So far, we have considered stoichiometric relationships on the basis of masses and moles. Often it is more convenient to add a substance into a reaction mixture in the form of a solution, rather than as a weighed sample of material. We can still make predictions of reactants used and products formed on the basis of mole-based stoichiometric relationships when we use solutions, because chemists define solution concentration terms based on the mole concept. But before we can take up solution concentration terminology, we need to understand how solutes dissolve in solvents and the kinds of reactions that can occur in solution.

**Learning Objective**

- Understand the terms electrolyte, strong electrolyte, weak electrolyte, and nonelectrolyte
- Know the solubility trends for simple ionic substances
- Know the kinds of reactions that can occur among electrolytes in aqueous solutions

**Success Criteria**

- Be able to identify which solutes will be strong electrolytes, weak electrolytes, or nonelectrolytes in aqueous solution
- Be able to predict the solubility or insolubility of simple ionic compounds in water
- Be able to predict reactions of mixed electrolyte solutions
- Be able to write balanced ionic and net ionic equations for reactions occurring when electrolyte solutions are mixed

**Electrolytes and Nonelectrolytes**

A solute that increases the electrical conductivity of a solvent when added to make a solution is an **electrolyte**. A solute that does not change the electrical conductivity when added to a solvent is a **nonelectrolyte**. Solutions of electrolytes conduct electricity through the movement of cations and anions, which are produced in solution when the solute dissolves. When an ionic substance dissolves in water, it breaks up into its component ions, which are free to move about in the solution.

\[ \text{NaCl(s)} \rightarrow \text{Na}^+(aq) + \text{Cl}^-(aq) \]

**electrolyte**
Substances that dissolve to give only molecules in solution do not conduct electricity and therefore are nonelectrolytes. Table sugar (sucrose) is a typical nonelectrolyte, because it produces no ions in solution.

\[C_{12}H_{22}O_{11}(s) \rightarrow C_{12}H_{22}O_{11}(aq)\]

nonelectrolyte

Not all molecular substances dissolve as molecules. For example, molecular acids break up to some extent to form \(H^+(aq)\) and an anion in solution. For example,

\[[HCl(g) \rightarrow H^+(aq) + Cl^–(aq)]\]
electrolyte

The \(H^+(aq)\) is actually present as the hydronium ion, \(H_3O^+(aq)\), so this reaction is better represented as follows:

\[[HCl(g) + H_2O \rightarrow H_3O^+(aq) + Cl^–(aq)]\]
electrolyte

If a substance produces virtually nothing other than ions in solution (i.e., there are essentially no molecules in solution), it will have the maximum possible conductivity for the amount of dissolved solute. Such substances are called strong electrolytes. Both NaCl and HCl are strong electrolytes. Ionic compounds, like NaCl, do not contain any molecules of the substance, and therefore they can only form ions in solution. Some ionic compounds, such as AgCl, are considered insoluble, because only a very small amount dissolves in a large quantity of water. Nonetheless, so-called insoluble ionic compounds do dissolve to some extent, and they do so by breaking up into cations and anions in solution. Therefore, all ionic compounds are strong electrolytes, regardless of their solubility. Electrolyte status and solubility are separate considerations.

As the examples of HCl and \(C_{12}H_{22}O_{11}\) show, some molecular compounds may be strong electrolytes or nonelectrolytes. Other molecular compounds may fall between these extremes. Molecular compounds that dissolve with a small portion of their molecules breaking up into ions will conduct electricity weakly. Thus, they are called weak electrolytes. Many acids (e.g., acetic acid) and most molecular bases (e.g., \(NH_3\)) are weak electrolytes.

\[[CH_3CO_2H(l) + H_2O \rightarrow H_3O^+(aq) + CH_3CO_2^–(aq)]\]
weak electrolyte

\[[NH_3(g) + H_2O \rightarrow NH_4^+(aq) + OH^–(aq)]\]
weak electrolyte

The reactions in each of these cases should be viewed as proceeding only partially to the right. (Later, we will consider these kinds of reactions in the context of the concept of equilibrium.) With weak electrolytes, the solute is present mainly as dissolved molecules, with only a relatively small number of ions produced in solution. Therefore, write all weak electrolytes in molecular form in ionic equations.
Q1

NaCl is a strong electrolyte when dissolved in water, but pure solid NaCl does not conduct electricity. Why?

