Three Major Classes of Chemical Reactions

4

Classifying the Countless Despite countless individual reactions, these silver chromate particles form through one of the three major classes of reactions discussed in this chapter.

Outline

Key Principles
to focus on while studying this chapter

- *Aqueous* chemical reactions are those that occur in water. Because of its *molecular shape* and uneven *distribution of electrons*, water dissolves many ionic and covalent substances. In water, many ionic compounds and a few simple, H-containing covalent compounds, such as HCl, *dissociate* into ions. ***(Section 4.1)***
- Three types of equations describe an aqueous reaction. A *molecular equation* shows all substances as intact compounds. A *total ionic equation* shows ions for all soluble substances. A *net ionic equation* is more useful because it omits *spectator ions* (those not involved in the reaction) and shows the *actual* chemical change taking place. ***(Section 4.2)***
- *Precipitation reactions* occur when soluble ionic compounds exchange ions (*metathesis*) and form an insoluble product (*precipitate*), in which the ions attract each other so strongly that their attraction to water molecules cannot pull them apart. ***(Section 4.3)***
- An *acid* produces H^+ ions in solution, and a *base* produces OH^- ions. In an *acid-base (neutralization) reaction*, the H^+ and the OH^- ions form water. Another way to view this process is that an acid *transfers a proton* to a base. An acid-base *titration* is used to measure the amount (mol) of acid (or base). ***(Section 4.4)***
- *Oxidation* is defined as *electron loss*, and *reduction* as *electron gain*. In an *oxidation-reduction (redox) reaction*, electrons move from one reactant to the other: the *reducing agent* is oxidized (loses the electrons), and the *oxidizing agent* is reduced (gains the electrons). Chemists use *oxidation number*, the number of electrons "owned" by each atom in a substance, to follow the change. ***(Section 4.5)***
- Many common redox reactions (which are sometimes classified as *combination, decomposition, displacement, or combustion*) involve elements as reactants or products. In an *activity series*, metals are ranked by their ability to reduce H^+ or displace the ion of a different metal from an aqueous solution. ***(Section 4.6)***

CONCEPTS & SKILLS TO REVIEW
before studying this chapter

- names and formulas of compounds (Section 2.8)
- nature of ionic and covalent bonding (Section 2.7)
- amount-mass-number conversions (Section 3.1)
- molarity and amount-mass-number conversions in solution (Section 3.5)
- balancing chemical equations (Section 3.3)
- calculating quantities of reactants and products (Section 3.4)

Rapid chemical changes occur among gas molecules as sunlight bathes the atmosphere or lightning rips through a stormy sky and strikes the sea. Aqueous reactions occur unceasingly in lakes, rivers, and oceans. And, in every cell of your body, thousands of reactions taking place right now enable you to function. Indeed, the amazing variety in nature is largely a consequence of the amazing variety of chemical reactions. With millions of reactions occurring in and around you, it would be impossible to describe them all. Fortunately, it isn't necessary because, when we survey even a small percentage of reactions, especially those in aqueous solution, a few major classes emerge.

4.1 • THE ROLE OF WATER AS A SOLVENT

For any reaction in solution, the solvent plays a role that depends on its chemical nature. Some solvents passively disperse the substances into individual molecules. But water is much more active, interacting strongly with the substances and even reacting with them in some cases. Nearly all environmental and biological reactions occur in water, so let's focus on how the water molecule interacts with both ionic and covalent solutes.

The Polar Nature of Water

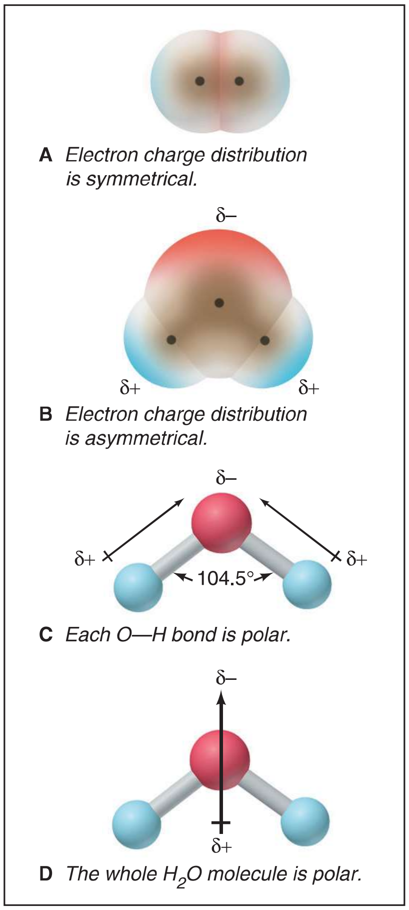
On the atomic scale, water's great solvent power arises from the *uneven distribution of electron charge* and a *bent molecular shape,* which create a *polar molecule:*

1. *Uneven charge distribution*. Recall from Section 2.7 that the electrons in a covalent bond are shared between the atoms. In a bond between identical atoms—as in H_2, Cl_2, O_2—the sharing is equal and electron charge is distributed evenly between the two nuclei (symmetrical shading in the space-filling model of Figure 4.1A). In covalent bonds between different atoms, the sharing is uneven because one atom attracts the electron pair more strongly than the other atom does.

For example, in each O—H bond of water, the shared electrons are closer to the O atom because an O atom attracts electrons more strongly than an H atom does. (You'll see why in Chapter 9.) This uneven charge distribution creates a *polar bond,* one with partially charged "poles." In Figure 4.1B, the asymmetrical shading shows this distribution, and the δ symbol indicates a partial charge. The O end is partially negative, represented by red shading and δ−, and the H end is partially positive, represented by blue shading and δ+.

2. *Bent molecular shape*. The sequence of the H—O—H atoms in water is not linear: the water molecule is bent with a bond angle of 104.5°. In the ball-and-stick model of Figure 4.1C, the *polar arrow* points to the negative pole, and the tail, shaped like a plus sign, marks the positive pole.

3. *Molecular polarity*. The combination of polar bonds and bent shape makes water a **polar molecule:** the region near the O atom is partially negative, and the region between the H atoms is partially positive (Figure 4.1D).



A *Electron charge distribution is symmetrical.*

B *Electron charge distribution is asymmetrical.*

C *Each O—H bond is polar.*

D *The whole H_2O molecule is polar.*

Figure 4.1 Electron distribution in molecules of H_2 and H_2O.

Ionic Compounds in Water

In this subsection, we consider two closely related aspects of aqueous solutions of ionic compounds—how they occur and how they behave. We also use a compound's formula to calculate the amount (mol) of each ion in solution.

How Ionic Compounds Dissolve: Replacement of Charge Attractions In an ionic solid, oppositely charged ions are held together by electrostatic attractions (see Figure 1.3C and Section 2.7). Water separates the ions by *replacing these attractions with others between several water molecules and each ion.* Picture a granule of a soluble ionic compound in water: the negative ends of some water molecules are

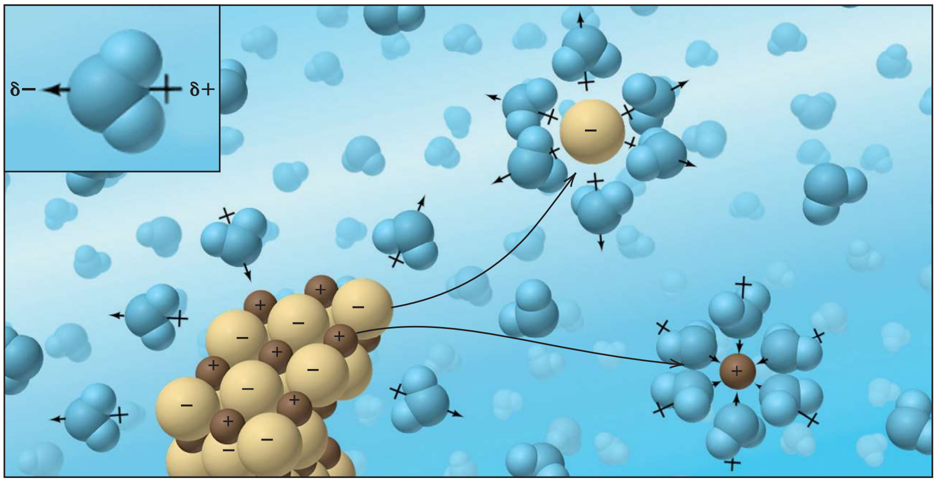


Figure 4.2 An ionic compound dissolving in water. The inset shows the polar arrow and partial charges (not shown in the rest of the scene) of each water molecule.

attracted to the cations, and the positive ends of other water molecules are attracted to the anions (Figure 4.2). Dissolution occurs because the *attractions between each type of ion and several water molecules outweigh the attractions between the ions*. Also, as the ions separate (dissociate) and become **solvated**—surrounded closely by solvent molecules—they *disperse randomly* in the solution.

For an ionic compound that doesn't dissolve in water, the attraction between ions is greater than the attraction between the ions and water. Actually, these so-called insoluble substances *do* dissolve to a very small extent, usually several orders of magnitude less than so-called soluble substances. For example, NaCl (a "soluble" compound) is over 4×10^4 times more soluble than AgCl (an "insoluble" compound):

$$\text{Solubility of NaCl in } H_2O \text{ at } 20°C = 365 \text{ g/L}$$
$$\text{Solubility of AgCl in } H_2O \text{ at } 20°C = 0.009 \text{ g/L}$$

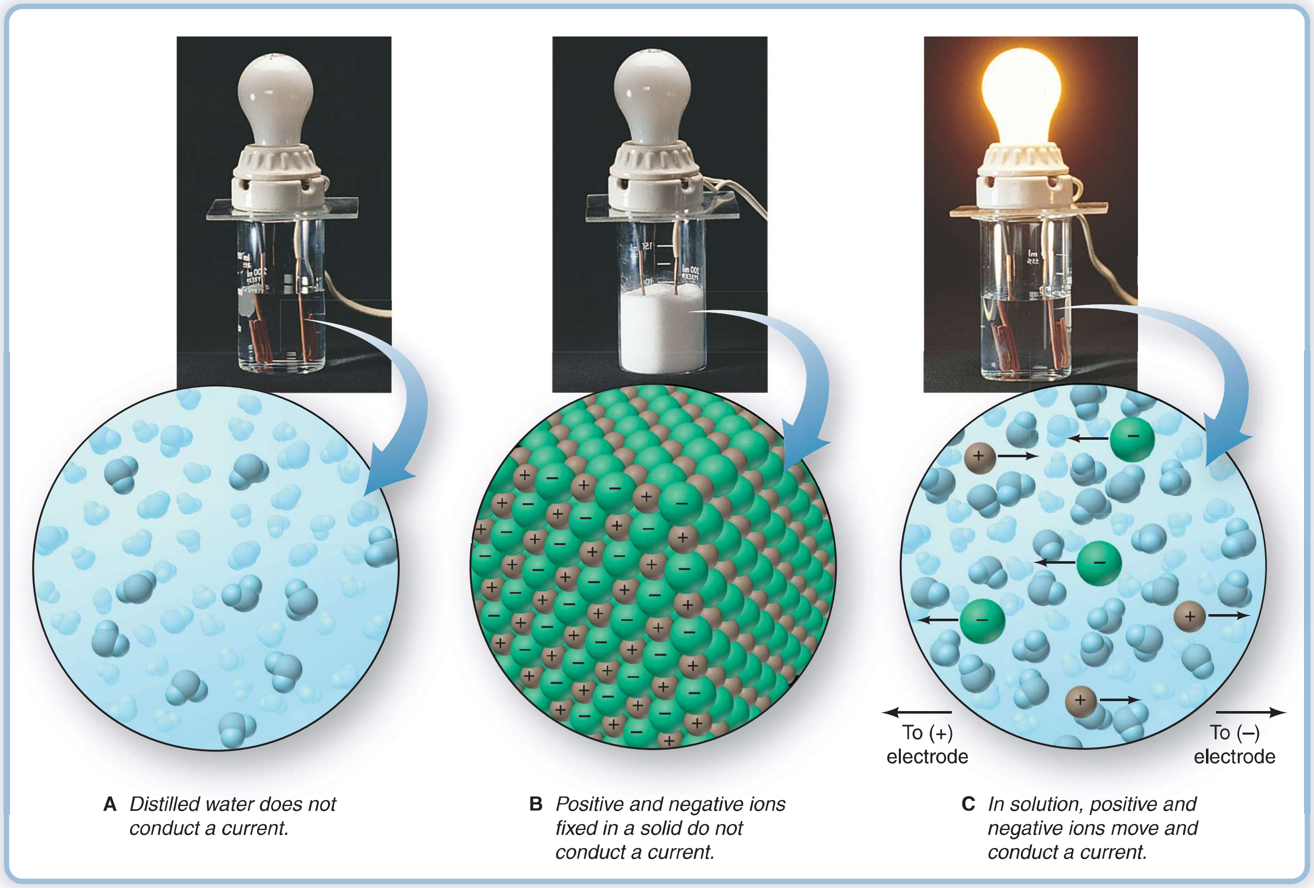
In Chapter 13, we'll highlight that dissolving involves more than a contest between the relative energies of attraction of ions for each other or for water. And we'll emphasize that it is favored by the greater freedom of motion the ions have when they leave the solid and disperse randomly through the solution.

How Ionic Solutions Behave: Electrolytes and Electrical Conductivity When an ionic compound dissolves, the solution's *electrical conductivity,* the flow of electric current, increases dramatically. When electrodes are immersed in distilled water (Figure 4.3A, *next page*) or pushed into an ionic solid (Figure 4.3B), no current flows, as shown by the unlit bulb. But in an aqueous solution of the compound, a large current flows, as shown by the lit bulb (Figure 4.3C). Current flow implies the *movement of charged particles:* when the ionic compound dissolves, the separate solvated ions move toward the electrode of opposite charge. A substance that conducts a current when dissolved in water is an **electrolyte.** Soluble ionic compounds are *strong* electrolytes because they dissociate completely and conduct a large current.

Calculating the Number of Moles of Ions in Solution *From the formula of the soluble ionic compound, we know the number of moles of each ion in solution*. For example, the equation for dissolving KBr in water to form solvated ions is

$$KBr(s) \xrightarrow{H_2O} K^+(aq) + Br^-(aq)$$

("H_2O" above the arrow means that water is the solvent, not a reactant.) Note that 1 mol of KBr dissociates into 2 mol of ions—1 mol of K^+ and 1 mol of Br^-. Sample Problems 4.1 and 4.2 apply these ideas, first with molecular scenes and then in calculations.



A *Distilled water does not conduct a current.*

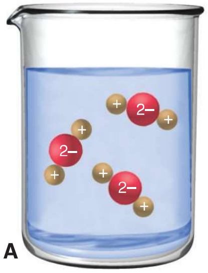
B *Positive and negative ions fixed in a solid do not conduct a current.*

C *In solution, positive and negative ions move and conduct a current.*

Figure 4.3 The electrical conductivity of ionic solutions.

Sample Problem 4.1 Using Molecular Scenes to Depict an Ionic Compound in Aqueous Solution

Problem **(a)** Which beaker best depicts the strong electrolyte potassium sulfate in aqueous solution (water molecules are not shown)?
(b) If each particle represents 0.1 mol, what is the total number of particles in solution?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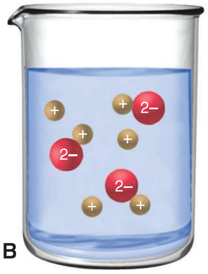
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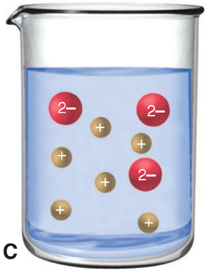
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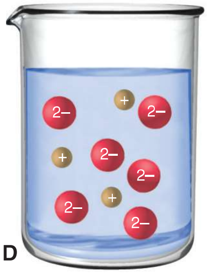

D

Plan **(a)** We determine the formula and write an equation for 1 mol of compound dissociating into ions. Potassium sulfate is a strong electrolyte, so it dissociates completely, but, in general, *polyatomic ions remain intact in solution.* **(b)** We count the number of separate particles, and then multiply by 0.1 mol and by Avogadro's number.

Solution **(a)** The formula is K_2SO_4, so the equation is

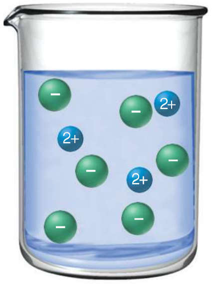
$$K_2SO_4(s) \xrightarrow{H_2O} 2K^+(aq) + SO_4^{2-}(aq)$$

There are two separate 1+ particles for every 2− particle, so beaker C is best.
(b) There are 9 particles, so the total amount (mol) of particles is 0.9 mol, and we have

$$\text{No. of particles} = 0.9\ \cancel{\text{mol}} \times \frac{6.022\times10^{23}\ \text{particles}}{1\ \cancel{\text{mol}}} = 5.420\times10^{23}\ \text{particles}$$

Check Rounding to check the math in (b) gives 0.9 × 6 = 5.4, so the answer seems correct. The number of particles is an exact number since we actually counted them; thus, the answer can have as many significant figures as in Avogadro's number.

FOLLOW-UP PROBLEM 4.1 **(a)** Which strong electrolyte is dissolved in water (water molecules not shown) in the beaker at right: LiBr, Cs_2CO_3, or $BaCl_2$?
(b) If each particle represents 0.05 mol, what mass (g) of compound was dissolved?



Sample Problem 4.2 Determining Amounts (mol) of Ions in Solution

Problem What amount (mol) of each ion is in each solution?
(a) 5.0 mol of ammonium sulfate dissolved in water
(b) 78.5 g of cesium bromide dissolved in water
(c) 7.42×10^{22} formula units of copper(II) nitrate dissolved in water
(d) 35 mL of 0.84 *M* zinc chloride

Plan We write an equation that shows 1 mol of compound dissociating into ions. **(a)** We multiply the number of moles of ions by 5.0. **(b)** We first convert grams to moles. **(c)** We first convert formula units to moles. **(d)** We first convert molarity and volume to moles.

Solution **(a)** $(NH_4)_2SO_4(s) \xrightarrow{H_2O} 2NH_4^+(aq) + SO_4^{2-}(aq)$

Calculating amount (mol) of NH_4^+ ions:

$$\text{Amount (mol) of } NH_4^+ = 5.0\ \cancel{\text{mol } (NH_4)_2SO_4} \times \frac{2\text{ mol } NH_4^+}{1\ \cancel{\text{mol } (NH_4)_2SO_4}} = 10.\text{ mol } NH_4^+$$

The formula shows 1 mol of SO_4^{2-} per mole of $(NH_4)_2SO_4$, so 5.0 mol of SO_4^{2-} is also present.

(b) $CsBr(s) \xrightarrow{H_2O} Cs^+(aq) + Br^-(aq)$

Converting from mass (g) to amount (mol):

$$\text{Amount (mol) of CsBr} = 78.5\ \cancel{\text{g CsBr}} \times \frac{1\text{ mol CsBr}}{212.8\ \cancel{\text{g CsBr}}} = 0.369\text{ mol CsBr}$$

Thus, 0.369 mol of Cs^+ and 0.369 mol of Br^- are present.

