

# Aqueous Solutions and Solubility Equilibria

## Chapter Preview

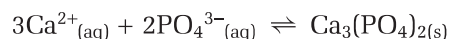
- 9.1** The Acid-Base Properties of Salt Solutions
- 9.2** Solubility Equilibria
- 9.3** Predicting the Formation of a Precipitate

## Prerequisite Concepts and Skills

Before you begin this chapter, review the following concepts and skills:

- solving equilibrium problems (Chapter 7, section 7.3)
- identifying conjugate acid-base pairs and comparing their strengths (Chapter 8, section 8.1)
- interpreting acid-base titration curves (Chapter 8, section 8.4)

The kidneys are sometimes called the master chemists of the body. They work to maintain the constant composition of the blood by helping to balance water and the various ions that are present in the blood. A very important equilibrium in the blood, which the kidneys help to control, involves calcium ions and phosphate ions.

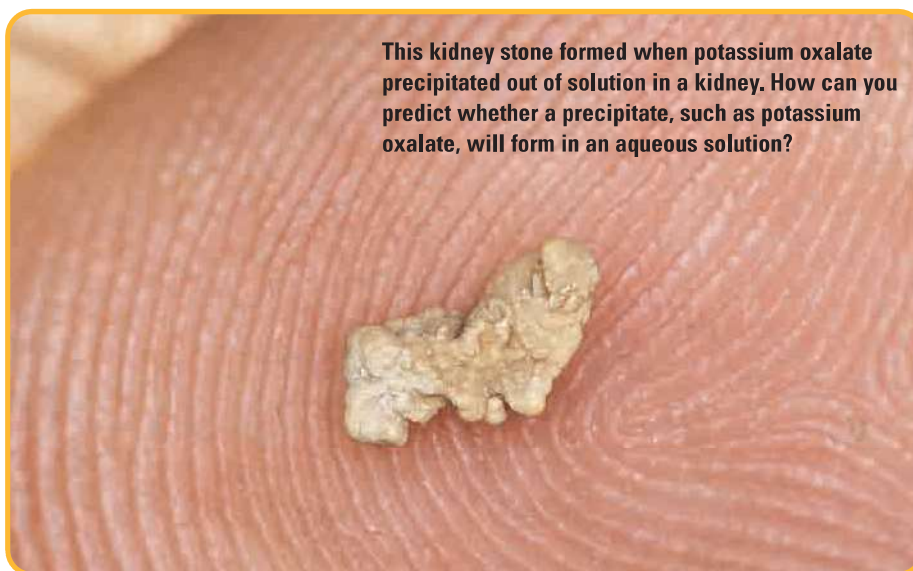


This equilibrium sometimes causes problems, however. For example, calcium phosphate helps to give bones their rigidity. If the kidneys remove too many phosphate ions from the blood due to disease, the position of equilibrium shifts to the left, as predicted by Le Châtelier's principle. More calcium phosphate dissolves in the blood, reducing bone density. The loss of too much calcium phosphate can lead to osteoporosis.

If the kidneys remove too many calcium ions from the blood, the equilibrium position *in the kidneys* shifts to the right. Solid calcium phosphate can form in the kidneys, producing kidney stones. Kidney stones, which are painful, can also form as the result of calcium oxalate precipitating in the kidneys. Precipitates of other compounds can affect different areas of the body: gallstones in the gall bladder and gout in the joints are two examples.

In this chapter, you will continue your study of acid-base reactions. You will find out how ions in aqueous solution can act as acids or bases. Then, by applying equilibrium concepts to ions in solution, you will be able to predict the solubility of ionic compounds in water and the formation of a precipitate.

This kidney stone formed when potassium oxalate precipitated out of solution in a kidney. How can you predict whether a precipitate, such as potassium oxalate, will form in an aqueous solution?



# The Acid-Base Properties of Salt Solutions

## 9.1

At the end of Chapter 8, you learned that when just enough acid and base have been mixed for a complete reaction, the solution can be acidic, neutral, or basic. The reaction between an acid and a base forms an aqueous solution of a salt. The properties of the dissolved salt determine the pH of a titration solution at equivalence. Figure 9.1 shows the acidic, basic, or neutral properties of three salt solutions.

