Chapter 4 Chemical Reactions and Solution Stoichiometry

In This Chapter...

The science of chemistry brings three central benefits to society. First, chemistry helps explain how the world works, principally by examining nature on the molecular scale. Second, chemical analysis is used to identify substances, both natural and artificial. This is evident every time a person's blood is tested to determine cholesterol level or when athletes undergo testing for banned drug use. Finally, the science of chemistry is unique in that it involves the ability to create new forms of matter by combining the elements and existing compounds in new but controlled ways. The creation of new chemical compounds is the subject of this chapter. Here, we explore the different types of chemical reactions, emphasizing the reactions that take place in aqueous solution.

Chapter Outline

- 4.1 Types of Chemical Reactions
- 4.2 Aqueous Solutions
- 4.3 Reactions in Aqueous Solution
- 4.4 Oxidation–Reduction Reactions
- 4.5 Stoichiometry of Reactions in Aqueous Solution

Chapter Review Chapter Summary Assignment

4.1 Types of Chemical Reactions

Section Outline

- 4.1a Combination Reactions
- 4.1b Decomposition Reactions
- 4.1c Displacement Reactions

Section Summary Assignment

Chemical reactions involve the transformation of matter, the reactants, into different materials, the products. You have learned how to represent chemical reactions using balanced chemical equations and how to calculate the quantities of material involved in a chemical reaction. We will now investigate the three common types of chemical reactions: combination reactions, decomposition reactions, and displacement reactions.

:

Opening Exploration 4.1 Chemical Reactions



4.1a Combination Reactions

A **combination reaction** is one in which typically two or more reactants, usually elements or compounds, combine to form one product, usually a compound. In one type of combination reaction, two elements combine to form a compound. For example, the elements hydrogen and oxygen combine to form water, giving off large amounts of energy in the process (**Figure 4.1.1**)

 $2 \operatorname{H}_2(g) + \operatorname{O}_2(g) \to 2 \operatorname{H}_2\operatorname{O}(g)$





This combination reaction is used to generate power from the main engines in the space shuttle. The large fuel tank has separate compartments containing liquefied hydrogen and oxygen, which are vaporized prior to mixing.

Other types of combination reactions include the combination of an element with a compound and the combination of two different compounds to form a new compound. For example, oxygen reacts with sulfur dioxide to make sulfur trioxide.

 $2 \operatorname{SO}_2(g) + \operatorname{O}_2(g) \to 2 \operatorname{SO}_3(g)$

Sulfur trioxide and water undergo a combination reaction to form sulfuric acid.

$$SO_3(g) + H_2O(\ell) \rightarrow H_2SO_4(aq)$$

Notice that in all combination reactions, the number of reactants is greater than the number of products (**Interactive Figure 4.1.2**).



Interactive Figure 4.1.2 Explore combination reactions.



Zinc reacts with iodine to form zinc iodide.

4.1b Decomposition Reactions

In a typical **decomposition reaction (Interactive Figure 4.1.3**), the number of products is greater than the number of reactants. The reaction is essentially the reverse of a combination reaction and usually results from the addition of thermal or electrical energy. For example, water is a very stable compound under typical conditions, but it can be made to decompose to its constituent elements by using electrical energy, a process called electrolysis.

$$2 \operatorname{H}_2 O(\ell) \to 2 \operatorname{H}_2(g) + O_2(g)$$

Metal carbonates such as calcium carbonate, CaCO₃, undergo decomposition when heated, giving off carbon dioxide gas as one of the products.

$$CaCO_3(s) \rightarrow CaO(s) + CO_2(g)$$

Interactive Figure 4.1.3 Explore decomposition reactions.



The decomposition of mercury(II) oxide

4.1c Displacement Reactions

Many common chemical reactions are classified as **displacement reactions**, reactions where the number of reactants is typically equal to the number of products. In displacement reactions, also called *exchange reactions*, one atom, ion, or molecular fragment displaces another. Displacement reactions can be single or double reactions.

Single Displacement Reactions In a **single displacement reaction**, one molecular fragment is exchanged for another.

$$AB + X \rightarrow XB + A$$

For example, when solid magnesium is placed in a solution of copper(II) chloride, the magnesium displaces the copper. In this case, the more reactive metal, magnesium, replaces the less reactive metal, copper.

$$CuCl_2(aq) + Mg(s) \rightarrow MgCl_2(aq) + Cu(s)$$

Another common single displacement reaction occurs when a metal reacts with water. In the reaction of sodium metal with water, the metal displaces a hydrogen atom in water, forming sodium hydroxide (Figure 4.1.4).

$$H_2O(\ell) + Na(s) \rightarrow H_2(g) + NaOH(aq)$$





Double Displacement Reactions A **double displacement reaction**, also called a *metathesis reaction*, occurs when two atoms, ions, or molecular fragments exchange.

$$\mathbf{AB} + \mathbf{XY} \to \mathbf{AY} + \mathbf{XB}$$

There are three common types of double displacement reactions, each of which will be discussed in greater detail later in this chapter.

Precipitation reactions are double displacement reactions that result in the formation of an insoluble compound. For example, when aqueous solutions of lead nitrate and potassium sulfate are combined, solid lead sulfate is formed (**Interactive Figure 4.1.5**).

 $Pb(NO_3)_2(aq) + K_2SO_4(aq) \rightarrow 2 KNO_3(aq) + PbSO_4(s)$



Interactive Figure 4.1.5 Explore displacement reactions.

Lead sulfate precipitates when solutions of lead nitrate and potassium sulfate are combined.

Many **acid–base reactions**, also called *neutralization reactions*, are double displacement reactions that result in the formation of water.

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

The H^+ and Na^+ ions exchange to form the products, water and sodium chloride.

Gas-forming reactions, reactions between ionic compounds and acids, are double displacement reactions that result in the formation of a gas, often carbon dioxide (**Figure 4.1.6**).



Figure 4.1.6 The reaction of calcium carbonate with an acid produces carbon dioxide gas.

When hydrochloric acid is added to solid nickel(II) carbonate, for example, a double displacement reaction takes place.

$$\begin{split} NiCO_3(s) + 2 \; HCl(aq) &\rightarrow NiCl_2(aq) + H_2CO_3(aq) \\ The carbonic acid, H_2CO_3, formed in the reaction decomposes into water and carbon dioxide gas. \\ H_2CO_3(aq) &\rightarrow H_2O(\ell) + CO_2(g) \end{split}$$

Thus, the net gas-forming reaction between nickel(II) carbonate and hydrochloric acid is written as $N_{\rm e}^{\rm VGP}$

 $NiCO_{3}(s) + 2 HCl(aq) \rightarrow NiCl_{2}(aq) + H_{2}O(\ell) + CO_{2}(g)$

Notice that the decomposition of carbonic acid makes this both a double displacement reaction and a decomposition reaction.

EXAMPLE PROBLEM: Identify reaction types.

Classify and balance each of the following reactions.

(a) $HNO_3(aq) + Ca(OH)_2(s) \rightarrow H_2O(\ell) + Ca(NO_3)_2(aq)$

(b) $Al(s) + Br_2(\ell) \rightarrow Al_2Br_6(s)$

SOLUTION:

You are asked to balance a chemical equation and classify the type of chemical reaction. **You are given** an unbalanced equation.

(a) This is a double displacement reaction, specifically an acid–base reaction. The H^+ and Ca^{2+} ions exchange to form the products of the reaction.

 $2 \text{ HNO}_3(aq) + \text{Ca}(\text{OH})_2(s) \rightarrow 2 \text{ H}_2\text{O}(\ell) + \text{Ca}(\text{NO}_3)_2(aq)$

(b) This is a combination reaction.

 $2 \operatorname{Al}(s) + 3 \operatorname{Br}_2(\ell) \to \operatorname{Al}_2\operatorname{Br}_6(s)$

4.1.1T: Tutorial Assignment Identify Reaction Types 4.1.1: Mastery Assignment Identify Reaction Types

4.2 Aqueous Solutions

Section Outline

4.2a Compounds in Aqueous Solution

4.2b Solubility of Ionic Compounds

Section Summary Assignment

Many chemical reactions take place in a **solvent**, a chemical species in which the chemical reactants are dissolved. A **solution** is a homogeneous mixture formed when a chemical species, a **solute**, is mixed with a solvent, typically a liquid. Much of the chemistry of life as well as much of the chemistry of commerce involves solutions in which water is the solvent. A compound dissolved in water is in an **aqueous** state, indicated with the symbol (aq) in chemical equations. We will examine the nature of compounds in aqueous solution and the way in which compounds can be classified by the electrical behavior of solutions containing them

Opening Exploration 4.2 Soluble or Insoluble? [Figure ID #4-8]—winter's photo?

4.2a Compounds in Aqueous Solutions

When an ionic compound such as sodium chloride dissolves in water, its constituent ions separate and become **solvated**, surrounded by solvent molecules. When water is the solvent, the ions are **hydrated**, and after hydration occurs, the individual ions have little contact with one another (**Interactive Figure 4.2.1**).

Interactive Figure 4.2.1 Explore the dissolution of NaCl.



Hydrated sodium and chloride ions

Notice that in Interactive Figure 4.2.1 the water molecules orient themselves so that the oxygen atoms are near the Na⁺ cations and the hydrogen atoms are near the Cl⁻ anions. This is due to the polar nature of water, a result of uneven electron distribution in water molecules. **[Flashforward 4.1 Anchor]** Water is a neutral compound, but the electrons in the covalent O—H bonds are distributed unevenly so that they are closer to oxygen than hydrogen. As a result, each H₂O molecule has a buildup of partial negative charge near the oxygen end of the molecule and partial positive charge near the hydrogen atoms. Thus, the negative end of a water molecule is strongly attracted to positively charged cations, and the positive end of each water molecule is attracted to anions.

Flashforward 4.1

In a covalent bond, electrons are attracted to two nuclei, but sometimes one nucleus attracts the electrons more strongly than the other. When one nucleus attracts the electrons more strongly, the bonding electrons are located closer to one nucleus than the other. This creates an uneven distribution of bond electron density and a polar bond (or polar covalent bond). When electrons experience the same attractive force to both nuclei, the bond is nonpolar. For a molecule to be polar, it must contain polar bonds and those bonds must be arranged such that there is an uneven charge distribution. (See Section 8.6.)

The dissolution of solid sodium chloride can be written as a chemical equation. $NaCl(s) \rightarrow Na^{+}(aq) + Cl^{-}(aq)$ Because the two types of ions are independent once dissolved, it does not matter where they originated. This means there is no difference between a hydrated Na^+ ion that came from dissolving NaCl and one that came from dissolving, for example, Na_2SO_4 .

Electrolytes The presence of hydrated ions in a solution affects the electrical conductivity of the solution. Using the simple conductivity apparatus shown in Figure 4.2.2, you can see that pure water does not conduct electricity but that a solution of NaCl does. The hydrated ions present in the aqueous NaCl solution carry the electrical charge from one electrode to the other, completing the circuit.

Interactive Figure 4.2.2 Explore the conductivity of aqueous solutions.



An aqueous sodium chloride solution conducts electricity.

Compounds that dissolve to form hydrated ions and increase the electrical conductivity of water are called **electrolytes**. Ionic compounds such as sodium chloride that dissociate 100% in water to form hydrated ions are **strong electrolytes**.

