(s) + 2H^+(aq) \rightarrow Ca^{2+}(aq) + CO_2(g) + H_2O$$
$$Mg(OH)_2(s) + 2H^+(aq) \rightarrow Mg^{2+}(aq) + H_2O$$

Using equations such as these, we can readily determine the amount of H^+ ion consumed by a given mass of antacid; let us say one gram. For $CaCO_3$,

$$1.00 \text{ g } CaCO_3 \times \frac{1 \text{ mol } CaCO_3}{100.0 \text{ g } CaCO_3} \times \frac{2 \text{ mol } H^+}{1 \text{ mol } CaCO_3}$$
$$= 0.0200 \text{ mol } H^+$$

Results of similar calculations give

0.0237 mol H^+/g $MgCO_3$, 0.0343 mol H^+/g $Mg(OH)_2$, 0.0385 mol H^+/g $Al(OH)_3$

We conclude that of these four antacids, $Al(OH)_3$ is the most "efficient," so far as getting rid of excess H^+ ions is concerned.

There is another, quite different way to solve the problem caused by acid indigestion. That is to use certain drugs known collectively as "H-2 blockers," scientifically known as H_2 receptor antagonists. They inhibit the release of H^+ ions into the stomach. Prescription drugs of this type have been used for some time to treat disorders of the stomach and esophagus. In 1994, pharmaceutical companies started selling several of these drugs over-the-counter (Figure B).

Another group of drugs, called proton pump inhibitors, have surpassed H-2 blockers in popularity. They are longer lasting and reduce acid secretion in gastric juices more effectively. They do this by an entirely different mechanism from H-2 receptor antagonists. These drugs can now also be found over-the-counter and go by the trade names Prilosec, Prevacid, and Zegerid, to name a few (Figure C). Omeprazole (a generic name) is also available.

Table A Antacids

Product	Antacids(s) Present	Product	Antacids(s) Present
Brioschi	$NaHCO_3$	Phillips	$Mg(OH)_2$
Gaviscon	$MgCO_3$, $Al(OH)_3$	Rolaids	$CaCO_3$, $Mg(OH)_2$
Gelusil	$Mg(OH)_2$, $Al(OH)_3$	Surpass	$CaCO_3$
Maalox	$Mg(OH)_2$, $Al(OH)_3$	Top Care	$MgCO_3$, $Al(OH)_3$
Mylanta	$Mg(OH)_2$, $Al(OH)_3$	Tums	$CaCO_3$

Figure A Some commercially available antacids.

Figure B Over-the-counter "H-2 blockers."

Figure C Over-the-counter proton pump inhibitors.

Key Concepts

1. Apply the precipitation diagram (Figures 4.2 and 4.3) to
   - predict solubility and precipitation reactions. **(Example 4.1; Problems 1–10)**
   - write net ionic equations for precipitation reactions. **(Examples 4.2, 4.3; Problems 5–10)**
2. Carry out stoichiometric calculations for reactions. **(Examples 4.3, 4.5, 4.10; Problems 11–16, 27–38, 59–70)**
3. With the aid of Tables 4.1 and 4.2 and Figure 4.10, write net ionic equations for acid-base reactions. **(Example 4.4; Problems 19–26)**
4. Determine oxidation numbers. **(Example 4.6, 4.7; Problems 39–42)**

Key Terms

amine
Arrhenius acid
Arrhenius base
equivalence point
half-equations
net ionic equation
neutralization
oxidation
oxidation number
oxidizing agent
precipitate
redox reaction
reducing agent
reduction
strong acid
strong base
titration
weak acid
weak base

Summary Problem

An aqueous solution of hydrogen chloride is called hydrochloric acid (Figure 4.18). It is widely used for a host of industrial purposes. It reacts with a wide variety of compounds.

(a) Write net ionic equations for the reaction between aqueous solutions of hydrochloric acid with

1. an aqueous solution of strontium hydroxide.
2. an aqueous solution of silver nitrate.
3. an aqueous solution of methylamine (CH_3NH_2).
4. iron(II) hydroxide. (The chloride ions react with iron(II) hydroxide to form metallic iron. Chlorate ions are also formed.)

(b) When 25.00 mL of 0.695 *M* HCl reacts with an excess of silver nitrate, a precipitate forms. How many grams of precipitate can be theoretically obtained?

(c) What volume of 0.2500 *M* strontium hydroxide is required to completely react with 75.00 mL of 0.07942 *M* HCl?

(d) When 37.5 mL of 0.439 *M* HCl reacts with 22.0 mL of 0.573 *M* ammonia, ammonium ions are formed. What is the concentration of each species in solution after reaction is complete? (Assume that volumes are additive.)

(e) An alloy containing aluminum is analyzed. All the aluminum in a 2.500-g sample of the alloy reacts with 212 mL of 0.493 *M* HCl. The equation for the reaction is:

$$2Al(s) + 6H^+(aq) \longrightarrow 2Al^{3+}(aq) + 3H_2(g)$$

1. What is the oxidizing agent?
2. Which element is oxidized?
3. Calculate the mass percent of aluminum in the alloy. (Assume that the only component of the alloy that reacts with HCl is aluminum.)