In this section, you will learn how to predict the pH of an aqueous solution of a salt. Predicting the pH is useful when you are performing a titration experiment, because you need to choose an indicator that changes colour at a pH value that is close to the pH at equivalence.

### Acidic and Basic Properties of Salts

The acidic or basic property of an aqueous solution of a salt results from reactions between water and the dissociated ions of the salt. Some ions do not react with water. They are neutral in solution. Ions that do react with water produce a solution with an excess of  $\text{H}_3\text{O}^+_{(\text{aq})}$  or  $\text{OH}^-_{(\text{aq})}$ . The extent of the reaction determines the pH of the solution. As you will see, the reaction between an ion and water is really just another acid-base reaction.

Is there a way to classify salts so that you can predict whether their solutions in water will be basic, acidic, or neutral? In the following ExpressLab, you will determine the pH values of solutions of various salts. Then you will analyze your results to decide if there is a pattern.

#### Section Preview/ Specific Expectations

In this section, you will

- **predict** qualitatively whether a solution of a specific salt will be acidic, basic, or neutral
- **solve** problems that involve acid-base titration data and the pH at the equivalence point
- **communicate** your understanding of the following terms: *equivalence point*, *end-point*



**Figure 9.1** Photograph (A) shows three aqueous salt solutions. Photograph (B) shows the solutions after a some universal indicator solution has been added to each one. The orange colour indicates an acidic solution, the yellow colour indicates a neutral solution, and the purple colour indicates a basic solution.



In this ExpressLab, you will measure the pH values of solutions of different salts with the same concentration in mol/L. The pH of a solution gives the relative  $[H_3O^+]$ , compared with the  $[OH^-]$ . From this information, you can infer which ion in the salt reacted with water to the greatest extent.

### Safety Precaution



- Some of the salts are irritants. Wear gloves and goggles at all times.

### Materials

dropper bottles containing 0.1 mol/L solutions of each of the following salts: ammonium chloride,  $NH_4Cl_{(aq)}$ ; sodium chloride,  $NaCl_{(aq)}$ ; sodium acetate,  $NaCH_3COO_{(aq)}$ ; potassium carbonate,  $K_2CO_{3(aq)}$   
unknown salt  
universal pH paper  
spot plate

### Procedure

- Copy the following table into your notebook and title it. Before you test each salt, write the formula of the salt in the appropriate box. (You will not be testing any salt that results from the reaction of a weak base and a weak acid.)

|             | Strong acid | Weak acid |
|-------------|-------------|-----------|
| Strong base |             |           |
| Weak base   |             |           |

- Copy the following table into your notebook, to record your observations. Give your table a title.

| Salt        | pH of aqueous solution |
|-------------|------------------------|
| $NH_4Cl$    |                        |
| $NaCl$      |                        |
| $NaCH_3COO$ |                        |
| $K_2CO_3$   |                        |
| unknown     |                        |

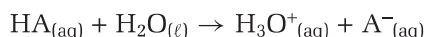
- Pour a small volume of one of the solutions into the well of a spot plate. Test the solution using universal pH paper. By comparing the colour of the paper, estimate the pH of the solution. Record your results in your table.
- Repeat step 3 for each of the solutions.

### Analysis

- An ion that does not react with water has no effect on the pH of water. If both the cation and the anion in a salt do not react with water, a solution of the salt will be neutral. Which salt consists of cations and anions that do not react with water? How did you classify this salt in terms of the strength of the acid and base used to form it?
- If a salt consists of one ion that does not react with water, and another ion that does, the pH of a solution of the salt will be affected by the ion that reacts with water.
  - Which salt(s) formed acidic solutions? Which ion accounts for the acidic nature of the solution?
  - Which salt(s) formed basic solutions? Which ion accounts for the basic nature of the solution?
- Classify your unknown salt in terms of the strength of the base and the acid from which the salt was formed.

### Salts That Dissolve and Form Neutral Solutions

In the following equation,  $HA_{(aq)}$  represents a strong acid, which dissociates completely in water.