Q2

Which of the following terms might apply to an ionic solute and why:

- strong electrolyte
- weak electrolyte
- nonelectrolyte

Q3

Which of the following terms might apply to a molecular solute:

- strong electrolyte
- weak electrolyte
- nonelectrolyte

Q4

Which kind(s) of solute particles (molecules, ions) exist in each of the following types of solutions? If more than one kind, which predominates?

- strong electrolyte
- weak electrolyte
- nonelectrolyte

Q5

Categorize each of the following solutes as strong electrolyte, weak electrolyte, or nonelectrolyte:

- \(\text{NaOH}\)
- \(\text{CH}_3\text{OH}\)
- \(\text{AgC}_2\text{H}_3\text{O}_2\)
- \(\text{HCO}_2\text{H}\)
- \(\text{NiSO}_4\)

Solubility Rules

A solute is considered **soluble** if an appreciable amount of it can be dissolved in a given amount of the solvent. For example, both table salt (NaCl) and table sugar (C\(_{11}H_{22}O_{11}\)) are soluble substances in water. A solute is considered **insoluble** if very little of it dissolves in a given amount of the solvent. For example, sand (SiO\(_2\)) is considered insoluble in water. Nonetheless, extremely small quantities of dissolved SiO\(_2\) can be found in a mixture of sand and water. As this suggests, solubility is a relative term. Virtually nothing is completely insoluble in water. As a rough guideline, we can classify solutes as soluble, insoluble, or sparingly soluble on the basis of the number of moles of solute dissolved per liter of solution.

- >0.10 mol/L: soluble
- <0.01 mol/L: insoluble
- 0.01 - 0.10 mol/L: sparingly soluble

Simple ionic compounds tend to have predictable solubilities, depending on the cations and anions of which they are composed. The following rules can be used to predict the solubilities of simple inorganic compounds (The following cations are considered in these general rules: **Group 1**, **Group 2**, \(\text{NH}_4^+\), \(\text{Ag}^+\), \(\text{Al}^{3+}\), \(\text{Cd}^{2+}\), \(\text{Co}^{2+}\), \(\text{Cr}^{3+}\), \(\text{Cu}^{2+}\), \(\text{Fe}^{2+}\), \(\text{Fe}^{3+}\), \(\text{Hg}_2^{2+}\), \(\text{Hg}^{2+}\), \(\text{Mn}^{2+}\), \(\text{Ni}^{2+}\), \(\text{Pb}^{2+}\), \(\text{Sn}^{2+}\), \(\text{Zn}^{2+}\).). You need to commit these rules to memory!

**Rule 1: Soluble Compounds**

- All nitrates (NO\(_3^-\)) and acetates (CH\(_3\)CO\(_2^-\)).
- All compounds with alkali-metal (Li\(^+\), Na\(^+\), K\(^+\), etc.) and ammonium (NH\(_4^+\)) cations.
- The halides Cl\(^-\), Br\(^-\), and I\(^-\), *except* those of Pb\(^{2+}\), Ag\(^+\), Hg\(_2^{2+}\), which are insoluble.
- Sulfates (SO\(_4^{2-}\)), *except* those of Sr\(^{2+}\), Ba\(^{2+}\), Pb\(^{2+}\), and Hg\(_2^{2+}\), which are insoluble. (CaSO\(_4\) is slightly soluble.)

**Rule 2: Insoluble Compounds**

- Carbonates (CO\(_3^{2-}\)) and phosphates (PO\(_4^{3-}\)), *except* those with alkali-metal and ammonium cations, which are soluble.
- Hydroxides (OH\(^-\)), *except* those with alkali-metal cations, which are soluble, and Ca(OH)\(_2\), Sr(OH)\(_2\), and Ba(OH)\(_2\), which are sparingly soluble.
- Sulfides (S\(^2-\)), *except* those with alkali-metal, calcium, and ammonium cations, which are soluble.