Answers

(a) 1. $H^+(aq) + OH^-(aq) \longrightarrow H_2O$
2. $Cl^-(aq) + Ag^+(aq) \longrightarrow AgCl(s)$
3. $CH_3NH_2(aq) + H^+(aq) \longrightarrow CH_3NH_3^+(aq)$
4. $3Fe(OH)_2(s) + Cl^-(aq) \longrightarrow 3Fe(s) + ClO_3^-(aq) + 3H_2O$

(b) 2.49 g

(c) 11.91 mL

(d) $NH_3 = 0$; $H^+ = 0.0648\ M$; $Cl^- = 0.277\ M$; $NH_4^+ = 0.212\ M$

(e) 1. H^+
2. Al
3. 37.6%

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Figure 4.18 Hydrochloric acid can be obtained from hardware stores, where it is called muriatic acid. This strong acid is used to clean metal and stone surfaces.

Questions and Problems

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

4-1 Precipitation Reactions

1. Write the formulas of the following compounds and decide which are soluble in water.
(**a**) sodium sulfate (**b**) iron(III) nitrate
(**c**) silver chloride (**d**) chromium(III) hydroxide

2. Follow the instructions for Question 1 for the following compounds:
(**a**) barium chloride
(**b**) magnesium hydroxide
(**c**) chromium(III) carbonate
(**d**) potassium phosphate

3. Describe how you would precipitate
(**a**) zinc carbonate from a solution of zinc nitrate.
(**b**) copper(II) phosphate from a solution of copper(II) chloride.
(**c**) barium sulfate from a solution of barium hydroxide.

4. Name the reagent, if any, that you would add to a solution of iron(III) chloride to precipitate
(**a**) iron(III) hydroxide.
(**b**) iron(III) carbonate.
(**c**) iron(III) phosphate.

5. Write net ionic equations for the formation of
(**a**) a precipitate when solutions of magnesium nitrate and potassium hydroxide are mixed.
(**b**) two different precipitates when solutions of silver(I) sulfate and barium chloride are mixed.

6. Write net ionic equations to explain the formation of
(**a**) a red precipitate when solutions of iron(III) nitrate and sodium hydroxide are mixed.
(**b**) two different precipitates when magnesium sulfate and barium hydroxide are mixed.

7. Decide whether a precipitate will form when the following solutions are mixed. If a precipitate forms, write a net ionic equation for the reaction.
(**a**) potassium nitrate and magnesium sulfate
(**b**) silver nitrate and potassium carbonate
(**c**) ammonium carbonate and cobalt(III) chloride
(**d**) sodium phosphate and barium hydroxide
(**e**) barium nitrate and potassium hydroxide

8. Follow the directions of Question 7 for solutions of the following:
(**a**) silver nitrate and sodium chloride
(**b**) cobalt(II) nitrate and sodium hydroxide
(**c**) ammonium phosphate and potassium hydroxide
(**d**) copper(II) sulfate and sodium carbonate
(**e**) lithium sulfate and barium hydroxide

9. Write a net ionic equation for any precipitation reaction that occurs when 1 *M* solutions of the following are mixed.
(**a**) copper(II) sulfate and sodium chloride
(**b**) manganese(II) nitrate and ammonium hydroxide
(**c**) silver nitrate and hydrochloric acid
(**d**) nickel(II) sulfate and potassium hydroxide
(**e**) ammonium carbonate and sodium nitrate

10. Follow the directions for Question 9 for the following pairs of solutions.
(**a**) sodium phosphate and barium chloride
(**b**) zinc sulfate and potassium hydroxide
(**c**) ammonium sulfate and sodium chloride
(**d**) cobalt(III) nitrate and sodium phosphate

11. What volume of 0.2500 *M* cobalt(III) sulfate is required to react completely with
(**a**) 25.00 mL of 0.0315 *M* calcium hydroxide?
(**b**) 5.00 g of sodium carbonate?
(**c**) 12.50 mL of 0.1249 *M* potassium phosphate?

12. What is the molarity of a 25.00 mL solution of iron(III) nitrate that reacts completely (100% yield) with
(**a**) 12.54 mL of 0.1488 *M* sodium carbonate?
(**b**) 7.58 g of potassium phosphate?
(**c**) 10.00 mL of 0.1573 *M* $Sr(OH)_2$?

13. A 50.00-mL sample of 0.0250 *M* silver nitrate is mixed with 0.0400 *M* chromium(III) chloride.
(**a**) What is the minimum volume of chromium(III) chloride required to completely precipitate silver chloride?
(**b**) How many grams of silver chloride are produced from (a)?

14. Aluminum ions react with carbonate ions to form an insoluble compound, aluminum carbonate.
(**a**) Write the net ionic equation for this reaction.
(**b**) What is the molarity of a solution of aluminum chloride if 30.0 mL is required to react with 35.5 mL of 0.137 *M* sodium carbonate?
(**c**) How many grams of aluminum carbonate are formed in (b)?

