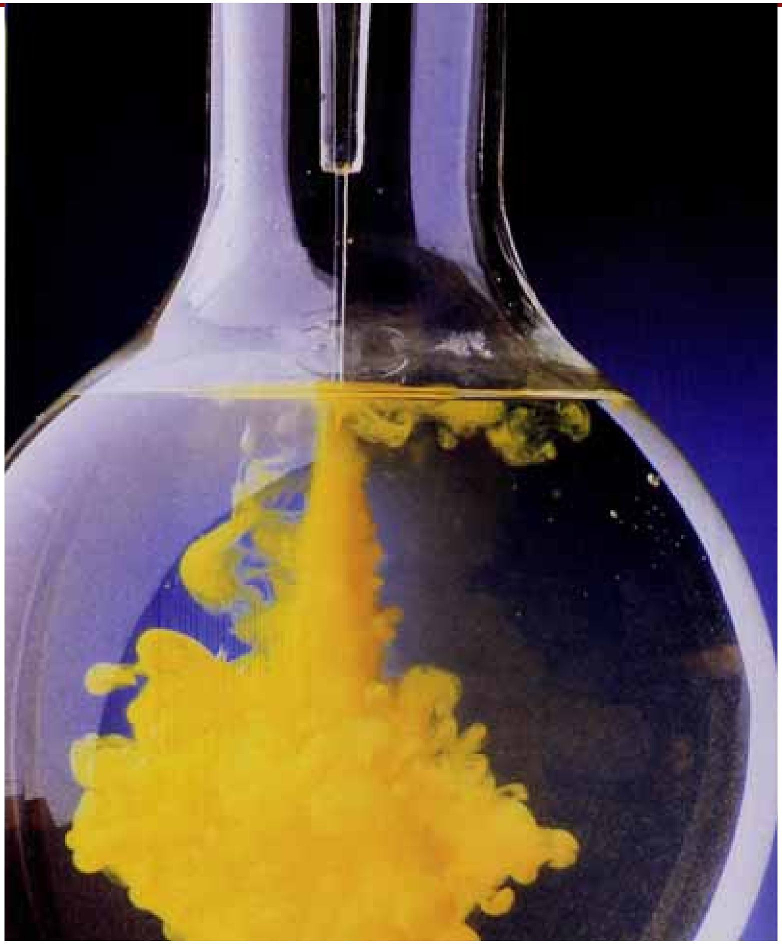
Chemistry

Zumdahl, 7th edition

歐亞書局

CH4 Types of Chemical Reactions and Solution Stoichiometry



Yellow lead(II) iodide is produced when lead(II) nitrate is mixed with potassium iodide.

Contents

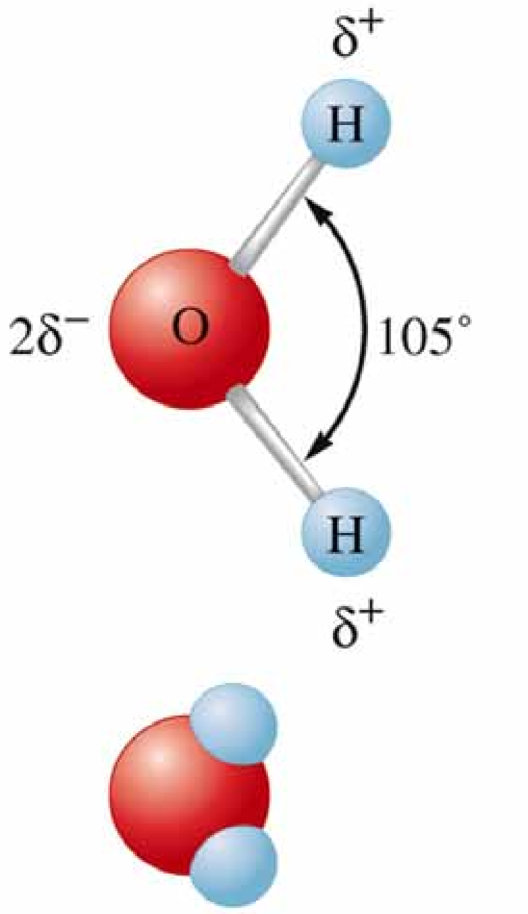
Introduction

- Much of the chemistry that affects each of us occurs among substances dissolved in water.
- We need to discuss the nature of solutions in which water is the dissolving medium, or solvent.
- These solutions are call **aqueous solutions**.

4.1 Water, the Common Solvent

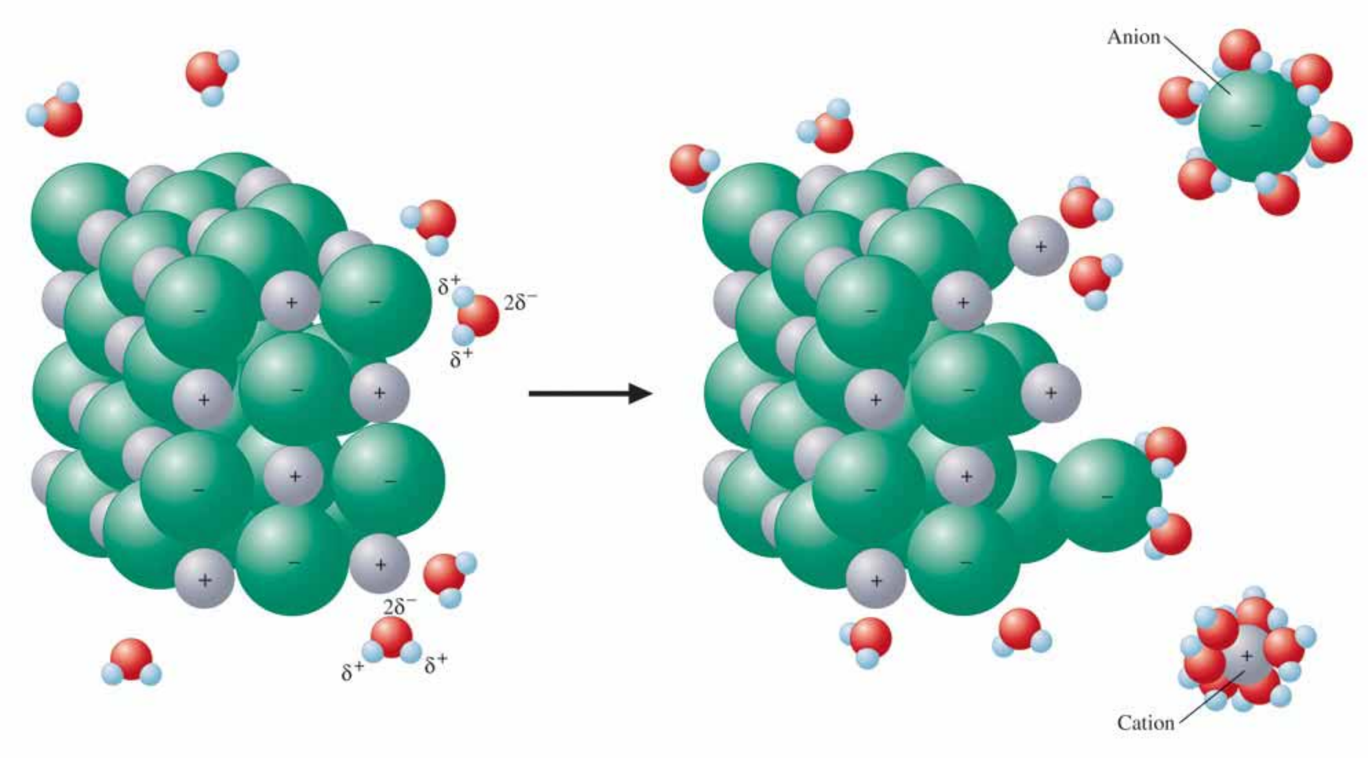
- Water is one of the most important substances on earth.
- One of the most valuable properties of water is its ability to dissolve many different substances.

Figure 4.1



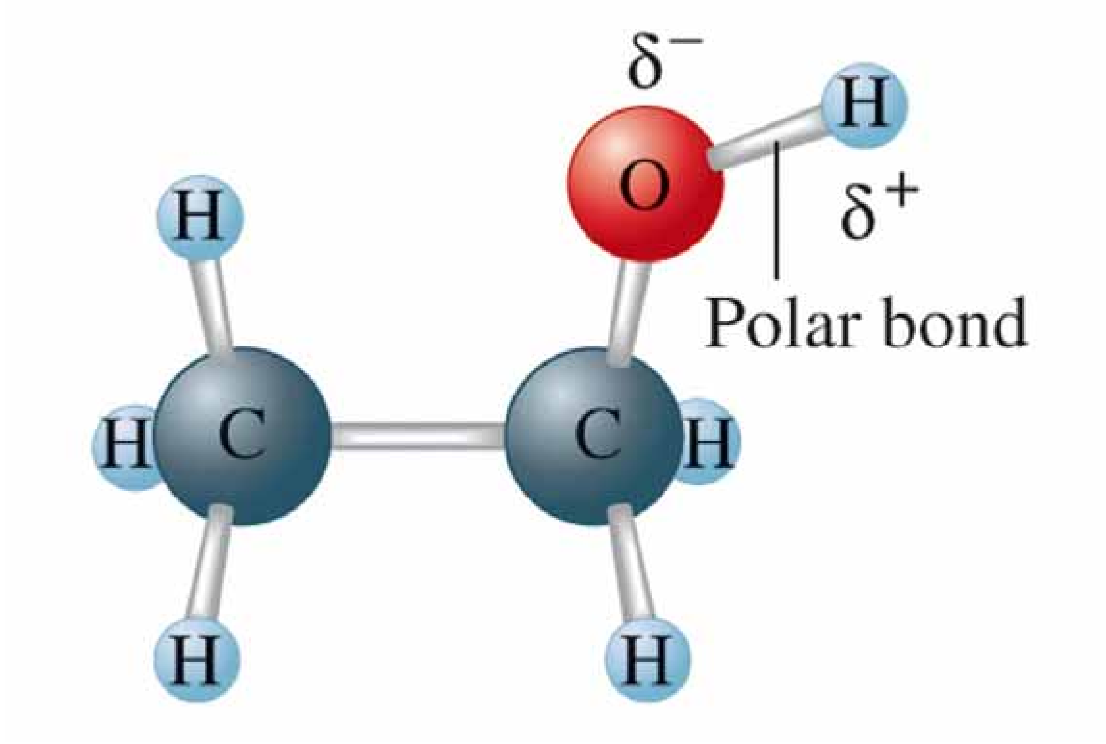
(top) The water molecule is polar.
(bottom) A space-filling model of the water molecule.

Figure 4.2



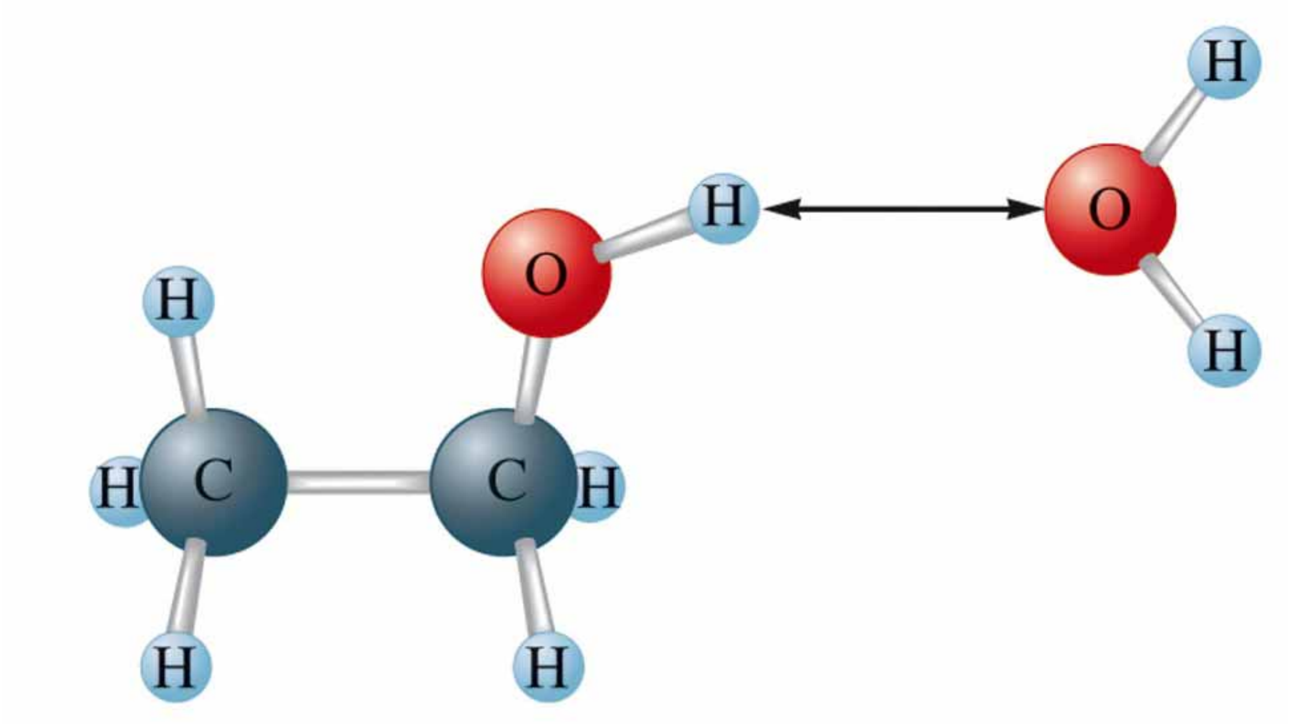
Polar water molecules interact with the positive and negative ions of a salt, assisting in the dissolving process.

Figure 4.3



(a) The ethanol molecule contains a polar O-H bond similar to those in the water molecule.

Figure 4.3



(b) The polar water molecule interacts strongly with the polar O-H bond in ethanol. This is a case of “like dissolving like.”

4.2 The Nature of Aqueous solutions: Strong and Weak Electrolytes

- In this section we will consider what happens when a substance, the **solute**, is dissolved in liquid water, the **solvent**.
- **Electrical conductivity**：Its ability to conduct an electric current.
- Pure water is not an electrical conductor.
- **Strong electrolytes**：conduct current very efficiently.
- **Weak electrolytes**：conduct only a small current.

- Nonelectrolytes：no current flow.
- An electrolyte is a substance that when dissolved in water produces a solution that can conduct electricity.
- As Arrhenius postulated, the extent to which a solution can conduct an electric current depends directly on the number of ions present.

Figure 4.4

Electrical conductivity of aqueous solutions. The circuit will be completed and will allow current to flow only when there are charge carriers (ions) in the solution. Note: Water molecules are present but not shown in these pictures. (a) A hydrochloric acid solution, which is a strong electrolyte, contains ions that readily conduct the current and give a brightly it bulb.