(c) $Cu(NO_3)_2(s) \xrightarrow{H_2O} Cu^{2+}(aq) + 2NO_3^-(aq)$

Converting from formula units to amount (mol):

$$\begin{aligned}\text{Amount (mol) of } Cu(NO_3)_2 &= 7.42\times10^{22}\ \cancel{\text{formula units } Cu(NO_3)_2} \\ &\quad \times \frac{1\text{ mol } Cu(NO_3)_2}{6.022\times10^{23}\ \cancel{\text{formula units } Cu(NO_3)_2}} \\ &= 0.123\text{ mol } Cu(NO_3)_2\end{aligned}$$

$$\text{Amount (mol) of } NO_3^- = 0.123\ \cancel{\text{mol } Cu(NO_3)_2} \times \frac{2\text{ mol } NO_3^-}{1\ \cancel{\text{mol } Cu(NO_3)_2}} = 0.246\text{ mol } NO_3^-$$

0.123 mol of Cu^{2+} is also present.

(d) $ZnCl_2(aq) \longrightarrow Zn^{2+}(aq) + 2Cl^-(aq)$

Converting from volume (mL) and molarity (mol/L) to amount (mol):

$$\text{Amount (mol) of } ZnCl_2 = 35\ \cancel{\text{mL}} \times \frac{1\ \cancel{\text{L}}}{10^3\ \cancel{\text{mL}}} \times \frac{0.84\text{ mol } ZnCl_2}{1\ \cancel{\text{L}}} = 2.9\times10^{-2}\text{ mol } ZnCl_2$$

$$\text{Amount (mol) of } Cl^- = 2.9\times10^{-2}\ \cancel{\text{mol } ZnCl_2} \times \frac{2\text{ mol } Cl^-}{1\ \cancel{\text{mol } ZnCl_2}} = 5.8\times10^{-2}\text{ mol } Cl^-$$

2.9×10^{-2} mol of Zn^{2+} is also present.

Check Round off to check the math and see if the relative numbers of moles of ions are consistent with the formula. For instance, in (a), 10 mol NH_4^+/5.0 mol SO_4^{2-} = $2NH_4^+$/$1SO_4^{2-}$, or $(NH_4)_2SO_4$. In (d), 0.029 mol Zn^{2+}/0.058 mol Cl^- = $1Zn^{2+}$/$2Cl^-$, or $ZnCl_2$.

FOLLOW-UP PROBLEM 4.2 What amount (mol) of each ion is in each solution?
(a) 2 mol of potassium perchlorate dissolved in water
(b) 354 g of magnesium acetate dissolved in water
(c) 1.88×10^{24} formula units of ammonium chromate dissolved in water
(d) 1.32 L of 0.55 *M* sodium bisulfate

Covalent Compounds in Water

Water dissolves many covalent (molecular) compounds also. Table sugar (sucrose, $C_{12}H_{22}O_{11}$), beverage (grain) alcohol (ethanol, CH_3CH_2OH), and automobile antifreeze (ethylene glycol, $HOCH_2CH_2OH$) are some familiar examples. All contain their own polar bonds, which interact with the bonds of water. However, most soluble covalent substances *do not* separate into ions, but remain intact molecules. For example,

$$HOCH_2CH_2OH(l) \xrightarrow{H_2O} HOCH_2CH_2OH(aq)$$

As a result, their aqueous solutions do not conduct an electric current, and these substances are **nonelectrolytes.** (As you'll see shortly, however, a small group of *H-containing molecules* that act as acids in aqueous solution *do* dissociate into ions.) Many other covalent substances, such as benzene (C_6H_6) and octane (C_8H_{18}), do not contain polar bonds, and these substances do not dissolve appreciably in water.

Summary of Section 4.1

- Because of polar bonds and a bent shape, the water molecule is polar, and water dissolves many ionic and covalent compounds.
- When an ionic compound dissolves, the attraction between each ion and water replaces the attraction between ions. Soluble ionic compounds are electrolytes because the ions are free to move and, thus, the solution conducts electricity.
- The formula of a soluble ionic compound shows the number of moles of each ion in solution per mole of compound dissolved.
- Water dissolves many covalent substances with polar bonds. These compounds are nonelectrolytes because the molecules remain intact and, thus, the solution does not conduct electricity. Covalent compounds without polar bonds are mostly insoluble in water.

4.2 • WRITING EQUATIONS FOR AQUEOUS IONIC REACTIONS

Chemists use three types of equations to represent aqueous ionic reactions. Let's examine a reaction to see what each type shows. When solutions of silver nitrate and sodium chromate are mixed, brick-red, solid silver chromate (Ag_2CrO_4) forms. Figure 4.4 depicts the reaction at the macroscopic level *(photos)*, the atomic level *(blow-up circles)*, and the symbolic level with the three types of equations (reacting ions are in red type):

- The **molecular equation** *(top)* reveals the least about the species that are actually in solution because *it shows all the reactants and products as if they were intact, undissociated compounds.* Only the designation for solid, (*s*), tells that a change has occurred:

  $$2AgNO_3(aq) + Na_2CrO_4(aq) \longrightarrow Ag_2CrO_4(s) + 2NaNO_3(aq)$$

- The **total ionic equation** *(middle)* is much more accurate because *it shows all the soluble ionic substances dissociated into ions.* The $Ag_2CrO_4(s)$ stands out as the only undissociated substance:

  $$2Ag^+(aq) + 2NO_3^-(aq) + 2Na^+(aq) + CrO_4^{2-}(aq) \longrightarrow Ag_2CrO_4(s) + 2Na^+(aq) + 2NO_3^-(aq)$$

  The charges balance: four positive and four negative for a net zero charge on the left, and two positive and two negative for a net zero charge on the right.

  Notice that $Na^+(aq)$ and $NO_3^-(aq)$ appear unchanged on both sides of the equation. These are called **spectator ions** (shown with pale colors in the atomic-level scenes). They are not involved in the actual chemical change but are present only as part of the reactants; that is, we can't add an Ag^+ ion without also adding an anion, in this case, the NO_3^- ion.

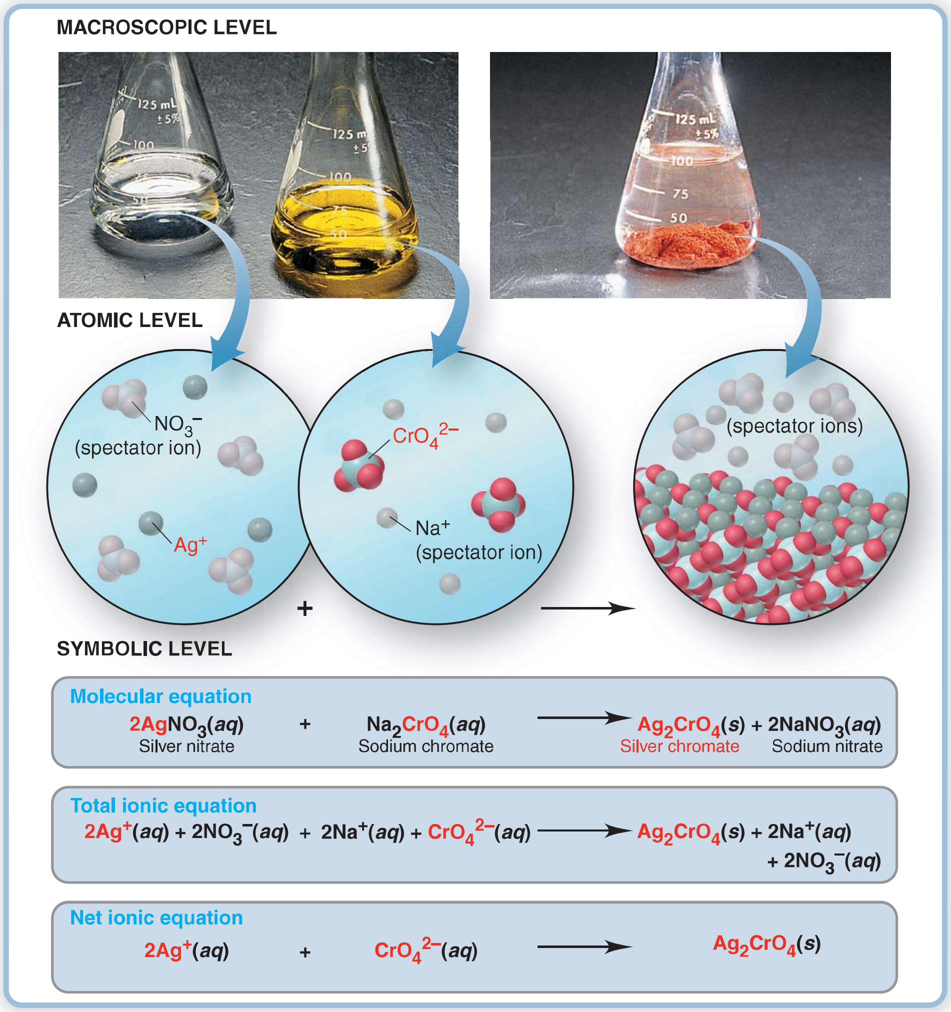


Figure 4.4 An aqueous ionic reaction and the three types of equations.

- The **net ionic equation** *(bottom)* is very useful because *it eliminates the spectator ions and shows only the actual chemical change:*

$$2Ag^+(aq) + CrO_4^{2-}(aq) \longrightarrow Ag_2CrO_4(s)$$

The formation of solid silver chromate from silver ions and chromate ions *is* the only change. To make that point clearly, suppose we mixed solutions of potassium chromate, $K_2CrO_4(aq)$, and silver acetate, $AgC_2H_3O_2(aq)$, instead of sodium chromate and silver nitrate. In that case, only the spectator ions would differ—$K^+(aq)$ and $C_2H_3O_2^-(aq)$ instead of $Na^+(aq)$ and $NO_3^-(aq)$.

Next, we'll apply these types of equations to three important classes of chemical reactions—precipitation, acid-base, and oxidation-reduction.

Summary of Section 4.2

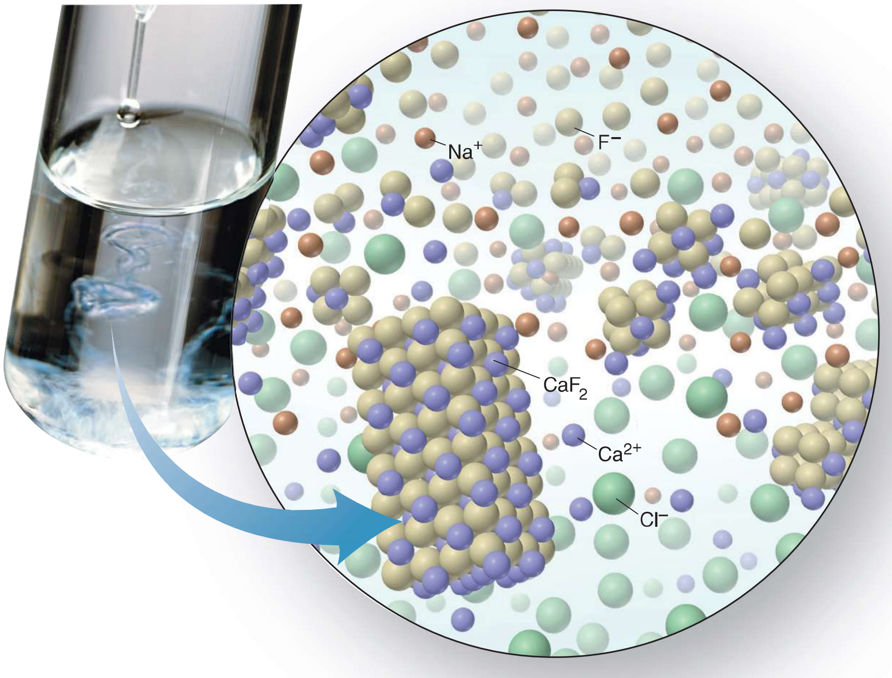
- A molecular equation shows all substances intact and undissociated into ions.
- A total ionic equation shows all soluble ionic compounds as separate, solvated ions. Spectator ions appear unchanged on both sides of the equation.
- A net ionic equation eliminates the spectator ions and, thus, shows only the actual chemical change.

4.3 • PRECIPITATION REACTIONS

Precipitation reactions occur commonly in both nature and commerce. Coral reefs and some gems and minerals form, in part, through this process. And the chemical industry employs precipitation methods to make several important inorganic compounds.

The Key Event: Formation of a Solid from Dissolved Ions

In a **precipitation reaction,** two soluble ionic compounds react to form an insoluble product, a **precipitate.** The reaction you saw between silver nitrate and sodium chromate is one example. Precipitates form for the same reason that some ionic compounds don't dissolve: the electrostatic attraction between the ions outweighs the tendency of the ions to remain solvated and move throughout the solution. When the two solutions are mixed, the ions collide and stay together, and a solid product "comes out of solution." Thus, the key event in a precipitation reaction is *the formation of an insoluble product through the net removal of ions from solution*. Figure 4.5 shows the process for calcium fluoride.



Molecular

$$CaCl_2(aq) + 2NaF(aq) \longrightarrow CaF_2(s) + 2NaCl(aq)$$

Total ionic

$$Ca^{2+}(aq) + 2Cl^-(aq) + 2Na^+(aq) + 2F^-(aq) \longrightarrow CaF_2(s) + 2Na^+(aq) + 2Cl^-(aq)$$

Net ionic

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

Figure 4.5 The precipitation of calcium fluoride. When aqueous solutions of NaF (from pipet) and $CaCl_2$ (in test tube) react, solid CaF_2 forms (water molecules are omitted for clarity).

Table 4.1 Solubility Rules for Ionic Compounds in Water

Soluble Ionic Compounds	Insoluble Ionic Compounds
1. All common compounds of Group 1A(1) ions (Li^+, Na^+, K^+, etc.) and ammonium ion (NH_4^+) are soluble.	1. All common metal hydroxides are insoluble, *except* those of Group 1A(1) and the larger members of Group 2A(2) (beginning with Ca^{2+}).
2. All common nitrates (NO_3^-), acetates (CH_3COO^- or $C_2H_3O_2^-$), and most perchlorates (ClO_4^-) are soluble.	2. All common carbonates (CO_3^{2-}) and phosphates (PO_4^{3-}) are insoluble, *except* those of Group 1A(1) and NH_4^+.
3. All common chlorides (Cl^-), bromides (Br^-), and iodides (I^-) are soluble, *except* those of Ag^+, Pb^{2+}, Cu^+, and Hg_2^{2+}. All common fluorides (F^-) are soluble, *except* those of Pb^{2+} and Group 2A(2).	3. All common sulfides are insoluble except those of Group 1A(1), Group 2A(2), and NH_4^+.
4. All common sulfates (SO_4^{2-}) are soluble, except those of Ca^{2+}, Sr^{2+}, Ba^{2+}, Ag^+, and Pb^{2+}.	

Predicting Whether a Precipitate Will Form

To predict whether a precipitate will form when we mix two aqueous ionic solutions, we refer to the short list of solubility rules in Table 4.1. Let's see how to apply these rules. When sodium iodide and potassium nitrate are each dissolved in water, their solutions consist of solvated, dispersed ions:

$$NaI(s) \xrightarrow{H_2O} Na^+(aq) + I^-(aq)$$
$$KNO_3(s) \xrightarrow{H_2O} K^+(aq) + NO_3^-(aq)$$

Three steps help us predict if a precipitate forms:

1. *Note the ions in the reactants.* The reactant ions are

$$Na^+(aq) + I^-(aq) + K^+(aq) + NO_3^-(aq) \longrightarrow ?$$

2. *Consider all possible cation-anion combinations.* In addition to NaI and KNO_3, which we know are soluble, the other cation-anion combinations are $NaNO_3$ and KI.
3. *Decide whether any combination is insoluble.* According to Table 4.1, no reaction occurs because all the combinations—NaI, KNO_3, $NaNO_3$, and KI—are soluble: Rules 1 and 2 say all compounds of Group 1A(1) ions and all nitrates are soluble.

Now, what happens if we substitute a solution of lead(II) nitrate, $Pb(NO_3)_2$, for the KNO_3 solution? The reactant ions are Na^+, I^-, Pb^{2+}, and NO_3^-. In addition to the two soluble reactants, NaI and $Pb(NO_3)_2$, the other two possible cation-anion combinations are $NaNO_3$ and PbI_2. According to Table 4.1, $NaNO_3$ is soluble (Rule 1), but PbI_2 is *not* (Rule 3). The total ionic equation shows the reaction that occurs as Pb^{2+} and I^- ions collide and form a precipitate:

$$2Na^+(aq) + 2I^-(aq) + Pb^{2+}(aq) + 2NO_3^-(aq) \longrightarrow 2Na^+(aq) + 2NO_3^-(aq) + PbI_2(s)$$

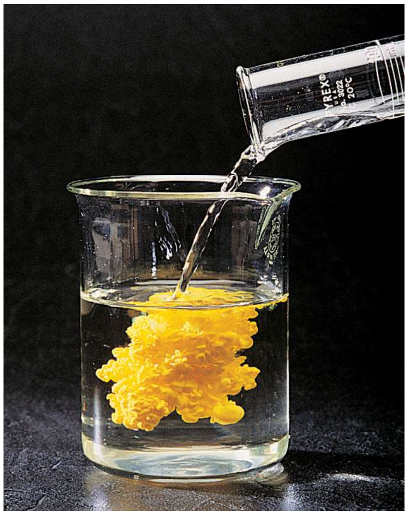
And the net ionic equation confirms it:

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

Metathesis Reactions The molecular equation for the reaction between $Pb(NO_3)_2$ and NaI shows *the ions exchanging partners* (Figure 4.6):

$$2NaI(aq) + Pb(NO_3)_2(aq) \longrightarrow PbI_2(s) + 2NaNO_3(aq)$$

Such reactions are called *double-displacement reactions,* or **metathesis** (pronounced *meh-TA-thuh-sis*) **reactions.** The processes that form Ag_2CrO_4 (Figure 4.4) and CaF_2 (Figure 4.5) are metathesis reactions, too. Sample Problems 4.2 and 4.3 provide practice in predicting if a precipitate forms.



$$2NaI(aq) + Pb(NO_3)_2(aq) \longrightarrow PbI_2(s) + 2NaNO_3(aq)$$

Figure 4.6 The precipitation of PbI_2, a metathesis reaction.

Sample Problem 4.3 Predicting Whether a Precipitation Reaction Occurs; Writing Ionic Equations

Problem Does a reaction occur when each of these pairs of solutions is mixed? If so, write balanced molecular, total ionic, and net ionic equations, and identify the spectator ions.

(a) Potassium fluoride(*aq*) + strontium nitrate(*aq*) ⟶

(b) Ammonium perchlorate(*aq*) + sodium bromide(*aq*) ⟶

Plan We note the reactant ions, write the cation-anion combinations, and refer to Table 4.1 to see if any are insoluble. For the molecular equation, we predict the products and write them all as intact compounds. For the total ionic equation, we write the soluble compounds as separate ions. For the net ionic equation, we eliminate the spectator ions.

Solution **(a)** In addition to the reactants, the two other ion combinations are strontium fluoride and potassium nitrate. Table 4.1 shows that strontium fluoride is insoluble, so a reaction *does* occur. Writing the molecular equation:

$$2KF(aq) + Sr(NO_3)_2(aq) \longrightarrow SrF_2(s) + 2KNO_3(aq)$$

Writing the total ionic equation:

$$2K^+(aq) + 2F^-(aq) + Sr^{2+}(aq) + 2NO_3^-(aq) \longrightarrow SrF_2(s) + 2K^+(aq) + 2NO_3^-(aq)$$

Writing the net ionic equation:

$$Sr^{2+}(aq) + 2F^-(aq) \longrightarrow SrF_2(s)$$

The spectator ions are K^+ and NO_3^-.

