7.3 Precipitation Reactions

The reaction that forms the scale in hot water pipes, eventually leading to major plumbing bills, belongs to a category of reactions called precipitation reactions. So does the reaction of calcium and magnesium ions with soap to create a solid scum in your bathtub and washing machine. Cadmium hydroxide, which is used in rechargeable batteries, is made from the precipitation reaction between water solutions of cadmium acetate and sodium hydroxide. This section describes the changes that occur in precipitation reactions, shows you how to predict when they take place, and shows you how to describe them using chemical equations.

Precipitation Reactions

OBJECTIVE 9

Precipitation reactions, such as the ones we will see in this section, belong to a general class of reactions called **double-displacement reactions**. (Double displacement reactions are also called **double-replacement**, **double-exchange**, or **metathesis reactions**.) Double displacement reactions have the following form, signifying that the elements in two reacting compounds change partners.

$$\mathrm{AB} + \mathrm{CD} \rightarrow \mathrm{AD} + \mathrm{CB}$$

Precipitation reactions take place between ionic compounds in solution. For example, in the precipitation reactions that we will see, A and C represent the cationic (or positively charged) portions of the reactants and products, and B and D represent the anionic (or negatively charged) portions of the reactants and products. The cation of the first reactant (A) combines with the anion of the second reactant (D) to form the product AD, and the cation of the second reactant (C) combines with the anion of the first reactant to form the product CB.

OBJECTIVE 10

Sometimes a double-displacement reaction has one product that is insoluble in water. As that product forms, it emerges, or precipitates, from the solution as a solid. This process is called **precipitation**, such a reaction is called a **precipitation reaction**, and the solid is called the **precipitate**. For example, when water solutions of calcium nitrate and sodium carbonate are mixed, calcium carbonate precipitates from the solution while the other product, sodium nitrate, remains dissolved.

This solid precipitates from the solution. It is a precipitate.

$$\mathrm{Ca(NO_3)_2}(aq) + \mathrm{Na_2CO_3}(aq) \rightarrow \mathrm{CaCO_3}(s) + 2\mathrm{NaNO_3}(aq)$$

One of the goals of this section is to help you to visualize the process described by this equation. Figures 7.10, 7.11, and 7.12 will help you do this.