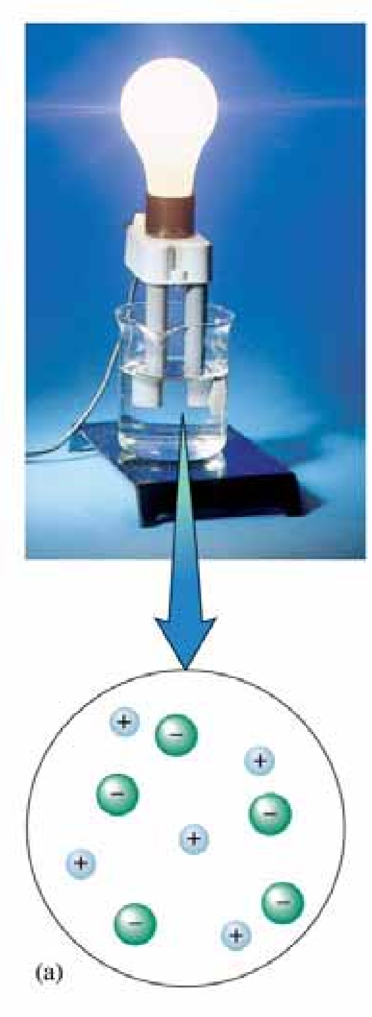
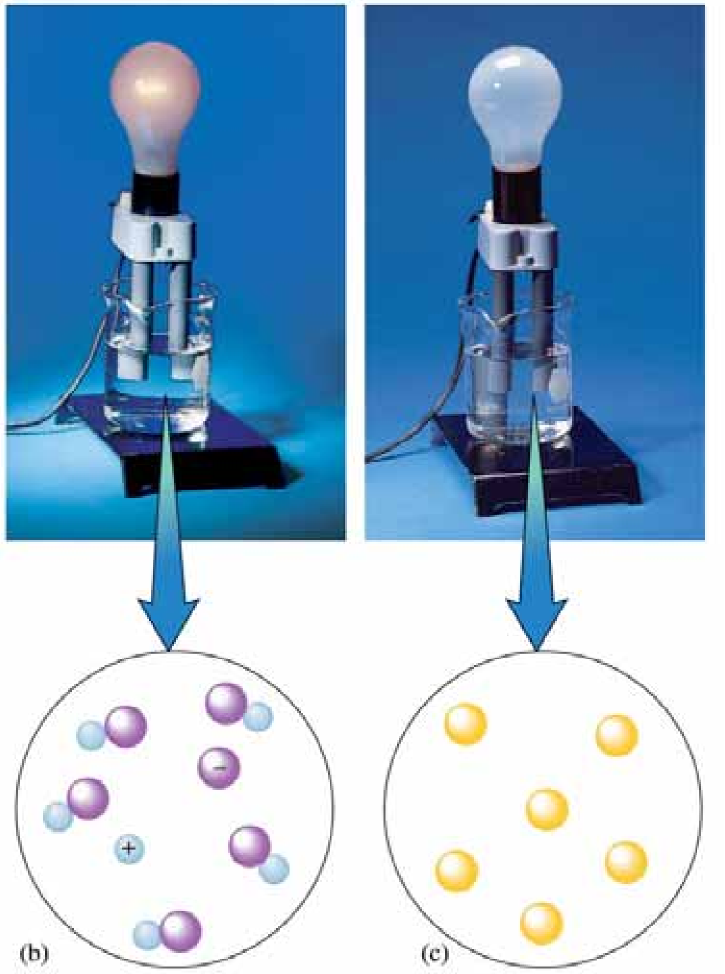


Figure 4.4

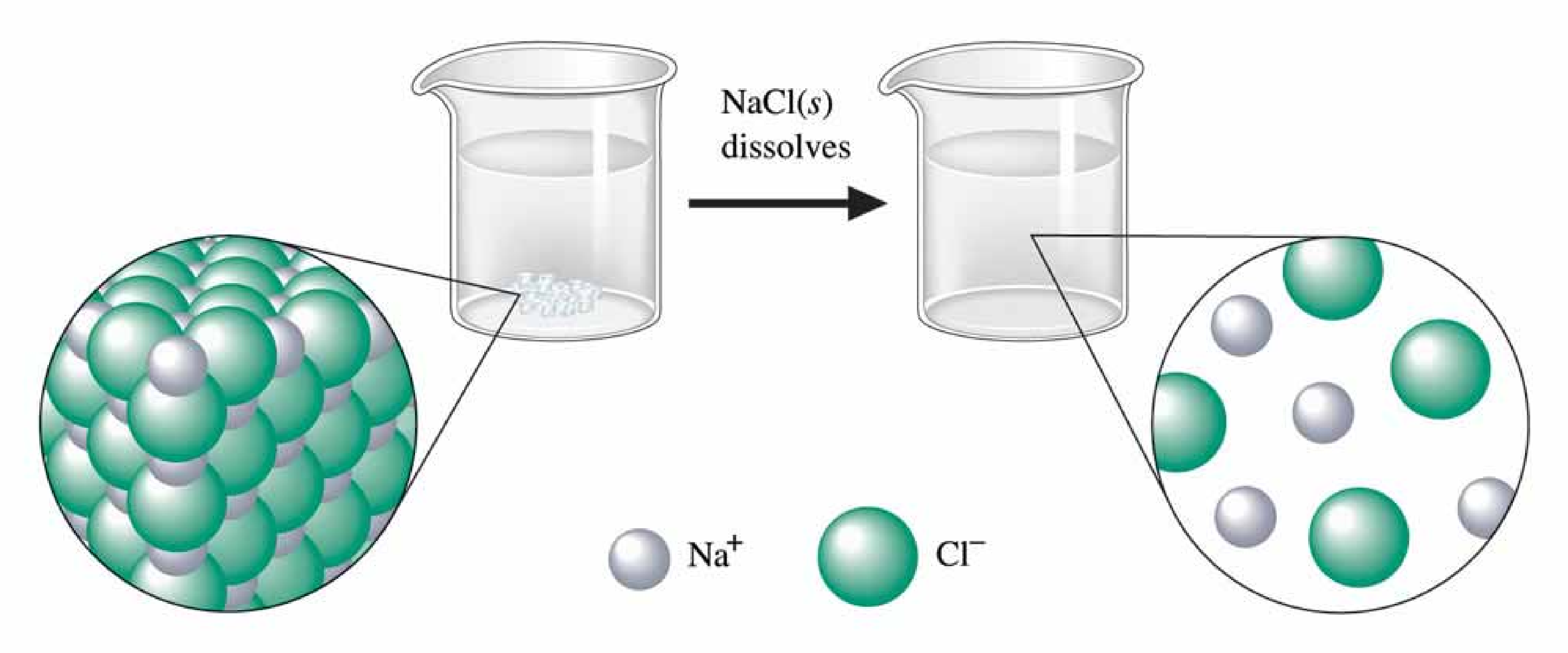


(b) An acetic acid solution, which is a weak electrolyte. The bulb is only dimly lit. (c) A sucrose solution, which is a nonelectrolyte, contains no ions and does not conduct a current. The bulb remains unlit.

Strong Electrolytes

- Strong electrolytes are substances that are completely ionized when they are dissolved in water, several classes of strong electrolytes: (1) soluble salts; (2) strong acids and (3) strong base.
- When NaCl dissolves in water, it produces hydrated Na^+ and Cl^- ions in the solution (see Fig. 4.5).

Figure 4.5



When solid NaCl dissolves, the Na$^+$ and Cl$^-$ ions are randomly dispersed in the water.

$$HCl \xrightarrow{H_2O} H^+(aq) + Cl^-(aq)$$

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

$$H_2SO_4 \xrightarrow{H_2O} H^+(aq) + HSO_4^-(aq)$$

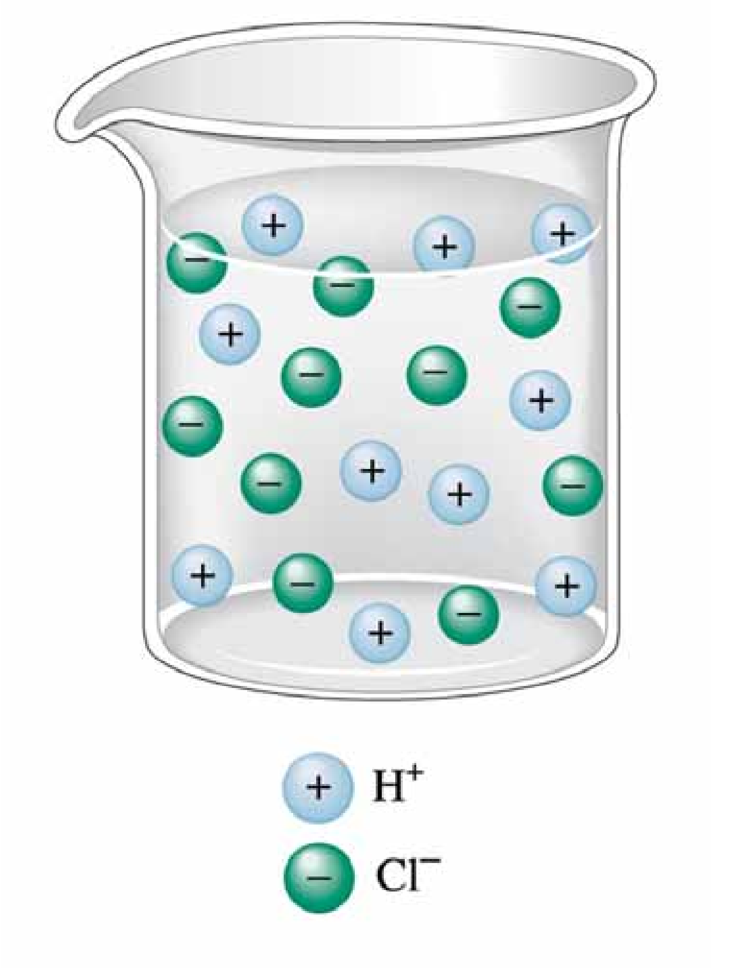
- **Acid** is a substance that produces H^+ ions (protons) when it is dissolved in eater.

- The Arrhenius definition of an acid is a substance that produces H^+ ions in solution.
- Strong electrolytes dissociate (ionize) completely in aqueous solution.

- Following facts are important :
  - Sulfuric acid, nitric acid, and hydrochloric acid are aqueous solutions and should be written in chemical equations as $H_2SO_4(aq)$, $HNO_3(aq)$, and $HCl(aq)$, respectively, although they often appear without the (*aq*) symbol.
  - A strong acid is one that completely dissociates into its ions. Thus if 100 molecules of HCl are dissolved in water, 100 H^+ ions and 100 Cl^- ions are produced. Virtually no HCl molecules exist in aqueous solutions (see Fig. 4.6)

- Sulfuic acid is a special case. The formula H_2SO_4 indicates the this acid can produce two H^+ ions per molecule when dissolved in water. However, only the first H^+ ion is completely dissociated. The second H^+ ion can be pulled off under certain conditions, which we will discuss later. Thus an aqueous solution of H_2SO_4 contains mostly H^+ ions and HSO_4^- ions.

Figure 4.6



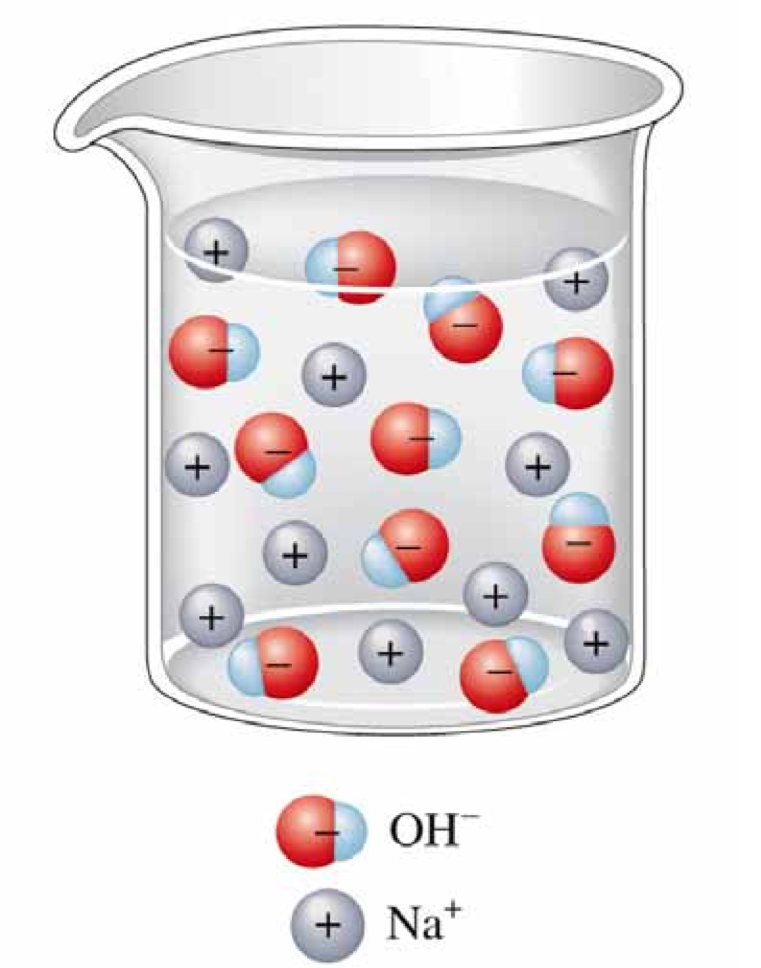
HCl(*aq*) is completely ionized.

- Another important class of strong electrolytes consists of the **strong base**, soluble ionic compounds containing the hydroxide ion (OH^-).
- The most common basic solutions are those produced when solid sodium hydroxide (NaOH) or potassium hydroxide (KOH) is dissolved in water to produce ions, as follows (see Fig. 4.7):

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

$$KOH(s) \xrightarrow{H_2O} K^+(aq) + OH^-(aq)$$

Figure 4.7



An aqueous solution of sodium hydroxide.

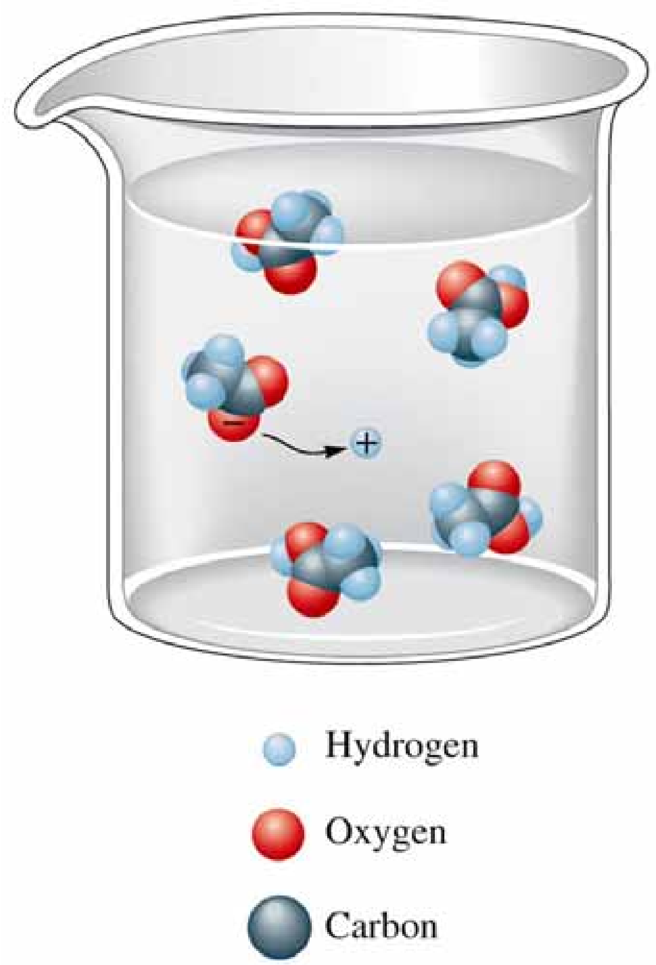
Weak Electrolytes

- Weak electrolytes dissociate (ionize) only to a small extent in aqueous solution.
- The main acidic component of vinegar is acetic acid ($HC_2H_3O_2$).
- The dissociation reaction for acetic acid in water can be written as follows:

$$HC_2H_3O_3(aq) \overset{H_2O}{\rightleftarrows} H^+(aq) + C_2H_3O_2^-(aq)$$

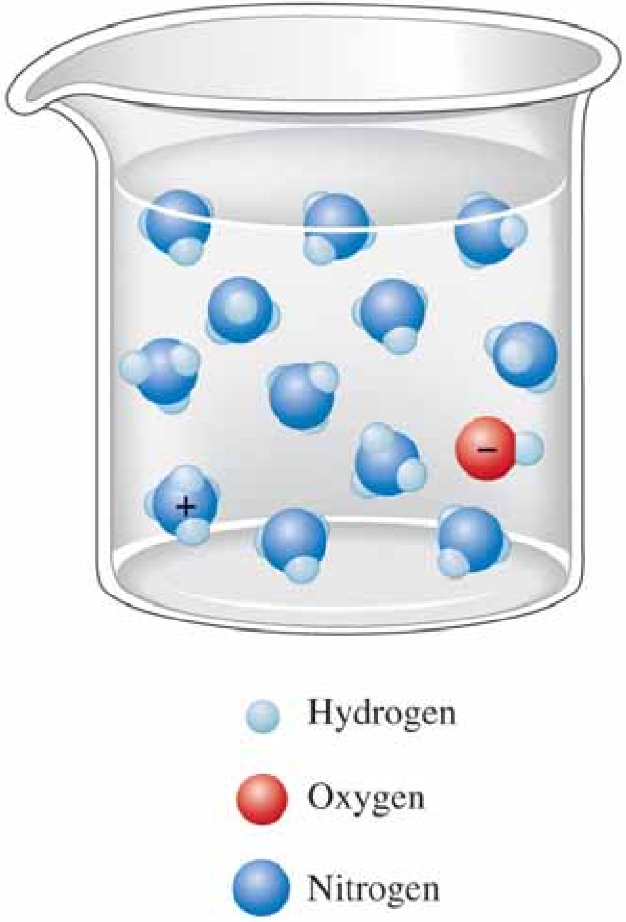
- In a solution containing 0.1 mole of $HC_2H_3O_2$ per liter, for every 100 molecules of $HC_2H_3O_2$ originally dissolved in water, approximately 99 molecules of $HC_2H_3O_2$ remain intact (see Fig. 4.8).
- Because acetic acid is a weak electrolyte, it is called a **weak acid**.