(b) The other ion combinations are ammonium bromide and sodium perchlorate. Table 4.1 shows that all ammonium, sodium, and most perchlorate compounds are soluble, and all bromides are soluble except those of Ag^+, Pb^{2+}, Cu^+, and Hg_2^{2+}. Therefore, ***no*** **reaction occurs.** The compounds remain as solvated ions.

FOLLOW-UP PROBLEM 4.3 Predict whether a reaction occurs, and if so, write balanced total and net ionic equations:

(a) Iron(III) chloride(*aq*) + cesium phosphate(*aq*) ⟶

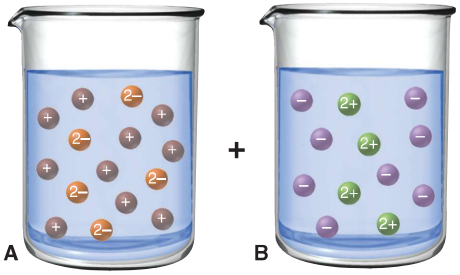
(b) Sodium hydroxide(*aq*) + cadmium nitrate(*aq*) ⟶

(c) Magnesium bromide(*aq*) + potassium acetate(*aq*) ⟶

(d) Silver nitrate(*aq*) + barium chloride(*aq*) ⟶

Sample Problem 4.4 Using Molecular Depictions in Precipitation Reactions

Problem The molecular views below depict reactant solutions for a precipitation reaction (with ions shown as colored spheres and water omitted for clarity):



(a) Which compound is dissolved in beaker A: KCl, Na_2SO_4, $MgBr_2$, or Ag_2SO_4?

(b) Which compound is dissolved in beaker B: NH_4NO_3, $MgSO_4$, $Ba(NO_3)_2$, or CaF_2?

(c) Name the precipitate and the spectator ions when solutions A and B are mixed, and write balanced molecular, total ionic, and net ionic equations for any reaction.

(d) If each particle represents 0.010 mol of ions, what is the maximum mass (g) of precipitate that can form (assuming complete reaction)?

Plan **(a)** and **(b)** From the depictions, we note the charge and number of each kind of ion and use Table 4.1 to determine the ion combinations that are soluble. **(c)** Once we know the combinations, Table 4.1 tells which two ions form the solid, so the other two are spectator ions. **(d)** This part is a limiting-reactant problem because the amounts of two species are involved. We count the number of each kind of ion that formed the solid. We multiply the number of each reactant ion by 0.010 mol and calculate the amount (mol) of product formed from each. Whichever ion forms less is limiting, so we use the molar mass of the precipitate to find mass (g).

Solution **(a)** In solution A, there are two 1+ particles for each 2− particle. Therefore, the dissolved compound cannot be KCl or $MgBr_2$. Of the remaining two choices, Ag_2SO_4 is insoluble, so the dissolved compound must be Na_2SO_4.

(b) In solution B, there are two 1− particles for each 2+ particle. Therefore, the dissolved compound cannot be NH_4NO_3 or $MgSO_4$. Of the remaining two choices, CaF_2 is insoluble, so the dissolved compound must be $Ba(NO_3)_2$.

(c) Of the two possible ion combinations, $BaSO_4$ and $NaNO_3$, $BaSO_4$ is insoluble, so Na^+ and NO_3^- are spectator ions.

Molecular: $Ba(NO_3)_2(aq) + Na_2SO_4(aq) \longrightarrow BaSO_4(s) + 2NaNO_3(aq)$

Total ionic: $Ba^{2+}(aq) + 2NO_3^-(aq) + 2Na^+(aq) + SO_4^{2-}(aq) \longrightarrow BaSO_4(s) + 2NO_3^-(aq) + 2Na^+(aq)$

Net ionic: $Ba^{2+}(aq) + SO_4^{2-}(aq) \longrightarrow BaSO_4(s)$

(d) Finding the ion that is the limiting reactant:

For Ba^{2+}:

$$\text{Amount (mol) of } BaSO_4 = 4\ \cancel{Ba^{2+}\text{ particles}} \times \frac{0.010\ \cancel{\text{mol }Ba^{2+}\text{ ion}}}{1\ \cancel{\text{particle}}} \times \frac{1\text{ mol }BaSO_4}{1\ \cancel{\text{mol }Ba^{2+}\text{ ions}}} = 0.040\text{ mol }BaSO_4$$

For SO_4^{2-}:

$$\text{Amount (mol) of } BaSO_4 = 5\ \cancel{SO_4^{2-}\text{ particles}} \times \frac{0.010\ \cancel{\text{mol }SO_4^{2-}\text{ ions}}}{1\ \cancel{\text{particle}}} \times \frac{1\text{ mol }BaSO_4}{1\ \cancel{\text{mol }SO_4^{2-}\text{ ions}}} = 0.050\text{ mol }BaSO_4$$

Therefore, Ba^{2+} ion is the limiting reactant.

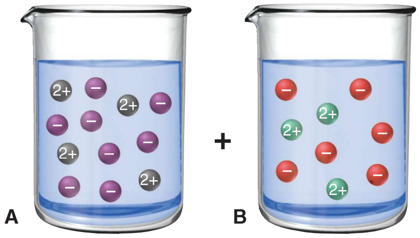
Calculating the mass (g) of product ($\mathcal{M}$ of $BaSO_4$ = 233.4 g/mol):

$$\text{Mass (g) of } BaSO_4 = 0.040\ \cancel{\text{mol }BaSO_4} \times \frac{233.4\text{ g }BaSO_4}{1\ \cancel{\text{mol }BaSO_4}} = 9.3\text{ g }BaSO_4$$

Check Counting the number of Ba^{2+} ions allows a more direct calculation for a check: four Ba^{2+} particles means the maximum mass of $BaSO_4$ that can form is

$$\text{Mass (g) of } BaSO_4 = 4\ \cancel{Ba^{2+}\text{ particles}} \times \frac{0.010\ \cancel{\text{mol }Ba^{2+}\text{ ions}}}{1\ \cancel{\text{particle}}} \times \frac{1\ \cancel{\text{mol }BaSO_4}}{1\ \cancel{\text{mol }Ba^{2+}\text{ ions}}} \times \frac{233.4\text{ g }BaSO_4}{1\ \cancel{\text{mol}}} = 9.3\text{ g }BaSO_4$$

FOLLOW-UP PROBLEM 4.4 Molecular views of the reactant solutions for a precipitation reaction are shown below (with ions represented as spheres and water molecules omitted):



(a) Which compound is dissolved in beaker A: $Zn(NO_3)_2$, KCl, Na_2SO_4, or $PbCl_2$?
(b) Which compound is dissolved in beaker B: $(NH_4)_2SO_4$, $Cd(OH)_2$, $Ba(OH)_2$, or KNO_3?
(c) Name the precipitate and the spectator ions when solutions A and B are mixed, and write balanced molecular, total ionic, and net ionic equations for the reaction.
(d) If each particle represents 0.050 mol of ions, what is the maximum mass (g) of precipitate that can form (assuming complete reaction)?

Summary of Section 4.3

- In a precipitation reaction, an insoluble ionic compound forms when solutions of two soluble ones are mixed. The electrostatic attraction between certain pairs of solvated ions is strong enough to overcome the attraction of each ion for water.
- Based on a set of solubility rules, we can predict whether a precipitate will form by noting which of all possible cation-anion combinations is insoluble.

4.4 • ACID-BASE REACTIONS

Aqueous acid-base reactions occur in processes as diverse as the metabolic action of proteins and carbohydrates, the industrial production of fertilizer, and the revitalization of lakes damaged by acid rain.

These reactions involve water as reactant or product, in addition to its common role as solvent. Of course, an **acid-base reaction** (also called a **neutralization reaction**) occurs when an acid reacts with a base, but the definitions of these terms and the scope of this reaction class have changed over the years. For our purposes at this point, we'll use definitions that apply to substances found commonly in the lab:

- *An **acid** is a substance that produces H^+ ions when dissolved in water.*

$$\mathrm{HX} \xrightarrow{\mathrm{H_2O}} \mathrm{H^+}(aq) + \mathrm{X^-}(aq)$$

- *A **base** is a substance that produces OH^- ions when dissolved in water.*

$$\mathrm{MOH} \xrightarrow{\mathrm{H_2O}} \mathrm{M^+}(aq) + \mathrm{OH^-}(aq)$$

(Other definitions are presented in Chapter 18.)

Table 4.2 Strong and Weak Acids and Bases

Acids

Strong
Hydrochloric acid, HCl
Hydrobromic acid, HBr
Hydriodic acid, HI
Nitric acid, HNO_3
Sulfuric acid, H_2SO_4
Perchloric acid, $HClO_4$

Weak (a few of many examples)
Hydrofluoric acid, HF
Phosphoric acid, H_3PO_4
Acetic acid, CH_3COOH (or $HC_2H_3O_2$)

Bases

Strong
Group 1A(1) hydroxides:
Lithium hydroxide, $LiOH$
Sodium hydroxide, $NaOH$
Potassium hydroxide, KOH
Rubidium hydroxide, $RbOH$
Cesium hydroxide, $CsOH$

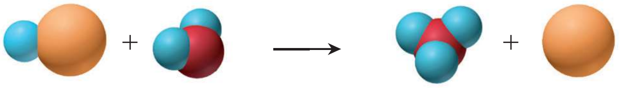
Heavy Group 2A(2) hydroxides:
Calcium hydroxide, $Ca(OH)_2$
Strontium hydroxide, $Sr(OH)_2$
Barium hydroxide, $Ba(OH)_2$

Weak (one of many examples)
Ammonia, NH_3

Acids and the Solvated Proton *Acidic solutions arise when certain covalent H-containing molecules dissociate into ions in water.* In every case, these molecules contain a *polar bond to H* in which the other atom pulls much more strongly on the electron pair. A good example is HBr. The Br end of the H—Br bond is partially negative, and the H end is partially positive. When hydrogen bromide gas dissolves in water, the poles of H_2O molecules are attracted to the oppositely charged poles of the HBr. The bond breaks, with H becoming the solvated cation $H^+(aq)$ and Br becoming the solvated anion $Br^-(aq)$:

$$\mathrm{HBr}(g) \xrightarrow{\mathrm{H_2O}} \mathrm{H^+}(aq) + \mathrm{Br^-}(aq)$$

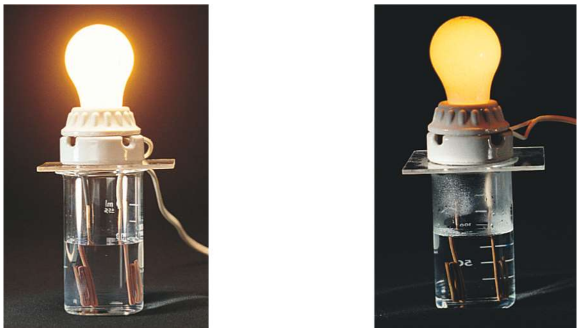
The solvated H^+ ion is a very unusual species. The H atom is a proton surrounded by an electron, so H^+ is just a proton. With a full positive charge concentrated in such a tiny volume, H^+ attracts the negative pole of water molecules so strongly that it forms a covalent bond to one of them. We'll emphasize this interaction by writing the solvated H^+ ion as a solvated H_3O^+ ion (hydronium ion):



$$\mathrm{HBr}(g) + \mathrm{H_2O}(l) \longrightarrow \mathrm{H_3O^+}(aq) + \mathrm{Br^-}(aq)$$

Acids and Bases as Electrolytes Acids and bases are categorized in terms of their "strength," the degree to which they dissociate into ions in water (Table 4.2):

- *Strong acids and strong bases dissociate completely into ions.* Therefore, like soluble ionic compounds, they are *strong* electrolytes and conduct a large current, as shown by the brightly lit bulb (Figure 4.7A).
- *Weak acids and weak bases dissociate very little into ions.* Most of their molecules remain intact. Therefore, they are *weak* electrolytes, which means they conduct a small current (Figure 4.7B).



A Strong acid (or base) = strong electrolyte

B Weak acid (or base) = weak electrolyte

Figure 4.7 Acids and bases as electrolytes.

Because a strong acid (or strong base) dissociates completely, we can find the molarity of H^+ (or OH^-) and the amount (mol) or number of each ion in solution. (You'll see how to determine these quantities for weak acids in Chapter 18.)

Sample Problem 4.5 Determining the Number of H^+ (or OH^-) Ions in Solution

Problem Nitric acid is a major chemical in the fertilizer and explosives industries. How many $H^+(aq)$ ions are in 25.3 mL of 1.4 *M* nitric acid?

Plan We know the volume (25.3 mL) and molarity (1.4 *M*) of nitric acid, and we need the number of $H^+(aq)$. We convert from mL to L and multiply by the molarity to find the amount (mol) of acid. Table 4.2 shows that nitric acid is a strong acid, so it dissociates completely. With the formula, we write a dissociation equation, which shows the amount (mol) of H^+ ions per mole of acid. We multiply that amount by Avogadro's number to find the number of $H^+(aq)$ ions (see the road map).

Solution Finding the amount (mol) of nitric acid:

$$\text{Amount (mol) of HNO}_3 = 25.3\ \cancel{\text{mL}} \times \frac{1\ \cancel{\text{L}}}{1000\ \cancel{\text{mL}}} \times \frac{1.4\ \text{mol}}{1\ \cancel{\text{L}}} = 0.035\ \text{mol}$$

Nitric acid is HNO_3, so we have:

$$HNO_3(l) \xrightarrow{H_2O} H^+(aq) + NO_3^-(aq)$$

Finding the number of H^+ ions:

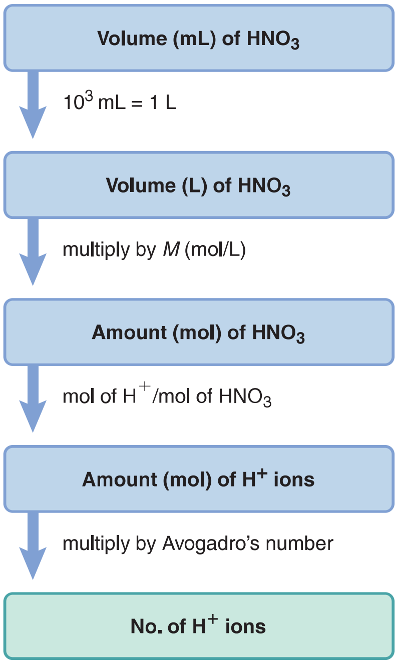
$$\text{No. of H}^+\ \text{ions} = 0.035\ \cancel{\text{mol HNO}_3} \times \frac{1\ \cancel{\text{mol H}^+}}{1\ \cancel{\text{mol HNO}_3}} \times \frac{6.022\times10^{23}\ \text{H}^+\ \text{ions}}{1\ \cancel{\text{mol H}^+}}$$

$$= \boxed{2.1\times10^{22}\ \text{H}^+\ \text{ions}}$$

Check The number of moles seems correct: 0.025 L × 1.4 mol/L = 0.035 mol, and multiplying by 6×10^{23} ions/mol gives 2×10^{22} ions.

FOLLOW-UP PROBLEM 4.5 How many $OH^-(aq)$ ions are present in 451 mL of 1.20 *M* potassium hydroxide?

Road Map



Structural Features of Acids and Bases A key structural feature appears in common laboratory acids and bases:

- *Acids.* Strong acids, such as HNO_3 and H_2SO_4, and weak acids, such as HF and H_3PO_4, have one or more H atoms as part of their structure, which are either completely released (strong) or partially released (weak) as protons in water.
- *Bases.* Strong bases have either OH^- (e.g., NaOH) or O^{2-} (e.g., K_2O) as part of their structure. The oxide ion is not stable in water and reacts to form OH^- ion:

$$O^{2-}(s) + H_2O(l) \longrightarrow 2OH^-(aq) \quad \text{so} \quad K_2O(s) + H_2O(l) \longrightarrow 2K^+(aq) + 2OH^-(aq)$$

Weak bases, such as ammonia, do not contain OH^- ions, but, as you'll see in later chapters, they all have an electron pair on N. Weak bases produce OH^- ions in a reaction that occurs to a small extent in water:

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

Weak Acids and Bases and the Equilibrium State The unusual yield arrow in the equation above for ammonia's reaction with water indicates that the *reaction proceeds in both directions.* Indeed, as we'll discuss in later chapters, most reactions behave this way: they seem to stop before they are complete (that is, before the limiting reactant is used up) because another reaction, the reverse of the first one, is taking place just as fast. As a result, *no further change in the amounts of reactants and products occurs,* and we say the reaction has reached a state of *equilibrium.*

The reversibility of reactions explains why weak acids and bases dissociate into ions to only a small extent: the dissociation becomes balanced by a reassociation. For example, when acetic acid dissolves in water, some of the CH_3COOH molecules react with water and form H_3O^+ and CH_3COO^- ions. As more ions form, they react with each other more often to re-form acetic acid and water, and this state is indicated by the special (equilibrium) arrow:

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

In fact, in 0.1 *M* CH_3COOH at 25°C, only about 1.3% of the acid molecules dissociate into ions. A similarly small percentage of ammonia molecules form ions when 0.1 *M* NH_3 reacts with water. We discuss the central idea of equilibrium and its applications for chemical and physical systems in Chapters 12, 13, and 17 through 21.

The Key Event: Formation of H_2O from H^+ and OH^-

To see the key event in acid-base reactions, we'll write the three types of aqueous ionic equations (with color) and focus on the reaction between the strong acid HCl and the strong base $Ba(OH)_2$:

- The molecular equation is

$$2HCl(aq) + Ba(OH)_2(aq) \longrightarrow BaCl_2(aq) + 2H_2O(l)$$

- HCl and $Ba(OH)_2$ dissociate completely, so the total ionic equation is

$$2H^+(aq) + 2Cl^-(aq) + Ba^{2+}(aq) + 2OH^-(aq) \longrightarrow Ba^{2+}(aq) + 2Cl^-(aq) + 2H_2O(l)$$

- In the net ionic equation, we eliminate the spectator ions, $Ba^{2+}(aq)$ and $Cl^-(aq)$:

$$2H^+(aq) + 2OH^-(aq) \longrightarrow 2H_2O(l) \quad \text{or} \quad H^+(aq) + OH^-(aq) \longrightarrow H_2O(l)$$

Thus, *the key event in aqueous reactions between a strong acid and a strong base is that an* H^+ *ion from the acid and an* OH^- *ion from the base form a water molecule.* Only the spectator ions differ from one strong acid–strong base reaction to another.

Like precipitation reactions, acid-base reactions occur through *the electrostatic attraction of ions and their removal from solution as the product.* In this case, rather than an insoluble ionic solid, the product is H_2O, which consists almost entirely of undissociated molecules. Actually, water molecules dissociate *very* slightly (which, as you'll see in Chapter 18, is very important), but the formation of water in an acid-base reaction results in an enormous net removal of H^+ and OH^- ions.

The molecular and total ionic equations above show that if you evaporate the water, the spectator ions remain: the ionic compound that results from the reaction of an acid and a base is called a **salt,** which in this case is barium chloride. Thus, in an aqueous neutralization reaction, *an acid and a base form a salt solution and water:*

$$\underset{\text{acid}}{HX(aq)} + \underset{\text{base}}{MOH(aq)} \longrightarrow \underset{\text{salt}}{MX(aq)} + \underset{\text{water}}{H_2O(l)}$$

Note that *the cation of the salt comes from the base and the anion from the acid.* Also note that acid-base reactions, like precipitation reactions, are metathesis (double-displacement) reactions.

