GENERAL CHEMISTRY

Principles and Modern Applications

TENTH EDITION

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Introduction to Reactions in Aqueous Solutions

5

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Introduction to Reactions in Aqueous Solutions

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5.1 The Nature of Aqueous Solutions

- Aqueous soln's (containing water)
- Aqueous soln's are found everywhere from seawater to living systems.
- Rxn in aqueous soln are important. bec.

---- water is

- (in)expensive and able to dissolve vast amount of substances,
- many subs. are dissociated into its ions which can participate in chem. rxn,

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Mental image of a solution at the molecular level

- The solvent molecules (rather tightly packed), greatly outnumber all other molecules. Water is the solvent in an aqueous solution, and our mental image of water might look something like Figure 5-1(a).
- Solute molecules or ions are present in much smaller number and are randomly distributed among the solvent molecules. Our mental image of an aqueous solution of air might look something like Figure 5-1(b).

Fig. 5.1 Molecular view of water and an aqueous solution of air

(a) Water is the solvent in an aqueous solution. Water molecules (red and white) are in close proximity in liquid water.

(b) An aqueous solution of air dissolved in water, N_2 and O_2. Dissolved oxygen (red) and nitrogen (blue) molecules are far apart, separated by water molecules.

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5.1 The Nature of Aqueous Solutions

- An important characteristic of an aqueous solution of ions is that it will conduct electricity, provided the concentration of ions is not too low.
- An aqueous solution of ions conducts electricity because the ions move essentially independently of each other, each one carrying a certain quantity of charge. (In a metallic conductor, such as copper or tungsten, electrons carry the charge.)
- Whether or not an aqueous solution is a conductor of electricity depends on the nature of the solute(s).
- Pure water contains so few ions that it does not conduct electric current. However, some solutes produce ions in solution, thereby making the solution an electrical conductor.
- Solutes that provide ions when dissolved in water are called electrolytes

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Electrolytes/ Ions

- Ions are individual groups of atoms that acquire a net electric charge by loosing or gaining electrons. Thus,

  - Mg^{+2} is a positively charged ion (cation), formed when a Mg atom loses 2 electrons.

  - Cl^-, Chloride ion ; NO_3^- ion, (anion) are negatively ions when they gain electrons

- in metallic conductors→ e^- 's carry the electric charge

- in electrically conducting aqueous soln. → ions carry the electric charge
- Pure water contains so few ions → not conduct electric current, however,

  - Some solutes can *dissociate* into ions in water and electric charge can be carried.These solutes are called *electrolytes*.

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Types of Electrolytes

Strong electrolyte is *completely ionized*.

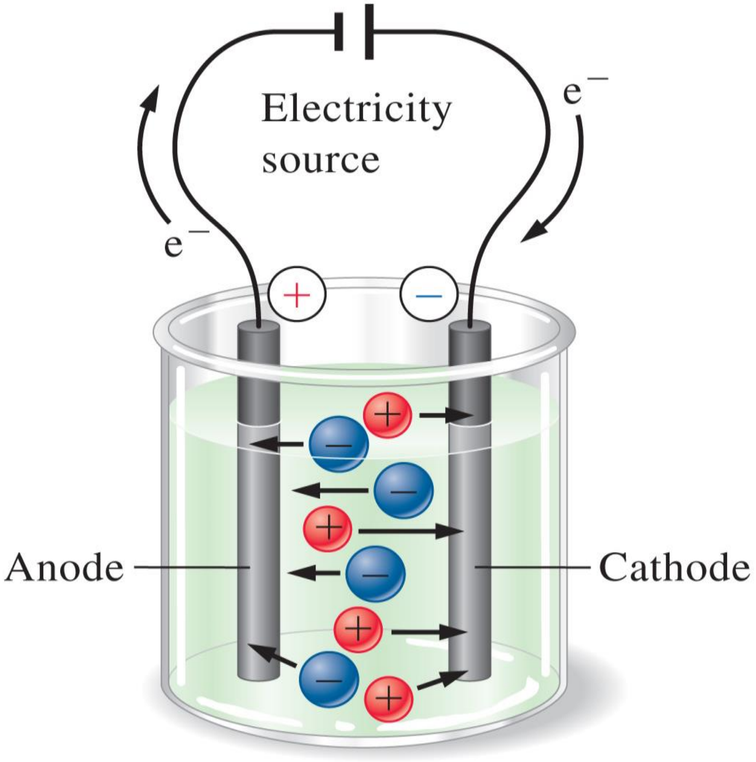
Good electrical conduction.

Weak electrolyte only *partially ionizes*

Fair conductor of electricity.

Non-electrolyte does not dissociate.

Poor conductor of electricity.



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▲ FIGURE 5–2

Conduction of electricity through a solution

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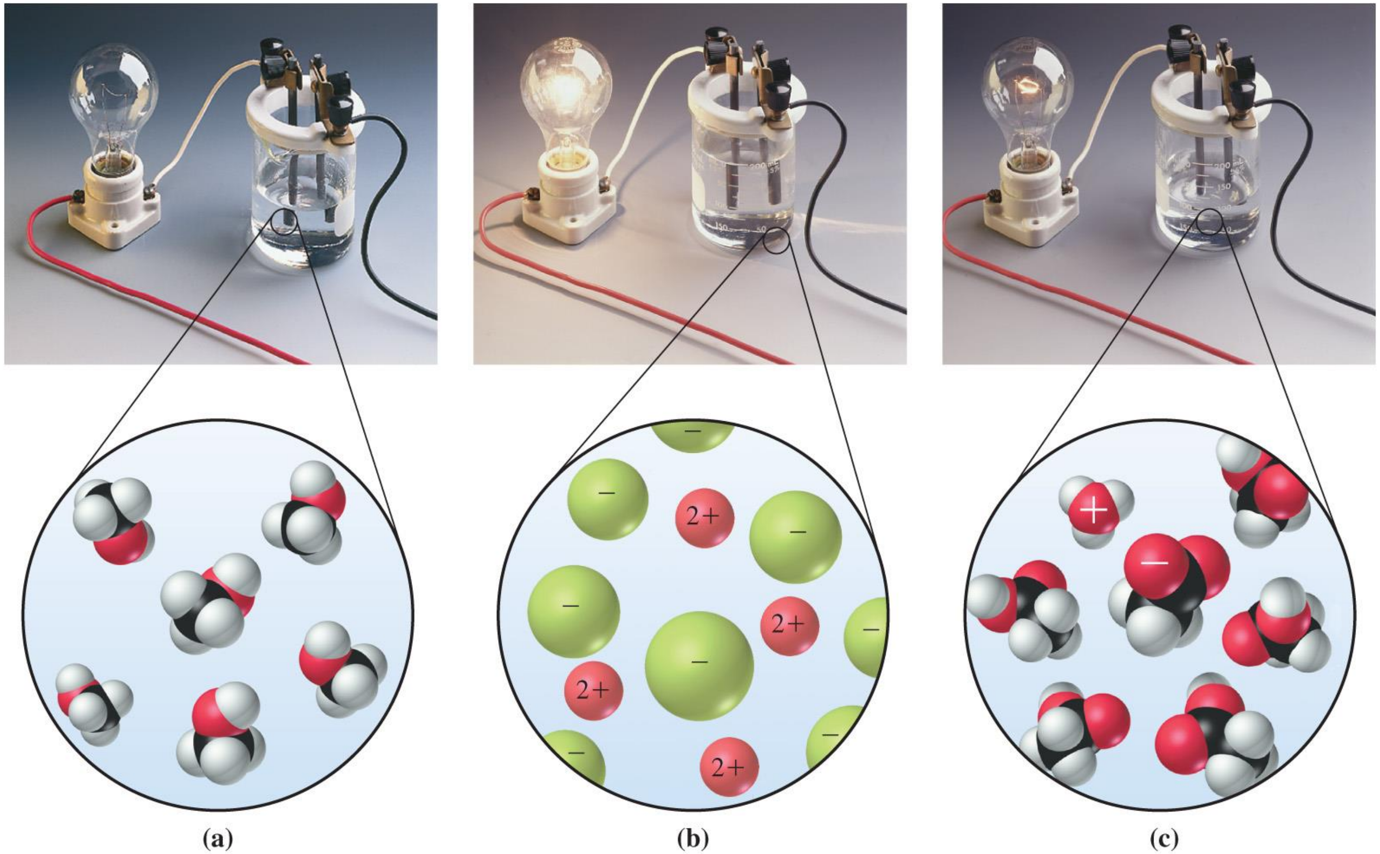

Three types of electrolytes .

(a) no ions present to speak of, only molecules. Methanol is a non-electrolyte in aqueous soln.

(b) the solute is present almost entirely as individual ions. $MgCl_2$ is a strong electrolyte in aq. soln.

(c), although most of the solute is present as molecules, a small fraction of the molecules ionize. CH3COOH is a weak electrolyte in aqueous solution. The CH_3COOH molecules that ionize produce acetate ions CH_3COO^- and H+ions

- Essentially all soluble ionic compounds and only a relatively few molecular compounds are strong electrolytes.
- Most molecular compounds are either nonelectrolytes or weak electrolytes.

A strong electrolyte:

$$MgCl_2(s) \longrightarrow Mg^{2+}(aq) + 2\ Cl^{-}(aq)$$

A weak electrolyte:

$$CH_3CO_2H(aq) \rightleftarrows CH_3CO_2^{-}(aq) + H^{+}(aq)$$

A non-electrolyte: $CH_3OH(aq)$

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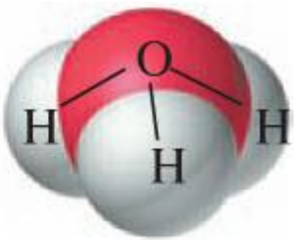
The hydrated proton

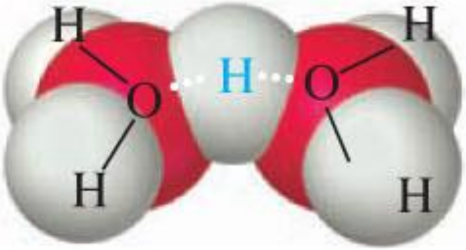
- The hydrogen cation is an interesting and important species that has been the subject of intensive research.

- The ion H^+ -a bare proton- is a small particle that interacts with the water molecules surrounding it. The simple hydrogen ion, H^+, does not exist in aqueous solutions.

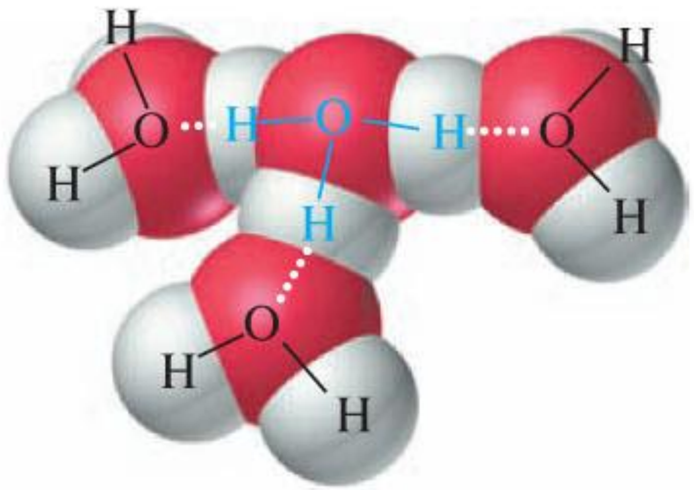
- Its actual form is as hydronium ion, H_3O^+ in which an H^+ ion is attached to an H_2O molecule. The hydronium ion, in turn, interacts with the water molecules surrounding it to form additional species $H_5O_2{}^+$ $H_7O_3{}^+$. These interactions are called hydration,



Hydronium ion
H_3O^+



A hydrated proton
$H_5O_2{}^+$



A hydrated proton
$H_9O_4{}^+$

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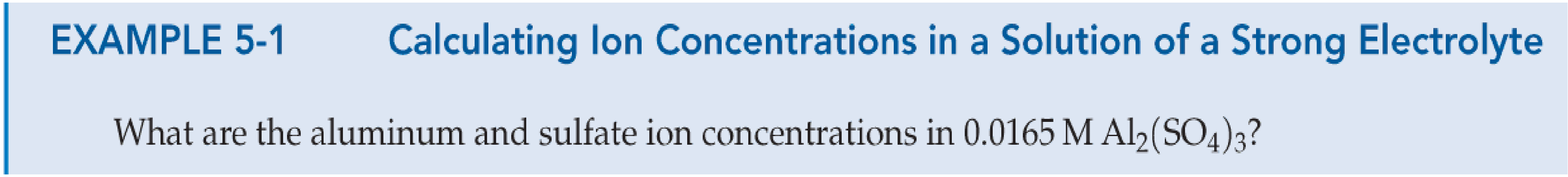
Relative Concentrations in Solution

$$MgCl_2(s) \rightarrow Mg^{2+}(aq) + 2\ Cl^{-}(aq)$$

In 0.0050 M $MgCl_2$:

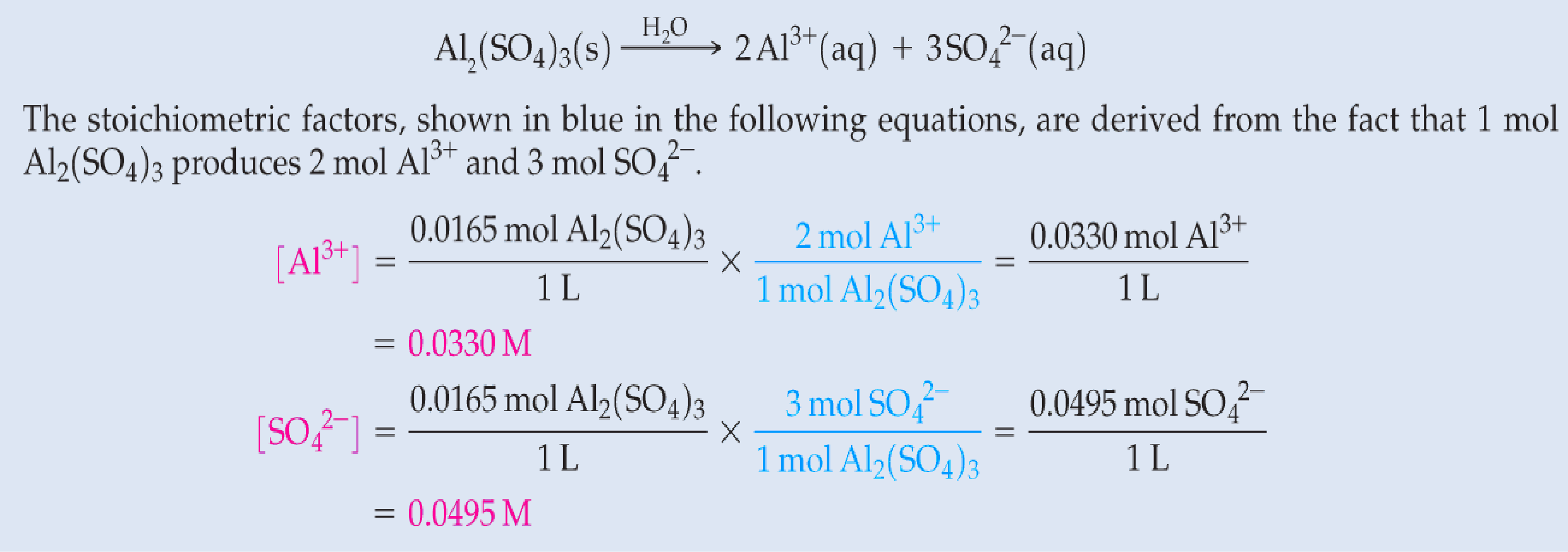
Stoichiometry is important.