Interpreting the equation from right to left, the conjugate base of the acid,  $A^-$ , has no tendency to combine with hydronium ions in water. Therefore, it is a weak base. In fact, the anion that is formed by a strong acid is a much weaker base than water, so it does not react with water. Consequently, when a salt that contains the anion of a strong acid is dissolved in water, the anion has no effect on the pH of the solution.

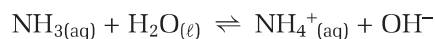
For example, the conjugate base of hydrochloric acid, HCl, is  $\text{Cl}^-$ . The chloride ion is a very weak base, so it does not react significantly with water. Therefore, the chloride ion, and the conjugate bases of other strong acids, do not affect the pH of an aqueous solution.

Similarly, the cations that form strong bases (the alkali metals and the metals below beryllium in Group 2 (IIA)) do not tend to react with hydroxide ions. These cations are weaker acids than water. Therefore, when a salt contains one of these ions (for example,  $\text{Na}^+$ ) the cation has no effect on the pH of an aqueous solution.

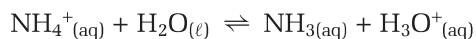
If a salt contains the cation of a strong base and the anion of a strong acid, neither ion reacts with water. Therefore, the solution has a pH of 7. Sodium chloride is an example of such a salt. It is formed by the reaction of sodium hydroxide (a strong base) and hydrochloric acid (a strong acid). *Salts of strong bases and strong acids dissolve in water and form neutral solutions.*

### Salts That Dissolve and Form Acidic Solutions

A weak base, such as aqueous ammonia, dissociates very little. Therefore, the equilibrium lies to the left.



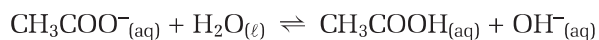
Interpreting this equation from right to left, the ammonium ion, (which is the conjugate acid of aqueous ammonia) is a relatively strong acid, compared to water. In solution, ammonium ions react with water, resulting in an acidic solution:



If a salt consists of the cation of a weak base and the anion of a strong acid, only the cation reacts with water. The solution has a pH that is less than 7. *Salts of weak bases and strong acids dissolve in water and form acidic solutions.*

### Salts That Dissolve and Form Basic Solutions

A weak acid, HA, forms a conjugate base,  $\text{A}^-$ , that is relatively strong. The reaction of such an anion with water results in a solution that is basic. For example, consider acetic acid,  $\text{CH}_3\text{COOH}_{(\text{aq})}$ , a weak acid. The conjugate base of acetic acid,  $\text{CH}_3\text{COO}^-_{(\text{aq})}$ , is relatively strong, compared to water. It reacts with water to form a basic solution.



If a salt consists of the cation of a strong base and the anion of a weak acid, such as  $\text{NaCH}_3\text{COO}$ , only the anion reacts significantly with water. The reaction produces hydroxide ions. Therefore, the solution will have a pH that is greater than 7. *Salts of strong bases and weak acids dissolve in water and form basic solutions.*

### Salts of Weak Bases and Weak Acids

If a salt consists of the cation of a weak base and the anion of a weak acid, both ions react with water. The solution is weakly acidic or weakly basic, depending on the relative strength of the ions that act as the acid or the base. You can determine which ion is stronger by comparing the values of  $K_a$  and  $K_b$  associated with the cation and the anion, respectively. *If  $K_a > K_b$ , the solution is acidic. If  $K_b > K_a$ , the solution is basic.*

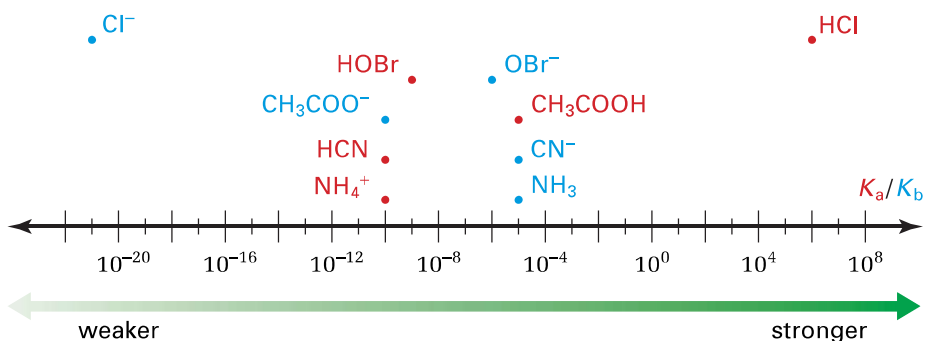


#### CHEM

#### FACT

A reaction between an ion and water is sometimes called a *hydrolysis* reaction. An ammonium ion hydrolyzes, but a sodium ion does not. An acetate ion hydrolyzes, but a chloride ion does not.

