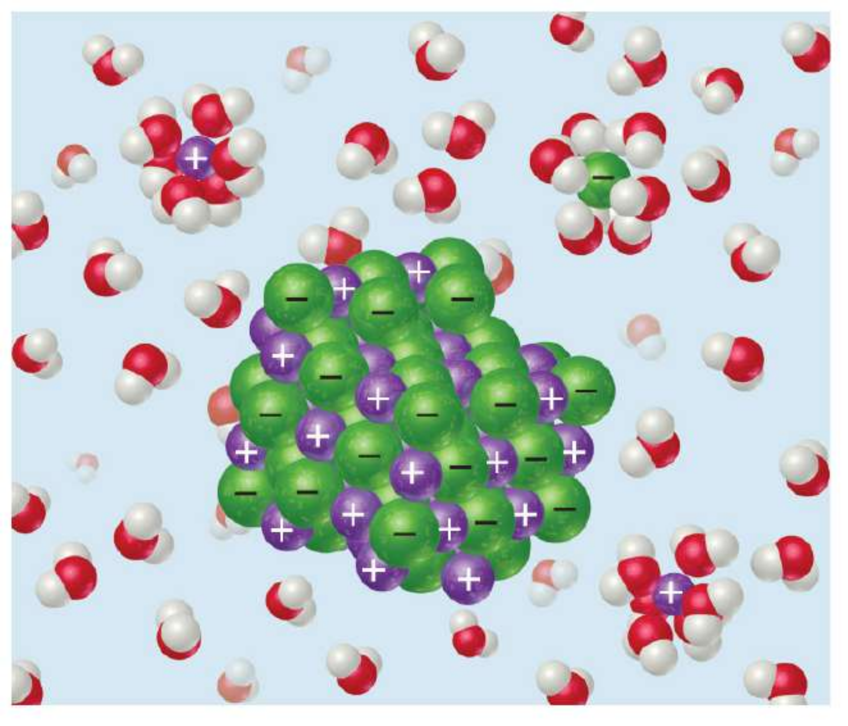
Chapter 4:
Reactions in Aqueous Solutions

4.1: General Properties of Aqueous Solutions

Solutions

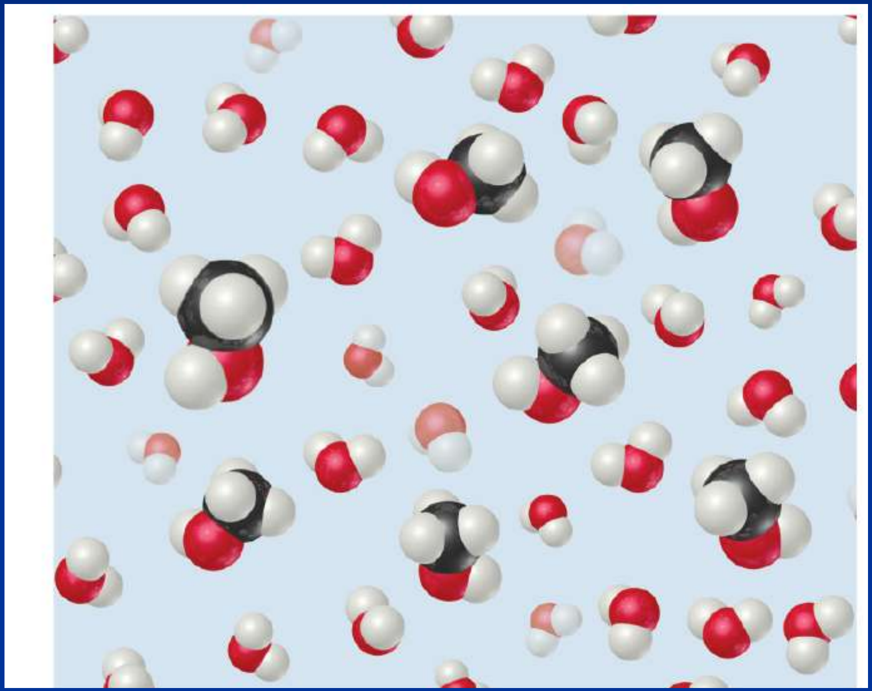
- Solutions are defined as homogeneous mixtures of two or more pure substances.
- The **solvent** is present in greatest abundance.
- All other substances are **solutes**.

Dissociation



- When an ionic substance dissolves in water, the solvent pulls the individual ions from the crystal and solvates them.
- This process is called **dissociation**.

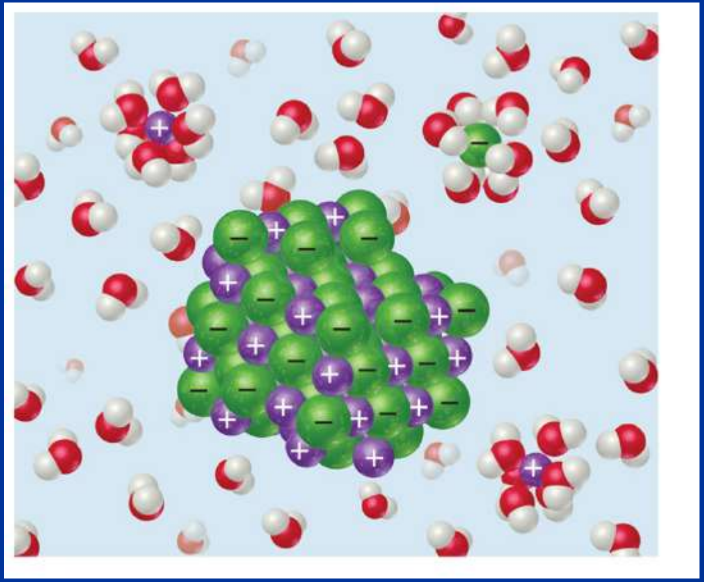
Electrolytes



- An **electrolyte** is a substances that dissociates into ions when dissolved in water.
- A **nonelectrolyte** may dissolve in water, but it does not dissociate into ions when it does so.

Electrolytes and Nonelectrolytes

	Strong Electrolyte	Weak Electrolyte	Nonelectrolyte
Ionic	All	None	None
Molecular	Strong acids (see Table 4.2)	Weak acids Weak bases	All other compounds



Soluble ionic compounds tend to be electrolytes.

Electrolytes and Nonelectrolytes

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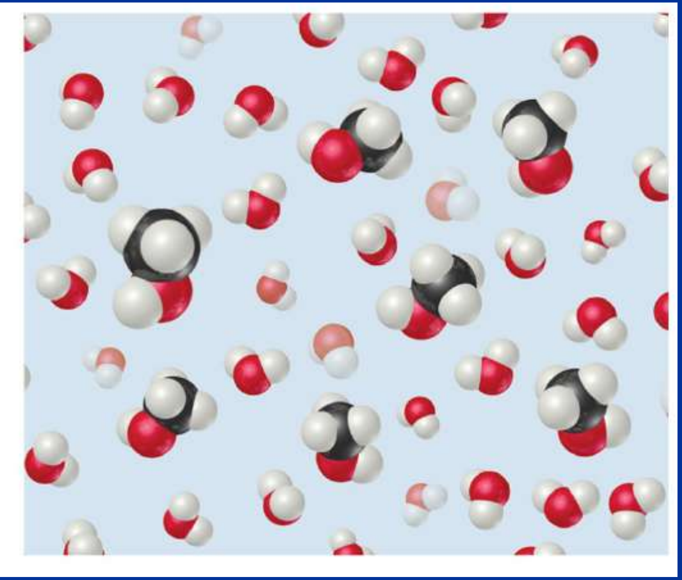
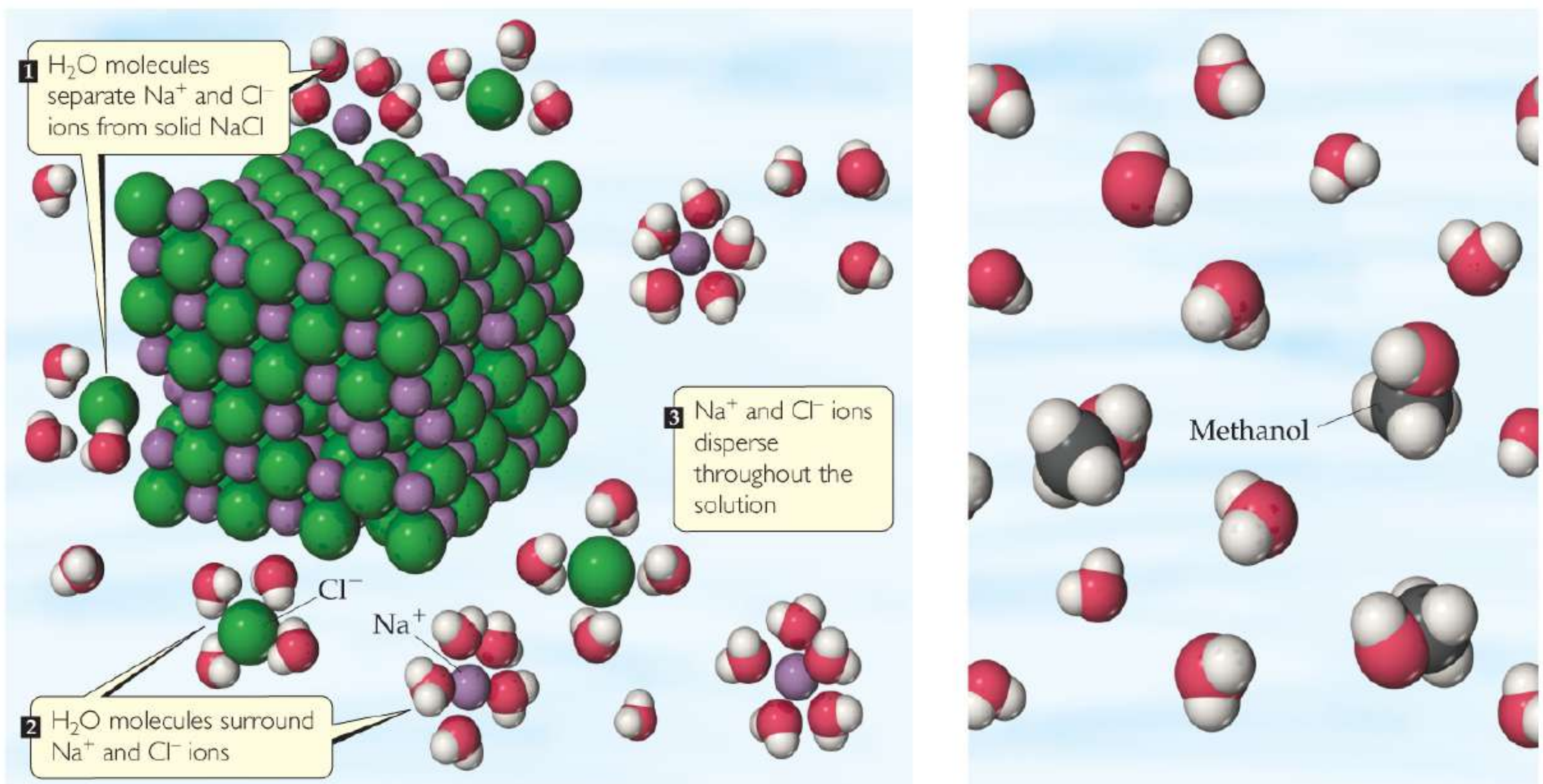


Molecular compounds tend to be nonelectrolytes, except for acids and bases.

Which solution, NaCl(*aq*) or CH_3OH(*aq*), conducts electricity?

a. NaCl(*aq*)

b. CH_3OH(*aq*)



(a) Ionic compounds like sodium chloride, NaCl, form ions when they dissolve.

(b) Molecular substances like methanol, CH_3OH, dissolve without forming ions.

What dissolved species are present in a solution of KCN?

a. $H_2O(l)$

b. $K^+(aq)$ and $H_2O(l)$

c. $CN^-(aq)$

d. $K^+(aq)$ and $CN^-(aq)$

What dissolved species are present in a solution of $NaClO_4$?

a. $H_2O(l)$

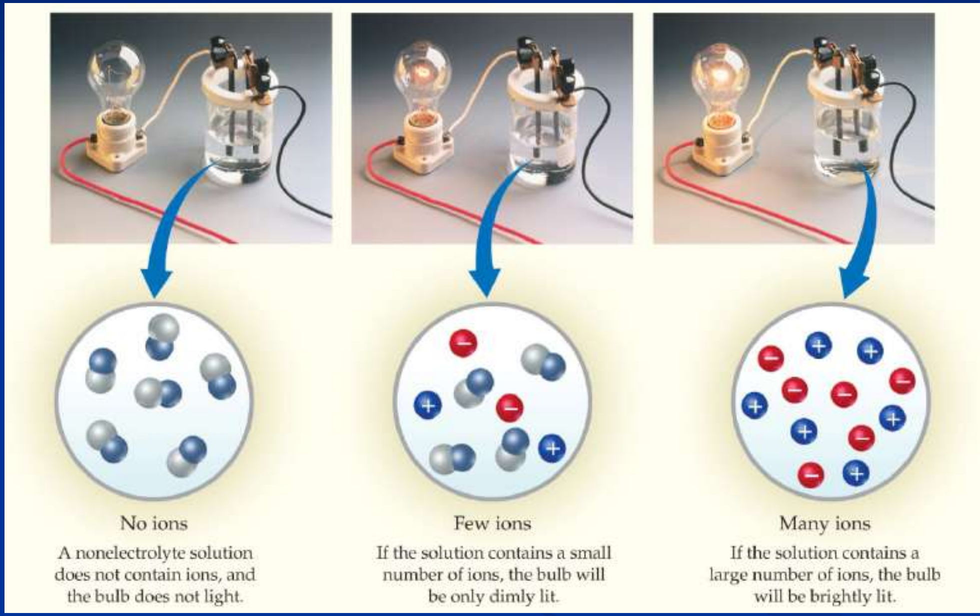
b. $Na^+(aq)$ and $H_2O(l)$

c. $ClO_4^-(aq)$

d. $Na^+(aq)$ and $ClO_4^-(aq)$

Electrolytes

- A **strong electrolyte** dissociates completely when dissolved in water.
- A **weak electrolyte** only dissociates partially when dissolved in water.