Figure 4.8



Acetic acid ($HC_2H_3O_2$) exists in water mostly as undissociated molecules. Only a small percentage of the molecules are ionized.

Figure 4.9



The reaction of NH_3 in water.

Nonelectrolytes

- Nonelectrolytes are substances the dissolve in water but do not produce any ions, as shown in Fig. 4.4(c).
- An example of a nonelectrolyte is ethanol.
- When ethanol dissolves, entire C_2H_5OH molecules are dispersed in the water.

4.3 The Composition of Solutions

- Chemical reactions often take place when two solutions are mixed.
- Stoichiometric calculations: (1) the *nature of the reaction*, which depends on the exact forms the chemicals take when dissolved, and (2) the *amounts of chemicals* present in the solutions, usually expressed as concentrations.

- **molarity** (*M*), which is defined as moles of solute per volume of solution in liters:

$$M = \text{molarity} = \frac{\text{moles of solute}}{\text{liters of solution}}$$

Sample Exercise 4.1 Calculation of Molarity I

Calculate molarity of a solution prepared by dissolving 11.5 g of solid NaOH in enough water to make 1.50 L of solution.

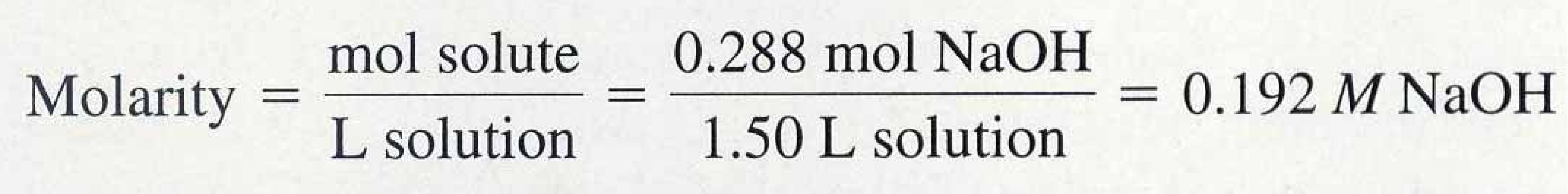
Solution

To find the molarity of the solution, we first compute th enumber of moles of solute using the molar mass of NaOH (40.00 g/mol):

$$11.5\ \cancel{\text{g NaOH}} \times \frac{1\ \text{mol NaOH}}{40.00\ \cancel{\text{g NaOH}}} = 0.288\ \text{mol NaOH}$$

Sample Exercise 4.1

To find the molarity of the solution, we first compute th enumber of moles of solute using the molar mass of NaOH (40.00 g/mol):



$$\text{Molarity} = \frac{\text{mol solute}}{\text{L solution}} = \frac{0.288 \text{ mol NaOH}}{1.50 \text{ L solution}} = 0.192\ M \text{ NaOH}$$

See Exercises 4.21 and 4.22

Sample Exercise 4.2 Calculation of Molarity II

Calculate molarity of a solution prepared by dissolving 1.56 g of gaseous HCl in enough water to make 26.8 mL of solution.

Solution

First we calculate the number of moles of HCl (molar mass ＝ 36.46 g/mol):

$$1.56\ \cancel{\text{g HCl}} \times \frac{1\ \text{mol HCl}}{36.46\ \cancel{\text{g HCl}}} = 4.28 \times 10^{-2}\ \text{mol HCl}$$

Sample Exercise 4.2

Next we must change the volume of hte solution to liters:

$$26.8\ \cancel{\text{mL}} \times \frac{1\ \text{L}}{1000\ \cancel{\text{mL}}} = 2.68 \times 10^{-2}\ \text{L}$$

Finally, we divide the moles of colution by the liters of solution:

$$\text{Molarity} = \frac{4.28 \times 10^{-2}\ \text{mol HCl}}{2.68 \times 10^{-2}\ \text{L solution}} = 1.60\ M\ \text{HCl}$$

See Exercises 4.21 and 4.22

- Standard solution is a *solution whose concentration is accurately known.*
- Standard solutions, often used in chemical analysis, can be prepared as shown in Fig. 4.10 and in sample Exercise 4.6.

Figure 4.10

Steps involved in the preparation of a standard aqueous solution. (a) Put a weighed amount of a substance (the solute) into the volumetric flask, and add a small quantity of water.

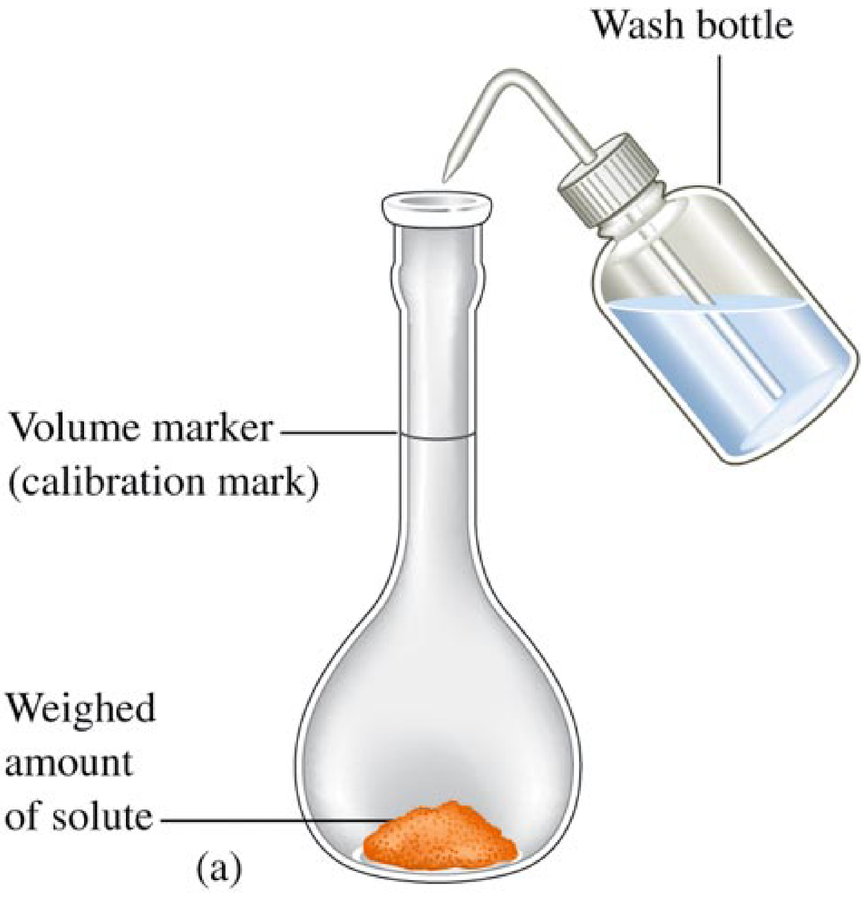
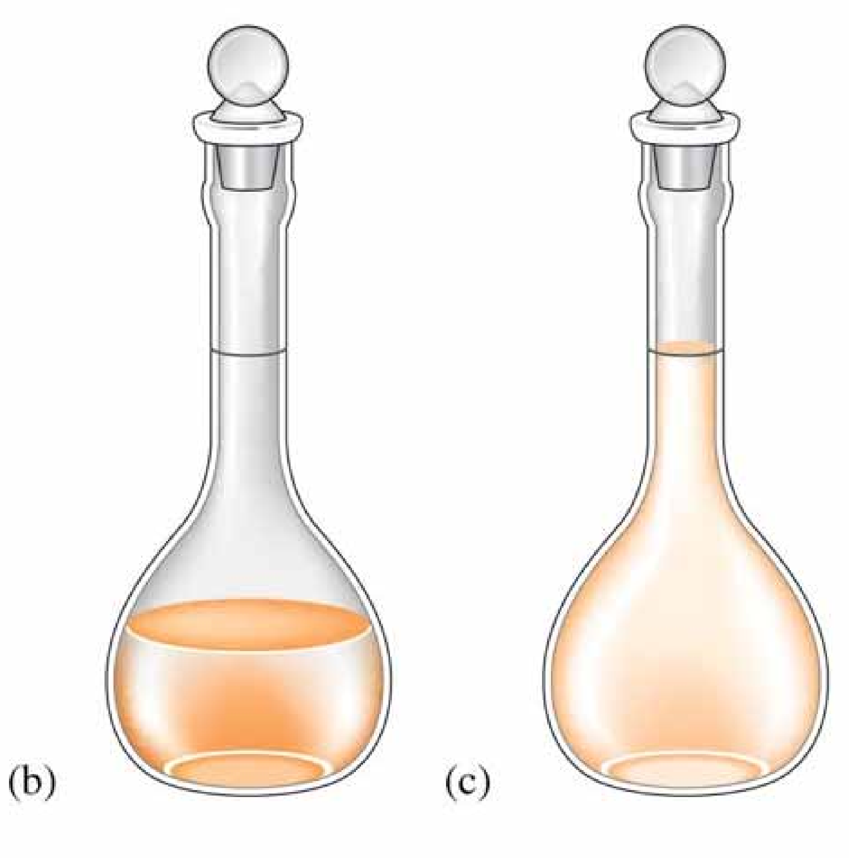


Figure 4.10

(b) Dissolve the solid in the water by gently swirling the flask (*with the stopper in place*). (c) Add more water (with gentle swirling) until the level of the solution just reaches the mark etched on the neck of the flask. The mix the solution thoroughly by inverting the flask several times.



Dilution

- Water is then added to achieve the molarity desired for a particular solution.
- The rule for **dilution**：

Moles of solute after dilution ＝ moles of solute before dilution

- A dilution procedure typically involves two types of glassware: a pipet and a volumetric flask.

- There are two common types of pipets: *volumetric* (or transfer) *pipets and measuring pipets*, as shown in Fig. 4.11.
- Volumetric pipets come in specific sizes, such as 5 mL, 10 mL, 25 mL, and so on.
- Measuring pipet as shown in Fig. 4.12.

Figure 4.11

(a) A measuring pipet is graduated and can be used to measure various volumes of liquid accurately. (b) A volumetric (transfer) pipet is designed to measure one volume accurately. When filled to the mark, it delivers the volume indicated on the piprt.

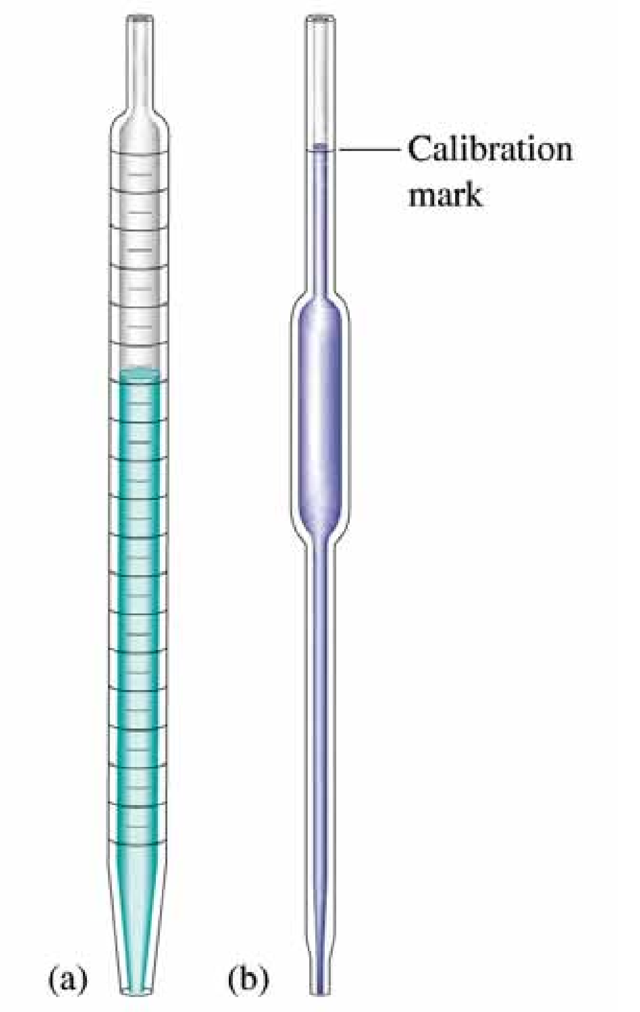
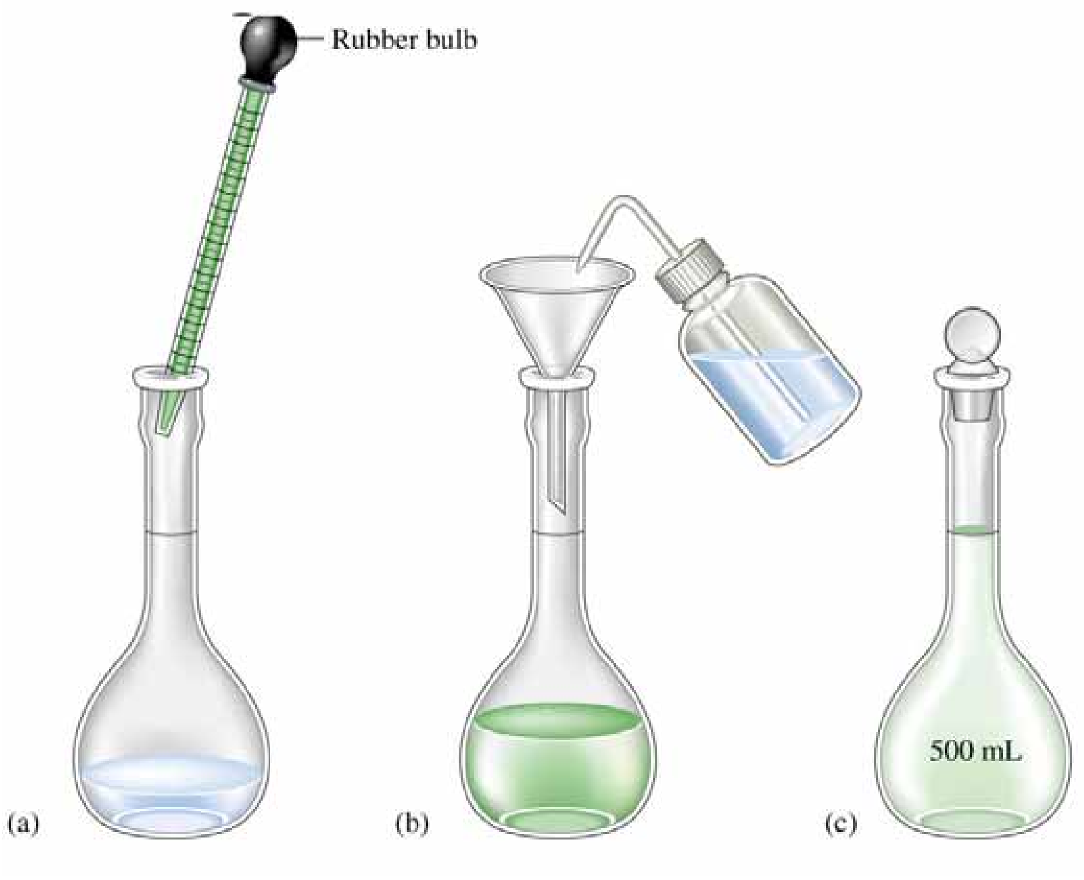


Figure 4.12

(a) A measuring pipet is used to transfer 28.7 mL of 17.4 *M* acetic acid solution to a volumetric flask. (b) Water is added to the flask to the calibration mark. (c) The resulting solution is 1.00 *M* acetic acid.