15. When Na_3PO_4 and $Ca(NO_3)_2$ are combined, the following reaction occurs:

$$2PO_4^{3-}(aq) + 3Ca^{2+}(aq) \longrightarrow Ca_3(PO_4)_2(s)$$

How many grams of $Ca_3(PO_4)_2(s)$ (MM = 310.18 g/mol) are obtained when 15.00 mL of 0.1386 *M* Na_3PO_4 are mixed with 20.00 mL of 0.2118 *M* $Ca(NO_3)_2$?

16. When solutions of aluminum sulfate and sodium hydroxide are mixed, a white gelatinous precipitate forms.
(**a**) Write a balanced net ionic equation for the reaction.
(**b**) What is the mass of the precipitate when 2.76 g of aluminum sulfate in 125 mL of solution is combined with 85.0 mL of 0.2500 *M* NaOH?
(**c**) What is the molarity of the ion in excess? (Ignore spectator ions and assume that volumes are additive.)

4-2 Acid-Base Reactions

17. Classify the following compounds as acids or bases, weak or strong.
(**a**) perchloric acid (**b**) cesium hydroxide
(**c**) carbonic acid, H_2CO_3 (**d**) ethylamine, $C_2H_5NH_2$

18. Follow the directions of Question 17 for
(**a**) hydrogen sulfide. (**b**) sulfuric acid.
(**c**) pyridine, C_5H_5N. (**d**) aluminum hydroxide.

19. For an acid-base reaction, what is the reacting species, that is, the ion or molecule that appears in the chemical equation, in the following acids?
(**a**) perchloric acid (**b**) hydriodic acid
(**c**) nitrous acid (**d**) nitric acid
(**e**) lactic acid, $HC_3H_5O_3$

20. Follow the directions of Question 19 for the following acids:
(**a**) hypochlorous acid (**b**) formic acid, $HCHO_2$
(**c**) acetic acid, $HC_2H_3O_2$ (**d**) hydrobromic acid
(**e**) sulfurous acid

21. For an acid-base reaction, what is the reacting species (the ion or molecule that appears in the chemical equation) in the following bases?
(**a**) barium hydroxide (**b**) trimethylamine $(CH_3)_3N$
(**c**) aniline, $C_6H_5NH_2$ (**d**) sodium hydroxide

22. Follow the directions of Question 21 for the following bases:
(**a**) toluidine, C_7H_9N (**b**) strontium hydroxide
(**c**) indol, C_8H_6NH (**d**) aqueous ammonia

23. Write a balanced net ionic equation for each of the following acid-base reactions in water.
(**a**) nitrous acid and barium hydroxide
(**b**) potassium hydroxide and hydrofluoric acid
(**c**) aniline ($C_6H_5NH_2$) and perchloric acid

24. Write a balanced net ionic equation for each of the following reactions in water.
(**a**) acetic acid, $HC_2H_3O_2$, with strontium hydroxide
(**b**) diethylamine, $(C_2H_5)NH$ with sulfuric acid
(**c**) aqueous hydrofluoric acid with sodium hydroxide

25. Consider the following generic equation:

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

For which of the following pairs would this be the correct prototype equation for the acid-base reaction in solution? If it is not correct, write the proper equation for the acid-base reaction between the pair.
(**a**) nitric acid and calcium hydroxide
(**b**) hydrochloric acid and CH_3NH_2
(**c**) hydrobromic acid and aqueous ammonia
(**d**) perchloric acid and barium hydroxide
(**e**) sodium hydroxide and nitrous acid

26. Consider the following generic equation

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

For which of the following pairs would this be the correct prototype equation for the acid-base reaction in solution? If it is not correct, write the proper equation for the acid-base reaction between the pair.
(**a**) hydrochloric acid and pyridine, C_5H_5N
(**b**) sulfuric acid and rubidium hydroxide
(**c**) potassium hydroxide and hydrofluoric acid
(**d**) ammonia and hydriodic acid
(**e**) strontium hydroxide and hydrocyanic acid

27. What is the molarity of a solution of nitric acid if 0.216 g of barium hydroxide is required to neutralize 20.00 mL of nitric acid?

28. How many milliliters of 0.2315 *M* sulfuric acid are required to neutralize 38.00 mL of 0.189 *M* ammonia?

29. What is the volume of 1.222 *M* sodium hydroxide required to react with
(**a**) 32.5 mL of 0.569 *M* sulfurous acid? (One mole of sulfurous acid reacts with two moles of hydroxide ion.)
(**b**) 5.00 g of oxalic acid, $H_2C_2O_4$? (One mole of oxalic acid reacts with two moles of hydroxide ion.)
(**c**) 15.0 g of concentrated acetic acid, $HC_2H_3O_2$, that is 88% by mass pure?

30. Consider several 25.00-mL solutions of perchloric acid. What is the molarity of the acid solution neutralized by
(**a**) 17.25 mL of 0.3471 *M* ethylamine ($C_2H_5NH_2$).
(**b**) 14.17 g of strontium hydroxide.
(**c**) 41.73 mL of an 18% (by mass) solution of ammonia (d = 0.9295 g/mL).

31. Analysis shows that a sample of H_2X (MM = 100.0 g/mol) reacts completely with 330.0 mL of 0.2000 *M* KOH.

$$H_2X(aq) + 2OH^-(aq) \longrightarrow X^{2-}(aq) + 2H_2O$$

What is the volume of the sample? (Density of H_2X = 1.200 g/mL.)