$[Mg^{2+}] = 0.0050\ M$ $[Cl^{-}] = 0.0100\ M$ $[MgCl_2] = 0\ M$



EXAMPLE 5-1 **Calculating Ion Concentrations in a Solution of a Strong Electrolyte**

What are the aluminum and sulfate ion concentrations in 0.0165 M $Al_2(SO_4)_3$?



$$Al_2(SO_4)_3(s) \xrightarrow{H_2O} 2\,Al^{3+}(aq) + 3\,SO_4^{2-}(aq)$$

The stoichiometric factors, shown in blue in the following equations, are derived from the fact that 1 mol $Al_2(SO_4)_3$ produces 2 mol Al^{3+} and 3 mol SO_4^{2-}.

$$[Al^{3+}] = \frac{0.0165\ \text{mol}\ Al_2(SO_4)_3}{1\ \text{L}} \times \frac{2\ \text{mol}\ Al^{3+}}{1\ \text{mol}\ Al_2(SO_4)_3} = \frac{0.0330\ \text{mol}\ Al^{3+}}{1\ \text{L}}$$

$$= 0.0330\ \text{M}$$

$$[SO_4^{2-}] = \frac{0.0165\ \text{mol}\ Al_2(SO_4)_3}{1\ \text{L}} \times \frac{3\ \text{mol}\ SO_4^{2-}}{1\ \text{mol}\ Al_2(SO_4)_3} = \frac{0.0495\ \text{mol}\ SO_4^{2-}}{1\ \text{L}}$$

$$= 0.0495\ \text{M}$$

5-2 Precipitation Reactions

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Qualitative test for Cl⁻ in tap water

Figure 5–6 ▲

- Precipitation reactions occur when certain cations and anions combine to produce an insoluble ionic solid called a **precipitate.**

- A test for the presence of chloride ion in water.

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

* The test involves the addition of a few drops of $AgNO_3(aq)$ to tap water. The formation of a precipitate of AgCl(s) confirms the presence of Cl-.

* In industry, precipitation reactions are used to manufacture numerous chemicals.

* In the extraction of magnesium metal from seawater, for instance, the first step is to precipitate Mg^{2+} as $Mg(OH)_2$.

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Net Ionic Equations:

$$AgNO_3(aq) + NaI(aq) \rightarrow AgI(s) + NaNO_3(aq)$$

$AgNO_3(aq)$

$NaI(aq)$

$AgI(s)$ (pale yellow)
$Na^+(aq)$ $NO_3^-(aq)$

▲ Figure 5–7

A precipitate of silver iodide

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Net Ionic Equations:

"whole formula form":

$$AgNO_3(aq) + NaI(aq) \rightarrow AgI(s) + NaNO_3(aq)$$

ionic form:

$$Ag^+(aq) + \cancel{NO_3^-(aq)} + \cancel{Na^+(aq)} + I^-(aq) \rightarrow AgI(s) + \overbrace{\cancel{Na^+(aq)} + \cancel{NO_3^-(aq)}}^{\text{Spectator ions}}$$

***Net ionic equation*:** $Ag^+(aq) + I^-(aq) \rightarrow AgI(s)$

A net ionic equation is an equation that includes only the actual participants in a reaction, with each participant denoted by the symbol or formula that best represents it.

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Predicting Precipitation Reactions

$AgNO_3(aq) + KBr(aq) \rightarrow ?$

- Write expression in ionic form

$Ag^+(aq) + NO_3^-(aq) + K^+(aq) + Br^-(aq) \rightarrow ?$

What will happen ? Two possibilities:

1- some cation-anion combination leads to an insoluble solid, a precipitate

(AgBr and KNO_3) OR

2- no such combination is possible, and there is no reaction at all.

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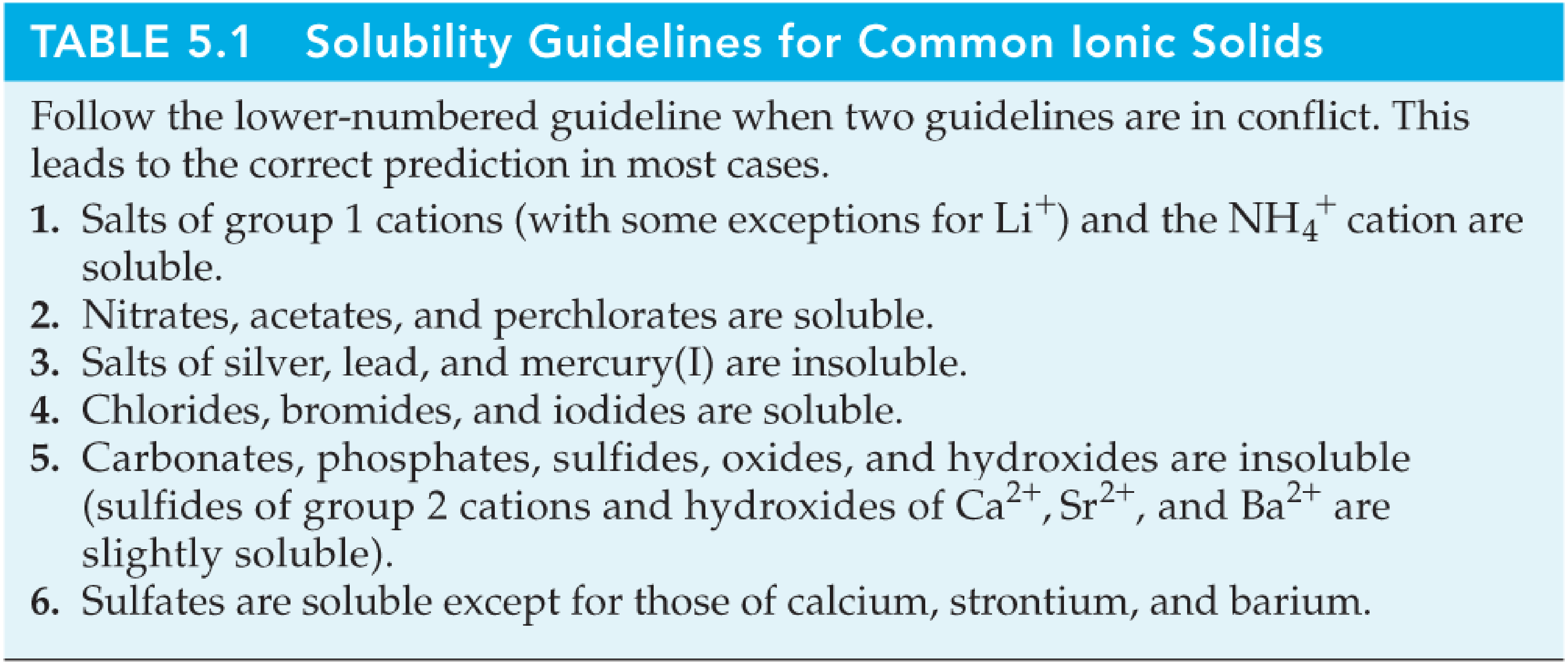

TABLE 5.1 Solubility Guidelines for Common Ionic Solids

Follow the lower-numbered guideline when two guidelines are in conflict. This leads to the correct prediction in most cases.

1. Salts of group 1 cations (with some exceptions for Li^+) and the NH_4^+ cation are soluble.
2. Nitrates, acetates, and perchlorates are soluble.
3. Salts of silver, lead, and mercury(I) are insoluble.
4. Chlorides, bromides, and iodides are soluble.
5. Carbonates, phosphates, sulfides, oxides, and hydroxides are insoluble (sulfides of group 2 cations and hydroxides of Ca^{2+}, Sr^{2+}, and Ba^{2+} are slightly soluble).
6. Sulfates are soluble except for those of calcium, strontium, and barium.

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- according to these guidelines, AgBr(s) is insoluble in water (because rule 3 takes precedence over rule 4) and should precipitate,
- whereas $KNO_3$is soluble (because of rule 1 and 2).

Written as an ionic equation, expression becomes

$$Ag^+(aq) + NO_3^-(aq) + K^+(aq) + Br^-(aq) \rightarrow AgBr(s) + K^+(aq) + NO_3^-(aq)$$

For the net ionic equation, we have

$$Ag^+(aq) + Br^-(aq) \rightarrow AgBr(s)$$

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EXAMPLE 5-2 Using Solubility Guidelines to Predict Precipitation Reactions

Predict whether a reaction will occur in each of the following cases. If so, write a net ionic equation for the reaction.

(a) $NaOH(aq) + MgCl_2(aq) \longrightarrow ?$
(b) $BaS(aq) + CuSO_4(aq) \longrightarrow ?$
(c) $(NH_4)_2SO_4(aq) + ZnCl_2(aq) \longrightarrow ?$

Solve

For each of **(a)**, **(b)** and **(c)**, apply the strategy described above.

(a) In aqueous solution, we get Na^+ and OH^- from NaOH and Mg^{2+} and Cl^- from $MgCl_2$. The combination of Na^+ and Cl^- gives NaCl, a soluble compound; thus, the Na^+ and Cl^- ions remain in solution. However, the Mg^{2+} and OH^- ions combine to produce $Mg(OH)_2$, an insoluble compound. The full, ionic equation is

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

With the elimination of spectator ions, we obtain

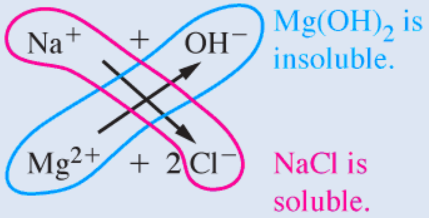
$$2\,OH^-(aq) + Mg^{2+}(aq) \longrightarrow Mg(OH)_2(s)$$

(b) In aqueous solution, we get Ba^{2+} and S^{2-} from BaS and Cu^{2+} and $SO_4{}^{2-}$ from $CuSO_4$. The Ba^{2+} and $SO_4{}^{2-}$ ions combine to form $BaSO_4$, an insoluble compound, and the Cu^{2+} and S^{2-} ions combine to form CuS, also an insoluble compound. The full ionic equation is

$$Ba^{2+}(aq) + S^{2-}(aq) + Cu^{2+}(aq) + SO_4{}^{2-}(aq) \longrightarrow BaSO_4(s) + CuS(s)$$

The equation above is also the net ionic equation because there are no spectator ions.

(c) We get $NH_4{}^+$, $SO_4{}^{2-}$, Zn^{2+}, and Cl^- ions in solution. Because all possible combinations of positive and negative ions lead to water soluble compounds, all of the ions remain in solution. No reaction occurs.



Assess

Problems of this type can also be solved by using a diagrammatic approach which is illustrated for part **(a)**.

As you gain experience, you should be able to go directly to a net ionic equation without first having to write an ionic equation that includes spectator ions.

a Inc.

5-3 Acid-Base Reactions

Ideas about acids and bases (or alkalis) date back to ancient times

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Acid: Latin *acidus*

Sour taste

Base: Arabic *al-qali*

Bitter taste

Acid-Base theory

Svante Arrhenius 1884

Brønsted and Lowry 1923

Figure 5-9 An acid, a base, and an acid–base indicator

The acidic nature of lemon juice is shown by the red color of the acid–base indicator methyl red. The basic nature of soap is indicated by the change in color of the indicator from red to yellow.

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Acids

- Svante Arrhenius , 1884
- an acid can be defined as a substance that provides hydrogen ions, **H^+** , in aqueous solution.

Different acids exhibit different tendencies for producing **H^+**

Strong Acids are molecular compounds that are almost completely ionized into **H^+** and accompanying anions when in aqueous solution

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

Weak acids are molecular compounds that have a weak tendency for producing H^+ ions; weak acids are incompletely ionized in aqueous solution

$$CH_3CO_2H(aq) \leftrightarrows H^+(aq) + CH_3CO_2^-(aq)$$

Double sided arrow

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Acids

Arrhenius definition

lead you to think that acids simply fall apart into **H⁺** ions and the accompanying anions when they are dissolved in water. However this is not the case.

-Brønsted and Lowry ,1923, a more modern approach

-proposed that the key process responsible for the properties of acids (and bases) was the transfer of an H^+ion (a proton) from one substance to another.

- For example, when acids dissolve in water, H^+ ions are transferred from acid molecules to water molecules, as shown below,

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

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

the acid molecules are acting as proton donors and the water molecules are acting as proton acceptors. According to the Brønsted-Lowry theory, an acid is a **proton donor.**

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Bases

-Svante Arrhenius , 1884

- A base is a substance that produces hydroxide ions in aqueous solution.

$$NaOH(aq) \xrightarrow{H_2O} Na^+(aq) + OH^-(aq)$$ Strong base

Weak bases: A base that is incompletely ionized in aqueous solution is a **weak base.**

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

Brønsted Lowry bases are **proton acceptors**.

NH_3 behaves as a proton acceptor (a Brønsted-Lowry base) and

H_2O behaves as a proton donor (a Brønsted-Lowry acid).