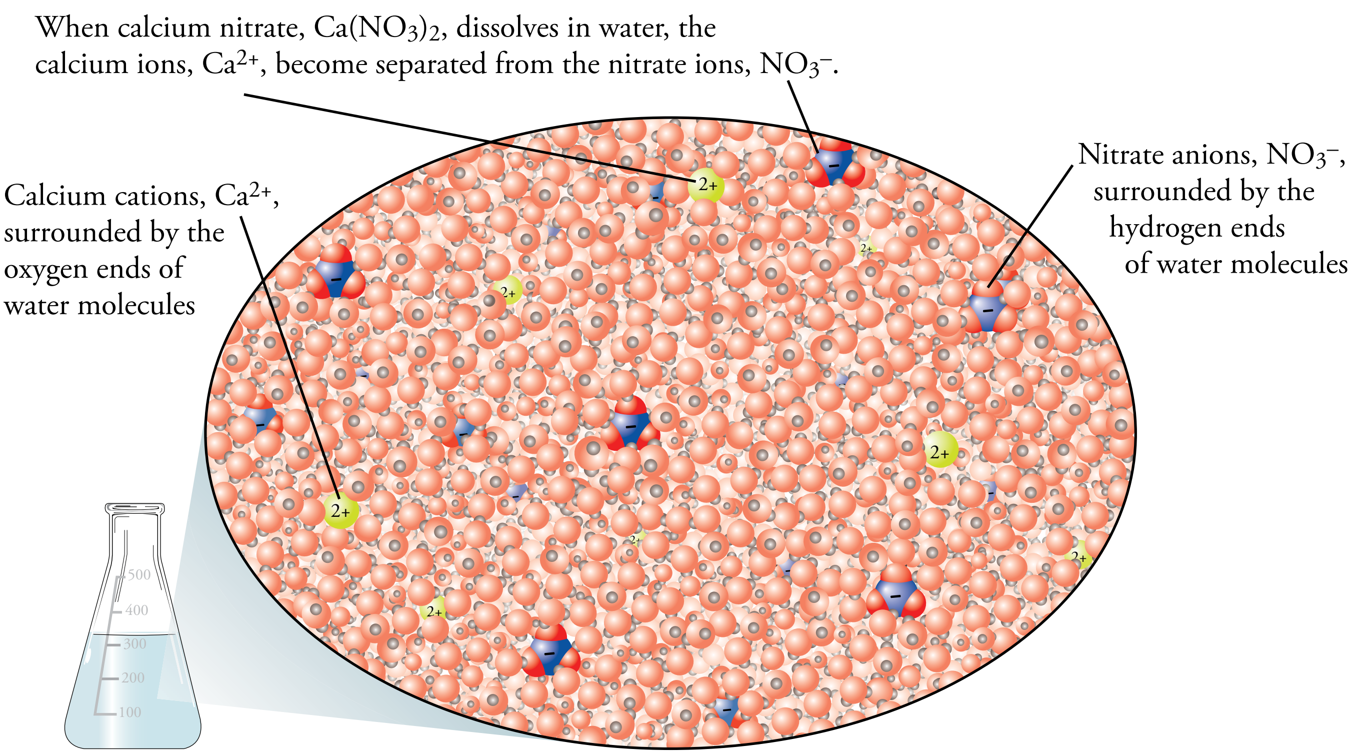
OBJECTIVE 10

First, let us imagine the particles making up the $Ca(NO_3)_2$ solution. Remember that when ionic compounds dissolve, the ions separate and become surrounded by water molecules. When $Ca(NO_3)_2$ dissolves in water (Figure 7.10), the Ca^{2+} ions separate from the NO_3^- ions, with the oxygen ends of water molecules surrounding the calcium ions, and the hydrogen ends of water molecules surrounding the nitrate ions.

An aqueous solution of sodium carbonate also consists of ions separated and surrounded by water molecules, much like the solution of calcium nitrate. If time were to stop at the instant that the solution of sodium carbonate was added to aqueous calcium nitrate, there would be four different ions in solution surrounded by water molecules: Ca^{2+}, NO_3^-, Na^+, and CO_3^{2-}. The oxygen ends of the water molecules surround the calcium and sodium ions, and the hydrogen ends of water molecules surround the nitrate and carbonate ions. Figure 7.11 on the next page shows the system at the instant just after solutions of calcium nitrate and sodium carbonate are combined and just before the precipitation reaction takes place. Because a chemical reaction takes place as soon as the $Ca(NO_3)_2$ and Na_2CO_3 solutions are combined, the four-ion system shown in this figure lasts for a very short time.

OBJECTIVE 10

Figure 7.10
Aqueous Calcium Nitrate
There are twice as many -1 nitrate ions as +2 calcium ions.