Sample Problem 4.6 Writing Ionic Equations for Acid-Base Reactions

Problem Write balanced molecular, total ionic, and net ionic equations for each of the following acid-base reactions and identify the spectator ions:

(a) Hydrochloric acid(*aq*) + potassium hydroxide(*aq*) ⟶

(b) Strontium hydroxide(*aq*) + perchloric acid(*aq*) ⟶

(c) Barium hydroxide(*aq*) + sulfuric acid(*aq*) ⟶

Plan All are strong acids and bases (see Table 4.2), so the actual reaction is between H^+ and OH^-. The products are H_2O and a salt solution of spectator ions. In (c), we note that the salt ($BaSO_4$) is insoluble (see Table 4.1), so there are no spectator ions.

Solution **(a)** Writing the molecular equation:

$$HCl(aq) + KOH(aq) \longrightarrow KCl(aq) + H_2O(l)$$

Writing the total ionic equation:

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

Writing the net ionic equation:

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

$K^+(aq)$ and $Cl^-(aq)$ are the spectator ions.

(b) Writing the molecular equation:

$$Sr(OH)_2(aq) + 2HClO_4(aq) \longrightarrow Sr(ClO_4)_2(aq) + 2H_2O(l)$$

Writing the total ionic equation:

$$Sr^{2+}(aq) + 2OH^-(aq) + 2H^+(aq) + 2ClO_4^-(aq) \longrightarrow Sr^{2+}(aq) + 2ClO_4^-(aq) + 2H_2O(l)$$

Writing the net ionic equation:

$$2OH^-(aq) + 2H^+(aq) \longrightarrow 2H_2O(l) \quad \text{or} \quad OH^-(aq) + H^+(aq) \longrightarrow H_2O(l)$$

$Sr^{2+}(aq)$ and $ClO_4^-(aq)$ are the spectator ions.

(c) Writing the molecular equation:

$$Ba(OH)_2(aq) + H_2SO_4(aq) \longrightarrow BaSO_4(s) + 2H_2O(l)$$

Writing the total ionic equation:

$$Ba^{2+}(aq) + 2OH^-(aq) + 2H^+(aq) + SO_4^{2-}(aq) \longrightarrow BaSO_4(s) + 2H_2O(l)$$

This is a neutralization *and* a precipitation reaction, so the net ionic equation is the same as the total ionic. There are no spectator ions.

FOLLOW-UP PROBLEM 4.6 Write balanced molecular, total ionic, and net ionic equations for the reaction between aqueous solutions of calcium hydroxide and nitric acid.

Proton Transfer in Acid-Base Reactions

When we take a closer look (with color) at the reaction between a strong acid and strong base, as well as reactions of weak acids with bases, a unifying pattern appears.

Reaction Between Strong Acid and Strong Base When HCl gas dissolves in water, the H^+ ion ends up bonded to a water molecule. Thus, hydrochloric acid actually consists of solvated H_3O^+ and Cl^- ions:

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

If we add NaOH solution, the total ionic equation shows that H_3O^+ *transfers a proton* to OH^- (leaving a water molecule written as H_2O, and forming a water molecule written as HOH):

$$\overbrace{[H_3O^+(aq) + Cl^-(aq)] + [Na^+(aq) + OH^-}^{H^+\ \text{transfer}}(aq)] \longrightarrow H_2O(l) + Cl^-(aq) + Na^+(aq) + HOH(l)$$

Without the spectator ions, the net ionic equation shows more clearly the *transfer of a proton* from H_3O^+ to OH^-:

$$\overbrace{H_3O^+(aq) \quad + \quad OH^-}^{H^+\ \text{transfer}}(aq) \longrightarrow H_2O(l) + HOH(l) \qquad [\text{or } 2H_2O(l)]$$

This equation is identical to the one we saw earlier (see p. 128),

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

with the additional H_2O molecule coming from the H_3O^+. Thus, an *acid-base reaction is a proton-transfer process.* In this case, the Cl^- and Na^+ ions remain in solution, and if the water is evaporated, they crystallize as the salt NaCl. Figure 4.8 on the next page shows this process on the atomic level. We'll discuss the proton-transfer concept thoroughly in Chapter 18.

Reactions of Weak Acids with Bases When solutions of sodium hydroxide and the weak acid acetic acid (CH_3COOH, Table 4.2) are mixed, the molecular equation is

$$CH_3COOH(aq) + NaOH(aq) \longrightarrow CH_3COONa(aq) + H_2O(l)$$

The total ionic equation is written differently for the reaction of a weak acid. Because acetic acid is weak and, thus, dissociates very little, it appears as *undissociated, intact molecules:*

$$CH_3COOH(aq) + Na^+(aq) + OH^-(aq) \longrightarrow CH_3COO^-(aq) + Na^+(aq) + H_2O(l)$$

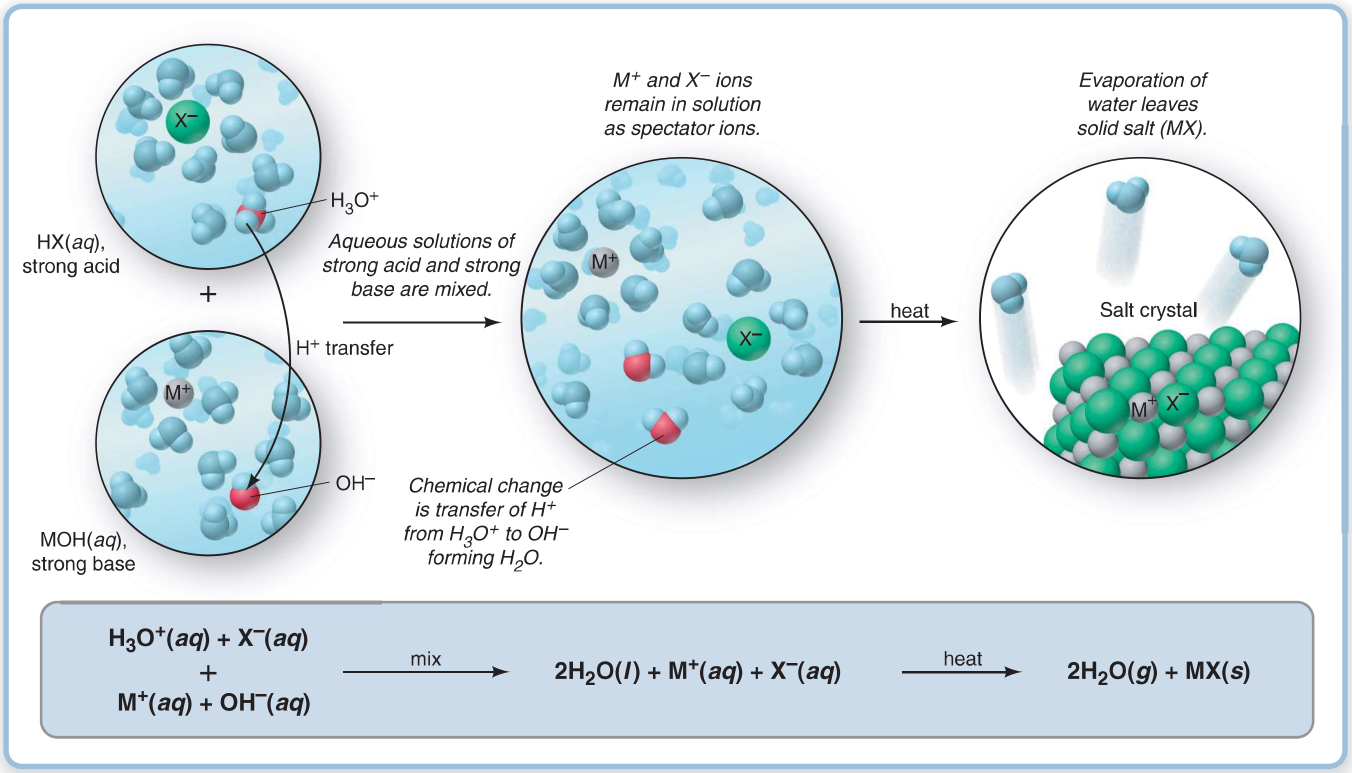


Figure 4.8 An aqueous strong acid–strong base reaction as a proton-transfer process.

The net ionic equation reveals that proton transfer occurs here as well, but directly from the weak acid rather than from H_3O^+:

$$CH_3COO\overbrace{H(aq) + OH^-}^{H^+\text{ transfer}}(aq) \longrightarrow CH_3COO^-(aq) + H_2O(l)$$

The only spectator ion is $Na^+(aq)$.

Quantifying Acid-Base Reactions by Titration

In any **titration,** *the known concentration of one solution is used to determine the unknown concentration of another.* In a typical acid-base titration, a *standardized* solution of base, one whose concentration is *known,* is added to a solution of acid whose concentration is *unknown (or vice versa).*

Figure 4.9A shows the laboratory setup for an acid-base titration with a known volume of acid and a few drops of indicator in a flask. An *acid-base indicator* is a substance whose color is different in acid than in base; the indicator used in the figure is phenolphthalein, which is pink in base and colorless in acid. (We examine indicators in Chapters 18 and 19.) Base is added from a buret, and the OH^- ions react with the H^+ ions. As the titration nears its end (Figure 4.9B), the drop of added base creates a temporary excess of OH^-, causing some indicator molecules to change to the basic color; they return to the acidic color when the flask is swirled. There are two key stages in the titration:

- The **equivalence point** occurs when *the amount (mol) of H^+ ions in the original volume of acid has reacted with the same amount (mol) of OH^- ions from the buret:*

  Amount (mol) of H^+ (originally in flask) = amount (mol) of OH^- (added from buret)

- The **end point** occurs when a tiny excess of OH^- ions changes the indicator permanently to its basic color (Figure 4.9C).

In calculations, such as in Sample Problem 4.7, we assume that this tiny excess of OH^- ions is insignificant and that *the amount of base needed to reach the end point is the same as the amount needed to reach the equivalence point.*

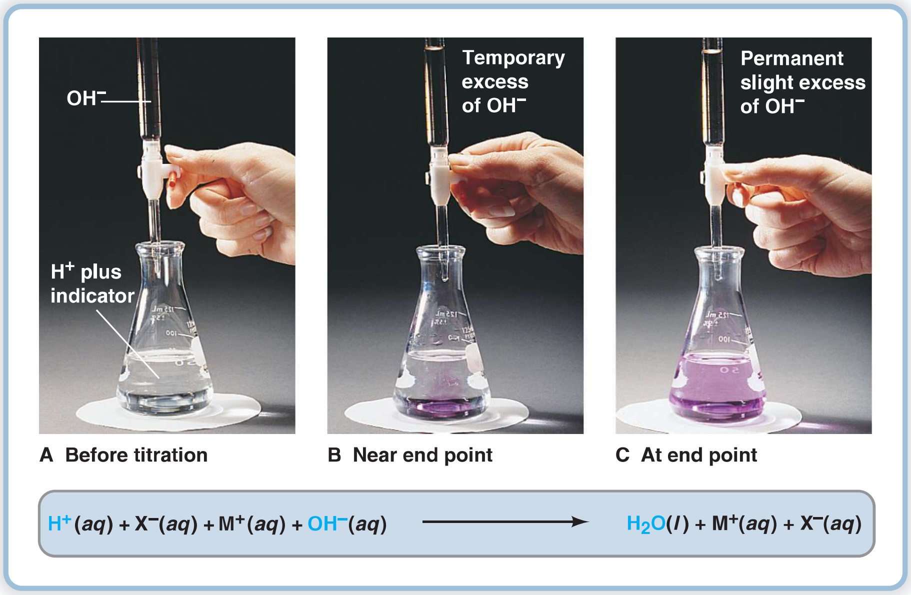


Figure 4.9 An acid-base titration.

Sample Problem 4.7 Finding the Concentration of an Acid from a Titration

Problem To standardize an HCl solution, you put 50.00 mL of it in a flask with a few drops of indicator and put 0.1524 *M* NaOH in a buret. The buret reads 0.55 mL at the start and 33.87 mL at the end point. Find the molarity of the HCl solution.

Plan We have to find the molarity of the acid from the volume of acid (50.00 mL), the initial (0.55 mL) and final (33.87 mL) volumes of base, and the molarity of the base (0.1524 *M*). First, we balance the equation. The volume of added base is the difference in buret readings, and we use the base's molarity to calculate the amount (mol) of base. Then, we use the molar ratio from the balanced equation to find the amount (mol) of acid originally present and divide by the acid's original volume to find the molarity (see the road map).

Solution Writing the balanced equation:

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

Finding the volume (L) of NaOH solution added:

$$\text{Volume (L) of solution} = (33.87\ \cancel{\text{mL}}\ \text{soln} - 0.55\ \cancel{\text{mL}}\ \text{soln}) \times \frac{1\ \text{L}}{1000\ \cancel{\text{mL}}}$$
$$= 0.03332\ \text{L soln}$$

Finding the amount (mol) of NaOH added:

$$\text{Amount (mol) of NaOH} = 0.03332\ \cancel{\text{L soln}} \times \frac{0.1524\ \text{mol NaOH}}{1\ \cancel{\text{L soln}}}$$
$$= 5.078\times10^{-3}\ \text{mol NaOH}$$

Finding the amount (mol) of HCl originally present: Since the molar ratio is 1/1,

$$\text{Amount (mol) of HCl} = 5.078\times10^{-3}\ \cancel{\text{mol NaOH}} \times \frac{1\ \text{mol HCl}}{1\ \cancel{\text{mol NaOH}}} = 5.078\times10^{-3}\ \text{mol HCl}$$

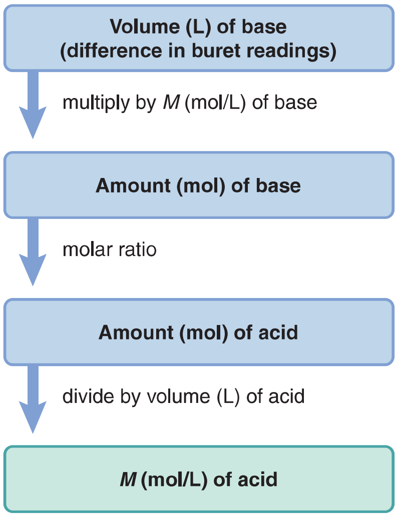
Calculating the molarity of HCl:

$$\text{Molarity of HCl} = \frac{5.078\times10^{-3}\ \text{mol HCl}}{50.00\ \cancel{\text{mL}}} \times \frac{1000\ \cancel{\text{mL}}}{1\ \text{L}} = \boxed{0.1016\ M\ \text{HCl}}$$

Check The answer makes sense: a large volume of less concentrated acid neutralized a small volume of more concentrated base. With rounding, the numbers of moles of H^+ and OH^- are about equal: 50 mL × 0.1 *M* H^+ = 0.005 mol = 33 mL × 0.15 *M* OH^-.

FOLLOW-UP PROBLEM 4.7 What volume of 0.1292 *M* $Ba(OH)_2$ would neutralize 50.00 mL of the HCl solution standardized in Sample Problem 4.7?

Road Map



Summary of Section 4.4

- In an acid-base (neutralization) reaction between an acid (an H^+-yielding substance) and a base (an OH^--yielding substance), H^+ and OH^- ions form H_2O.
- Strong acids and bases dissociate completely in water (strong electrolytes); weak acids and bases dissociate slightly (weak electrolytes).
- An acid-base reaction involves the transfer of a proton from an acid to a base.
- Since weak acids dissociate very little, ionic equations show a weak acid as an intact molecule transferring its proton to the base.
- In a titration, the known concentration of one solution is used to determine the concentration of the other.

4.5 • OXIDATION-REDUCTION (REDOX) REACTIONS

Oxidation-reduction (redox) reactions include the formation of a compound from its elements (and the reverse process), all combustion reactions, the generation of electricity in batteries, the production of cellular energy, and many others. In fact, redox reactions are so widespread that many do not occur in solution at all. In this section, we examine the key event in the redox process and discuss important terminology.

The Key Event: Net Movement of Electrons Between Reactants

The key chemical event in an **oxidation-reduction** (or **redox**) **reaction** is the *net movement of electrons from one reactant to another*. The movement occurs from the reactant (or atom in the reactant) with *less* attraction for electrons to the reactant (or atom) with *more* attraction for electrons.

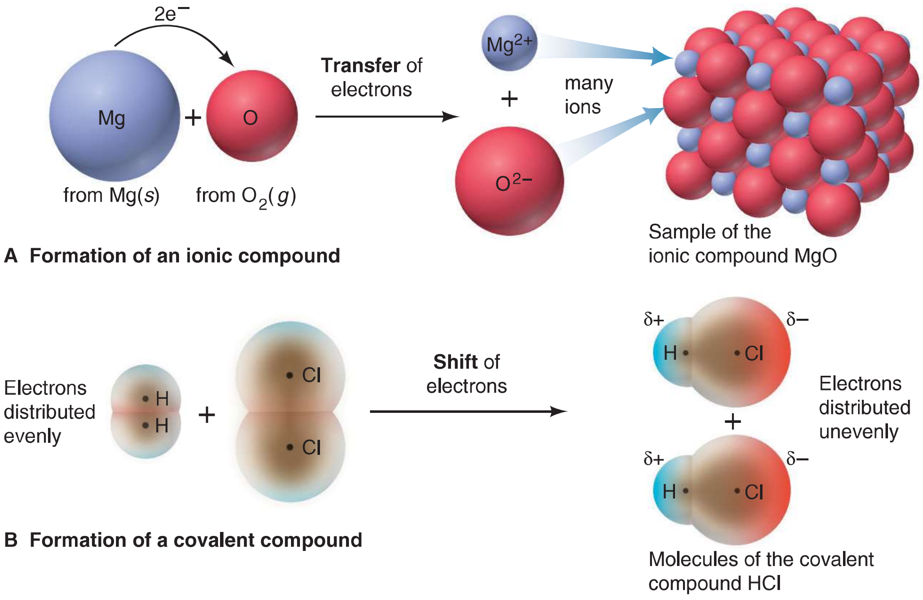
This process occurs in the formation of both ionic and covalent compounds:

- *Ionic compounds: transfer of electrons.* In the reaction that forms MgO from its elements (see Figure 3.6), the balanced equation is

$$2Mg(s) + O_2(g) \longrightarrow 2MgO(s)$$

Figure 4.10A shows that each Mg atom loses two electrons and each O atom gains them. This loss and gain is a ***transfer** of electrons* away from each Mg atom to each O atom. The resulting Mg^{2+} and O^{2-} ions aggregate into an ionic solid.

Figure 4.10 The redox process in the formation of (A) ionic and (B) covalent compounds from their elements.



- *Covalent compounds: shift of electrons.* During the formation of a covalent compound from its elements, there is more of a ***shift*** *of electrons* than a full transfer. Thus, *ions do not form*. Consider the formation of HCl gas:

$$H_2(g) + Cl_2(g) \longrightarrow 2HCl(g)$$

To see the electron movement, we'll compare the electron distribution in reactant and product. As Figure 4.10B shows, in H_2 and Cl_2, the electrons are shared equally between the atoms *(symmetrical shading)*. Because the Cl atom attracts electrons more than the H atom, in HCl, the electrons are shared unequally *(asymmetrical shading)*. Electrons shift away from H and toward Cl, so the Cl atom has more negative charge (*red* and $\delta-$) than it had in Cl_2, and the H atom has less negative charge (*blue* and $\delta+$) than it had in H_2.