NaCl(s)
$$\xrightarrow{100\%}$$
 Na⁺(aq) + Cl⁻(aq)

There are many examples of compounds that dissolve in water but do not form ions, such as sucrose $(C_{12}H_{22}O_{11})$ and ethanol (CH₃CH₂OH). These compounds are **nonelectrolytes** and form aqueous solutions that do not conduct electricity. **Weak electrolytes**, such as acetic acid, are compounds whose solutions conduct electricity only slightly. These compounds dissolve in water and form ions, but they do not dissociate completely. For example, when acetic acid is added to water, the solution contains non-ionized acetic acid molecules along with hydrated H⁺ and CH₃CO₂⁻ ions.

$$CH_3CO_2H(aq) \xrightarrow{less than 100\%} CH_3CO_2^{-}(aq) + H^+(aq)$$

4.2b Solubility of Ionic Compounds

Many ionic compounds are **soluble** in water; that is, they dissolve in water to form solutions containing hydrated ions. Ionic compounds that do not dissolve to an appreciable extent are **insoluble** in water. Recall that ionic compounds consist of individual cations and anions held together by ionic forces in a three-dimensional arrangement. When a soluble ionic compound dissolves in water, strong hydration forces between ions and water molecules replace these ionic forces. If the ionic forces are very strong, however, the compound does not dissociate into hydrated ions and it does not dissolve in water.

A precipitation reaction occurs when an insoluble ionic compound is the product of an exchange reaction. Predicting the solubility of ionic compounds, therefore, allows us to determine whether a solid, called a **precipitate**, might form when solutions containing ionic compounds are mixed. We

can use general trends in the solubility of ionic compounds containing commonly encountered ions to predict whether an ionic compound will be soluble in water, as shown in Interactive **Table 4.2.1**.

Soluble Ionic Compounds	Exceptions
All sodium (Na ^{$+$}), potassium (K ^{$+$}), and	
ammonium (NH_4^+) salts	
All nitrate (NO_3^-), acetate ($CH_3CO_2^-$), chlorate	
(ClO_3^{-}) , and perchlorate (ClO_4^{-}) salts	
All chloride (Cl^-), bromide (Br^-), and iodide (I^-)	Compounds also containing lead, silver, or
salts	mercury(I) $(Pb^{2+}, Ag^{+}, Hg_{2}^{2+})$
All fluoride (F ⁻) salts	Compounds also containing calcium, strontium,
	barium, or lead (Ca^{2+} , Sr^{2+} , Ba^{2+} , Pb^{2+})
All sulfate (SO_4^{2-}) salts	Compounds also containing calcium, silver,
	mercury(I), strontium, barium, or lead (Ca^{2+} , Ag^+ ,
	$Hg_2^{2+}, Sr^{2+}, Ba^{2+}, Pb^{2+})$
Insoluble Ionic Compounds	Exceptions
Hydroxide (OH^{-}) and oxide (O^{2-}) compounds	Compounds also containing sodium, potassium,
	or barium (Na ⁺ , K ⁺ , Ba ²⁺)
Sulfide (S ²⁻) salts	Compounds also containing sodium, potassium,
	ammonium, or barium (Na ⁺ , K ⁺ , NH ₄ ⁺ , Ba ²⁺)
Carbonate (CO_3^{2-}) and phosphate (PO_4^{3-}) salts	Compounds also containing sodium, potassium,
	or ammonium (Na ⁺ , K ⁺ , NH ₄ ⁺)
Soluble compounds are defined as those that disso	lve to the extent of 1 g or more per 100 g water.

Interactive Table 4.2.1 Solubility Rules for Ionic Compounds in Water

Notice that classification of ionic compound solubility is primarily based on the anion in the compound. When classifying an ionic compound as soluble or insoluble, first determine whether the anion present is typically found in soluble or insoluble compounds. Next, see if the cation in the compound results in an exception to the solubility guidelines.

For example, sodium nitrate, NaNO₃, is a soluble ionic compound because it contains the NO₃⁻ ion, an anion found in soluble compounds. Calcium nitrate, Ca(NO₃)₂, is also soluble because it too contains the NO₃⁻ anion. Silver chloride, AgCl, is an insoluble compound even though compounds containing Cl⁻ are generally soluble. As shown in Interactive Table 4.2.1, when the chloride ion is paired with Ag⁺, Hg₂²⁺, or Pb²⁺, an insoluble compound results.

Calcium carbonate, CaCO₃, is an insoluble compound. The presence of the carbonate ion $(CO_3^{2^-})$ places this compound in the group of generally insoluble compounds. The only exceptions to this rule are carbonate compounds containing NH_4^+ , K^+ , or Na^+ ions.

EXAMPLE PROBLEM: Characterize the solubility of ionic compounds.

Classify each of the compounds as soluble or insoluble in water:

- (a) Lead chloride
- (b) Magnesium iodide
- (c) Nickel sulfide

SOLUTION:

You are asked to classify a compound as soluble or insoluble in water. **You are given** the name of a compound. (a) Lead chloride, $PbCl_2$, is insoluble in water. As shown in Interactive Table 4.2.1, ionic compounds containing the chloride ion are generally soluble, but lead chloride is an exception to this rule.

(b) Magnesium iodide, MgI_2 , is soluble in water. As shown in Interactive Table 4.2.1, most ionic compounds that contain the iodide ion are soluble in water, with the exception of PbI_2 , AgI, and Hg_2I_2 .

(c) Nickel sulfide, NiS, is insoluble in water. As shown in Interactive Table 4.2.1, most metal sulfides are insoluble in water.

4.2.1T: Tutorial Assignment Characterize the Solubility of Ionic Compounds **4.2.1:** Mastery Assignment Characterize the Solubility of Ionic Compounds

4.3 Reactions in Aqueous Solution

Section Outline

- 4.3a Precipitation Reactions
- 4.3b Net Ionic Equations
- 4.3c Acid–Base Reactions
- 4.3d Gas-Forming Reactions

Section Summary Assignment

When solutions containing soluble ionic compounds are mixed, the hydrated ions intermingle. Whether or not one of the three common exchange reactions—precipitation reactions, acid–base reactions and gas-forming reactions—occurs, depends on the identity of the ions in solution. In this section, we explore how to predict when these double displacement reactions will occur and how to use the reactions to synthesize a desired ionic compound.

Opening Exploration 4.3: Reactions in Water







4.3a Precipitation Reactions

A precipitation reaction occurs when a solution, originally containing dissolved species, produces a solid, which generally is denser and falls to the bottom of the reaction vessel (**Interactive Figure 4.3.1**).



Interactive Figure 4.3.1 Explore a precipitation reaction

The precipitation of lead iodide

The most common precipitation reactions occurring in aqueous solution involve the formation of an insoluble ionic compound when two solutions containing soluble compounds are mixed.

Consider what happens when an aqueous solution of NaCl is added to an aqueous solution of AgNO₃. The first solution contains hydrated Na⁺ and Cl⁻ ions and the second solution, Ag^+ and NO_3^- ions.

$$NaCl(s) \rightarrow Na^{+}(aq) + Cl^{-}(aq)$$

AgNO₃(s) \rightarrow Ag⁺(aq) + NO₃⁻(aq)

When mixed, a double displacement reaction takes place, forming the soluble compound NaNO₃ and the insoluble compound AgCl. In the reaction vessel the Ag^+ and Cl^- ions combine, and a white solid precipitates from the solution. As the solid precipitates, the Na⁺ and NO₃⁻ ions remain in solution. The overall double displacement reaction is represented by the following balanced equation:

$$NaCl(aq) + AgNO_3(aq) \rightarrow AgCl(s) + NaNO_3(aq)$$

When determining whether a precipitation reaction will occur, first identify the ions present when the two solutions are mixed and then see if an exchange of ions results in an insoluble ionic compound. If an insoluble compound can form, a precipitation reaction occurs. If no combination of ions results in an insoluble compound, no net reaction occurs and the two solutions mix without the formation of a precipitate.

For example, consider the reaction of calcium nitrate with sodium carbonate. Calcium nitrate is a soluble compound (all ionic compounds containing the NO_3^- ion are soluble), and sodium carbonate is a soluble compound (all ionic compounds containing the Na^+ ion are soluble).

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

 $Na_2CO_3(s) \rightarrow 2 Na^+(aq) + CO_3(aq)$

An exchange of ions pairs Ca^{2+} with CO_3^{2-} to form $CaCO_3$ and Na^+ with NO_3^- to form $NaNO_3$. Calcium carbonate is an insoluble compound (most ionic compounds containing the carbonate ion are insoluble), and $NaNO_3$ is soluble. A precipitation reaction occurs, and the balanced equation is

$$Ca(NO_3)_2(aq) + Na_2CO_3(aq) \rightarrow CaCO_3(s) + 2 NaNO_3(aq)$$

EXAMPLE PROBLEM: Predict products and write equations for precipitation reactions.

(a) When aqueous solutions of $Pb(NO_3)_2$ and KI are mixed, does a precipitate form?

(b) Write a balanced equation for the precipitation reaction that occurs when aqueous solutions of copper(II) iodide and potassium hydroxide are combined.

SOLUTION:

You are asked to predict whether a precipitate will form during a chemical reaction and to write a balanced equation for a precipitation reaction.

You are given the identity of two reactants.

(a) Yes, a solid precipitate, PbI₂, forms when these solutions are mixed: $Pb(NO_3)_2(aq) + KI(aq) \rightarrow PbI_2(s) + 2 KNO_3(aq)$

(b) $CuI_2(aq) + 2 \text{ KOH}(aq) \rightarrow Cu(OH)_2(s) + 2 \text{ KI}(aq)$

4.3.1T: Tutorial Assignment Predict Products and Write Equations for Precipitation Reactions

4.3.1: Mastery Assignment Predict Products and Write Equations for Precipitation Reactions

4.3b Net Ionic Equations

In the equation for the formation of solid AgCl shown previously, three of the species, NaCl, AgNO₃, and NaNO₃, are strong electrolytes that dissociate 100% into ions in aqueous solution. It is therefore possible to write the balanced equation in its completely ionized form:

 $Na^+(aq) + Cl^-(aq) + Ag^+(aq) + NO_3^-(aq) \rightarrow AgCl(s) + Na^+(aq) + NO_3^-(aq)$ Two of the ionic species, Na^+ and NO_3^- , do not change during the reaction; they are present in exactly the same form in the reactants and the products. These unchanged ions are called **spectator ions** because they do not participate in the chemical reaction. A **net ionic equation** is written by removing the spectator ions from the completely ionized equation and shows only the chemical species that participate in the chemical reaction.

Completely ionized equation:

 $Na^{+}(aq) + Cl^{-}(aq) + Ag^{+}(aq) + NO_{3}^{-}(aq) \rightarrow AgCl(s) + Na^{+}(aq) + NO_{3}^{-}(aq)$ spectator ion spectator ion spectator ions

Net ionic equation:

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

For precipitation reactions, net ionic equations are written following the steps in **Interactive Table 4.3.1**.

Step 1	Write a balanced chemical equation for the precipitation reaction.
Step 2	Identify all strong electrolytes (soluble compounds) in the reaction and write them in their completely ionized form.
Step 3	Identify the spectator ions in the reaction.
Step 4	Remove spectator ions and write the reaction using only the species that remain.

Interactive Table 4.3.1 Writing Net Ionic Equations for Precipitation Reactions

For example, consider the reaction between calcium nitrate and sodium carbonate.