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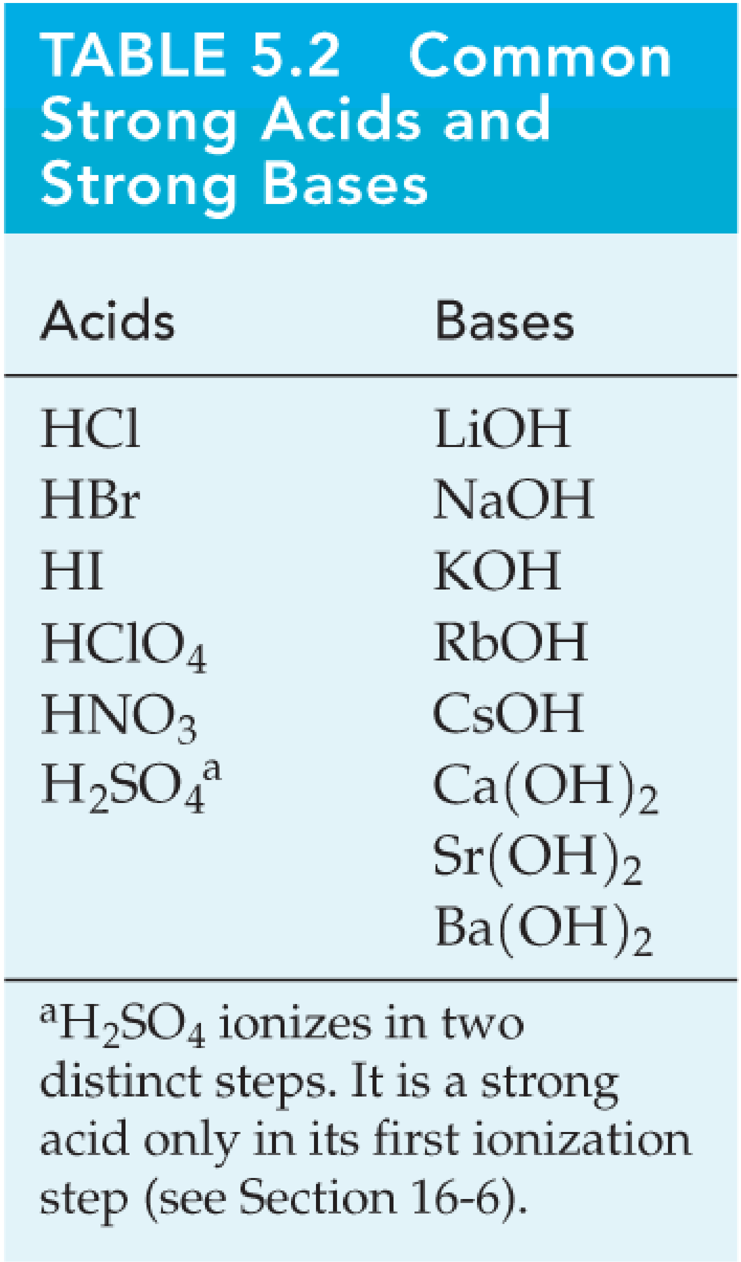

TABLE 5.2 Common Strong Acids and Strong Bases

Acids	Bases
HCl	LiOH
HBr	NaOH
HI	KOH
$HClO_4$	RbOH
HNO_3	CsOH
H_2SO_4[a]	$Ca(OH)_2$
	$Sr(OH)_2$
	$Ba(OH)_2$

[a] H_2SO_4 ionizes in two distinct steps. It is a strong acid only in its first ionization step (see Section 16-6).

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Acidic and Basic solutions:

* When dissolved in water,

- an acid produces H^+ ions and
- a base produces OH^- ions.

- However, experiment shows small numbers of OH^- and H^+ ions are present even in pure water.
- In pure water, the following reaction occurs to a limited extent, hence the use of a double arrow

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

$[H^+]_{water} = [OH^-]_{water} = 1.0 * 10^{-7}$ M at 25

$[H^+] > 1.0 * 10^{-7}$ M acidic

$[OH^-] > 1.0 * 10^{-7}$ M basic

An acidic solution has $[H^+] > [H^+]_{water}$

A basic solution has $[OH^-] > [OH^-]_{water}$

An acidic solution has an excess of H^+ ions (compared with pure water), and a basic solution has an excess of OH^- ions.

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Neutralization:

In a **neutralization reaction,** an acid and a base react to form water and an aqueous solution of an ionic compound called a **salt. Thus, in molecular form,**

$$\underset{\textit{base}}{\mathrm{NaOH(aq)}} + \underset{\textit{acid}}{\mathrm{HCl(aq)}} \rightarrow \underset{\textit{salt}}{\mathrm{NaCl(aq)}} + \underset{\textit{water}}{\mathrm{H_2O(l)}}$$

$$\underset{\textit{base}}{\mathrm{NH_3\,(aq)}} + \underset{\textit{acid}}{\mathrm{HCl(aq)}} \rightarrow \underset{\textit{salt}}{\mathrm{NH_4^{+}(aq) + Cl^{-}}}$$

All the neutralization reactions given above involve a strong acid or a strong base and all of them go essentially to completion, that is, until the limiting reagent is used up. Thus, we use a single arrow rather than a double arrow in the equations for these reactions.

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Recognizing Acids and Bases:

- Acids have *ionizable* hydrogen atoms, which are generally identified by the way in which the formula of an acid is written

  CH_3CO_2H or $HC_2H_3O_2$ acidic hydrogen, ionizable

  CH_4, hydrogens are not ionizable, neither an acid nor a base

- Bases are often indicated by combination of hydroxide ion with various metal cations.

  NaOH, KOH

- To identify a weak base, we usually need a chemical equation for the ionization reaction

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

$$Na_2CO_3(s) + H_2O(l) \rightarrow HCO_3^-(aq) + 2\,Na^+(aq) + OH^-(aq)$$

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More Acid–Base Reactions:

- $Mg(OH)_2$ is a base because it contains OH^-
- but this compound is quite insoluble in water.
- If an acid added, becomes soluble through neutralization

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

$$Mg(OH)_2(s) + 2\ CH_3CO_2H(aq) \rightarrow$$

$$Mg^{2+}(aq) + 2\ CH_3CO_2^-(aq) + 2\ H_2O(l)$$

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More Acid–Base Reactions:

$CaCO_3$ in Limestone and marble.

$$CaCO_3(s) + 2\ H^+(aq) \rightarrow Ca^{2+}(aq) + H_2CO_3(aq)$$

But: $$H_2CO_3(aq) \rightarrow H_2O(l) + CO_2(g)$$

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

-Thus, a gas is given off when reacts with an acid and dissolves.

- This rxn is responsible for the erosion of marble statues by acid rain.

▲ FIGURE 5-10
Damage caused by acid rain

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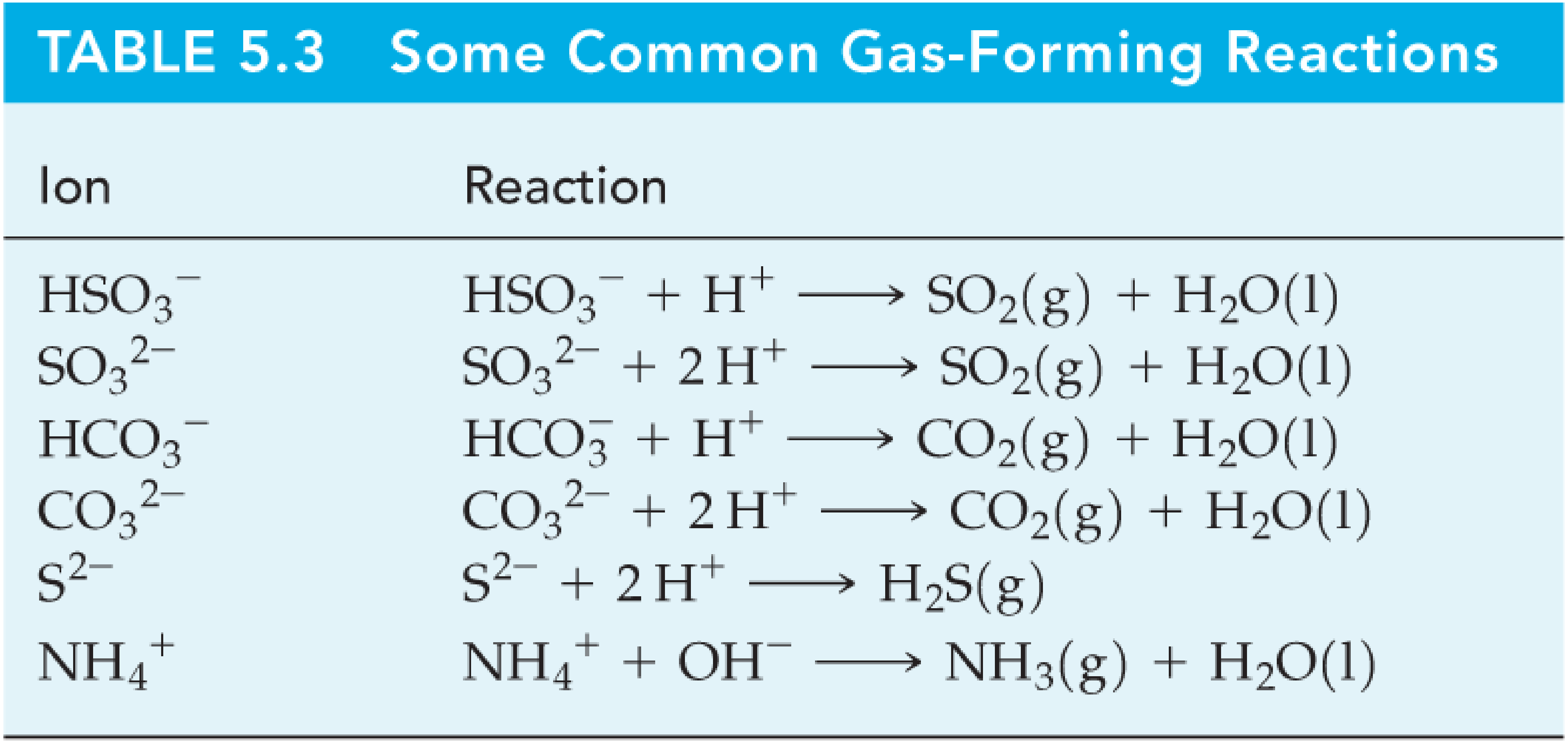

TABLE 5.3 Some Common Gas-Forming Reactions

Ion	Reaction
HSO_3^-	$HSO_3^- + H^+ \longrightarrow SO_2(g) + H_2O(l)$
SO_3^{2-}	$SO_3^{2-} + 2\,H^+ \longrightarrow SO_2(g) + H_2O(l)$
HCO_3^-	$HCO_3^- + H^+ \longrightarrow CO_2(g) + H_2O(l)$
CO_3^{2-}	$CO_3^{2-} + 2\,H^+ \longrightarrow CO_2(g) + H_2O(l)$
S^{2-}	$S^{2-} + 2\,H^+ \longrightarrow H_2S(g)$
NH_4^+	$NH_4^+ + OH^- \longrightarrow NH_3(g) + H_2O(l)$

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EXAMPLE 5-3 Writing Equations for Acid–Base Reactions

Write a net ionic equation to represent the reaction of **(a)** aqueous strontium hydroxide with nitric acid; **(b)** solid aluminum hydroxide with hydrochloric acid.

Solve

(a) $2\,HNO_3(aq) + Sr(OH)_2(aq) \longrightarrow Sr(NO_3)_2(aq) + 2\,H_2O(l)$

Ionic form:

$$2\,H^+(aq) + 2\,NO_3^-(aq) + Sr^{2+}(aq) + 2\,OH^-(aq) \longrightarrow Sr^{2+}(aq) + 2\,NO_3^-(aq) + 2\,H_2O(l)$$

Net ionic equation: Delete the spectator ions (Sr^{2+} and NO_3^-).

$$2\,H^+(aq) + 2\,OH^-(aq) \longrightarrow 2\,H_2O(l)$$

or, more simply,

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

(b) $Al(OH)_3(s) + 3\,HCl(aq) \longrightarrow AlCl_3(aq) + 3\,H_2O(l)$

Ionic form:

$$Al(OH)_3(s) + 3\,H^+(aq) + 3\,Cl^-(aq) \longrightarrow Al^{3+}(aq) + 3\,Cl^-(aq) + 3\,H_2O(l)$$

Net ionic equation: Delete the spectator ion (Cl^-).

$$Al(OH)_3(s) + 3\,H^+(aq) \longrightarrow Al^{3+}(aq) + 3\,H_2O(l)$$

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5-4 Oxidation-Reduction Reactions:

- Practical applications of oxidation reduction reactions can be traced back thousands of years.

- The metal needed to make tools was obtained by heating copper or iron ores, Cu_2O or hematite Fe_2O_3, in the presence of C

- Hematite is converted to iron in a blast furnace.

$$Fe_2O_3(s) + 3\ CO(g) \xrightarrow{\Delta} 2\ Fe(l) + 3\ CO_2(g)$$

Fe^{3+} is reduced to metallic iron.

CO(g) is oxidized to carbon dioxide.

- A commonly used term to describe a reaction in which a substance gains O atoms is *oxidation, and a reaction* in which a substance loses O atoms is *reduction.*
- Oxidation and reduction always occur together. and such a reaction is called an *oxidation reduction, or redox reaction.*

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- The oxygen in Fe_2O_3 can also be removed by igniting a finely divided mixture of Fe_2O_3 and Al. Iron atoms of iron(III) oxide give up O atoms to Al atoms, producing Al_2O_3. Known as thermite reaction.

$$Fe_2O_3(s) + 2\ Al(s) \rightarrow Al_2O_3(s) + 2\ Fe(l)$$

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Figure 5-11
Thermite Reaction

- Definitions of oxidation and reduction based solely on the transfer of O atoms are too restrictive. By using broader definitions, many reactions in aqueous solution can be described as oxidation reduction reactions, even when no oxygen is involved.

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Oxidation State Changes:

Assign oxidation states:

$$\overset{3+\ \ 2-}{Fe_2O_3(s)} + 3\ \overset{2+\ 2-}{CO(g)} \xrightarrow{\Delta} 2\ \overset{0}{Fe(l)} + 3\ \overset{4+\ \ 2-}{CO_2(g)}$$

Fe^{3+} is reduced to metallic iron.
CO(g) is oxidized to carbon dioxide.

- In terms of oxidation state changes,

  * in an oxidation process, the O.S. of some element increases;

  * in a reduction process, the O.S. of some element decreases.

* Even though we assess oxidation state changes by element, oxidation and reduction involve the entire species in which the element is found. Thus, for the reaction above, the whole compound Fe_2O_3 is reduced, not just the Fe atoms; and CO is oxidized, not just the C atom

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EXAMPLE 5-4 Identifying Oxidation–Reduction Reactions

Indicate whether each of the following is an oxidation–reduction reaction.

(a) $MnO_2(s) + 4\,H^+(aq) + 2\,Cl^-(aq) \longrightarrow Mn^{2+}(aq) + 2\,H_2O(l) + Cl_2(g)$

(b) $H_2PO_4^-(aq) + OH^-(aq) \longrightarrow HPO_4^{2-}(aq) + H_2O(l)$

Analyze

In each case, indicate the oxidation states of the elements on both sides of the equation, and look for changes.