**Q6**

Indicate whether the following ionic compounds are soluble or insoluble.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Solubility</th>
<th>Compound</th>
<th>Solubility</th>
</tr>
</thead>
<tbody>
<tr>
<td>PbCl(_2)</td>
<td></td>
<td>Pb(CH(_3)CO(_2))</td>
<td></td>
</tr>
</tbody>
</table>
When two electrolytes are mixed together, it is possible for the cations from one electrolyte to become associated with the anions of the other electrolyte and vice versa. In many cases the result is merely a solution in which the two kinds of cations and two kinds of anions commingle. However, in some cases, the new cation-anion association results in a compound that separates from solution. In such cases, a chemical reaction has occurred, which is called a metathesis reaction (also called double displacement or exchange reaction). Metathesis occurs when a new cation-anion pairing would result in any of the following:

1. an insoluble compound (a precipitate),
2. neutralization (an acid-base reaction), or
3. a gas or other molecular species.

We will consider precipitation reactions first. What (if anything) would happen if we mix solutions of \((\text{NH}_4)_2\text{SO}_4(aq)\) and \(\text{BaCl}_2(aq)\)? Let us switch the ion pairs:

\[
(\text{NH}_4)_2\text{SO}_4(aq) + \text{BaCl}_2(aq) \rightarrow
\]

The combination of \(\text{NH}_4^+(aq)\) ions with \(\text{Cl}^-(aq)\) would be the same as the solution produced by the soluble strong electrolyte \(\text{NH}_4\text{Cl}(aq)\). Therefore, this pair does not produce a new product. However, the combination of \(\text{Ba}^{2+}(aq)\) ions with \(\text{SO}_4^{2-}(aq)\) ions would form insoluble \(\text{BaSO}_4(s)\), which would precipitate out of the solution as a new product. We could represent this reaction with the following molecular equation:
\[(NH_4)_2SO_4(aq) + BaCl_2(aq) \rightarrow BaSO_4(s) + 2 NH_4Cl(aq)\]

The term “molecular equation” is used figuratively here, because of course ionic compounds are not composed of molecules corresponding to their empirical formulas. It is generally more useful to represent a metathetical reaction by an ionic equation, in which those species that are soluble strong electrolytes are broken up into their component ions. In this form, the metathesis reaction between $(NH_4)_2SO_4(aq)$ and $BaCl_2(aq)$ is written as follows:

\[2 NH_4^+(aq) + SO_4^{2–}(aq) + Ba^{2+}(aq) + 2 Cl^–(aq) \rightarrow BaSO_4(s) + 2 NH_4^+(aq) + 2 Cl^–(aq)\]

Notice that equal numbers of $NH_4^+(aq)$ ions and $Cl^–(aq)$ ions appear on both sides of the equation. Nothing really happens to them, so they are spectator ions, which can be eliminated from the equation. The resulting net ionic equation is

\[Ba^{2+}(aq) + SO_4^{2–}(aq) \rightarrow BaSO_4(s)\]

Notice that if we did not know (from the Rules of Solubility) that $BaSO_4$ is insoluble, we could not predict this metathetical reaction. You need to commit these rules to memory!

Q7

When two electrolyte solutions are mixed, new pairings of cations and anions may or may not result in a metathetical reaction. In order for a real reaction to take place, what possible products must a particular cation-anion pair produce?

Q8

Write balanced ionic and net ionic equations for the reaction that occurs when each of the following pairs of solutions are mixed. If no precipitate forms, write “no reaction”.

- $(AgNO_3(aq) + NaI(aq))$
- $(Pb(NO_3)2(aq) + K_2SO_4(aq))$
- $(Mg(NO_3)_2(aq) + K_2SO_4(aq))$
- $(Ca(NO_3)_2(aq) + (NH_4)_3PO_4(aq))$

Acid-Base Reactions

For the time being, we will be using the Arrhenius definition of acids and bases:

- acid: a substance that produces $H^+(aq)$ in solution
- base: a substance that produces $OH^–(aq)$ in solution

The $H^+$ ion is actually just a proton, so acids are sometimes seen as proton donors. In keeping with this, acids that can give one $H^+$ ion per acid molecule (e.g., HCl, HNO$_3$) are called monoprotic, while those acids that can give more than
one H⁺ ion per acid molecule are called **polyprotic**, or more specifically diprotic (e.g., H₂SO₄), triprotic (e.g., H₃PO₄), etc., according to the number of H⁺ ions that can be produced per acid molecule.