Step 1 $Ca(NO_3)_2(aq) + Na_2CO_3(aq) \rightarrow CaCO_3(s) + 2 NaNO_3(aq)$

Step 2 Strong electrolytes (soluble compounds): Ca(NO₃)₂, Na₂CO₃(aq) and NaNO₃(aq) Ca²⁺(aq) + 2 NO₃⁻(aq) + 2 Na⁺(aq) + CO₃²⁻(aq) \rightarrow CaCO₃(s) + 2 Na⁺(aq) + 2 NO₃⁻(aq)

Step 3 Spectator ions: NO₃⁻ and Na⁺

Step 4

 $Ca^{2+}(aq) + 2 NO_3 (aq) + 2 Na^+(aq) + CO_3^{2-}(aq) \longrightarrow CaCO_3(s) + 2 Na^+(aq) + 2 NO_3 (aq)$ $Ca^{2+}(aq) + CO_3^{2-}(aq) \rightarrow CaCO_3(s)$

In upcoming sections we will describe writing net ionic equations for other types of reactions in aqueous solution

EXAMPLE PROBLEM: Write Net Ionic Equations for Precipitation Reactions

Write the net ionic equation for the precipitation reaction that occurs when aqueous solutions of sodium sulfide and chromium(III) acetate are combined.

SOLUTION:

You are asked to write a net ionic equation for a chemical reaction. You are given the identity of the reactants.

Step 1. 3 Na₂S(aq) + 2 Cr(CH₃CO₂)₃(aq) \rightarrow 6 NaCH₃CO₂(aq) + Cr₂S₃(s) **Step 2.** Strong electrolytes (soluble compounds): Na₂S(aq), Cr(CH₃CO₂)₃, and NaCH₃CO₂(aq)

$$6 \operatorname{Na}^{+}(aq) + 3 \operatorname{S}^{2-}(aq) + 2 \operatorname{Cr}^{3+}(aq) + 6 \operatorname{CH}_{3}\operatorname{CO}_{2}^{-}(aq) \rightarrow 6 \operatorname{Na}^{+}(aq) + 6 \operatorname{CH}_{3}\operatorname{CO}_{2}^{-}(aq) + 6 \operatorname{CH}_{3}\operatorname{CO}_{2}^{-}(aq)$$

 $Cr_2S_3(s)$

Step 3. Spectator ions: Na⁺ and CH₃CO₂⁻

Step 4.

$$6 \text{ Na}^{\pm}(\text{aq}) + 3 \text{ S}^{2-}(\text{aq}) + 2 \text{ Cr}^{3+}(\text{aq}) + 6 \text{ CH}_3 \text{C} \Theta_2 \text{ (aq)} \longrightarrow 6 \text{ Na}^{\pm}(\text{aq}) + 6 \text{ CH}_3 \text{C} \Theta_2 \text{ (aq)} + \text{Cr}_2 \text{S}_3(\text{s})$$

 $3 \text{ S}^{2-}(\text{aq}) + 2 \text{ Cr}^{3+}(\text{aq}) \rightarrow \text{Cr}_2\text{S}_3(\text{s})$

4.3.2T: Tutorial Assignment Write Net Ionic Equations for Precipitation Reactions **4.3.2:** Mastery Assignment Write Net Ionic Equations for Precipitation Reactions

4.3c Acid–Base Reactions

Acid–base reactions are a second example of double displacement (exchange) reactions that take place in aqueous solution. Acids and bases are common materials, found in foods (citric acid gives lemons their sour taste; acetic acid is one component of vinegar) and household materials (sodium hydroxide and ammonia are bases found in many cleaning products). There are many ways to define acids and bases. **[Flashforward 4.2 Anchor]** In one of the simplest definitions, an **acid** is a species that produces H^+ ions when dissolved in water and a **base** is a species that increases the amount of OH^- ions in a solution. Bases also react with H^+ ions and can therefore also be described as proton (H^+) acceptors. Acids and bases are electrolytes that produce hydrated ions in aqueous solution.

Flashforward 4.2

The definition of an acid and a base we use in this chapter is the Arrhenius definition, where an acid is a substance containing hydrogen that, when dissolved in water, increases the concentration of H^+ ions, and a base is a substance containing the hydroxide group that, when dissolved in water, increases the concentration of OH^- ions. The Brønsted–Lowry definition is a broader description of the nature of acids and bases (see **Section 16.1**). A Brønsted–Lowry acid is a substance that can donate a proton (H^+ ion), and a Brønsted–Lowry base is a substance that can accept a proton (H^+ ion). The Brønsted–Lowry definition allows us to define a larger number of compounds as acids or bases and describe acid–base reactions that take place in solvents other than water (such as ethanol or benzene).

An acid–base reaction is also known as a neutralization reaction because the reaction can result in a solution that is neutral. That is, it no longer has acidic or basic properties. For example, consider the reaction of nitric acid (HNO₃) and sodium hydroxide (NaOH).

$$\frac{\text{HNO}_3(\text{aq}) + \text{NaOH}(\text{aq}) \rightarrow \text{H}_2\text{O}(\ell) + \text{NaNO}_3(\text{aq})}{acid \ base \ water \ salt}$$

This reaction between an acid and a base produces water and a **salt**, an ionic compound formed as the result of an acid–base reaction that consists of a cation donated from a base and an anion donated from an acid. Notice that this is also a double displacement reaction. The base in this reaction, NaOH, acts as a proton acceptor, combining with H^+ to form water.

Acids Nitric acid is a strong acid because it is a strong electrolyte that ionizes 100% in aqueous solution. Acetic acid is an example of a **weak acid**, a weak electrolyte that does not completely ionize in solution (Interactive Table 4.3.2)

$$\begin{array}{l} \mathsf{HNO}_3(\mathsf{aq}) \xrightarrow[ionized]{100\%} \mathsf{H}^+(\mathsf{aq}) + \mathsf{NO}_3^-(\mathsf{aq}) \\ \mathsf{CH}_3\mathsf{CO}_2\mathsf{H}(\mathsf{aq}) \xrightarrow[ionized]{\operatorname{less than 100\%}} \mathsf{H}^+(\mathsf{aq}) + \mathsf{CH}_3\mathsf{CO}_2^-(\mathsf{aq}) \end{array}$$

There are six important strong acids in aqueous solution (Interactive Table 4.3.2) and numerous weak acids. Many weak acids are **organic acids**, compounds made up mostly of carbon, hydrogen, and oxygen that also contain the -C(O)OH structural group (**Figure 4.3.2**).

Strong Acids		Weak Acids	Weak Acids	
HCl	Hydrochloric acid	CH ₃ CO ₂ H	Acetic acid	
HBr	Hydrobromic acid	$H_3C_6H_5O_5$	Citric acid	
HI	Hydroiodic acid	$H_2C_2O_4$	Oxalic acid	
HNO ₃	Nitric acid	HF	Hydrofluoric acid	
H_2SO_4	Sulfuric acid	H_3PO_4	Phosphoric acid	
HClO ₄	Perchloric acid	H ₂ CO ₃	Carbonic acid	

Interactive Table 4.3.2 Some Important Acids



Figure 4.3.2 Molecular models of some organic acids

Some acids can produce more than one mole of H^+ ions per mole of acid. An acid that produces only one mole of H^+ ions per mole of acid is a **monoprotic acid**. Sulfuric acid, H_2SO_4 , and carbonic acid, H_2CO_3 , are examples of **diprotic acids**, acids that can dissociate to form two moles of H^+ ions per mole of acid.

$$H_2SO_4(aq) \rightarrow H^+(aq) + HSO_4^-(aq)$$
$$HSO_4^-(aq) \rightarrow H^+(aq) + SO_4^{-2}(aq)$$

Bases Bases are also characterized as being either strong or weak (Interactive Table 4.3.3). All common strong bases are hydroxide salts such as NaOH and KOH. Weak bases are most often compounds containing a nitrogen atom such as ammonia, NH₃, and trimethylamine, (CH₃)₃N.

Strong Bases		Weak Bases	
LiOH	Lithium hydroxide	NH ₃	Ammonia
NaOH	Sodium hydroxide	$(CH_3)_3N$	Trimethylamine
КОН	Potassium hydroxide	CH ₃ CH ₂ NH ₂	Ethylamine
Ca(OH) ₂	Calcium hydroxide		

Interactive Table 4.3.3 Some Important Bases

When added to water, strong bases act as strong electrolytes and are ionized completely. For example, when NaOH is added to water, it forms hydrated Na^+ and OH^- ions.

NaOH(s)
$$\xrightarrow{100\%}$$
 Na⁺(aq) + OH⁻(aq)

When added to water, weak bases also increase the concentration of hydroxide ion (OH^{-}) but do so by reacting with water. For example, NH_3 is a weak base and reacts with water to form NH_4^+ and OH^- ions.

$$NH_3(g) + H_2O(\ell) \xrightarrow{\text{less than 100\%}} NH_4^+(aq) + OH^-(aq)$$

Like a weak acid, a weak base is a weak electrolyte that does not completely ionize. In a solution of NH₃, for example, only about 1% of the NH₃ molecules react with water.

Net Ionic Equations for Acid–Base Reactions The net ionic equation for a strong acid–strong base reaction is written by first writing a completely ionized equation.

 $H^+(aq) + NO_3^-(aq) + Na^+(aq) + OH^-(aq) \rightarrow H_2O(\ell) + Na^+(aq) + NO_3^-(aq)$ Identifying the spectator ions that remain unchanged during the reaction (Na⁺ and NO₃⁻) and removing them results in the net ionic equation for most strong acid–strong base reactions. $H^+(aq) + OH^-(aq) \rightarrow H_2O(\ell)$

The net ionic equation for the reaction of strong acids or bases with weak acids or bases also involves writing a completely ionized equation and identifying any spectator ions. For example, consider the reaction of hydrochloric acid with the weak base ammonia.

 $HCl(aq) + NH_3(aq) \rightarrow NH_4Cl(aq)$

In this reaction, the base acts as a proton acceptor, accepting H^+ from the acid to form the ammonium ion, NH_4^+ . Writing the equation in its completely ionized form,

 $H^+(aq) + Cl^-(aq) + NH_3(aq) \rightarrow NH_4^+(aq) + Cl^-(aq)$

Ammonium chloride, NH₄Cl, is a soluble ionic compound that dissociates completely in aqueous solution. Removing the spectator ion (Cl⁻) results in the following net ionic equation: $H^+(aq) + NH_2(aq) \rightarrow NH_4^+(aq)$

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

For acid–base reactions, net ionic equations are written following the steps in **Interactive Table 4.3.4**.

Interactive Table 4.3.4	Writing Net Ionic Ed	quations for Acid–Base Reactions
--------------------------------	----------------------	----------------------------------

Step 1	Write a balanced chemical equation for the acid-base reaction.
Step 2	Identify all strong electrolytes (strong acids and bases and soluble ionic compounds) in the reaction and write them in their completely ionized form.
Step 3	Identify the spectator ions in the reaction.
Step 4	Remove spectator ions and write the reaction using only the species that remain.

EXAMPLE PROBLEM: Write net ionic equations for acid-base reactions.

Write the net ionic equation for the reaction that occurs when aqueous solutions of potassium hydroxide and phosphoric acid are combined.

SOLUTION:

You are asked to write the net ionic equation for an acid–base reaction. **You are given** the identity of the reactants in the acid–base reaction.