Solve

(a) The O.S. of Mn decreases from +4 in MnO_2 to +2 in Mn^{2+}. MnO_2 is reduced to Mn^{2+}. The O.S. of O remains at −2 throughout the reaction, and that of H, at +1. The O.S. of Cl increases from −1 in Cl^- to 0 in Cl_2. Cl^- is oxidized to Cl_2. The reaction is an oxidation–reduction reaction.

(b) The O.S. of H is +1 on both sides of the equation. Oxygen remains at O.S. −2 throughout. The O.S. of phosphorus is +5 in $H_2PO_4^-$ and also +5 in HPO_4^{2-}. There are no changes in O.S. This is not an oxidation–reduction reaction. (It is, in fact, an acid–base reaction.)

Assess

Because many redox reactions involve H^+, OH^-, or insoluble ionic compounds, it is easy to confuse a redox reaction with an acid–base or a precipitation reaction. It is important that you remember the defining features of each type of reaction. Precipitation reactions involve the combination of ions in solution to produce an insoluble precipitate, acid–base reactions involve proton (H^+) transfer, and redox reactions involve electron transfer and changes in oxidation states.

PRACTICE EXAMPLE A: Identify whether each of the following is an oxidation–reduction reaction.

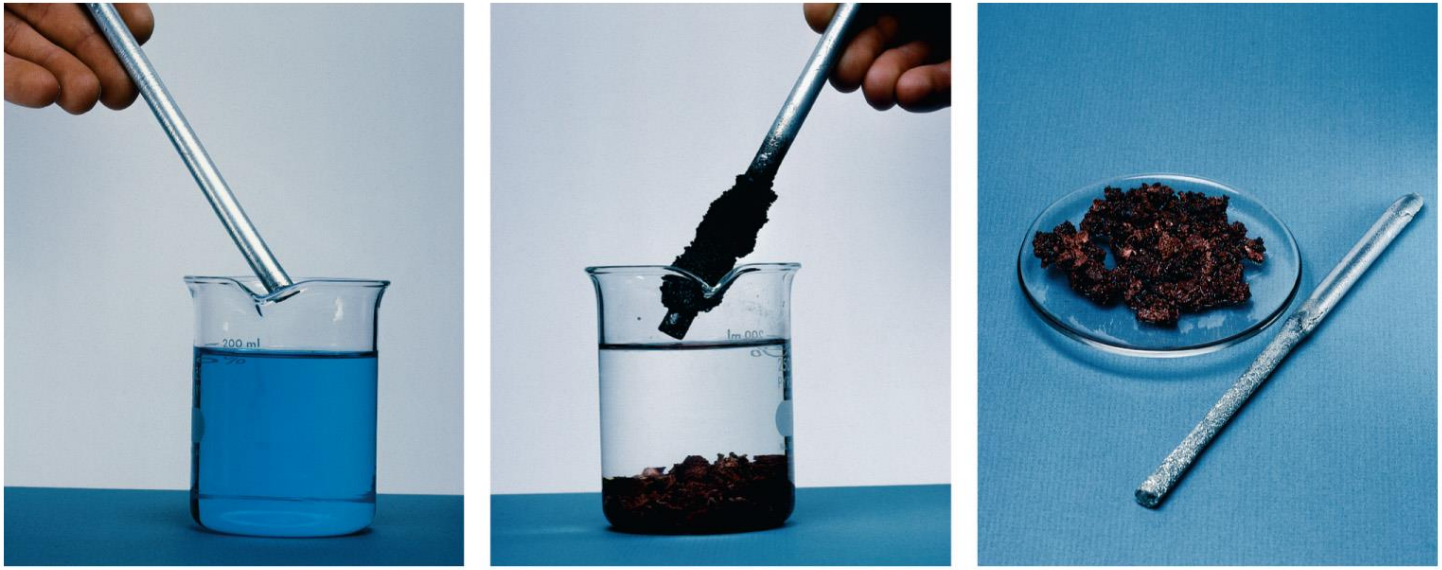
(a) $(NH_4)_2SO_4(aq) + Ba(NO_3)_2(aq) \longrightarrow BaSO_4(s) + 2\,NH_4NO_3(aq)$

(b) $2\,Pb(NO_3)_2(s) \longrightarrow 2\,PbO(s) + 4\,NO_2(g) + O_2(g)$

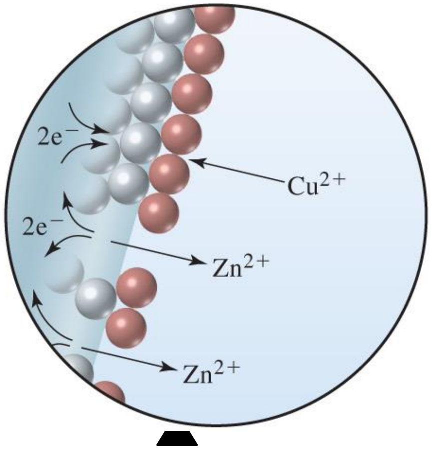
PRACTICE EXAMPLE B: Identify the species that is oxidized and the species that is reduced in the reaction below.

$$5\,VO^{2+}(aq) + MnO_4^-(aq) + H_2O(l) \longrightarrow 5\,VO_2^+(aq) + Mn^{2+}(aq) + 2\,H^+(aq)$$

Oxidation and Reduction Half-Reactions:



(a) (b) (c)



(a) A zinc rod above an aqueous solution of copper(II) sulfate.

(b) Following immersion of the Zn rod in the $CuSO_4$ (aq) for several hours, the blue color of Cu^{2+}(aq) disappears and a deposit of copper forms on the rod

$$Zn(s) + Cu^{2+}(aq) \rightarrow Zn^{2+}(aq) + Cu(s)$$

Figure 5-12 **An oxidation-reduction reaction**

$Zn(s) + Cu^{2+}(aq) \rightarrow Zn^{2+}(aq) + Cu(s)$

The reaction can be represented by two half-reactions.

Oxidation: $Zn(s) \rightarrow Zn^{2+}(aq) + 2\,e^{-}$

Reduction: $Cu^{2+}(aq) + 2\,e- \rightarrow Cu(s)$

Overall: $Cu^{2+}(aq) + Zn(s) \rightarrow Cu(s) + Zn^{2+}(aq)$

Oxidation O.S. of some element *increases* in the reaction.
Electrons are on the right of the equation

Reduction O.S. of some element *decreases* in the reaction.
Electrons are on the left of the equation.

Oxidation and reduction half-reactions must always occur together, and the total number of electrons associated with the oxidation must *equal the* total number associated with the reduction.

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EXAMPLE 5-5 Representing an Oxidation–Reduction Reaction Through Half-Equations and an Overall Equation

Write equations for the oxidation and reduction processes that occur and the overall equation for the reaction of iron with hydrochloric acid solution to produce $H_2(g)$ and Fe^{2+}. The reaction is shown in Figure 5-13.

Analyze

The reactants are Fe(s) and HCl(aq), and the products are $H_2(g)$ and $FeCl_2(aq)$, a soluble ionic compound. In the reaction, the oxidation state of iron changes from 0 in Fe to +2 in $FeCl_2$, and the oxidation state of hydrogen changes from +1 in HCl to 0 in H_2. Thus, iron is oxidized and hydrogen is reduced.

Solve

The balanced chemical equations are as follows.

$$\begin{array}{ll} \textit{Oxidation:} & \mathrm{Fe(s)} \longrightarrow \mathrm{Fe^{2+}(aq)} + 2\,e^- \\ \textit{Reduction:} & \underline{2\,\mathrm{H^+(aq)} + 2\,e^- \longrightarrow \mathrm{H_2(g)}} \\ \textit{Overall:} & \mathrm{Fe(s)} + 2\,\mathrm{H^+(aq)} \longrightarrow \mathrm{Fe^{2+}(aq)} + \mathrm{H_2(g)} \end{array}$$

Assess

This example illustrates that iron dissolves in acid solution. Iron is a major component of steel and the reaction in this example contributes to the corrosion of steel that is exposed to air and moisture. For example, H^+ ions from acid rain cause Fe atoms in steel to become oxidized to Fe^{2+} ions. The oxidation of iron creates small pits in the steel surface and leads to corrosion.

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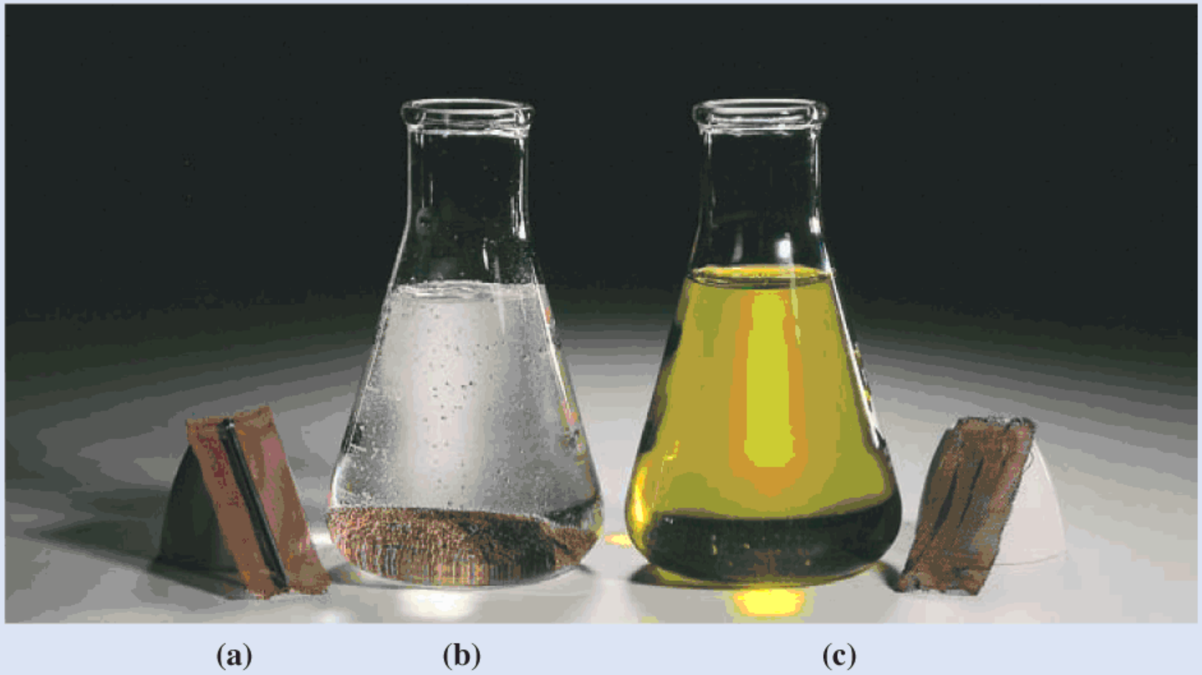

▲ FIGURE 5-13
Displacement of H^+ (aq) by iron—Example 5-5 illustrated
(a) An iron nail is wrapped in a piece of copper screen. **(b)** The nail and screen are placed in HCl(aq). Hydrogen gas is evolved as the nail reacts. **(c)** The nail reacts completely and produces Fe^{2+}(aq), but the copper does not react.

-Why does Fe react with HCl (aq) displacing H_2(g) whereas Cu does not?

Why does Fe form Fe^{2+} and not Fe^{3+} in this reaction?

-relative abilities of Fe and Cu atoms to give up electrons-(to become oxidized)

-Fe gives up electrons more easily than does Cu; also, Fe is more readily oxidized to Fe^{2+} than it is to Fe^{3+}

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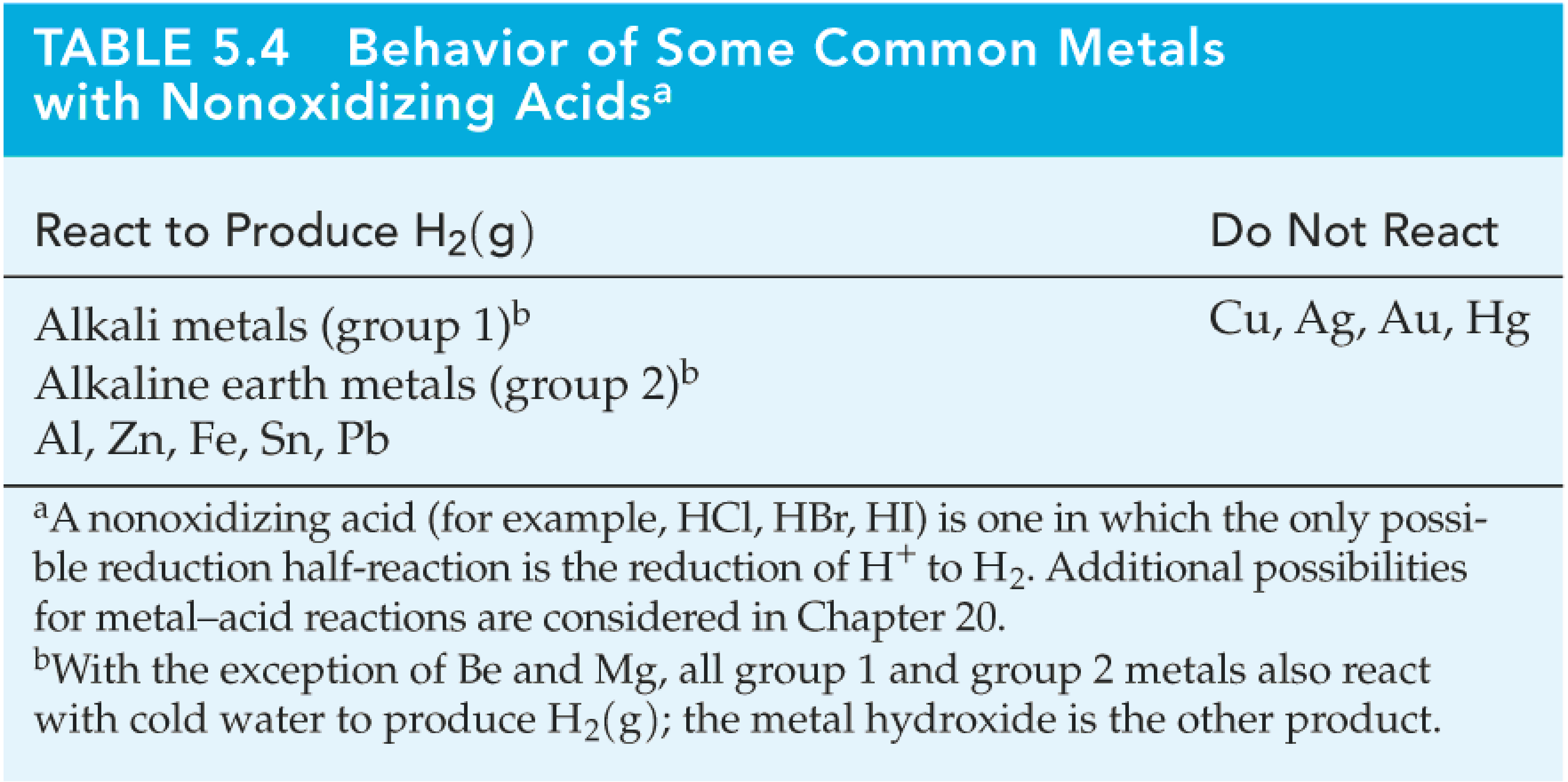

TABLE 5.4 Behavior of Some Common Metals with Nonoxidizing Acids[a]

React to Produce $H_2(g)$	Do Not React
Alkali metals (group 1)[b]	Cu, Ag, Au, Hg
Alkaline earth metals (group 2)[b]	
Al, Zn, Fe, Sn, Pb	

[a] A nonoxidizing acid (for example, HCl, HBr, HI) is one in which the only possible reduction half-reaction is the reduction of H^+ to H_2. Additional possibilities for metal–acid reactions are considered in Chapter 20.