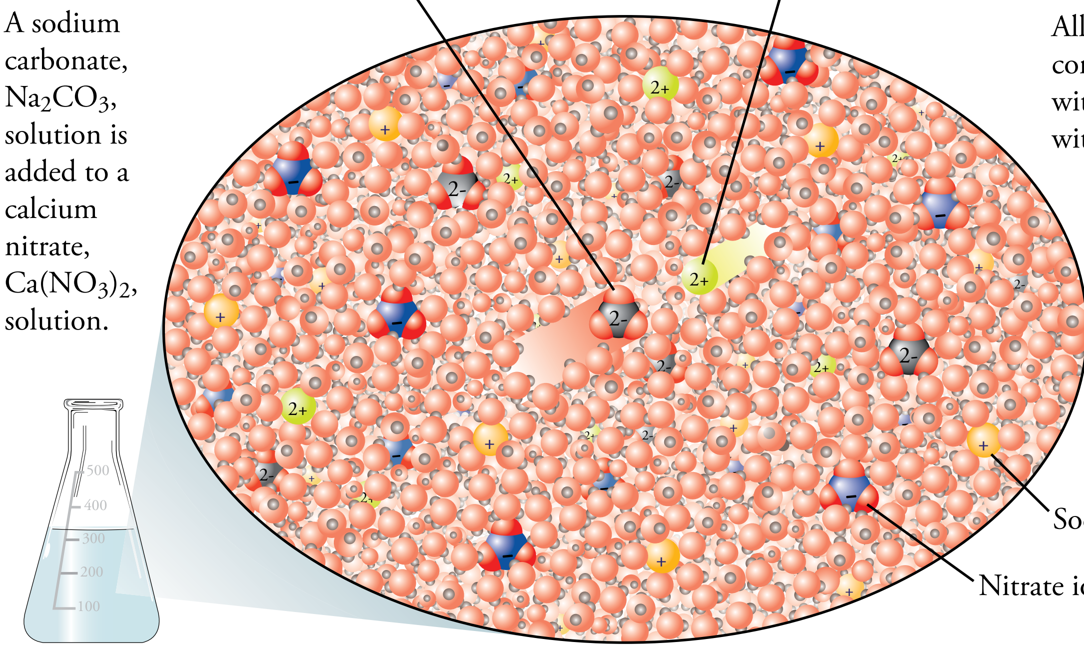


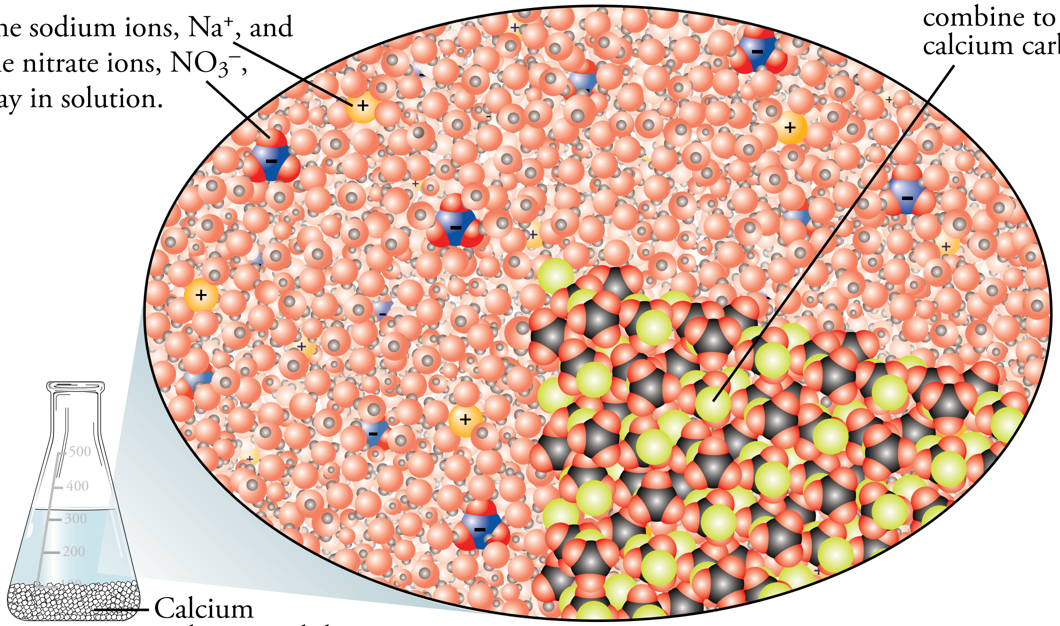
Figure 7.11
Mixture of $Ca(NO_3)_2(aq)$ and $Na_2CO_3(aq)$ at the Instant They Are Combined

Objective 10

Objective 10

The ions in solution move in a random way, like any particle in a liquid, so they will constantly collide with other ions. When two cations or two anions collide, they repel each other and move apart. When a calcium ion and a nitrate ion collide, they may stay together for a short time, but the attraction between them is too weak to keep them together when water molecules collide with them and push them apart. The same is true for the collision between sodium ions and carbonate ions. After colliding, they stay together for only an instant before water molecules break them apart again.