Step 1. 3 KOH(aq) + H₃PO₄(aq) \rightarrow 3 H₂O(ℓ) + K₃PO₄(aq)

Step 2. KOH is a strong base, and K₃PO₄ is a soluble ionic compound.

 $3 \text{ K}^{+}(aq) + 3 \text{ OH}^{-} + \text{H}_{3}\text{PO}_{4}(aq) \rightarrow 3 \text{ H}_{2}\text{O}(\ell) + 3 \text{ K}^{+}(aq) + \text{PO}_{4}^{-3}(aq)$

Notice that H₃PO₄ is a weak acid and therefore is not written in an ionized form.

Step 3. K^+ is a spectator ion.

Step 4

 $3 \text{ K}^{\pm}(\text{aq}) + 3 \text{ OH}^{-} + \text{H}_{3}\text{PO}_{4}(\text{aq}) \longrightarrow 3 \text{ H}_{2}\text{O}(\ell) + 3 \text{ K}^{\pm}(\text{aq}) + \text{PO}_{4}^{3-}(\text{aq})$

 $3 \text{ OH}^- + \text{H}_3\text{PO}_4(\text{aq}) \rightarrow 3 \text{ H}_2\text{O}(\ell) + \text{PO}_4^{3-}(\text{aq})$

4.3.3T: Tutorial Assignment Write Net Ionic Equations for Acid–Base Reactions **4.3.3:** Mastery Assignment Write Net Ionic Equations for Acid–Base Reactions

4.3d Gas-Forming Reactions

A third double displacement reaction commonly encountered in the laboratory is the reaction of an ionic compound with an acid to form a gas. These gas-forming reactions, introduced previously in this chapter, are a special type of acid–base reaction involving less obvious bases such as $CuCO_3$ and Na_2SO_3 (Figure 4.3.3).



Figure 4.3.3 Alka-seltzer contains an acid (citric acid) and a base (sodium bicarbonate) that react to form carbon dioxide gas.

When the gas-forming reaction involves a metal carbonate, one product of the reaction is carbon dioxide gas. Consider the reaction between copper(II) carbonate and hydrochloric acid.

$$CuCO_3(s) + 2 HCl(aq) \rightarrow CuCl_2(aq) + H_2CO_3(aq)$$

As shown previously, one product of the double displacement reaction, H_2CO_3 , undergoes a decomposition reaction to produce gaseous carbon dioxide and water.

$$H_2CO_3(aq) \rightarrow H_2O(\ell) + CO_2(g)$$

The net reaction, therefore, is

 $CuCO_3(s) + 2 HCl(aq) \rightarrow CuCl_2(aq) + CO_2(g) + H_2O(\ell)$

The procedure for writing net ionic equations for gas-forming reactions is similar to that used for precipitation and acid–base net ionic equations, as shown in Interactive Table 4.3.5.

Step 1	Write a balanced chemical equation for the gas-forming reaction.
Step 2	Identify all strong electrolytes (strong acids and bases and soluble ionic compounds) in the reaction and write them in their completely ionized form.
Step 3	Identify the spectator ions in the reaction.
Step 4	Remove spectator ions and write the reaction using only the species that remain.

nteractive Table 4.3.5	Writing Net	Ionic Equations for	or Gas-Forming Reactions
------------------------	-------------	----------------------------	--------------------------

Applying these steps to the reaction between copper(II) carbonate and hydrochloric acid,

Step 1
$$CuCO_3(s) + 2 HCl(aq) \rightarrow CuCl_2(aq) + CO_2(g) + H_2O(\ell)$$

Step 2 HCl is a strong base and CuCl₂ is a soluble ionic compound.

$$CuCO_3(s) + 2 H^+(aq) + 2 Cl^-(aq) \rightarrow Cu^{2+}(aq) + 2 Cl^-(aq) + CO_2(g) + H_2O(\ell)$$

Step 3 Chloride ions (Cl⁻) are spectator ions in this reaction.

Step 4

 $CuCO_{3}(s) + 2 H^{+}(aq) + 2 Cl^{-}(aq) \longrightarrow Cu^{2+}(aq) + 2 Cl^{-}(aq) + CO_{2}(g) + H_{2}O(\ell)$

$$CuCO_3(s) + 2 H^+(aq) \rightarrow Cu^{2+}(aq) + CO_2(g) + H_2O(\ell)$$

When a gas-forming reaction involves an ionic compound that is not a metal carbonate, it is not always easy to predict the products of the reaction. For example, sodium sulfite, Na₂SO₃, reacts with hydrochloric acid to form gaseous sulfur dioxide.

$$Ia_2SO_3(aq) + 2 HCl(aq) \rightarrow 2 NaCl(aq) + SO_2(g) + H_2O(\ell)$$

The net ionic equation for this reaction is

$$\mathrm{SO_3}^{2-}(\mathrm{aq}) + 2 \mathrm{H}^+(\mathrm{aq}) \rightarrow \mathrm{SO_2}(\mathrm{g}) + \mathrm{H_2O}(\ell)$$

EXAMPLE PROBLEM: Write net ionic equations for gas-forming reactions.

Write a net ionic equation for the reaction that occurs when aqueous hydroiodic acid is combined with solid zinc carbonate.

SOLUTION:

You are asked to write the net ionic equation for a gas-forming reaction.

You are given the identity of the reactants in the gas-forming reaction.

Step 1. 2 HI(aq) + ZnCO₃(s) \rightarrow ZnI₂(aq) + H₂O(ℓ) + CO₂(g)

Note that H₂CO₃ is formed in the reaction but undergoes a decomposition reaction to produce gaseous carbon dioxide and water.

Step 2. HI is a strong acid and ZnI_2 is a soluble ionic compound.

 $2 \text{ H}^{+}(aq) + 2 \text{ I}^{-}(aq) + \text{ZnCO}_{3}(s) \rightarrow \text{Zn}^{2+}(aq) + 2 \text{ I}^{-}(aq) + \text{H}_{2}\text{O}(\ell) + \text{CO}_{2}(g)$

Step 3. The iodide ion (I^-) is a spectator ion in this reaction. **Step 4.**

 $2 H^{+}(aq) + 2 I^{-}(aq) + ZnCO_{3}(s) \longrightarrow Zn^{2+}(aq) + 2 I^{-}(aq) + H_{2}O(\ell) + CO_{2}(g)$

 $2 \operatorname{H}^{+}(aq) + \operatorname{ZnCO}_{3}(s) \rightarrow \operatorname{Zn}^{2+}(aq) + \operatorname{H}_{2}O(\ell) + \operatorname{CO}_{2}(g)$

4.3.4T: Tutorial Assignment Write Net Ionic Equations for Gas-Forming Reactions 4.3.4: Mastery Assignment Write Net Ionic Equations for Gas-Forming Reactions

4.4 Oxidation–Reduction Reactions

Section Outline

- 4.4a Oxidation and Reduction
- 4.4b Oxidation Numbers and Oxidation States
- 4.4c Recognizing Oxidation–Reduction Reactions

Section Summary Assignment

The two simplest particles in chemistry are the proton and the electron. Whereas acid-base chemistry involves a transfer of protons, H^+ ions, between acids and bases, many other reactions involve the transfer of electrons. These electron-transfer reactions are known as **oxidation-reduction reactions**, or *redox reactions*. Most of the combination, decomposition, and single displacement reactions described earlier in this chapter are oxidation-reduction reactions.



Opening Exploration 4.4: An Oxidation–Reduction Reaction

4.4a Oxidation and Reduction

Oxidation is the loss of one or more electrons from a chemical species, and **reduction** is the gain of one or more electrons. For example, consider the single displacement reaction involving zinc metal and a solution of copper(II) nitrate (Interactive Figure 4.4.1). If a piece of zinc metal is immersed in a $Cu(NO_3)_2$ solution, a thin coating of copper metal quickly forms on the zinc.

Interactive Figure 4.4.1 Investigate oxidation and reduction.



Zinc metal reacts with aqueous Cu²⁺ ions to form copper metal and aqueous Zn²⁺ ions.

Complete equation:	$Zn(s) + 2 Cu(NO_3)_2(aq) \rightarrow Zn(NO_3)_2(aq) + Cu(s)$
Net ionic equation:	$Zn(s) + Cu^{2+}(aq) \rightarrow Zn^{2+}(aq) + Cu(s)$

In this oxidation–reduction reaction, zinc gives up two electrons to form Zn^{2+} and the copper(II) ions gain two electrons to form copper metal, Cu. Thus, Zn is oxidized and Cu²⁺ is reduced.



Notice that in order for a species to be oxidized and give up electrons, some other species must gain the electrons lost. The electron-acceptor species in an oxidation–reduction reaction is called the **oxidizing agent**. Because the oxidizing agent gains electrons, it is reduced. The **reducing agent** donates electrons to the species that is reduced and is therefore oxidized. In summary,

- An oxidizing agent oxidizes another substance and is reduced.
- A reducing agent reduces another substance and is oxidized.

In the reaction of zinc with copper(II) ions,

$Zn(s) + Cu^{2+}(aq) \rightarrow Zn^{2+}(aq) + Cu(s)$		
Loses 2 e ⁻	Gains 2 e ⁻	
oxidized	reduced	
reducing agent	oxidizing agent	

The equation for an oxidation–reduction reaction can be broken down in a way that emphasizes the gain and loss of electrons. A **half-reaction** shows only the species involved in oxidation or reduction and also includes the electrons lost or gained by each species. Adding the oxidation and reduction half-reactions results in the net ionic equation. Notice that in the half-reactions that follow, the total number of electrons lost by Zn is equal to the total number of electrons gained by Cu^{2+} .

Oxidation half-reaction:	$Zn(s) \rightarrow Zn^{2+}(aq) + 2 e^{-}$
Reduction half-reaction:	$Cu^{2+}(aq) + 2 e^{-} \rightarrow Cu(s)$
Net ionic equation:	$Zn(s) + Cu^{2+}(aq) \rightarrow Zn^{2+}(aq) + Cu(s)$

The term *oxidation* originally referred to the addition of oxygen, the most commonly encountered oxidizing agent, to an element or compound. When molecular oxygen reacts with a metal, for example, each O_2 molecule gains four electrons (two for each O atom) and is reduced to form oxide ions. Halogens, F_2 , Cl_2 , Br_2 , and I_2 , are also very good oxidizing agents.

Metals are generally good reducing agents that are easily oxidized to form positively charged ions, and they show a range of reducing ability. For example, alkali and alkaline earth metals are excellent reducing agents, as is aluminum. On the other hand, the coinage metals, Cu, Ag, and Au, are poor reducing agents. This is why they are useful for making coins; they do not oxidize easily and therefore do not corrode.

4.4b Oxidation Numbers and Oxidation States

In the reaction of zinc and copper(II) ions, it is easy to see in the net ionic equation the flow of electrons from Zn to Cu^{2+} . In many other cases involving more complex compounds and ions, the electron transfer is more difficult to discern. To aid in identifying oxidizing and reducing agents, a system of electron counting has been developed to identify species that are either gaining or losing electrons during a reaction. This system involves the assignment of oxidation numbers to elements, ions, and atoms in compounds.