4.4 Types of Chemical Reactions

Types of Solution Reactions

- Precipitation reactions
- Acid-base reactions
- Oxidation-reduction reactions

4.5 Precipitation Reactions

- When two solutions are mixed, an insoluble substance sometimes forms; that is, a solid forms and separates from the solution.
- Such a reaction is called a **precipitation reaction**, and the solid that forms is called a **precipitate**.
- A precipitation reaction occurs when an aqueous solution of potassium chromate, $K_2CrO_4(aq)$, which is yellow, is added to a colorless aqueous solution containing barium nitrate, $Ba(NO_3)_2(aq)$.

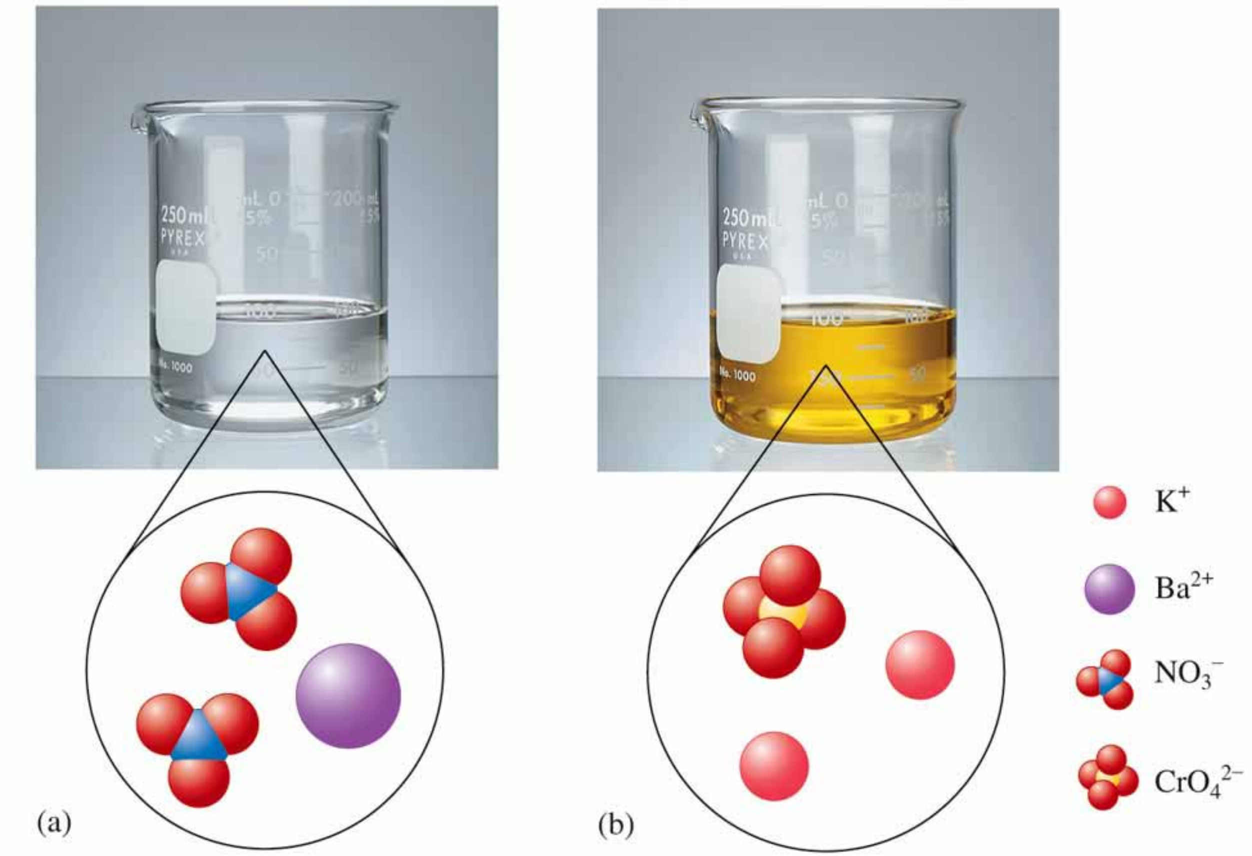
Figure 4.13

When yellow aqueous potassium chromate is added to a colorless barium nitrate solution, yellow barium chromate precipitates.

- *Remember: In virtually every case, when a solid containing ions dissolves in water, the ions separate* and move around independently.
- That is, $Ba(NO_3)_2(aq)$ does not contain $Ba(NO_3)_2$ units; it contains separated Ba^{2+} and NO_3^- ions. See Fig. 4.14(a).
- We can represent the mixing of $K_2CrO_4(aq)$ and $Ba(NO_3)_2(aq)$ in two ways. First,

$$K_2CrO_4(aq) + Ba(NO_3)_2(aq) \longrightarrow \text{products}$$

Figure 4.14



Reactant solutions: (a) $Ba(NO_3)_2(aq)$ and (b) $K_2CrO_4(aq)$.

- A much more accurate representation is

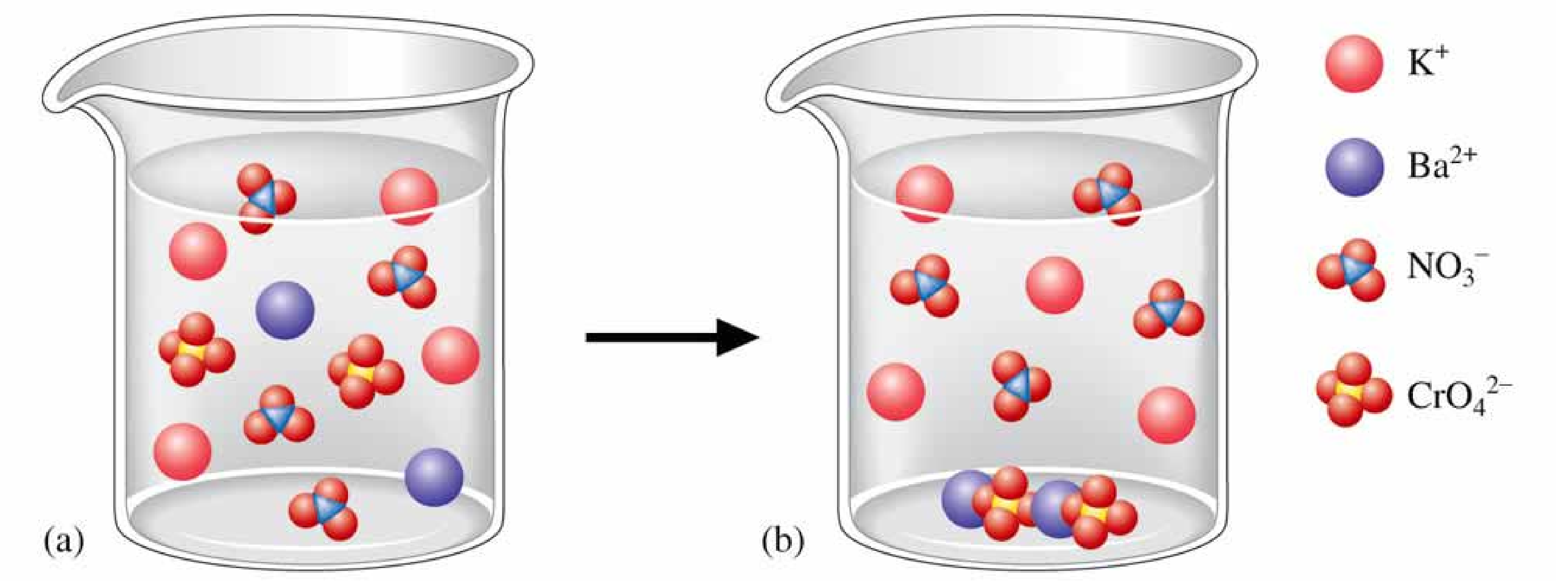
$$\underbrace{2K^{+}(aq) + CrO_4^{2-}(aq)}_{\text{The ions in } K_2CrO_4(aq)} + \underbrace{Ba^{2+}(aq) + 2NO_3^{-}(aq)}_{\text{The ions in } Ba_2(NO_3)_2(aq)} \rightarrow \text{products}$$

- Thus the mixed solution contains the ions:

$$K^{+} \qquad CrO_4^{2-} \qquad Ba^{2+} \qquad NO_3^{-}$$

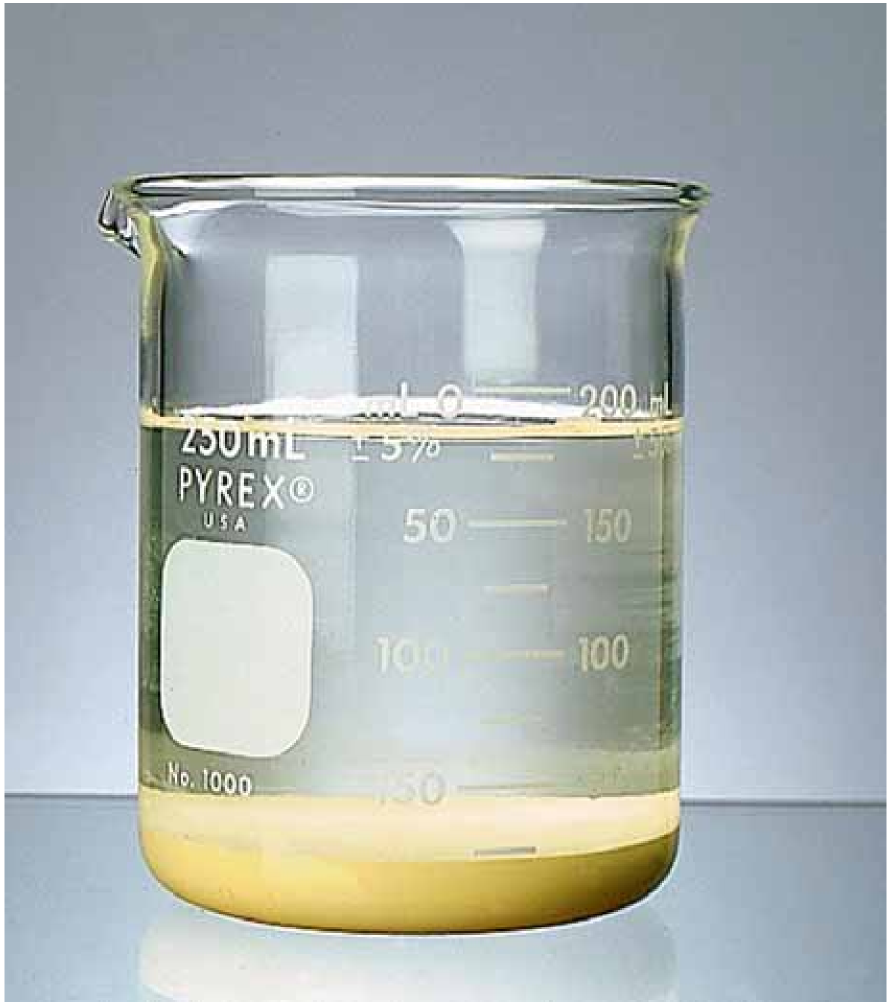
As illustrated in Fig. 4.15(a).

Figure 4.15



The reaction of $K_2CrO_4(aq)$ and $Ba(NO_3)_2(aq)$. (a) The molecular-level "picture" of the mixed solution before any reaction has occurred. (b) The molecular-level "picture" of the solution after the reaction has occurred to form $BaCrO_4(s)$. *Note:* $BaCrO_4(s)$ is not molecular. It actually contains Ba^{2+} and CrO_4^{2-} ions packed together in a lattice.

Figure 4.15



(c) A photo of the solution after the reaction has occurred, showing the solid $BaCrO_4$ on the bottom.

- Some things that will help us predict the products of
  1. When ions form a solid compound, the compound must have a zero net charge.
  2. Most ionic materials contain only two types of ions: one type of cation and one type of anion (for example, NaCl, KOH, Na_3SO_4, K_2CrO_4, $Co(NO_3)_2$, HN_3Cl, Na_2CO_3).
- The possible combinations of a given cation and a given anion from the list of ions K^+, CrO_4^{2-}, Ba^{2+}, NO_3^- are

K_2CrO_4 KNO_3 $BaCrO_4$ $Ba(NO_3)_2$

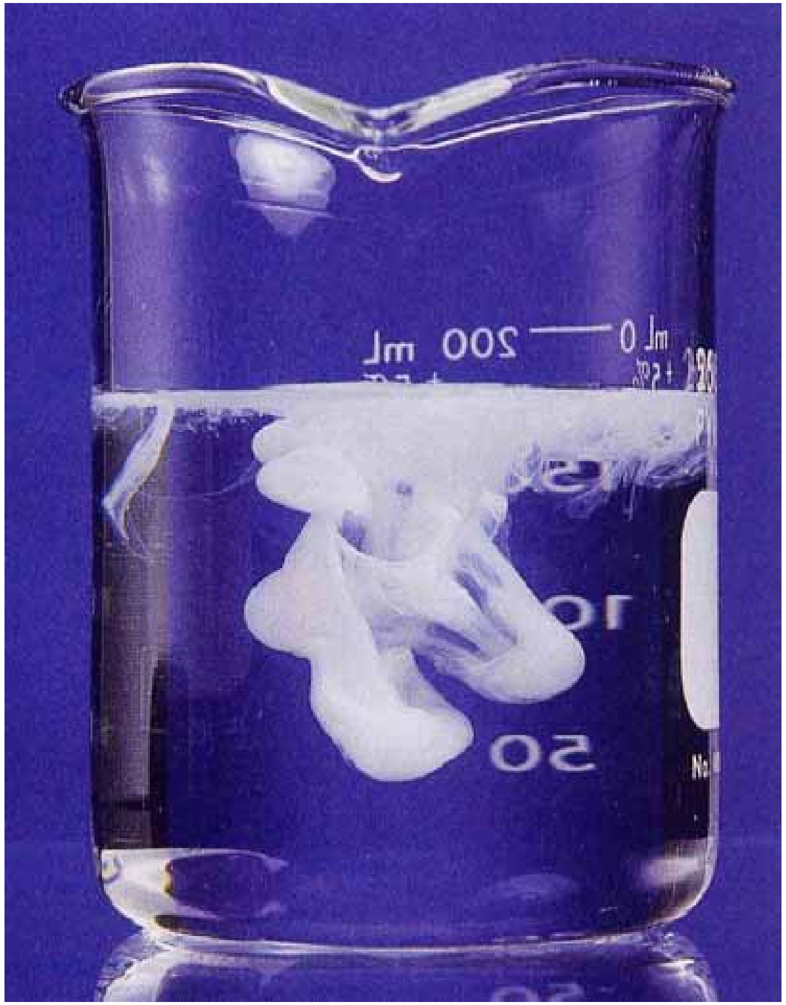
- The only real possibilities for the solid that formed are

KNO_3 and $BaCrO_4$

- When an aqueous solution of silver nitrate is added to an aqueous solution of potassium chloride, a white precipitate forms, as shown in Fig. 4.16.

$$\underbrace{Ag^+,\ NO_3^-}_{\text{In silver nitrate solution}} + \underbrace{K^+,\ Cl^-}_{\text{In potassium chloride solution}} \rightarrow \underbrace{Ag^+,\ NO_3^-,\ K^+,\ Cl^-}_{\text{Combined solution, before reaction}} \longrightarrow \text{white solid}$$

Figure 4.16



Precipitation of silver chloride by mixing solutions of silver nitrate and potassium chloride. The K^+ and NO_3^- ions remain in solution.

- Since $AgNO_3$ and KCl are the substances dissolved in the two reactant solutions, KNO_3 is quite soluble in water.

$$AgNO_3(aq) + KCl(aq) \longrightarrow AgCl(s) + KNO_3(aq)$$

- Figure 4.17 shows the result of mixing aqueous solutions of $AgNO_3$ and KCl, including a microscopic visualization of the reaction.