32. A student tries to determine experimentally the molar mass of aspirin (HAsp). She takes 1.00 g of aspirin, dissolves it in water, and neutralizes it with 17.6 mL of 0.315 *M* KOH. The equation for the reaction is

$$HAsp(aq) + OH^-(aq) \longrightarrow Asp^-(aq) + H_2O$$

What is the molar mass of aspirin?

33. Sulfuric acid is needed in a lead storage battery. A 25.00-mL sample of "battery acid" taken from a functioning battery requires 53.7 mL of 4.552 *M* NaOH for complete neutralization. What is the molarity of the battery acid?

34. For a product to be called "vinegar," it must contain at least 5.0% acetic acid, $HC_2H_3O_2$, by mass. A 10.00-g sample of a "raspberry vinegar" is titrated with 0.1250 *M* $Ba(OH)_2$ and required 37.50 mL for complete neutralization. Can the product be called a "vinegar"?

35. The percentage of sodium hydrogen carbonate, $NaHCO_3$, in a powder for stomach upsets is found by titrating with 0.275 *M* hydrochloric acid. If 15.5 mL of hydrochloric acid is required to react with 0.500 g of the sample, what is the percentage of sodium hydrogen carbonate in the sample?
The balanced equation for the reaction that takes place is

$$NaHCO_3(s) + H^+(aq) \longrightarrow Na^+(aq) + CO_2(g) + H_2O$$

36. A capsule of vitamin C, a weak acid, is analyzed by titration with 0.450 *M* potassium hydroxide. It is found that 5.94 mL of the base are required to react with the contents of a capsule. If the contents have a mass of 0.634 g, what is the mass percent of vitamin C ($C_6H_8O_6$) in the capsule? (One mol of vitamin C reacts with one mol of OH^-.)

37. An artificial fruit beverage contains 12.0 g of tartaric acid, $H_2C_4H_4O_6$, to achieve tartness. It is titrated with a basic solution that has a density of 1.045 g/cm^3 and contains 5.00 mass percent KOH. What volume of the basic solution is required? (One mole of tartaric acid reacts with two moles of hydroxide ion.)

38. Lactic acid, $C_3H_6O_3$, is the acid present in sour milk. A 0.100-g sample of pure lactic acid requires 12.95 mL of 0.0857 *M* sodium hydroxide for complete reaction. How

many moles of hydroxide ion are required to neutralize one mole of lactic acid?

4-3 Oxidation-Reduction Reactions

39. Assign oxidation numbers to each element in
(**a**) nitrogen oxide
(**b**) ammonia
(**c**) potassium peroxide
(**d**) chlorate ion (ClO_3^-)

40. Assign oxidation numbers to each element in
(**a**) methane (**b**) carbonate ion (CO_3^{2-})
(**c**) iodate ion (IO_4^-) (**d**) hydrazine (N_2H_4)

41. Assign oxidation numbers to each element in
(**a**) ClO_3^- (**b**) H_2SO_3 (**c**) K_2O_2 (**d**) Na_3N

42. Assign oxidation numbers to each element in
(**a**) HIO_3 (**b**) $NaMnO_4$ (**c**) SnO_2
(**d**) NOF (**e**) NaO_2

43. Classify each of the following half-reactions as oxidation or reduction.
(**a**) $O_2(g) \longrightarrow O^{2-}(aq)$
(**b**) $MnO_4^-(aq) \longrightarrow MnO_2(s)$
(**c**) $Cr_2O_7^{2-}(aq) \longrightarrow Cr^{3+}(aq)$
(**d**) $Cl^-(aq) \longrightarrow Cl_2(g)$

44. Classify each of the following half-equations as oxidation or reduction.
(**a**) $CH_3OH(aq) \longrightarrow CO_2(g)$
(**b**) $NO_3^-(aq) \longrightarrow NH_4^+(aq)$
(**c**) $Fe^{3+}(aq) \longrightarrow Fe(s)$
(**d**) $V^{2+}(aq) \longrightarrow VO_3^-(aq)$

45. Classify each of the following half-equations as oxidation or reduction.
(**a**) $Mn^{2+}(aq) \longrightarrow MnO_4^-(aq)$
(**b**) $CrO_4^{2-}(aq) \longrightarrow Cr^{3+}(aq)$
(**c**) $PbO_2(s) \longrightarrow Pb^{2+}(aq)$
(**d**) $ClO_2^-(aq) \longrightarrow ClO^-(aq)$

46. Classify each of the following half-reactions as oxidation or reduction.
(**a**) $TiO_2(s) \longrightarrow Ti^{3+}(aq)$
(**b**) $Zn^{2+}(aq) \longrightarrow Zn(s)$
(**c**) $NH_4^+(aq) \longrightarrow N_2(g)$
(**d**) $CH_3OH(aq) \longrightarrow CH_2O(aq)$

47. For each unbalanced equation given below
- write unbalanced half-reactions.
- identify the species oxidized and the species reduced.
- identify the oxidizing and reducing agents.