Some Essential Redox Terminology

This subsection introduces certain key terms that describe central ideas of the redox process.

- **Oxidation** is the *loss* of electrons.
- **Reduction** is the *gain* of electrons.

During the formation of MgO, Mg undergoes oxidation (loss of electrons), and O_2 undergoes reduction (gain of electrons). The loss and gain are simultaneous, but we can imagine them occurring separately:

Oxidation (electron loss by Mg): $Mg \longrightarrow Mg^{2+} + 2e^-$

Reduction (electron gain by O_2): $\frac{1}{2}O_2 + 2e^- \longrightarrow O^{2-}$

(Throughout the chapter, blue type indicates oxidation, and red type reduction.)

- The **oxidizing agent** is the species doing the oxidizing (causing the electron loss).
- The **reducing agent** is the species doing the reducing (causing the electron gain).

One reactant acts on the other. During the reaction that forms MgO, *O_2 oxidizes Mg,* so O_2 is the oxidizing agent, and *Mg reduces O_2*, so Mg is the reducing agent.

Note the give and take of electrons: O_2 takes the electrons that Mg gives up, or, put the other way around, Mg gives up the electrons that O_2 takes. This means that

- *The oxidizing agent is reduced:* it takes electrons (gains them).
- *The reducing agent is oxidized:* it gives up electrons (loses them).

In the formation of HCl, *Cl_2 oxidizes H_2* (H loses some electron charge and Cl gains it), which is the same as saying that *H_2 reduces Cl_2*. The reducing agent, H_2, is oxidized, and the oxidizing agent, Cl_2, is reduced.

Using Oxidation Numbers to Monitor Electron Charge

Chemists have devised a "bookkeeping" system to monitor which atom loses electron charge and which atom gains it: each atom in a molecule (or formula unit) is assigned an **oxidation number (O.N.),** or *oxidation state,* which is the charge the atom would have *if* electrons were transferred completely, not shared.

Each element in a binary *ionic* compound has a full charge because the atom transferred its electron(s), and so the atom's oxidation number equals the ionic charge. But, each element in a *covalent* compound (or in a polyatomic ion) has a partial charge because the electrons shifted away from one atom and toward the other. For these cases, we determine oxidation number by a set of rules (Table 4.3, *next page;* you'll learn the atomic basis of the rules in Chapters 8 and 9).

An O.N. has the sign *before* the number (as in +2), whereas an ionic charge has the sign *after* the number (as in 2+). Also, unlike a unitary ionic charge, as in Na^+ or Cl^-, an O.N. of +1 or −1 retains the numeral. For example, we don't write the sodium ion as Na^{+1}, but the O.N. of the Na^+ ion is +1, not merely +.

Table 4.3 Rules for Assigning an Oxidation Number (O.N.)

General Rules

1. For an atom in its elemental form (Na, O_2, Cl_2, etc.): O.N. = 0
2. For a monatomic ion: O.N. = ion charge (with the sign *before* the numeral)
3. The sum of O.N. values for the atoms in a molecule or formula unit of a compound equals zero. The sum of O.N. values for the atoms in a polyatomic ion equals the ion's charge.

Rules for Specific Atoms or Periodic Table Groups

1. For Group 1A(1):	O.N. = +1 in all compounds
2. For Group 2A(2):	O.N. = +2 in all compounds
3. For hydrogen:	O.N. = +1 in combination with nonmetals
	O.N. = −1 in combination with metals and boron
4. For fluorine:	O.N. = −1 in all compounds
5. For oxygen:	O.N. = −1 in peroxides
	O.N. = −2 in all other compounds (except with F)
6. For Group 7A(17):	O.N. = −1 in combination with metals, nonmetals (except O), and other halogens lower in the group

Sample Problem 4.8 Determining the Oxidation Number of Each Element in a Compound (or Ion)

Problem Determine the oxidation number (O.N.) of each element in these species:
(a) Zinc chloride **(b)** Sulfur trioxide **(c)** Nitric acid **(d)** Dichromate ion

Plan We determine the formulas and consult Table 4.3, including the general rules that the O.N. values for a compound add up to zero and those for a polyatomic ion add up to the ion's charge.

Solution **(a)** $ZnCl_2$. The sum of O.N.s must equal zero. The O.N. of the Zn^{2+} ion is +2, so the O.N. of each Cl^- ion is −1, for a total of −2.
(b) SO_3. The O.N. of each oxygen is −2, for a total of −6. The O.N.s must add up to zero, so the O.N. of S is +6.
(c) HNO_3. The O.N. of H is +1, so the O.N.s of the atoms in NO_3^- must add up to −1 to equal the charge of the polyatomic ion and give zero for the compound. The O.N. of each O is −2, for a total of −6. Therefore, the O.N. of N is +5.
(d) $Cr_2O_7^{2-}$. The O.N. of each O is −2, so the total for seven O atoms is −14. Therefore, each Cr must have an O.N. of +6 in order for the sum of the O.N.s to equal the charge of the ion: +12 + (−14) = −2.

FOLLOW-UP PROBLEM 4.8 Determine the O.N. of each element in the following:
(a) Scandium oxide (Sc_2O_3) **(b)** Gallium chloride ($GaCl_3$)
(c) Hydrogen phosphate ion **(d)** Iodine trifluoride

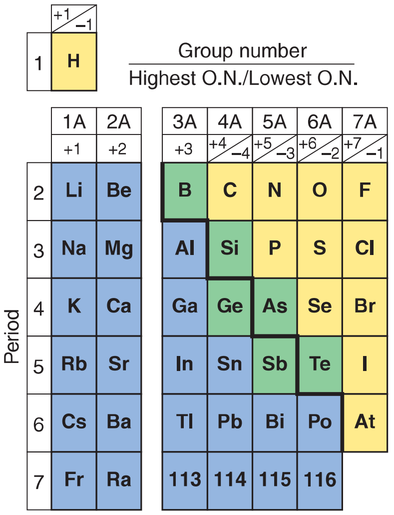


Figure 4.11 Highest and lowest oxidation numbers of reactive main-group elements.

The periodic table is a great help in learning the highest and lowest oxidation numbers of most main-group elements (Figure 4.11):

- For most main-group elements, the A-group number (1A, 2A, and so on) is the *highest* oxidation number (always positive) of any element in the group. The only exceptions are O, which never has an O.N. of +6, and F, which never has an O.N. of +7.
- For main-group nonmetals and some metalloids, the A-group number minus 8 is the *lowest* oxidation number (always negative) of any element in the group.

For example, the highest oxidation number of S (Group 6A) is +6, as in SF_6, and the lowest is (6 − 8), or −2, as in FeS and other metal sulfides.

Using O.N.s to Identify Oxidizing and Reducing Agents By assigning an oxidation number to each atom, we can see which species was oxidized and which reduced and, thus, which is the oxidizing agent and which the reducing agent:

- If an atom has a higher (more positive or less negative) O.N. in the product than it had in the reactant, the reactant that contains that atom was oxidized (lost electrons) and is the reducing agent. Thus, *oxidation is shown by an increase in O.N.*
- If an atom has a lower (more negative or less positive) O.N. in the product than it had in the reactant, the reactant that contains that atom was reduced (gained electrons) and is the oxidizing agent. Thus, *reduction is shown by a decrease in O.N.*

Sample Problem 4.9 Identifying Oxidizing and Reducing Agents

Problem Identify the oxidizing agent and the reducing agent in each of the following:

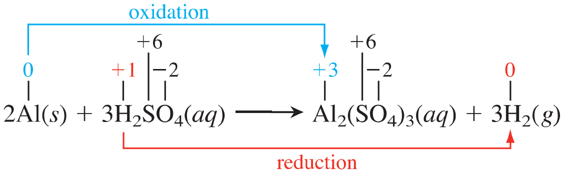
(a) $2Al(s) + 3H_2SO_4(aq) \longrightarrow Al_2(SO_4)_3(aq) + 3H_2(g)$

(b) $PbO(s) + CO(g) \longrightarrow Pb(s) + CO_2(g)$

(c) $2H_2(g) + O_2(g) \longrightarrow 2H_2O(g)$

Plan We assign an O.N. to each atom (or ion). The reducing agent contains an atom that is oxidized (O.N. *increased* from left to right in the equation). The oxidizing agent contains an atom that is reduced (O.N. *decreased*). We mark the changes with tie-lines.

Solution (a) Assigning oxidation numbers:



$$\overset{0}{2Al}(s) + 3\overset{+1}{H_2}\overset{+6}{S}\overset{-2}{O_4}(aq) \longrightarrow \overset{+3}{Al_2}(\overset{+6}{S}\overset{-2}{O_4})_3(aq) + 3\overset{0}{H_2}(g)$$

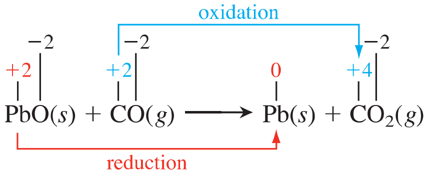
The O.N. of Al increased from 0 to +3 (Al lost electrons), so Al was oxidized;

Al is the reducing agent.

The O.N. of H decreased from +1 to 0 (H gained electrons), so H^+ was reduced;

H_2SO_4 is the oxidizing agent.

(b) Assigning oxidation numbers:



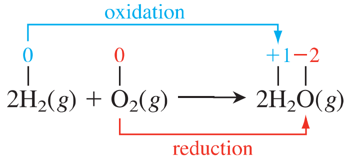
$$\overset{+2}{Pb}\overset{-2}{O}(s) + \overset{+2}{C}\overset{-2}{O}(g) \longrightarrow \overset{0}{Pb}(s) + \overset{+4}{C}\overset{-2}{O_2}(g)$$

Pb decreased its O.N. from +2 to 0, so PbO was reduced; PbO is the oxidizing agent.

C increased its O.N. from +2 to +4, so CO was oxidized; CO is the reducing agent.

When a reactant (in this case, CO) becomes a product with more O atoms (CO_2), it is oxidized; when a reactant (PbO) becomes a product with fewer O atoms (Pb), it is reduced.

(c) Assigning oxidation numbers:



$$2\overset{0}{H_2}(g) + \overset{0}{O_2}(g) \longrightarrow 2\overset{+1}{H_2}\overset{-2}{O}(g)$$

O_2 was reduced (O.N. of O decreased from 0 to −2); O_2 is the oxidizing agent.

H_2 was oxidized (O.N. of H increased from 0 to +1); H_2 is the reducing agent.

Oxygen is always the oxidizing agent in a combustion reaction.

FOLLOW-UP PROBLEM 4.9 Identify each oxidizing agent and each reducing agent:

(a) $2Fe(s) + 3Cl_2(g) \longrightarrow 2FeCl_3(s)$ **(b)** $2C_2H_6(g) + 7O_2(g) \longrightarrow 4CO_2(g) + 6H_2O(g)$

(c) $5CO(g) + I_2O_5(s) \longrightarrow I_2(s) + 5CO_2(g)$

Be sure to remember that *transferred electrons are never free because the reducing agent loses electrons and the oxidizing agent gains them **simultaneously.*** In other words, a complete reaction *cannot* be "an oxidation" *or* "a reduction"; it must be an oxidation-reduction. Figure 4.12 summarizes redox terminology.

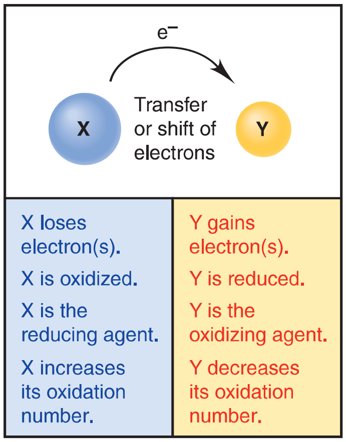


Figure 4.12 A summary of terminology for redox reactions.

Summary of Section 4.5

- When one reactant has a greater attraction for electrons than another, there is a net movement of electrons, and a redox reaction takes place. Electron gain (reduction) and electron loss (oxidation) occur simultaneously.
- Assigning oxidation numbers to all atoms in a reaction is a method for identifying a redox reaction. The species that is oxidized (contains an atom that increases in oxidation number) is the reducing agent; the species that is reduced (contains an atom that decreases in oxidation number) is the oxidizing agent.

4.6 • ELEMENTS IN REDOX REACTIONS

In many redox reactions, such as those in Sample Problem 4.9, *atoms occur as an element on one side of an equation and as part of a compound on the other*. While there are many redox reactions that do *not* involve free elements, we'll focus here on the many others that do. One way to classify these is by comparing the *numbers* of reactants and products. With that approach, we have three types—*combination, decomposition,* and *displacement;* one other type involving elements is *combustion*. In this section, we survey each type with several examples.

Combination Redox Reactions

In a combination redox reaction, two or more reactants, at least one of which is an element, form a compound:

$$\mathrm{X} + \mathrm{Y} \longrightarrow \mathrm{Z}$$

Combining Two Elements Two elements may react to form binary ionic or covalent compounds. Here are some important examples:

1. *Metal and nonmetal form an ionic compound.* A metal, such as aluminum, reacts with a nonmetal, such as oxygen. The change in O.N.s shows that the metal is oxidized, so it is the reducing agent; the nonmental is reduced, so it is the oxidizing agent:

$$4\overset{0}{\mathrm{Al}}(s) + 3\overset{0}{\mathrm{O}}_2(g) \longrightarrow 2\overset{+3}{\mathrm{Al}}_2\overset{-2}{\mathrm{O}}_3(s)$$

Figure 3.6 (p. 87) shows the redox reaction between magnesium metal and oxygen on the macroscopic and atomic scales.

2. *Two nonmetals form a covalent compound.* In one of thousands of examples, ammonia forms from nitrogen and hydrogen in a reaction that occurs in industry on an enormous scale:

$$\overset{0}{\mathrm{N}}_2(g) + 3\overset{0}{\mathrm{H}}_2(g) \longrightarrow 2\overset{-3}{\mathrm{N}}\overset{+1}{\mathrm{H}}_3(g)$$

Combining Compound and Element Many binary covalent compounds react with nonmetals to form larger compounds. Many nonmetal oxides react with additional O_2 to form "higher" oxides (those with more O atoms in each molecule). For example,

$$2\overset{+2}{\mathrm{N}}\overset{-2}{\mathrm{O}}(g) + \overset{0}{\mathrm{O}}_2(g) \longrightarrow 2\overset{+4}{\mathrm{N}}\overset{-2}{\mathrm{O}}_2(g)$$

Similarly, many nonmetal halides combine with additional halogen to form "higher" halides:

$$\overset{+3}{\mathrm{P}}\overset{-1}{\mathrm{Cl}}_3(l) + \overset{0}{\mathrm{Cl}}_2(g) \longrightarrow \overset{+5}{\mathrm{P}}\overset{-1}{\mathrm{Cl}}_5(s)$$

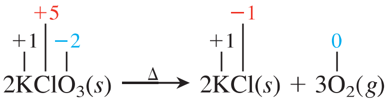
Decomposition Redox Reactions

In a *decomposition redox reaction,* a compound forms two or more products, at least one of which is an element:

$$Z \longrightarrow X + Y$$

In any decomposition reaction, the reactant absorbs enough energy for one or more bonds to break. The energy can take several forms, but the most important are decomposition by heat (thermal) and by electricity (electrolytic). The products are either elements or elements and smaller compounds.

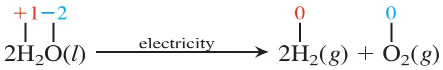
Thermal Decomposition When the energy absorbed is heat, the reaction is called a *thermal decomposition*. (A Greek delta, Δ, above the yield arrow indicates strong heating is required.) Many metal oxides, chlorates, and perchlorates release oxygen when strongly heated. Heating potassium chlorate is a method for forming small amounts of oxygen in the laboratory; the same reaction occurs in some explosives and fireworks:



$$2\overset{+1}{K}\overset{+5}{Cl}\overset{-2}{O}_3(s) \xrightarrow{\Delta} 2\overset{+1}{K}\overset{-1}{Cl}(s) + 3\overset{0}{O}_2(g)$$

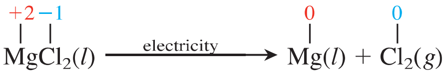
Notice that the lone reactant is the oxidizing *and* the reducing agent.

Electrolytic Decomposition In the process of electrolysis, a compound absorbs electrical energy and decomposes into its elements. In the early 19th century, the observation of the electrolysis of water was crucial for establishing atomic masses:



$$2\overset{+1}{H}_2\overset{-2}{O}(l) \xrightarrow{\text{electricity}} 2\overset{0}{H}_2(g) + \overset{0}{O}_2(g)$$

Many active metals, such as sodium, magnesium, and calcium, are produced industrially by electrolysis of their molten halides:



$$\overset{+2}{Mg}\overset{-1}{Cl}_2(l) \xrightarrow{\text{electricity}} \overset{0}{Mg}(l) + \overset{0}{Cl}_2(g)$$

(We examine the details of electrolysis and its role in the industrial recovery of several elements in Chapter 21.)

Displacement Redox Reactions and Activity Series

In any *displacement reaction,* the number of substances on the two sides of the equation remains the same, but atoms (or ions) exchange places. There are two types:

1. In *double*-displacement (metathesis) reactions, such as precipitation and acid-base reactions (Sections 4.3 and 4.4), atoms (or ions) of two *compounds* exchange places; these reactions are *not* redox processes:

$$AB + CD \longrightarrow AC + BD$$

2. In *single*-displacement reactions, one of the substances is an *element;* therefore, *all single-displacement reactions* ***are*** *redox processes:*

$$X + YZ \longrightarrow XZ + Y$$

In solution, single-displacement reactions occur when an atom of one element displaces the ion of another: if the displacement involves metals, the atom *reduces* the ion; if it involves nonmetals (specifically halogens), the atom *oxidizes* the ion. In two *activity series*—one for metals and one for halogens—the elements are ranked in order of their ability to displace hydrogen (for metals) and one another.

The Activity Series of the Metals Metals are ranked by their ability to displace H_2 from various sources and another metal from solution. In all displacements of H_2, the metal is the reducing agent (O.N. increases), and water or acid is the oxidizing agent (O.N. of H decreases). The activity series of the metals is based on these facts:

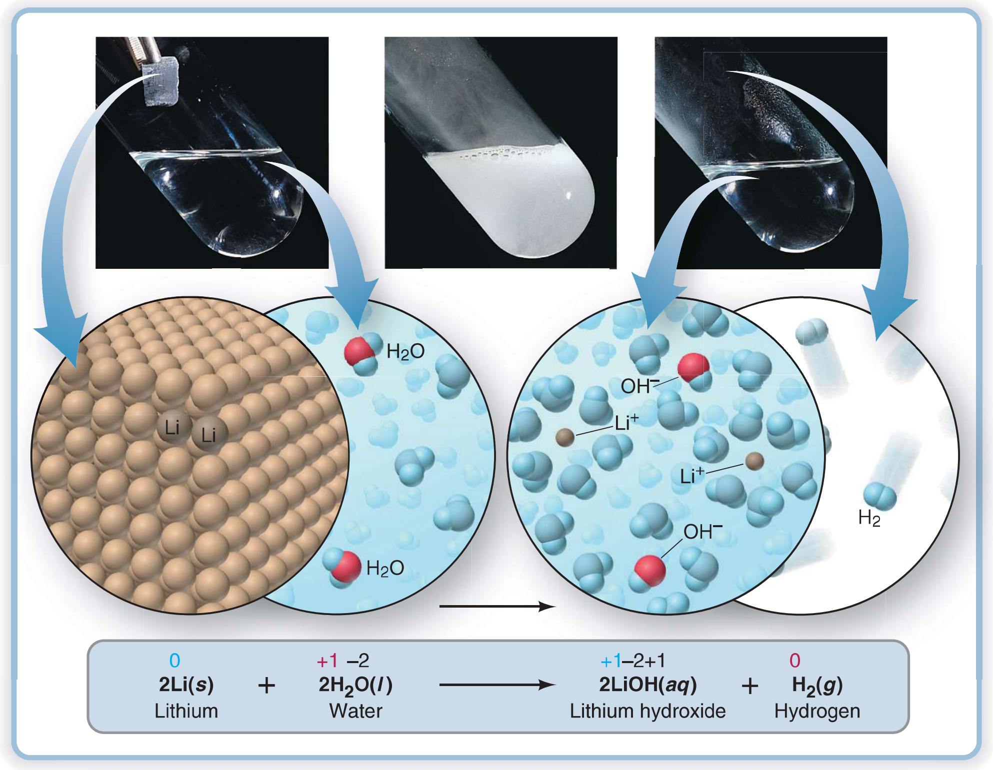


Figure 4.13 The active metal lithium displaces hydrogen from water. Only water molecules involved as products of the reaction are red and blue.