The **oxidation number**, also called *oxidation state* of an atom, represents the number of electrons that have been gained (if the oxidation number is negative) or lost (if the oxidation number is positive) from the neutral atom. Oxidation numbers are primarily used to identify the transfer of electrons in an oxidation–reduction reaction and are not always representative of the actual charge carried by an atom in a compound. Oxidation numbers are assigned according to the rules shown in **Table 4.4.1**.

Rule	Example
1. Each atom in a pure element has an	Fe in Fe(s) oxidation number = 0
oxidation number of zero.	Each O in $O_2(g)$ oxidation number = 0
2. A monoatomic ion has an oxidation	Cl in Cl ^{$-$} oxidation number = -1
number equal to the ion charge.	Mg in Mg ²⁺ oxidation number = $+2$
3. In compounds, halogens (F, Cl, Br, I)	Each F in CF_4 oxidation number = -1
have an oxidation number of -1 .	Each Cl in ClF ₃ oxidation number = $+3$
Exception: When halogens are combined with	
oxygen or fluorine, the oxidation number of Cl,	
Br, and I is not –1.	
4. In compounds, oxygen has an oxidation	Each O in CO ₂ oxidation number = -2
number of –2.	Each O in H_2O_2 oxidation number = -1
Exception: In compounds containing the peroxide	
ion $(O_2^{2^{-}})$, oxygen has an oxidation number of	
-1.	
5. When combined with nonmetals,	Each H in CH_4 oxidation number = +1
hydrogen is assigned an oxidation number of +1.	H in LiH oxidation number = -1
With metals, hydrogen has an oxidation number	
of -1.	
6. The sum of the oxidation numbers for all	CO_2
atoms in an ion is equal to the overall charge on	(C oxidation number) $+ 2 \times$ (O oxidation
the ion. For a neutral compound, the sum of all of	number) = 0
the oxidation numbers is equal to zero.	(C oxidation number) $+ 2 \times (-2) = 0$
	C oxidation number = $+4$
	ClO ₄ ⁻
	(Cl oxidation number) $+ 4 \times$ (O oxidation
	number) = -1
	(Cl oxidation number) $+ 4 \times (-2) = -1$
	Cl oxidation number = $+7$

Table 4.4.1 Rules for Assigning Oxidation Numbers

EXAMPLE PROBLEM: Assign oxidation numbers.

Determine the oxidation number of each atom in K₂CrO₄

SOLUTION:

You are asked to assign oxidation numbers to elements in a compound. **You are given** the formula of the compound.

This compound contains two K^+ ions, each of which has an oxidation number of +1. Each of the four O atoms has an oxidation number of -2, for a total of -8. The oxidation number of Cr is found using the K and O oxidation numbers and the overall charge on the compound.

charge on K_2CrO_4 = sum of K oxidation numbers + chromium oxidation number + sum of oxygen oxidation numbers

0 = 2(+1) +oxidation number Cr + 4(-2)

The oxidation number of Cr is therefore +6. This number does not represent the actual charge on Cr in K_2CrO_4 .

4.4.1T: Tutorial Assignment Assign Oxidation Numbers

4.4.1: Mastery Assignment Assign Oxidation Numbers

4.4c Recognizing Oxidation–Reduction Reactions

We can generally predict the products of acid-base and precipitation reactions. This is not the case for oxidation-reduction reactions. In these reactions, predicting the products is beyond the scope of this introductory textbook. That being said, you should be able to recognize an oxidation-reduction reaction and be able to predict when one is likely to occur, if not what products will be formed.

Oxidation-reduction reactions always involve a change in the oxidation number of one or more atoms. Therefore, the most certain means of determining whether a reaction is an oxidation-reduction reaction is to determine the oxidation numbers of all elements in the reaction. If any of the oxidation numbers change when proceeding from reactants to products, the reaction is an oxidation-reduction reaction.

For example, consider the following reaction.

 $Cl_2(g) + H_3AsO_4(aq) \rightarrow HAsO_2(aq) + 2 HClO(aq)$

First, assign oxidation numbers for all atoms.

 $Cl_2(g) + H_3AsO_4(aq) \rightarrow HAsO_2(aq) + 2 HClO(aq)$

 $(0) \qquad (+1)(+5)(-2) \qquad (+1)(+3)(-2) \qquad (+1)(+1)(-2)$

Any element with a change in oxidation number when proceeding from reactants to products has been oxidized or reduced. In the preceding reaction, the oxidation number of chlorine increases from 0 (in Cl_2) to +1 (in HClO). The oxidation number has increased because each chlorine atom has lost an electron. Chlorine, Cl_2 , has been oxidized to HClO and is the reducing agent. The oxidation number of arsenic decreases from +5 (in H_3AsO_4) to +3 (in HAsO₂). The oxidation number has decreased because each arsenic atom has gained two electrons. H_3AsO_4 has been reduced to HAsO₂ and is the oxidizing agent.

Some general guidelines can also help make it easier to recognize oxidation–reduction reactions. For example, oxidation–reduction reactions often involve one or more common oxidizing and reducing agents (**Interactive Table 4.4.2**).

Oxidizing Agent	Reaction Product	Reducing Agent	Reaction Product
O ₂ (oxygen)	O^{2-} (oxide ion) or an	H ₂ (hydrogen) or	H^+ (hydrogen ion) or H
	oxygen-containing	hydrogen-containing	combined in H ₂ O
	molecular compound	molecular compound	
H ₂ O ₂ (hydrogen	$H_2O(\ell)$	C (carbon) used to	CO and CO ₂
peroxide)	- ()	reduce metal oxides	
F_2 , Cl_2 , Br_2 , or I_2	F^{-} , Cl^{-} , Br^{-} , or I^{-} (halide	M, metals such as Na,	M^{n+} , metal ions such as
(halogens)	ions)	K, Fe, or Al	$Na^{+}, K^{+}, Fe^{3+}, or Al^{3+}$
$Cr_2O_7^{2-}$ (dichromate ion)	Cr ³⁺ (chromium(III) ion),		
	in acid solution		
MnO_4^{-} (permanganate	Mn ²⁺ (manganese(II)		
ion)	ion), in acid solution		

Interactive Table 4.4.2 Common Oxidizing and Reducing Agents

As shown in **Interactive Table 4.4.1**, reactions involving a pure element are usually oxidation– reduction reactions. Also, almost all reactions involving compounds with atoms in very high or very low oxidation states are oxidation–reduction reactions. For example, Mn has a very high oxidation number of +7 in the permanganate ion, MnO_4^- . The permanganate ion is a strong oxidizing agent because reactions involving the ion almost always involve it being reduced to a lower oxidation number.

Finally, all combustion reactions and most explosive reactions are oxidation–reduction reactions. In reactions that involve the burning of organic matter in air, the organic material is the reducing agent and O_2 in air is the oxidizing agent.

EXAMPLE PROBLEM: Identify oxidizing and reducing agents.

Identify the oxidizing agent and the reducing agent in the following reactions:

(a) $2 \text{ K}(s) + 2 \text{ H}_2\text{O}(\ell) \rightarrow 2 \text{ KOH}(aq) + \text{H}_2(g)$

(b) $I_2(s) + 2 Br^{-}(aq) \rightarrow 2 I^{-}(aq) + Br_2(\ell)$

SOLUTION:

You are asked to identify the oxidizing and reducing agents in a reaction. You are given a chemical equation.

(a) Potassium metal is a common reducing agent, and in this reaction it is oxidized to form the potassium ion, K^+ . Water is therefore the oxidizing agent. The hydrogen in water is reduced to elemental H₂.

(b) Iodine, I_2 , is a halogen and is a common oxidizing agent. Elemental iodine is reduced to form the iodide ion, I^- , and Br^- , the reducing agent, is oxidized to form elemental bromine, Br_2 .

4.4.2T: Tutorial Assignment Identify Oxidizing and Reducing Agents: Tutorial Assignment **4.4.2:** Mastery Assignment Identify Oxidizing and Reducing Agents

4.5 Stoichiometry of Reactions in Aqueous Solution

Section Outline

- 4.5a Solution Concentration and Molarity
- 4.5b Preparing Solutions of Known Concentration
- 4.5c Solution Stoichiometry
- 4.5d Titrations

Section Summary Assignment

In the previous chapter we analyzed weight relations between reactants and products. Here we extend the quantitative study of chemical reactions to those reactions occurring in aqueous solution.

Opening Exploration 4.5 Why is Concentration Important? [Figure ID #4-27] Winters photo

4.5a Solution Concentration and Molarity

To work with quantities of materials in aqueous solution, first we must measure the amount of solute dissolved in a solvent. We will work with the **concentration** of a solute in a solution, a quantitative measure of the amount of material dissolved in a known quantity of solvent or solution (**Figure 4.5.1**).



Figure 4.5.1 The concentration of hydrogen peroxide in this solution is indicated on the label.

There are many measurements of concentration, including weight percent, parts per million (ppm), and molarity. The most common concentration used in the chemistry lab is **molarity** (**M**), the amount of solute (in moles) dissolved in exactly 1 liter of solution (**Equation 4.1**)

molarity (M) =
$$\frac{\text{moles of solute}}{1 \text{ L of solution}}$$
 (4.1)

It is helpful to always think of molarity as a ratio because it can be used as a conversion factor in calculations, converting between the amount (in moles) of solute in a solution and the volume (in liters) of a solution.

Square brackets are placed around the formula of a solute to indicate a concentration in molarity units. For example, reporting a concentration as [NaCl] = 0.15 M means that the amount of sodium chloride dissolved in a solution is 0.15 mol per liter of solution, or the NaCl concentration is 0.15 molar.

To determine the concentration of a solute in a solution in units of molarity, first calculate the amount of solute present (in moles) and then divide that amount by the volume of the solution, in units of liters (L). For example, the concentration (M) of 250. mL of solution that contains 14.5 g $CaCl_2$ is calculated as follows.

First, determine the amount of solute present.

$$14.5 \text{ g CaCl}_2 \times \frac{1 \text{ mol CaCl}_2}{111.0 \text{ g}} = 0.131 \text{ mol CaCl}_2$$

Next, convert the solution volume to units of liters.

250. mL ×
$$\frac{1 \text{ L}}{1000 \text{ mL}}$$
 = 0.250 L

Finally, use Equation 4.1 to calculate the concentration of the solution.

$$[CaCl_2] = \frac{0.131 \text{ mol } CaCl_2}{0.250 \text{ L}} = 0.524 \text{ M } CaCl_2$$

EXAMPLE PROBLEM: Calculate solution concentration in molarity units.

A student weighs out 5.33 g of NiBr₂ and transfers it to a 100.-mL volumetric flask, adds enough water to dissolve the solid, and then adds water to the 100-mL mark on the neck of the flask. Calculate the concentration (in molarity units) of nickel bromide in the resulting solution.

SOLUTION:

You are asked to calculate the concentration of a solution in molarity units.

You are given the identity of the solute, the amount of solute in the solution, and the total volume of the solution.

First determine the amount of solute present.