Figure 4.17

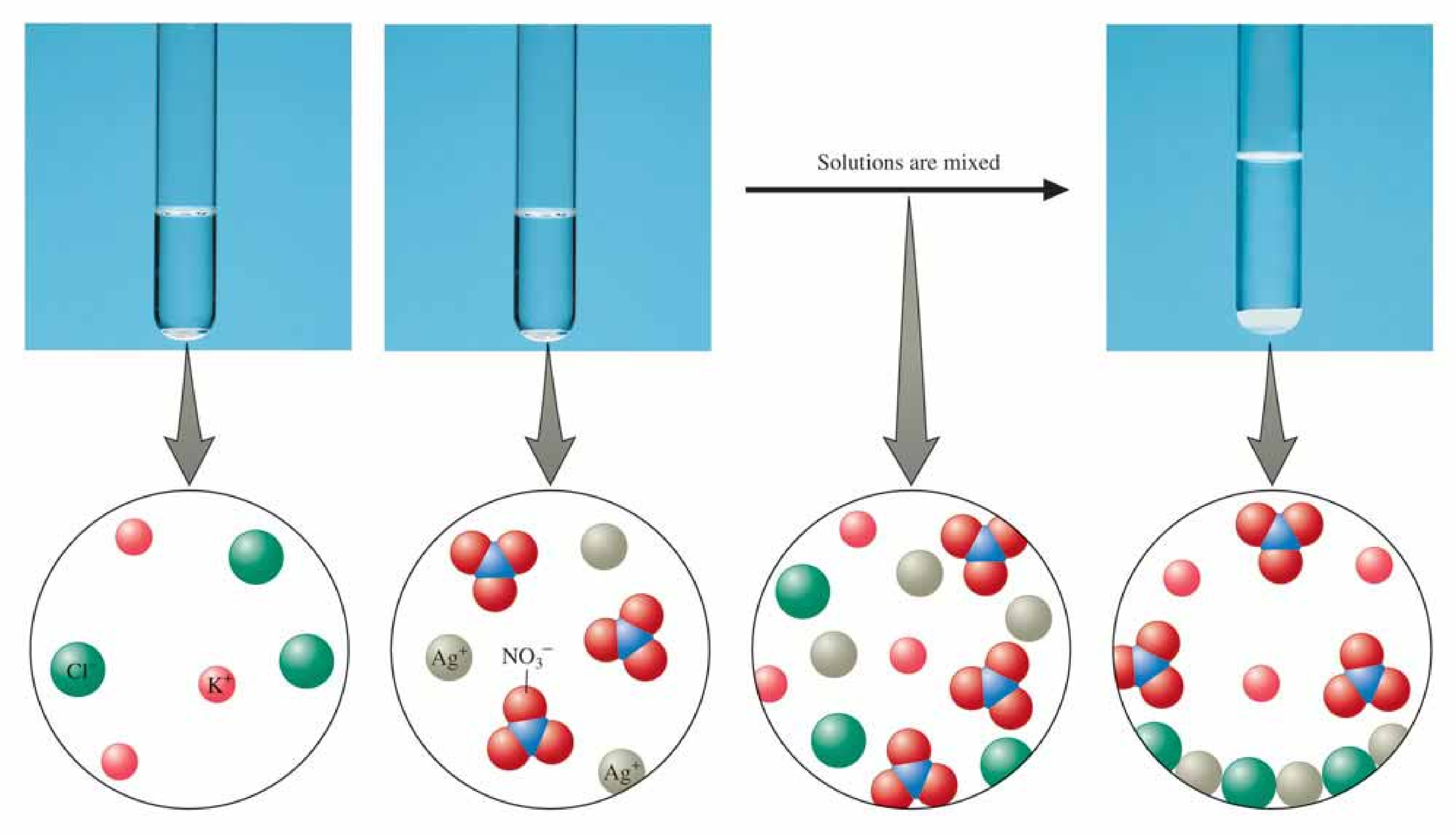


Figure 4.17

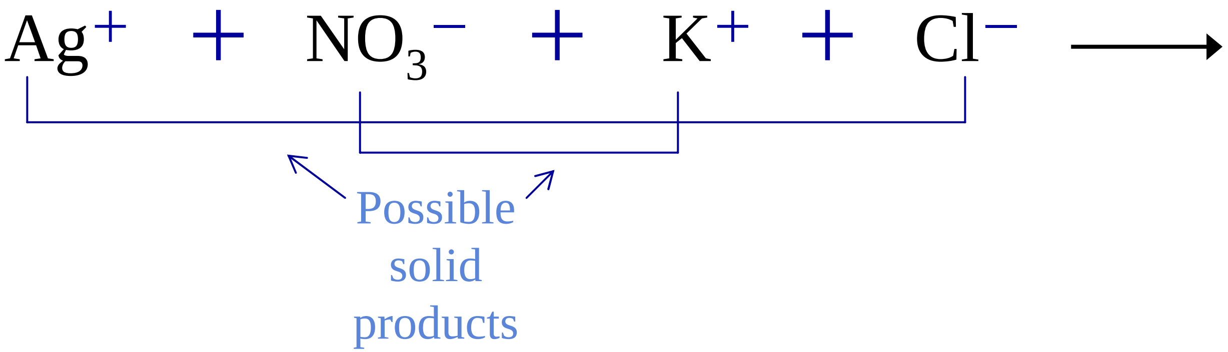
Photos and accompanying molecular-level representations illustrating the reaction of KCl(*aq*) with $AgNO_3$(*aq*) to form AgCl(*s*). Note that it is not possible to have a photo of the mixed solution before the reaction occurs, because it is an imaginary step that we use to help visualize the reaction. Actually, the reaction occurs immediately when the two solutions are mixed.

- The phrase *slightly soluble* used in the solubility rules in Table 4.1 means that the tiny amount of solid that dissolves is not noticeable.
- *Insoluble and slightly soluble* are often used interchangeably.

TABLE 4.1 Simple Rules for the Solubility of Salts in Water

1. Most nitrate (NO_3^-) salts are soluble.
2. Most salts containing the alkali metal ions (Li^+, Na^+, K^+, Cs^+, Rb^+) and the ammonium ion (NH_4^+) are soluble.
3. Most chloride, bromide, and iodide salts are soluble. Notable exceptions are salts containing the ions Ag^+, Pb^{2+}, and Hg_2^{2+}.
4. Most sulfate salts are soluble. Notable exceptions are $BaSO_4$, $PbSO_4$, Hg_2SO_4, and $CaSO_4$.
5. Most hydroxide salts are only slightly soluble. The important soluble hydroxides are NaOH and KOH. The compounds $Ba(OH)_2$, $Sr(OH)_2$, and $Ca(OH)_2$ are marginally soluble.
6. Most sulfide (S^{2-}), carbonate (CO_3^{2-}), chromate (CrO_4^{2-}), and phosphate (PO_4^{3-}) salts are only slightly soluble.

- When solutions containing ionic substances are mixed, it will be helpful in determining the products if you think in terms of *ion interchange*.



$$Ag^{+} + NO_3^{-} + K^{+} + Cl^{-} \longrightarrow$$

Possible solid products

- The solubility rules in Table 4.1 allow us to predict whether either product forms as a solid.

Sample Exercise 4.8 Predicting Reaction Products

Using the solubility rules in Table 4.1, predict what will happen when the following pairs of solutions are mixed.

a. $KNO_3(aq)$ and $BaCl_2(aq)$

b. $Na_2SO_4(aq)$ and $Pb(NO_3)_2(aq)$

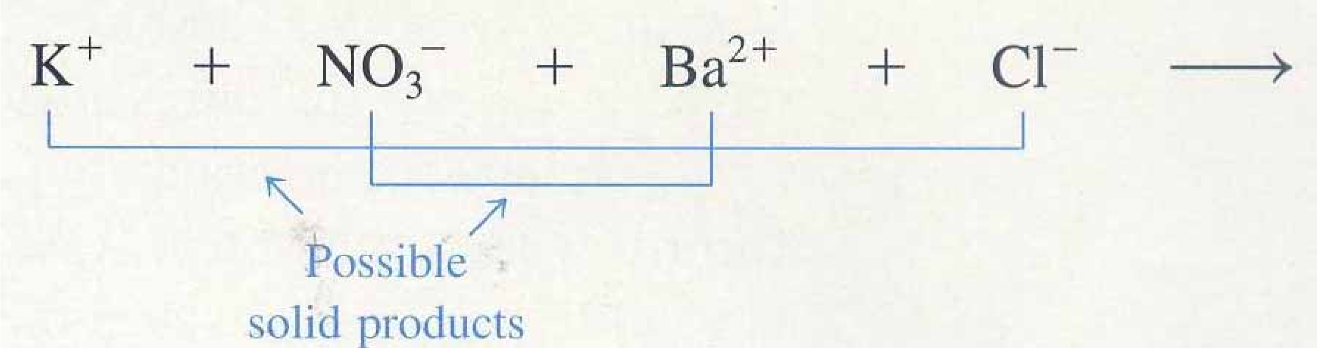
c. $KOH(aq)$ and $Fe(NO_3)_3(aq)$

Lead sulfate is a white solid.

Sample Exercise 4.8

Solution

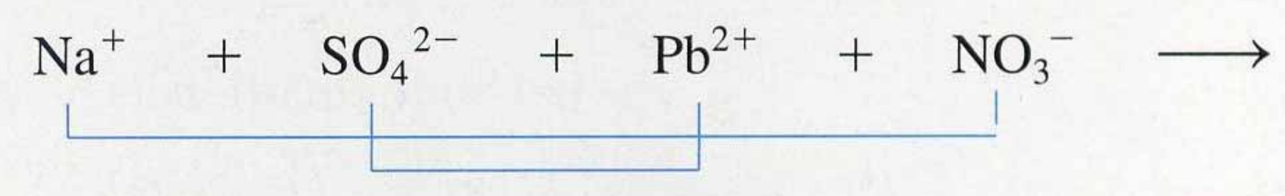
a.



Thus no precipitate forms when KNO_3(*aq*) and $BaCl_2$(*aq*) are mixed. All the ions remain dissolved in solution. No chemical reaction occurs.

Sample Exercise 4.8

b.



$$Na^+ + SO_4^{2-} + Pb^{2+} + NO_3^- \longrightarrow$$

The compound $NaNO_3$ is soluble, but $PbSO_4$ is insoluble.When these solutions are mixed, $PbSO_4$ will precipitate from the solution. The balanced equation is

$$Na_2SO_4(aq) + Pb(NO_3)_2(aq) \longrightarrow PbSO_4(s) + 2NaNO_3(aq)$$

c.

$$3KOH(aq) + Fe(NO_3)_3(aq) \longrightarrow Fe(OH)_3(s) + 3KNO_3(aq)$$

Sample Exercise 4.8

Both K^+ and NO_3^- salts are silyble. $Fe(OH)_3$ is only slightly soluble.

See Exercises 4.37 and 4.38

Solid $Fe(OH)_3$ forms when aqueous KOH and $Fe(NO_3)_3$ are mixed.

4.6 Describing Reactions in Solution

- The overall or formula equation for this reaction:

$$K_2CrO_4(aq) + Ba(NO_3)_2(aq) \longrightarrow BaCrO_4(s) + 2KNO_3(aq)$$

- Although the formula equation shows the reactants and products of the reaction, it does not give a correct picture of what actually occurs in solution.
- The **complete ionic equation**

$$2K^+(aq) + CrO_4^{2-}(aq) + Ba^{2+}(aq) + 2NO_3^-(aq) \longrightarrow BaCrO_4(s) + 2K^+(aq) + 2NO_3^-(aq)$$

- In a complete ionic equation, all substances that are strong electrolytes are represented as ions.
- The ions that do not participate directly in the reaction are called **spectator ions**.
- The ions that participate in this reaction are the Ba^{2+} and CrO_4^{2-}

$$Ba^{2+}(aq) + CrO_4^{2-}(aq) \longrightarrow BaCrO_4(s)$$

- This equation, called the **net ionic equation**.

Three Types of Equations Are Used to Describe Reactions in Solution

- The **formula equation** gives the overall reaction stoichiometry but not necessarily the actual forms of the reactants and products in solution.
- The **complete ionic equation** represents as ions all reactants and products that are strong electrolytes.
- The **net ionic equation** includes only those solution components undergoing a change. Spectator ions are not included.

Sample Exercise 4.9 **Writing Equations for Reactions**

For each of the following reactions, write the formula equation, the complete ionic equation, and the net ionic equation.

a. Aqueous potassium chloride is added to aqueous sliver nitrate to form a silver chloride precipitate plus aqueous potassium nitrate.

b. Aqueous potassium hydroxide is mixed with aqueous iron(III) nitrate to form a precipitate of iron(III) hydroxide and aqueous potassium nitrate.

Sample Exercise 4.9

Solution

a. Formula Equation

$$KCl(aq) + AgNO_3(aq) \longrightarrow AgCl(s) + KNO_3(aq)$$

Complete Ionic Equation

(*Remember: Any ionic compound dissolved in water will be present as the separated ions.*)

$$\underset{\substack{\text{Spectator}\\ \text{ion}}}{\overset{}{\underset{\uparrow}{K^+(aq)}}} + Cl^-(aq) + Ag^+(aq) + \underset{\substack{\text{Spectator}\\ \text{ion}}}{\underset{\uparrow}{NO_3^-(aq)}} \longrightarrow \underset{\substack{\text{Solid,}\\ \text{not written}\\ \text{as separate ions}}}{\underset{\uparrow}{AgCl(s)}} + \underset{\substack{\text{Spectator}\\ \text{ion}}}{\underset{\uparrow}{K^+(aq)}} + \underset{\substack{\text{Spectator}\\ \text{ion}}}{\underset{\uparrow}{NO_3^-(aq)}}$$

Sample Exercise 4.9

Canceling the spectator ions

$$\cancel{K^+}(aq) + Cl^-(aq) + Ag^+(aq) + \cancel{NO_3^-}(aq) \longrightarrow AgCl(s) + \cancel{K^+}(aq) + \cancel{NO_3^-}(aq)$$

gives the following net ionic equation.

Net Ionic Equation

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

b. Formula Equation

$$3KOH(aq) + Fe(NO_3)_3(aq) \longrightarrow Fe(OH)_3(s) + 3KNO_3(aq)$$

Sample Exercise 4.9

Complete Ionic Equation

$$3K^{+}(aq) + 3OH^{-}(aq) + Fe^{3+}(aq) + 3NO_3^{-}(aq) \longrightarrow Fe(OH)_3(s) + 3K^{+}(aq)$$

Net Ionic Equation

$$3OH^{-}(aq) + Fe^{3+}(aq) \longrightarrow Fe(OH)_3(s)$$

See Exercises 4.39 and 4.44

4.7 Stoichiometry of Precipitation Reactions

- *These same principles apply to reactions that take place in solutions.*

Sample Exercise 4.10 Determining the Mass of Product Formed

Calculate the mass of solid NaCl that must be added to 1.50 L of a 0.100 *M* $AgNO_3$ solution to precipitate all the Ag^+ ions in the form of AgCl.