- **monoprotic**: \[HCl(aq) \rightarrow H^+(aq) + Cl^–(aq)\]
- **diprotic**: \[H₂SO₄(aq) \rightarrow H^+(aq) + H_SO₄^–(aq)\] \[HSO₄^–(aq) \rightleftharpoons H^+(aq) + SO₄^{2–}(aq)\]

An ionic hydroxide compound is a base (e.g., NaOH), because it dissolves in water to give OH⁻(aq) ions.

- **ionic base**: \[NaOH(s) \rightarrow Na^+(aq) + OH^–(aq)\]

Molecular bases, such as ammonia and amines, do not contain \((OH^-)\) ions but produce hydroxide ions when dissolved in water:

- **molecular base (ammonia)**: \[NH_3(aq) + H_2O(l) \rightarrow NH_4^+(aq) + OH^–(aq)\]
- **molecular base (an amine)**: \[CH_3NH₂(aq) + H₂O(l) \rightarrow CH_3NH_3^+(aq) + OH^–(aq)\]

Acids that are strong electrolytes are called **strong acids**, and those that are weak electrolytes are called **weak acids**. Thus, HCl is a strong acid, and CH₃CO₂H is a weak acid. Most acids are weak, with a few notable exceptions. *If you learn to recognize the common strong acids, you may assume that any other acid is weak unless told otherwise.* Similarly, bases that are strong electrolytes are **strong bases**, and those that are weak electrolytes are **weak bases**. Most strong bases are ionic hydroxide compounds, which are strong electrolytes like all other ionic compounds. Thus NaOH is a strong base. Molecular bases, such as NH₃ and CH₃NH₂, are generally weak.

**Neutralization** is the fundamental reaction between an acid and a base in which H⁺ from the acid is transferred either to OH⁻ from the base or to the base itself (if a weak base). Water is a product when H⁺(aq) and OH⁻(aq) combine:

\[H^+(aq) + OH^–(aq) \rightleftharpoons H_2O(l)\]

A cation results when H⁺(aq) is transferred to a weak base, as shown by the following neutralization of ammonia:

\[NH_3(aq) + H^+(aq) \rightleftharpoons NH_4^+(aq)\]

When a weak acid is neutralized, hydrogen ion must break away from the acid to combine with OH⁻(aq), as shown by the following neutralization reaction for acetic acid:

\[CH_3CO₂H(aq) + OH^–(aq) \rightarrow CH_3CO₂^–(aq) + H_2O(l)\]

In all cases, the resulting anion formed from the acid and the cation formed from the base produce a **salt** in solution.

As we have seen with precipitation reactions, we can write equations for neutralizations in three forms: (a) molecular, (b) ionic, and (c) net ionic. Let us consider the three types of equations for the neutralization of the strong acid HCl(aq) with the strong base NaOH(aq).

- **Molecular equation**: \[\underbrace{HCl(aq)}_{\text{acid}} + \underbrace{NaOH(aq)}_{\text{acid}} \rightarrow H_2O(l) + \underbrace{NaCl(aq)}_{\text{salt}}\]
Again, the term “molecular equation” is used in a figurative sense only. As we know, both HCl(aq) and NaOH(aq) are strong electrolytes, so in solution they are actually present only as their component ions. If we write the reaction in this form, we have an ionic equation.

\[
\text{Ionic Equation: } \left[H^+(aq) + \cancel{Cl^–(aq)} + \cancel{Na^+(aq)} + OH^–(aq) \rightarrow H_2O(l) + \cancel{Na^+(aq)} + \cancel{Cl^–(aq)}\right]
\]

In this representation, nothing really happens to \(Na^+(aq)\) and \(Cl^–(aq)\). They are merely spectator ions, which can be canceled across the equation. When this is done, we obtain a net ionic equation.

\[
\text{Net ionic equation: } \left[H^+(aq) + OH^–(aq) \rightarrow H_2O(l)\right]
\]