5.33 g NiBr₂ ×
$$\frac{1 \text{ mol NiBr}_2}{218.5 \text{ g}}$$
 = 0.0244 mol NiBr₂

Use Equation 4.1 to calculate the concentration of the solution.

$$[\text{NiBr}_2] = \frac{0.0244 \text{ mol NiBr}_2}{0.100 \text{ L}} = 0.244 \text{ M NiBr}_2$$

4.5.1T: Tutorial Assignment Calculate Solution Concentration in Molarity Units 4.5.1: Mastery Assignment Calculate Solution Concentration in Molarity Units

The concentration of a solute in a solution can be used along with the compound formula to determine the concentration of a specific ionic species in a solution. For example, the concentration of calcium ions and chloride ions in the 0.524-M CaCl₂ solution is calculated here:

$$[Ca^{2+}] = \frac{0.524 \text{ mol } CaCl_2}{1 \text{ L}} \times \frac{1 \text{ mol } Ca^{2+}}{1 \text{ mol } CaCl_2} = 0.524 \text{ M}$$
$$[Cl^{\$}] = \frac{0.524 \text{ mol } CaCl_2}{1 \text{ L}} \times \frac{2 \text{ mol } Cl^{\$}}{1 \text{ mol } CaCl_2} = 1.05 \text{ M}$$

As shown in this calculation and in Interactive Figure 4.5.2, the chloride ion concentration is twice that of the calcium ion concentration because the ions are present in a 2:1 ratio in the compound formula, CaCl₂.

Interactive Figure 4.5.2 Determine ion concentrations.



In an aqueous solution of CaCl2, the chloride ion concentration is twice the calcium ion concentration.

EXAMPLE PROBLEM: Calculate ion concentration.

In the laboratory, a student adds 15.8 g of sodium sulfate to a 500.-mL volumetric flask and adds water to the mark on the neck of the flask. Calculate the concentration (in mol/L) of sodium sulfate, the sodium ion, and the sulfate ion in the solution.

SOLUTION:

You are asked to calculate the concentration of a solution and the concentration of the ions in the solution.

You are given the identity of the solute, the amount of solute in the solution, and the total volume of the solution.

First determine the concentration of sodium sulfate.

15.8 g Na₂SO₄ ×
$$\frac{1 \text{ mol Na}_2 \text{SO}_4}{142.0 \text{ g}} = 0.111 \text{ mol Na}_2 \text{SO}_4$$

$$[Na_2SO_4] = \frac{0.111 \text{ mol } Na_2SO_4}{0.500 \text{ L}} = 0.222 \text{ M } Na_2SO_4$$

Use the compound stoichiometry to determine the ion concentration in the solution.

$$>[Na^{+}] = \frac{0.222 \text{ M Na}_{2}\text{SO}_{4}}{1 \text{ L}} \times \frac{2 \text{ mol Na}^{+}}{1 \text{ mol Na}_{2}\text{SO}_{4}} = 0.444 \text{ M Na}^{+}$$

$$[SO_4^{2\check{S}}] = \frac{0.222 \text{ M Na}_2 SO_4}{1 \text{ L}} \times \frac{1 \text{ mol } SO_4^{2\check{S}}}{1 \text{ mol } Na_2 SO_4} = 0.222 \text{ M } SO_4^{2\check{S}}$$

4.5.2T: Tutorial Assignment Calculate Ion Concentration **4.5.2:** Mastery Assignment Calculate Ion Concentration

The concentration of a solution can also be used to determine the volume of a solution that contains a specific amount of solute or the amount of solute in a given volume of solution. That is, a concentration in units of molarity can be used as a conversion factor to convert between the amount of solute in a solution (in moles) and the volume of a solution (in liters). For example, the volume of a 0.264-M solution of AgNO₃ needed to provide 18.6 g of the ionic compound is calculated next.

First, determine the amount of AgNO₃ needed in units of moles.

$$18.6 \text{ g AgNO}_3 \times \frac{1 \text{ mol AgNO}_3}{169.9 \text{ g}} = 0.109 \text{ mol AgNO}_3 \text{ needed}$$

Next, use the amount of AgNO₃ needed and the solution concentration to calculate the volume of solution needed.

$$0.109 \text{ mol AgNO}_3 \times \frac{1 \text{ L solution}}{0.264 \text{ mol AgNO}_3} = 0.415 \text{ L solution}$$

Notice that in this case, the concentration of the solution is inverted when used as a conversion factor so that the units cancel correctly, resulting in an answer with volume units.

EXAMPLE PROBLEM: Use molarity as a conversion factor.

Calculate the mass (in grams) of magnesium iodide that must be added to a 250-mL volumetric flask in order to prepare 250 mL of a 0.169-M aqueous solution of the salt.

SOLUTION:

You are asked to calculate the mass of solute required to make a solution of known volume and concentration.

You are given the identity of the solute, the volume of the solution, and the concentration of the solution.

First determine the amount of magnesium iodide needed using the concentration and volume of the desired solution.

$$0.250 \text{ L} \times \frac{0.169 \text{ mol MgI}_2}{1 \text{ L}} = 0.0423 \text{ mol MgI}_2$$

Use the amount of magnesium iodide to determine the mass of solid needed to prepare the solution.

$$0.423 \text{ mol } MgI_2 \times \frac{278.1 \text{ g}}{1 \text{ mol } MgI_2} = 118 \text{ g } MgI_2$$

4.5.3T: Tutorial Assignment Use Molarity as a Conversion Factor

4.5.3: Mastery Assignment Use Molarity as a Conversion Factor

4.5b Preparing Solutions of Known Concentration

One of the most important skills learned by chemists is how to accurately prepare a solution of known concentration. This process has two parts: First, calculate the quantities that must be combined to make the solution; then correctly prepare the solution in the laboratory. We will describe both parts here, but it is only by practicing in the chemistry lab that you can become proficient in the skills necessary to prepare a solution correctly.

The laboratory equipment necessary for this process must allow you to accurately measure the volume of a solution. **Volumetric glassware** is laboratory glassware that has been carefully calibrated to contain very accurate volumes or allow for the measurement of very accurate volumes (**Interactive Figure 4.5.3**). Volumetric flasks are typically used to make solutions of known concentration. These flasks are generally available with volumes of 25 mL, 50 mL, 100 mL, 250 mL, 1 L, and 2 L. Although the flasks can hold more than the stated volume, a mark is placed on the neck of the flask that denotes a specific volume; filling the flask to that mark ensures that it holds the stated volume of liquid.

Interactive Figure 4.5.3 Select the correct glassware

[Figure ID #4-30]Winters photo

A collection of volumetric and nonvolumetric laboratory glassware

Two methods are used to make a solution of known concentration: the **direct addition** method and the **dilution** method.

Direct Addition Method The direct addition method is generally used to prepare solutions with relatively high concentrations of solute, whereas the dilution method is generally used to prepare more dilute solutions.

For example, the direct addition method can be used to prepare 100. mL of a 0.200-M solution of sucrose, $C_{12}H_{22}O_{11}$. First, calculate the quantity (in grams) of sucrose needed to make the solution. Using the volume of the desired solution and the desired concentration, calculate the amount of sucrose needed (in moles).

100. mL solution
$$\times \frac{1 \text{ L}}{1000 \text{ mL}} = 0.100 \text{ L}$$
 solution
0.100 L solution $\times \frac{0.200 \text{ mol sucrose}}{1 \text{ L solution}} = 0.0200 \text{ mol sucrose needed}$

Next, calculate the quantity of sucrose needed, in units of grams.

$$0.0200 \text{ mol } C_{12}H_{22}O_{11} \times \frac{342.3 \text{ g}}{1 \text{ mol } C_{12}H_{22}O_{11}} = 6.85 \text{ g} C_{12}H_{22}O_{11}$$

To make 100. mL of a 0.200-M solution of sucrose, weigh out 6.85 g of sucrose on a laboratory balance and carefully add it to a 100-mL volumetric flask. Add a small amount of water to the flask and swirl until the sucrose dissolves completely. Add additional water to the flask, mixing as each portion is added. Carefully add water to the volumetric flask until the bottom of the meniscus sits on the mark on the neck of the flask. Invert the flask to mix the contents (**Interactive Figure 4.5.4**).

Interactive Figure 4.5.4 Make a solution by direct addition.



The materials required to make a solution by direct addition

EXAMPLE PROBLEM: Use the Direct Addition Method

Describe the steps involved in preparing 500. L of a 0.125-M potassium nitrate solution using solid potassium nitrate, a 500-mL volumetric flask, and deionized water.

SOLUTION:

You are asked to describe the steps in making a solution of known volume and concentration using the direct addition method.

You are given the volume and concentration of the desired solution and the identity of the solute.

Calculate the amount of KNO3 required to prepare the solution.

$$0.500 \text{ L} \times \frac{0.125 \text{ mol KNO}_3}{1 \text{ L}} \times \frac{101.1 \text{ g}}{1 \text{ mol KNO}_3} = 6.32 \text{ g KNO}_3$$

To make the solution, weigh out 6.32 g of KNO₃ on a laboratory balance and carefully add it to a 500-mL volumetric flask. Add a small amount of deionized water to the flask and swirl until the solid dissolves completely. Add additional water to the flask, mixing as each portion is added. Carefully add water to the volumetric flask until the bottom of the meniscus sits on the mark on the neck of the flask. Invert the flask to mix the contents.

4.5.4T: Tutorial Assignment Use the Direct Addition Method 4.5.4: Mastery Assignment Use the Direct Addition Method

Dilution Method The dilution method is used to prepare very dilute solutions because it is difficult to weigh small amounts of solute with great accuracy. In the dilution method, the solution is prepared by diluting a more concentrated existing solution with a known concentration. For example, we can use a 0.600-M NiCl₂ stock solution to prepare 50.0 mL of solution that is 0.0125 M in NiCl₂.

First, use the concentration and volume of the desired solution to calculate the amount of solute (in moles) needed from the stock solution.

50.0 mL solution
$$\times \frac{1 \text{ L}}{1000 \text{ mL}} = 0.0500 \text{ L}$$
 solution
0.0500 L solution $\times \frac{0.0125 \text{ mol NiCl}_2}{1 \text{ L solution}} = 6.25 \times 10^{\text{§4}} \text{ mol NiCl}_2 \text{ needed}$

Next, use the amount of solute needed and the concentration of the stock solution to calculate the volume of stock solution that contains the desired amount of NiCl₂.

$$6.25 \times 10^{\$4} \text{ mol NiCl}_2 \times \frac{1 \text{ L solution}}{0.600 \text{ mol NiCl}_2} = 1.04 \times 10^{\$3} \text{ L}$$

To prepare the solution, transfer 1.04×10^{-3} L (1.04 mL) of the 0.600-M stock solution to a 50.0-mL volumetric flask using a graduated pipette and follow the procedure outline previously for using a volumetric flask (**Interactive Figure 4.5.5**).

Interactive Figure 4.5.5 Make a solution by dilution.



The materials required to make a solution by dilution

When using the dilution method to prepare a solution of known concentration, remember that the total amount of solute is the same in both the measured volume of the more concentrated stock solution and in the dilute solution created. This means we can use a simple equation (Equation 4.2) to calculate the volume or concentration of either the stock solution or the more dilute solution. Equation 4.2 is based on the fact that the concentration and volume of any solution can be used to calculate the amount of solute present in a solution.

amount of solute (mol) = solution concentration $\left(\frac{\text{mol}}{\text{L}}\right) \times \text{solution volume (L)} = C \times V$

Because the amount of solute (in moles) in the measured volume of concentrated solution is equal to the amount of solute (in moles) in the diluted solution,

mol solute in concentrated solution = mol solute in dilute solution

and

$$C_{\rm conc} \times V_{\rm conc} = C_{\rm dil} \times V_{\rm dil}$$
(4.2)

where C_{conc} and V_{conc} are the concentration (mol/L) and volume (L) of the concentrated solution and C_{dil} and V_{dil} are the concentration (mol/L) and volume (L) of the diluted solution.