Solution

When added to the $AgNO_3$ solution (which contains Ag^+ and NO_3^- ions), the solid NaCl dissolves to yield Na^+ and Cl^- ions. Thus the mixed solution contains the ions

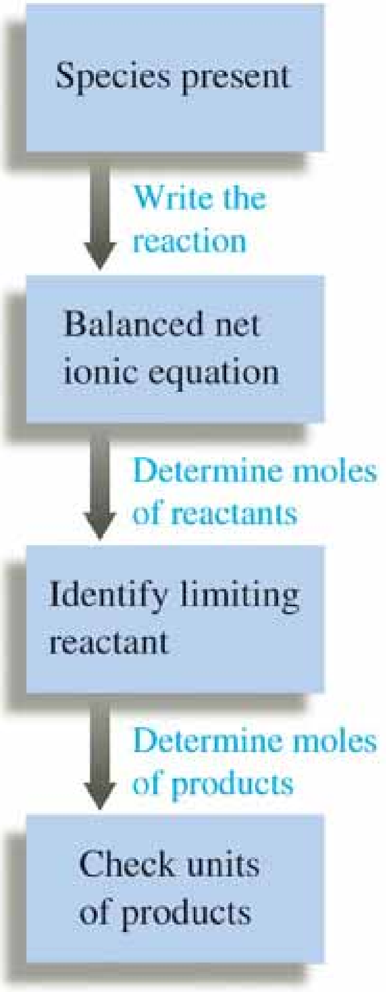
$$Ag^+ \qquad NO_3^- \qquad Na^+ \qquad Cl^-$$

Sample Exercise 4.10

Note from Table 4.1 that $NaNO_3$ is soluble and AgCl is incoluble. Therefore, solid AgCl forms according to the following net ionic equation:

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

In this case we must add enough Cl^- ions to react with all the Ag^+ ions present. Thus we must calculate the moles of Ag^+ ions present in 1.50 l of a 0.100 M $AgNO_3$



Species present

Write the reaction

Balanced net ionic equation

Determine moles of reactants

Identify limiting reactant

Determine moles of products

Check units of products

Sample Exercise 4.10

solution (remember that a 0.100 M $AgNO_3$ solution contains 0.100 M Ag^+ ions and 0.100 M NO_3^- ions):

$$1.50\ \cancel{L} \times \frac{0.100\ \text{mol Ag}^+}{\cancel{L}} = 0.150\ \text{mol Ag}^+$$

Because Ag^+ and Cl^- react in a 1:1 ratio, 0.150 mol Cl^- ions and thus 0.150 mol NaCl are required. We calculate the mass of NaCl reauired as follows:

$$0.150\ \cancel{\text{mol NaCl}} \times \frac{58.45\ \text{g NaCl}}{\cancel{\text{mol NaCl}}} = 8.77\ \text{g NaCl}$$

See Exercises 4.47

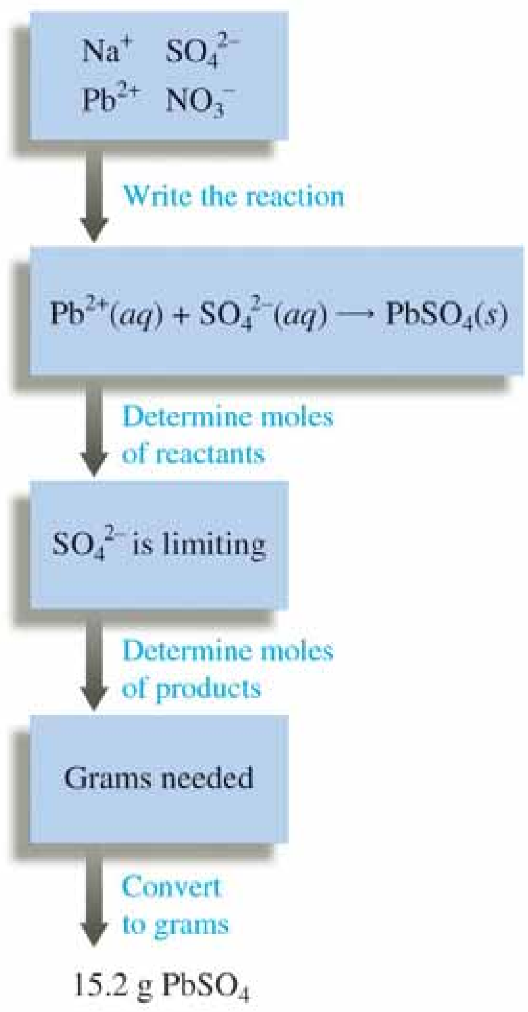
Solving Stoichiometry Problems for Reactions in Solution

1. Identify the species present in the combined solution, and determine what reaction occurs.
2. Write the balanced net ionic equation for the reaction.
3. Calculate the moles of reactants.
4. Determine which reactant is limiting.
5. Calculate the moles of product or products, as required.
6. Convert to grams or other units, as required.

Sample Exercise 4.11

Determining the Mass of Product Formed

When aqueous solutions of Na_2SO_4 and $Pb(NO_3)_2$ are mixed, $PbSO_4$ precipitates. Calculate the mass of $PbSO_4$ formed when 1.25 L of 0.0500 *M* $Pb(NO_3)_2$ and 2.00 L of 0.0250 *M* Na_2SO_4 are mixed.



4.8 Acid-Base Reactions

- An acid is a substance that produces H^+ ions when dissolved in water, and a base is a substance that produces OH^- ions.
- Such a definition was provided by Johannes N. Brønsted (1879-1947) and Thomas M. Lowry (1874-1936), who defined acids and bases as follows:

An **acid** is a proton donor.

A **base** is a proton acceptor.

- When an aqueous solution of hydrogen chloride (HCl) is mixed with an aqueous solution of sodium hydroxide (NaOH), the combined solution contains the ions H^+, Cl^-, Na^+, and OH^-.
- The separated ions are present because HCl is a strong acid and NaOH is a strong base.
- From Table 4.1 we can see that NaCl is soluble in water and thus will not precipitate.
- Large quantities of H^+ and OH^- ions cannot coexist in solution.

- They react to form H_2O molecules:

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

- Consider mixing an aqueous solution of acetic acid ($HC_2H_3O_2$) with an aqueous solution of potassium hydroxide (KOH).
- A possible precipitation reaction could occur between K^+ and OH^-.
- We know that KOH is soluble, so precipitation does not occur.

- The net ionic equation for this reaction is

$$\mathrm{OH^{-} + HC_2H_3O_2}(aq) \longrightarrow \mathrm{H_2O}(l) + \mathrm{C_2H_3O_2^{-}}(aq)$$

- This reaction illustrates a very important general principle: *The hydroxide ion is such a strong base that for purposes of stoichiometric calculations it can be assumed to react completely with any weak acid that we will encounter.*

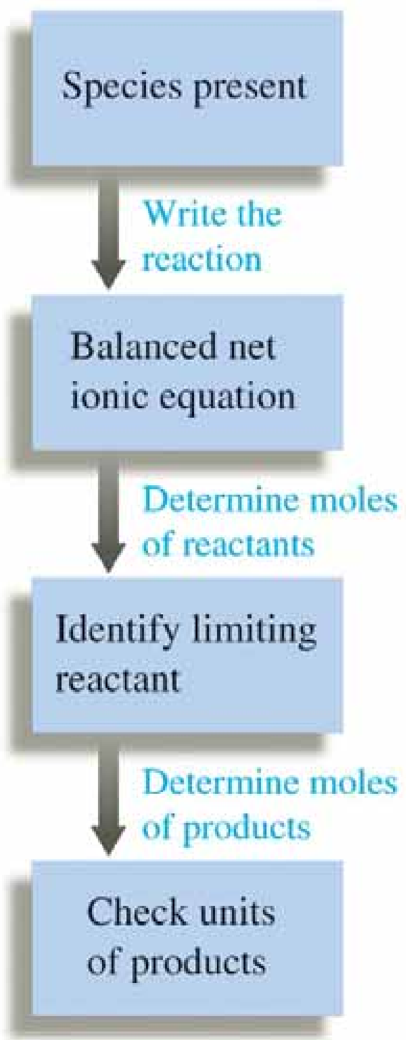
Performing Calculations for Acid-Base Reactions

1. List the species present in the combined solution before any reaction occurs, and decide what reaction will occur.
2. Write the balanced net ionic equation for the reaction.
3. Calculate the moles of reactants. For reactions in solution, use the volumes of the original solutions and their molarities.
4. Determine the limiting reactant where appropriate.

5 **Calculate the moles of the required reactant or product.**

6 **Convert to grams or volume (of solution), as required.**

- An acid-base reaction is often called a **neutralization reaction**. When just enough base is added to react exactly with the acid in a solution, we say the acid has been neutralized.



Species present

Write the reaction

Balanced net ionic equation

Determine moles of reactants

Identify limiting reactant

Determine moles of products

Check units of products

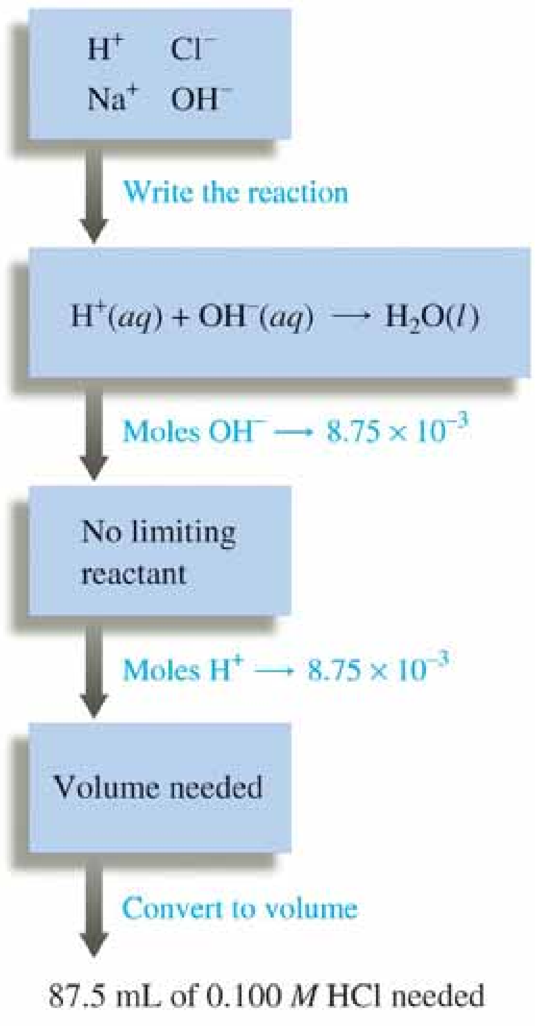
Sample Exercise 4.12 Neutralization Reactions I

What volume of a 0.100 *M* HCl solution is needed to neutralize 25.0 mL of 0.350 *M* NaOH?

Ans. $H^+(aq) + OH^-(aq) \rightarrow H_2O(l)$

$0.100 \times V_{HCl} = 0.350 \times 25.0/1000$

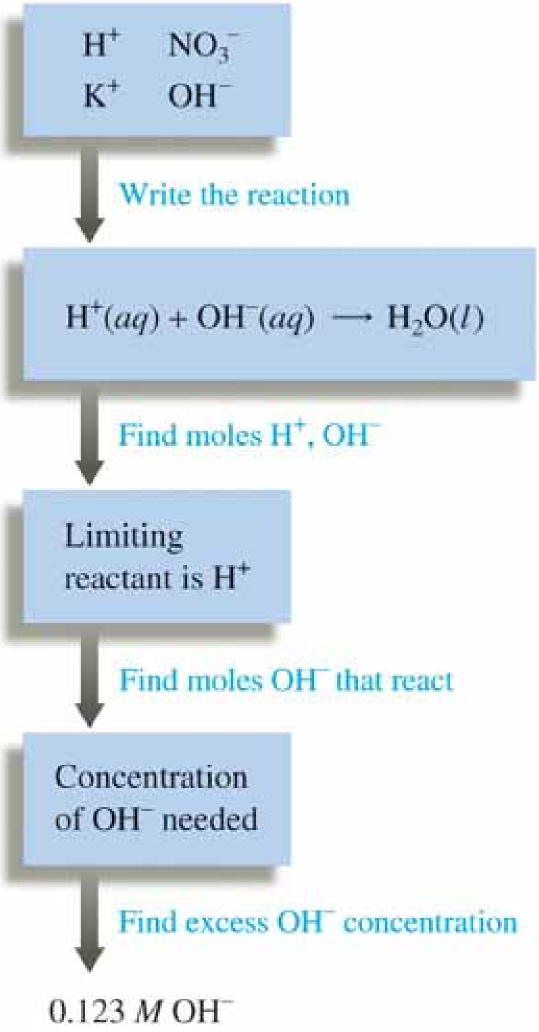
$V_{HCl} = 0.0875\ L = 87.5\ mL$



Sample Exercise 4.13

Neutralization Reactions II

In a certain experiment, 28.0 mL of 0.250 *M* HNO_3 and 53.0 mL of 0.320 *M* KOH are mixed. Calculate the amount of water formed in the resulting reaction. What is the concentration of H^+ or OH^- ions in excess after the reaction goes to completion?



28.0 mL of 0.250 *M* HNO_3 and 53.0 mL of 0.320 *M* KOH

28.0/1000 x 0.250 = 7.00 x 10^{-3} mol H^+

53.0/1000 x 0.320 = 1.70 x 10^{-2} mol OH^-

H^+ is limiting reactant

The amount of water formed = 18 x 7 x 10^{-3} = 0.13 g

$[OH^-]$ = 0.017-0.007)/(0.028 + 0.053) = 0.123 M

Acid-Base Titrations

- **Volumetric analysis** is a technique for determining the amount of a certain substance by doing a titration.
- A **titration** involves delivery of a measured volume of a solution of known concentration into a solution containing the substance being analyzed.
- The point in the titration where enough titrant has been added to react exactly with the analyte is called the **equivalence point** or the **stoichiometric point**.

- **Indicator**, a substance added at the beginning of the titration that changes color at (or very near) the equivalence point.
- The following three requirements must be met for a titration to be successful:

1. The exact reaction between titrant and analyte must be know (and rapid).
2. The stoichiometric (equivalence) point must be marked accurately.
3. The volume of titrant required to reach the stoichiometric point must be known accurately.

- When an acid is titrated with a base, the phenolphthalein remains colorless until after the acid is consumed and the first drop of excess base is added.
- In this case, the endpoint (the solution changes from colorless to pink) occurs approximately one drop of base beyond the stoichiometric point.
- This type of titration is illustrated in the three photos in Fig. 4.18.

Figure 4.18

The titration of acid with a base. (a) The titrant (the base) is in the buret, and the flask contains the acid solution along with a small amount of indicator. (b) As base is added drop by drop to the acid solution in the flask during the titration, the indicator changes color, but the color disappears on mixing.

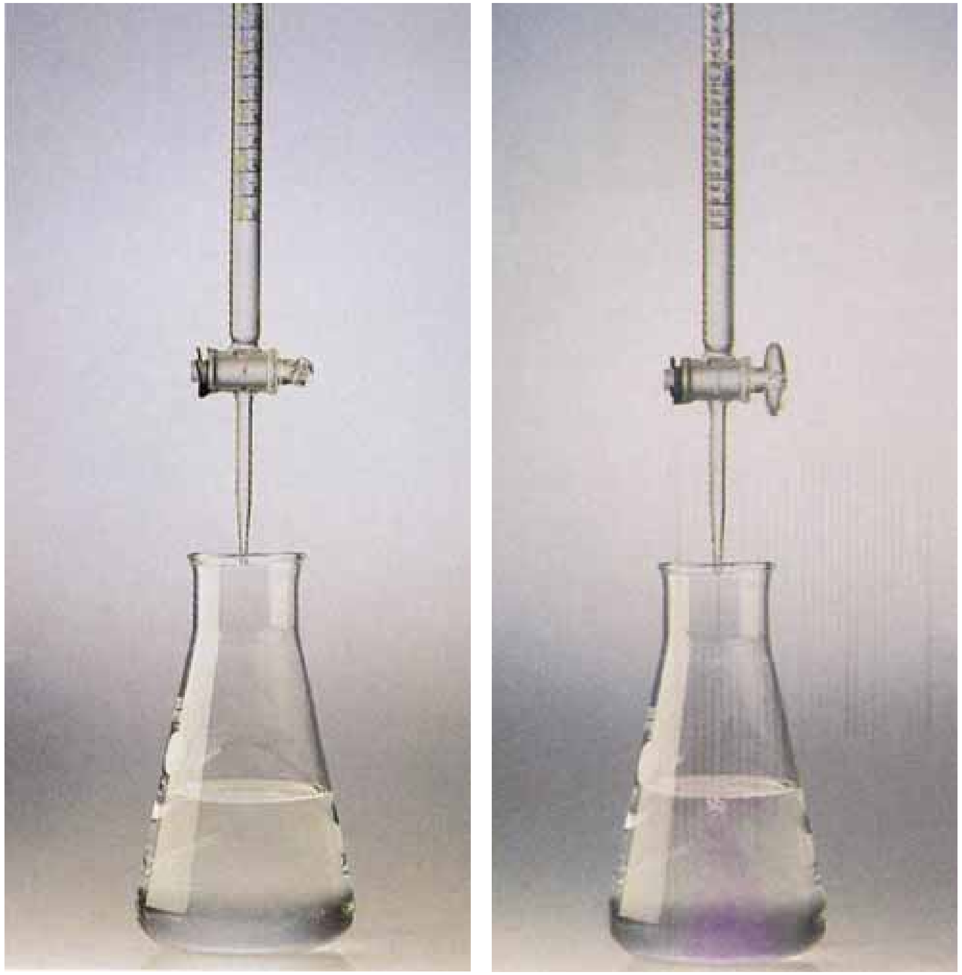


Figure 4.18

(c) The stoichiometric (equivalence) point is marked by a permanent indicator color change. The volume of base added is the difference between the final and initial buret readings.