When calcium ions and carbonate ions collide, however, they stay together longer because the attraction between them is stronger than the attractions between the other pairs of ions. They might eventually be knocked apart, but while they are together, other calcium ions and carbonate ions can collide with them. When another Ca^{2+} or CO_3^{2-} ion collides with a $CaCO_3$ pair, a trio forms. Other ions collide with the trio to form clusters of ions that then grow to become small **crystals**—solid particles whose component atoms, ions, or molecules are arranged in an organized, repeating pattern. Many crystals form throughout the system, so the solid $CaCO_3$ at first appears as a cloudiness in the mixture. The crystals eventually settle to the bottom of the container (Figures 7.11 and 7.12).



Objective 10

Figure 7.12
Product Mixture for the Reaction of $Ca(NO_3)_2(aq)$ and $Na_2CO_3(aq)$

The equation that follows, which is often called a **complete ionic equation**, describes the forms taken by the various substances in solution. The ionic compounds dissolved in the water are described as separate ions, and the insoluble ionic compound is described with a complete formula.

$$\underbrace{Ca^{2+}(aq) + 2NO_3^-(aq) + 2Na^+(aq) + CO_3^{2-}(aq)}_{\text{Described as separate ions}} \rightarrow \underbrace{CaCO_3(s)}_{\text{Solid precipitate}} + \underbrace{2Na^+(aq) + 2NO_3^-(aq)}_{\text{Described as separate ions}}$$

Objective 10

The sodium and nitrate ions remain unchanged in this reaction. They were separate and surrounded by water molecules at the beginning, and they are still separate and surrounded by water molecules at the end. They were important in delivering the calcium and carbonate ions to solution (the solutions were created by dissolving solid calcium nitrate and solid sodium carbonate in water), but they did not actively participate in the reaction. When ions play this role in a reaction, we call them **spectator ions**.

Because spectator ions are not involved in the reaction, they are often left out of the chemical equation. The equation written without the spectator ions is called a **net ionic equation**.

Spectator ions are eliminated. Spectator ions

$$Ca^{2+}(aq) + 2NO_3^-(aq) + 2Na^+(aq) + CO_3^{2-}(aq) \rightarrow CaCO_3(s) + 2Na^+(aq) + 2NO_3^-(aq)$$

Net ionic equation: $Ca^{2+}(aq) + CO_3^{2-}(aq) \rightarrow CaCO_3(s)$

We call the equation that shows the complete formulas for all of the reactants and products the **complete equation**, or, sometimes, the **molecular equation**.

$$Ca(NO_3)_2(aq) + Na_2CO_3(aq) \rightarrow CaCO_3(s) + 2NaNO_3(aq)$$

You can find an animation that shows this precipitation reaction at the textbook's Web site.

Predicting Water Solubility

In order to predict whether a precipitation reaction will take place when two aqueous ionic compounds are mixed, you need to be able to predict whether the possible products of the double-displacement reaction are soluble or insoluble in water.

When we say that one substance is soluble in another, we mean that they can be mixed to a significant degree. More specifically, chemists describe the **solubility** of a substance as the maximum amount of it that can be dissolved in a given amount of solvent at a particular temperature. This property is often described in terms of the maximum number of grams of solute that will dissolve in 100 milliliters (or 100 grams) of solvent. For example, the water solubility of calcium nitrate is 121.2 g $Ca(NO_3)_2$ per 100 mL water at 25 °C. This means that when calcium nitrate is added steadily to 100 mL of water at 25 °C, it will dissolve until 121.2 g $Ca(NO_3)_2$ have been added. If more $Ca(NO_3)_2$ is added to the solution, it will remain in the solid form.

When we say an ionic solid is insoluble in water, we do not mean that none of the solid dissolves. There are always some ions that can escape from the surface of an ionic solid in water and go into solution. Thus, when we say that calcium carbonate is insoluble in water, what we really mean is that the solubility is very low (0.0014 g $CaCO_3$ per 100 mL H_2O at 25 °C).

OBJECTIVE 11

Solubility is difficult to predict with confidence. The most reliable way to obtain a substance's solubility is to look it up on a table of physical properties in a reference book. When that is not possible, you can use the following guidelines for predicting whether some substances are soluble or insoluble in water. They are summarized in Table 7.1.

- Ionic compounds with group 1 (or 1A) metallic cations or ammonium cations, NH_4^+, form soluble compounds no matter what the anion is.

- Ionic compounds with acetate, $C_2H_3O_2^-$, or nitrate, NO_3^-, ions form soluble compounds no matter what the cation is.
- Compounds containing chloride, Cl^-, bromide, Br^-, or iodide, I^-, ions are water-soluble except with silver ions, Ag^+ and lead(II) ions, Pb^{2+}.
- Compounds containing the sulfate ion, SO_4^{2-}, are water-soluble except with barium ions, Ba^{2+}, and lead(II) ions, Pb^{2+}.
- Compounds containing carbonate, CO_3^{2-}, phosphate, PO_4^{3-}, or hydroxide, OH^-, ions are insoluble in water except with group 1 metallic ions and ammonium ions.

Table 7.1 Water Solubility of Ionic Compounds

Objective 11

Category	Ions	Except with these ions	Examples
Soluble cations	Group 1 metallic ions and ammonium, NH_4^+	No exceptions	Na_2CO_3, $LiOH$, and $(NH_4)_2S$ are soluble.
Soluble anions	NO_3^- and $C_2H_3O_2^-$	No exceptions	$Bi(NO_3)_3$, and $Co(C_2H_3O_2)_2$ are soluble.
Usually soluble anions	Cl^-, Br^-, and I^-	Soluble with some exceptions, including with Ag^+ and Pb^{2+}	$CuCl_2$ is water soluble, but $AgCl$ is insoluble.
	SO_4^{2-}	Soluble with some exceptions, including with Ba^{2+} and Pb^{2+}	$FeSO_4$ is water soluble, but $BaSO_4$ is insoluble.
Usually insoluble	CO_3^{2-}, PO_4^{3-}, and OH^-	Insoluble with some exceptions, including with group 1 elements and NH_4^+	$CaCO_3$, $Ca_3(PO_4)_2$, and $Mn(OH)_2$ are insoluble in water, but $(NH_4)_2CO_3$, Li_3PO_4, and $CsOH$ are soluble.

Exercise 7.2 - Predicting Water Solubility

Objective 11

Predict whether each of the following is soluble or insoluble in water.

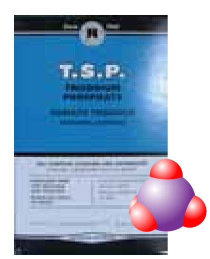
a. $Hg(NO_3)_2$ (used to manufacture felt)

b. $BaCO_3$ (used to make radiation resistant glass for color TV tubes)

c. K_3PO_4 (used to make liquid soaps)

d. $PbCl_2$ (used to make other lead salts)

e. $Cd(OH)_2$ (in storage batteries)



Sodium phosphate (or trisodium phosphate), Na_3PO_4, is an all-purpose cleaner.

You can find a computer tutorial that will provide more practice predicting water solubility at the textbook's Web site.

The study sheet on the next page will guide you in predicting whether precipitation reactions take place and help you write chemical equations for precipitation reactions.

Sample Study Sheet 7.2 Predicting Precipitation Reactions and Writing Precipitation Equations

OBJECTIVE 12

TIP-OFF You are asked to predict whether a precipitation reaction will take place between two aqueous solutions of ionic compounds, and if the answer is yes, to write the complete equation for the reaction.

GENERAL STEPS

Step 1 Determine the formulas for the possible products using the general double-displacement equation. (Remember to consider ion charges when writing your formulas.)

$$AB + CD \rightarrow AD + CB$$

STEP 2 Predict whether either of the possible products is water-insoluble. If either possible product is insoluble, a precipitation reaction takes place, and you may continue with step 3. If neither is insoluble, write "No reaction."

STEP 3 Follow these steps to write the complete equation.

- Write the formulas for the reactants separated by a + sign.
- Separate the formulas for the reactants and products with an arrow.
- Write the formulas for the products separated by a + sign.
- Write the physical state for each formula.
  The insoluble product will be followed by (*s*).
  Water-soluble ionic compounds will be followed by (*aq*).
- Balance the equation.

EXAMPLES See Examples 7.6-7.8.

EXAMPLE 7.6 - Predicting Precipitation Reactions

OBJECTIVE 12

Predict whether a precipitate will form when water solutions of silver nitrate, $AgNO_3(aq)$, and sodium phosphate, $Na_3PO_4(aq)$, are mixed. If there is a precipitation reaction, write the complete equation that describes the reaction.

Solution

Step 1 *Determine the possible products using the general double-displacement equation.*

$$AB + CD \rightarrow AD + CB$$

In $AgNO_3$, Ag^+ is A, and NO_3^- is B. In Na_3PO_4, Na^+ is C, and PO_4^{3-} is D. The possible products from the mixture of $AgNO_3(aq)$ and $Na_3PO_4(aq)$ are Ag_3PO_4 and $NaNO_3$. (Remember to consider charge when you determine the formulas for the possible products.)

$$AgNO_3(aq) + Na_3PO_4(aq) \quad \text{to} \quad Ag_3PO_4 + NaNO_3$$

Step 2 *Predict whether either of the possible products is water-insoluble.*

According to our solubility guidelines, most phosphates are insoluble, and compounds with Ag^+ are not listed as an exception. Therefore, silver phosphate, Ag_3PO_4, which is used in photographic emulsions, would be insoluble. Because compounds containing Na^+ and NO_3^- are soluble, $NaNO_3$ is soluble.

Step 3 *Write the complete equation.* (Don't forget to balance it.)

$$\mathbf{3AgNO_3(aq) + Na_3PO_4(aq) \rightarrow Ag_3PO_4(s) + 3NaNO_3(aq)}$$

Example 7.7 - Predicting Precipitation Reactions

Objective 12

Predict whether a precipitate will form when water solutions of barium chloride, $BaCl_2(aq)$, and sodium sulfate, $Na_2SO_4(aq)$, are mixed. If there is a precipitation reaction, write the complete equation that describes the reaction.

Solution

Step 1 In $BaCl_2$, A is Ba^{2+}, and B is Cl^-. In Na_2SO_4, C is Na^+, and D is SO_4^{2-}. The possible products from the reaction of $BaCl_2(aq)$ and $Na_2SO_4(aq)$ are $BaSO_4$ and NaCl.

$$BaCl_2(aq) + Na_2SO_4(aq) \quad \text{to} \quad BaSO_4 + NaCl$$

Step 2 According to our solubility guidelines, most sulfates are soluble, but $BaSO_4$ is an exception. It is insoluble and would precipitate from the mixture. Because compounds containing Na^+ (and most containing Cl^-) are soluble, NaCl is soluble.

Step 3

$$\mathbf{BaCl_2(aq) + Na_2SO_4(aq) \rightarrow BaSO_4(s) + 2NaCl(aq)}$$

This is the reaction used in industry to form barium sulfate, which is used in paint preparations and in x-ray photography.

Example 7.8 - Predicting Precipitation Reactions

Objective 12

Predict whether a precipitate will form when lead(II) nitrate, $Pb(NO_3)_2(aq)$, and sodium acetate, $NaC_2H_3O_2(aq)$, are mixed. If there is a precipitation reaction, write the complete equation that describes the reaction.

Solution

Step 1 The possible products from the mixture of $Pb(NO_3)_2(aq)$ and $NaC_2H_3O_2(aq)$ are $Pb(C_2H_3O_2)_2$ and $NaNO_3$.

$$Pb(NO_3)_2(aq) + NaC_2H_3O_2(aq) \quad \text{to} \quad Pb(C_2H_3O_2)_2 + NaNO_3$$

Step 2 According to our solubility guidelines, compounds with nitrates and acetates are soluble, so both $Pb(C_2H_3O_2)_2$ and $NaNO_3$ are soluble. **There is no precipitation reaction.**

Exercise 7.3 - Precipitation Reactions

Objective 12

Predict whether a precipitate will form when each of the following pairs of water solutions is mixed. If there is a precipitation reaction, write the complete equation that describes the reaction.

a. $CaCl_2(aq) + Na_3PO_4(aq)$

b. $KOH(aq) + Fe(NO_3)_3(aq)$

c. $NaC_2H_3O_2(aq) + CaSO_4(aq)$

d. $K_2SO_4(aq) + Pb(NO_3)_2(aq)$

Having Trouble?

Are you having trouble with the topics in this chapter? People often do. To complete each of the lessons in it successfully, you need to have mastered the skills taught in previous sections. Here is a list of the things you need to know how to do to solve the problems at the end of this chapter. Work through these items in the order presented, and be sure you have mastered each before going on to the next.

- Convert between names and symbols for the common elements. See Table 3.1.
- Identify whether an element is a metal or a nonmetal. See Section 3.3.
- Determine the charges on many of the monatomic ions. See Figure 5.3.
- Convert between the names and formulas for polyatomic ions. See Table 6.3.
- Convert between the names and formulas for ionic compounds. See Section 6.1.
- Balance chemical equations. See Section 7.1.
- Predict the products of double-displacement reactions. See Section 7.3.
- Predict whether ionic compounds are soluble or insoluble in water. See Section 7.3.

Special Topic 7.1 Hard Water and Your Hot Water Pipes

A precipitation reaction that is a slight variation on the one depicted in Figures 7.11 and 7.12 helps explain why a solid scale forms more rapidly in your hot water pipes than in your cold water pipes.

We say water is hard if it contains calcium ions, magnesium ions, and in many cases, iron ions. These ions come from rocks in the ground and dissolve into the water that passes through them. For example, limestone rock is calcium carbonate, $CaCO_3(s)$, and dolomite rock is a combination of calcium carbonate and magnesium carbonate, written as $CaCO_3{\bullet}MgCO_3(s)$. Water alone will dissolve very small amounts of these minerals, but carbon dioxide dissolved in water speeds the process.

$$CaCO_3(s) + CO_2(g) + H_2O(l) \rightarrow Ca^{2+}(aq) + 2HCO_3^-(aq)$$

If the water were removed from the product mixture, calcium hydrogen carbonate, $Ca(HCO_3)_2$, would form, but this compound is much more soluble than calcium carbonate and does not precipitate from our tap water.

When hard water is heated, the reverse of this reaction occurs, and the calcium and hydrogen carbonate ions react to reform solid calcium carbonate.

$$Ca^{2+}(aq) + 2HCO_3^-(aq) \rightarrow CaCO_3(s) + CO_2(g) + H_2O(l)$$

Thus, in your hot water pipes, solid calcium carbonate precipitates from solution and collects as scale on the inside of the pipes. After we have discussed acid-base reactions in Chapter 8, it will be possible to explain how the plumber can remove this obstruction.