- *The most reactive metals displace H_2 from liquid water*. Group 1A(1) metals and Ca, Sr, and Ba from Group 2A(2) displace H_2 from water (Figure 4.13).
- *Slightly less reactive metals displace H_2 from steam.* Heat supplied by steam is needed for less reactive metals such as Al and Zn to displace H_2:

$$2\overset{0}{\text{Al}}(s) + 6\overset{+1}{\text{H}}_2\overset{-2}{\text{O}}(g) \xrightarrow{\Delta} 2\overset{+3}{\text{Al}}(\overset{-2}{\text{O}}\overset{+1}{\text{H}})_3(s) + 3\overset{0}{\text{H}}_2(g)$$

- *Still less reactive metals displace H_2 from acids.* The higher concentration of H^+ in acid solutions is needed for even less reactive metals such as Ni and Sn to displace H_2 (Figure 4.14). For nickel, the net ionic equation is

$$\overset{0}{\text{Ni}}(s) + 2\overset{+1}{\text{H}}{}^+(aq) \longrightarrow \overset{+2}{\text{Ni}}{}^{2+}(aq) + \overset{0}{\text{H}}_2(g)$$

- *The least reactive metals cannot displace H_2 from any source.* Fortunately, precious metals, such as silver, gold, and platinum, do *not* react with water or acid.
- *An atom of one metal displaces the ion of another.* Comparisons of metal reactivity show, for example, that Zn metal displaces Cu^{2+} ion from aqueous $CuSO_4$:

$$\overset{+2}{\text{Cu}}{}^{2+}(aq) + \overset{+6}{\text{S}}\overset{-2}{\text{O}}{}_4{}^{2-}(aq) + \overset{0}{\text{Zn}}(s) \longrightarrow \overset{0}{\text{Cu}}(s) + \overset{+2}{\text{Zn}}{}^{2+}(aq) + \overset{+6}{\text{S}}\overset{-2}{\text{O}}{}_4{}^{2-}(aq)$$

Figure 4.14 The displacement of H_2 from acid by nickel.

And Figure 4.15 shows that Cu metal displaces silver (Ag^+) ion from solution; therefore, zinc is more reactive than copper, which is more reactive than silver.

Many such reactions form the basis of the **activity series of the metals.** Note these two points from Figure 4.16:

- Elements higher on the list are stronger reducing agents than elements lower down; in other words, any metal can reduce the ions of metals below it.
- From higher to lower, a metal can displace H_2 (reduce H^+) from water, steam, acid, or not at all.

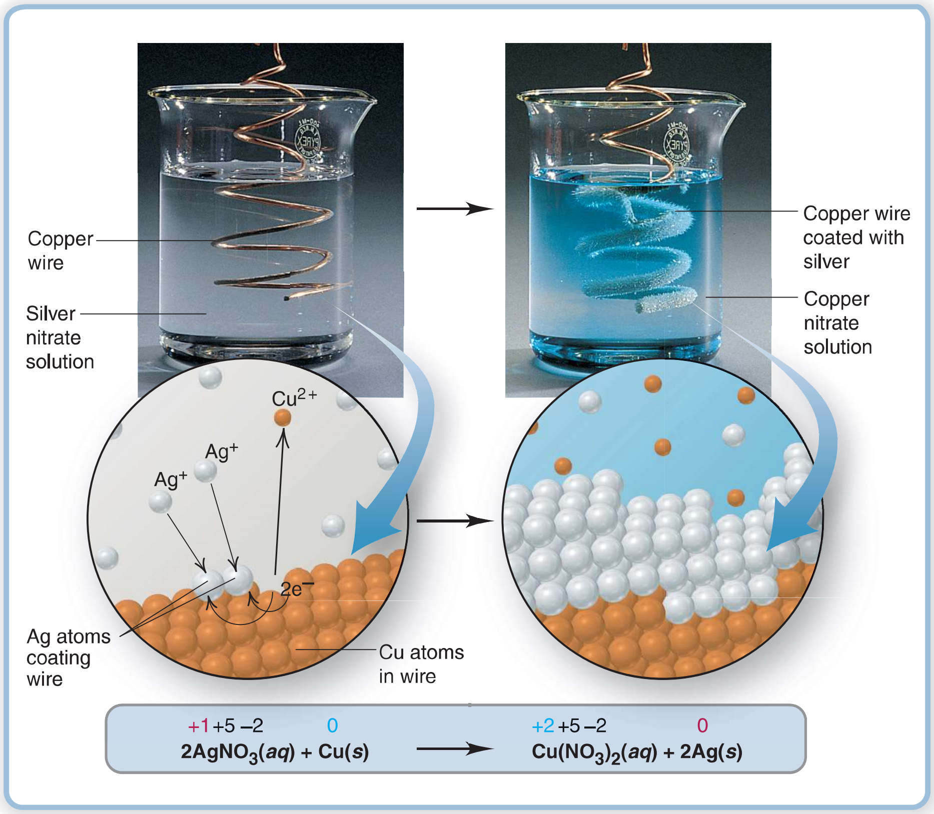


Figure 4.15 A more reactive metal (Cu) displacing the ion of a less reactive metal (Ag^+) from solution.

Consider the metals we've just discussed: Li, Al, and Ni lie above H_2, while Ag lies below it; also, Zn lies above Cu, which lies above Ag. The most reactive metals on the list are in Groups 1A(1) and 2A(2) of the periodic table, and the least reactive are Cu, Ag, and Au in Group 1B(11) and Hg in 2B(12).

The Activity Series of the Halogens Reactivity of the elements decreases down Group 7A(17), so we have

$$F_2 > Cl_2 > Br_2 > I_2$$

A halogen higher in the group is a stronger oxidizing agent than one lower down. Thus, elemental chlorine can oxidize bromide ions *(below)* or iodide ions from solution, and elemental bromine can oxidize iodide ions:

$$2\overset{-1}{Br^-}(aq) + \overset{0}{Cl_2}(aq) \longrightarrow \overset{0}{Br_2}(aq) + 2\overset{-1}{Cl^-}(aq)$$

Combustion Reactions

Combustion is the process of combining with oxygen, most commonly with the release of heat and the production of light, as in a flame. Combustion reactions are not classified by the number of reactants and products, but *all of these reactions are redox processes* because elemental oxygen is a reactant:

$$2CO(g) + O_2(g) \longrightarrow 2CO_2(g)$$

The combustion reactions that we commonly use to produce energy involve coal, petroleum, gasoline, natural gas, or wood as a reactant. These mixtures consist of substances with many C—C and C—H bonds, which break during the reaction, and each C and H atom combines with oxygen to form CO_2 and H_2O. The combustion of butane is typical:

$$2C_4H_{10}(g) + 13O_2(g) \longrightarrow 8CO_2(g) + 10H_2O(g)$$

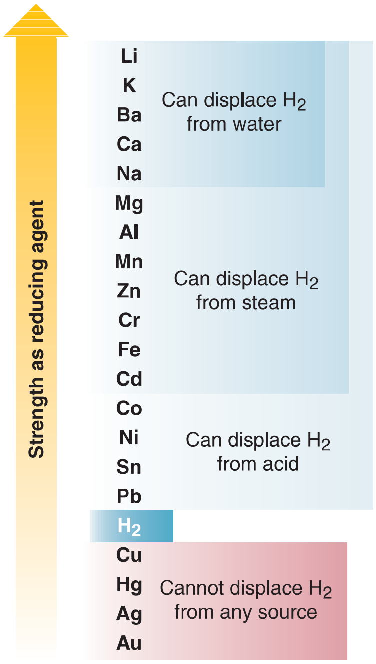


Figure 4.16 The activity series of the metals. The most active metal (strongest reducing agent) is at the top, and the least active metal (weakest reducing agent) is at the bottom.

Biological *respiration* is a multistep combustion process that occurs within our cells when we "burn" foodstuffs, such as glucose, for energy:

$$C_6H_{12}O_6(s) + 6O_2(g) \longrightarrow 6CO_2(g) + 6H_2O(g) + \text{energy}$$

Sample Problem 4.10 Identifying the Type of Redox Reaction

Problem Classify each of the following redox reactions as a combination, decomposition, or displacement reaction, write a balanced molecular equation for each, as well as total and net ionic equations for part (c), and identify the oxidizing and reducing agents:

(a) Magnesium(s) + nitrogen(g) ⟶ magnesium nitride(s)
(b) Hydrogen peroxide(l) ⟶ water + oxygen gas
(c) Aluminum(s) + lead(II) nitrate(aq) ⟶ aluminum nitrate(aq) + lead(s)

Plan To decide on reaction type, recall that combination reactions produce fewer products than reactants, decomposition reactions produce more products, and displacement reactions have the same number of reactants and products. The oxidation number (O.N.) becomes more positive for the reducing agent and less positive for the oxidizing agent.

Solution **(a)** Combination: two substances form one. This reaction occurs, along with formation of magnesium oxide, when magnesium burns in air, which is mostly N_2:

$$3\overset{0}{Mg}(s) + \overset{0}{N_2}(g) \longrightarrow \overset{+2}{Mg_3}\overset{-3}{N_2}(s)$$

Mg is the reducing agent; N_2 is the oxidizing agent.

(b) Decomposition: one substance forms two. Because hydrogen peroxide is very unstable and breaks down from heat, light, or just shaking, this reaction occurs within every bottle of this common household antiseptic:

$$2\overset{+1}{H_2}\overset{\overset{-1}{-1}}{O_2}(l) \longrightarrow 2\overset{+1}{H_2}\overset{-2}{O}(l) + \overset{0}{O_2}(g)$$

H_2O_2 is both the oxidizing *and* the reducing agent. The O.N. of O in peroxides is −1. It is shown in blue *and* red because it both increases to 0 in O_2 and decreases to −2 in H_2O.

(c) Displacement: two substances form two others. As Figure 4.16 shows, Al is more active than Pb and, thus, displaces it from aqueous solution:

$$2\overset{0}{Al}(s) + 3\overset{+2}{Pb}(\overset{+5}{N}\overset{-2}{O_3})_2(aq) \longrightarrow 2\overset{+3}{Al}(\overset{+5}{N}\overset{-2}{O_3})_3(aq) + 3\overset{0}{Pb}(s)$$

Al is the reducing agent; $Pb(NO_3)_2$ is the oxidizing agent.

The total ionic equation is

$$2Al(s) + 3Pb^{2+}(aq) + 6NO_3^-(aq) \longrightarrow 2Al^{3+}(aq) + 6NO_3^-(aq) + 3Pb(s)$$

The net ionic equation is

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

FOLLOW-UP PROBLEM 4.10 Classify each of the following redox reactions as a combination, decomposition, or displacement reaction, write a balanced molecular equation for each, as well as total and net ionic equations for parts (b) and (c), and identify the oxidizing and reducing agents:

(a) $S_8(s) + F_2(g) \longrightarrow SF_4(g)$
(b) $CsI(aq) + Cl_2(aq) \longrightarrow CsCl(aq) + I_2(aq)$
(c) $Ni(NO_3)_2(aq) + Cr(s) \longrightarrow Ni(s) + Cr(NO_3)_3(aq)$

Summary of Section 4.6

- A reaction that has an element as reactant or product is a redox reaction.
- In combination redox reactions, elements combine to form a compound, or a compound and an element combine.

- In decomposition redox reactions, compounds break down by absorption of heat or electricity into elements or into a compound and an element.
- In displacement redox reactions, one element displaces the ion of another from solution.
- Activity series rank elements in order of ability to displace each other. A more reactive metal can displace (reduce) hydrogen ion or the ion of a less reactive metal from solution. A more reactive halogen can displace (oxidize) the ion of a less reactive halogen from solution.
- Combustion releases heat through a redox reaction of a substance with O_2.

CHAPTER REVIEW GUIDE

The following sections provide many aids to help you study this chapter. (Numbers in parentheses refer to pages, unless noted otherwise.)

Learning Objectives

These are concepts and skills to review after studying this chapter.

Related section (§), sample problem (SP), and upcoming end-of-chapter problem (EP) numbers are listed in parentheses.

1. Understand how water dissolves an ionic compound compared to a covalent compound and which solution contains an electrolyte; use a compound's formula to find moles of ions in solution (§4.1) (SPs 4.1, 4.2) (EPs 4.1–4.19)
2. Understand the key events in precipitation and acid-base reactions and use ionic equations to describe them; distinguish between strong and weak acids and bases and calculate an unknown concentration from a titration (§4.2–4.4) (SPs 4.3–4.7) (EPs 4.20–4.47)
3. Understand the key event in the redox process; determine the oxidation number of any element in a compound; identify the oxidizing and reducing agents in a reaction (§4.5) (SPs 4.8, 4.9) (EPs 4.48–4.60)
4. Identify three important types of redox reactions that involve elements: combination, decomposition, displacement (§4.6) (SP 4.10) (EPs 4.61–4.75)

Key Terms

These important terms appear in boldface in the chapter and are defined again in the Glossary.

Section 4.1
polar molecule (116)
solvated (117)
electrolyte (117)
nonelectrolyte (120)

Section 4.2
molecular equation (120)
total ionic equation (120)
spectator ion (120)
net ionic equation (121)

Section 4.3
precipitation reaction (122)
precipitate (122)
metathesis reaction (123)

Section 4.4
acid-base (neutralization) reaction (126)
acid (126)
base (126)
salt (128)
titration (130)
equivalence point (130)
end point (130)

Section 4.5
oxidation-reduction (redox) reaction (132)
oxidation (133)
reduction (133)
oxidizing agent (133)
reducing agent (133)
oxidation number (O.N.) (or oxidation state) (133)

Section 4.6
activity series of the metals (138)

BRIEF SOLUTIONS TO FOLLOW-UP PROBLEMS

Compare your own solutions to these calculation steps and answers.

4.1 The compound is $BaCl_2$.

$$\text{Mass (g) of BaCl}_2 = 9\ \cancel{\text{particles}} \times \frac{0.05\ \cancel{\text{mol particles}}}{1\ \cancel{\text{particle}}} \times \frac{1\ \cancel{\text{mol BaCl}_2}}{3\ \cancel{\text{mol particles}}} \times \frac{208.2\ \text{g BaCl}_2}{1\ \cancel{\text{mol BaCl}_2}} = 31.2\ \text{g BaCl}_2$$

4.2 (a) $KClO_4(s) \xrightarrow{H_2O} K^+(aq) + ClO_4^-(aq)$;
2 mol of K^+ and 2 mol of ClO_4^-

(b) $Mg(C_2H_3O_2)_2(s) \xrightarrow{H_2O} Mg^{2+}(aq) + 2C_2H_3O_2^-(aq)$;
2.49 mol of Mg^{2+} and 4.97 mol of $C_2H_3O_2^-$

(c) $(NH_4)_2CrO_4(s) \xrightarrow{H_2O} 2NH_4^+(aq) + CrO_4^{2-}(aq)$;
6.24 mol of NH_4^+ and 3.12 mol of CrO_4^{2-}

(d) $NaHSO_4(s) \xrightarrow{H_2O} Na^+(aq) + HSO_4^-(aq)$;
0.73 mol of Na^+ and 0.73 mol of HSO_4^-

4.3 (a) $Fe^{3+}(aq) + 3Cl^-(aq) + 3Cs^+(aq) + PO_4^{3-}(aq) \longrightarrow FePO_4(s) + 3Cl^-(aq) + 3Cs^+(aq)$

$Fe^{3+}(aq) + PO_4^{3-}(aq) \longrightarrow FePO_4(s)$

(b) $2Na^+(aq) + 2OH^-(aq) + Cd^{2+}(aq) + 2NO_3^-(aq) \longrightarrow 2Na^+(aq) + 2NO_3^-(aq) + Cd(OH)_2(s)$

$2OH^-(aq) + Cd^{2+}(aq) \longrightarrow Cd(OH)_2(s)$

(c) No reaction occurs

(d) $2Ag^+(aq) + 2NO_3^-(aq) + Ba^{2+}(aq) + 2Cl^-(aq) \longrightarrow 2AgCl(s) + 2NO_3^-(aq) + Ba^{2+}(aq)$

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

BRIEF SOLUTIONS TO FOLLOW-UP PROBLEMS (continued)

4.4 (a) Beaker A contains a solution of $\mathrm{Zn(NO_3)_2}$.
(b) Beaker B contains a solution of $\mathrm{Ba(OH)_2}$.
(c) The precipitate is zinc hydroxide, and the spectator ions are $\mathrm{Ba^{2+}}$ and $\mathrm{NO_3^-}$.

Molecular: $\mathrm{Zn(NO_3)_2}(aq) + \mathrm{Ba(OH)_2}(aq) \longrightarrow \mathrm{Zn(OH)_2}(s) + \mathrm{Ba(NO_3)_2}(aq)$

Total ionic:
$\mathrm{Zn^{2+}}(aq) + \mathrm{2NO_3^-}(aq) + \mathrm{Ba^{2+}}(aq) + \mathrm{2OH^-}(aq) \longrightarrow \mathrm{Zn(OH)_2}(s) + \mathrm{Ba^{2+}}(aq) + \mathrm{2NO_3^-}(aq)$

Net ionic: $\mathrm{Zn^{2+}}(aq) + \mathrm{2OH^-}(aq) \longrightarrow \mathrm{Zn(OH)_2}(s)$

(d) The $\mathrm{OH^-}$ ion is limiting.