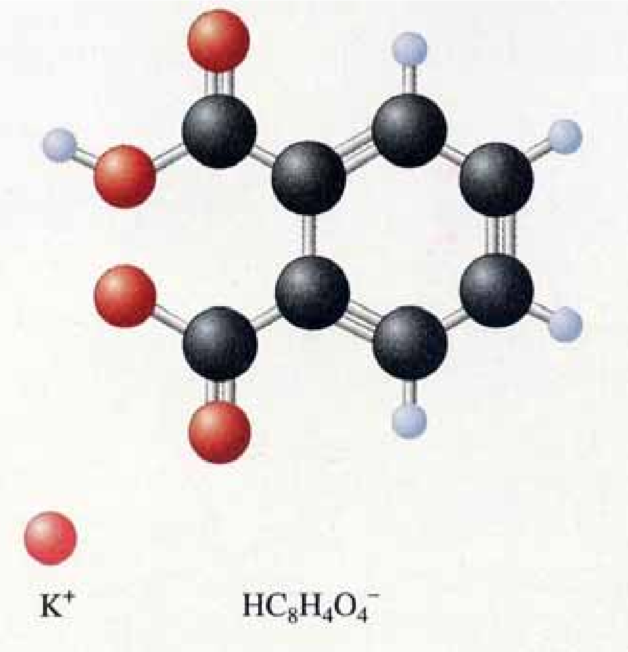
Sample Exercise 4.14

Neutralization Titration

A student carries out an experiment to standardize (determine the exact concentration of) a sodium hydroxide solution. To do this, the student weighs out a 1.3009-g sample of potassium hydrogen phthalate ($KHC_8H_4O_4$, often abbreviated KHP). KHP (molar mass 204.22 g/mol) has one acidic hydrogen. The student dissolves the KHP in distilled water, adds phenolphthalein as an indicator, and titrates the resulting solution with the sodium hydroxide solution to the phenolphthalein endpoint. The different between the final and initial buret

Sample Exercise 4.14

Readings indicates that 41.20 mL of the sodium hydroxide solution is required to react exactly with the 1.3009 g KHP. Calculate the concentration of the sodium hydroxide solution.



Sample Exercise 4.14

Solution

Aqueous sodium hydroxide contains the Na^+ and OH^- ions, and $KHC_8H_4O_4$ dissolves in water to give the K^+ and $HC_8H_4O_4^-$ ions. As the titration proceeds, the mixed solution contains the following ions: K^+, $HC_8H_4O_4^-$, Na^+, OH^-. The OH^- will remove an H^+ from the $HC_8H_4O_4^-$ to give the following net ionic reaction:

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

Sample Exercise 4.14

Since the reaction exhibits 1:1 stoichiometry, we know that 41.20 mL of the sodium hydroxide solution must contain exactly the same number of moles of OH^- as there are moles of $HC_8H_4O_4^-$ in 1.3009 g $KHC_8H_4O_4$. We calculate the moles of $KHC_8H_4O_4$ in the usual way:

$$1.3009\ \cancel{\text{g KHC}_8\text{H}_4\text{O}_4} \times \frac{1\ \text{mol KHC}_8\text{H}_4\text{O}_4}{204.22\ \cancel{\text{g KHC}_8\text{H}_4\text{O}_4}} = 6.3701 \times 10^{-3}\ \text{mol KHC}_8\text{H}_4\text{O}_4$$

This means that 6.3701×10^{-3} mol OH^- must be added to react with the 6.3701×10^{-3} mol $HC_8H_4O_4^-$. Thus

Sample Exercise 4.14

41.20 mL (4.120×10^{-2} L) of the sodium hydroxide solution must contain 6.3701×10^{-3} mol OH^- (and Na^+), and the concertration of the sodium hydroxide solution is

$$\text{Molarity of NaOH} = \frac{\text{mol NaOH}}{\text{L solution}} = \frac{6.3701 \times 10^{-3}\ \text{mol NaOH}}{4.120 \times 10^{-2}\ \text{L}}$$
$$= 0.1546\ M$$

This standard sodium hydroxide solution can now be used in other experiments (see Sample Exercise 4.15).

See Exercises 4.47

4.9 Oxidation-Reduction Reactions

- We have seen that many important substances are ionic. Sodium chloride, can be formed by the reaction of elemental sodium and chlorine:

$$2\text{Na}(s) + \text{Cl}_2(g) \longrightarrow 2\text{NaCl}(s)$$

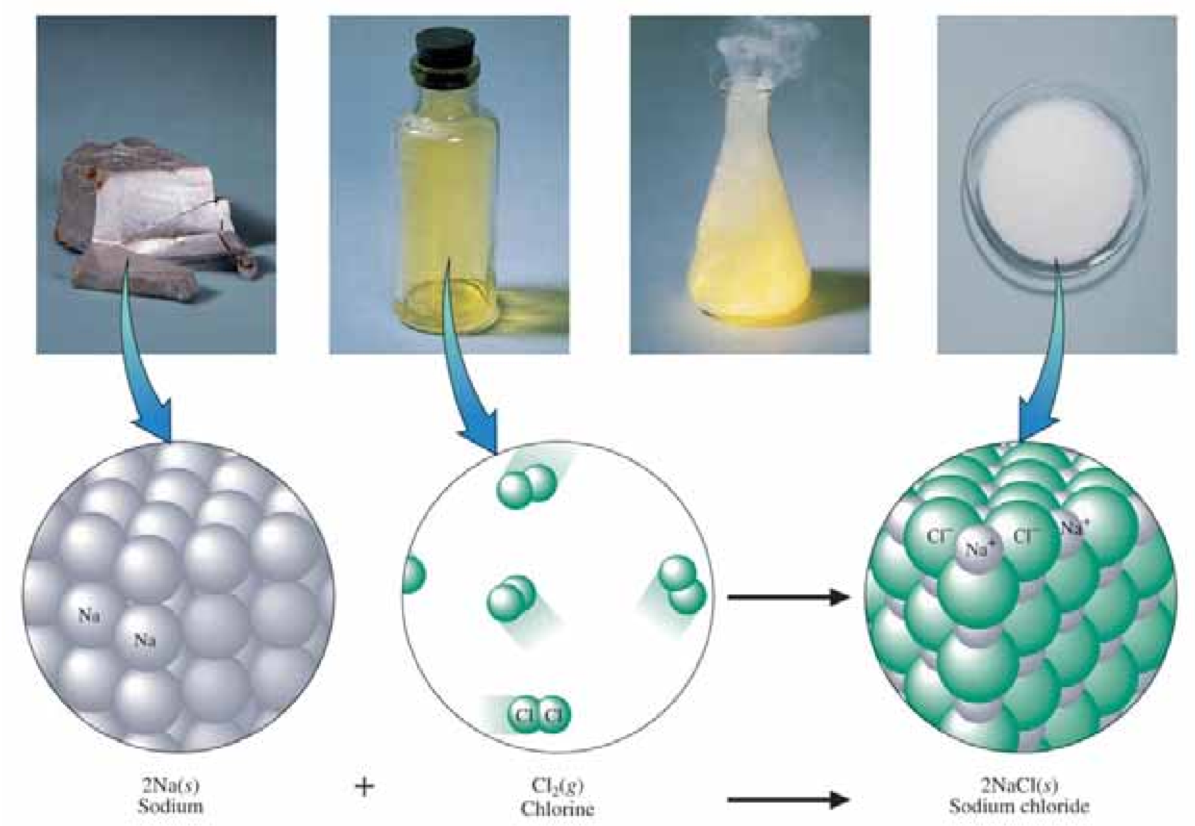
- This process is represented in Fig. 4.19.
- *Reaction like this one, in which one or more electrons are transferred, are called* ***oxidation-reduction reactions*** *or* ***redox reactions****.*

- Many important chemical reactions involve oxidation and reduction.
- Combustion reactions, which provide most of the energy to power our civilization, also involve oxidation and reduction.
- An example is the reaction of methane with oxygen:

$$CH_4(g) + 2O_2(g) \longrightarrow CO_2(g) + 2H_2O(g) + \text{energy}$$

- Even though none of the reactants or products in this reaction is ionic, the reaction is still assumed to involve a transfer of electrons from carbon to oxygen.

Figure 4.19



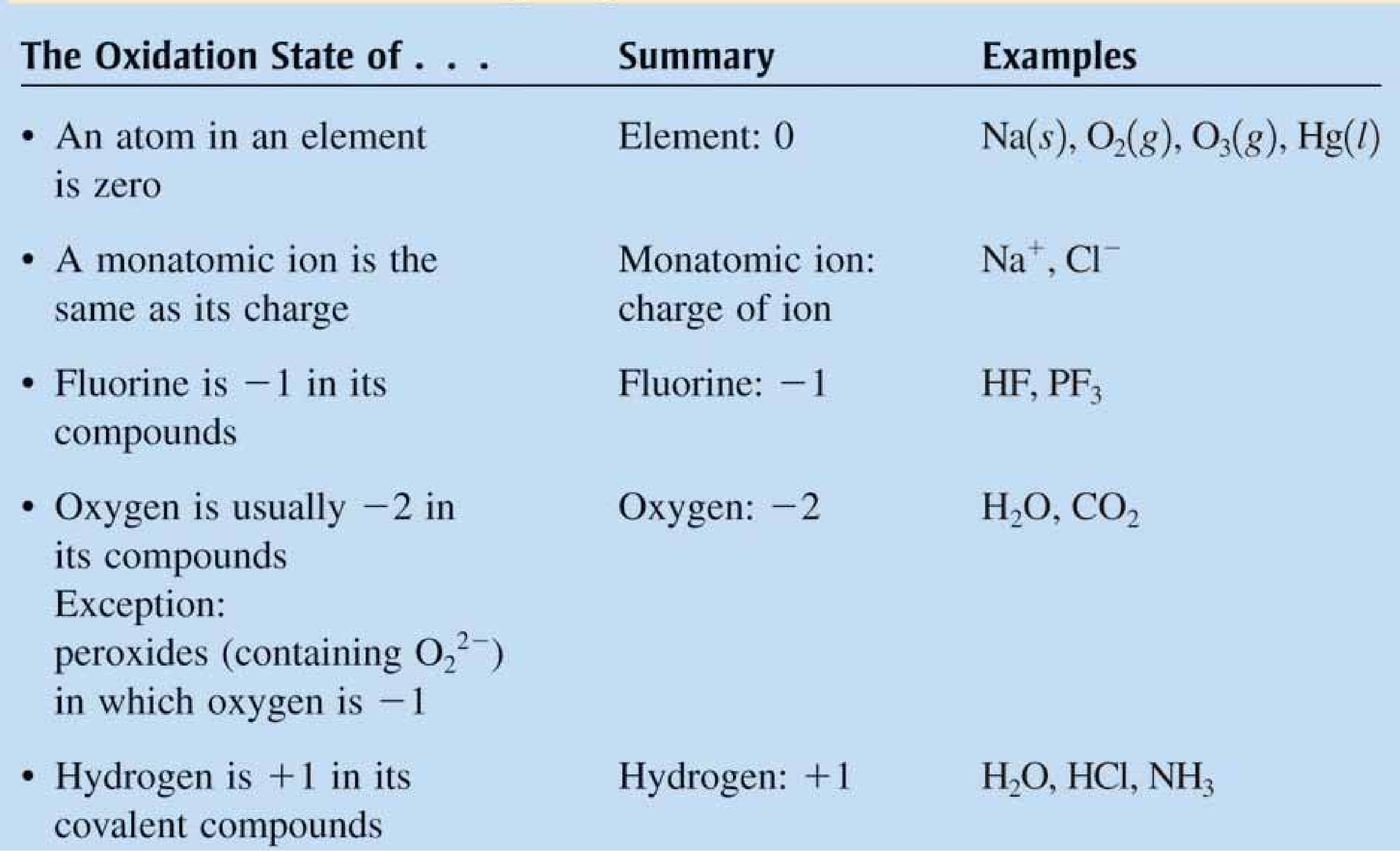
The reaction of solid sodium and gaseous chlorine to form solid sodium chloride.

Oxidation States

- The oxidation states of atoms in covalent compounds are obtained by arbitrarily assigning the electrons (which are actually shared) to particular atoms.
- We do this as follows: For a covalent bond between two identical atoms, the electrons are split equally between the two.
- In cases where two different atoms are involved (and the electrons are thus shared unequally), the shared electrons are assigned completely to the atom that has the stronger attraction for electrons.

- A series of rules for assigning oxidation states that are summarized in Table 4.2.
- To apply these rules recognize that *the sum of the oxidation states must be zero for an electrically neutral compound.*

TABLE 4.2 Rules for Assigning Oxidation States



The Oxidation State of . . .	Summary	Examples
• An atom in an element is zero	Element: 0	Na(*s*), O_2(*g*), O_3(*g*), Hg(*l*)
• A monatomic ion is the same as its charge	Monatomic ion: charge of ion	Na^+, Cl^-
• Fluorine is −1 in its compounds	Fluorine: −1	HF, PF_3
• Oxygen is usually −2 in its compounds Exception: peroxides (containing O_2^{2-}) in which oxygen is −1	Oxygen: −2	H_2O, CO_2
• Hydrogen is +1 in its covalent compounds	Hydrogen: +1	H_2O, HCl, NH_3

Oxidation of copper metal by nitric acid. The copper atoms lose two electrons to form Cu^{2+} ions, which give a deep green color that becomes turquoise when diluted with water.

Sample Exercise 4.16

Assigning Oxidation States

Assign oxidation states to all atoms in the following.

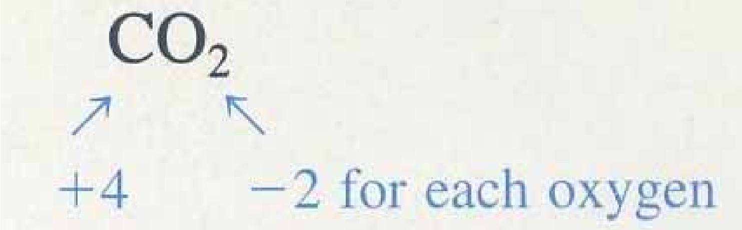
a. CO_2

b. SF_6

c. NO_3^-

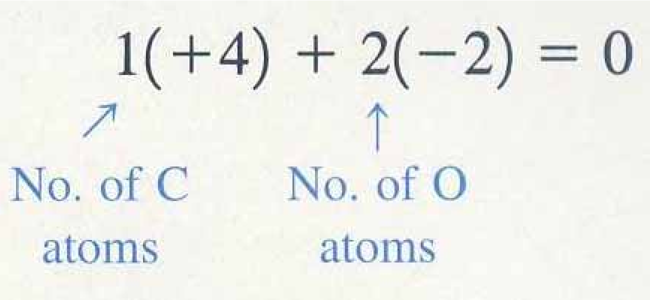
Solution

a. The oxidation state of oxygen is －2.



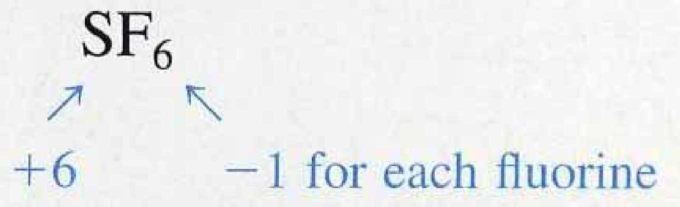
Sample Exercise 4.16

The sum is zero as required:



$$\underset{\substack{\nearrow\\\text{No. of C}\\\text{atoms}}}{1}(+4) + \underset{\substack{\uparrow\\\text{No. of O}\\\text{atoms}}}{2}(-2) = 0$$

b.