(**a**) $Ag(s) + NO_3^-(aq) \longrightarrow Ag^+(aq) + NO(g)$
(**b**) $CO_2(g) + H_2O(l) \longrightarrow C_2H_4(g) + O_2(g)$

48. Follow the directions of Question 47 for the following unbalanced equations:
(**a**) $As_2O_3(s) + MnO_4^-(aq) \longrightarrow H_3AsO_4(aq) + Mn^{2+}(aq)$
(**b**) $N_2H_4(l) + CO_3^{2-}(aq) \longrightarrow N_2(g) + CO(g)$

49. A solution of potassium permanganate reacts with oxalic acid, $H_2C_2O_4$, to form carbon dioxide and solid manganese(IV) oxide (MnO_2) according to the equation

$$3H_2C_2O_4(aq) + 2MnO_4^-(aq) + 2H^+(aq) \longrightarrow 6CO_2(g) + 2MnO_2(s) + 4H_2O$$

(**a**) If 20.0 mL of 0.300 *M* potassium permanganate are required to react with 13.7 mL of oxalic acid, what is the molarity of the oxalic acid?
(**b**) What is the mass of manganese(IV) oxide formed?

50. The vanadium (V) ion in a 0.5000-g sample of ore is converted to VO^{2+} ions. The amount of VO^{2+} in solution can be determined by reaction with an acid solution of $KMnO_4$. The balanced equation for the reaction is

$$5VO^{2+}(aq) + MnO_4^-(aq) + 11H_2O \longrightarrow Mn^{2+}(aq) + 5V(OH_4)^+(aq) + 2H^+(aq)$$

What is the mass percent of vanadium in the ore if 26.45 mL of 0.02250 *M* permanganate solution is required for complete reaction?

51. Hydrogen gas is bubbled into a solution of barium hydroxide that has sulfur in it. The equation for the reaction that takes place is

$$H_2(g) + S(s) + 2OH^-(aq) \longrightarrow S^{2-}(aq) + 2H_2O$$

What volume of 0.349 *M* $Ba(OH)_2$ is required to react completely with 3.00 g of sulfur?

52. Consider the reaction between silver and nitric acid for which the equation is

$$Ag(s) + 2H^+(aq) + NO_3^-(aq) \longrightarrow Ag^+(aq) + NO_2(g) + H_2O$$

If 42.50 mL of 12.0 *M* nitric acid furnishes enough H^+ to react with silver, how many grams of silver react?

53. The molarity of iodine in solution can be determined by titration with arsenious acid, H_3AsO_4. The unbalanced equation for the reaction is

$$H_3AsO_3(aq) + I_2(aq) + H_2O \longrightarrow 2I^-(aq) + H_3AsO_4(aq) + 2H^+(aq)$$

A 243-mL solution of aqueous iodine is prepared by dissolving iodine crystals in water. A fifty-mL portion of the solution requires 15.42 mL of 0.134 *M* H_3AsO_3 for complete reaction. What is the molarity of the solution? How many grams of iodine were added to the solution?

54. A wire weighing 0.250 g and containing 92.50% Fe is dissolved in HCl. The iron is completely oxidized to Fe^{3+} by bromine water. The solution is then treated with tin(II) chloride to bring about the reaction

$$Sn^{2+}(aq) + 2Fe^{3+}(aq) \longrightarrow 2Fe^{2+}(aq) + Sn^{4+}(aq) + H_2O$$

If 22.0 mL of tin(II) chloride solution is required for complete reaction, what is the molarity of the tin(II) chloride solution?

55. Glycerol ($C_3H_8O_3$) is commonly used as an additive to moisturizers. The amount of glycerol added can be determined by titration with permanganate in basic solution.

$$14MnO_4^-(aq) + C_3H_8O_3(aq) + 20OH^-(aq) \longrightarrow 14MnO_4^{2-}(aq) + 3CO_3^{2-}(aq) + 14H_2O$$

How many milliliters of 6.15 *M* $KMnO_4$ are required to completely react with 7.25 mL of an aqueous solution of glycerol (d = 1.144 g/mL) that is 51.6% by mass?

56. Laws passed in some states define a drunk driver as one who drives with a blood alcohol level of 0.10% by mass or

higher. The level of alcohol can be determined by titrating blood plasma with potassium dichromate according to the following equation

$$16H^+(aq) + 2Cr_2O_7^{2-}(aq) + C_2H_5OH(aq) \longrightarrow 4Cr^{3+}(aq) + 2CO_2(g) + 11H_2O$$

Assuming that the only substance that reacts with dichromate in blood plasma is alcohol, is a person legally drunk if 38.94 mL of 0.0723 *M* potassium dichromate is required to titrate a 50.0-g sample of blood plasma?

Unclassified

57. A sample of limestone weighing 1.005 g is dissolved in 75.00 mL of 0.2500 *M* hydrochloric acid. The following reaction occurs:

$$CaCO_3(s) + 2H^+(aq) \longrightarrow Ca^{2+}(aq) + CO_2(g) + H_2O$$

It is found that 19.26 mL of 0.150 *M* NaOH is required to titrate the excess HCl left after reaction with the limestone. What is the mass percent of $CaCO_3$ in the limestone?