EXAMPLE PROBLEM: Use the dilution method to make a solution.

In the laboratory, a student dilutes 21.5 mL of a 10.0-M nitric acid solution to a total volume of 125 mL. What is the concentration of the diluted solution?

SOLUTION:

You are asked to calculate the concentration of a diluted solution.

You are given the volume and concentration of the concentrated solution and the volume of the diluted solution.

First, calculate the amount of HNO₃ in the concentrated sample.

$$0.0215 \text{ L} \times \frac{10.0 \text{ mol HNO}_3}{1 \text{ L}} = 0.215 \text{ mol HNO}_3 \text{ in the concentrated sample}$$

Use the amount of HNO_3 and the volume of the diluted sample to calculate the concentration of the dilute solution.

$$\frac{0.215 \text{ mol HNO}_3}{0.125 \text{ L}} = 1.72 \text{ M HNO}_3$$

You can also use the equation $C_{\text{conc}} \times V_{\text{conc}} = C_{\text{dil}} \times V_{\text{dil}}$ to calculate the concentration of the diluted solution.

$$C_{\text{conc}} \times V_{\text{conc}} = C_{\text{dil}} \times V_{\text{dil}}$$
(10.0 M HNO₃)(21.5 mL) = (C_{\text{dil}})(125 mL)

$$C_{\text{dil}} = 1.72 \text{ M HNO}_3$$

Notice that the volume units cancel and do not need to be in units of liters.

4.5.5T: Tutorial Assignment Use the Dilution Method to Make a Solution 4.5.5: Mastery Assignment Use the Dilution Method to Make a Solution

4.5c Solution Stoichiometry

The central premise of stoichiometry is that the amount of matter produced in a chemical reaction can be determined using the mole relationship provided by a balanced chemical equation. The amount of

reactants and products can be determined from mass (in grams) or, as we have just seen, from the volume and concentration of a solution. As shown in **Interactive Figure 4.5.6**, the stoichiometric relationships between reactants and products developed in Chapter 3 can be expanded to include using the volume and concentration of a solution to determining amounts of reactant and product.



Interactive Figure 4.5.6 Explore stoichiometric relationships involving aqueous solutions.

A flow chart for stoichiometry calculations

For example, the mass of $PbCrO_4$ produced when 50.0 mL of a 0.400-M $Pb(NO_3)_2$ solution is mixed with an excess of 0.100 M Na_2CrO_4 is calculated as follows:



Step 1. Write a balanced chemical equation.

Pb(NO₃)₂(aq) + Na₂CrO₄(aq) → 2 NaNO₃(aq) + PbCrO₄(s) **Step 2.** Calculate moles of limiting reactant. 0.400 mol Pb(NO₃) = 1 J

$$\frac{1.400 \text{ mol Pb}(\text{NO}_3)_2}{1 \text{ L}} \times \frac{1 \text{ L}}{1000 \text{ mL}} \times 50.0 \text{ mL} = 0.0200 \text{ mol Pb}(\text{NO}_3)_2$$

Step 3. Calculate moles of product.

$$0.0200 \text{ mol Pb}(\text{NO}_3)_2 \times \frac{1 \text{ mol Pb}(\text{CrO}_4)}{1 \text{ mol Pb}(\text{NO}_3)_2} = 0.0200 \text{ mol Pb}(\text{CrO}_4)$$

Step 4. Calculate mass of product.

$$0.0200 \text{ mol PbCrO}_4 \times \frac{323.2 \text{ g}}{1 \text{ mol PbCrO}_4} = 6.46 \text{ g PbCrO}_4$$

EXAMPLE PROBLEM: Use solution stoichiometry.

Calculate the volume (in mL) of 0.715 M HNO₃ needed to react completely with 6.35 g of CaCO₃ in a gas-forming reaction.

SOLUTION:

You are asked to calculate the volume of a solution required to completely consume a reactant. **You are given** the concentration of the solution and the mass of the reactant that will be consumed.

Step 1. Write a balanced chemical equation for the gas-forming reaction.

$$2 \text{HNO}_3(aq) + \text{CaCO}_3(s) \rightarrow \text{Ca}(\text{NO}_3)_2(aq) + \text{H}_2\text{O}(\ell) + \text{CO}_2(g)$$

Step 2. Calculate moles of calcium carbonate available to react with HNO₃.

$$6.35 \text{ g CaCO}_3 \times \frac{1 \text{ mol CaCO}_3}{100.1 \text{ g}} = 0.0634 \text{ mol CaCO}_3$$

Step 3. Use the reaction stoichiometry to calculate moles of HNO₃ required to react with the available CaCO₃.

$$0.0634 \text{ mol CaCO}_3 \times \frac{2 \text{ mol HNO}_3}{1 \text{ mol CaCO}_3} = 0.127 \text{ mol HNO}_3$$

Step 4. Use the concentration and amount of HNO_3 solution to calculate the volume of nitric acid needed.

volume of HNO₃ solution = 0.127 mol HNO₃ × $\frac{1 \text{ L}}{0.715 \text{ mol HNO}_3}$ × $\frac{10^3 \text{ mL}}{1 \text{ L}}$ = 177 mL

4.5.6T: Tutorial Assignment Use Solution Stoichiometry

4.5.6: Mastery Assignment Use Solution Stoichiometry

4.5d Titrations

A **titration** is an application of solution stoichiometry in which a solution of known concentration is used to analyze a solution of unknown concentration. The two most common types of titrations are acid–base titrations and oxidation–reduction titrations.

Acid–Base Titrations An acid–base titration is used in analytical laboratories to accurately determine the concentration of an acid or base solution or the molar mass of an unknown acid or base. In an acid–base titration, an aqueous solution of a base (or acid) is placed in a buret and slowly added to a solution of an acid (or base) in a flask until the reaction is complete. An **acid–base indicator**, a dye that shows by a change in color when the acid–base reaction is complete, is added to the solution in the flask before the titration is begun. The most common acid–base indicator used in the general chemistry laboratory is phenolphthalein, an organic dye that is colorless in acidic solutions and pink in basic solutions.

The **equivalence point** in an acid–base titration is the point at which the acid (or base) in the flask has been consumed completely by the base (or acid) that has been added from the buret. That is, $[H^+] = [OH^-]$ at the equivalence point in an acid–base titration.

The steps involved in an acid–base titration calculation are similar to those in any solution stoichiometry problem. Consider, for example, the titration of 30.0 mL of tartaric acid ($H_2C_4H_4O_6$, a diprotic acid) solution with 0.354 M NaOH (**Interactive Figure 4.5.7**). In this titration, 28.79 mL of NaOH is required to reach the equivalence point in the titration. The concentration of the tartaric acid solution is determined as shown in the following steps.

Step 1. Write a balanced equation for the acid–base reaction.

 $H_2C_4H_4O_6(aq) + 2 \text{ NaOH}(aq) \rightarrow Na_2C_4H_4O_6(aq) + 2 H_2O(\ell)$

Step 2. Use the volume and concentration of the NaOH solution to calculate the amount of base added to the acid solution during the titration.

28.79 mL solution
$$\times \frac{1 \text{ L}}{1000 \text{ mL}} \times \frac{0.354 \text{ mol NaOH}}{1 \text{ L solution}} = 0.0102 \text{ mol NaOH}$$

Step 3. Use the balanced equation to determine the amount of acid present in the flask.

$$0.0102 \text{ mol NaOH} \times \frac{1 \text{ mol } \text{H}_2\text{C}_4\text{H}_4\text{O}_6}{2 \text{ mol NaOH}} = 0.00510 \text{ mol } \text{H}_2\text{C}_4\text{H}_4\text{O}_6$$

Step 4. Use the amount of acid and the volume of the acid solution to determine the concentration of the tartaric acid solution.

$$\frac{0.00510 \text{ mol } \text{H}_2\text{C}_4\text{H}_4\text{O}_6}{30.0 \text{ mL solution}} \times \frac{1000 \text{ mL}}{1 \text{ L}} = 0.170 \text{ M}$$

Interactive Figure 4.5.7 Explore acid–base titrations.







The titration of tartaric acid with sodium hydroxide

EXAMPLE PROBLEM: Determine an unknown concentration or volume using an acid-base titration.

Calculate the volume of 0.106 M barium hydroxide required to neutralize 18.7 mL of a 0.288-M hydrochloric acid solution.

SOLUTION:

You are asked to calculate the volume of base solution required to neutralize an aqueous solution containing an acid.

You are given the concentration of the base, the identity of the base, the concentration and volume of the acid solution, and the identity of the acid.

Step 1. Write a balanced equation for the acid–base reaction.

$$2 \operatorname{HCl}(aq) + \operatorname{Ba}(OH)_2(aq) \rightarrow \operatorname{BaCl}_2(aq) + 2 \operatorname{H}_2O(\ell)$$

Step 2. Use the volume and concentration of the HCl solution to calculate the amount of acid neutralized during the titration.

18.7 mL HCl solution
$$\times \frac{1 \text{ L}}{1000 \text{ mL}} \times \frac{0.288 \text{ mol HCl}}{1 \text{ L solution}} = 0.00536 \text{ mol HCl}$$

Step 3. Use the balanced equation to determine the amount of base required to neutralize the acid.

$$0.00536 \text{ mol HCl} \times \frac{1 \text{ mol Ba(OH)}_2}{2 \text{ mol HCl}} = 0.00268 \text{ mol Ba(OH)}_2$$

Step 4. Use the amount of base and the concentration of the base solution to determine the volume of barium hydroxide solution required to neutralize the acid solution.

volume Ba(OH)₂ solution = 0.00268 mol Ba(OH)₂ × $\frac{1 \text{ L}}{0.106 \text{ mol Ba(OH)}_2}$ × $\frac{1000 \text{ mL}}{1 \text{ L}}$ = 25.3 mL

This type of calculation is often performed before beginning a titration in order to estimate the amount of solution in the buret required to reach the equivalence point.

4.5.7T: Tutorial Assignment Determine an Unknown Concentration or Volume Using an Acid– Base Titration

4.5.7: Mastery Assignment Determine an Unknown Concentration or Volume Using an Acid-Base Titration

It is often important to have an accurate concentration of an acid or base solution. With standardization, another type of acid–base titration, the concentration of an acid or base is determined accurately by the use of either a primary standard or another solution whose concentration has already been determined. A **primary standard** is an acid or base that can be obtained in a very pure form, such as potassium hydrogen phthalate, $KHC_8H_4O_4$ (often abbreviated KHP), or sodium carbonate, Na_2CO_3 . The steps involved in standardization calculations are very similar to other acid–base titration calculations, as shown in the following example.

EXAMPLE PROBLEM: Use a primary standard to determine an unknown concentration using an acid–base titration.

>Potassium hydrogen phthalate is a solid, monoprotic acid frequently used in the laboratory as a primary standard. It has the unwieldy formula of $KHC_8H_4O_4$. This is often written in shorthand notation as KHP. If 37.1 mL of a barium hydroxide solution is needed to neutralize 1.83 g of KHP, what is the concentration (in mol/L) of the barium hydroxide solution?

SOLUTION:

You are asked to determine the concentration of a solution containing a base.

You are given the mass of primary standard used, the volume of base solution required to neutralize the primary standard, and the identity of the base and the primary standard.