[b] With the exception of Be and Mg, all group 1 and group 2 metals also react with cold water to produce $H_2(g)$; the metal hydroxide is the other product.

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5-5 Balancing Oxidation-Reduction Equations

Electrons are transferred from one substance to another and so we must keep track of electrons and the charge that these electrons carry.

Few can be balanced by inspection.

$$2\,MnO_4^- + H_2O_2 + 6\,H^+ \longrightarrow 2\,Mn^{2+} + 3\,O_2 + 4\,H_2O \tag{5.19}$$

$$2\,MnO_4^- + 3\,H_2O_2 + 6\,H^+ \longrightarrow 2\,Mn^{2+} + 4\,O_2 + 6\,H_2O \tag{5.20}$$

$$2\,MnO_4^- + 5\,H_2O_2 + 6\,H^+ \longrightarrow 2\,Mn^{2+} + 5\,O_2 + 8\,H_2O \tag{5.21}$$

$$2\,MnO_4^- + 7\,H_2O_2 + 6\,H^+ \longrightarrow 2\,Mn^{2+} + 6\,O_2 + 10\,H_2O \tag{5.22}$$

Systematic approach is required.

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The Half-Equation Method:

- Write and balance separate half-equations for oxidation and reduction.
- Adjust coefficients in the two half-equations so that the same number of electrons appear in each half-equation.
- Add together the two half-equations (canceling out electrons) to obtain the balanced overall equation

* This first step in this method actually involves several steps. A detailed description of the method is given in Table 5.5. The method is appropriate for reactions that occur in an acidic solution. Because an acidic solution contains an excess of ions, the method uses ions in balancing the half-equations.

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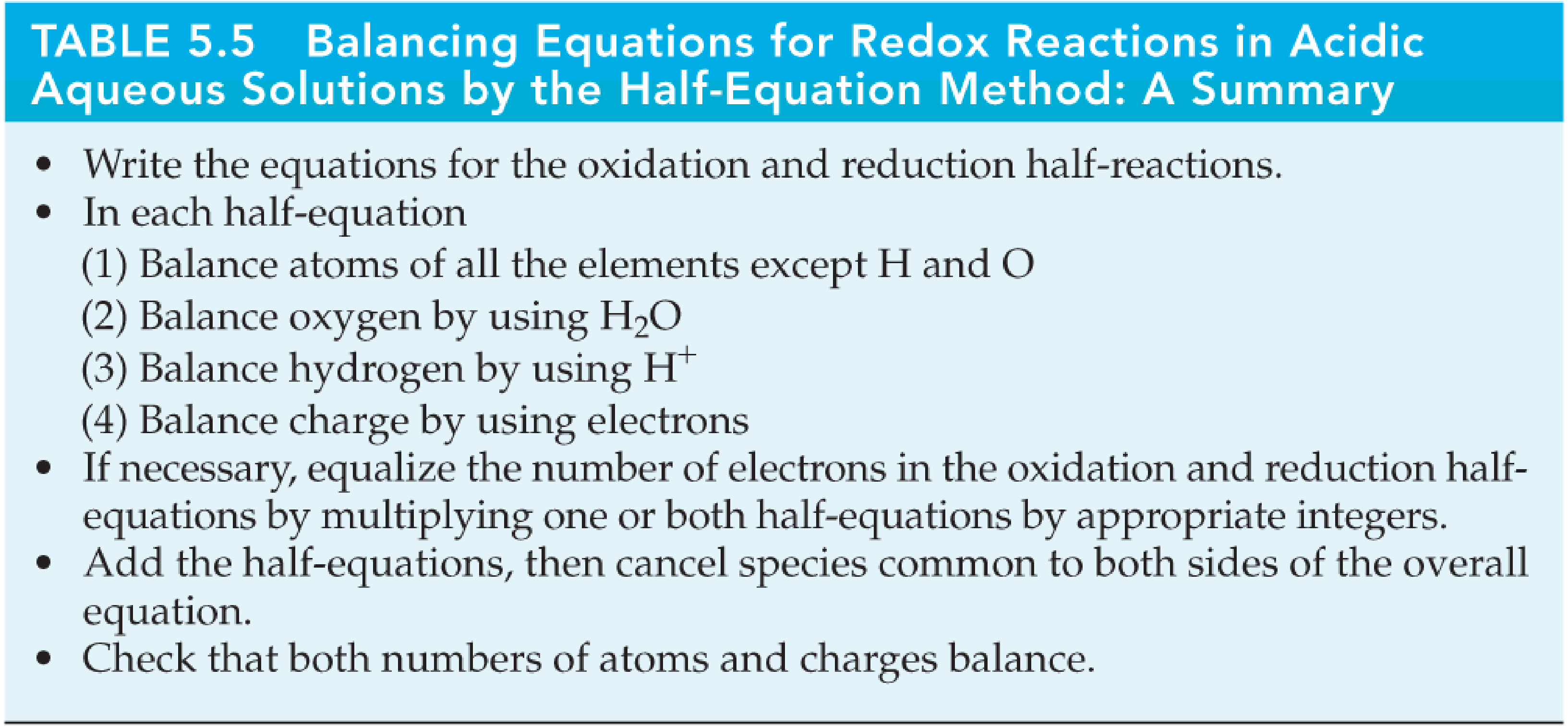

TABLE 5.5 Balancing Equations for Redox Reactions in Acidic Aqueous Solutions by the Half-Equation Method: A Summary

- Write the equations for the oxidation and reduction half-reactions.
- In each half-equation
  (1) Balance atoms of all the elements except H and O
  (2) Balance oxygen by using H_2O
  (3) Balance hydrogen by using H^+
  (4) Balance charge by using electrons
- If necessary, equalize the number of electrons in the oxidation and reduction half-equations by multiplying one or both half-equations by appropriate integers.
- Add the half-equations, then cancel species common to both sides of the overall equation.
- Check that both numbers of atoms and charges balance.

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EXAMPLE 5-6 Balancing the Equation for a Redox Reaction in an Acidic Solution

The reaction described by expression (5.23) below is used to determine the sulfite ion concentration present in wastewater from a papermaking plant. Use the half-equation method to obtain a balanced equation for this reaction in an acidic solution.

$$SO_3^{2-}(aq) + MnO_4^-(aq) \longrightarrow SO_4^{2-}(aq) + Mn^{2+}(aq) \qquad \textbf{(5.23)}$$

Analyze

The reaction occurs in acidic aqueous solution. We can use the method summarized in Table 5.5 to balance it.

Solve

The O.S. of sulfur increases from +4 in SO_3^{2-} to +6 in SO_4^{2-}. The O.S. of Mn decreases from +7 in MnO_4^- to +2 in Mn^{2+}. Thus, SO_3^{2-} is oxidized and MnO_4^- is reduced.

Step 1. *Write skeleton half-equations based on the species undergoing oxidation and reduction.* The half-equations are

$$SO_3^{2-}(aq) \longrightarrow SO_4^{2-}(aq)$$
$$MnO_4^-(aq) \longrightarrow Mn^{2+}(aq)$$

Step 2. *Balance each half-equation for numbers of atoms, in this order:*

- atoms other than H and O
- O atoms, by adding H_2O with the appropriate coefficient
- H atoms, by adding H^+ with the appropriate coefficient

The other atoms (S and Mn) are already balanced in the half-equations. To balance O atoms, we add one H_2O molecule to the left side of the first half-equation and four to the right side of the second.

$$SO_3^{2-}(aq) + H_2O(l) \longrightarrow SO_4^{2-}(aq)$$
$$MnO_4^-(aq) \longrightarrow Mn^{2+}(aq) + 4\,H_2O(l)$$

To balance H atoms, we add two H^+ ions to the right side of the first half-equation and eight to the left side of the second.

$$SO_3^{2-}(aq) + H_2O(l) \longrightarrow SO_4^{2-}(aq) + 2\,H^+(aq)$$
$$MnO_4^-(aq) + 8\,H^+(aq) \longrightarrow Mn^{2+}(aq) + 4\,H_2O(l)$$

(continued)

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Step 3. *Balance each half-equation for electric charge.* Add the number of electrons necessary to get the same electric charge on both sides of each half-equation. By doing this, you will see that the half-equation in which electrons appear on the right side is the *oxidation half-equation*. The other half-equation, with electrons on the left side, is the *reduction half-equation.*

Oxidation:

$$SO_3^{2-}(aq) + H_2O(l) \longrightarrow SO_4^{2-}(aq) + 2\,H^+(aq) + 2\,e^-$$

(net charge on each side, −2)

Reduction:

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

(net charge on each side, +2)

Step 4. *Obtain the overall redox equation by combining the half-equations.* Multiply the oxidation half-equation by 5 and the reduction half-equation by 2. This results in 10 e^- on each side of the overall equation. These terms cancel out. *Electrons must not appear in the final equation.*

Overall:

$$\begin{array}{l} 5\,SO_3^{2-}(aq) + 5\,H_2O(l) \longrightarrow 5\,SO_4^{2-}(aq) + 10\,H^+(aq) + \cancel{10\,e^-} \\ 2\,MnO_4^-(aq) + 16\,H^+(aq) + \cancel{10\,e^-} \longrightarrow 2\,Mn^{2+}(aq) + 8\,H_2O(l) \\ \hline 5\,SO_3^{2-}(aq) + 2\,MnO_4^-(aq) + 5\,H_2O(l) + 16\,H^+(aq) \longrightarrow \\ \qquad 5\,SO_4^{2-}(aq) + 2\,Mn^{2+}(aq) + 8\,H_2O(l) + 10\,H^+(aq) \end{array}$$

Step 5. *Simplify.* The overall equation should not contain the same species on both sides. Subtract 5 H_2O from each side of the equation in step 4. This leaves 3 H_2O on the right. Also subtract 10 H^+ from each side, leaving 6 H^+ on the left.

$$5\,SO_3^{2-}(aq) + 2\,MnO_4^-(aq) + 6\,H^+(aq) \longrightarrow 5\,SO_4^{2-}(aq) + 2\,Mn^{2+}(aq) + 3\,H_2O(l)$$

Step 6. *Verify.* Check the overall equation to ensure that it is balanced both for numbers of atoms and electric charge. For example, show that in the balanced equation from step 5, the net charge on each side of the equation is −6: $(5 \times 2-) + (2 \times 1-) + (6 \times 1+) = (5 \times 2-) + (2 \times 2+) = -6$.

Assess

The final check completed in step 6 gives us confidence that our result is correct. This is an important step; always take the time to complete it. It is also worth pointing out that, in this example, there was only one atom per formula that was oxidized or reduced. (Refer to the skeleton half-equations given in step 1.) Many students have difficulty balancing half-equations in which more than one atom per formula is oxidized or reduced, as is the case when $Cr_2O_7^{2-}$ is reduced to Cr^{3+}. Had we used $Cr_2O_7^{2-}$ instead of MnO_4^- in equation (5.23), the balanced chemical equation for the reaction would have been $3\,SO_3^{2-} + Cr_2O_7^{2-} + 8\,H^+ \rightarrow 3\,SO_4^{2-} + 2\,Cr^{3+} + 4\,H_2O$.

PRACTICE EXAMPLE A: Balance the equation for this reaction in acidic solution.

$$Fe^{2+}(aq) + MnO_4^-(aq) \longrightarrow Fe^{3+}(aq) + Mn^{2+}(aq)$$

PRACTICE EXAMPLE B: Balance the equation for this reaction in acidic solution.

$$UO^{2+}(aq) + Cr_2O_7^{2-}(aq) \longrightarrow UO_2^{2+}(aq) + Cr^{3+}(aq)$$

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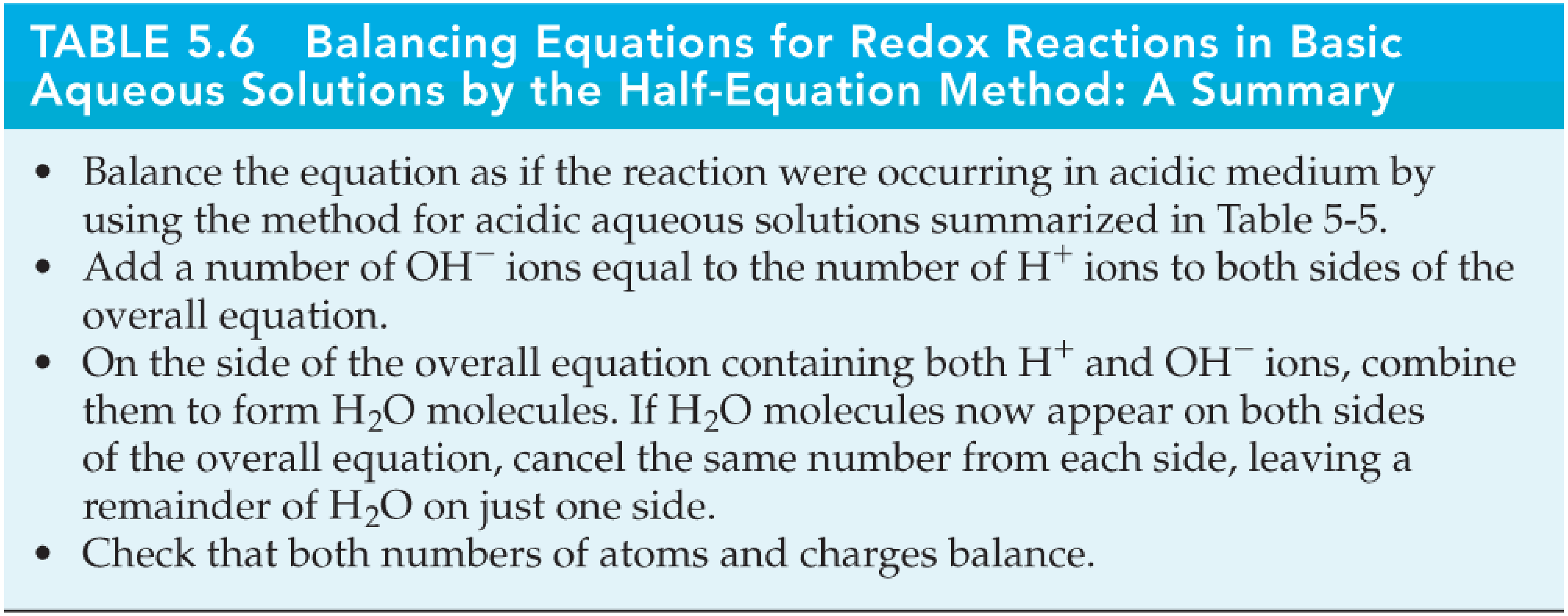

TABLE 5.6 Balancing Equations for Redox Reactions in Basic Aqueous Solutions by the Half-Equation Method: A Summary

- Balance the equation as if the reaction were occurring in acidic medium by using the method for acidic aqueous solutions summarized in Table 5-5.
- Add a number of OH^- ions equal to the number of H^+ ions to both sides of the overall equation.
- On the side of the overall equation containing both H^+ and OH^- ions, combine them to form H_2O molecules. If H_2O molecules now appear on both sides of the overall equation, cancel the same number from each side, leaving a remainder of H_2O on just one side.
- Check that both numbers of atoms and charges balance.

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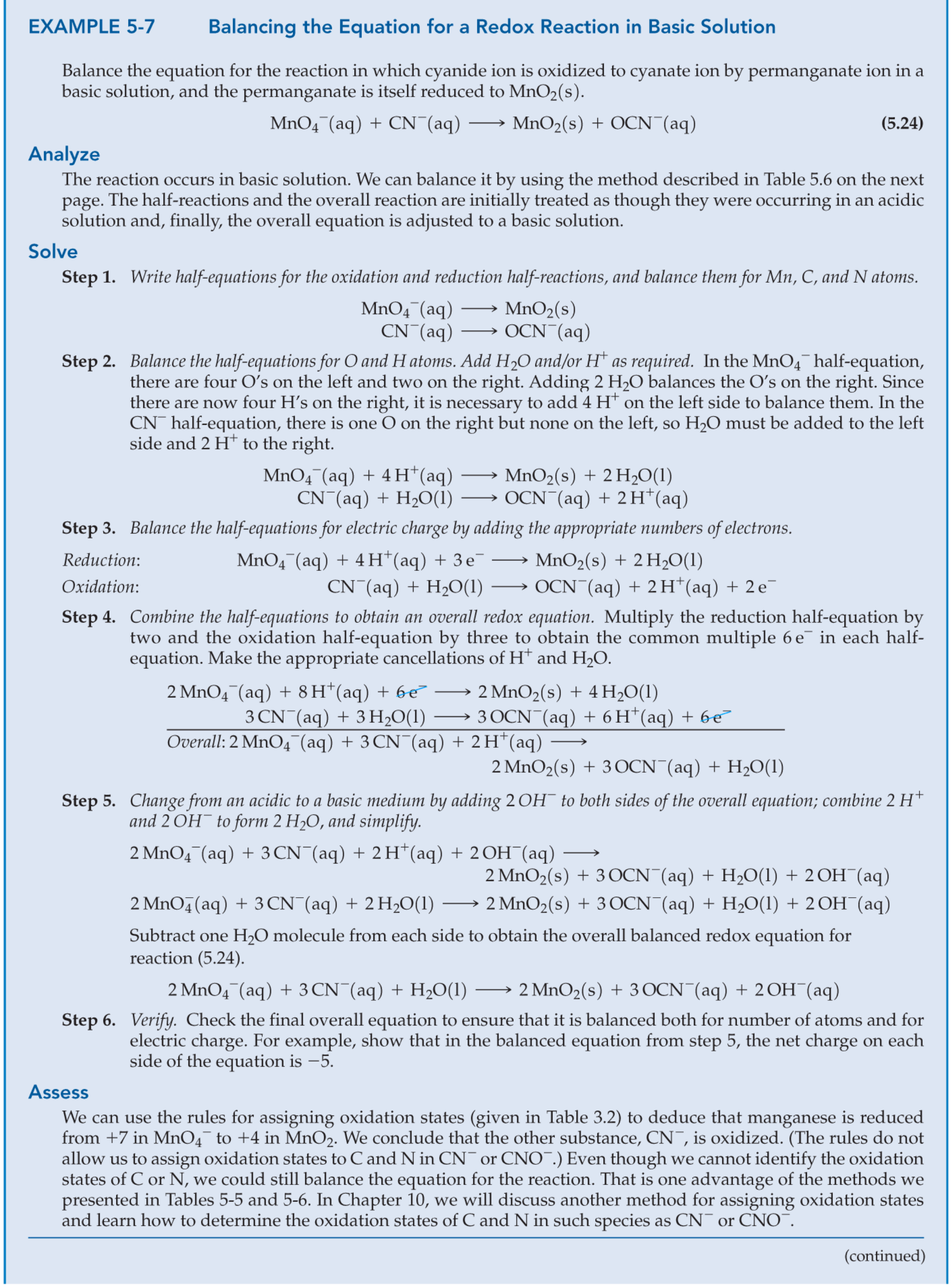

EXAMPLE 5-7 Balancing the Equation for a Redox Reaction in Basic Solution

Balance the equation for the reaction in which cyanide ion is oxidized to cyanate ion by permanganate ion in a basic solution, and the permanganate is itself reduced to $MnO_2(s)$.

$$MnO_4^-(aq) + CN^-(aq) \longrightarrow MnO_2(s) + OCN^-(aq) \qquad \textbf{(5.24)}$$

Analyze

The reaction occurs in basic solution. We can balance it by using the method described in Table 5.6 on the next page. The half-reactions and the overall reaction are initially treated as though they were occurring in an acidic solution and, finally, the overall equation is adjusted to a basic solution.

Solve

Step 1. *Write half-equations for the oxidation and reduction half-reactions, and balance them for Mn, C, and N atoms.*

$$\begin{aligned} MnO_4^-(aq) &\longrightarrow MnO_2(s) \\ CN^-(aq) &\longrightarrow OCN^-(aq) \end{aligned}$$

Step 2. *Balance the half-equations for O and H atoms. Add H_2O and/or H^+ as required.* In the MnO_4^- half-equation, there are four O's on the left and two on the right. Adding 2 H_2O balances the O's on the right. Since there are now four H's on the right, it is necessary to add 4 H^+ on the left side to balance them. In the CN^- half-equation, there is one O on the right but none on the left, so H_2O must be added to the left side and 2 H^+ to the right.

$$\begin{aligned} MnO_4^-(aq) + 4\,H^+(aq) &\longrightarrow MnO_2(s) + 2\,H_2O(l) \\ CN^-(aq) + H_2O(l) &\longrightarrow OCN^-(aq) + 2\,H^+(aq) \end{aligned}$$

Step 3. *Balance the half-equations for electric charge by adding the appropriate numbers of electrons.*

Reduction: $MnO_4^-(aq) + 4\,H^+(aq) + 3\,e^- \longrightarrow MnO_2(s) + 2\,H_2O(l)$

Oxidation: $CN^-(aq) + H_2O(l) \longrightarrow OCN^-(aq) + 2\,H^+(aq) + 2\,e^-$

Step 4. *Combine the half-equations to obtain an overall redox equation.* Multiply the reduction half-equation by two and the oxidation half-equation by three to obtain the common multiple $6\,e^-$ in each half-equation. Make the appropriate cancellations of H^+ and H_2O.

$$\begin{aligned} 2\,MnO_4^-(aq) + 8\,H^+(aq) + \cancel{6\,e^-} &\longrightarrow 2\,MnO_2(s) + 4\,H_2O(l) \\ 3\,CN^-(aq) + 3\,H_2O(l) &\longrightarrow 3\,OCN^-(aq) + 6\,H^+(aq) + \cancel{6\,e^-} \\ \hline \textit{Overall: } 2\,MnO_4^-(aq) + 3\,CN^-(aq) + 2\,H^+(aq) &\longrightarrow \\ & 2\,MnO_2(s) + 3\,OCN^-(aq) + H_2O(l) \end{aligned}$$

Step 5. *Change from an acidic to a basic medium by adding $2\,OH^-$ to both sides of the overall equation; combine $2\,H^+$ and $2\,OH^-$ to form $2\,H_2O$, and simplify.*

$$\begin{aligned} & 2\,MnO_4^-(aq) + 3\,CN^-(aq) + 2\,H^+(aq) + 2\,OH^-(aq) \longrightarrow \\ & \qquad 2\,MnO_2(s) + 3\,OCN^-(aq) + H_2O(l) + 2\,OH^-(aq) \\ & 2\,MnO_4^-(aq) + 3\,CN^-(aq) + 2\,H_2O(l) \longrightarrow 2\,MnO_2(s) + 3\,OCN^-(aq) + H_2O(l) + 2\,OH^-(aq) \end{aligned}$$

Subtract one H_2O molecule from each side to obtain the overall balanced redox equation for reaction (5.24).

$$2\,MnO_4^-(aq) + 3\,CN^-(aq) + H_2O(l) \longrightarrow 2\,MnO_2(s) + 3\,OCN^-(aq) + 2\,OH^-(aq)$$

Step 6. *Verify.* Check the final overall equation to ensure that it is balanced both for number of atoms and for electric charge. For example, show that in the balanced equation from step 5, the net charge on each side of the equation is −5.

Assess

We can use the rules for assigning oxidation states (given in Table 3.2) to deduce that manganese is reduced from +7 in MnO_4^- to +4 in MnO_2. We conclude that the other substance, CN^-, is oxidized. (The rules do not allow us to assign oxidation states to C and N in CN^- or CNO^-.) Even though we cannot identify the oxidation states of C or N, we could still balance the equation for the reaction. That is one advantage of the methods we presented in Tables 5-5 and 5-6. In Chapter 10, we will discuss another method for assigning oxidation states and learn how to determine the oxidation states of C and N in such species as CN^- or CNO^-.

(continued)

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Disproportionation Reactions:

The same substance is both oxidized **and** reduced.

Some have practical significance

Hydrogen peroxide

$$2\ H_2O_2(aq) \rightarrow H_2O(l) + O_2(g)$$

the oxidation state of oxygen changes from -1 in H_2O_2 to -2 in H_2O (a reduction) and to 0 in O_2 (an oxidation).

Sodium thiosulphate

$$2\ S_2O_3{}^{-2}(aq) + 2\ H^+(aq) \rightarrow S(s) + SO_2(g) + H_2O(l)$$

* The oxidation states of S are +2 in $S_2O_3{}^{-2}$, and 0 in S, and +4 in SO_2.Thus, $S_2O_3{}^{-2}$ is simultaneously oxidized and reduced.

* Solutions of sodium thiosulfate $Na_2S_2O_3{}^{-2}$ are often used in the laboratory in redox reactions, and stock solutions of it sometimes develop small deposits of sulfur, a pale yellow solid, over time.

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The same substance appears on the left side in each half-equation for a disproportionation reaction. The balanced half-equations and overall equation for reaction (5.26) are given below.

$$\begin{array}{lrcl}
\textit{Oxidation:} & S_2O_3^{2-}(aq) + H_2O(l) & \longrightarrow & 2\,SO_2(g) + 2\,H^+(aq) + \cancel{4e^-} \\
\textit{Reduction:} & S_2O_3^{2-}(aq) + 6\,H^+(aq) + \cancel{4e^-} & \longrightarrow & 2\,S(s) + 3\,H_2O(l) \\
\hline
 & 2\,S_2O_3^{2-}(aq) + 4\,H^+(aq) & \longrightarrow & 2\,S(s) + 2\,SO_2(g) + 2\,H_2O(l) \\
\textit{Overall:} & S_2O_3^{2-}(aq) + 2\,H^+(aq) & \longrightarrow & S(s) + SO_2(g) + H_2O(l)
\end{array}$$

Antiseptic action of hydrogen peroxide solution

▲ Figure 5–14

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5-6 Oxidizing and Reducing Agents.

* An oxidizing agent (oxidant)

- causes another substance to be oxidized
- contains an element whose oxidation state decreases in a redox reaction
- gains electrons (electrons are found on the left side of its half-equation)
- is reduced

* A reducing agent (reductant)

- causes another substance to be reduced
- contains an element whose oxidation state increases in a redox reaction
- loses electrons (electrons are found on the right side of its half-equation)
- is oxidized

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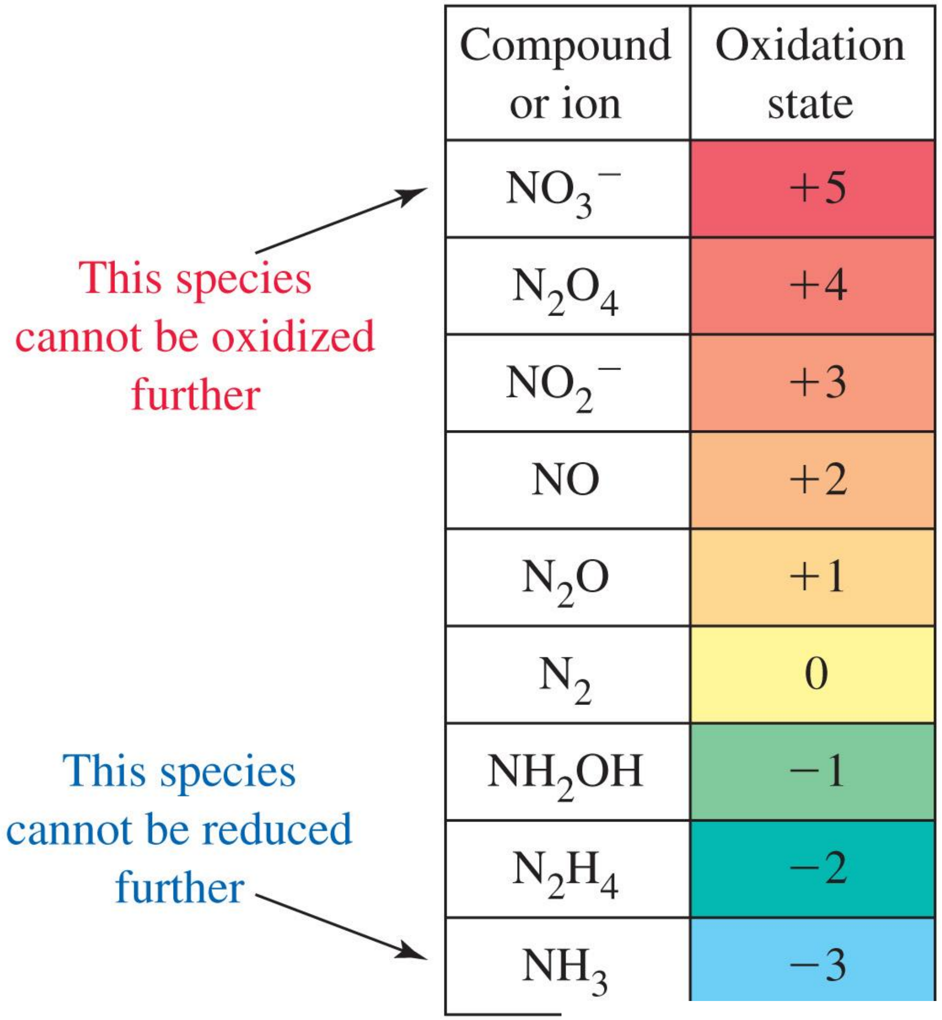

Compound or ion	Oxidation state
NO_3^-	+5
N_2O_4	+4
NO_2^-	+3
NO	+2
N_2O	+1
N_2	0
NH_2OH	−1
N_2H_4	−2
NH_3	−3

This species cannot be oxidized further

This species cannot be reduced further

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▲ Figure 5–15

Oxidation states of nitrogen: Identifying oxidizing and reducing agents

- In NO_3^- and N_2O_4 nitrogen is in one of its highest possible oxidation states (O.S). These species are usually oxidizing agents in redox reactions.
- In N_2H_4 and NH_3 nitrogen is in one of its lowest oxidation states. These species are usually reducing agents.

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A)When these two liquid compounds are mixed, a vigorous reaction takes place:

$$N_2O_4(l) + 2\,N_2H_4(l) \longrightarrow 3\,N_2(g) + 4\,H_2O(g)$$

B) Certain substances in which the oxidation state of an element is between its highest and lowest possible values may act as oxidizing agents in some instances and reducing agents in others. For example, in the reaction of hydrazine with hydrogen to produce ammonia, hydrazine acts as an oxidizing agent.

$$N_2H_4(l) + H_2(g) \longrightarrow 2\,NH_3(g)$$

C) Ozone, a triatomic form of oxygen, is an oxidizing agent used in water purification, as in the oxidation of the organic compound phenol

$$C_6H_5OH(aq) + 14\,O_3(g) \longrightarrow 6\,CO_2(g) + 3\,H_2O(l) + 14\,O_2(g)$$

D) Thiosulfate ion, is an important reducing agent. One of its industrial uses is as an antichlor to destroy residual chlorine from the bleaching of fibers

$$S_2O_3^{2-}(aq) + 4\,Cl_2(aq) + 5\,H_2O(l) \longrightarrow 2\,HSO_4^{-}(aq) + 8\,H^{+}(aq) + 8\,Cl^{-}(aq)$$

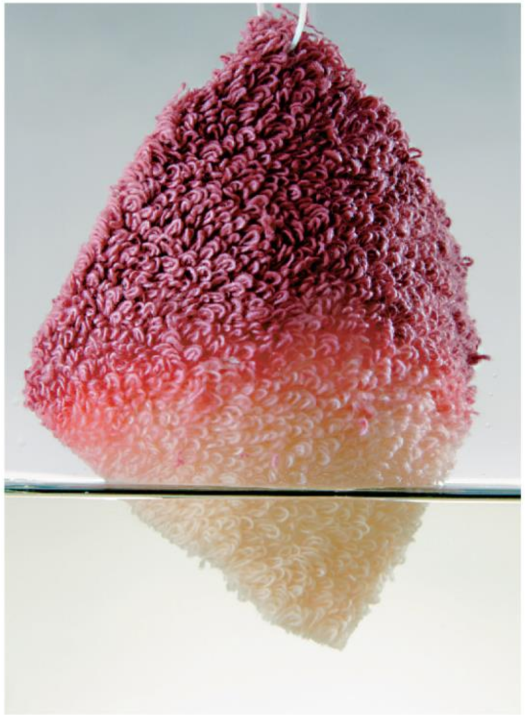

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Figure 5-16

Bleaching action of NaOCl(aq)

* Aqueous sodium hypochlorite, NaOCl(aq), is a powerful oxidizing agent. It is the active ingredient in many liquid chlorine bleaches. The bleaching action of NaOCl(aq) is associated with the reduction of the OCl - ion to Cl- ; the electrons required for the reduction come from colored compounds in stains

* A red cloth becomes white when immersed in NaOCl(aq), which oxidizes the red pigment to colorless products

▲

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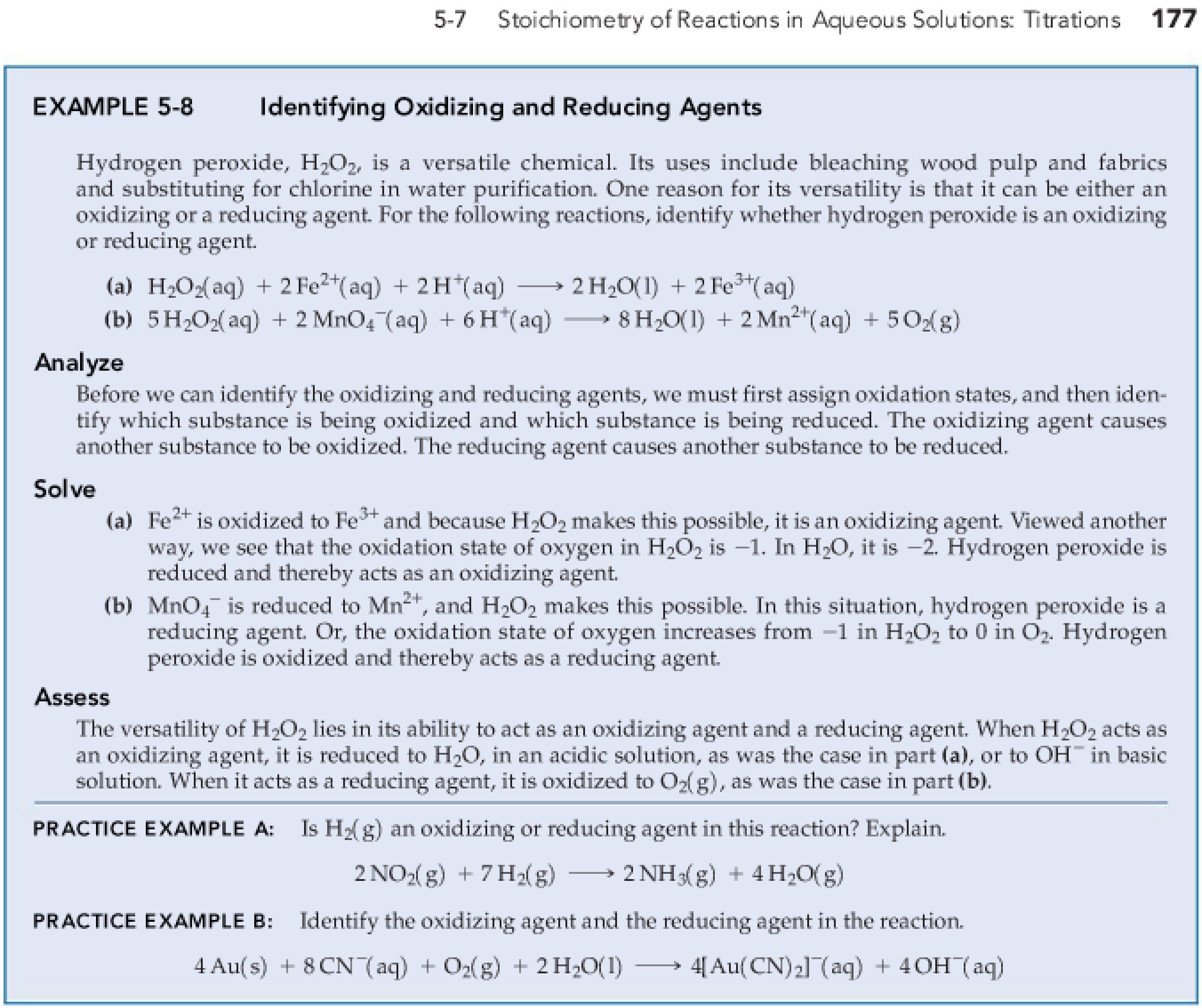

EXAMPLE 5-8 Identifying Oxidizing and Reducing Agents

Hydrogen peroxide, H_2O_2, is a versatile chemical. Its uses include bleaching wood pulp and fabrics and substituting for chlorine in water purification. One reason for its versatility is that it can be either an oxidizing or a reducing agent. For the following reactions, identify whether hydrogen peroxide is an oxidizing or reducing agent.

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

(b) $5\,H_2O_2(aq) + 2\,MnO_4^-(aq) + 6\,H^+(aq) \longrightarrow 8\,H_2O(l) + 2\,Mn^{2+}(aq) + 5\,O_2(g)$

Analyze

Before we can identify the oxidizing and reducing agents, we must first assign oxidation states, and then identify which substance is being oxidized and which substance is being reduced. The oxidizing agent causes another substance to be oxidized. The reducing agent causes another substance to be reduced.

Solve

(a) Fe^{2+} is oxidized to Fe^{3+} and because H_2O_2 makes this possible, it is an oxidizing agent. Viewed another way, we see that the oxidation state of oxygen in H_2O_2 is -1. In H_2O, it is -2. Hydrogen peroxide is reduced and thereby acts as an oxidizing agent.

(b) MnO_4^- is reduced to Mn^{2+}, and H_2O_2 makes this possible. In this situation, hydrogen peroxide is a reducing agent. Or, the oxidation state of oxygen increases from -1 in H_2O_2 to 0 in O_2. Hydrogen peroxide is oxidized and thereby acts as a reducing agent.

Assess

The versatility of H_2O_2 lies in its ability to act as an oxidizing agent and a reducing agent. When H_2O_2 acts as an oxidizing agent, it is reduced to H_2O, in an acidic solution, as was the case in part **(a)**, or to OH^- in basic solution. When it acts as a reducing agent, it is oxidized to $O_2(g)$, as was the case in part **(b)**.

PRACTICE EXAMPLE A: Is $H_2(g)$ an oxidizing or reducing agent in this reaction? Explain.

$$2\,NO_2(g) + 7\,H_2(g) \longrightarrow 2\,NH_3(g) + 4\,H_2O(g)$$

PRACTICE EXAMPLE B: Identify the oxidizing agent and the reducing agent in the reaction.

$$4\,Au(s) + 8\,CN^-(aq) + O_2(g) + 2\,H_2O(l) \longrightarrow 4[Au(CN)_2]^-(aq) + 4\,OH^-(aq)$$

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5-7 Stoichiometry of Reactions in Aqueous Solutions: Titrations.

Titration

Carefully controlled addition of one solution to another.

The trick is to stop the titration at the point where both reactants have reacted completely, a condition called the **equivalence point** of the titration.

Equivalence Point

Both reactants have reacted completely, the two reactants have combined in stoichiometric proportions; both have been consumed, and neither remains in excess.

Indicators

Substances which change colour near an equivalence point.

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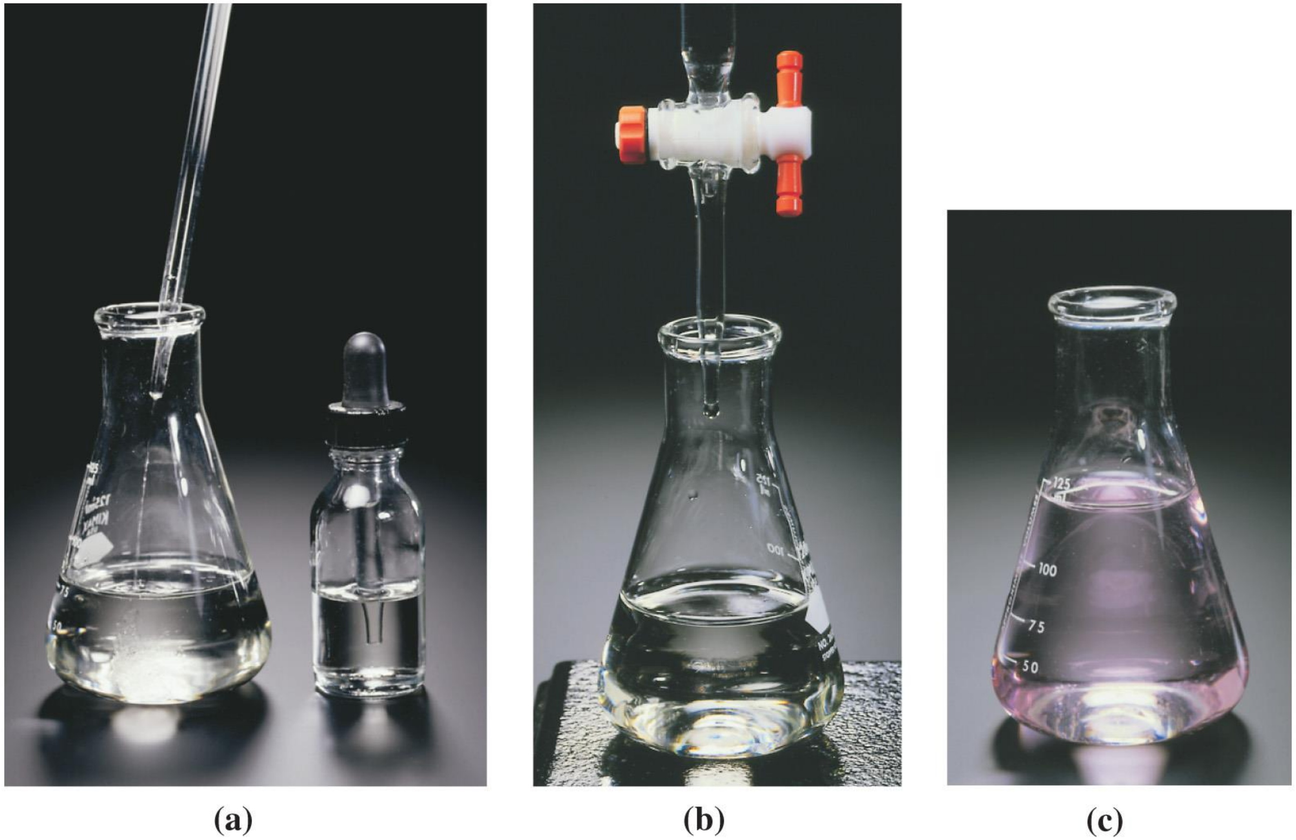
5.0 mL CH_3CO_2H

A few drops
phenolpthalein

Add 0.1000 M NaOH

The “endpoint”
(close to the equivalence point)



An acid–base titration—Example 5-9 illustrated

(a) A 5.00 mL sample of vinegar, a small quantity of water, and a few drops of phenolphthalein indicator are added to a flask. (b) 0.1000 M NaOH from a previously filled buret is slowly added. (c) As long as the acid is in excess, the solution in the flask remains colorless. When the acid has been neutralized, an additional drop of NaOH(aq) causes the solution to become slightly basic. The phenolphthalein indicator turns a light pink. The first lasting appearance of the pink color is taken to be the equivalence point of the titration.

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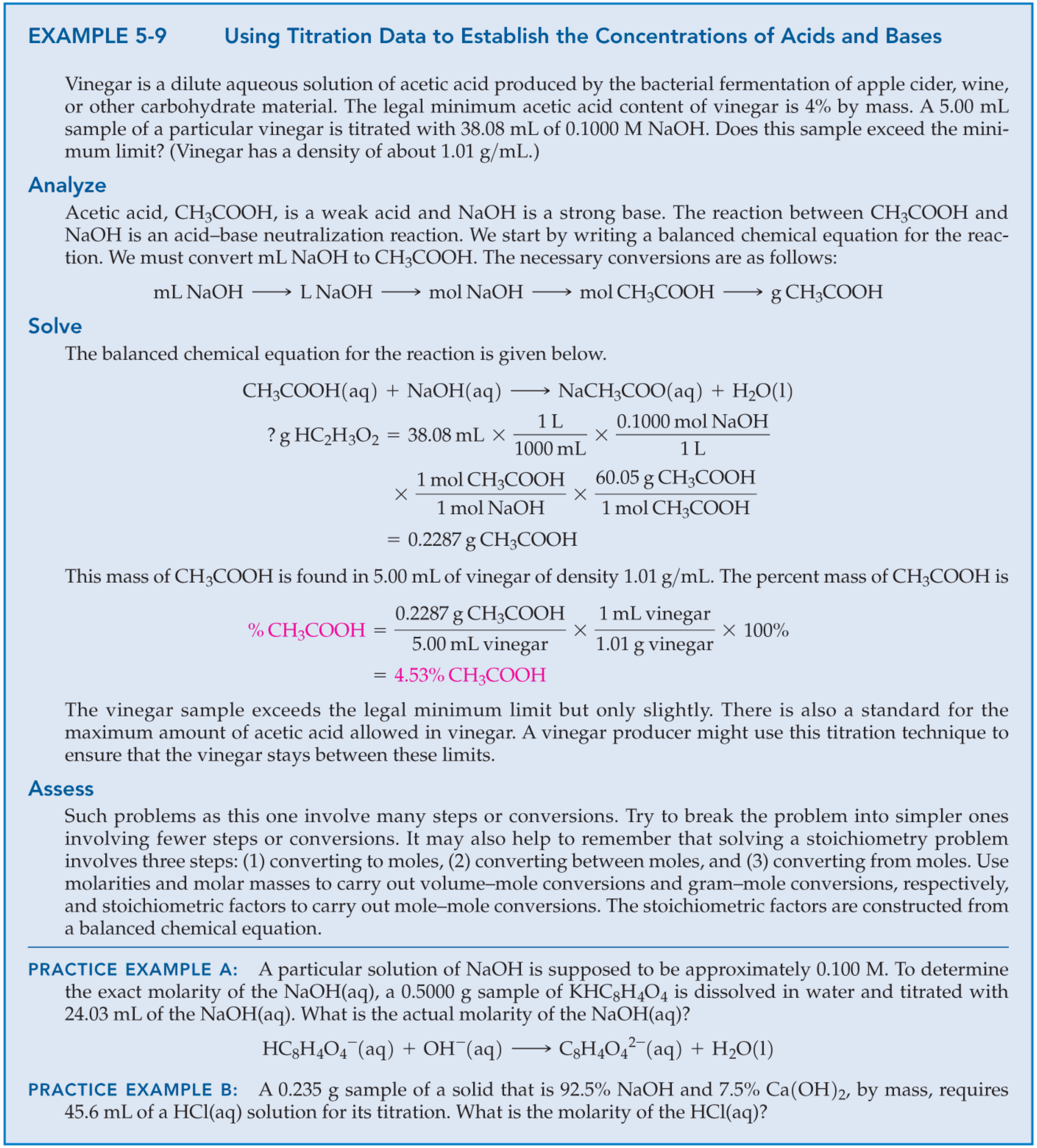

EXAMPLE 5-9 Using Titration Data to Establish the Concentrations of Acids and Bases

Vinegar is a dilute aqueous solution of acetic acid produced by the bacterial fermentation of apple cider, wine, or other carbohydrate material. The legal minimum acetic acid content of vinegar is 4% by mass. A 5.00 mL sample of a particular vinegar is titrated with 38.08 mL of 0.1000 M NaOH. Does this sample exceed the minimum limit? (Vinegar has a density of about 1.01 g/mL.)

Analyze

Acetic acid, CH_3COOH, is a weak acid and NaOH is a strong base. The reaction between CH_3COOH and NaOH is an acid–base neutralization reaction. We start by writing a balanced chemical equation for the reaction. We must convert mL NaOH to CH_3COOH. The necessary conversions are as follows:

$$\text{mL NaOH} \longrightarrow \text{L NaOH} \longrightarrow \text{mol NaOH} \longrightarrow \text{mol } CH_3COOH \longrightarrow \text{g } CH_3COOH$$

Solve

The balanced chemical equation for the reaction is given below.

$$CH_3COOH(aq) + NaOH(aq) \longrightarrow NaCH_3COO(aq) + H_2O(l)$$

$$? \text{ g } HC_2H_3O_2 = 38.08 \text{ mL} \times \frac{1 \text{ L}}{1000 \text{ mL}} \times \frac{0.1000 \text{ mol NaOH}}{1 \text{ L}}$$

$$\times \frac{1 \text{ mol } CH_3COOH}{1 \text{ mol NaOH}} \times \frac{60.05 \text{ g } CH_3COOH}{1 \text{ mol } CH_3COOH}$$

$$= 0.2287 \text{ g } CH_3COOH$$

This mass of CH_3COOH is found in 5.00 mL of vinegar of density 1.01 g/mL. The percent mass of CH_3COOH is

$$\% \, CH_3COOH = \frac{0.2287 \text{ g } CH_3COOH}{5.00 \text{ mL vinegar}} \times \frac{1 \text{ mL vinegar}}{1.01 \text{ g vinegar}} \times 100\%$$

$$= 4.53\% \, CH_3COOH$$

The vinegar sample exceeds the legal minimum limit but only slightly. There is also a standard for the maximum amount of acetic acid allowed in vinegar. A vinegar producer might use this titration technique to ensure that the vinegar stays between these limits.

Assess

Such problems as this one involve many steps or conversions. Try to break the problem into simpler ones involving fewer steps or conversions. It may also help to remember that solving a stoichiometry problem involves three steps: (1) converting to moles, (2) converting between moles, and (3) converting from moles. Use molarities and molar masses to carry out volume–mole conversions and gram–mole conversions, respectively, and stoichiometric factors to carry out mole–mole conversions. The stoichiometric factors are constructed from a balanced chemical equation.

PRACTICE EXAMPLE A: A particular solution of NaOH is supposed to be approximately 0.100 M. To determine the exact molarity of the NaOH(aq), a 0.5000 g sample of $KHC_8H_4O_4$ is dissolved in water and titrated with 24.03 mL of the NaOH(aq). What is the actual molarity of the NaOH(aq)?

$$HC_8H_4O_4^-(aq) + OH^-(aq) \longrightarrow C_8H_4O_4^{2-}(aq) + H_2O(l)$$

PRACTICE EXAMPLE B: A 0.235 g sample of a solid that is 92.5% NaOH and 7.5% $Ca(OH)_2$, by mass, requires 45.6 mL of a HCl(aq) solution for its titration. What is the molarity of the HCl(aq)?

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Standardization:

- Determination of the exact molarity of a solution, usually to three or four significant figures, is called standardization of a solution

- It is not so important that the concentration be a round number (as 0.1000 vs. 0.1035 M), but rather that the concentration be accurately known.

Procedure:

- Suppose we need a $KMnO_4$ solution of exactly known molarity, close to 0.020 M. We cannot prepare this solution by weighing out the required amount of $KMnO_4$ and dissolving it in water. The solid is not pure, and its actual purity (that is, the mass percent) is *not known.*

- *Conversely, we* can obtain iron wire in essentially pure form and allow the wire to react with an acid to yield Fe^{+2} (aq).

- Fe^{+2} (aq) is oxidized to Fe^{+3} (aq) by $KMnO_4$ in an acidic solution. By determining the volume of $KMnO_4$ required to oxidize a known quantity of Fe^{+2} (aq), we can calculate the exact molarity of the $KMnO_4$(aq).

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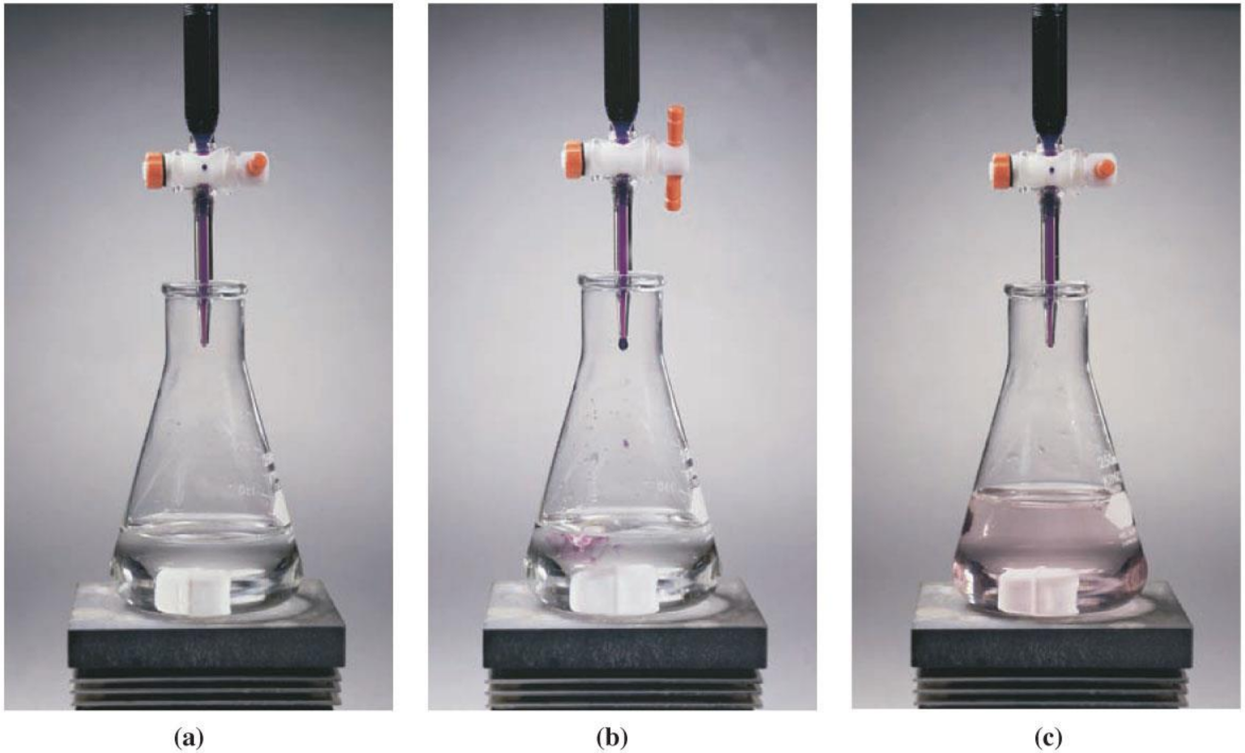
(a) (b) (c)

▲ FIGURE 5-18

Standardizing a solution of an oxidizing agent through a redox titration—Example 5-10 illustrated

(a) The solution contains a known amount of and the buret is filled with the intensely colored $KMnO_4$(aq) to be standardized.

(b) As it is added to the strongly Fe^{2+},acidic solution of Fe^{2+}(aq), the $KMnO_4$(aq) is immediately decolorized as a result of reaction (5.27).

(c) When all the Fe^{2+} has been oxidized to Fe^{3+}additional $KMnO_4$(aq) has nothing left to oxidize and the solution turns a distinctive pink. Even a fraction of a drop of the $KMnO_4$(aq) beyond the equivalence point is sufficient to cause this pink coloration.

EXAMPLE 5-10 Standardizing a Solution for Use in Redox Titrations

A piece of iron wire weighing 0.1568 g is converted to $Fe^{2+}(aq)$ and requires 26.24 mL of a $KMnO_4(aq)$ solution for its titration. What is the molarity of the $KMnO_4(aq)$?

$$5\,Fe^{2+}(aq) + MnO_4^{-}(aq) + 8\,H^{+}(aq) \longrightarrow 5\,Fe^{3+}(aq) + Mn^{2+}(aq) + 4\,H_2O(l) \qquad \textbf{(5.27)}$$

Analyze

The key to a titration calculation is that the amounts of two reactants consumed in the titration are stoichiometrically equivalent—neither reactant is in excess. We are given an amount of Fe (0.156 g) and must determine the number of moles of $KMnO_4$ in the 26.24 mL sample. The following conversions are required:

$$\text{g Fe} \longrightarrow \text{mol Fe} \longrightarrow \text{mol Fe}^{2+} \longrightarrow \text{mol MnO}_4^{-} \longrightarrow \text{mol KMnO}_4$$

The third conversion, from mol Fe^{2+} to mol MnO_4^{-}, requires a stoichiometric factor constructed from the coefficients in equation (5.27).

Solve

First, determine the amount (in moles) of $KMnO_4$ consumed in the titration.

$$\begin{aligned} ?\ \text{mol KMnO}_4 &= 0.1568\ \text{g Fe} \times \frac{1\ \text{mol Fe}}{55.847\ \text{g Fe}} \times \frac{1\ \text{mol Fe}^{2+}}{1\ \text{mol Fe}} \\ &\quad \times \frac{1\ \text{mol MnO}_4^{-}}{5\ \text{mol Fe}^{2+}} \times \frac{1\ \text{mol KMnO}_4}{1\ \text{mol MnO}_4^{-}} \\ &= 5.615 \times 10^{-4}\ \text{mol KMnO}_4 \end{aligned}$$

The volume of solution containing the 5.615×10^{-4} mol $KMnO_4$ is 26.24 mL $=$ 0.02624 L, which means that

$$\text{concn KMnO}_4 = \frac{5.615 \times 10^{-4}\ \text{mol KMnO}_4}{0.02624\ \text{L}} = 0.02140\ \text{M KMnO}_4$$