58. The iron content of hemoglobin is determined by destroying the hemoglobin molecule and producing small water-soluble ions and molecules. The iron in the aqueous solution is reduced to iron(II) ion and then titrated against potassium permanganate. In the titration, iron(II) is oxidized to iron(III) and permanganate is reduced to manganese(II) ion. A 5.00-g sample of hemoglobin requires 32.3 mL of a 0.002100 *M* solution of potassium permanganate. The reaction with permanganate ion is

$$MnO_4^-(aq) + 8H^+(aq) + 5Fe^{2+}(aq) \longrightarrow Mn^{2+}(aq) + 5Fe^{3+}(aq) + 4H_2O$$

What is the mass percent of iron in hemoglobin?

59. In order to determine the purity of ammonium sulfate, a sample with a mass of 0.850 g is dissolved in KOH. The equation for the reaction that takes place is

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

The ammonia liberated is distilled into a flask that contains 50.00 mL of 0.250 *M* HCl. Not all the HCl is consumed. The excess HCl reacts with 17.3 mL of 0.120 *M* NaOH. What is the mass percent of $(NH_4)_2SO_4$ in the sample?

60. Gold metal will dissolve only in *aqua regia,* a mixture of concentrated hydrochloric acid and concentrated nitric acid in a 3:1 volume ratio. The products of the reaction between gold and the concentrated acids are $AuCl_4^-(aq)$, $NO(g)$, and H_2O. The equation for this reaction where HNO_3 and HCl are strong acids is

$$Au(s) + 4Cl^-(aq) + 4H^+(aq) + NO_3^-(aq) \longrightarrow AuCl_4^-(aq) + NO(g) + 2H_2O$$

(**a**) What stoichiometric ratio of hydrochloric acid to nitric acid should be used?

(**b**) What volumes of 12 *M* HCl and 16 *M* HNO_3 are required to furnish the Cl^- and NO_3^- ions to react with 25.0 g of gold?

61. Cisplatin, $Pt(NH_3)_2Cl_2$, is a drug widely used in chemotherapy. It can react with the weak base pyridine, C_6H_5N. Suppose 3.11 g of cisplatin are treated with 2.00 mL of pyridine (d = 0.980 g/mL). The unreacted pyridine is then titrated with HCl according to the following reaction:

$$C_6H_5N(l) + H^+(aq) \longrightarrow C_6H_5NH^+(aq)$$

The complete reaction requires 31.2 mL of 0.0245 *M* HCl.

(**a**) How many moles of pyridine were unused in the cisplatin reaction?

(**b**) How many moles of pyridine would react with one mole of cisplatin?

62. Ten mL of concentrated H_3PO_4 (91.7% by mass, d = 1.69 g/mL) was accidentally poured into a beaker containing 20.0 g of NaOH. Not all the NaOH was consumed. How many grams of NaOH were left unreacted? The equation for the reaction is

$$H_3PO_4(aq) + 3OH^-(aq) \longrightarrow 3H_2O + PO_4^{3-}(aq)$$

Conceptual Questions

63. Consider the following balanced redox reaction in basic medium.

$$3Sn^{2+}(aq) + Cr_2O_7^{2-}(aq) + 4H_2O \longrightarrow 3Sn^{4+}(aq) + Cr_2O_3(s) + 8\,OH^-(aq)$$

(**a**) What is the oxidizing agent?

(**b**) What species has the element that increases its oxidation number?

(**c**) What species contains the element with the highest oxidation number?

(**d**) If the reaction were to take place in acidic medium, what species would not be included in the reaction?

64. Identify the type of aqueous reaction using the symbols **PPT** for precipitation, **SA/SB** for strong acid–strong base, **SA/WB** for strong acid–weak base, **WA/SB** for weak acid–strong base, and **NR** for no reaction.

(**a**) $CH_3CH_2NH_2 + HCl$

(**b**) $Ca(OH)_2 + HF$

(**c**) $Ca(OH)_2 + Na_3PO_4$

(**d**) $Ag_2SO_4 + BaCl_2$

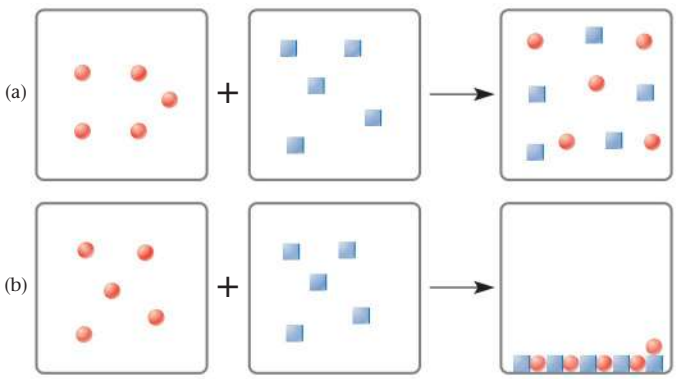
(**e**) $Mg(NO_3)_2 + NaCl$

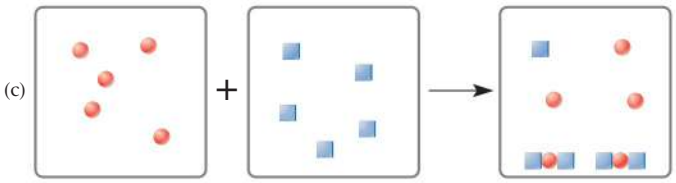
65. Using circles to represent cations and squares to represent anions, show pictorially the reactions that occur between aqueous solutions of

(**a**) Fe^{3+} and OH^-.