In the cases of weak acids and weak bases, the principal species in solution are molecules. The ions that weak acids and bases form in pure water are only minor components of the solution composition. For this reason, weak acids and all other weak electrolytes are shown in molecular form when writing ionic or net ionic equations. For example, the neutralization of the weak acid acetic acid (here abbreviated as HOAc) can be represented as follows:

\[
\begin{align*}
\text{Molecular equation: } &\quad [\text{HOAc}(aq) + \text{NaOH}(aq) \rightarrow \text{H}_2\text{O}(l) + \text{NaOAc}(aq)] \\
\text{Ionic Equation: } &\quad [\text{HOAc}(aq) + \text{Na}^+(aq) + \text{OH}^–(aq) \rightarrow \text{H}_2\text{O}(l) + \text{Na}^+(aq) + \text{OAc}^–(aq)] \\
\text{Net Ionic Equation: } &\quad [\text{HOAc}(aq) + \text{OH}^–(aq) \rightarrow \text{H}_2\text{O}(l) + \text{OAc}^–(aq)]
\end{align*}
\]

Notice that only the Na\(^+[aq]\) ions are spectator ions in this case. The acetate ion is part of acetic acid on the left. It only becomes a free ion as a result of the neutralization. In similar manner, we can represent the neutralization of the weak base ammonia as follows:

\[
\begin{align*}
\text{Molecular equation: } &\quad [\text{NH}_3(aq) + \text{HCl}(aq) \rightarrow \text{NH}_4\text{Cl}(aq)] \\
\text{Ionic Equation: } &\quad [\text{NH}_3(aq) + \text{H}^+(aq) + \text{Cl}^–(aq) \rightarrow \text{NH}_4^+(aq) + \text{Cl}^–(aq)] \\
\text{Net Ionic Equation: } &\quad [\text{NH}_3(aq) + \text{H}^+(aq) \rightarrow \text{NH}_4^+(aq)]
\end{align*}
\]

Note that only the chloride ion is a spectator ion in this case. The \(\text{H}^+(aq)\) on the left is not a spectator ion, because it becomes part of the molecular polyatomic ion \(\text{NH}_4^+(aq)\) on the right.

**Q9**

Indicate whether each of the following is an acid or base, whether it is strong or weak, and show how you would write it (as molecules or ions) in an ionic equation. HCl and NH\(_3\) are given as examples.

<table>
<thead>
<tr>
<th>formula</th>
<th>acid/base</th>
<th>strong/weak</th>
<th>written in solution as</th>
</tr>
</thead>
<tbody>
<tr>
<td>HCl</td>
<td>acid</td>
<td>strong</td>
<td>(H^+(aq) + \text{Cl}^–(aq))</td>
</tr>
<tr>
<td>NH(_3)</td>
<td>base</td>
<td>weak</td>
<td>(\text{NH}_3(aq))</td>
</tr>
<tr>
<td>HCO(_2)H</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CH(_3)NH(_2)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>formula</td>
<td>acid/base</td>
<td>strong/weak</td>
<td>written in solution as</td>
</tr>
<tr>
<td>---------</td>
<td>-----------</td>
<td>-------------</td>
<td>----------------------</td>
</tr>
<tr>
<td>HClO₄</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>HOCl</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**Q10**

Write balanced net ionic equations for the following neutralizations. (Start by writing ionic equations, and then cancel any spectator ions.) Remember to write all weak electrolytes and molecular species in molecular form.

- \((\text{KOH(aq)} + \text{HCO}_2\text{H(aq)})\)
- \((\text{HNO}_3\text{(aq)} + \text{Ca(OH)}_2\text{(aq)})\)
- \((\text{CH}_3\text{NH}_2\text{(aq)} + \text{HBr(aq)})\)
- \((\text{NaC}_2\text{H}_3\text{O}_2\text{(aq)} + \text{HNO}_3\text{(aq)})\)