Mass (g) of $\mathrm{Zn(OH)_2}$

$$= 6\ \cancel{\mathrm{OH^-\ particles}} \times \frac{0.050\ \cancel{\mathrm{mol\ OH^-\ ions}}}{1\ \cancel{\mathrm{OH^-\ particle}}} \times \frac{1\ \cancel{\mathrm{mol\ Zn(OH)_2}}}{2\ \cancel{\mathrm{mol\ OH^-\ ions}}} \times \frac{99.43\ \mathrm{g\ Zn(OH)_2}}{1\ \cancel{\mathrm{mol\ Zn(OH)_2}}}$$
$$= 15\ \mathrm{g\ Zn(OH)_2}$$

4.5 No. of $\mathrm{OH^-}$ ions $= 451\ \cancel{\mathrm{mL}} \times \dfrac{1\ \cancel{\mathrm{L}}}{10^3\ \cancel{\mathrm{mL}}}$

$$\times \frac{1.20\ \cancel{\mathrm{mol\ KOH}}}{1\ \cancel{\mathrm{L\ soln}}} \times \frac{1\ \cancel{\mathrm{mol\ OH^-}}}{1\ \cancel{\mathrm{mol\ KOH}}} \times \frac{6.022\times10^{23}\ \mathrm{OH^-\ ions}}{1\ \cancel{\mathrm{mol\ OH^-}}}$$
$$= 3.26\times10^{23}\ \mathrm{OH^-}$$

4.6 $\mathrm{Ca(OH)_2}(aq) + \mathrm{2HNO_3}(aq) \longrightarrow \mathrm{Ca(NO_3)_2}(aq) + \mathrm{2H_2O}(l)$
$\mathrm{Ca^{2+}}(aq) + \mathrm{2OH^-}(aq) + \mathrm{2H^+}(aq) + \mathrm{2NO_3^-}(aq) \longrightarrow \mathrm{Ca^{2+}}(aq) + \mathrm{2NO_3^-}(aq) + \mathrm{2H_2O}(l)$
$\mathrm{H^+}(aq) + \mathrm{OH^-}(aq) \longrightarrow \mathrm{H_2O}(l)$

4.7 $\mathrm{Ba(OH)_2}(aq) + \mathrm{2HCl}(aq) \longrightarrow \mathrm{BaCl_2}(aq) + \mathrm{2H_2O}(l)$
Volume (L) of soln

$$= 50.00\ \cancel{\mathrm{mL\ HCl\ soln}} \times \frac{1\ \mathrm{L}}{10^3\ \cancel{\mathrm{mL}}} \times \frac{0.1016\ \cancel{\mathrm{mol\ HCl}}}{1\ \cancel{\mathrm{L\ soln}}}$$
$$\times \frac{1\ \cancel{\mathrm{mol\ Ba(OH)_2}}}{2\ \cancel{\mathrm{mol\ HCl}}} \times \frac{1\ \cancel{\mathrm{L\ soln}}}{0.1292\ \cancel{\mathrm{mol\ Ba(OH)_2}}}$$
$$= 0.01966\ \mathrm{L}$$

4.8 (a) O.N. of Sc = +3; O.N. of O = −2
(b) O.N. of Ga = +3; O.N. of Cl = −1
(c) O.N. of H = +1; O.N. of P = +5; O.N. of O = −2
(d) O.N. of I = +3; O.N. of F = −1

4.9 (a) Fe is the reducing agent; $\mathrm{Cl_2}$ is the oxidizing agent.
(b) $\mathrm{C_2H_6}$ is the reducing agent; $\mathrm{O_2}$ is the oxidizing agent.
(c) CO is the reducing agent; $\mathrm{I_2O_5}$ is the oxidizing agent.

4.10 (a) Combination: $\mathrm{S_8}(s) + \mathrm{16F_2}(g) \longrightarrow \mathrm{8SF_4}(g)$
$\mathrm{S_8}$ is the reducing agent; $\mathrm{F_2}$ is the oxidizing agent.
(b) Displacement:
$\mathrm{2CsI}(aq) + \mathrm{Cl_2}(aq) \longrightarrow \mathrm{2CsCl}(aq) + \mathrm{I_2}(aq)$
$\mathrm{2Cs^+}(aq) + \mathrm{2I^-}(aq) + \mathrm{Cl_2}(aq) \longrightarrow \mathrm{2Cs^+}(aq) + \mathrm{2Cl^-}(aq) + \mathrm{I_2}(aq)$
$\mathrm{2I^-}(aq) + \mathrm{Cl_2}(aq) \longrightarrow \mathrm{2Cl^-}(aq) + \mathrm{I_2}(aq)$
$\mathrm{Cl_2}$ is the oxidizing agent; CsI is the reducing agent.
(c) Displacement:
$\mathrm{3Ni(NO_3)_2}(aq) + \mathrm{2Cr}(s) \longrightarrow \mathrm{3Ni}(s) + \mathrm{2Cr(NO_3)_3}(aq)$
$\mathrm{3Ni^{2+}}(aq) + \mathrm{6NO_3^-}(aq) + \mathrm{2Cr}(s) \longrightarrow \mathrm{3Ni}(s) + \mathrm{2Cr^{3+}}(aq) + \mathrm{6NO_3^-}(aq)$
$\mathrm{3Ni^{2+}}(aq) + \mathrm{2Cr}(s) \longrightarrow \mathrm{3Ni}(s) + \mathrm{2Cr^{3+}}(aq)$
Cr is the reducing agent; $\mathrm{Ni(NO_3)_2}$ is the oxidizing agent.

PROBLEMS

Problems with **colored** numbers are answered in Appendix E. Sections match the text and provide the numbers of relevant sample problems. Bracketed problems are grouped in pairs (indicated by a short rule) that cover the same concept. Comprehensive Problems are based on material from any section or previous chapter.

The Role of Water as a Solvent

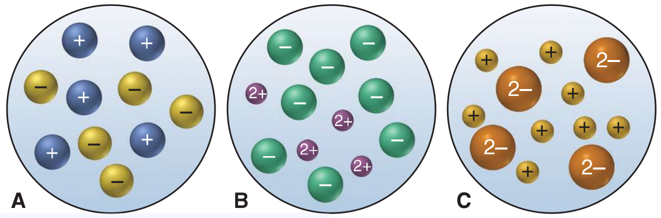
(Sample Problems 4.1 and 4.2)

4.1 What two factors cause water to be polar?

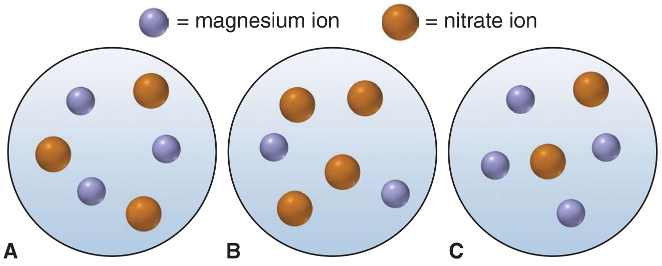
4.2 What must be present in an aqueous solution for it to conduct an electric current? What general classes of compounds form solutions that conduct?

4.3 What occurs on the molecular level when an ionic compound dissolves in water?

4.4 Which of the following scenes best represents how the ions occur in an aqueous solution of: (a) $\mathrm{CaCl_2}$; (b) $\mathrm{Li_2SO_4}$; (c) $\mathrm{NH_4Br}$?



4.5 Which of the following scenes best represents a volume from a solution of magnesium nitrate?



4.6 Why are some ionic compounds soluble in water and others are not?

4.7 Some covalent compounds dissociate into ions in water. What atom do these compounds have in their structures? What type of solution do they form? Name three examples of such a solution.

4.8 Is each of the following very soluble in water? Explain.
(a) Benzene, $\mathrm{C_6H_6}$ (b) Sodium hydroxide
(c) Ethanol, $\mathrm{CH_3CH_2OH}$ (d) Potassium acetate

4.9 Is each of the following very soluble in water? Explain.
(a) Lithium nitrate (b) Glycine, $\mathrm{H_2NCH_2COOH}$
(c) Pentane (d) Ethylene glycol, $\mathrm{HOCH_2CH_2OH}$

4.10 Does an aqueous solution of each of the following conduct an electric current? Explain.
(a) Cesium bromide (b) Hydrogen iodide

4.11 Does an aqueous solution of each of the following conduct an electric current? Explain.
(a) Potassium sulfate (b) Sucrose, $C_{12}H_{22}O_{11}$

4.12 How many total moles of ions are released when each of the following dissolves in water?
(a) 0.75 mol of K_3PO_4 (b) 6.88×10^{-3} g of $NiBr_2\cdot3H_2O$
(c) 2.23×10^{22} formula units of $FeCl_3$

4.13 How many total moles of ions are released when each of the following dissolves in water?
(a) 0.734 mol of Na_2HPO_4 (b) 3.86 g of $CuSO_4\cdot5H_2O$
(c) 8.66×10^{20} formula units of $NiCl_2$

4.14 How many moles and how many ions of each type are present in each of the following?
(a) 130. mL of 0.45 *M* aluminum chloride
(b) 9.80 mL of a solution containing 2.59 g lithium sulfate/L
(c) 245 mL of a solution containing 3.68×10^{22} formula units of potassium bromide per liter

4.15 How many moles and how many ions of each type are present in each of the following?
(a) 88 mL of 1.75 *M* magnesium chloride
(b) 321 mL of a solution containing 0.22 g aluminum sulfate/L
(c) 1.65 L of a solution containing 8.83×10^{21} formula units of cesium nitrate per liter

4.16 How many moles of H^+ ions are present in the following aqueous solutions?
(a) 1.40 L of 0.25 *M* perchloric acid
(b) 6.8 mL of 0.92 *M* nitric acid
(c) 2.6 L of 0.085 *M* hydrochloric acid

4.17 How many moles of H^+ ions are present in the following aqueous solutions?
(a) 1.4 mL of 0.75 *M* hydrobromic acid
(b) 2.47 mL of 1.98 *M* hydriodic acid
(c) 395 mL of 0.270 *M* nitric acid

4.18 To study a marine organism, a biologist prepares a 1.00-kg sample to simulate the ion concentrations in seawater. She mixes 26.5 g of NaCl, 2.40 g of $MgCl_2$, 3.35 g of $MgSO_4$, 1.20 g of $CaCl_2$, 1.05 g of KCl, 0.315 g of $NaHCO_3$, and 0.098 g of NaBr in distilled water. (a) If the density of the solution is 1.025 g/cm^3, what is the molarity of each ion? (b) What is the total molarity of alkali metal ions? (c) What is the total molarity of alkaline earth metal ions? (d) What is the total molarity of anions?

4.19 Water "softeners" remove metal ions such as Ca^{2+} and Fe^{3+} by replacing them with enough Na^+ ions to maintain the same number of positive charges in the solution. If 1.0×10^3 L of "hard" water is 0.015 *M* Ca^{2+} and 0.0010 *M* Fe^{3+}, how many moles of Na^+ are needed to replace these ions?

Writing Equations for Aqueous Ionic Reactions

4.20 Write two sets of equations (both molecular and total ionic) with different reactants that have the same net ionic equation as the following equation:

$$Ba(NO_3)_2(aq) + Na_2CO_3(aq) \longrightarrow BaCO_3(s) + 2NaNO_3(aq)$$

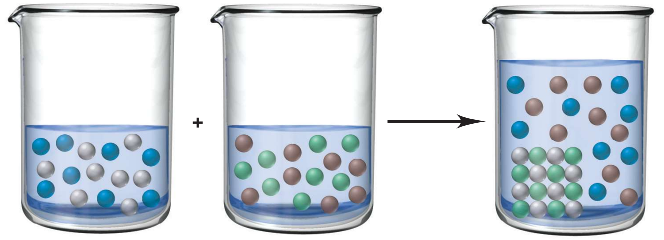
Precipitation Reactions

(Sample Problems 4.3 and 4.4)

4.21 Why do some pairs of ions precipitate and others do not?

4.22 Use Table 4.1 to determine which of the following combinations leads to a precipitation reaction. How can you identify the spectator ions in the reaction?
(a) Calcium nitrate(aq) + sodium chloride(aq) $\longrightarrow$
(b) Potassium chloride(aq) + lead(II) nitrate(aq) $\longrightarrow$

4.23 The beakers represent the aqueous reaction of $AgNO_3$ and NaCl. Silver ions are gray. What colors are used to represent NO_3^-, Na^+, and Cl^-? Write molecular, total ionic, and net ionic equations for the reaction.



4.24 Complete the following precipitation reactions with balanced molecular, total ionic, and net ionic equations:
(a) $Hg_2(NO_3)_2(aq) + KI(aq) \longrightarrow$
(b) $FeSO_4(aq) + Sr(OH)_2(aq) \longrightarrow$

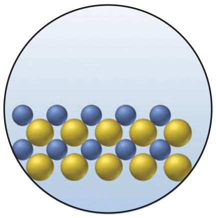
4.25 Complete the following precipitation reactions with balanced molecular, total ionic, and net ionic equations:
(a) $CaCl_2(aq) + Cs_3PO_4(aq) \longrightarrow$
(b) $Na_2S(aq) + ZnSO_4(aq) \longrightarrow$

4.26 When each of the following pairs of aqueous solutions is mixed, does a precipitation reaction occur? If so, write balanced molecular, total ionic, and net ionic equations:
(a) Sodium nitrate + copper(II) sulfate
(b) Ammonium bromide + silver nitrate

4.27 When each of the following pairs of aqueous solutions is mixed, does a precipitation reaction occur? If so, write balanced molecular, total ionic, and net ionic equations:
(a) Potassium carbonate + barium hydroxide
(b) Aluminum nitrate + sodium phosphate

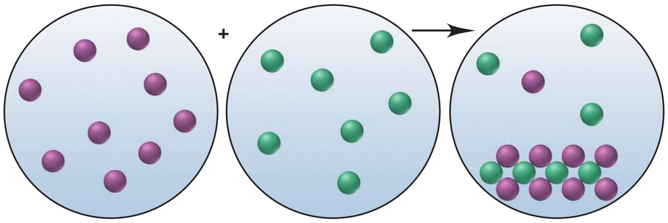
4.28 If 38.5 mL of lead(II) nitrate solution reacts completely with excess sodium iodide solution to yield 0.628 g of precipitate, what is the molarity of lead(II) ion in the original solution?

4.29 If 25.0 mL of silver nitrate solution reacts with excess potassium chloride solution to yield 0.842 g of precipitate, what is the molarity of silver ion in the original solution?



4.30 With ions shown as spheres and solvent molecules omitted for clarity, the circle *(right)* illustrates the solid formed when a solution containing K^+, Mg^{2+}, Ag^+, or Pb^{2+} *(blue)* is mixed with one containing ClO_4^-, NO_3^-, or SO_4^{2-} *(yellow)*. (a) Identify the solid. (b) Write a balanced net ionic equation for the reaction. (c) If each sphere represents 5.0×10^{-4} mol of ion, what mass of product forms?

4.31 The precipitation reaction between 25.0 mL of a solution containing a cation *(purple)* and 35.0 mL of a solution containing an anion *(green)* is depicted below (with ions shown as spheres and solvent molecules omitted for clarity).



(a) Given the following choices of reactants, write balanced total ionic and net ionic equations that best represent the reaction:
(1) $KNO_3(aq) + CuCl_2(aq) \longrightarrow$
(2) $NaClO_4(aq) + CaCl_2(aq) \longrightarrow$
(3) $Li_2SO_4(aq) + AgNO_3(aq) \longrightarrow$
(4) $NH_4Br(aq) + Pb(CH_3COO)_2(aq) \longrightarrow$
(b) If each sphere represents 2.5×10^{-3} mol of ion, find the total number of ions present.
(c) What is the mass of solid formed?

4.32 The mass percent of Cl^- in a seawater sample is determined by titrating 25.00 mL of seawater with $AgNO_3$ solution, causing a precipitation reaction. An indicator is used to detect the end point, which occurs when free Ag^+ ion is present in solution after all the Cl^- has reacted. If 53.63 mL of 0.2970 *M* $AgNO_3$ is required to reach the end point, what is the mass percent of Cl^- in the seawater (*d* of seawater = 1.024 g/mL)?

4.33 Aluminum sulfate, known as *cake alum,* has a wide range of uses, from dyeing leather and cloth to purifying sewage. In aqueous solution, it reacts with base to form a white precipitate. (a) Write balanced total and net ionic equations for its reaction with aqueous NaOH. (b) What mass of precipitate forms when 185.5 mL of 0.533 *M* NaOH is added to 627 mL of a solution that contains 15.8 g of aluminum sulfate per liter?

Acid-Base Reactions

(Sample Problems 4.5 to 4.7)

4.34 Is the total ionic equation the same as the net ionic equation when $Sr(OH)_2(aq)$ and $H_2SO_4(aq)$ react? Explain.

4.35 (a) Name three common strong acids. (b) Name three common strong bases. (c) What is a characteristic behavior of a strong acid or a strong base?

4.36 (a) Name three common weak acids. (b) Name one common weak base. (c) What is the major difference between a weak acid and a strong acid or between a weak base and a strong base, and what experiment would you perform to observe it?

4.37 (a) The net ionic equation for the aqueous neutralization reaction between acetic acid and sodium hydroxide is different from that for the reaction between hydrochloric acid and sodium hydroxide. Explain by writing balanced net ionic equations. (b) For a solution of acetic acid in water, list the major species in decreasing order of concentration.

4.38 Complete the following acid-base reactions with balanced molecular, total ionic, and net ionic equations:
(a) Potassium hydroxide(aq) + hydrobromic acid(aq) $\longrightarrow$
(b) Ammonia(aq) + hydrochloric acid(aq) $\longrightarrow$

4.39 Complete the following acid-base reactions with balanced molecular, total ionic, and net ionic equations:
(a) Cesium hydroxide(aq) + nitric acid(aq) $\longrightarrow$
(b) Calcium hydroxide(aq) + acetic acid(aq) $\longrightarrow$

4.40 Limestone (calcium carbonate) is insoluble in water but dissolves when a hydrochloric acid solution is added. Write balanced total ionic and net ionic equations, showing hydrochloric acid as it actually exists in water and the reaction as a proton-transfer process.

4.41 Zinc hydroxide is insoluble in water but dissolves when a nitric acid solution is added. Why? Write balanced total ionic and net ionic equations, showing nitric acid as it actually exists in water and the reaction as a proton-transfer process.

4.42 If 25.98 mL of 0.1180 *M* KOH solution reacts with 52.50 mL of CH_3COOH solution, what is the molarity of the acid solution?

4.43 If 26.25 mL of 0.1850 *M* NaOH solution reacts with 25.00 mL of H_2SO_4, what is the molarity of the acid solution?

4.44 An auto mechanic spills 88 mL of 2.6 *M* H_2SO_4 solution from an auto battery. How many milliliters of 1.6 *M* $NaHCO_3$ must be poured on the spill to react completely with the sulfuric acid?

4.45 One of the first steps in the enrichment of uranium for use in nuclear power plants involves a displacement reaction between UO_2 and aqueous HF:

$$UO_2(s) + HF(aq) \longrightarrow UF_4(s) + H_2O(l) \text{ [unbalanced]}$$

How many liters of 2.40 *M* HF will react with 2.15 kg of UO_2?

4.46 An unknown amount of acid can often be determined by adding an excess of base and then "back-titrating" the excess. A 0.3471-g sample of a mixture of oxalic acid, which has two ionizable protons, and benzoic acid, which has one, is treated with 100.0 mL of 0.1000 *M* NaOH. The excess NaOH is titrated with 20.00 mL of 0.2000 *M* HCl. Find the mass % of benzoic acid.

4.47 A mixture of bases can sometimes be the active ingredient in antacid tablets. If 0.4826 g of a mixture of $Al(OH)_3$ and $Mg(OH)_2$ is neutralized with 17.30 mL of 1.000 *M* HNO_3, what is the mass % of $Al(OH)_3$ in the mixture?

Oxidation-Reduction (Redox) Reactions

(Sample Problems 4.8 to 4.9)

4.48 Why must every redox reaction involve an oxidizing agent and a reducing agent?

4.49 In which of the following equations does sulfuric acid act as an oxidizing agent? In which does it act as an acid? Explain.
(a) $4H^+(aq) + SO_4^{2-}(aq) + 2NaI(s) \longrightarrow$
$2Na^+(aq) + I_2(s) + SO_2(g) + 2H_2O(l)$
(b) $BaF_2(s) + 2H^+(aq) + SO_4^{2-}(aq) \longrightarrow 2HF(aq) + BaSO_4(s)$

4.50 Give the oxidation number of nitrogen in the following:
(a) NH_2OH (b) N_2F_4 (c) NH_4^+ (d) HNO_2

4.51 Give the oxidation number of sulfur in the following:
(a) $SOCl_2$ (b) H_2S_2 (c) H_2SO_3 (d) Na_2S

4.52 Give the oxidation number of arsenic in the following:
(a) AsH_3 (b) $H_2AsO_4^-$ (c) $AsCl_3$

4.53 Give the oxidation number of phosphorus in the following:
(a) $H_2P_2O_7^{2-}$ (b) PH_4^+ (c) PCl_5

4.54 Give the oxidation number of manganese in the following:
(a) MnO_4^{2-} (b) Mn_2O_3 (c) $KMnO_4$

4.55 Give the oxidation number of chromium in the following:
(a) CrO_3 (b) $Cr_2O_7^{2-}$ (c) $Cr_2(SO_4)_3$

4.56 Identify the oxidizing and reducing agents in the following:
(a) $5H_2C_2O_4(aq) + 2MnO_4^-(aq) + 6H^+(aq) \longrightarrow$
$2Mn^{2+}(aq) + 10CO_2(g) + 8H_2O(l)$

(b) $3Cu(s) + 8H^+(aq) + 2NO_3^-(aq) \longrightarrow 3Cu^{2+}(aq) + 2NO(g) + 4H_2O(l)$

4.57 Identify the oxidizing and reducing agents in the following:

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

(b) $2H^+(aq) + H_2O_2(aq) + 2Fe^{2+}(aq) \longrightarrow 2Fe^{3+}(aq) + 2H_2O(l)$

4.58 Identify the oxidizing and reducing agents in the following:

(a) $8H^+(aq) + 6Cl^-(aq) + Sn(s) + 4NO_3^-(aq) \longrightarrow SnCl_6^{2-}(aq) + 4NO_2(g) + 4H_2O(l)$

(b) $2MnO_4^-(aq) + 10Cl^-(aq) + 16H^+(aq) \longrightarrow 5Cl_2(g) + 2Mn^{2+}(aq) + 8H_2O(l)$

4.59 Identify the oxidizing and reducing agents in the following:

(a) $8H^+(aq) + Cr_2O_7^{2-}(aq) + 3SO_3^{2-}(aq) \longrightarrow 2Cr^{3+}(aq) + 3SO_4^{2-}(aq) + 4H_2O(l)$

(b) $NO_3^-(aq) + 4Zn(s) + 7OH^-(aq) + 6H_2O(l) \longrightarrow 4Zn(OH)_4^{2-}(aq) + NH_3(aq)$

4.60 A person's blood alcohol (C_2H_5OH) level can be determined by titrating a sample of blood plasma with a potassium dichromate solution. The balanced equation is

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

If 35.46 mL of 0.05961 M $Cr_2O_7^{2-}$ is required to titrate 28.00 g of plasma, what is the mass percent of alcohol in the blood?

Elements in Redox Reactions

(Sample Problem 4.10)

4.61 Which type of redox reaction leads to each of the following?

(a) An increase in the number of substances

(b) A decrease in the number of substances

(c) No change in the number of substances

4.62 Why do decomposition redox reactions typically have compounds as reactants, whereas combination redox and displacement redox reactions have one or more elements?

4.63 Which of the types of reactions discussed in Section 4.6 commonly produce more than one compound?

4.64 Balance each of the following redox reactions and classify it as a combination, decomposition, or displacement reaction:

(a) $Sb(s) + Cl_2(g) \longrightarrow SbCl_3(s)$

(b) $AsH_3(g) \longrightarrow As(s) + H_2(g)$

(c) $Zn(s) + Fe(NO_3)_2(aq) \longrightarrow Zn(NO_3)_2(aq) + Fe(s)$

4.65 Balance each of the following redox reactions and classify it as a combination, decomposition, or displacement reaction:

(a) $Mg(s) + H_2O(g) \longrightarrow Mg(OH)_2(s) + H_2(g)$

(b) $Cr(NO_3)_3(aq) + Al(s) \longrightarrow Al(NO_3)_3(aq) + Cr(s)$

(c) $PF_3(g) + F_2(g) \longrightarrow PF_5(g)$

4.66 Predict the product(s) and write a balanced equation for each of the following redox reactions:

(a) $N_2(g) + H_2(g) \longrightarrow$

(b) $NaClO_3(s) \xrightarrow{\Delta}$

(c) $Ba(s) + H_2O(l) \longrightarrow$

4.67 Predict the product(s) and write a balanced equation for each of the following redox reactions:

(a) $Fe(s) + HClO_4(aq) \longrightarrow$

(b) $S_8(s) + O_2(g) \longrightarrow$

(c) $BaCl_2(l) \xrightarrow{\text{electricity}}$

4.68 Predict the product(s) and write a balanced equation for each of the following redox reactions:

(a) Cesium + iodine $\longrightarrow$

(b) Aluminum + aqueous manganese(II) sulfate $\longrightarrow$

(c) Sulfur dioxide + oxygen $\longrightarrow$

(d) Butane and oxygen $\longrightarrow$

(e) Write a balanced net ionic equation for (b).

4.69 Predict the product(s) and write a balanced equation for each of the following redox reactions:

(a) Pentane (C_5H_{12}) + oxygen $\longrightarrow$

(b) Phosphorus trichloride + chlorine $\longrightarrow$

(c) Zinc + hydrobromic acid $\longrightarrow$

(d) Aqueous potassium iodide + bromine $\longrightarrow$

(e) Write a balanced net ionic equation for (d).

4.70 How many grams of O_2 can be prepared from the thermal decomposition of 4.27 kg of HgO? Name and calculate the mass (in kg) of the other product.

4.71 How many grams of chlorine gas can be produced from the electrolytic decomposition of 874 g of calcium chloride? Name and calculate the mass (in g) of the other product.

4.72 In a combination reaction, 1.62 g of lithium is mixed with 6.50 g of oxygen.

(a) Which reactant is present in excess?

(b) How many moles of product are formed?

(c) After reaction, how many grams of each reactant and product are present?

4.73 In a combination reaction, 2.22 g of magnesium is heated with 3.75 g of nitrogen.

(a) Which reactant is present in excess?

(b) How many moles of product are formed?

(c) After reaction, how many grams of each reactant and product are present?

4.74 A mixture of $CaCO_3$ and CaO weighing 0.693 g was heated to produce gaseous CO_2. After heating, the remaining solid weighed 0.508 g. Assuming all the $CaCO_3$ broke down to CaO and CO_2, calculate the mass percent of $CaCO_3$ in the original mixture.

4.75 Before arc welding was developed, a displacement reaction involving aluminum and iron(III) oxide was commonly used to produce molten iron (the thermite process). This reaction was used, for example, to connect sections of iron rails for train tracks. Calculate the mass of molten iron produced when 1.50 kg of aluminum reacts with 25.0 mol of iron(III) oxide.

Comprehensive Problems

4.76 Nutritional biochemists have known for decades that acidic foods cooked in cast-iron cookware can supply significant amounts of dietary iron (ferrous ion). (a) Write a balanced net ionic equation, with oxidation numbers, that supports this fact. (b) Measurements show an increase from 3.3 mg of iron to 49 mg of iron per $\frac{1}{2}$-cup (125-g) serving during the slow preparation of tomato sauce in a cast-iron pot. How many ferrous ions are present in a 26-oz (737-g) jar of the tomato sauce?

4.77 The brewing industry uses yeast to convert glucose to ethanol. The baking industry uses the carbon dioxide produced in the same reaction to make bread rise:

$$C_6H_{12}O_6(s) \xrightarrow{\text{yeast}} 2C_2H_5OH(l) + 2CO_2(g)$$

How many grams of ethanol can be produced from 100. g of glucose? What volume of CO_2 is produced? (Assume 1 mol of gas occupies 22.4 L at the conditions used.)

4.78 A chemical engineer determines the mass percent of iron in an ore sample by converting the Fe to Fe^{2+} in acid and then reacting the Fe^{2+} with MnO_4^-. A 1.1081-g sample was dissolved in acid, and it reacted completely with 39.32 mL of 0.03190 *M* $KMnO_4$. The balanced equation is

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

Calculate the mass percent of iron in the ore.

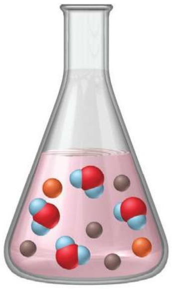
4.79 You are given solutions of HCl and NaOH and must determine their concentrations. You use 27.5 mL of NaOH to titrate 100. mL of HCl and 18.4 mL of NaOH to titrate 50.0 mL of 0.0782 *M* H_2SO_4. Find the unknown concentrations.

4.80 The flask *(right)* represents the products of the titration of 25 mL of sulfuric acid with 25 mL of sodium hydroxide.

(a) Write balanced molecular, total ionic, and net ionic equations for the reaction.

(b) If each orange sphere represents 0.010 mol of sulfate ion, how many moles of acid and of base reacted?

(c) What are the molarities of the acid and the base?



4.81 On a lab exam, you have to find the concentrations of the monoprotic (one proton per molecule) acids HA and HB. You are given 43.5 mL of HA solution in one flask. A second flask contains 37.2 mL of HA, and you add enough HB solution to it to reach a final volume of 50.0 mL. You titrate the first HA solution with 87.3 mL of 0.0906 *M* NaOH and the mixture of HA and HB in the second flask with 96.4 mL of the NaOH solution. Calculate the molarity of the HA and HB solutions.

4.82 Nitric acid, a major industrial and laboratory acid, is produced commercially by the multistep Ostwald process, which begins with the oxidation of ammonia:

Step 1. $4NH_3(g) + 5O_2(g) \longrightarrow 4NO(g) + 6H_2O(l)$

Step 2. $2NO(g) + O_2(g) \longrightarrow 2NO_2(g)$

Step 3. $3NO_2(g) + H_2O(l) \longrightarrow 2HNO_3(l) + NO(g)$

(a) What are the oxidizing and reducing agents in each step?

(b) Assuming 100% yield in each step, what mass (in kg) of ammonia must be used to produce 3.0×10^4 kg of HNO_3?

4.83 For the following aqueous reactions, complete and balance the molecular equation and write a net ionic equation:

(a) Manganese(II) sulfide + hydrobromic acid
(b) Potassium carbonate + strontium nitrate
(c) Potassium nitrite + hydrochloric acid
(d) Calcium hydroxide + nitric acid
(e) Barium acetate + iron(II) sulfate
(f) Barium hydroxide + hydrocyanic acid
(g) Copper(II) nitrate + hydrosulfuric acid
(h) Magnesium hydroxide + chloric acid

4.84 Various data can be used to find the composition of an alloy (a metallic mixture). Show that calculating the mass % of Mg in a magnesium-aluminum alloy (d = 2.40 g/cm^3) using each of the following pieces of data gives the same answer (within rounding): (a) a sample of the alloy has a mass of 0.263 g (d of Mg = 1.74 g/cm^3; d of Al = 2.70 g/cm^3); (b) an identical sample reacting with excess aqueous HCl forms 1.38×10^{-2} mol of H_2; (c) an identical sample reacting with excess O_2 forms 0.483 g of oxide.

4.85 Sodium peroxide (Na_2O_2) is often used in self-contained breathing devices, such as those used in fire emergencies, because it reacts with exhaled CO_2 to form Na_2CO_3 and O_2. How many liters of respired air can react with 80.0 g of Na_2O_2 if each liter of respired air contains 0.0720 g of CO_2?

4.86 Magnesium is used in airplane bodies and other lightweight alloys. The metal is obtained from seawater in a process that includes precipitation, neutralization, evaporation, and electrolysis. How many kilograms of magnesium can be obtained from 1.00 km^3 of seawater if the initial Mg^{2+} concentration is 0.13% by mass (d of seawater = 1.04 g/mL)?

4.87 Physicians who specialize in sports medicine routinely treat athletes and dancers. Ethyl chloride, a local anesthetic commonly used for simple injuries, is the product of the combination of ethylene with hydrogen chloride:

$$C_2H_4(g) + HCl(g) \longrightarrow C_2H_5Cl(g)$$

If 0.100 kg of C_2H_4 and 0.100 kg of HCl react: (a) How many molecules of gas (reactants plus products) are present when the reaction is complete? (b) How many moles of gas are present when half the product forms?

4.88 Carbon dioxide is removed from the atmosphere of space capsules by reaction with a solid metal hydroxide. The products are water and the metal carbonate.

(a) Calculate the mass of CO_2 that can be removed by reaction with 3.50 kg of lithium hydroxide.

(b) How many grams of CO_2 can be removed by 1.00 g of each of the following: lithium hydroxide, magnesium hydroxide, and aluminum hydroxide?

4.89 Calcium dihydrogen phosphate, $Ca(H_2PO_4)_2$, and sodium hydrogen carbonate, $NaHCO_3$, are ingredients of baking powder that react to produce CO_2, which causes dough or batter to rise:

$$Ca(H_2PO_4)_2(s) + NaHCO_3(s) \longrightarrow CO_2(g) + H_2O(g) + CaHPO_4(s) + Na_2HPO_4(s)$$

[unbalanced]

If the baking powder contains 31% $NaHCO_3$ and 35% $Ca(H_2PO_4)_2$ by mass:

(a) How many moles of CO_2 are produced from 1.00 g of baking powder?

(b) If 1 mol of CO_2 occupies 37.0 L at 350°F (a typical baking temperature), what volume of CO_2 is produced from 1.00 g of baking powder?

4.90 In a titration of HNO_3, you add a few drops of phenolphthalein indicator to 50.00 mL of acid in a flask. You quickly add 20.00 mL of 0.0502 *M* NaOH but overshoot the end point, and the solution turns deep pink. Instead of starting over, you add 30.00 mL of the acid, and the solution turns colorless. Then, it takes 3.22 mL of the NaOH to reach the end point.

(a) What is the concentration of the HNO_3 solution?

(b) How many moles of NaOH were in excess after the first addition?

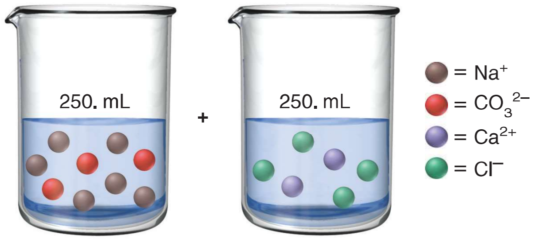
4.91 The active compound in Pepto-Bismol contains C, H, O, and Bi.

(a) When 0.22105 g of it was burned in excess O_2, 0.1422 g of bismuth(III) oxide, 0.1880 g of carbon dioxide, and 0.02750 g of water were formed. What is the empirical formula of this compound?

(b) Given a molar mass of 1086 g/mol, determine the molecular formula.

(c) Complete and balance the acid-base reaction between bismuth(III) hydroxide and salicylic acid ($HC_7H_5O_3$), which is used to form this compound.
(d) A dose of Pepto-Bismol contains 0.600 mg of active ingredient. If the yield of the reaction in part (c) is 88.0%, what mass (in mg) of bismuth(III) hydroxide is required to prepare one dose?

4.92 Two aqueous solutions contain the ions indicated below.



(a) Write balanced molecular, total ionic, and net ionic equations for the reaction that occurs when the solutions are mixed.
(b) If each sphere represents 0.050 mol of ion, what mass (in g) of precipitate forms, assuming 100% yield?
(c) What is the concentration of each ion in solution after reaction?

4.93 In 1997 and 2009, at United Nations conferences on climate change, many nations agreed to expand their research efforts to develop renewable sources of carbon-based fuels. For more than a quarter century, Brazil has been engaged in a program to replace gasoline with ethanol derived from the root crop manioc (cassava).
(a) Write separate balanced equations for the complete combustion of ethanol (C_2H_5OH) and of gasoline (represented by the formula C_8H_{18}).
(b) What mass of oxygen is required to burn completely 1.00 L of a mixture that is 90.0% gasoline ($d = 0.742$ g/mL) and 10.0% ethanol ($d = 0.789$ g/mL) by volume?
(c) If 1.00 mol of O_2 occupies 22.4 L, what volume of O_2 is needed to burn 1.00 L of the mixture?
(d) Air is 20.9% O_2 by volume. What volume of air is needed to burn 1.00 L of the mixture?

4.94 In a car engine, gasoline (represented by C_8H_{18}) does not burn completely, and some CO, a toxic pollutant, forms along with CO_2 and H_2O. If 5.0% of the gasoline forms CO:
(a) What is the ratio of CO_2 to CO molecules in the exhaust?
(b) What is the mass ratio of CO_2 to CO?
(c) What percentage of the gasoline must form CO for the mass ratio of CO_2 to CO to be exactly 1/1?

4.95 The amount of ascorbic acid (vitamin C; $C_6H_8O_6$) in tablets is determined by reaction with bromine and then titration of the hydrobromic acid with standard base:

$$C_6H_8O_6(aq) + Br_2(aq) \longrightarrow C_6H_6O_6(aq) + 2HBr(aq)$$
$$HBr(aq) + NaOH(aq) \longrightarrow NaBr(aq) + H_2O(l)$$

A certain tablet is advertised as containing 500 mg of vitamin C. One tablet was dissolved in water and reacted with Br_2. The solution was then titrated with 43.20 mL of 0.1350 *M* NaOH. Did the tablet contain the advertised quantity of vitamin C?

4.96 In the process of *pickling,* rust is removed from newly produced steel by washing the steel in hydrochloric acid:

(1) $6HCl(aq) + Fe_2O_3(s) \longrightarrow 2FeCl_3(aq) + 3H_2O(l)$

During the process, some iron is lost as well:

(2) $2HCl(aq) + Fe(s) \longrightarrow FeCl_2(aq) + H_2(g)$

(a) Which reaction, if either, is a redox process? (b) If reaction 2 did not occur and all the HCl were used, how many grams of Fe_2O_3 could be removed and $FeCl_3$ produced in a 2.50×10^3-L bath of 3.00 *M* HCl? (c) If reaction 1 did not occur and all the HCl were used, how many grams of Fe could be lost and $FeCl_2$ produced in a 2.50×10^3-L bath of 3.00 *M* HCl? (d) If 0.280 g of Fe is lost per gram of Fe_2O_3 removed, what is the mass ratio of $FeCl_2$ to $FeCl_3$?

4.97 At liftoff, a space shuttle uses a solid mixture of ammonium perchlorate and aluminum powder to obtain great thrust from the volume change of solid to gas. In the presence of a catalyst, the mixture forms solid aluminum oxide and aluminum trichloride and gaseous water and nitrogen monoxide.
(a) Write a balanced equation for the reaction, and identify the reducing and oxidizing agents.
(b) How many total moles of gas (water vapor and nitrogen monoxide) are produced when 50.0 kg of ammonium perchlorate reacts with a stoichiometric amount of Al?
(c) What is the change in volume from this reaction? (*d* of $NH_4ClO_4 = 1.95$ g/cc, Al = 2.70 g/cc, $Al_2O_3 = 3.97$ g/cc, and $AlCl_3 = 2.44$ g/cc; assume 1 mol of gas occupies 22.4 L.)