(**b**) Na^+ and PO_4^{3-}.

66. Assuming that circles represent cations and squares represent anions, match the incomplete net ionic equations to their pictorial representations.

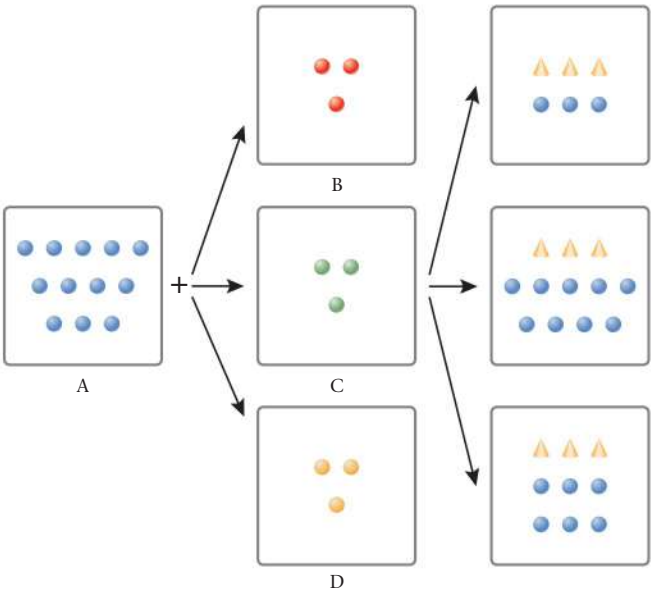




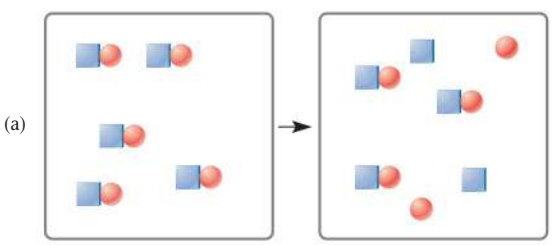
(1) $2Na^+ + SO_4^{2-} \longrightarrow$ _____
(2) $Mg^{2+} + 2OH^- \longrightarrow$ _____
(3) $Ba^{2+} + CO_3^{2-} \longrightarrow$ _____

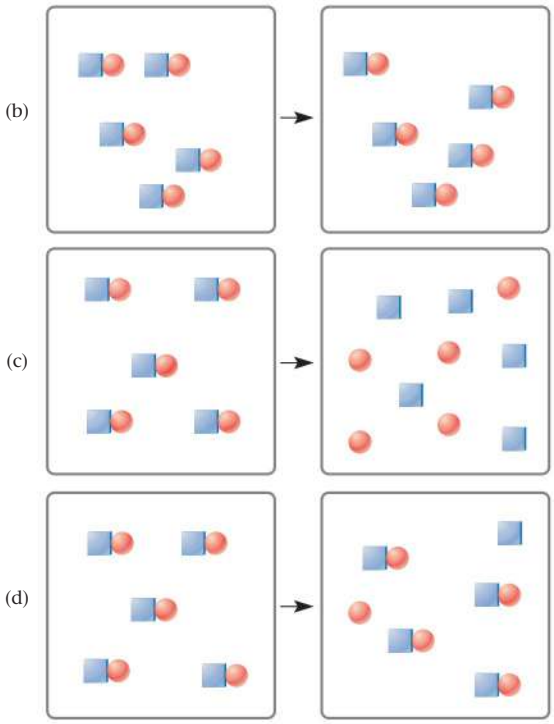
67. Consider four beakers. Beaker A has an aqueous solution of NaOH in which the OH^- ions are represented by blue circles. Beaker B has a weak acid; HX is represented by red circles. Beaker C has a weak acid; H_2X is represented by green circles. Beaker D has a weak acid; H_3X is represented by yellow circles. X^- ions are represented by triangles. Match the pictorial representations with the reactions given below.

(**a**) $HX(aq) + OH^-(aq) \longrightarrow X^-(aq) + H_2O$
(**b**) $H_2X(aq) + 2OH^-(aq) \longrightarrow X^-(aq) + 2H_2O$
(**c**) $H_3X(aq) + 3OH^-(aq) \longrightarrow X^-(aq) + 3H_2O$



68. The following figures represent species before and after they are dissolved in water. Classify each species as weak electrolyte, strong electrolyte, or nonelectrolyte. You may assume that species that dissociate during solution break up as ions.





69. A student is asked to identify the metal nitrate present in an aqueous solution. The cation in the solution can be either Na^+, Ba^{2+}, Ag^+, or Ni^{2+}. Results of solubility experiments are as follows:

unknown + chloride ions—no precipitate
unknown + carbonate ions—precipitate
unknown + sulfate ions—precipitate

What is the cation in the solution?

70. Three students titrate different samples of the same solution of HCl to obtain its molarity. Below are their data.

Student A: 20.00 mL HCl + 20.00 mL H_2O 0.100 *M* NaOH used to titrate to the equivalence point
Student B: 20.00 mL HCl + 40.00 mL H_2O 0.100 *M* NaOH used to titrate to the equivalence point
Student C: 20.00 mL HCl + 20.00 mL H_2O 0.100 *M* $Ba(OH)_2$ used to titrate to the equivalence point.

All the students calculated the molarities correctly. Which (if any) of the following statements are true?

(**a**) The molarity calculated by A is half that calculated by B.
(**b**) The molarity calculated by A is equal to that calculated by C.
(**c**) The molarity calculated by B is twice that calculated by C.
(**d**) The molarity calculated by A is twice that calculated by B.
(**e**) The molarity calculated by A is equal to that calculated by B.

Challenge Problems

71. Calcium in blood or urine can be determined by precipitation as calcium oxalate, CaC_2O_4. The precipitate is dissolved in strong acid and titrated with potassium permanganate. The equation for reaction is

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

A 24-hour urine sample is collected from an adult patient, reduced to a small volume, and titrated with 26.2 mL of 0.0946 *M* $KMnO_4$. How many grams of calcium oxalate are in the sample? Normal range for Ca^{2+} output for an adult is 100 to 300 mg per 24 hour. Is the sample within the normal range?

72. Stomach acid is approximately 0.020 *M* HCl. What volume of this acid is neutralized by an antacid tablet that weighs 330 mg and contains 41.0% $Mg(OH)_2$, 36.2% $NaHCO_3$, and 22.8% NaCl? The reactions involved are

$$Mg(OH)_2(s) + 2H^+(aq) \longrightarrow Mg^{2+}(aq) + 2H_2O$$

$$HCO_3^-(aq) + H^+(aq) \longrightarrow CO_2(g) + H_2O$$

73. Copper metal can reduce silver ions to metallic silver. The copper is oxidized to copper ions according to the reaction

$$2Ag^+(aq) + Cu(s) \longrightarrow Cu^{2+}(aq) + 2Ag(s)$$

A copper strip with a mass of 2.00 g is dipped into a solution of $AgNO_3$. After some time has elapsed, the copper strip is coated with silver. The strip is removed from the solution, dried, and weighed. The coated strip has a mass of 4.18 g. What are the masses of copper and silver metals in the strip? (*Hint:* Remember that the copper metal is being used up as silver metal forms.)

74. A solution contains both iron(II) and iron(III) ions. A 50.00-mL sample of the solution is titrated with 35.0 mL of 0.0280 *M* $KMnO_4$, which oxidizes Fe^{2+} to Fe^{3+}. The permanganate ion is reduced to manganese(II) ion. The equation for this reaction is

$$MnO_4^-(aq) + 8H^+(aq) + 5Fe^{2+}(aq) \longrightarrow Mn^{2+}(aq) + 5Fe^{3+}(aq) + 4H_2O$$

Another 50.00-mL sample of the solution is treated with zinc, which reduces all the Fe^{3+} to Fe^{2+}. The equation for this reaction is

$$2Fe^{3+}(aq) + Zn(s) \longrightarrow 2Fe^{2+}(aq) + Zn^{2+}(aq)$$

The resulting solution is again titrated with 0.0280 *M* $KMnO_4$; this time 48.0 mL is required. What are the concentrations of Fe^{2+} and Fe^{3+} in the solution?

75. A student is given 0.930 g of an unknown acid, which can be either oxalic acid, $H_2C_2O_4$, or citric acid, $H_3C_6H_5O_7$. To determine which acid she has, she titrates the unknown acid with 0.615 *M* NaOH. The equivalence point is reached when 33.6 mL are added. What is the unknown acid?

76. Solid iron(III) hydroxide is added to 625 mL of 0.280 *M* HCl. The resulting solution is acidic and titrated with 238.2 mL of 0.113 *M* NaOH. What mass of iron(III) hydroxide was added to the HCl?

77. A 300.0-g sample of a solid is made up of a uniform mixture of $NaNO_3$, $MgCl_2$, and $BaCl_2$. A 100.0-g sample of the mixture is dissolved in water and treated with an excess of KOH. The precipitate from the reaction has a mass of 13.47 g. The remaining 200.0-g sample is also dissolved in water and treated with an aqueous solution of $AgNO_3$. The resulting precipitate has a mass of 195.8 g. What are the masses of $NaNO_3$, $MgCl_2$, and $BaCl_2$ in the 300.0-g sample?

78. When 85.0 mL of 0.250 *M* $Ba(OH)_2$ solution is added to 85.00 mL of 0.250 *M* $Al(NO_3)_3$ solution, a white gelatinous precipitate of $Al(OH)_3$ is formed. Assuming 100% yield,

(**a**) what mass (in grams) of $Al(OH)_3$ is formed?

(**b**) what is the molarity of each of the ions Ba^{2+}, OH^-, Al^{3+}, NO_3^- in the resulting solution?