**Gas Forming Reactions**

Cation-anion combinations can sometimes produce a molecular gas species, which often will be evident as bubbles in the solution. Learn to recognize the following gas-forming net ionic equations:

\[
\text{HCO}_3^-\text{(aq)} + \text{H}^+\text{(aq)} \rightleftharpoons \text{CO}_2\text{(g)} + \text{H}_2\text{O(l)} \\
\text{CO}_3^{2-}\text{(aq)} + 2 \text{H}^+\text{(aq)} \rightleftharpoons \text{CO}_2\text{(g)} + \text{H}_2\text{O(l)} \\
\text{SO}_3^{2-}\text{(aq)} + 2 \text{H}^+\text{(aq)} \rightleftharpoons \text{SO}_2\text{(g)} + \text{H}_2\text{O(l)} \\
\text{S}^{2-}\text{(aq)} + 2 \text{H}^+\text{(aq)} \rightleftharpoons \text{H}_2\text{S(g)} \\
\text{NH}_4^+\text{(aq)} + \text{OH}^-\text{(aq)} \rightleftharpoons \text{NH}_3\text{(g)} + \text{H}_2\text{O(l)}
\]

Note that all of these are really acid-base neutralization reactions. The only thing that makes them different is that they form a gas.

**Q11**

Write balanced net ionic equations for the following, remembering to write all solids, liquids, weak electrolytes, or molecular species in molecular form. (Start by writing ionic equations, and then cancel any spectator ions.)

- \((\text{NH}_4\text{Cl(aq)} + \text{Ca(OH)}_2\text{(aq)} \rightarrow)\)
- \((\text{PbS(s)} + \text{HNO}_3\text{(aq)} \rightarrow)\)
- \((\text{NaHCO}_3\text{(aq)} + \text{CH}_3\text{CO}_2\text{H(aq)} \rightarrow)\)
- \((\text{CaCO}_3\text{(s)} + \text{HCl(aq)} \rightarrow)\)
Summary: Recognizing Electrolytes

How can we know whether something is a strong electrolyte, weak electrolyte, or nonelectrolyte? For the purposes of this course, use these criteria to determine the electrolyte classification of a substance dissolved in water (aqueous solution):

1. All ionic compounds are strong electrolytes, because they mostly break up into ions as they dissolve in water. Even insoluble ionic compounds (e.g., AgCl, PbSO₄, CaCO₃) are strong electrolytes, because the small amounts that dissolve in water do so principally as ions; i.e., there is virtually no undissociated form of the compound in solution.

2. Molecular compounds may be nonelectrolytes, weak electrolytes, or strong electrolytes, depending on whether they dissolve without ion formation, a little ion formation, or mostly ion formation, respectively. Examples:

<table>
<thead>
<tr>
<th>Molecular Compound</th>
<th>Electrolyte Type</th>
<th>Species in Solution</th>
</tr>
</thead>
<tbody>
<tr>
<td>sucrose (table sugar)</td>
<td>nonelectrolyte</td>
<td>molecules only</td>
</tr>
<tr>
<td>acetic acid (HC₂H₃O₂ = HOAc)</td>
<td>weak electrolyte</td>
<td>molecules and ions</td>
</tr>
<tr>
<td>hydrogen chloride (HCl)</td>
<td>strong electrolyte</td>
<td>ions only</td>
</tr>
</tbody>
</table>

3. Strong acids and strong bases are strong electrolytes [e.g., HCl(aq), H₂SO₄ (aq), HClO₄(aq); NaOH(aq)]. There are virtually no molecules of a strong acid or base in solution, only ions.

Summary: Representing Electrolytes and Nonelectrolytes in Ionic Equations

When writing ionic and net ionic equations, we observe the following conventions:

1. Write all molecular compounds in molecular form. Examples:
   - \(\text{C}_{11}\text{H}_{22}\text{O}_{11}(aq)\)
   - \(\text{H}_2\text{O}(l)\)
   - \(\text{CO}_2(g)\)

2. Write all weak electrolytes in molecular form, because molecules (not ions) are the principal species in solution. Examples:
   - \(\text{CH}_3\text{CO}_2\text{H}(aq) \text{ not } \text{H}^+(aq) + \text{CH}_3\text{CO}_2^-(aq)\)
   - \(\text{NH}_3(aq) \text{ not } \text{NH}_4^+(aq) + \text{OH}^-(aq)\)

3. Write soluble strong electrolytes as ions and insoluble strong electrolytes as combined solids (i.e., so-called "molecular form"). Examples:
   - \(\text{NaCl}(aq) = \text{Na}^+(aq) + \text{Cl}^-(aq)\)
   - \(\text{AgCl}(s) = \text{AgCl}(s)\)