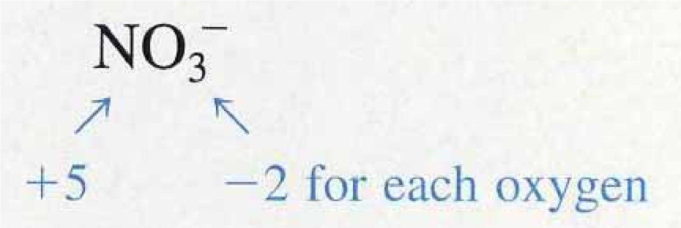


$$\underset{\substack{\nearrow\\+6}}{\mathrm{S}}\;\underset{\substack{\nwarrow\\-1\text{ for each fluorine}}}{\mathrm{F}_6}$$

Reality Check: $+6 + 6(-1) = 0$

Sample Exercise 4.16

c.



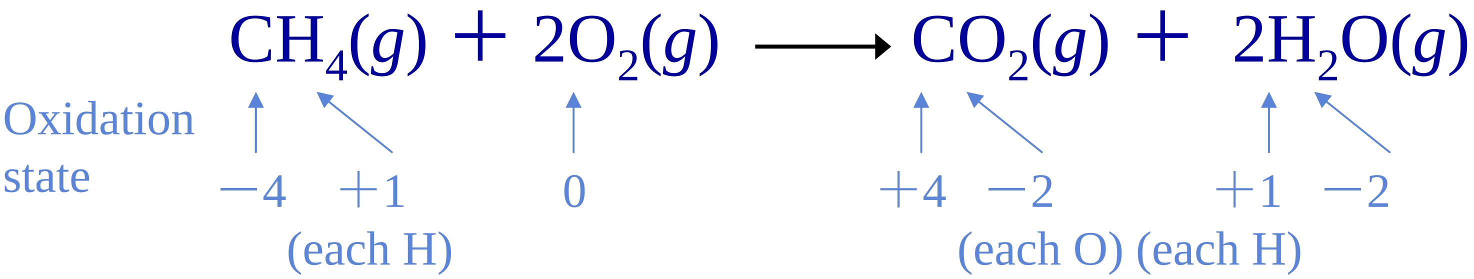
Reality Check: $+5 + 3(-2) = -1$

See Exercises 4.67 through 4.70

- For Fe_3O_4, the rules assume that all the iron atoms are equal, when in fact this compound can best be viewed as-containing four O^{2-} ions, two Fe^{3+} ions, and one Fe^{2+} ion per formula unit.

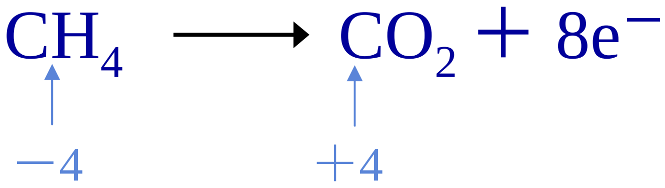
Magnetite is a magnetic ore containing Fe_3O_4. Note that the compass needle points toward the ore.

The Characteristics of Oxidation-Reduction Reactions



$$CH_4(g) + 2O_2(g) \longrightarrow CO_2(g) + 2H_2O(g)$$

- Note that the oxidation state for oxygen in O_2 is 0 because it is in elemental form.
- Note that carbon undergoes a change in oxidation state from −4 in CH_4 to +4 in CO_2.



$$CH_4 \longrightarrow CO_2 + 8e^-$$

- Each oxygen changes from an oxidation state of 0 in O_2 to -2 in H_2O and CO_2, signifying a gain of two electrons per atom.

$$\underset{\substack{\uparrow \\ 0}}{2O_2} + 8e^- \longrightarrow \underset{\substack{\nwarrow \qquad \nearrow \\ 4(-2) = -8}}{CO_2 + 2H_2O}$$

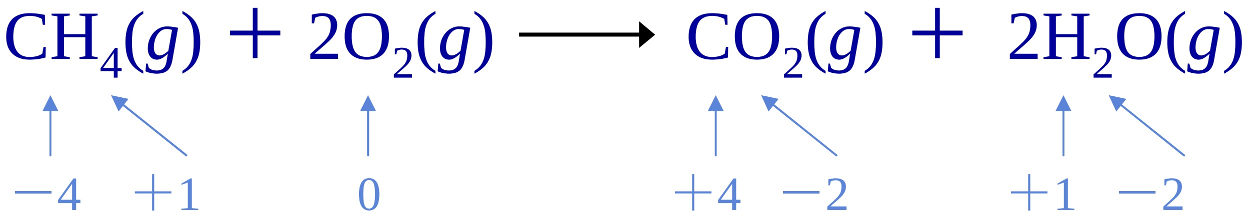
- **Oxidation** is an increase in oxidation state (a loss of electrons).

- **Reduction** is a decrease in oxidation state (a gain of electrons). Thus in the reaction.

$$\underset{\underset{0}{\uparrow}}{2Na(s)} + \underset{\underset{0}{\uparrow}}{Cl_2(g)} \longrightarrow 2\underset{\underset{+1}{\uparrow}}{Na}\underset{\underset{-1}{\nwarrow}}{Cl}(s)$$

- Cl_2 is called the oxidizing agent (electron acceptor), and Na is called the reducing agent (electron donor). These terms are summarized in Fig. 4.20.

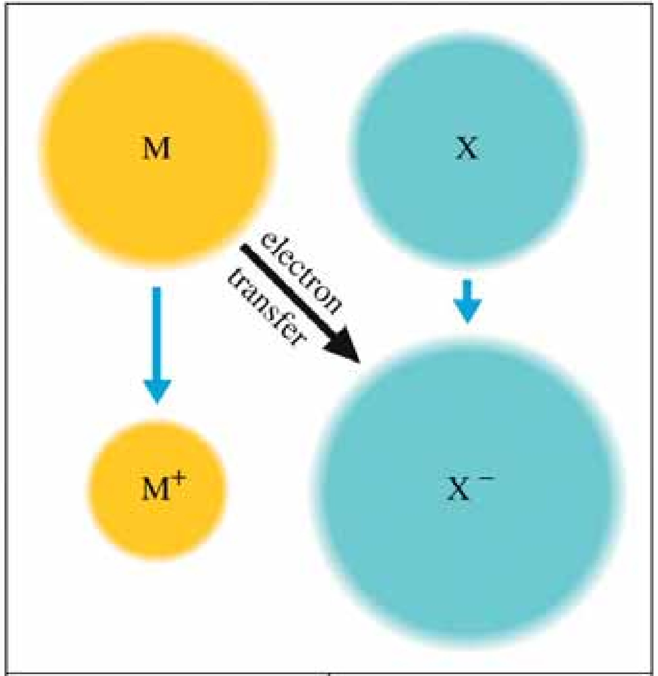
- Concerning the reaction



$$\underset{-4\quad +1}{CH_4(g)} + \underset{0}{2O_2(g)} \longrightarrow \underset{+4\quad -2}{CO_2(g)} + \underset{+1\quad -2}{2H_2O(g)}$$

- Carbon is oxidized because there has been an increase in its oxidation state (carbon has formally lost electrons).
- Oxygen is reduced because there has been a decrease in its oxidation state (oxygen has formally gained electrons).
- CH_4 is the reducing agent.
- O_2 is the oxidizing agent.

Figure 4.20



Oxidized	Reduced
loses electrons	*gains* electrons
oxidation state *increases*	oxidation state *decreases*
reducing agent	*oxidizing* agent

A summary of an oxidation-reduction process, in which M is oxidized and X is reduced.

4.10 Balancing Oxidation-Reduction Equations

The Half-Reaction Method for Balancing Oxidation-Reduction Reactions in Aqueous Solutions

- For oxidation-reduction reactions that occur in aqueous solution, it is useful to separate the reaction into two **half-reactions**: involving oxidation and the other involving reduction.

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

- The substance being *reduced*,

$$Ce^{4+}(aq) \longrightarrow Ce^{3+}(aq)$$

- The substance being *oxidized*,

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

- The general procedure is to balance the equations for the half-reactions separately and then to add them to obtain the overall balanced equation.

The Half-Reaction Method for Balancing Equations for Oxidation-Reduction Reactions Occurring in Acidic Solution

1 Write separate equations for the oxidation and reduction half-reactions.

2 For each half-reaction,

a. Balance all the element except hydrogen and oxygen.

b. Balance oxygen using H_2O.

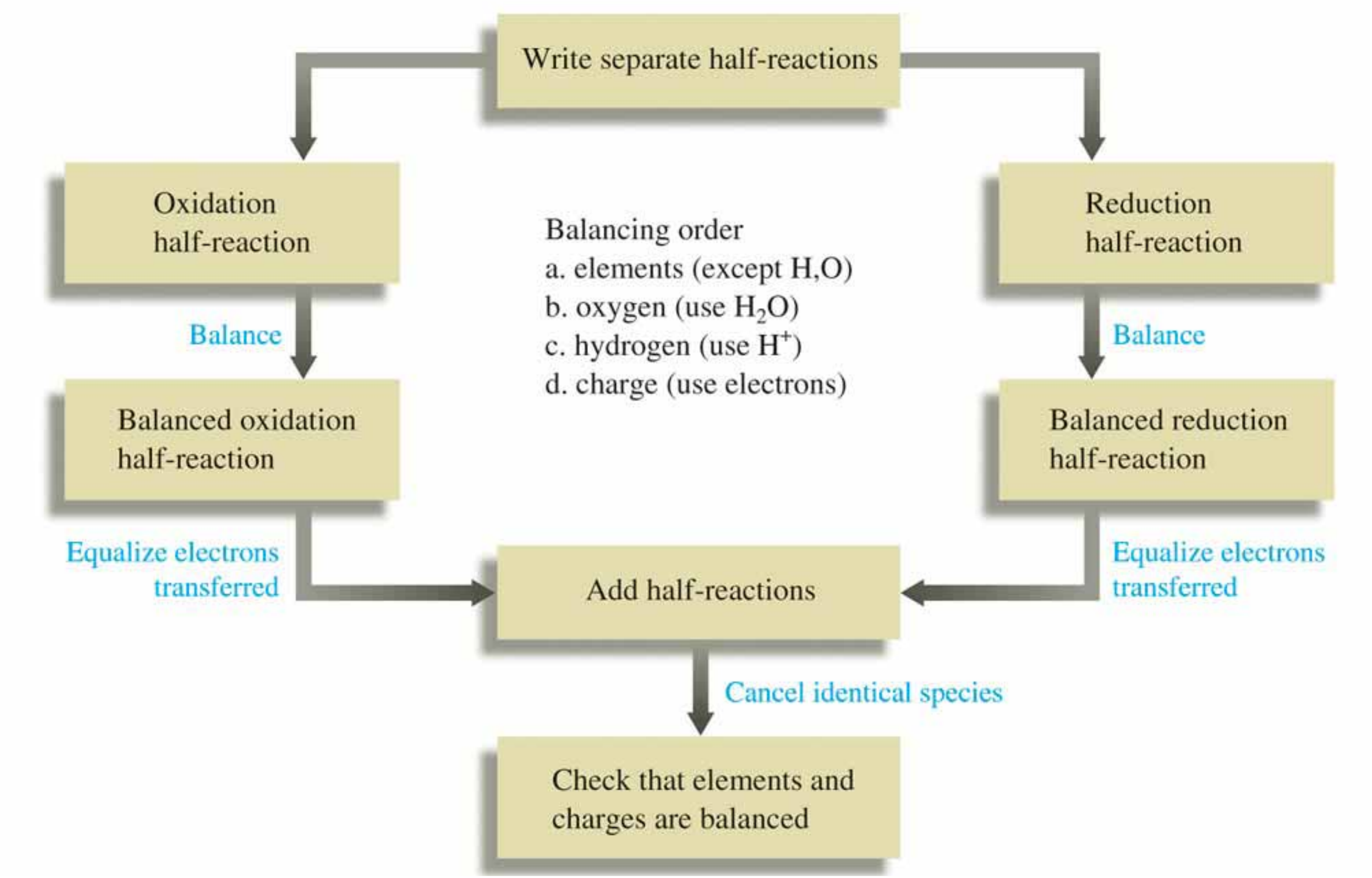
c. Balance hydrogen using H^+.

d. Balance the charge using electrons.

3 If necessary, multiply one or both balanced half-reactions by an integer to equalize the number of electrons transferred in the two half-reactions.

4. **Add the half-reactions, and cancel identical species.**
5. **Check that the elements and charges are balanced.**

- These steps are summarized by the following flowchart:



Write separate half-reactions

Oxidation half-reaction

Reduction half-reaction

Balance

Balance

Balanced oxidation half-reaction

Balanced reduction half-reaction

Balancing order
a. elements (except H,O)
b. oxygen (use H_2O)
c. hydrogen (use H^+)
d. charge (use electrons)

Equalize electrons transferred

Equalize electrons transferred

Add half-reactions

Cancel identical species

Check that elements and charges are balanced

- We will illustrate this method by balancing the equation for the reaction between permanganate and iron(II) ions in acidic solution:

$$\mathrm{MnO_4^-}(aq) + \mathrm{Fe^{2+}}(aq) \xrightarrow{\text{Acid}} \mathrm{Fe^{3+}}(aq) + \mathrm{Mn^{2+}}(aq)$$

1 *Identify and write equations for the half-reactions.*

$$\underset{+7}{\mathrm{Mn}}\,\underset{-2\text{ (each O)}}{\mathrm{O_4^-}} \longrightarrow \underset{+2}{\mathrm{Mn^{2+}}}$$

- This is the reduction half-reaction.

$$\underset{\substack{\uparrow \\ +2}}{Fe^{2+}} \longrightarrow \underset{\substack{\uparrow \\ +3}}{Fe^{3+}}$$

➡ **2** *Balance each half-reaction.*

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

a. The manganese is balanced.

b. We balance oxygen by adding $4H_2O$ to the right side of the equation:

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

c. Balance hydrogen by adding $8H^+$ to the left side:

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

d. Balance the charge using electrons.

$$8H^+(aq) + MnO_4^-(aq) \qquad Mn^{2+}(aq) + 4H_2O(l)$$

$$\underbrace{8+ \quad + \quad 1-}_{7+} \qquad\qquad \underbrace{2+ \quad + \quad 0}_{2+}$$

We can equalize the charges by adding five electrons to the left side:

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

Both the *elements* and the *charges* are now balanced.

For the oxidation reaction

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

$$\underbrace{\mathrm{Fe}^{2+}(aq)}_{2+} \longrightarrow \underbrace{\mathrm{Fe}^{3+}(aq)}_{3+}$$

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

3 *Equalize the electron transfer in the two half-reactions.*

$$5\mathrm{Fe}^{2+}(aq) \longrightarrow 5\mathrm{Fe}^{3+}(aq) + 5\mathrm{e}^{-}$$

➡ **4** *Add the half-reactions.*

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

Note that the electrons cancel (as they must) to give the final balanced equation:

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

➡ **5** *Check that elements and charges are balanced.*

Elements balance:

$$5Fe,\ 1\ Mn,\ 4O,\ 8H \longrightarrow 5Fe,\ 1\ Mn,\ 4O,\ 8H$$

Charges balance:

$$5(2+) + (1-) + 8(1+) = 17+ \longrightarrow 5(3+) + (2+) + 0 = 17+$$

The equation is balanced.

The Half-Reaction Method for Balancing Equations for Oxidation-Reduction Reactions Occurring in Basic Solution

1. Use the half-reaction method as specified for acidic solutions to obtain the final balanced equation as *if H^+ ions were present*.
2. To both sides of the equation obtained above, add a number of OH^- ions that is equal to the number of H^+ ions. (We want to eliminate H^+ by forming H_2O.)
3. Form H_2O on the side containing both H^+ and OH^- ions, and eliminate the number of H_2O molecules that appear on both sides of the equation.
4. Check that elements and charges are balanced.

- This method is summarized by the following flowchart: