10.0 **INTRODUCTION**

Thus far, our study of chemistry has focused on pure substances (elements and compounds). However, most chemical reactions occur in mixtures, which can be classified as either *heterogeneous* or *homogeneous*. The properties of a *heterogeneous* mixture vary within the mixture. If you were to sample a heterogeneous mixture of oil in water, you would find its properties to be those of either oil or water, depending on where the mixture was sampled. A *homogeneous* mixture is characterized by uniform properties throughout; for example, the sweetness of a homogeneous mixture of sugar dissolved in water is the same everywhere in the mixture. Homogeneous mixtures are called *solutions*, the topic of this chapter.

Solutions are all around us. The atmosphere is a solution of gases in gases (mainly oxygen and nitrogen). Vinegar is a solution of a liquid in a liquid (acetic acid in water). A carbonated beverage is a solution of a gas in a liquid (carbon dioxide in water). Sweetened water is a solution of a solid in a liquid (sugar dissolved in water). Solder is a solution of a solid in a solid (tin in lead). These are but a few examples of the types of solutions we deal with every day.

Each of the components of a solution is characterized as either the *solvent* or a *solute*. There is only one solvent in a solution, but there can be several solutes. If there is only one liquid present, it is the solvent and any gases or solids that are dissolved in it are solutes. If more than one liquid is present, the liquid in the greater amount is usually considered to be the solvent. For example, a carbonated, non-diet soft drink is a solution made with *solid* sugar, *liquid* water, and *gaseous* carbon dioxide. Water is the only liquid, so it is the solvent, while the sugar and the carbon dioxide are solutes.
THE OBJECTIVES OF CHAPTER 10 ARE TO:

- define and describe solutions;
- define various units of concentration;
- define solubility and describe the solution process;
- present simple principles for predicting solubilities;
- describe the function of detergents;
- define electrolytes and the nature of their aqueous solutions;
- introduce net equations; and
- describe solubility equilibria and define the solubility product constant.

## 10.1 CONCENTRATION

The relative amounts of solute and solvent in a solution are important characteristics of the solution. They are usually given in terms of the **concentration** of the solute in the solvent or solution. There are many concentration units, but we will consider only three.

<table>
<thead>
<tr>
<th>Unit</th>
<th>Definition</th>
</tr>
</thead>
<tbody>
<tr>
<td>%(m/m)</td>
<td>percent by mass grams of solute/100 g of solution</td>
</tr>
<tr>
<td>%(V/V)</td>
<td>percent by volume mL of solute/100 mL of solution</td>
</tr>
<tr>
<td>M</td>
<td>molarity moles of solute/L of solution</td>
</tr>
</tbody>
</table>

**Percent by mass** is most commonly used in solid solutions. A 60/40 solder is a solution of lead and tin that is 60% lead and 40% tin by mass. **Percent by volume** is used for solutions of liquids in liquids. Ethylene glycol (C₂H₆O₂) is a common antifreeze, which gives a maximum freezing protection in a 50% mixture by volume. Thus, your car is best protected from freezing when half of the volume of the solution in the cooling system is ethylene glycol and half is water. The grain alcohol or ethanol (C₂H₅OH) content in alcoholic beverages is given in terms of **proof**, which is simply twice the percent by volume of the alcohol in the solution. Thus, 100 mL of 90 proof rum contains 45 mL of C₂H₅OH.

The mole is the most useful measure of amount in a chemistry laboratory because it is easily related to the number of molecules or ions, so **molarity** is a very common unit of concentration in the laboratory. A solution of sugar that is composed of 0.10 mole of sugar (C₁₂H₂₂O₁₁) in a liter of solution is said to have a concentration of 0.10 M (read as 0.10 molar). The molarity of a solute is represented by enclosing its formula in square brackets; thus, the above sugar solution is one in which [C₁₂H₂₂O₁₁] = 0.10 M.
Example 10.1

A solution is prepared by dissolving a teaspoon (4.8 g) of sugar (C\textsubscript{12}H\textsubscript{22}O\textsubscript{11}; M\textsubscript{m} = 342 g/mol) in enough water to make 100 mL of solution.

a) What is the concentration of sugar in g/mL?

\[
\text{conc. of sugar} = \frac{4.8 \text{ g C}_{12}\text{H}_{22}\text{O}_{11}}{100 \text{ mL solution}} = 0.048 \text{ g C}_{12}\text{H}_{22}\text{O}_{11}/\text{mL solution}
\]

b) What is the concentration of the sugar in mol/L?

\[
\text{conc. of sugar} = \frac{4.8 \text{ g C}_{12}\text{H}_{22}\text{O}_{11}}{342 \text{ g C}_{12}\text{H}_{22}\text{O}_{11}} = \frac{0.014 \text{ mol C}_{12}\text{H}_{22}\text{O}_{11}}{1 \text{ L solution}} = 0.14 \text{ M}
\]

c) How many moles of sugar are in 35 mL of the solution?

\[
\text{mol of sugar} = \frac{35 \text{ mL solution}}{1000 \text{ mL solution}} \times \frac{0.14 \text{ mol C}_{12}\text{H}_{22}\text{O}_{11}}{1 \text{ L solution}} = 0.0049 \text{ mol C}_{12}\text{H}_{22}\text{O}_{11}
\]

The density of solids was discussed in Chapter 8, but density is also an important characteristic of pure liquids and solutions. Density (d) is mass per unit volume, 

\[
d = \frac{\text{mass of sample}}{\text{volume of sample}}
\]

The density of water is 1.0 g/cm\textsuperscript{3}, which means that 1 cubic centimeter of water has a mass of 1.0 g. The density of lead is 11.3 g/cm\textsuperscript{3}. Thus, lead is much denser than water, which is the reason that lead does not float on water.

Example 10.2

What is the molarity of pure water?

The question essentially asks for the number of moles of water that are present in one liter of pure water. The problem can be solved by finding the mass of a liter of water and determining the number of moles it contains. The density of water is 1.0 g/mL, and its molar mass is 18.0 g/mol.

\[
1000 \text{ mL H}_2\text{O} \times \frac{1.0 \text{ g H}_2\text{O}}{1 \text{ mL H}_2\text{O}} \times \frac{1 \text{ mol H}_2\text{O}}{18 \text{ g H}_2\text{O}} = 56 \text{ mol H}_2\text{O}
\]

There are 56 moles of water molecules in a liter. Thus, liquid water is 56 M. One liter of a 0.1 M sugar solution contains 0.1 mol of sugar and 56 mol of water. This means that there are ~560 water molecules for every sugar molecule in the solution!
10.2 THE SOLUTION PROCESS

There is usually a limit to how much solute can dissolve in a given amount of solvent at a given temperature. This limit is called the **solubility** of the solute in that solvent at that temperature. Solutions in which the concentration of the solute has reached this level are said to be **saturated**. Substances are often classified as soluble or insoluble in a solvent, but solubilities vary continuously. In this text, substances with solubilities of 0.1 M or greater are considered to be **soluble**; those with solubilities between 0.1 and 0.01 M are referred to as **moderately soluble**, and those with solubilities below 0.01 M are called **insoluble**. Thus, a saturated solution of NaCl in water is about 7 M, so NaCl is soluble in water; a saturated solution of MgSO\(_4\) is 0.015 M, so MgSO\(_4\) is moderately soluble in water; a saturated solution of silver chloride is only about 10\(^{-5}\) M, so AgCl is considered to be insoluble in water. Two substances, such as water and ethanol that are soluble in one another in all proportions are said to be **miscible**.

**Example 10.3**

Given the following solubilities of some fluorides in 100 mL of water at 25 °C, classify each as soluble, moderately soluble, or insoluble.

a) 2.56 g NiF\(_2\) (\(M_m = 96.7\) g/mol)

Molarity is moles of solute per liter of solution, using the factor-label method we obtain

\[
\frac{2.56 \text{ g NiF}_2}{100 \text{ mL}} \times \frac{1000 \text{ mL}}{1 \text{ L}} \times \frac{1 \text{ mol NiF}_2}{96.7 \text{ g NiF}_2} = \frac{0.265 \text{ mol NiF}_2}{1 \text{ L}} = 0.265 \text{ M}
\]

The solubility in water is greater than 0.1 M. We conclude that NiF\(_2\) is **soluble** in water.

b) 0.075 g CuF\(_2\) (\(M_m = 102\) g/mol)

Proceed as in Part A.

\[
\frac{0.075 \text{ g CuF}_2}{100 \text{ mL}} \times \frac{1000 \text{ mL}}{1 \text{ L}} \times \frac{1 \text{ mol CuF}_2}{102 \text{ g CuF}_2} = \frac{7.4 \times 10^{-3} \text{ mol CuF}_2}{1 \text{ L water}} = 7.4 \times 10^{-3} \text{ M}
\]

The solubility of CuF\(_2\) is less than 0.01 M, so we conclude that CuF\(_2\) is **insoluble** in water.

c) 0.417 g S\(_2\)F\(_2\) (\(M_m = 102\) g/mol)

\[
\frac{0.417 \text{ g S}_2\text{F}_2}{100 \text{ mL}} \times \frac{1000 \text{ mL}}{1 \text{ L}} \times \frac{1 \text{ mol S}_2\text{F}_2}{102 \text{ g S}_2\text{F}_2} = \frac{0.0409 \text{ mol S}_2\text{F}_2}{1 \text{ L water}} = 0.0409 \text{ M}
\]

The solubility of S\(_2\)F\(_2\) is between 0.01 M and 0.1 M, so it is **moderately soluble** in water.
Consider the solution process in which substance A dissolves in a solvent to make a solution. If A is a solid, we can represent the process as

\[ A(s) \rightarrow A(\text{solution}) \quad \Delta H_{\text{solution}} \]

\( \Delta H_{\text{solution}} \) is the enthalpy (or heat) of solution. Recall from Section 9.8 that the extent of a reaction depends upon the value of \( \Delta G^\circ \). Thus, A is considered soluble if \( \Delta G^\circ_{\text{solution}} \) is not large and positive.* We can apply Equation 9.6 to the solution process to obtain \( \Delta G^\circ_{\text{solution}} = \Delta H^\circ_{\text{solution}} - T \Delta S^\circ_{\text{solution}} \), where \( \Delta S^\circ_{\text{solution}} \) is the standard entropy of solution. There are competing factors that tend to keep \( \Delta S^\circ_{\text{solution}} \) small, so \( \Delta H^\circ_{\text{solution}} \) usually dominates the solution process. We use the approximation that a substance is soluble if its heat of solution is negative or only slightly positive.

In Section 9.4, the enthalpy of a reaction was approximated in terms of the energy required to break reactant bonds and form product bonds. Dissolving a molecular solute can be viewed in the same manner; that is, existing interactions must be broken and new interactions must be formed. The difference is that, in the solution process, the interactions are intermolecular rather than intramolecular.

As discussed in Chapter 7, molecular substances are held in the liquid and solid states by a combination of three intermolecular forces: dispersion, dipole-dipole, and hydrogen bonding. If the solute is an ionic compound, it is maintained in the solid state by ionic bonds. In order for the solute to dissolve, it must disperse itself uniformly into the solvent. Consequently, the solution process can be understood in terms of three steps, each with its own contribution to the enthalpy of solution:

1. \( \Delta H_{\text{solute}} \) is the enthalpy required to separate solute particles. \( \Delta H_{\text{solute}} > 0 \).
2. \( \Delta H_{\text{solvent}} \) is the energy required to create the “cavities” in the solvent that will be occupied by the solute particles. \( \Delta H_{\text{solvent}} > 0 \).
3. \( \Delta H_{\text{mixing}} \) is the enthalpy change that occurs when the solute and the solvent particles interact. \( \Delta H_{\text{mixing}} < 0 \).

As shown in Equation 10.1, the enthalpy of solution is the sum of three enthalpy terms,

\[ \Delta H_{\text{solution}} = \Delta H_{\text{solute}} + \Delta H_{\text{solvent}} + \Delta H_{\text{mixing}} \quad \text{Eq. 10.1} \]

A substance is soluble in a solvent so long as the energy required to break the solute-solute and solvent-solvent interactions is not much greater than the energy released when the solute-solvent interactions are established. However, solute-solvent interactions are comparable to solvent-solvent and solute-solute interactions only if all of the interactions are of the same type, which is summarized by the rule that like dissolves like.

* \( \Delta G^\circ > 0 \) implies only that the equilibrium concentration of A is less than 1 M (the standard state). Thus, it is slightly positive when \([A] = 0.1 \text{ M}\), our definition of soluble.
Ionic substances and polar molecules are more soluble in polar solvents, while nonpolar molecules are more soluble in nonpolar solvents.

Figure 10.1 demonstrates the solution process for dissolving a polar solute in water. $\Delta H_{\text{solute}} > 0$ for a solid or liquid composed of polar molecules because energy is required to overcome the dipolar and dispersion forces. $\Delta H_{\text{solvent}} > 0$ because dipolar and H-bonding forces must be overcome to separate water molecules and create cavities for the solute molecules. Energy is released ($\Delta H_{\text{mixing}} < 0$) when regions of opposite charge on solute and solvent interact. If the solute is not polar, $\Delta H_{\text{mixing}} \approx 0$, the entire process is endothermic, and the solute is insoluble.

The combined process of creating a cavity in the solvent and placing the solute into the cavity (steps 2 and 3 above) is known as solvation. Thus, we can write

$$\Delta H_{\text{solvation}} = \Delta H_{\text{solvent}} + \Delta H_{\text{mixing}}$$

Eq. 10.2

The solute is said to be solvated, because it is surrounded by and interacting with solvent molecules. In the special case where the solvent is water, the process is called hydration and the solute is said to be hydrated.

Example 10.4

a) Which has the greater solubility in water, HBr or Br₂?

HBr is a polar molecule, and Br₂ is a nonpolar molecule, so HBr is more soluble in polar substances such as water.

b) Which is the better solvent for I₂, CS₂(l) or H₂O(l)?

Iodine is a nonpolar molecule and dissolves best in nonpolar solvents. Because water is polar, it is a poor solvent for nonpolar molecules such as I₂. Carbon disulfide, on the other hand, is nonpolar (CS₂ is linear, and both electron regions around the carbon are identical), and is a much better solvent for nonpolar molecules such as I₂. (In fact, I₂ is almost 1,000 times more soluble in CS₂ than in H₂O.)

c) In which solvent would KCl be more soluble, CCl₄ or water?

KCl is ionic, and ionic substances are most soluble in polar solvents. Thus, KCl is more soluble in water than in a nonpolar solvent such as CCl₄.

Figure 10.1 The Solution Process

a) A polar solid solute (blue end is positive and red end is negative) and a liquid solvent (H₂O in the figure).
b) The solute particles are separated.
c) Solvent molecules are separated to produce cavities (labeled 1 through 4).
d) The solute particles enter the cavities and interact with the solvent to produce a solution.
10.3 ORGANIC COMPOUNDS

Many of the compounds encountered outside the chemistry laboratory, such as vitamins, carbohydrates, grease, oils, gasoline, paint removers, plastics, and dyes, are organic compounds. **Organic compounds** are based on carbon, and their number is limitless because of the manner in which carbon atoms can bond to one another (Chapter 13). We now examine the solubility of this important class of compounds in water.

Gasoline and water ‘don’t mix’, and, based on the discussion in Section 10.2, we conclude that the reason they do not mix is that they do not interact with one another very well. Gasoline is a solution of many organic compounds, most of which are hydrocarbons like octane (Figure 10.2a). **Hydrocarbons** are compounds that contain only carbon and hydrogen atoms. The C and H atoms in octane form CH₃ and CH₂ groups connected by C-C single bonds. CH₃ groups and CH₂ groups are not polar, so octane molecules interact with each other only through dispersion forces. Consequently, octane molecules do not interact well with the polar and strongly hydrogen-bonded water molecules. Thus, when a hydrocarbon enters water, the water molecules position themselves so as to form highly ordered, ice-like cages around each of the hydrocarbon molecules. These cages form to optimize the hydrogen bonding between the water molecules in the vicinity of the hydrocarbon because they cannot hydrogen bond to the hydrocarbon. Formation of a highly ordered cage results in a large negative entropy of solution, which assures that the free energy of solution is large and positive and the hydrocarbon is not water soluble. This effect is called the **hydrophobic effect**. The hydrophobic effect is especially important in biochemistry where it leads to membrane formation. Compounds with many CH₂ groups, which interact very poorly with water, are said to be hydrophobic, while polar molecules and ions, which interact strongly with water, are hydrophilic. Octane is hydrophobic, but not all organic molecules are. For example, sucrose (table sugar) is a hydrophilic substance because it contains many O-H groups (Figure 10.2b) that hydrogen bond with water.

Alcohols are organic molecules that contain one or more hydroxyl (OH) groups. Our discussion and Table 10.1 center around alcohols with the generic formula ROH, where R is CH₃(CH₂)_n (n = 0 to 6). Each alcohol contains a hydrophilic (OH) and a hydrophobic (R) region, and its solubility in water depends upon n, number of CH₂ groups in the hydrophobic chain. When n is small (0, 1, or 2), the OH group dominates and the alcohol is hydrophilic. Thus, CH₃OH (methanol or wood alcohol), CH₃CH₂OH (ethanol or grain
alcohol) and $\text{CH}_3(\text{CH}_2)_2\text{OH}$ (rubbing alcohol) are all miscible with water. However, as the hydrophobic chain gets longer, the alcohol becomes more hydrophobic, and its solubility in water drops. By the time $n$ is six, the solubility has dropped down to 0.015 M. Similarly, increasing the number of hydroxyl groups increases the hydrophilic nature of the alcohol and its solubility in water. For example, the solubility of $\text{CH}_3(\text{CH}_2)_3\text{OH}$ in water is only 0.059 M, but $\text{HO}(\text{CH}_2)_3\text{OH}$, which differs only by the substitution of a hydrophilic OH for a hydrophobic $\text{CH}_3$, is miscible with water.

Acetone, $(\text{CH}_3)_2\text{C}=\text{O}$ (Figure 10.3), is a common laboratory solvent because many organic substances are soluble in it, and it is miscible with water. Acetone contains $\text{CH}_3$ groups that interact with other organic compounds through dispersion forces, so many organic substances dissolve in acetone. However, it also contains a polar C=O group, which makes the molecule hydrophilic. As with alcohols, the water solubility of compounds like this depends upon the lengths of the carbon chains; as the hydrophobic portion of the molecule increases, its solubility in water decreases. For example, $(\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2)_2\text{C}=\text{O}$ is only slightly soluble in water.

**Example 10.4**

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**Example 10.5**

Indicate whether each of the following substances is more soluble in water or in ether, $\text{C}_2\text{H}_5$-$\text{O}$-$\text{C}_2\text{H}_5$, a solvent with nonpolar components similar to those in acetone. See the margin for structures.

a) **Decane**

Decane is a hydrophobic molecule with no hydrophilic (polar) regions. Consequently, it is soluble in ether but not in water.

b) **Dodecanedioic acid**

Dodecanedioic acid has two hydrophilic regions, the COOH groups at either end, and it also has a large hydrophobic region (ten CH$_2$ groups) in the center. In this case, the hydrophobic region dominates, and the acid is soluble in ether but not in water.

c) **Ethanedioic (oxalic) acid**

Oxalic acid has two hydrophilic groups but no hydrophobic region. It is soluble in water but not in ether.

d) **Sodium propanoate**

Ionic substances are always more soluble in water than in ether.
10.4 DETERGENTS AND MICELLES

Water is the most common household solvent because it is plentiful and easily handled. While ionic substances, such as table salt, or those substances with which it can hydrogen bond, such as sugar (Figure 10.2b), are water soluble, grease, oil, and most dirt are hydrophobic and do not dissolve in water. These hydrophobic substances are frequently soluble in common laboratory solvents, such as acetone or ether, but these solvents are too costly and dangerous for general use. If water is to be used as a solvent for removing hydrophobic materials from clothing and dishes, some other substance, one that is both hydrophilic so it will be soluble in water and hydrophobic so it can dissolve dirt, must be added to the water. Such substances are called detergents.

A detergent is a substance that has a hydrophobic region consisting of a long carbon chain (referred to as the ‘tail’) and a hydrophilic region in the form of an ionic or polar group (referred to as the ‘head’) at one end. Figure 10.4 shows four representations of sodium dodecyl sulfate (SDS), $\text{C}_{12}\text{H}_{25}\text{SO}_{4}\text{Na}$, a common synthetic detergent found in shampoos and toothpastes. SDS readily dissolves in water to yield $\text{Na}^{+}$ and $\text{C}_{12}\text{H}_{25}\text{SO}_{4}\text{Na}^{-}$ ions. The ionic sulfate ‘head’ makes it water soluble, while the hydrophobic $\text{C}_{12}\text{H}_{25}$ ‘tail’ interacts with the nonpolar grease through dispersion forces. The 12-carbon tail of SDS is quite short for a detergent as most detergents have tails containing 15 to 19 carbon atoms, which makes them more hydrophobic and better at dissolving grease. Soaps are detergents that are derived from fatty acids (Section 13.4) and have the general formula $\text{RCOONa}$, where $\text{R}$ is a hydrophobic tail and the $\text{COO}^{-}$ group is the polar head.

When a small amount of SDS is placed in water, the hydrophobic effect is so strong that the hydrophobic tails stick out of the water, while the polar heads remain in the water. The result is a monolayer (a layer that is only one molecule thick) lying on the surface of the water (Figure 10.5). If the hydrophobic tails are forced into the water by an increase in concentration coupled with agitation to accelerate the process, they interact with one another to form spherical aggregates called micelles (pronounced ‘my-cells’). Figure 10.6 shows a cross-sectional view of a micelle sphere. The polar heads are pointed toward the water and form the surface of the sphere making the sphere water soluble. The interior of the sphere is a liquid hydrocarbon composed of the hydrophobic tails interacting through dispersion forces. A small micelle contains 80 - 100 detergent molecules. Grease and oil molecules are hydrophobic and interact well with the hydrocarbon interior of the micelle. As a result, the grease and oil dissolve in the hydrocarbon liquid. We wash our clothes and
dishes by adding a detergent, agitating it to accelerate the formation of micelles that
dissolve the hydrophobic dirt, and then rinsing the micelles and the captured oil and grease
down the drain.

**Example 10.6**

Which would form a better micelle, sodium acetate (NaC\(_2\)H\(_3\)O\(_2\)) or sodium palmitate
(NaC\(_{16}\)H\(_{31}\)O\(_2\))? Explain.

The CH\(_3\) group of the acetate ion is not hydrophobic enough for acetate to form micelles.
Sodium acetate is soluble in water. The CH\(_3\)(CH\(_2\))\(_{14}\) chain of the palmitate ion is very
hydrophobic, so the ion makes an excellent micelle.

**10.5 ELECTROLYTES**

In Chapter 8, we saw that ionic substances form extended solids in which there are no
clearly defined ‘ionic molecules.’ Rather, each ion is surrounded by some number (the
coordination number) of ions of opposite charge. In this section, we consider the nature of
solutions composed of ionic substances dissolved in water by examining their ability to
conduct electricity. Consider the apparatus shown in Figure 10.7. How brightly the light
bulb glows depends upon how well charge flows from one electrode to the other, i.e., how
well charge flows through the solution. The movement of charge through the solution is
due to the migration of ions, not free electrons. The light bulb does not glow when the
electrodes are immersed in pure water or in a 0.1 M sugar solution because there are no
ions in these solutions. The bulb glows very brightly when the solution is 0.1 M NaCl, but
it does not glow at if solid sodium chloride is used. Thus, an aqueous solution of NaCl is a
good conductor of electricity, but the solid is not. The difference between the solution and
the solid is that the ions in solution are mobile, while those in the solid are not. Conduction
in the solution results from a migration of ions as Na\(^{1+}\) ions migrate toward the negative

![Figure 10.7 Solutions of electrolytes conduct electricity](image)
electrode and Cl\(^{1-}\) ions migrate toward the positive electrode. Substances that dissociate completely into ions when they dissolve in water are said to be **strong electrolytes**, substances that dissociate only partially in water are **weak electrolytes**, and substances that do not dissociate in water are called **nonelectrolytes**. Table 10.2 summarizes the results of several other solutions.

Ionic compounds are strong electrolytes, so when a solid ionic compound is dissolved in water, it goes into solution completely as ions.\(^\ast\) For example,

\[
\begin{align*}
\text{NaCl(s)} & \rightarrow \text{Na}^{1+} + \text{Cl}^{1-} \\
\text{MgCl}_2(s) & \rightarrow \text{Mg}^{2+} + 2\text{Cl}^{1-} \\
\text{K}_2\text{S(s)} & \rightarrow 2\text{K}^{1+} + \text{S}^{2-}
\end{align*}
\]

A solution of NaCl contains only Na\(^{1+}\) and Cl\(^{1-}\) ions; there are no NaCl molecules. Note that the chemical equation for the dissociation must have the same stoichiometry as the substance. Thus, the formula MgCl\(_2\) indicates that there are 2Cl\(^{1-}\) ions for every one Mg\(^{2+}\) ion, so the dissociation must express the same stoichiometry. Many ionic compounds contain polyatomic ions,\(^\dagger\) but the bonds that hold the atoms in polyatomic ions are covalent and do not dissociate in water, so polyatomic ions enter solution in tact.

\[
\begin{align*}
\text{NaNO}_3(s) & \rightarrow \text{Na}^{1+} + \text{NO}_3^{1-} \\
\text{MgSO}_4(s) & \rightarrow \text{Mg}^{2+} + \text{SO}_4^{2-} \\
\text{K}_3\text{PO}_4(s) & \rightarrow 3\text{K}^{1+} + \text{PO}_4^{3-}
\end{align*}
\]

Ionic compounds are not the only class of compounds that are electrolytes; acids and bases are electrolytes as well. The first chemical definition of acids and bases was made by Svante Arrhenius.

**Arrhenius acids** are substances that produce H\(^{1+}\) ions when dissolved in water.

**Arrhenius bases** are compounds that produce OH\(^{-}\) ions when dissolved in water.

Acids can be identified because the acidic protons are usually written first in their chemical formulas. For example, H\(_2\)S is an acid, so the protons appear first in its formula, but NH\(_3\) is not, so the protons do not appear first in its formula. In Arrhenius theory, acids ionize in water in a manner similar to ionic substances, but only **strong acids** ionize completely. The common strong acids are HCl, HBr, HI, HNO\(_3\), HClO\(_4\), and H\(_2\)SO\(_4\). For example, the following chemical equations represent the Arrhenius view of dissolving HCl, HNO\(_3\), and HClO\(_4\) in water:

\[
\begin{align*}
\text{HCl(g)} & \rightarrow \text{H}^{1+} + \text{Cl}^{1-} \\
\text{HNO}_3(l) & \rightarrow \text{H}^{1+} + \text{NO}_3^{1-} \\
\text{HClO}_4(l) & \rightarrow \text{H}^{1+} + \text{ClO}_4^{1-}
\end{align*}
\]

Most acids dissociate only partially in water, so they are **weak acids**. Weak acids are weak electrolytes because they produce only small amounts of H\(^{1+}\) and the anion in water. HF, HNO\(_2\), and HClO\(_2\) are examples of weak acids. The light bulb glows only dimly in a 0.1 M solution of a weak electrolyte because there are far fewer ions to conduct the electricity.

### Table 10.2 Conduction in some 0.1 M aqueous solutions

<table>
<thead>
<tr>
<th>Solution</th>
<th>Glow(^a)</th>
<th>Type of Solution</th>
<th>Particles in Solution</th>
</tr>
</thead>
<tbody>
<tr>
<td>pure water</td>
<td>none</td>
<td>nonelectrolyte</td>
<td>H(_2)O molecules</td>
</tr>
<tr>
<td>NaCl</td>
<td>bright</td>
<td>strong electrolyte</td>
<td>Na(^{1+}) + Cl(^{1-}) ions</td>
</tr>
<tr>
<td>HCl</td>
<td>bright</td>
<td>strong electrolyte</td>
<td>H(^{1+}) + Cl(^{1-}) ions</td>
</tr>
<tr>
<td>HF</td>
<td>dim</td>
<td>weak electrolyte</td>
<td>mostly HF molecules</td>
</tr>
<tr>
<td>sugar</td>
<td>none</td>
<td>nonelectrolyte</td>
<td>C(<em>{12})H(</em>{22})O(_{11}) molecules</td>
</tr>
<tr>
<td>NaNO(_3)</td>
<td>bright</td>
<td>strong electrolyte</td>
<td>Na(^{1+}) + NO(_3^{1-}) ions</td>
</tr>
<tr>
<td>NaOH</td>
<td>bright</td>
<td>strong electrolyte</td>
<td>Na(^{1+}) + OH(^{-}) ions</td>
</tr>
<tr>
<td>CH(_3)OH</td>
<td>none</td>
<td>nonelectrolyte</td>
<td>CH(_3)OH molecules</td>
</tr>
<tr>
<td>NH(_3)</td>
<td>dim</td>
<td>weak electrolyte</td>
<td>mostly NH(_3) molecules</td>
</tr>
</tbody>
</table>

\(^a\) “Glow” refers to the light bulb in Figure 10.7.

\(^\ast\) Unless stated otherwise, it is understood that an isolated ion is in aqueous solution, so we drop the (aq) for clarity when writing ions.

\(^\dagger\) A list of some common polyatomic ions can be found in Table 4.1, which is reproduced on the last page facing the back cover.
Hydrofluoric acid is a weak acid as less than 10% of the HF molecules in a typical solution dissociate into their ions. To emphasize the fact that there are many more molecules than ions in a solution of a weak acid, the solution process is written with equilibrium arrows:

\[
\text{HF}(\text{aq}) \rightleftharpoons \text{H}^+ + \text{F}^- \\
\text{HNO}_2(\text{aq}) \rightleftharpoons \text{H}^+ + \text{NO}_2^- \\
\text{HClO}_2(\text{aq}) \rightleftharpoons \text{H}^+ + \text{ClO}_2^-
\]

Metal hydroxides are the most common strong bases:

\[
\text{NaOH}(\text{s}) \rightarrow \text{Na}^+ + \text{OH}^- \\
\text{Ba(OH)}_2(\text{s}) \rightarrow \text{Ba}^{2+} + 2\text{OH}^-
\]

Most weak bases are also ionic and produce \(\text{OH}^-\) ions as the result of the reaction of the anion with water. For example, \(\text{F}^-\) and \(\text{NO}_2^-\) ions are weak bases:

\[
\text{F}^- + \text{H}_2\text{O} \rightleftharpoons \text{HF} + \text{OH}^- \\
\text{NO}_2^- + \text{H}_2\text{O} \rightleftharpoons \text{HNO}_2(\text{aq}) + \text{OH}^-
\]

Ammonia is the most common example of a molecular substance that is a weak base:

\[
\text{NH}_3(\text{aq}) + \text{H}_2\text{O} \rightleftharpoons \text{NH}_4^+ + \text{OH}^-
\]

Sugar is a nonelectrolyte because it retains its molecular identity when it dissolves. The chemical equation for dissolving sugar in water is

\[
\text{C}_{12}\text{H}_{22}\text{O}_{11}(\text{s}) \rightarrow \text{C}_{12}\text{H}_{22}\text{O}_{11}(\text{aq})
\]

**ION CONCENTRATIONS IN SOLUTIONS OF STRONG ELECTROLYTES**

Ionic compounds, such as NaCl, are strong electrolytes, because all of the solid NaCl that dissolves dissociates into ions. Thus, a solution labeled 0.10 M NaCl contains Na\(^{1+}\) and Cl\(^{-}\) ions, but no NaCl molecules. The ions react independently of one another; a chloride ion in a solution of NaCl is the same as one in a solution of KCl or MgCl\(_2\). Thus, it is the concentration of the ion, not the parent compound that is important in solution chemistry. To convert from the concentration of the parent compound to that of any ion requires the stoichiometry of the chemical equation for the dissociation, which is given by the stoichiometry of the compound. For example, to determine the concentration of chloride ions in a 0.10 M MgCl\(_2\) solution, we recognize that there are two moles of chloride ions for every one mole of MgCl\(_2\), and write the following:

\[
[\text{Cl}^-] = \frac{0.10 \text{ mol MgCl}_2}{1 \text{ L solution}} \times \frac{2 \text{ mol Cl}^-}{1 \text{ mol MgCl}_2} = \frac{0.20 \text{ mol Cl}^-}{1 \text{ L solution}} = 0.20 \text{ M}
\]

An aqueous solution that is labeled 0.10 M MgCl\(_2\), is 0.10 M in Mg\(^{2+}\) ions and 0.20 M in Cl\(^{-}\) ions, but it contains no MgCl\(_2\)!
Example 10.7

What are the concentrations of the ions in the following solutions?

a) 0.0364 M \text{BaCl}_2

Barium chloride is an ionic compound and a strong electrolyte, so it dissociates into its
component ions when it dissolves: \text{BaCl}_2 \rightarrow \text{Ba}^{2+} + 2\text{Cl}^{-}. Use stoichiometry to determine
the concentrations of the ions

\[
[\text{Ba}^{2+}] = \frac{0.0364 \text{ mol BaCl}_2}{1 \text{ L solution}} \times \frac{1 \text{ mol Ba}^{2+}}{1 \text{ mol BaCl}_2} = \frac{0.0364 \text{ mol Ba}^{2+}}{1 \text{ L solution}} = 0.0364 \text{ M}
\]

\[
[\text{Cl}^{-}] = \frac{0.0364 \text{ mol BaCl}_2}{1 \text{ L solution}} \times \frac{2 \text{ mol Cl}^{-}}{1 \text{ mol BaCl}_2} = \frac{0.0728 \text{ mol Cl}^{-}}{1 \text{ L solution}} = 0.0728 \text{ M}
\]

b) 0.108 M \text{K}_3\text{PO}_4

\text{PO}_4^{3-} is the phosphate ion, so the dissociation is \text{K}_3\text{PO}_4 \rightarrow 3\text{K}^{+} + \text{PO}_4^{3-}, and the ion
concentrations are determined as follows:

\[
[\text{K}^{+}] = \frac{0.108 \text{ mol K}_3\text{PO}_4}{1 \text{ L solution}} \times \frac{3 \text{ mol K}^{+}}{1 \text{ mol K}_3\text{PO}_4} = \frac{0.324 \text{ mol K}^{+}}{1 \text{ L solution}} = 0.324 \text{ M}
\]

\[
[\text{PO}_4^{3-}] = \frac{0.108 \text{ mol K}_3\text{PO}_4}{1 \text{ L solution}} \times \frac{1 \text{ mol PO}_4^{3-}}{1 \text{ mol K}_3\text{PO}_4} = \frac{0.108 \text{ mol PO}_4^{3-}}{1 \text{ L solution}} = 0.108 \text{ M}
\]

10.6 ELECTROLYTE SOLUTIONS

Ionic bonds must be broken when an ionic substance dissolves, but ionic bonds are strong
interactions, so \(\Delta H_{\text{solute}}\) is large and positive. Thus, \(\Delta H_{\text{solvation}}\), the enthalpy of solvation
(hydration in this case because the solvent is water), must be large and negative for an
ionic substance to dissolve in water. In other words, the interaction between the water
molecules and the ions must be very strong. This strong interaction arises because water
has a strong dipole (Section 7.2), which points from the center of the hydrogen atoms
toward the electronegative oxygen atom (Figure 10.8).

When a crystal of sodium chloride is placed in water, \text{H}_2\text{O} molecules approach it with
their dipoles aligned to interact with the ions at the surface (Figure 10.9). Consequently,
the negative end of the water dipole points toward the positive \text{Na}^{+} ions, and the positive
end of the dipole points toward the negative \text{Cl}^{-} ions (Figure 10.9a). As the ions are pulled
into solution by the water molecules, more and more water molecules surround them. The
ions become solvated or hydrated in this case because water is the solvent. Keep in mind
that pure water is \(\sim 56 \text{ M}\) (Section 10.1), so a 0.1 M solution of sodium chloride contains

Figure 10.8 The water dipole
(a) The region in red carries negative charge, while the one in blue is positively charged.
(b) The dipole, which is represented by the arrow, points from the center of positive charge toward the
center of negative charge.

Figure 10.9 Dissolving NaCl in water
(a) Water molecules approach the crystal such that the positive ends of the water dipoles align with chloride ions and the
negative ends align with sodium ions.
(b) The ions are pulled into solution and are surrounded by water molecules. We say that the ions are solvated or, in
this case, hydrated.
~560 H₂O molecules for each NaCl unit or ~280 H₂O molecules for each Na<sup>+</sup> ion and ~280 H₂O molecules for each Cl<sup>-</sup> ion. In Figure 10.9, there are about only ~10 H₂O molecules for each ion, but there are actually hundreds in a typical solution.

Figure 10.9 demonstrates the difference between the environments of the ions in solid and aqueous NaCl. In the solid (Figure 10.9a), all interactions are between Na<sup>+</sup> and Cl<sup>-</sup> ions, so the solid is represented as NaCl. In aqueous NaCl (Figure 10.9b), each ion is hydrated, so its interactions are with water; interactions with other ions are very weak due to the high dielectric (ε) of water. Consequently, an aqueous solution of a salt is usually represented as the separated ions: Na<sup>+</sup> + Cl<sup>-</sup>

### 10.7 DISSOLUTION OF IONIC SUBSTANCES

The process whereby an ionic substance dissolves in water is called dissolution*. The chemical equation for the dissolution of calcium carbonate is

\[
\text{CaCO}_3(s) \rightarrow \text{Ca}^{2+} + \text{CO}_3^{2-}
\]

As an approximation, we assume that an ionic substance is soluble when the force of attraction between its ions in solution is small enough that the ions can exist separately in solution; i.e., the force is not great enough that the separated ions attract one another to reverse the dissolution process. The force of attraction is described by Coulomb’s law, \( F = \frac{kq_1q_2}{\varepsilon r^2} \) (Equation 1.3). We conclude that an ionic substance is soluble when

- \( r \) is very large. \( r \) is the property of the solution because it is the distance between the ions in the solution. \( r \) depends only upon concentration; ions in concentrated solutions are closer than ions in dilute solutions. If a substance is soluble, then the force of attraction cannot be great even at moderate concentration, so \( r \) cannot be very large.

- \( \varepsilon \) is large. \( \varepsilon \) is the dielectric constant of the solvent and measures how well the solvent screens the charges in solution. The dielectric constants for some common solvents are given in Table 10.3. The dielectric constant of water is about 40 times greater than that of a nonpolar solvent such as hexane (C₆H₁₄). This means that the force of attraction of two oppositely charged ions separated by the same distance is 40 times greater in C₆H₁₄ than in water, which is another reason that ionic substances are more soluble in water.

- \( q_1q_2 \) is small. The product of the charges on the ions is the only factor that is a property of the ionic solute. Recall that the charges on ions typically fall in the range of -3 to +3, thus \( 1 \leq |q_1q_2| \leq 9 \). If the magnitude of the charge on either ion is one, \(|q_1q_2| \) cannot exceed 3, but if neither charge is 1, then \(|q_1q_2| \) cannot be less than 4. Consequently, we expect that ionic compounds containing highly charged ions will not be as soluble in water as those containing +1 and -1 ions because the force of attraction between highly charged ions is too strong.

* Dissolution means a decomposition of a whole into its parts. Here, it refers to the breaking apart of an ionic solid into its constituent ions in solution.

### Table 10.3 Dielectric constants of selected solvents at 20 °C

<table>
<thead>
<tr>
<th>Solvent Name</th>
<th>Formula</th>
<th>( \varepsilon )</th>
</tr>
</thead>
<tbody>
<tr>
<td>acetic acid</td>
<td>CH₃COOH</td>
<td>6.20</td>
</tr>
<tr>
<td>acetone</td>
<td>(CH₃)₂C=O</td>
<td>21.0</td>
</tr>
<tr>
<td>benzene</td>
<td>C₆H₆</td>
<td>2.28</td>
</tr>
<tr>
<td>carbon disulfide</td>
<td>CS₂</td>
<td>2.63</td>
</tr>
<tr>
<td>carbon tetrachloride</td>
<td>CCl₄</td>
<td>2.24</td>
</tr>
<tr>
<td>dimethyl sulfoxide</td>
<td>(CH₃)₂S=O</td>
<td>47.2</td>
</tr>
<tr>
<td>ether</td>
<td>(C₂H₅)₂O</td>
<td>4.27</td>
</tr>
<tr>
<td>ethanol</td>
<td>C₂H₅OH</td>
<td>25.3</td>
</tr>
<tr>
<td>hexane</td>
<td>C₆H₁₄</td>
<td>1.89</td>
</tr>
<tr>
<td>methanol</td>
<td>CH₃OH</td>
<td>33.0</td>
</tr>
<tr>
<td>water</td>
<td>H₂O</td>
<td>80.10</td>
</tr>
</tbody>
</table>

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The effect of the $q_1q_2$ product on the solubility of ionic compounds is summarized by the **Solubility Rules** shown in Table 10.4. The rules should be considered to be *rules of thumb* only; they summarize many, but not *all* cases. Rules 1 and 2 indicate that if either ion is +1 or -1 then the salt is likely to be soluble. Rule 3 continues with this theme but indicates what appear to be some exceptions to the +1/-1 rule. However, recall from Section 5.2 that late metals, such as those in Rule 3 are highly electronegative, so their bonds to halides have substantial covalent character and are not very ionic. Thus, Coulomb’s Law is not applicable to those halides. Rule 4 indicates that sulfate is the only ion having a charge different from +1 or -1 that forms compounds that are usually soluble in water. Rule 5 states that *any compound that is not listed as soluble in Rules 1 through 4 should be assumed to be insoluble.*

**Example 10.8**

a) Which of the following compounds can be used to make a solution that is 0.1 M in Pb$^{2+}$ ions?  PbSO$_4$, Pb(NO$_3$)$_2$, PbI$_2$, and Pb(OH)$_2$

To make a 0.1 M solution, you must use a substance that is soluble. PbSO$_4$ is not soluble (Rule 4), Pb(NO$_3$)$_2$ is soluble (Rule 2), PbI$_2$ is not soluble (Rule 3), and Pb(OH)$_2$ is not soluble (Rule 5). Thus, only Pb(NO$_3$)$_2$ is soluble and can be used to make the solution.

b) Which of the following compounds can be used to make a solution that is 0.1 M in CrO$_4^{2-}$ ions?  K$_2$CrO$_4$, BaCrO$_4$, (NH$_4$)$_2$CrO$_4$, FeCrO$_4$, and Ag$_2$CrO$_4$

CrO$_4^{2-}$ ions are not listed in the solubility rules, so we assume that all of its compounds are insoluble unless the cation is the ammonium ion or a Group 1A metal (Rule 1). Therefore, K$_2$CrO$_4$ and (NH$_4$)$_2$CrO$_4$ could be used, but none of the others are soluble enough to make the solution.

**10.8 PRECIPITATION OF IONIC SUBSTANCES**

The ions in solution are mobile, so when two solutions are mixed the ions in one solution encounter those from the other solution. If their interaction is strong enough, they precipitate from solution as an insoluble solid. **Precipitation** is the reverse of dissolution. The chemical equation for the precipitation of Ca$^{2+}$ and CO$_3^{2-}$ ions from solution is

$$Ca^{2+} + CO_3^{2-} → CaCO_3(s)$$

Two ions precipitate from an aqueous solution if the compound they form is insoluble; i.e., when $r$ is small (the solution is too concentrated) and/or $q_1q_2$ is large. To determine if a precipitate forms when two solutions are mixed, we use the solubility rules to see if the

---

**Table 10.4 Solubility Rules for Ionic Compounds in water**

<table>
<thead>
<tr>
<th>Rule</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rule 1</td>
<td>Compounds of NH$_4^{+}$ and group 1A metal ions are soluble.</td>
</tr>
<tr>
<td>Rule 2</td>
<td>Compounds of NO$_3^{-}$, ClO$_4^{-}$, ClO$_3^{-}$, and C$_2$H$_3$O$_2^{-}$ are soluble.</td>
</tr>
<tr>
<td>Rule 3</td>
<td>Compounds of Cl$^{-}$, Br$^{-}$, and I$^{-}$ are soluble except those of Ag$^{+}$, Cu$^{+}$, Tl$^{+}$, Hg$_2^{2+}$ and Pb$^{2+}$.</td>
</tr>
<tr>
<td>Rule 4</td>
<td>Compounds of SO$_4^{2-}$ are soluble except those of Ca$^{2+}$, Sr$^{2+}$, Ba$^{2+}$, and Pb$^{2+}$.</td>
</tr>
<tr>
<td>Rule 5</td>
<td>Most other ionic compounds are insoluble; i.e., most other combinations of ions form precipitates in water.</td>
</tr>
</tbody>
</table>
combination of the cation in one compound with the anion in the other results in a compound that is insoluble. For example, consider mixing solutions of AgNO\textsubscript{3} and NaCl. Both substances are strong electrolytes, so they are found as their separated ions in aqueous solution. Thus, we represent the two solutions in different boxes as follows:

\[
\begin{align*}
1 & : \text{Ag}^{+} + \text{NO}_3^- \\
2 & : \text{Na}^{+} + \text{Cl}^- 
\end{align*}
\]

We then designate the two new cation-anion combinations that are possible in the mixed solution by the lines labeled 1 and 2. The possibilities for opposite charge interaction are therefore

1) Ag\textsuperscript{+} + Cl\textsuperscript{-} \\
2) Na\textsuperscript{+} + NO\textsubscript{3}\textsuperscript{-}

Rule 3 states that AgCl is insoluble, so it precipitates from solution, while NaNO\textsubscript{3} is soluble (Rules 1 and 2) and does not precipitate.

\[\text{Example 10.9}\]

Write the formula of the precipitate that forms when the following aqueous solutions are mixed or write none if no precipitate is expected.

\begin{enumerate}
\item[a)] Solutions of FeSO\textsubscript{4} and KOH
Express the solutions as the separated ions as shown in the margin and determine the new cation-anion combinations. (1) Fe\textsuperscript{2+} + OH\textsuperscript{-} and (2) K\textsuperscript{+} + SO\textsubscript{4}\textsuperscript{2-}. No precipitate results from the K\textsuperscript{+} + SO\textsubscript{4}\textsuperscript{2-} combination (Rules 1 and 4), but neither Fe\textsuperscript{2+} nor OH\textsuperscript{-} are listed in the solubility rules, so combination (1) produces an insoluble compound (Rule 5). The +2 charge on Fe\textsuperscript{2+} requires 2OH\textsuperscript{-}, so the formula of the precipitate is Fe(OH)\textsubscript{2}.

\item[b)] Solutions of Pb(ClO\textsubscript{4})\textsubscript{2} and CuSO\textsubscript{4}
As shown in the margin, the new cation-anion combinations that are possible upon mixing are (1) Pb\textsuperscript{2+} + SO\textsubscript{4}\textsuperscript{2-} and (2) Cu\textsuperscript{2+} + ClO\textsubscript{4}\textsuperscript{-}. No precipitate results from Cu\textsuperscript{2+} + ClO\textsubscript{4}\textsuperscript{-} (Rule 2), but the combination of Pb\textsuperscript{2+} + SO\textsubscript{4}\textsuperscript{2-} is insoluble (Rule 4). The formula of the precipitate is PbSO\textsubscript{4}.

\item[c)] Solutions of K\textsubscript{3}PO\textsubscript{4} and CoCl\textsubscript{2}
Mixing introduces the following interactions: 1) K\textsuperscript{+} + Cl\textsuperscript{-} and 2) Co\textsuperscript{2+} + PO\textsubscript{4}\textsuperscript{3-}. Combination (1) results in KCl, which is soluble (Rules 1 and 3). Neither Co\textsuperscript{2+} nor PO\textsubscript{4}\textsuperscript{3-} is listed in the solubility rules, so combination (2) produces a precipitate. The lowest common multiple of the +2 and -3 charges is 6, so three cations and two anions are required in the formula. The precipitate is cobalt(II) phosphate: Co\textsubscript{3}(PO\textsubscript{4})\textsubscript{2}.
\end{enumerate}
Example 10.10

a) A solution is known to contain Ba\(^{2+}\) and/or Ag\(^{+}\) ions. Which ion is present if the addition of Cl\(^{-}\) ions does not cause a precipitate, but the addition of SO\(_4\)^{2-} does?

BaCl\(_2\) is soluble, but AgCl is not (Rule 3), so the solution cannot contain Ag\(^{+}\) ions because AgCl does not precipitate. Ag\(_2\)SO\(_4\) is soluble, but BaSO\(_4\) is not (Rule 4), so the precipitate must be BaSO\(_4\). We conclude that the solution contains Ba\(^{2+}\) but not Ag\(^{+}\) ions.

b) A solution is known to contain Br\(^{-}\) and/or OH\(^{-}\) ions. Which ion is present if the addition of Pb\(^{2+}\) ions causes a precipitate, but the addition of Fe\(^{2+}\) does not?

Neither PbBr\(_2\) (Rule 3) and Pb(OH)\(_2\) (Rule 5) are soluble, so the precipitate could be due to either anion. However, FeBr\(_2\) is soluble (Rule 3), while Fe(OH)\(_2\) is not, so the lack of precipitate with the addition of Fe\(^{2+}\) rules out the presence of OH\(^{-}\) ions. We conclude that the solution contains Br\(^{-}\), but not OH\(^{-}\) ions.

The reaction that occurs when solutions of silver nitrate and sodium chloride are mixed could be represented by the following chemical equation:

\[ \text{AgNO}_3(aq) + \text{NaCl}(aq) \rightarrow \text{AgCl}(s) + \text{NaNO}_3(aq) \]

The fact that silver chloride precipitated is indicated by showing that it is a solid, while all others are aqueous (in solution). However, strong electrolytes are typically represented by their ions in aqueous solutions, so the reaction mixture could also be represented as

\[ \text{Ag}^{+} + \text{NO}_3^{-} + \text{Na}^{+} + \text{Cl}^{-} \rightarrow \text{AgCl}(s) + \text{Na}^{+} + \text{NO}_3^{-} \]

As indicated by the blue rectangles, the sodium and nitrate ions are unchanged during the reaction; each ion is surrounded by hundreds of water molecules before and after the reaction. Ions that do not participate in the reaction but are present throughout are called spectator ions. Both Na\(^{+}\) and NO\(_3\)^{-} are spectator ions in the above. Because these ions do not participate in the reaction, they are not included in the net equation, which shows only those species that change. The net equation for the precipitation of silver chloride, regardless of the source of the ions, is written as follows:

\[ \text{Ag}^{+} + \text{Cl}^{-} \rightarrow \text{AgCl}(s) \]

Net equations indicate only the changes that occur during a chemical reaction. They are most important when dealing with aqueous reactions of ionic substances. We will use them extensively in the next two chapters when we discuss redox (reduction-oxidation) reactions and acid-base reactions. In balancing a net reaction containing ions, it is important to realize that charge balance is as important as atom balance.
Example 10.11

Write net equations for the precipitation reactions in example 10.9.

a) Solutions of FeSO₄ and KOH

The precipitate is Fe(OH)₂, so 2OH⁻ ions are required for each Fe²⁺ ion.

\[ \text{Fe}^{2+} + 2\text{OH}^- \rightarrow \text{Fe(OH)}_2 \]

b) Solutions of Pb(ClO₄)₂ and CuSO₄

The precipitate is PbSO₄. There is 1:1 ratio of ions, so the net equation is

\[ \text{Pb}^{2+} + \text{SO}_4^{2-} \rightarrow \text{PbSO}_4 \]

c) Solutions of K₃PO₄ and CoCl₂

The precipitate is Co₃(PO₄)₂, so 3Co²⁺ and 2PO₄³⁻ are required.

\[ 3\text{Co}^{2+} + 2\text{PO}_4^{3-} \rightarrow \text{Co}_3(\text{PO}_4)_2 \]

Example 10.12

Write net equations for the reactions occurring when solutions of the following substances are mixed. Indicate ‘no reaction’ if no precipitate is expected to form.

a) Potassium iodide + lead nitrate

\[ \text{K}^+ + \text{I}^- + \text{Pb}^{2+} + \text{NO}_3^- \]

1. No reaction because KNO₃ is soluble by Rules 1 and 2.
2. PbI₂ precipitates by Rule 3.
   
   Net reaction: Pb²⁺ + 2I⁻ → PbI₂(s).

b) Sodium phosphate + silver nitrate

\[ \text{Na}^+ + \text{PO}_4^{3-} + \text{Ag}^{+} + \text{NO}_3^- \]

1. No reaction because NaNO₃ is soluble by Rules 1 and 2.
2. Ag₃PO₄ precipitates by Rule 5.
   
   Net reaction: 3Ag⁺ + PO₄³⁻ → Ag₃PO₄(s).
c) Ammonium sulfate + sodium phosphate

\[ \text{NH}_4^+ + \text{SO}_4^{2-} + \text{Na}^+ + \text{PO}_4^{3-} \]

1. No reaction because (NH_4)_3PO_4 is soluble by Rule 1.
2. No reaction because Na_2SO_4 is soluble by Rules 1 and 4.

No reaction occurs when these solutions are mixed.

The following are left as student activities. The answers are on the following page.

d) Lead nitrate + potassium chromate

e) Barium acetate + ammonium sulfate

f) Cobalt(II) chloride + sodium phosphate

g) Ammonium sulfate + silver nitrate

10.9 SOLUBILITY EQUILIBRIA

The precipitation and dissolution processes are in dynamic equilibrium in a saturated solution; \textit{i.e.}, the rate at which the solid dissolves equals the rate at which the ions precipitate. For CaCO_3(s), the chemical equation that represents this equilibrium is

\[ \text{CaCO}_3(s) \rightleftharpoons \text{Ca}^{2+} + \text{CO}_3^{2-} \]

The concentrations of the ions in the saturated solution can be used to determine the equilibrium constant for the reaction, or they can be determined from the equilibrium constant, if it is known. As discussed in Section 9.11, solutes enter the equilibrium
constant expression as their molar concentrations raised to an exponent equal to their coefficient in the balanced equation, while solids enter the expression as 1. Substances on the right (products) are in the numerator, and substances on the left (reactants) are in the denominator. Thus, the equilibrium constant expression for the dissolution of CaCO$_3$ is

$$K_{sp} = \frac{[Ca^{2+}][CO_{3}^{2-}]}{1} = [Ca^{2+}][CO_{3}^{2-}] = 4.8 \times 10^{-9}$$

Eq. 10.3

The equilibrium constant, which involves only a product of concentrations (there is no denominator), is called the solubility product constant and given the symbol $K_{sp}$. A small value for $K_{sp}$ means that the product of the concentrations of the ions present at equilibrium is very small, which indicates that the substance is not very soluble. The $K_{sp}$ of CaCO$_3$ is $4.8 \times 10^{-9}$ at 298K, $K_{sp} < 1$, so it is an insoluble compound. Table 10.5 shows the solubility product constants of a few other insoluble salts. In a saturated solution of AgCl ($K_{sp} = 1.8 \times 10^{-10}$), $[Ag^{+}] \sim 10^{-5}$ M, while in a saturated solution of Ag$_2$S ($K_{sp} = 8 \times 10^{-48}$), $[Ag^{+}] \sim 10^{-17}$ M. Thus, silver chloride may be fairly insoluble, but Ag$_2$S is even more insoluble.

<table>
<thead>
<tr>
<th>Compound</th>
<th>$K_{sp}$</th>
<th>Compound</th>
<th>$K_{sp}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>AgCl</td>
<td>$1.8 \times 10^{-10}$</td>
<td>Ag$_2$S</td>
<td>$6.3 \times 10^{-50}$</td>
</tr>
<tr>
<td>Ag$_2$CrO$_4$</td>
<td>$1.1 \times 10^{-12}$</td>
<td>CaSO$_4$</td>
<td>$2.4 \times 10^{-5}$</td>
</tr>
<tr>
<td>AgI</td>
<td>$8.3 \times 10^{-17}$</td>
<td>BaSO$_4$</td>
<td>$1.1 \times 10^{-10}$</td>
</tr>
</tbody>
</table>

Example 10.13
The $K_{sp}$ of zinc carbonate is $1.0 \times 10^{-10}$. Write the process and the expression that correspond to that value.

The process is the dissolution of ZnCO$_3$ in water. In this process, the ionic bonds between the Zn$^{2+}$ ions and the CO$_3^{2-}$ ions are broken, but the covalent C-O bonds within the carbonate ion remain intact. The chemical process and $K_{sp}$ expression are

$$ZnCO_3(s) \rightleftharpoons Zn^{2+} + CO_3^{2-} \quad K_{sp} = [Zn^{2+}][CO_3^{2-}] = 1.0 \times 10^{-10}$$

Example 10.14
The $K_{sp}$ of iron(III) hydroxide is $1.6 \times 10^{-38}$. Write the process and the expression that correspond to that value.

Three OH$^{−}$ ions are required for each Fe$^{3+}$ ion, so the chemical formula is Fe(OH)$_3$. In addition, three hydroxide ions must be produced in the dissolution, so the hydroxide ion concentration must be cubed in the $K_{sp}$ expression.

$$Fe(OH)_3(s) \rightleftharpoons Fe^{3+} + 3OH^{−} \quad K_{sp} = [Fe^{3+}][OH^{−}]^3 = 1.6 \times 10^{-39}$$

Answers to student exercises in Example 10.12

d) Pb$^{2+}$ + CrO$_4^{2−}$ → PbCrO$_4$
e) Ba$^{2+}$ + SO$_4^{2−}$ → BaSO$_4$
f) $3Co^{2+}$ + $2PO_4^{3−}$ → $Co_3(PO_4)_2$
g) No reaction
Example 10.15

The hydroxide ion concentration in pure water is $1.0 \times 10^{-7}$ M. What is the maximum concentration of Fe$^{3+}$ that can exist at that hydroxide ion concentration?

From Example 10.14,

$$K_{sp} = 1.6 \times 10^{-39} = [Fe^{3+}][OH^{-}]^3$$

Solving for the Fe$^{3+}$ ion concentration, we obtain

$$[Fe^{3+}] = \frac{K_{sp}}{[OH^{-}]^3}$$

Substitution of the given $K_{sp}$ and the fact that $[OH^{-}] = 1.0 \times 10^{-7}$ M in pure water yields

$$[Fe^{3+}] = \frac{1.6 \times 10^{-39}}{(1.0 \times 10^{-7})^3} = 1.6 \times 10^{-18} \text{ M}$$

Thus, it is not possible to obtain high concentrations of iron(III) in water due to the precipitation of iron(III) hydroxide!

10.10 CHAPTER SUMMARY AND OBJECTIVES

Solutions are homogeneous mixtures characterized by the concentration of a solute in a solvent. The most useful and common unit of concentration in the chemistry laboratory is molarity, the number of moles of solute present in a liter of solution. The maximum concentration of solute that can be obtained in solution is called the solubility of the solute in that solvent at that temperature. The enthalpy of solution involves three terms: 1) the enthalpy required to loosen the solute particles from their interactions with one another; 2) the enthalpy required to create cavities in the solvent to accommodate the particles, and 3) the enthalpy released when the solute-solvent interactions are established. The first two terms are endothermic, while the third term is exothermic. Because $\Delta S$ is usually positive, the free energy of solution will be negative when the exothermic term is not much less than the sum of the two endothermic terms. This consideration is summarized in the rule like dissolves like: compounds with similar types of intermolecular forces are soluble in one another.

Compounds with many CH$_2$ groups interact so poorly with water that they are said to be hydrophobic. Consequently, many organic compounds are insoluble in water. However, there are a number of hydrophilic organic compounds that readily dissolve in water due to the presence of polar groups such as –OH, or ionic groups such as –OSO$_3^-$, that interact
well with water. Organic compounds are soluble in water as long as they contain hydrophilic regions and their hydrophobic regions are not very large. Substances with both large hydrophobic regions and ionic regions can form spherical micelles when they are agitated in water. Detergents form micelles that function by dissolving the grease and oils into the hydrophobic micelle interior. The grease-and-oil containing micelles can be rinsed away because the hydrophilic ionic heads of the micelles are water soluble.

Electrolytes are substances whose aqueous solutions conduct electricity. The conduction of electricity is the result of the mobility of ions in solution. Ionic substances are strong electrolytes, while covalent substances are nonelectrolytes. Ions in aqueous solution are hydrated, which means they are surrounded by many water molecules that screen the ions from one another. In a saturated aqueous solution of an ionic solid, the dissolution and precipitation processes occur at the same rate, and the equilibrium constant for dissolution is called the solubility product constant, $K_{sp}$.

After studying the material presented in this chapter, you should be able to:

1. calculate the molarity of a solution from the mass of solute and the volume of the solution or the number of moles of solute in a given volume of solution of known molarity (Section 10.1);
2. describe the solution process, including the factors that contribute to the enthalpy of solution (Section 10.2);
3. explain and use the rule “like dissolves like” (Section 10.2);
4. classify compounds as hydrophilic or hydrophobic (Section 10.3);
5. explain the action of micelles and detergents (Section 10.4);
6. classify substances as strong, weak, or nonelectrolytes (Section 10.5);
7. determine the concentrations of all ions in a solution from the concentration of the parent compound (Section 10.6);
8. explain how ionic compounds dissolve in water (Section 10.7);
9. write the chemical equation for the dissolution of an ionic substance (Section 10.7);
10. use the solubility rules to predict whether a precipitate should form when aqueous solutions of ionic compounds are mixed (Section 10.8);
11. differentiate between spectator ions and reacting ions and write net equations for precipitation reactions (Section 10.8);
12. write the expression that relates the concentrations of the ions in a saturated solution to the solubility product of a substance (Section 10.9) and
13. calculate the concentration of an ion in a saturated solution given the $K_{sp}$ and the concentrations of the other ions (Section 10.9).
10.11 EXERCISES

1. Distinguish between the terms ‘solute’ and ‘solvent.’ Give an example of a solution and identify each component.

2. Distinguish between ‘homogenous’ and ‘heterogeneous’ mixtures. Give an example of each.

Review Appendix C (Molarity) if you need help on Exercises 3-8.

3. What is the concentration of nitrate ion in each of the following solutions?
   a) 0.25 M KNO₃
   b) 0.10 M Al(NO₃)₃
   c) 0.20 M Ca(NO₃)₂

4. What is the concentration of all ions in each of the following solutions?
   a) 0.16 M CaCl₂
   b) 0.080 M Na₂SO₄
   c) 0.060 M KBr

5. A solution is prepared by dissolving 25.0 g of sodium sulfate in enough water to prepare 250 mL of solution.
   a) What is the molarity of sodium sulfate in the solution?
   b) What are the molarities of the sodium and sulfate ions in the solution?
   c) How many moles of sodium ions are present in 17 mL of the solution?

6. A solution is labeled 0.0650 M K₃PO₄.
   a) How many moles of K¹⁺ ions are present in 500 mL of this solution?
   b) How many moles of PO₄³⁻ ions are present in 500 mL of this solution?
   c) How many grams of K₃PO₄ are present in 50 mL of this solution?

7. A solution of K₂SO₄, which has a volume of 75.0 mL, contains 0.0048 moles of potassium ions. What is the molarity of the K₂SO₄ solution?

8. What mass of KCl is required to make 45 mL of a 0.13 M KCl solution? How many moles of chloride ion are present in the solution?

9. What are the two steps involved in solvation?

10. Explain the meaning of like dissolves like.

11. Explain the hydrophobic effect.

12. Indicate whether each of the following substances are more soluble in H₂O or C₆H₁₄:
   a) KI  b) C₆H₁₈  c) grease  d) CH₃(CH₂)₁₂OH

13. Indicate whether each of the following substances are more soluble in H₂O or C₆H₁₄:
   a) HF  b) CH₃OH  c) NaC₂H₅O₂  d) CH₄

14. What are the characteristics of a good detergent?

15. Differentiate between a monolayer and a micelle. Under what conditions is a detergent expected to form in each?

16. Represent CH₃(CH₂)₁₅COONa with symbol shown in Figure 10.4d.

17. Identify each of the following as a weak, strong, or nonelectrolyte:
   a) CCl₄  b) NH₄NO₃  c) H₂CO₃  d) HNO₃  e) CH₃OH

18. Identify each of the following as a weak, strong, or nonelectrolyte:
   a) KF  b) CH₃Cl  c) HF  d) NH₃  e) CH₃COONa

19. What are the predominant solute species in aqueous solutions of the following? Write the molecule or the separated ions as appropriate.
   a) CO₂  b) CaCl₂  c) PF₃  d) K₂Cr₂O₇  e) KOH

20. What are the predominant solute species in aqueous solutions of the following? Write the molecule or the separated ions as appropriate.
   a) CoCl₃  b) Pb(NO₃)₂  c) NH₄F  d) C₂H₅OH  e) BrF₃

21. What is the ratio of the force of attraction experienced by Ca²⁺ and SO₄²⁻ to that experienced by Al³⁺ and Cl⁻? Assume that the ions are the same distance apart and in the same medium.

22. What is the ratio of the force of attraction experienced by Na¹⁺ and Cl⁻ to that experienced by Al³⁺ and P³⁻? Assume that the ions are the same distance apart and in the same medium.

23. What property of water makes it a good solvent for ionic compounds? How is this property expressed in Coulomb’s Law?

24. Which solid(s) can be used to make a solution that is 0.1 M in Pb²⁺ ions?
   a) Pb(ClO₄)₂  b) PbCl₂  c) PbCrO₄  d) PbCO₃  e) PbS

25. Which solid(s) can be used to make a solution that is 0.1 M in Zn²⁺ ions?
   a) Zn(ClO₄)₂  b) ZnCl₂  c) ZnCrO₄  d) ZnCO₃  e) ZnS

26. Which solid(s) can be used to make a solution that is 0.1 M in SO₄²⁻ ions?
   a) PbSO₄  b) K₂SO₄  c) CuSO₄  d) BaSO₄  e) FeSO₄

27. Which solid(s) can be used to make a solution that is 0.1 M in CrO₄²⁻ ions?
   a) ZnCrO₄  b) K₂CrO₄  c) CuCrO₄  d) BaCrO₄  e) FeCrO₄
28. A student finds two unlabelled jars, one is BaSO4 and the other is Na2SO4. Suggest an easy way to determine which jar contains Na2SO4.

29. A solution is known to contain one of the following cations: Na1+, Ag1+, or Fe2+. The addition of chloride ion to part of the solution had no apparent effect, but addition of CrO4^{2-} ion resulted in a precipitate. What is the identity of the cation in the original solution?

30. A solution is known to contain one of the following anions: Cl1-, SO4^{2-}, or NO31-. What is the identity of the anion if a precipitate was observed with the addition of Pb2+, but no precipitate formed with the addition of Ag1+?

31. Write net equations for any precipitation reactions that occur when the following 0.1 M solutions are mixed or write 'no reaction' if appropriate.
   a) manganese(II) chloride + sodium sulfide
   b) iron(III) chloride + sodium carbonate
   c) potassium sulfide + zinc nitrate
   d) silver sulfate + barium iodide
   e) lead acetate + lithium hydroxide
   f) ammonium phosphate + copper(II) sulfate

32. Write net equations for any precipitation reactions that occur when the following 0.1 M solutions are mixed or write 'no reaction' if appropriate.
   a) potassium chromate + nickel(II) chloride
   b) cadmium nitrate + ammonium carbonate
   c) manganese(II) acetate + zinc sulfate
   d) lithium perchlorate + silver acetate
   e) barium nitrate + silver sulfate
   f) cesium hydroxide + iron(III) acetate

33. Write the chemical equation of the dissolution of the following salts in water and give the Ksp expression.
   a) FeS
   b) PbCl2
   c) Ca3(PO4)2

34. Write the chemical equation of the dissolution of the following salts in water and give the Ksp expression.
   a) Al(OH)3
   b) Fe2S3
   c) CoPO4

35. What is the maximum concentration of Fe^{2+} ions that can exist in a solution in which [OH^1-] = 1.0x10^{-7} M? Ksp (Fe(OH)2)= 8.0x10^{-16}

36. What is the maximum concentration of Pb^{2+} ions that can exist in a solution which is 0.10 M in chloride ion? Ksp (PbCl2)= 1.7x10^{-5}.

37. What is the Ksp of AgCN if the concentrations of silver and cyanide ions in a saturated solution of silver cyanide are each 1.1x10^{-8} M?

38. What is the Ksp of BaCO3 if the concentrations of barium and carbonate ions in a saturated solution of barium carbonate are each 9.0x10^{-5} M?

Review Appendix D4 if you need help on Exercises 39 - 42.

39. A student mixes 1.50 L of 0.20 M K2CrO4 and 1.20 L of 0.30 M AgNO3.
   a) Write the net reaction that occurs.
   b) How many moles of CrO4^{2-} ion were added?
   c) How many moles of Ag1+ ion were added?
   d) How many moles of Ag2CrO4 precipitate?
   e) How many grams of Ag2CrO4 precipitate?

40. A student mixes 25.0 mL of 0.20 M KCl and 15.0 mL of 0.30 M Pb(NO3)2.
   a) Write the net reaction that occurs.
   b) How many moles of Cl1- ion were added?
   c) How many moles of Pb2+ ion were added?
   d) How many moles of PbCl2 precipitate?
   e) How many grams of PbCl2 precipitate?

41. A student mixes 0.36 L of 0.10 M Ba(ClO4)2 and 0.52 L of 0.10 M Na2SO4.
   a) Write the net reaction that occurs.
   b) How many moles of SO4^{2-} ion were added?
   c) How many moles of Ba^{2+} ion were added?
   d) How many moles of BaSO4 precipitate?
   e) How many grams of BaSO4 precipitate?

42. A student mixes 78 mL of 0.17 M Fe(NO3)3 and 85 mL of 0.20 M Na2CO3.
   a) Write the net reaction that occurs.
   b) How many moles of CO3^{2-} ion were added?
   c) How many moles of Fe^{3+} ion were added?
   d) How many moles of Fe2(CO3)3 precipitate?
   e) How many grams of Fe2(CO3)3 precipitate?