Strong Electrolytes Are…

- Strong acids
- Strong bases

Strong Acids	Strong Bases
Hydrochloric, HCl	Group 1A metal hydroxides ($LiOH$, $NaOH$, KOH, $RbOH$, $CsOH$)
Hydrobromic, HBr	Heavy group 2A metal hydroxides [$Ca(OH)_2$, $Sr(OH)_2$, $Ba(OH)_2$]
Hydroiodic, HI	
Chloric, $HClO_3$	
Perchloric, $HClO_4$	
Nitric, HNO_3	
Sulfuric, H_2SO_4	

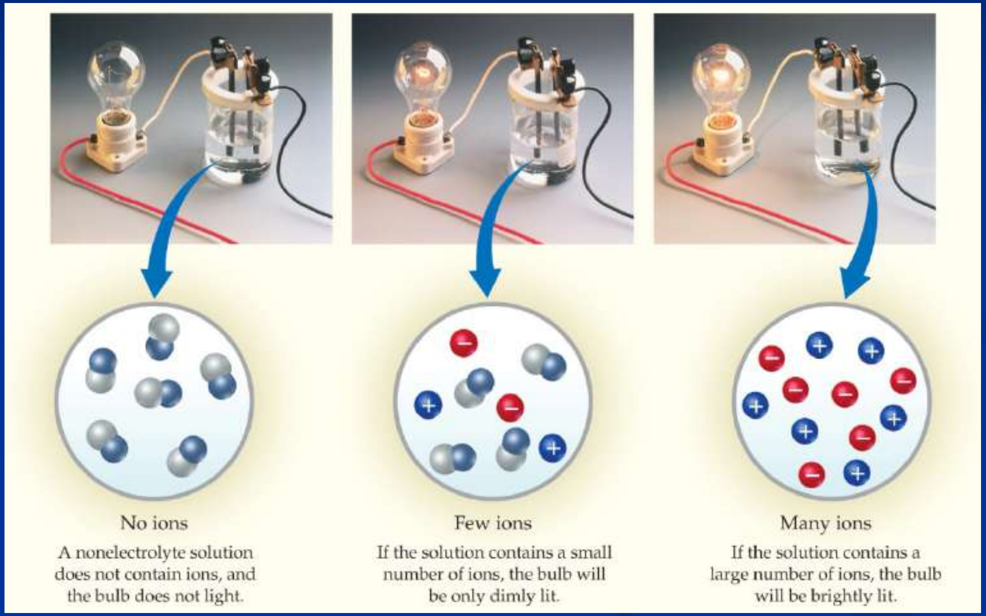
Strong Electrolytes Are…

- Strong acids
- Strong bases
- Soluble ionic salts

Soluble Ionic Compounds		Important Exceptions
Compounds containing	NO_3^-	None
	CH_3COO^-	None
	Cl^-	Compounds of Ag^+, Hg_2^{2+}, and Pb^{2+}
	Br^-	Compounds of Ag^+, Hg_2^{2+}, and Pb^{2+}
	I^-	Compounds of Ag^+, Hg_2^{2+}, and Pb^{2+}
	SO_4^{2-}	Compounds of Sr^{2+}, Ba^{2+}, Hg_2^{2+}, and Pb^{2+}
Insoluble Ionic Compounds		**Important Exceptions**
Compounds containing	S^{2-}	Compounds of NH_4^+, the alkali metal cations, and Ca^{2+}, Sr^{2+}, and Ba^{2+}
	CO_3^{2-}	Compounds of NH_4^+ and the alkali metal cations
	PO_4^{3-}	Compounds of NH_4^+ and the alkali metal cations
	OH^-	Compounds of the alkali metal cations, and NH_4^+, Ca^{2+}, Sr^{2+}, and Ba^{2+}

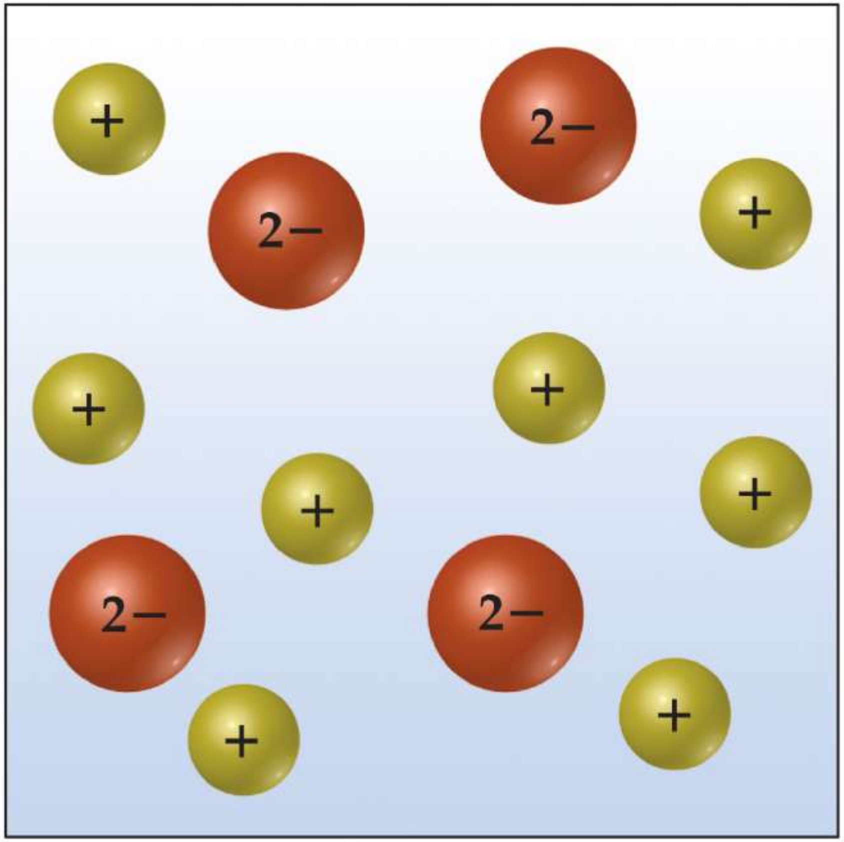
Which solute will cause the light bulb in Figure 4.2 to glow most brightly, CH_3OH, NaOH, or CH_3COOH?

a. $CH_3OH(aq)$
b. $NaOH(aq)$
c. $CH_3COOH(aq)$
d. Cannot determine



Sample Exercise 4.1 Relating Relative Numbers of Anions and Cations to Chemical Formulas

The diagram on the right represents an aqueous solution of one of the following compounds: $MgCl_2$, KCl, or K_2SO_4. Which solution does the drawing best represent?



Practice Exercise 1

If you have an aqueous solution that contains 1.5 moles of HCl, how many moles of ions are in the solution?

(a) 1.0

(b) 1.5

(c) 2.0

(d) 2.5

(e) 3

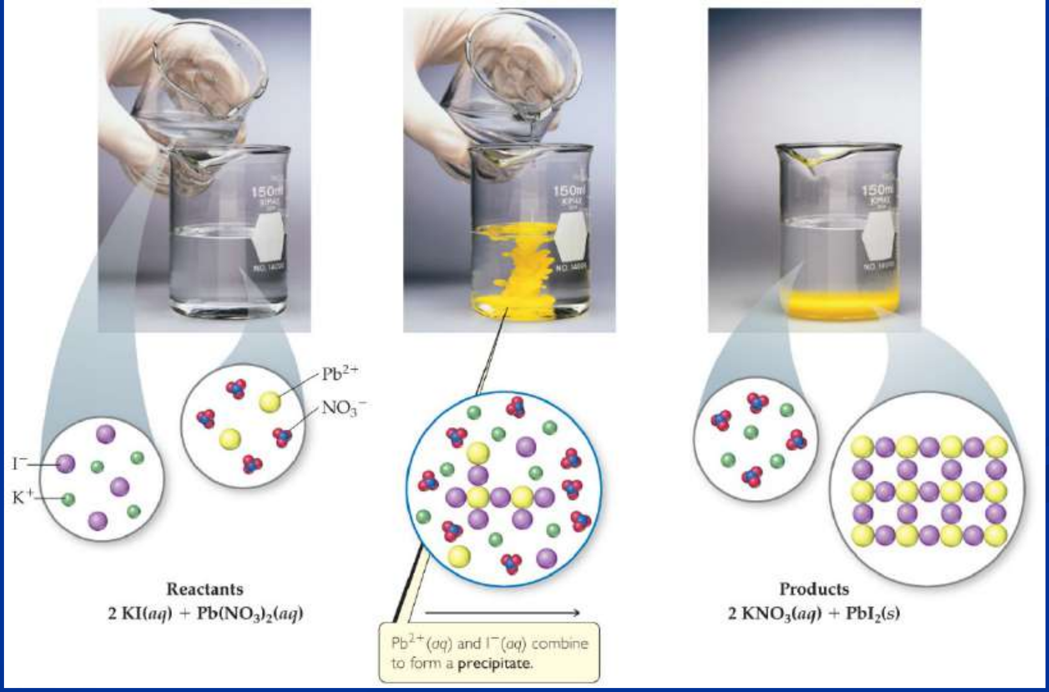
Practice Exercise 2

- If there are six cations in each of the following solutions, how many anions are there?
  - $NiSO_4$
  - $Ca(NO_3)_2$
  - Na_3PO_4
  - $Al_2(SO_4)_3$

4.2 Precipitation Reactions

Precipitation Reactions

When two solutions containing soluble salts are mixed, sometimes an insoluble salt will be produced. A salt "falls" out of solution, like snow out of the sky. This solid is called a **precipitate**.



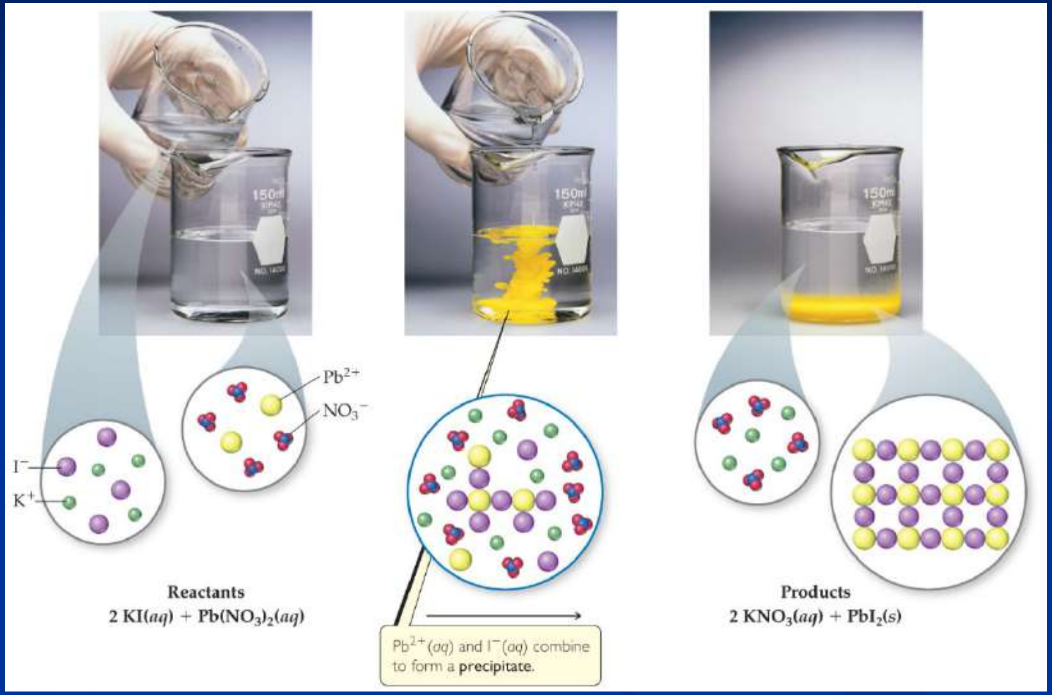
Which ions remain in solution after PbI_2 precipitation is complete?

a. K^+ and I^-

b. Pb^{2+} and I^-

c. K^+ and NO_3^-

d. Pb^{2+} and NO_3^-



Solubility of Ionic Compounds

- Not all ionic compounds dissolve in water.
- A list of **solubility rules** is used to decide what combination of ions will dissolve.

Table 4.1 Solubility Guidelines for Common Ionic Compounds in Water

Soluble Ionic Compounds		Important Exceptions
Compounds containing	NO_3^-	None
	CH_3COO^-	None
	Cl^-	Compounds of Ag^+, Hg_2^{2+}, and Pb^{2+}
	Br^-	Compounds of Ag^+, Hg_2^{2+}, and Pb^{2+}
	I^-	Compounds of Ag^+, Hg_2^{2+}, and Pb^{2+}
	SO_4^{2-}	Compounds of Sr^{2+}, Ba^{2+}, Hg_2^{2+}, and Pb^{2+}
Insoluble Ionic Compounds		**Important Exceptions**
Compounds containing	S^{2-}	Compounds of NH_4^+, the alkali metal cations, Ca^{2+}, Sr^{2+}, and Ba^{2+}
	CO_3^{2-}	Compounds of NH_4^+ and the alkali metal cations
	PO_4^{3-}	Compounds of NH_4^+ and the alkali metal cations
	OH^-	Compounds of NH_4^+, the alkali metal cations, Ca^{2+}, Sr^{2+}, and Ba^{2+}

Sample Exercise 4.2: Using Solubility Rules

- Classify as soluble or insoluble:
  - A) sodium carbonate
  - B) lead (II) sulfate
  - C) cobalt (II) hydroxide
  - D) barium nitrate
  - E) ammonium phosphate

Practice Exercise 1

Which of the following compounds is insoluble in water?

(a) $(NH_4)_2S$
(b) $CaCO_3$
(c) $NaOH$
(d) Ag_2SO_4
(e) $Pb(CH_3COO)_2$

Metathesis (Exchange) Reactions (Double Replacement)

- Metathesis comes from a Greek word that means "to transpose."
- It appears the ions in the reactant compounds exchange, or transpose, ions.

$$\mathbf{Ag}NO_3\,(aq) + K\mathbf{Cl}\,(aq) \longrightarrow \mathbf{AgCl}\,(s) + KNO_3\,(aq)$$

Completing and Balancing Metathesis Equations

- Steps to follow

1) Use the chemical formulas of the reactants to determine which ions are present.
2) Write formulas for the products: cation from one reactant, anion from the other. Use charges to write proper subscripts.
3) Check your solubility rules. If either product is insoluble, a precipitate forms.
4) Balance the equation.

Solution Chemistry

- It is helpful to pay attention to *exactly* what species are present in a reaction mixture (i.e., solid, liquid, gas, aqueous solution).
- If we are to understand reactivity, we must be aware of just what is changing during the course of a reaction.

Sample Exercise 4.3 & Practice Exercises

1) Write a balanced equation, predicting the precipitate, when solutions of $BaCl_2$ and K_2SO_4 are mixed.
2) Will a precipitate form when barium nitrate and potassium hydroxide are mixed?
3) Write a balanced equation, predicting the precipitate, when solutions of $Fe_2(SO_4)_3$ and LiOH are mixed.

Ways to Write Metathesis Reactions

1) Molecular equation
2) Complete ionic equation
3) Net ionic equation

Molecular Equation

The **molecular equation** lists the reactants and products in their molecular form.

$$Pb(NO_3)_2\,(aq) + 2\,KI\,(aq) \longrightarrow PbI_2\,(s) + 2\,KNO_3\,(aq)$$

Ionic Equation

- In the **ionic equation** all strong electrolytes (strong acids, strong bases, and soluble ionic salts) are dissociated into their ions.
- This more accurately reflects the species that are found in the reaction mixture.

$$Pb^{+2}\,(aq) + 2\,NO_3^-\,(aq) + 2\,K^+\,(aq) + 2\,I^-\,(aq) \longrightarrow$$
$$PbCl_2\,(s) + 2\,K^+\,(aq) + 2\,NO_3^-\,(aq)$$

Net Ionic Equation

- To form the net ionic equation, cross out anything that does not change from the left side of the equation to the right.
- The only things left in the equation are those things that change (i.e., react) during the course of the reaction.
- Those things that didn't change (and were deleted from the net ionic equation) are called **spectator ions**.

$$Pb^{+2}\,(aq) + 2\,\cancel{NO_3^{-}}\,(aq) + \cancel{2\,K^{+}}\,(aq) + 2\,I^{-}\,(aq) \longrightarrow$$

$$PbCl_2\,(s) + \cancel{2\,K^{+}}\,(aq) + \cancel{2\,NO_3^{-}}\,(aq)$$

Which ions, if any, are spectator ions in this reaction?

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

a. $Ag^{+}(aq)$ and $Cl^{-}(aq)$

b. $NO_3^{-}(aq)$ and $Cl^{-}(aq)$

c. $Na^{+}(aq)$ and $NO_3^{-}(aq)$

d. No spectator ions are involved.

Writing Net Ionic Equations

1. Write a balanced molecular equation.
2. Dissociate all strong electrolytes.
3. Cross out anything that remains unchanged from the left side to the right side of the equation.
4. Write the net ionic equation with the species that remain.

Sample Exercise 4.4: Writing a Net Ionic Equation

1) Write the molecular, complete ionic and net ionic equations for mixing solutions of calcium chloride and sodium carbonate.
2) Write the molecular, complete ionic and net ionic equations for mixing solutions of silver nitrate and potassium phosphate.

Practice Exercise 1

- What happens when you mix an aqueous solution of sodium nitrate with an aqueous solution of barium chloride?

(a) There is no reaction; all possible products are soluble.

- **(b)** Only barium nitrate precipitates

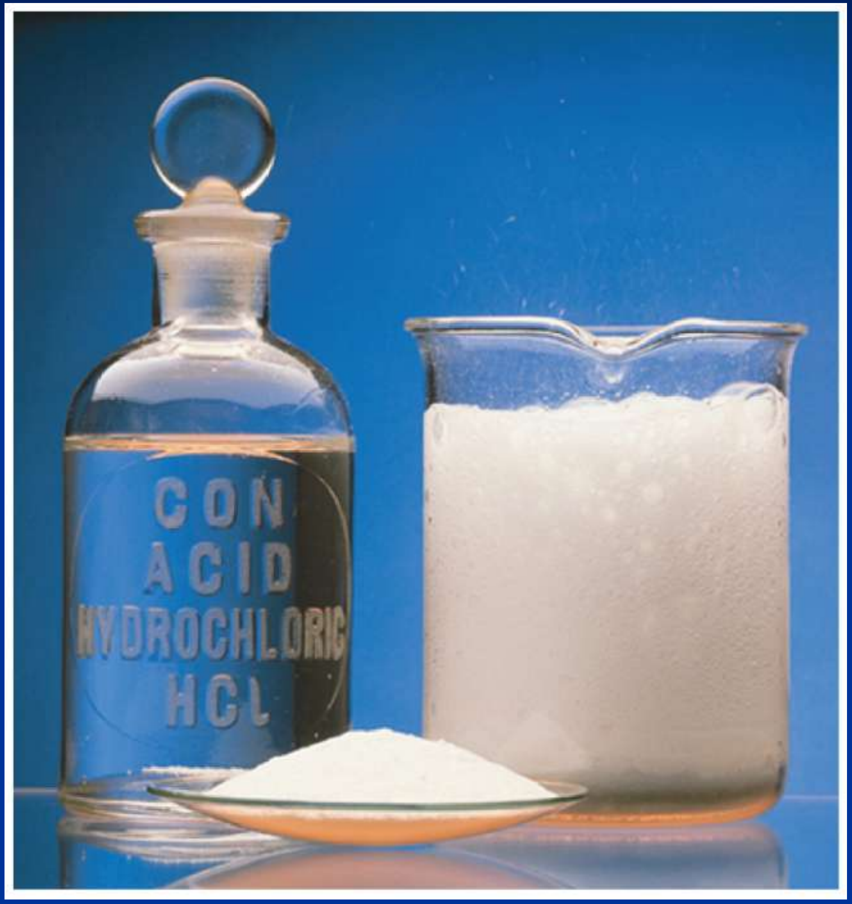
(c) Only sodium chloride precipitates

(d) Both barium nitrate and sodium chloride precipitate

(e) Nothing; barium chloride is not soluble

4.3 Acids, Bases, and Neutralization Reactions

Acids



- **Arrhenius** defined acids as substances that increase the concentration of H^+ when dissolved in water.
- **Brønsted and Lowry** defined them as proton donors.

Acids

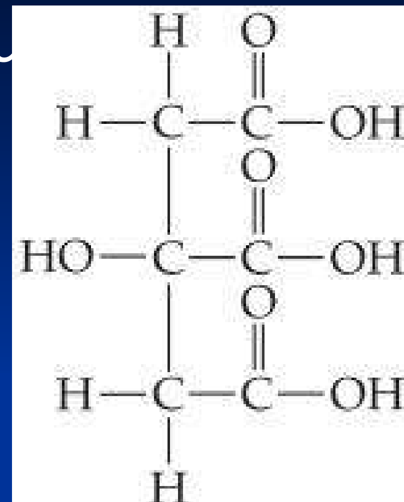
There are only seven strong acids:

- Hydrochloric (HCl)
- Hydrobromic (HBr)
- Hydroiodic (HI)
- Nitric (HNO_3)
- Sulfuric (H_2SO_4)
- Chloric ($HClO_3$)
- Perchloric ($HClO_4$)

Acids

- Monoprotic
- Polyprotic
  - Occurs in two or more steps
- Ionizable Hs

The structural formula of citric acid, a main component of citru



How many $H^+(aq)$ can be generated by each citric acid molecule dissolved in water?

a. 0

b. 1

c. 2

d. 3

Bases

- **Arrhenius** defined bases as substances that increase the concentration of OH^- when dissolved in water.
- **Brønsted and Lowry** defined them as proton acceptors.

Bases

The strong bases are the soluble metal salts of hydroxide ion:

- Alkali metals
- Calcium
- Strontium
- Barium

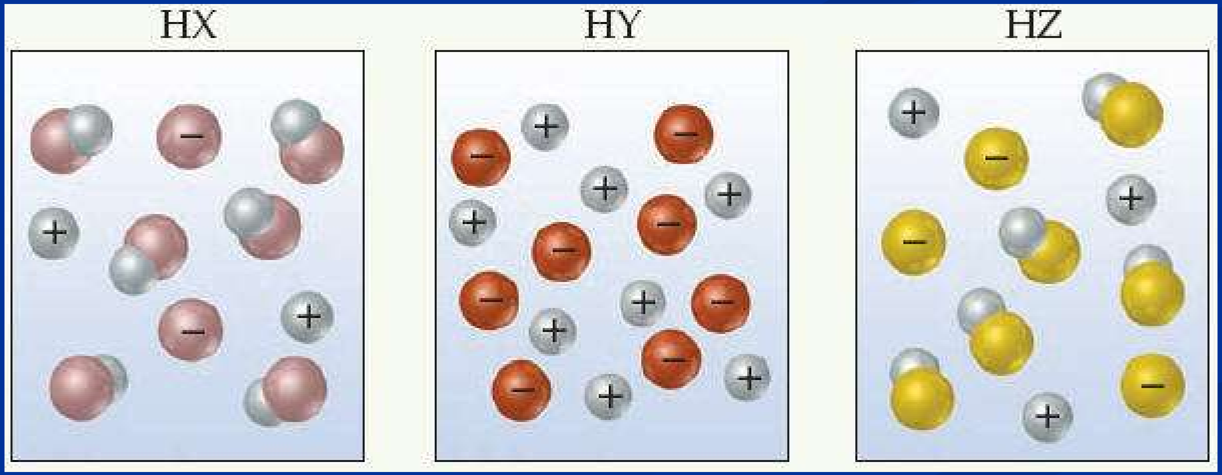
Why isn't $Al(OH)_3$ classified as a strong base?

a. $Al(OH)_3$ is not basic in water.
b. $Al(OH)_3$ is insoluble in water.
c. $Al(OH)_3$ is a strong acid in water, not basic.
d. $Al(OH)_3$ is a weak acid in water, not basic.

Which of the following is a strong acid: H_2SO_3, HBr, CH_3COOH?

Sample Exercise 4.5 Comparing Acid Strengths

The following diagrams represent aqueous solutions of three acids (HX, HY, and HZ) with water molecules omitted for clarity. Rank them from strongest to weakest.



Practice Exercise 1

A set of aqueous solutions are prepared containing different acids at the same concentration: acetic acid, chloric acid and hydrobromic acid. Which solution(s) are the most electrically conductive?

(a) chloric acid

(b) hydrobromic acid

(c) acetic acid

(d) both chloric acid and hydrobromic acid

(e) all three solutions have the same electrical conductivity.

Sample Exercise 4.5 Writing a Net Ionic Equation

Practice Exercise 2

Imagine a diagram showing 10 Na^+ ions and 10 OH^- ions. If this solution were mixed with the one pictured on the previous slide for HY, what would the diagram look like that represents the solution after any possible reaction? (H^+ ions will react with ions to form H_2O.)

Sample Exercise 4.6: Classify the following as a strong electrolyte, weak electrolyte, or nonelectrolyte

- $CaCl_2$
- HNO_3
- C_2H_5OH
- HCOOH
- KOH

Practice Exercise 1

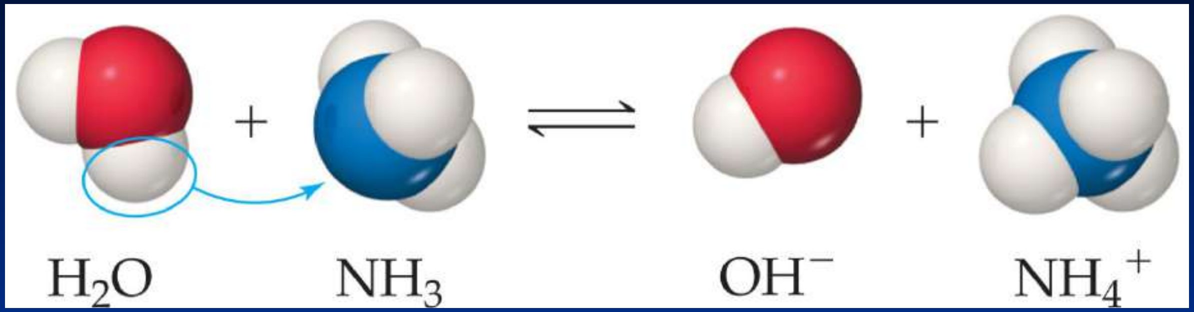
Which of these substances, when dissolved in water, is a strong electrolyte?

(a) ammonia
(b) hydrofluoric acid
(c) folic acid
(d) sodium nitrate
(e) sucrose

Practice Exercise 2

Consider solutions in which 0.1 mol of each of the following compounds is dissolved in 1 L of water: $Ca(NO_3)_2$, $C_6H_{12}O_6$, $NaCH_3COO$, CH_3COOH. Rank the solutions in order of increasing electrical conductivity, based on the fact that the greater the number of ions in solution, the greater the conductivity.

Acid-Base Reactions



- In an acid–base reaction, the acid (H_2O above) donates a proton (H^+) to the base (NH_3 above).
- Reactions between an acid and a base are called **neutralization reactions**.
- When the base is a metal hydroxide, water and a **salt** (an ionic compound) are produced.

Neutralization Reactions

When a strong acid (like HCl) reacts with a strong base (like NaOH), the net ionic equation is circled below:

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

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

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

Sample Exercise 4.7

1. Write a balanced molecular equation for the reaction between aqueous solutions of acetic acid CH_3COOH and barium hydroxide $Ba(OH)_2$. Then write the net ionic equation.
2. Write a balanced molecular equation for the reaction between aqueous solutions of phosphorous acid H_3PO_4 and potassium hydroxide KOH. Then write the net ionic equation.

Practice Exercise 1

Which is the correct net ionic equation for the reaction of aqueous ammonia with nitric acid?

(a) $NH_4^+(aq) + H^+(aq) \longrightarrow NH_5^{2+}(aq)$
(b) $NH_3(aq) + NO_3^-(aq) \longrightarrow NH_2^-(aq) + HNO_3(aq)$
(c) $NH_2^-(aq) + H^+(aq) \longrightarrow NH_3(aq)$
(d) $NH_3(aq) + H^+(aq) \longrightarrow NH_4^+(aq)$
(e) $NH_4^+(aq) + NO_3^-(aq) \longrightarrow NH_4NO_3(aq)$

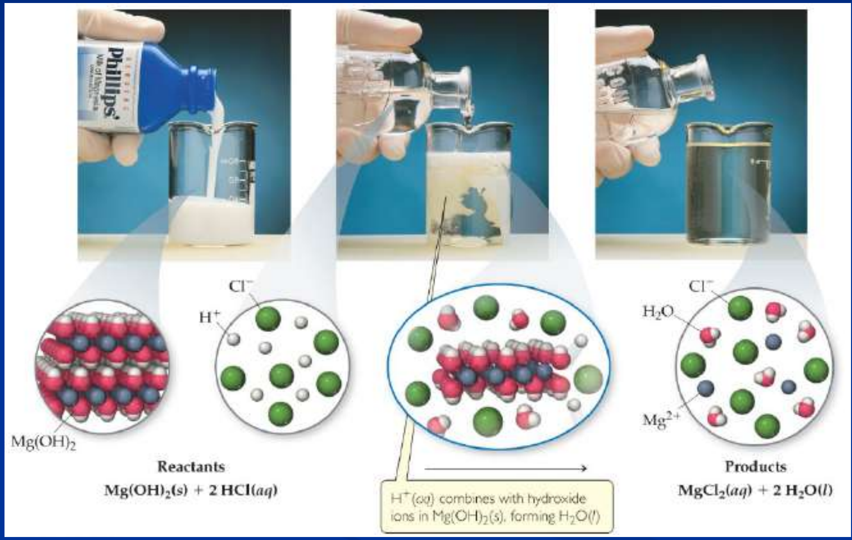
Adding just a few drops of hydrochloric acid would not be sufficient to dissolve all the $Mg(OH)_2(s)$. Why not?

a. Insufficient chloride ions are added to react with all of the solid magnesium hydroxide.

b. Insufficient hydrogen ions are added to react with all of the solid magnesium hydroxide.

c. Magnesium hydroxide reacts only slowly with hydrochloric acid.

d. A neutralization reaction does not occur.



Gas-Forming Reactions

- Some metathesis reactions do not give the product expected.
- In this reaction, the expected product (H_2CO_3) decomposes to give a gaseous product (CO_2).

$$CaCO_3\,(s) + HCl\,(aq) \longrightarrow CaCl_2\,(aq) + CO_2\,(g) + H_2O\,(l)$$

Gas-Forming Reactions

When a carbonate or bicarbonate reacts with an acid, the products are a salt, carbon dioxide, and water.

$$CaCO_3\ (s) + HCl\ (aq) \longrightarrow CaCl_2\ (aq) + CO_2\ (g) + H_2O\ (l)$$

$$NaHCO_3\ (aq) + HBr\ (aq) \longrightarrow NaBr\ (aq) + CO_2\ (g) + H_2O\ (l)$$

Gas-Forming Reactions

Similarly, when a sulfite reacts with an acid, the products are a salt, sulfur dioxide, and water.

$$SrSO_3\ (s) + 2\ HI\ (aq) \longrightarrow SrI_2\ (aq) + SO_2\ (g) + H_2O\ (l)$$

Gas-Forming Reactions

- This reaction gives the predicted product, but you had better carry it out in the hood, or you will be *very* unpopular!
- But just as in the previous examples, a gas is formed as a product of this reaction.

$$Na_2S\ (aq) + H_2SO_4\ (aq) \longrightarrow Na_2SO_4\ (aq) + H_2S\ (g)$$

By analogy to examples given in the text, predict what gas forms when Na_2SO_3(*s*) reacts with HCl(*aq*).

a. SO_2(*g*)

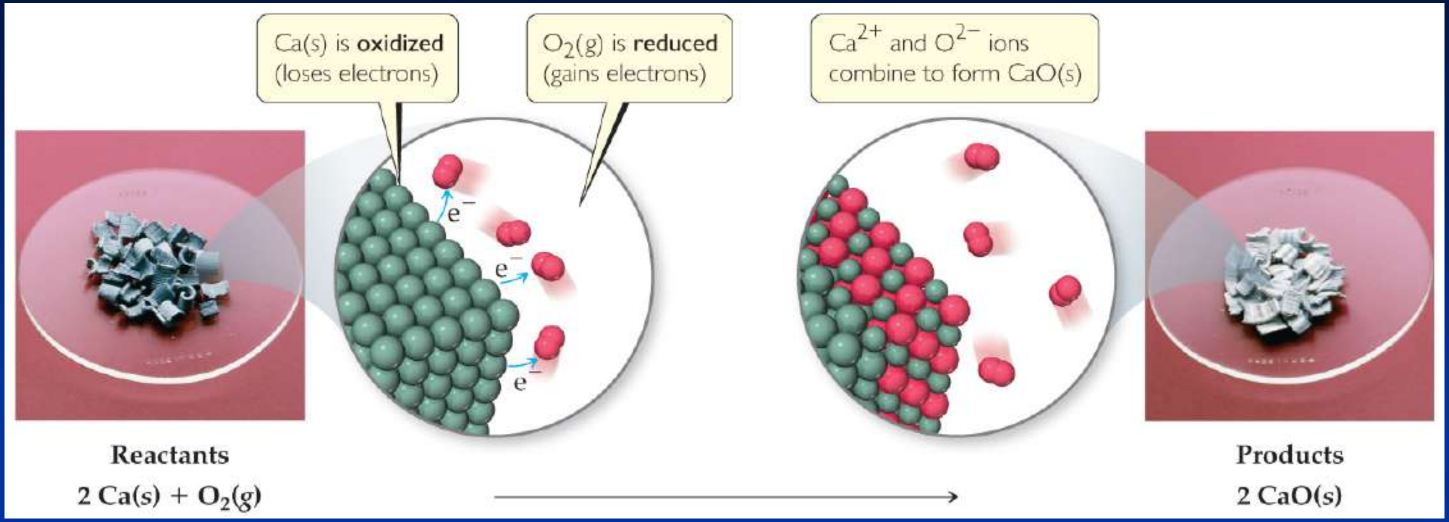
b. H_2(*g*)

c. CO_2(*g*)

d. H_2S(*g*)

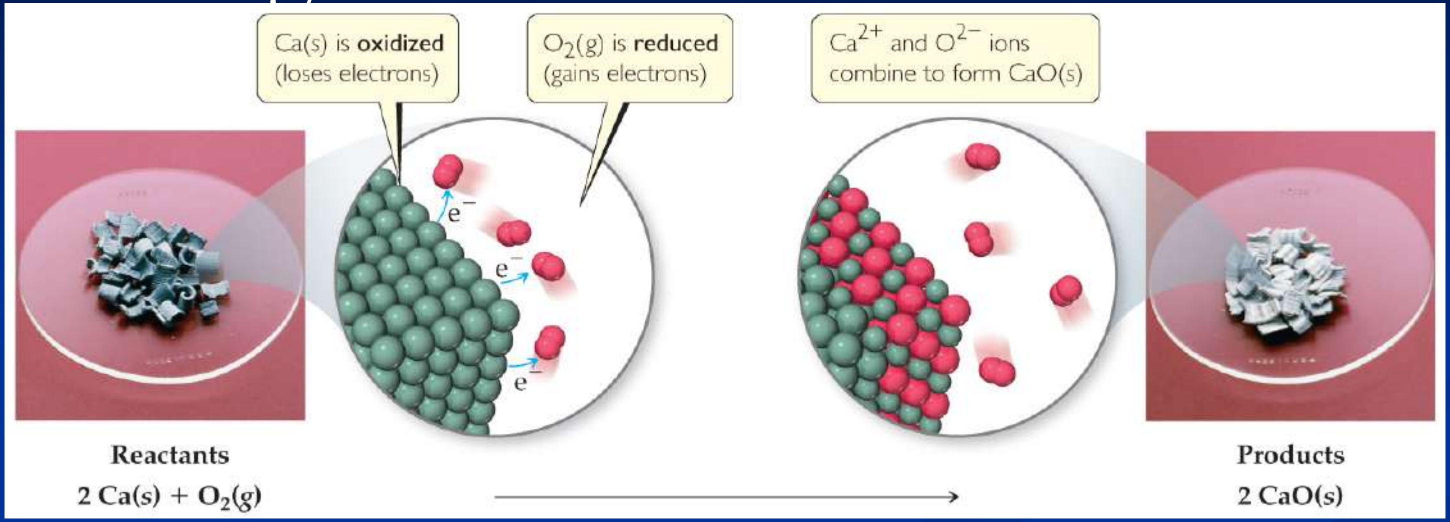
4.4 Oxidation-Reduction Reactions

Oxidation-Reduction Reactions



- Loss of electrons is **oxidation.**
- Gain of electrons is **reduction.**
- One cannot occur without the other.
- The reactions are often called **redox reactions.**

How many electrons does each oxygen atom gain during the course of this reaction?



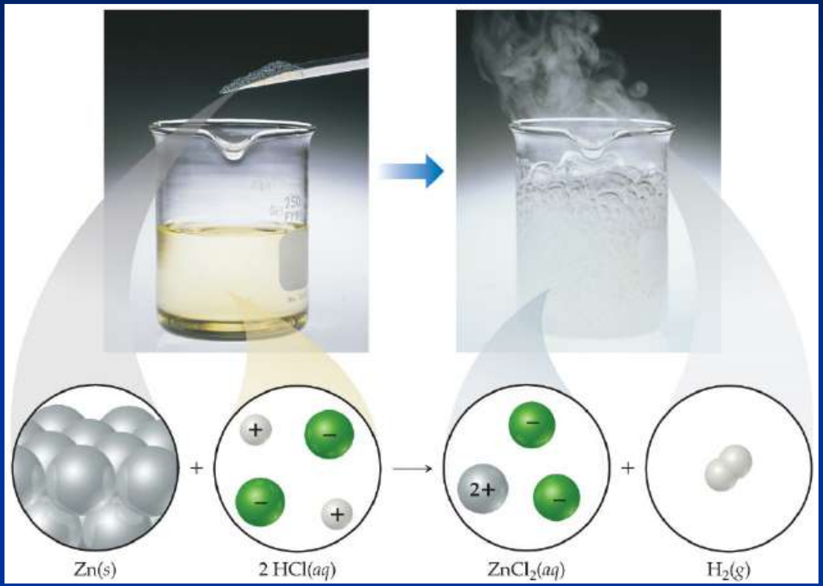
a. None

b. One

c. Two

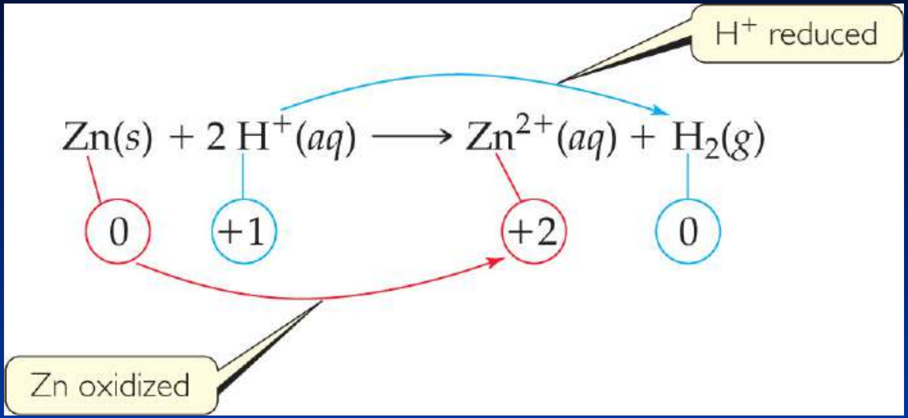
d. Four

Oxidation Numbers



- To keep track of what loses electrons and what gains them, we assign **oxidation numbers**.
- If the oxidation number increases for an element, that element is oxidized.
- If the oxidation number decreases for an element, that element is reduced.

Oxidation and Reduction



- A species is **oxidized** when it loses electrons.
  - Zinc loses two electrons, forming the Zn^{2+} ion.
- A species is **reduced** when it gains electrons.
  - H^+ gains an electron, forming H_2.
- An **oxidizing agent** causes something else to be oxidized (H^+); a **reducing agent** causes something else to be reduced (Zn).

Assigning Oxidation Numbers

1. Elements in their elemental form have an oxidation number of 0.
2. The oxidation number of a monatomic ion is the same as its charge.

Assigning Oxidation Numbers

3. Nonmetals tend to have negative oxidation numbers, although some are positive in certain compounds or ions.
   - Oxygen has an oxidation number of −2, except in the peroxide ion, which has an oxidation number of −1.
   - Hydrogen is −1 when bonded to a metal and +1 when bonded to a nonmetal.

Assigning Oxidation Numbers

3. Nonmetals tend to have negative oxidation numbers, although some are positive in certain compounds or ions.
   - Fluorine always has an oxidation number of −1.
   - The other halogens have an oxidation number of −1 when they are negative; they can have positive oxidation numbers, however, most notably in oxyanions.

Assigning Oxidation Numbers

4. The sum of the oxidation numbers in a neutral compound is 0.
5. The sum of the oxidation numbers in a polyatomic ion is the charge on the ion.

What is the oxidation number of nitrogen in aluminum nitride, AlN?

a. +1
b. –1
c. –2
d. –3

What is the oxidation number of nitrogen in nitric acid, HNO_3?

a. +6

b. +5

c. +4

d. –1

Sample Exercise 4.8

- Determine the oxidation number of sulfur in each of the following:
- H_2S
- S_8
- SCl_2
- Na_2SO_3
- SO_4^{2-}

Practice Exercise 1

In which compound is the oxidation state of oxygen –1?

(a) O_2

(b) H_2O

(c) H_2SO_4

(d) H_2O_2

(e) KCH_3COO

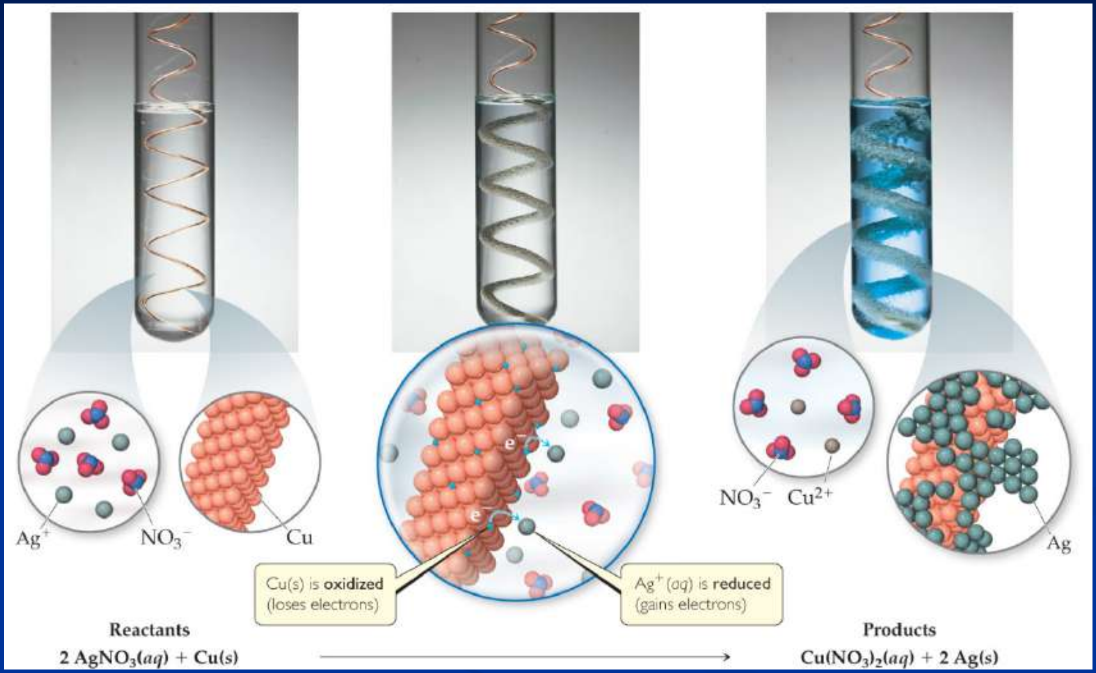
Practice Exercise 2

What is the oxidation state of the boldfaced element in each of the following: **(a)** $\mathbf{P}_2O_5$, **(b)** $Na\mathbf{H}$, **(c)** $\mathbf{Cr}_2O_7^{2-}$, **(d)** $\mathbf{Sn}Br_4$, **(e)** $Ba\mathbf{O}_2$?

Displacement Reactions

In **displacement reactions**, ions oxidize an element.

In this reaction, silver ions oxidize copper metal:



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

The reverse reaction does NOT occur. Why not?

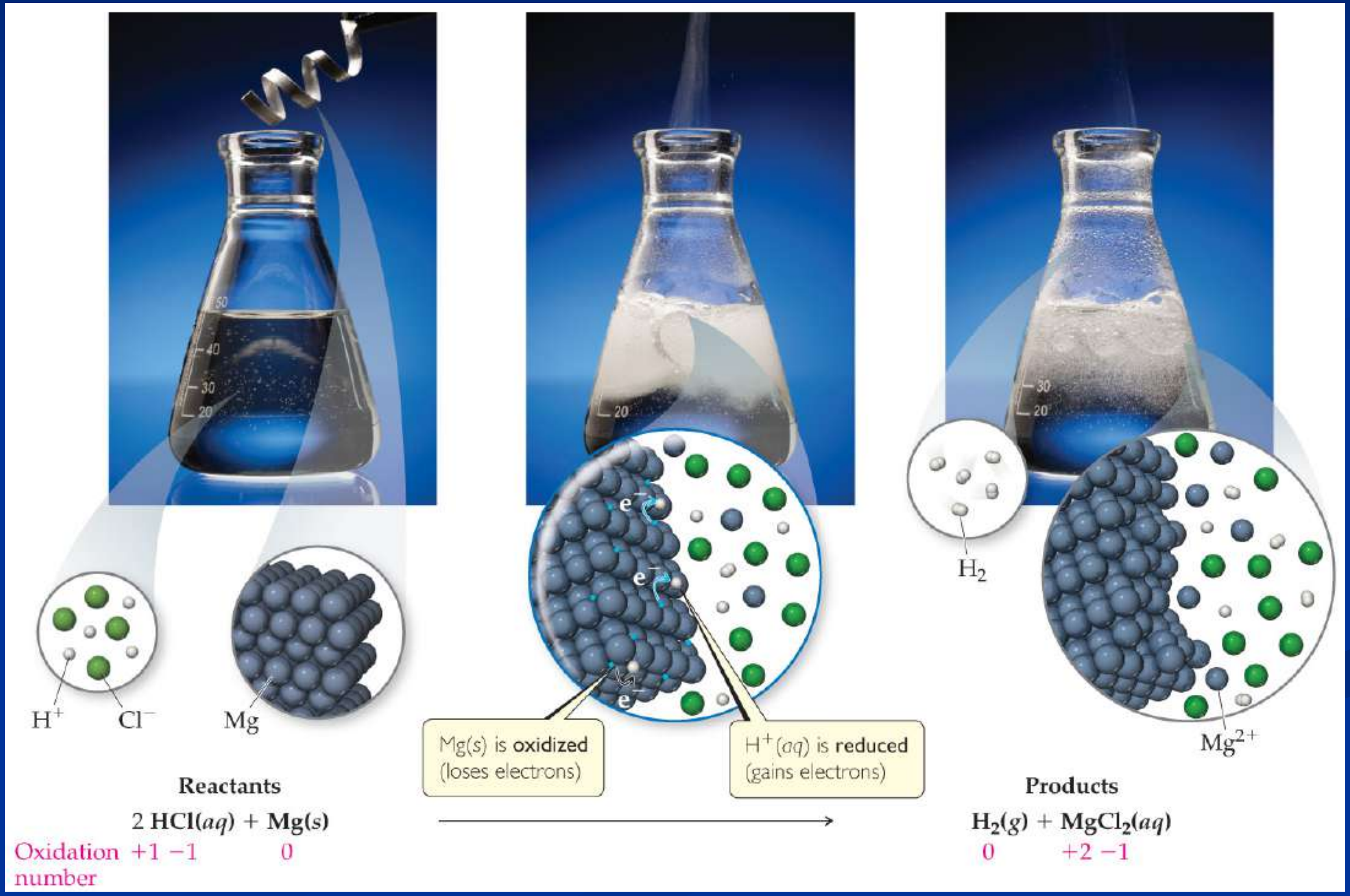
How many moles of hydrogen gas would be produced for every mole of magnesium added into the HCl solution?

a. None

b. One

c. Two

d. Four



Sample Exercise 4.9

- 1)Write the balanced molecular and net ionic equations for the reaction of aluminum with hydrobromic acid.

Practice Exercise 1

Which of the following statements is true about the reaction between zinc and copper sulfate?

(a) Zinc is oxidized, and copper on is reduced.

(b) Zinc is reduced, and copper ion is oxidized

(c) All reactants and products are soluble strong electrolytes

(d) The oxidation state of copper in copper sulfate is 0

(e) More than one of the previous choices are true.

Practice Exercise 2

- Write the balanced molecular and net ionic equations for the reaction between magnesium and cobalt (II) sulfate. What is oxidized and what is reduced?

Activity Series

Table 4.5 Activity Series of Metals in Aqueous Solution

Metal	Oxidation Reaction
Lithium	$Li(s) \longrightarrow Li^{+}(aq) + e^{-}$
Potassium	$K(s) \longrightarrow K^{+}(aq) + e^{-}$
Barium	$Ba(s) \longrightarrow Ba^{2+}(aq) + 2e^{-}$
Calcium	$Ca(s) \longrightarrow Ca^{2+}(aq) + 2e^{-}$
Sodium	$Na(s) \longrightarrow Na^{+}(aq) + e^{-}$
Magnesium	$Mg(s) \longrightarrow Mg^{2+}(aq) + 2e^{-}$
Aluminum	$Al(s) \longrightarrow Al^{3+}(aq) + 3e^{-}$
Manganese	$Mn(s) \longrightarrow Mn^{2+}(aq) + 2e^{-}$
Zinc	$Zn(s) \longrightarrow Zn^{2+}(aq) + 2e^{-}$
Chromium	$Cr(s) \longrightarrow Cr^{3+}(aq) + 3e^{-}$
Iron	$Fe(s) \longrightarrow Fe^{2+}(aq) + 2e^{-}$
Cobalt	$Co(s) \longrightarrow Co^{2+}(aq) + 2e^{-}$
Nickel	$Ni(s) \longrightarrow Ni^{2+}(aq) + 2e^{-}$
Tin	$Sn(s) \longrightarrow Sn^{2+}(aq) + 2e^{-}$
Lead	$Pb(s) \longrightarrow Pb^{2+}(aq) + 2e^{-}$
Hydrogen	$H_2(g) \longrightarrow 2H^{+}(aq) + 2e^{-}$
Copper	$Cu(s) \longrightarrow Cu^{2+}(aq) + 2e^{-}$
Silver	$Ag(s) \longrightarrow Ag^{+}(aq) + e^{-}$
Mercury	$Hg(l) \longrightarrow Hg^{2+}(aq) + 2e^{-}$
Platinum	$Pt(s) \longrightarrow Pt^{2+}(aq) + 2e^{-}$
Gold	$Au(s) \longrightarrow Au^{3+}(aq) + 3e^{-}$

Ease of oxidation increases

- Elements higher on the activity series are more reactive.
- They are more likely to exist as ions.

Metal/Acid Displacement Reactions

- The elements above hydrogen will react with acids to produce hydrogen gas.
- The metal is oxidized to a cation.

Does a reaction occur when an aqueous solution of $NiCl_2(aq)$ is added to a test tube containing strips of metallic zinc?

a. Yes

b. No

Table 4.5 Activity Series of Metals in Aqueous Solution

Metal	Oxidation Reaction
Lithium	$Li(s) \longrightarrow Li^{+}(aq) + e^{-}$
Potassium	$K(s) \longrightarrow K^{+}(aq) + e^{-}$
Barium	$Ba(s) \longrightarrow Ba^{2+}(aq) + 2e^{-}$
Calcium	$Ca(s) \longrightarrow Ca^{2+}(aq) + 2e^{-}$
Sodium	$Na(s) \longrightarrow Na^{+}(aq) + e^{-}$
Magnesium	$Mg(s) \longrightarrow Mg^{2+}(aq) + 2e^{-}$
Aluminum	$Al(s) \longrightarrow Al^{3+}(aq) + 3e^{-}$
Manganese	$Mn(s) \longrightarrow Mn^{2+}(aq) + 2e^{-}$
Zinc	$Zn(s) \longrightarrow Zn^{2+}(aq) + 2e^{-}$
Chromium	$Cr(s) \longrightarrow Cr^{3+}(aq) + 3e^{-}$
Iron	$Fe(s) \longrightarrow Fe^{2+}(aq) + 2e^{-}$
Cobalt	$Co(s) \longrightarrow Co^{2+}(aq) + 2e^{-}$
Nickel	$Ni(s) \longrightarrow Ni^{2+}(aq) + 2e^{-}$
Tin	$Sn(s) \longrightarrow Sn^{2+}(aq) + 2e^{-}$
Lead	$Pb(s) \longrightarrow Pb^{2+}(aq) + 2e^{-}$
Hydrogen	$H_2(g) \longrightarrow 2H^{+}(aq) + 2e^{-}$
Copper	$Cu(s) \longrightarrow Cu^{2+}(aq) + 2e^{-}$
Silver	$Ag(s) \longrightarrow Ag^{+}(aq) + e^{-}$
Mercury	$Hg(l) \longrightarrow Hg^{2+}(aq) + 2e^{-}$
Platinum	$Pt(s) \longrightarrow Pt^{2+}(aq) + 2e^{-}$
Gold	$Au(s) \longrightarrow Au^{3+}(aq) + 3e^{-}$

Ease of oxidation increases

Does a reaction occur when $NiCl_2(aq)$ is added to a test tube containing $Zn(NO_3)_2(aq)$?

a. Yes

b. No

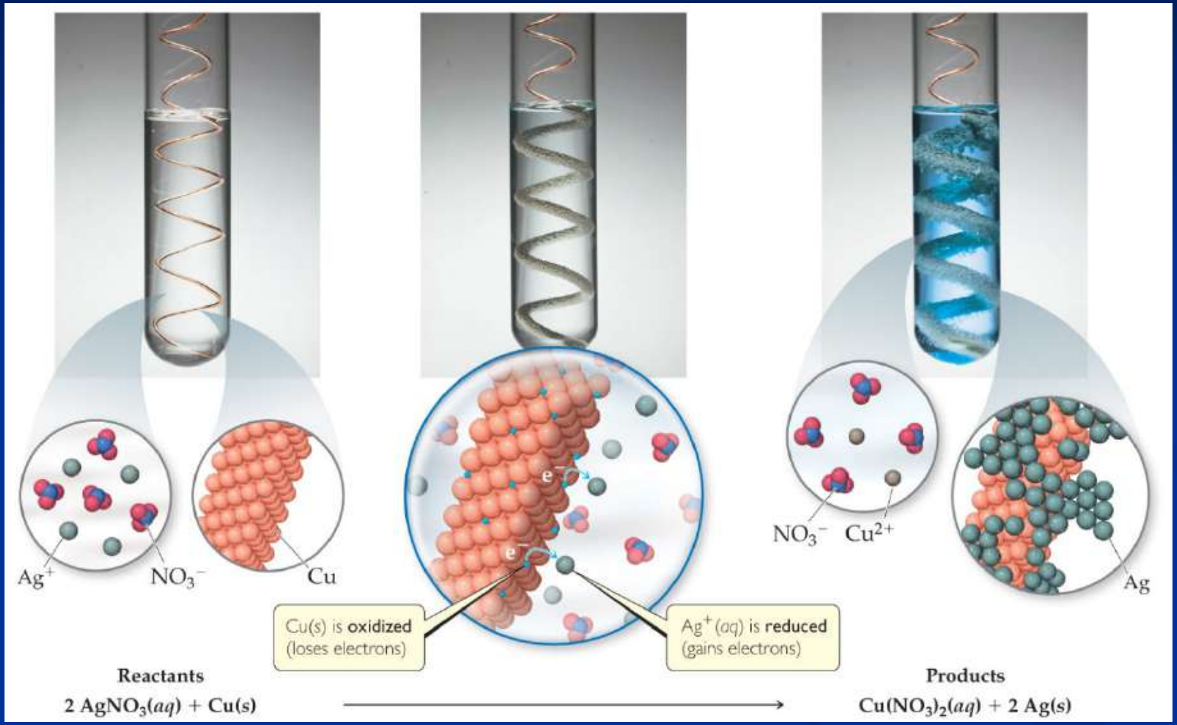
Why does the solution turn blue?

a. Cu^{2+} (*aq*) ions are blue.

b. NO_3^- (*aq*) ions are blue.

c. Ag(*s*) is blue.

d. H_2O is blue.



Sample Exercise 4.10 Determining When an Oxidation-Reduction Reaction Can Occur

Will an aqueous solution of iron(II) chloride oxidize magnesium metal? If so, write the balanced molecular and net ionic equations for the reaction.

Practice Exercise 1

Which of these metals is the easiest to oxidize?

(a) gold
(b) Lithium
(c) Iron
(d) Sodium
(e) aluminum

Practice Exercise 2

- Which of the following metals will be oxidized by $Pb(NO_3)_2$: Zn, Cu, Fe?

20.2 Balancing Oxidation-Reduction Reactions

Half-Reactions

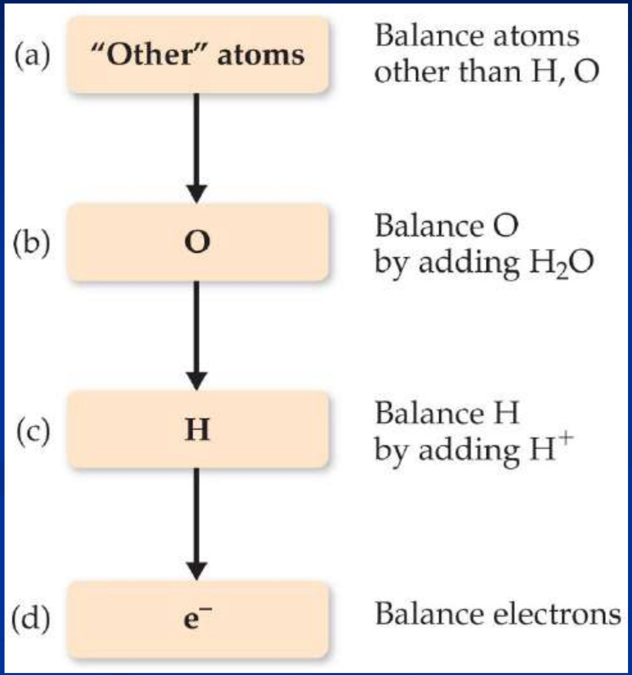
- The oxidation and reduction are written and balanced separately.
- We will use them to balance a redox reaction.
- For example, when Sn^{2+} and Fe^{3+} react,

$$\textit{Oxidation:} \quad Sn^{2+}(aq) \longrightarrow Sn^{4+}(aq) + 2e^-$$

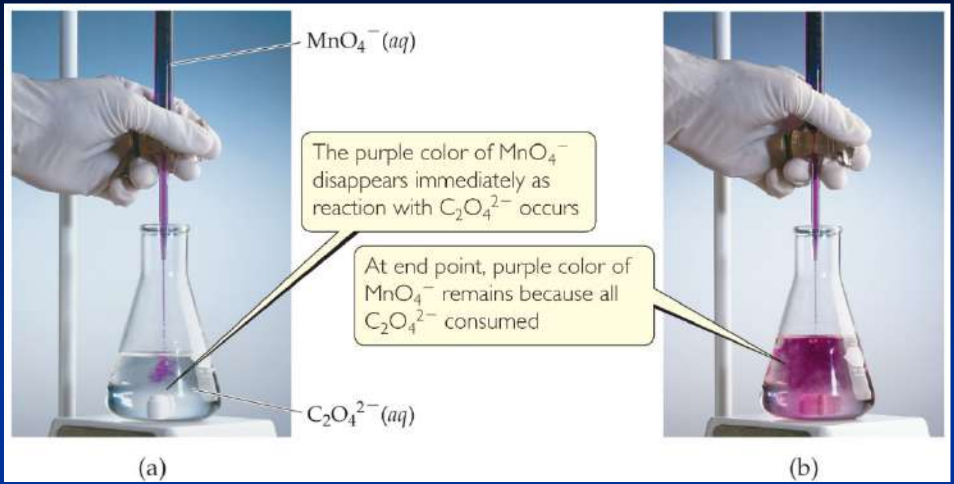
$$\textit{Reduction:} \quad 2\,Fe^{3+}(aq) + 2e^- \longrightarrow 2\,Fe^{2+}(aq)$$

Balancing Redox Equations: The Half-Reactions Method (a Synopsis)

1) Make two half-reactions (oxidation and reduction).
2) Balance atoms other than O and H. Then, balance O and H using H_2O/H^+.
3) Add electrons to balance charges.
4) Multiply by common factor to make electrons in half-reactions equal.
5) Add the half-reactions.
6) Simplify by dividing by common factor or converting H^+ to OH^- if basic.
7) Double-check atoms and charges balance!



The Half-Reaction Method



Consider the reaction between MnO_4^- and $C_2O_4^{2-}$:

$$MnO_4^-(aq) + C_2O_4^{2-}(aq) \longrightarrow Mn^{2+}(aq) + CO_2(aq)$$

- Assigning oxidation numbers shows that Mn is reduced $(+7 \rightarrow +2)$ and C is oxidized $(+3 \rightarrow +4)$.

Oxidation Half-Reaction

$$C_2O_4^{2-} \longrightarrow CO_2$$

To balance the carbon, we add a coefficient of 2:

$$C_2O_4^{2-} \longrightarrow 2\ CO_2$$

Oxidation Half-Reaction

$$C_2O_4^{2-} \longrightarrow 2\ CO_2$$

The oxygen is now balanced as well. To balance the charge, we must add two electrons to the right side:

$$C_2O_4^{2-} \longrightarrow 2\ CO_2 + 2e^-$$

Reduction Half-Reaction

$$MnO_4^- \longrightarrow Mn^{2+}$$

The manganese is balanced; to balance the oxygen, we must add four waters to the right side:

$$MnO_4^- \longrightarrow Mn^{2+} + 4\ H_2O$$

Reduction Half-Reaction

$$MnO_4^- \longrightarrow Mn^{2+} + 4\ H_2O$$

To balance the hydrogen, we add $8H^+$ to the left side:

$$8\ H^+ + MnO_4^- \longrightarrow Mn^{2+} + 4\ H_2O$$

Reduction Half-Reaction

$$8\ H^+ + MnO_4^- \longrightarrow Mn^{2+} + 4\ H_2O$$

To balance the charge, we add $5e^-$ to the left side:

$$5e^- + 8\ H^+ + MnO_4^- \longrightarrow Mn^{2+} + 4\ H_2O$$

Combining the Half-Reactions

Now we combine the two half-reactions together:

$$C_2O_4^{2-} \longrightarrow 2\ CO_2 + 2e^-$$

$$5e^- + 8\ H^+ + MnO_4^- \longrightarrow Mn^{2+} + 4\ H_2O$$

To make the number of electrons equal on each side, we will multiply the first reaction by 5 and the second by 2:

Combining the Half-Reactions

$$5\ C_2O_4^{2-} \longrightarrow 10\ CO_2 + 10e^-$$

$$10e^- + 16\ H^+ + 2\ MnO_4^- \longrightarrow 2\ Mn^{2+} + 8\ H_2O$$

When we add these together, we get

$$10e^- + 16\ H^+ + 2\ MnO_4^- + 5\ C_2O_4^{2-} \longrightarrow$$
$$2\ Mn^{2+} + 8\ H_2O + 10\ CO_2 + 10e^-$$

Combining the Half-Reactions

$$10e^{-} + 16\ H^{+} + 2\ MnO_4^{-} + 5\ C_2O_4^{2-} \longrightarrow$$
$$2\ Mn^{2+} + 8\ H_2O + 10\ CO_2 + 10e^{-}$$

The only thing that appears on both sides is the electrons. Subtracting them, we are left with

$$16\ H^{+} + 2\ MnO_4^{-} + 5\ C_2O_4^{2-} \longrightarrow$$
$$2\ Mn^{2+} + 8\ H_2O + 10\ CO_2$$

(Verify that the equation is balanced by counting atoms and charges on each side of the equation.)

Sample Exercise 20.2 Balancing Redox Equations in Acidic Solution

Complete and balance this equation by the method of half-reactions:

$$Cr_2O_7^{2-}(aq) + Cl^-(aq) \longrightarrow Cr^{3+}(aq) + Cl_2(g) \quad \text{(acidic solution)}$$

Practice Exercise 1

If you complete and balance the following equation in acidic solution

$$Mn^{2+}(aq) + NaBiO_3(s) \rightarrow Bi^{3+}(aq) + MnO_4^{-}(aq) + Na^{+}(aq)$$

how many water molecules are there in the balanced equation (for the reaction balanced with the smallest whole-number coefficients)? **(a)** Four on the reactant side, **(b)** Three on the product side, **(c)** One on the reactant side, **(d)** Seven on the product side, **(e)** Two on the product side.

Practice Exercise 2

Complete and balance the following equations using the method of half-reactions. Both reactions occur in acidic solution.

(a) $Cu(s) + NO_3^-(aq) \longrightarrow Cu^{2+}(aq) + NO_2(g)$

(b) $Cr_2O_7^{2-} + H_2S \rightarrow Cr^{2+} + S$

Balancing in Basic Solution

- A reaction that occurs in basic solution can be balanced as if it occurred in acid.
- Once the equation is balanced, add OH^- to each side to "neutralize" the H^+ in the equation and create water in its place.
- If this produces water on both sides, subtract water from each side so it appears on only one side of the equation.

Sample Exercise 20.3 Balancing Redox Equations in Basic Solution

Complete and balance this equation for a redox reaction that takes place in basic solution:

$$CN^-(aq) + MnO_4^-(aq) \longrightarrow CNO^-(aq) + MnO_2(s) \qquad \text{(basic solution)}$$

Practice Exercise 1

If you complete and balance the following oxidation–reduction reaction in basic solution

$$NO_2^-\,(aq) + Al(s) \rightarrow NH_3(aq) + Al(OH)_4^-\,(aq)$$

how many hydroxide ions are there in the balanced equation (for the reaction balanced with the smallest whole-number coefficients)?
(a) One on the reactant side, **(b)** One on the product side, **(c)** Four on the reactant side, **(d)** Seven on the product side, **(e)** None

Practice Exercise 2

Complete and balance the following equations for oxidation-reduction reactions that occur in basic solution:

$$Cr(OH)_3(s) + ClO^-(aq) \longrightarrow CrO_4^{2-}(aq) + Cl_2(g)$$

(b) $Pb(OH)_3^- + OCl^- \rightarrow PbO_2 + Cl^-$

4.5 Concentrations of Solutions

Molarity

- Two solutions can contain the same compounds but be quite different because the proportions of those compounds are different.
- Molarity is one way to measure the concentration of a solution.

$$\text{Molarity } (M) = \frac{\text{moles of solute}}{\text{volume of solution in liters}}$$

Which is more concentrated, a solution prepared by dissolving 21.0 g of NaF (0.500 mol) in enough water to make 500 mL of solution or a solution prepared by dissolving 10.5 g (0.250 mol) of NaF in enough water to make 100 mL of solution?

a. 21.0 g of NaF dissolved in water to make 500 mL of solution

b. 10.5 g of NaF dissolved in water to make 100 mL of solution

Sample Exercise 4.11

1) Calculate the molarity of a solution made by dissolving 23.4 g of sodium sulfate in enough water to form 125 mL of solution.
2) Calculate the molarity of a solution made by dissolving 5.00 g glucose ($C_6H_{12}O_6$) in sufficient water to form exactly 100 mL of solution.

Practice Exercise 1

What is the molarity of a solution that is made by dissolving 3.68 g of sucrose ($C_{12}H_{22}O_{11}$) in sufficient water to form 275.0 mL of solution?

(a) 13.4 M
(b) 7.43×10^{-2} M
(c) 3.91×10^{-2} M
(d) 7.43×10^{-5} M
(e) 3.91×10^{-5} M

Calculating Molar Concentration of Ions

- When an ionic compound dissolves, the relative concentrations of the ions introduced into the solution depend on the chemical formula of the compound.
- Ex. A 1.0 M solution of Na_2SO_4 would have 2.0 M Na^+ ions and 1M SO_4^{2-} ions

Sample Exercise 4.12

1) What are the molar concentrations of each of the ions present in 0.025 M aqueous solution of calcium nitrate?
2) What is the molar concentration of K^+ ions in a 0.015 M solution of potassium carbonate?

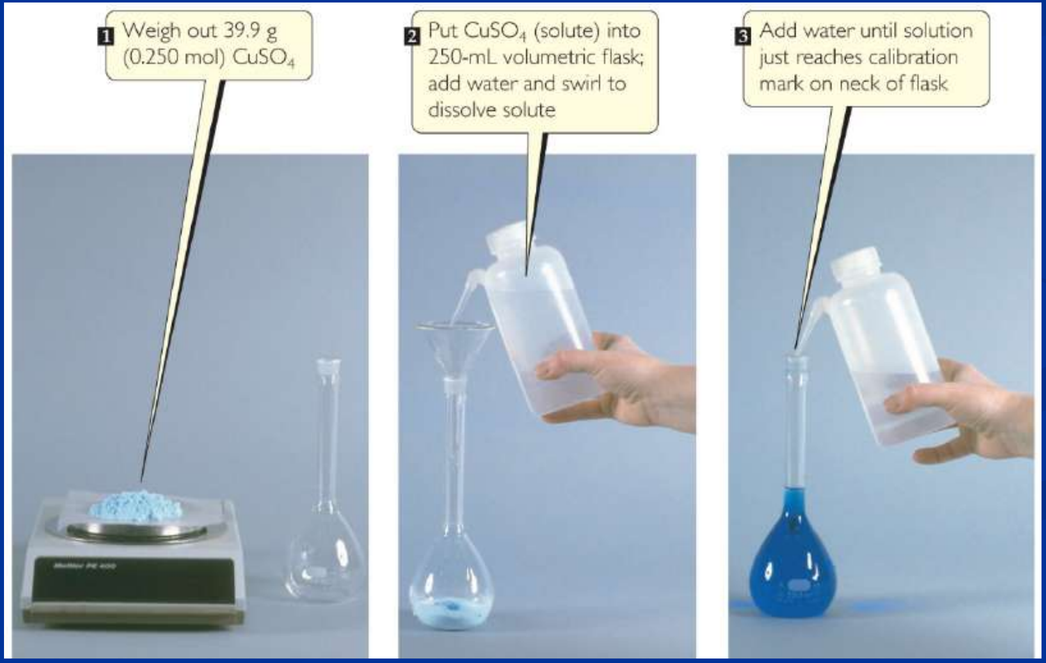
Practice Exercise 1

What is the ratio of the concentration of potassium ions to the concentration of carbonate ions in a 0.015 *M* solution of potassium carbonate?

(a) 1:0.015
(b) 0.015:1
(c) 1:1
(d) 1:2
(e) 2:1

Mixing a Solution

- To create a solution of a known molarity, weigh out a known mass (and, therefore, number of moles) of the solute.
- Then add solute to a volumetric flask, and add solvent to the line on the neck of the flask.



Sample Exercise 4.13

1) How many grams of Na_2SO_4 are required to make 0.350 L of 0.500 M Na_2SO_4?

2) How many grams of Na_2SO_4 are there in 15 mL of 0.50 M Na_2SO_4?

3) How many milliliters of 0.50 M Na_2SO_4 solution are needed to provide 0.038 mol of this salt?

Practice Exercise 1

What is the concentration of ammonia in a solution made by dissolving 3.75 g of ammonia in 120.0 L of water?

(a) 1.84×10^{-3} *M*

(b) 3.78×10^{-2} *M*

(c) 0.0313 *M*

(d) 1.84 *M*

(e) 7.05 *M*

Dilution

- One can also dilute a more concentrated solution by
  - Using a pipet to deliver a volume of the solution to a new volumetric flask, and
  - Adding solvent to the line on the neck of the new flask.

Dilution

The molarity of the new solution can be determined from the equation

$$M_c \times V_c = M_d \times V_d,$$

where M_c and M_d are the molarity of the concentrated and dilute solutions, respectively, and V_c and V_d are the volumes of the two solutions.

How is the molarity of a 0.50 *M* KBr solution changed when water is added to double its volume?

a. The concentration (molarity) remains the same.
b. The new concentration is 0.25 *M*.
c. The new concentration is 1.00 *M*.
d. The new concentration is 2.50 *M*.

Sample Exercise 4.14

How many milliliters of 3.0 M H_2SO_4 are needed to make 450 mL of 0.10 M H_2SO_4?

Practice Exercise 1

What volume of a 1.00 *M* stock solution of glucose must be used to make 500.0 mL of a 1.75×10^{-2} *M* glucose solution in water?

(a) 1.75 mL
(b) 8.75 mL
(c) 48.6 mL
(d) 57.1 mL
(e) 28,570 mL

Practice Exercise 2

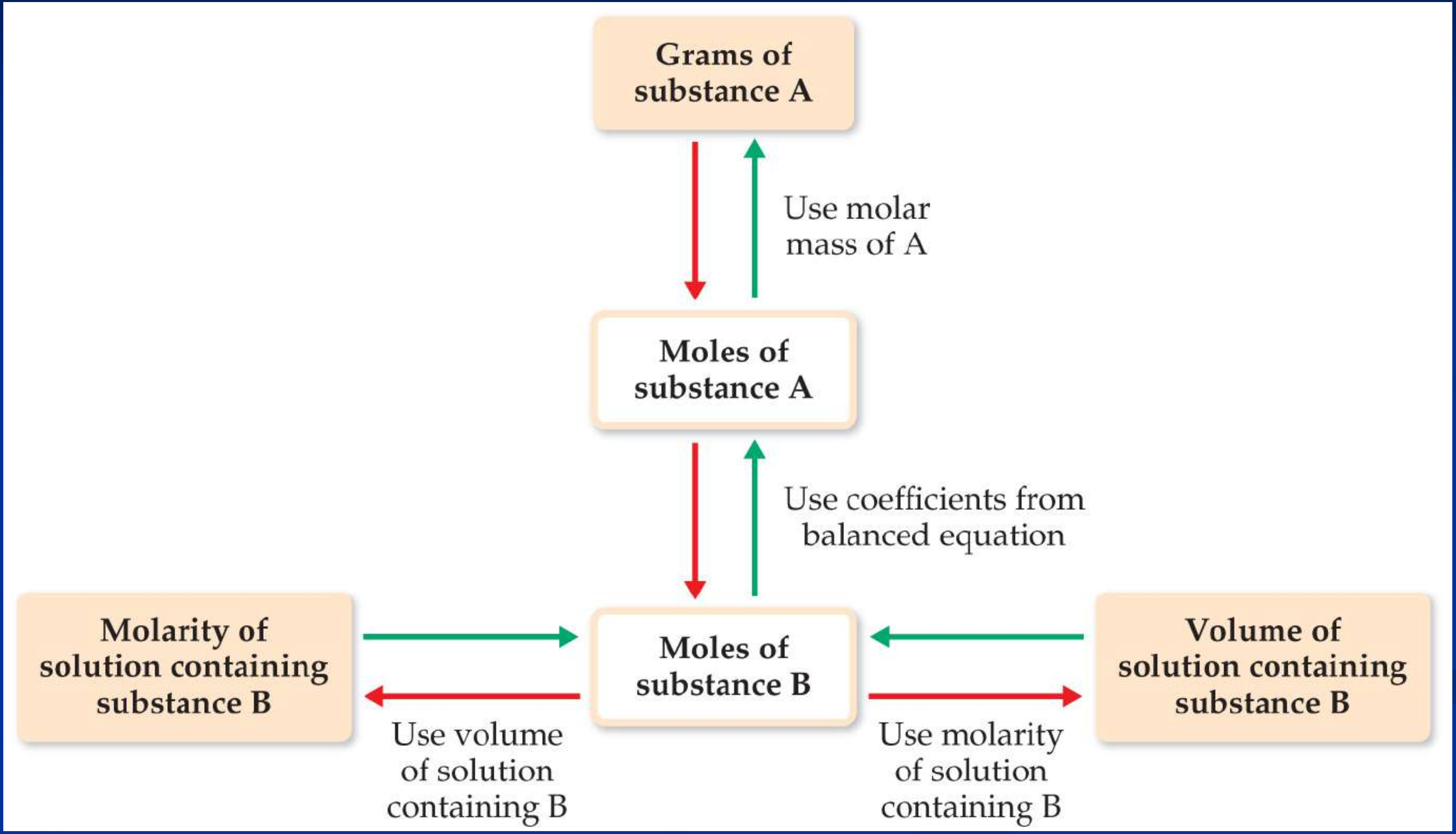
1) What volume of 2.50 M lead (II) nitrate solution contains 0.0500 mol of Pb^{2+}?

2) How many milliliters of 5.0 M $K_2Cr_2O_7$ solution must be diluted to prepare 250 mL of 0.10 M solution?

3) If 10.0 mL of a 10.0 M stock solution of NaOH is diluted to 250 mL, what is the concentration of the resulting solution?

4.6 Solution Stoichiometry and Chemical Analysis

Using Molarities in Stoichiometric Calculations



Sample Exercise 4.15

1) How many grams of $Ca(OH)_2$ are needed to neutralize 25.0 mL of 0.100 M HNO_3?
2) How many grams of NaOH are needed to neutralize 20.0 mL of 0.150 M H_2SO_4 solution?
3) How many liters of 0.500 M HCl are needed to react completely with 0.100 mol of $Pb(NO_3)_2$, forming a precipitate of $PbCl_2$?

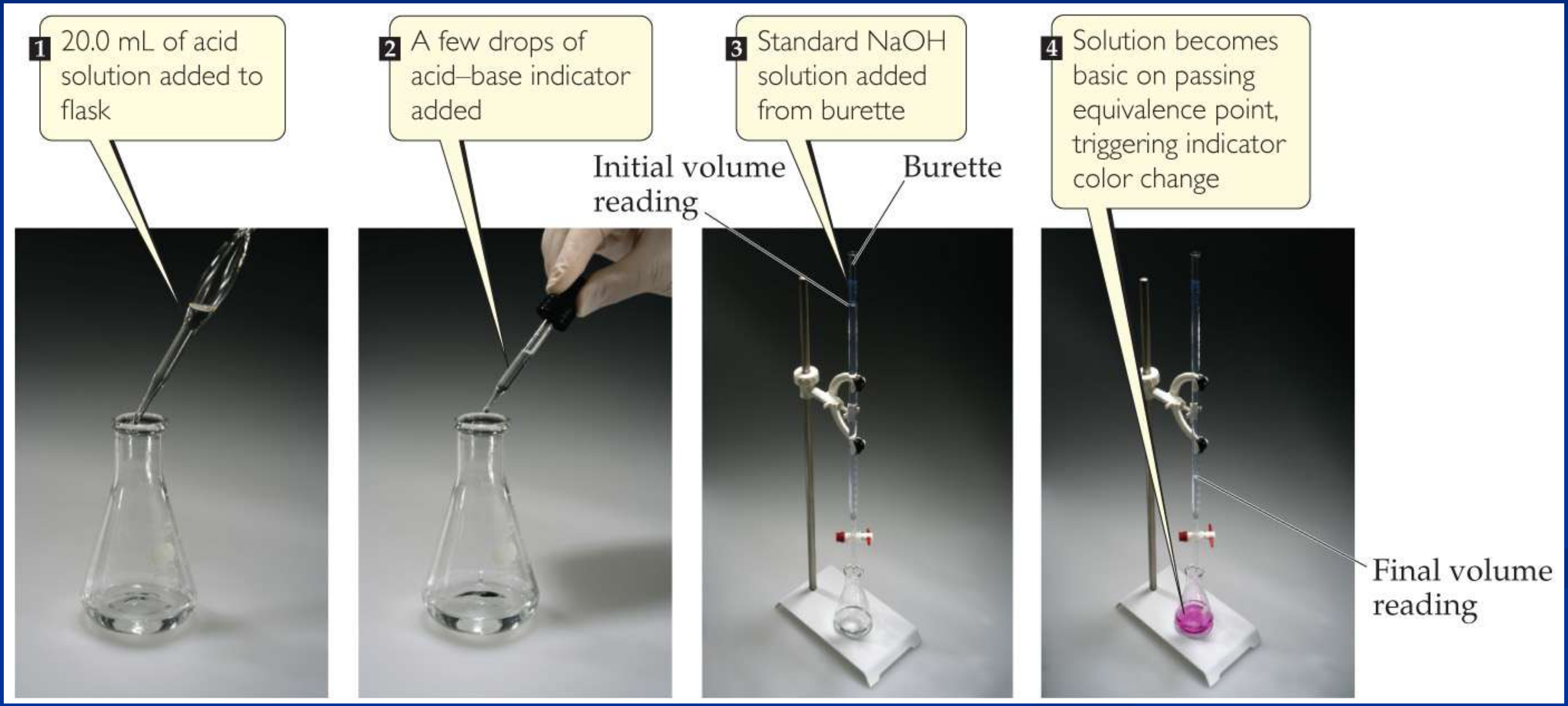
Practice Exercise 1

How many milligrams of sodium sulfide are needed to completely react with 25.00 mL of a 0.0100 *M* aqueous solution of cadmium nitrate, to form a precipitate of CdS(*s*)?

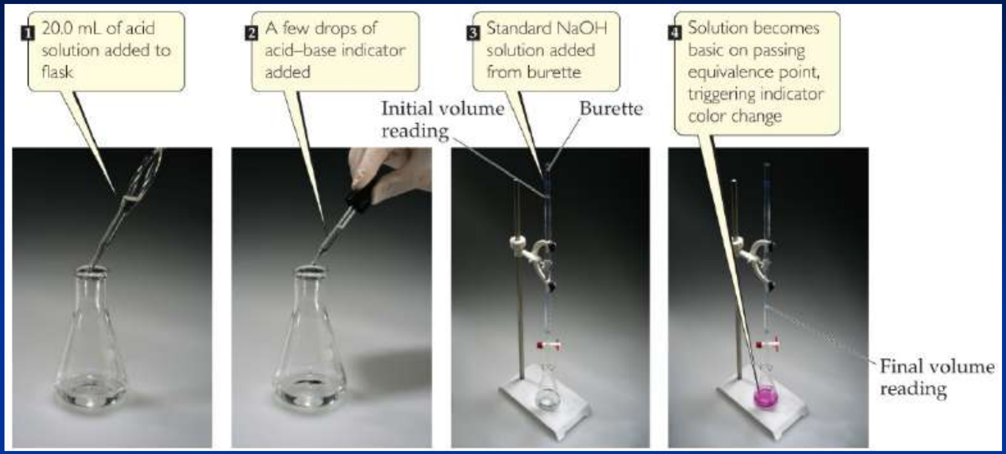
(a) 13.8 mg
(b) 19.5 mg
(c) 23.5 mg
(d) 32.1 mg
(e) 39.0 mg

Titration

A **titration** is an analytical technique in which one can calculate the concentration of a solute in a solution.



How would the volume of standard solution added change if that solution were $Ba(OH)_2(aq)$ instead of $NaOH(aq)$?



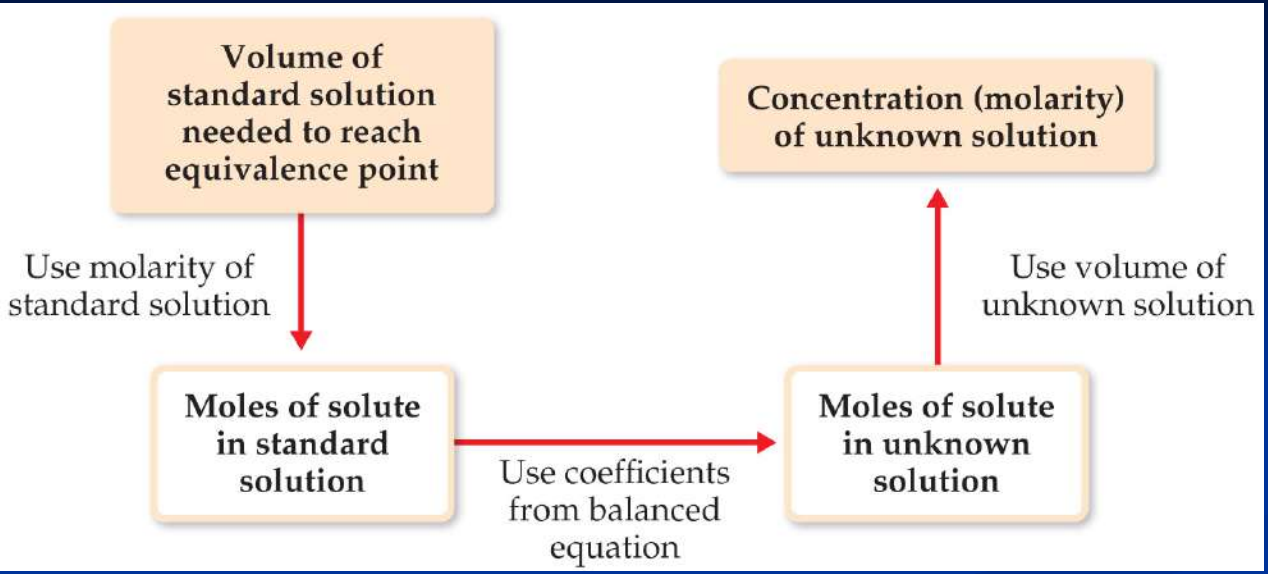
a. Increase by one-half the volume used for titration with NaOH.

b. Increase by two the volume used for titration with NaOH.

c. Decrease by two the volume used for titration with NaOH.

d. Decrease by one-half the volume used for titration with NaOH.

Titration



- A solution of known concentration, called a **standard solution**, is used to determine the unknown concentration of another solution.
- The reaction is complete at the **equivalence point**.

Sample Exercise 4.16

1) 45.7 mL of 0.500 M H_2SO_4 is required to neutralize a 20.0-mL sample of NaOH solution. What is the concentration of the NaOH solution?
2) What is the molarity of an NaOH solution if 48.0 mL is needed to neutralize 35.0 mL of 0.144 M H_2SO_4?

Practice Exercise 1

What is the molarity of an HCl solution if 27.3 mL of it neutralizes 134.5 mL of 0.0165 *M* $Ba(OH)_2$?

(a) 0.0444 *M*

(b) 0.0813 *M*

(c) 0.163 *M*

(d) 0.325 *M*

(e) 3.35 *M*

Sample Exercise 4.17

- The quantity of Cl^- in a municipal water supply is determined by titrating the sample with Ag^+. The reaction taking place during the titration is
- $Ag^+_{(aq)} + Cl^-_{(aq)} \rightarrow AgCl_{(s)}$
- The end point in this type of titration is marked by a change in color of a special type of indicator. How many grams of chloride ion are in a sample of the water if 20.2 mL of 0.100 M Ag^+ is needed to react with all the chloride in the sample? If the sample has a mass of 10.0 g, what percent Cl^- does it contain?

Practice Exercise 1

A mysterious white powder is found at a crime scene. A simple chemical analysis concludes that the powder is a mixture of sugar and the weak base morphine ($C_{17}H_{19}NO_3$). The crime lab takes 10.00 mg of the mysterious white powder, dissolves it in 100.00 mL water, and titrates it to the equivalence point with 2.84 mL of a standard 0.0100 *M* HCl solution. What is the percentage of morphine in the white powder? **(a)** 8.10%, **(b)** 17.3%, **(c)** 32.6%, **(d)** 49.7%, **(e)** 81.0%

Practice Exercise 2

A sample of an iron ore is dissolved in acid, and the iron is converted to Fe^{2+}. The sample is then titrated with 47.20 mL of 0.02240 *M* MnO_4^- solution. The oxidation-reduction reaction that occurs during titration is as follows:

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

(a) How many moles of MnO_4^- were added to the solution? **(b)** How many moles of Fe^{2+} were in the sample? **(c)** How many grams of iron were in the sample? **(d)** If the sample had a mass of 0.8890 g, what is the percentage of iron in the sample?

Sample Integrative Exercise

A sample of 70.5 mg of potassium phosphate is added to 15.0 mL of 0.050 M silver nitrate resulting in the formation of a precipitate.

Write the balanced molecular equation.

What is the limiting reactant?

Calculate the theoretical yield in grams, of the precipitate that forms.