Step 1. Write a balanced equation for the acid–base reaction.

 $2 \text{ KHC}_8\text{H}_4\text{O}_4(aq) + \text{Ba}(\text{OH})_2(aq) \rightarrow \text{Ba}(\text{KC}_8\text{H}_4\text{O}_4(aq) + 2 \text{H}_2\text{O}(\ell)$

Step 2. Use the mass of the primary standard, KHP, and the balanced equation to determine the amount of $Ba(OH)_2$ in the solution.

$$1.83 \text{ g } \text{KHC}_{8}\text{H}_{4}\text{O}_{4} \times \frac{1 \text{ mol } \text{KHC}_{8}\text{H}_{4}\text{O}_{4}}{204.2 \text{ g}} \times \frac{1 \text{ mol } \text{Ba}(\text{OH})_{2}}{2 \text{ mol } \text{KHC}_{8}\text{H}_{4}\text{O}_{4}} = 0.00448 \text{ mol } \text{Ba}(\text{OH})_{2}$$

Step 3. Use the amount of base and the volume of the base solution to determine the concentration of the barium hydroxide solution.

 $\frac{0.00448 \text{ mol Ba}(\text{OH})_2}{37.1 \text{ mL solution}} \times \frac{1000 \text{ mL}}{1 \text{ L}} = 0.121 \text{ M Ba}(\text{OH})_2$

4.5.8T: Tutorial Assignment Use a Primary Standard to Determine an Unknown Concentration Using an Acid–Base Titration

4.5.8: Mastery Assignment Use a Primary Standard to Determine an Unknown Concentration Using an Acid–Base Titration

A third type of acid–base titration calculation involves the determination of the molar mass of an acid or base. For example, as shown in Interactive Figure 4.5.8, an acid–base titration can be used to calculate the effective molecular mass of the basic chemicals found in the ashes produced by burning firewood.

Interactive Figure 4.5.8 Determine the molar mass of an unknown using an acid–base titration.

The ashes produced from burning firewood are basic.

EXAMPLE PROBLEM: Use an acid-base titration to calculate the molar mass of an acid.

A 0.125-g sample of an unknown monoprotic acid is dissolved in water and titrated with standardized sodium hydroxide. The equivalence point in the titration is reached after the addition of 20.59 mL of 0.0193 M NaOH to the sample of the unknown acid. Calculate the molar mass of the acid.

SOLUTION:

You are asked to calculate the molar mass of an unknown monoprotic acid.

You are given the mass of the acid sample, the volume and concentration of base required to neutralize the acid sample, the identity of the base, and the fact that the acid is monoprotic.

Step 1. Write a balanced equation for the acid–base reaction. In this case we do not know the identity of the acid, but we know it is monoprotic; therefore, we can use the general formula HA to represent the unknown acid in an equation.

$$HA(aq) + NaOH(aq) \rightarrow H_2O(\ell) + NaA(aq)$$

Step 2. Use the volume and concentration of the NaOH solution to calculate the amount of base used to neutralize the acid during the titration.

20.59 mL NaOH solution
$$\times \frac{1 \text{ L}}{1000 \text{ mL}} \times \frac{0.0193 \text{ mol NaOH}}{1 \text{ L solution}} = 3.97 \times 10^{\text{\$4}} \text{ mol NaOH}$$

Step 3. Use the balanced equation to determine the amount of acid in the flask.

$$3.97 \times 10^{\$4} \text{ mol NaOH} \times \frac{1 \text{ mol HA}}{1 \text{ mol NaOH}} = 3.97 \times 10^{\$4} \text{ mol HA}$$

Step 4. Use the mass of the acid sample and the amount of acid (in mol) in the sample to calculate the molar mass of the unknown acid.

molar mass of HA =
$$\frac{0.125 \text{ g}}{3.97 \times 10^{84} \text{ mol}} = 315 \text{ g/mol}$$

4.59T: Tutorial Assignment Use an Acid–Base Titration to Calculate the Molar Mass of an Acid4.5.9: Mastery Assignment Use an Acid–Base Titration to Calculate the Molar Mass of an Acid

Oxidation–Reduction Titrations An **oxidation–reduction titration** uses an oxidation–reduction reaction to analyze a solution of unknown concentration. The equivalence point in an oxidation–reduction reaction occurs when the reactants are consumed and often is detected by a color change in one of the reactants.

EXAMPLE PROBLEM: Determine an unknown volume or concentration using an oxidationreduction titration.

The concentration of a hydrogen peroxide solution is determined by titrating it with a 0.275-M solution of potassium permanganate. The balanced net ionic equation for the reaction is

$$5 \text{ H}_2\text{O}_2(aq) + 6 \text{ H}^+(aq) + 2 \text{ MnO}_4^-(aq) \rightarrow 5 \text{ O}_2(g) + 2 \text{ Mn}^{2+}(aq) + 8 \text{ H}_2\text{O}(\ell)$$

In one experiment, 17.3 mL of the 0.275-M KMnO₄ solution is required to react completely with 25.0 mL of the hydrogen peroxide solution. Calculate the concentration of the hydrogen peroxide solution.

SOLUTION:

You are asked to calculate the concentration of a solution using an oxidation–reduction titration. **You are given** the balanced oxidation–reduction reaction, the volume and concentration of the titrant, and the volume of the solution of unknown concentration.

Step 1. Calculate the amount of KMnO₄ added to the flask during the titration.

17.3 mL KMnO₄ solution ×
$$\frac{1 \text{ L}}{1000 \text{ mL}}$$
 × $\frac{0.275 \text{ mol KMnO}_4}{1 \text{ L solution}} = 0.00476 \text{ mol KMnO}_4$

Step 2. Use the balanced equation to determine the amount of hydrogen peroxide in the sample.

$$0.00476 \text{ mol } \text{KMnO}_4 \times \frac{5 \text{ mol } \text{H}_2\text{O}_2}{2 \text{ mol } \text{KMnO}_4} = 0.0119 \text{ mol } \text{H}_2\text{O}_2$$

Step 3. Use the amount of hydrogen peroxide and the volume of the sample to calculate the solution concentration.

$$\frac{0.0119 \text{ mol } \text{H}_2\text{O}_2}{25.0 \text{ mL}} \times \frac{1000 \text{ mL}}{1 \text{ L}} = 0.475 \text{ M} \text{ H}_2\text{O}_2$$

The equivalence point in this titration is indicated by the color of the solution. As the purple KMnO₄ solution is added to the flask containing H_2O_2 , the colorless Mn^{2+} ion is formed. At the equivalence point a slight excess of KMnO₄ is present in the flask and the solution has a faint purple color.

4.5.10T: Tutorial Assignment Determine an Unknown Volume or Concentration Using an Oxidation–Reduction Titration

4.5.10: Mastery Assignment Determine an Unknown Volume or Concentration Using an Oxidation–Reduction Titration

Chapter Review

Key Concepts

4.1 Types of Chemical Reactions

- In a combination reaction, two or more reactants combine to form one product (4.1a).
- A decomposition reaction is often the reverse of a combination reaction, and the number of products in this type of reaction is typically greater than the number of reactants (4.1b).

- In displacement reactions, also called exchange reactions, one atom, ion, or molecular fragment displaces another (4.1c).
- Double-displacement reactions are also called metathesis reactions. Examples include precipitation reactions and acid–base reactions (4.1c).

4.2 Aqueous Solutions

- A solution is formed when a solute is mixed with a solvent (4.2).
- A compound dissolved in water is in an aqueous state (4.2).
- Species dissolved in a solvent are solvated (or hydrated when water is the solvent) (4.2a).
- An electrolyte increases the electrical conductivity of water (4.2a).
- Electrolytes are characterized as strong or weak; a species that does not increase the electrical conductivity of water is a nonelectrolyte (4.2a).
- Ionic compounds can be soluble or insoluble in water; their solubility is predicted using solubility rules for ionic compounds in water (4.2b).

4.3 Reactions in Aqueous Solution

- A precipitation is an exchange reaction that results in the formation of an insoluble ionic compound, a precipitate (4.3a).
- Ionic species that are unchanged during an exchange reaction are called spectator ions (4.3b).
- A net ionic equation is a chemical equation for a reaction written without spectator ions (4.3b).
- Acid-base reactions, which occur between an acid and a base, are typically exchange reactions where a proton is transferred between the acid and base and water and an ionic salt are formed (4.3c).
- Acids and bases can be characterized as strong (strong electrolytes) or weak (weak electrolytes) (4.3c).
- A monoprotic acid produces one mole of H⁺ ions per mole of acid, and a diprotic acid produces two moles of H⁺ per mole of acid (4.3c).
- A gas-forming reaction is an exchange reaction that has a gas as one of its products (4.3d)

4.4 Oxidation–Reduction Reactions

- An oxidation-reduction reaction involves the exchange of electrons between two or more species (4.4).
- Oxidation is the loss of one or more electrons from a chemical species and reduction is the gain of one or more electrons (4.4a).
- An oxidizing agent is reduced in an oxidation-reduction reaction, and a reducing agent is oxidized in an oxidation-reduction reaction (4.4a).
- A half-reaction shows only the oxidation *or* reduction in the oxidation–reduction reaction (4.4a).
- The oxidation number (or oxidation state) of an atom is assigned using a set of rules (4.4b).

• Oxidation numbers are used to identify the species oxidized or reduced in an oxidation-reduction reaction (4.4c).

4.5 Stoichiometry of Reactions in Aqueous Solution

- Concentration is a quantitative measure of the amount of solute dissolved in a solvent (4.5a).
- Molarity is a concentration unit defined as moles of solute dissolved in 1 liter of solution (4.5a).
- Two methods of making solutions of known concentration are the direct addition method and the dilution method (4.5b).
- The concentration of a solution can be used, along with the solution volume, to determine the number of moles of solute in a sample (4.5c).
- In a titration, a solution of known concentration is used to analyze a solution of unknown concentration (4.5d).
- Acid–base titrations use an acid–base reaction to analyze an unknown solution (4.5d).
- The equivalence point in an acid–base titration occurs when all of the acid and base are consumed (4.5d).
- A primary standard can be used, along with an acid–base titration, to determine the concentration of an unknown acid or base solution (4.5d).
- Oxidation-reduction titrations use an oxidation-reduction reaction to analyze an unknown solution (4.5d).

Key Equations

molarity (M)	moles of solute	(4 1)
	1 L of solution	(4.1)
$C_{\rm conc} \times V_{\rm conc} = C_{\rm dil} \times V_{\rm dil}$		(4.2)

Key Terms

4.1 Types of Chemical Reactions

>combination reaction decomposition reaction displacement reactions single displacement reaction double displacement reaction precipitation reactions acid–base reactions gas-forming reactions

4.2 Aqueous Solutions

solvent solution solute aqueous solvated hydrated electrolytes strong electrolytes nonelectrolytes weak electrolytes soluble insoluble precipitate

4.3 Reactions in Aqueous Solution

spectator ions net ionic equation acid base salt strong acid weak acid organic acids monoprotic acid diprotic acids

4.4 Oxidation–Reduction Reactions

oxidation-reduction reactions oxidation reduction oxidizing agent reducing agent half-reaction oxidation number

4.5 Stoichiometry of Reactions in Aqueous Solution

concentration molarity (M) volumetric glassware direct addition dilution titration acid–base titration acid–base indicator equivalence point primary standard oxidation–reduction titration