**Figure 9.2** The values of  $K_a$  and  $K_b$  are shown for acid-base conjugate pairs. A strong acid, such as  $\text{HCl}_{(\text{aq})}$ , forms a conjugate base,  $\text{Cl}^-_{(\text{aq})}$ , that is too weak to react significantly with water. A weaker acid, such as  $\text{CH}_3\text{COOH}_{(\text{aq})}$ , forms a conjugate base,  $\text{CH}_3\text{COO}^-_{(\text{aq})}$ , that is strong enough to react significantly with water.



The following list summarizes the acidic and basic properties of salts. Table 9.1 shows the acid-base properties of salts in relation to the acids and bases that react to form them.

#### Acidic and Basic Properties of Salts

- The salt of a strong acid/weak base dissolves to form an acidic solution.
- The salt of a weak acid/strong base dissolves to form a basic solution.
- The salt of a weak acid/weak base dissolves to form an acidic solution if  $K_a$  for the cation is greater than  $K_b$  for the anion. The solution is basic if  $K_b$  for the anion is greater than  $K_a$  for the cation.

**Table 9.1** The Acid-Base Properties of Various Salts

|  | Anion derived from a strong acid   | Anion derived from a weak acid   |
|--|--|--|
| <b>Cation derived from a strong base</b> | Reaction with water:<br>neither ion<br>Solution: neutral<br>Examples: $\text{NaCl}$ , $\text{K}_2\text{SO}_4$ , $\text{Ca}(\text{NO}_3)_2$             | Reaction with water:<br>only the anion<br>Solution: basic<br>Examples: $\text{NaCH}_3\text{COO}$ , $\text{KF}$ , $\text{Mg}(\text{HSO}_4)_2$   |
| <b>Cation derived from a weak base</b>   | Reaction with water:<br>only the cation<br>Solution: acidic<br>Examples: $\text{NH}_4\text{Cl}$ , $\text{NH}_4\text{NO}_3$ , $\text{NH}_4\text{ClO}_4$ | Reaction with water:<br>both ions<br>Solution: neutral if $K_a = K_b$ ,<br>acidic if $K_a > K_b$ ,<br>basic if $K_b > K_a$<br>Examples: $\text{NH}_4\text{CN}$ (basic), $(\text{NH}_4)_2\text{S}$ (basic), $\text{NH}_4\text{NO}_2$ (acidic) |

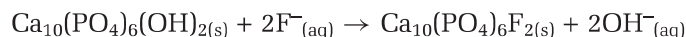
### Sodium Fluoride: A Basic Salt That Protects Teeth

Sugar is a common ingredient in prepared foods. When sugar remains on your teeth, bacteria in your mouth convert it into an acid. The principal constituent of tooth enamel is a mineral called hydroxyapatite,  $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$ . Hydroxyapatite reacts with acids to form solvated ions and water. (Solvated ions are ions surrounded by solvent particles.) Eventually, a cavity forms in the enamel.

To help prevent acid from damaging tooth enamel, many water treatment plants add small concentrations (about 1 ppm) of salts, such as  $\text{NaF}$ ,



to the water. You may notice that a fluoride salt has also been added to your toothpaste. Fluoride ions displace  $\text{OH}^-$  from hydroxyapatite to form fluoroapatite,  $\text{Ca}_{10}(\text{PO}_4)_6\text{F}_2$ , as shown in the equation below.



The fluoride ion is a much weaker base than the hydroxide ion, and fluoroapatite is therefore less reactive towards acids.

The following Sample Problem shows you how to predict the acidity or basicity of aqueous salt solutions.

### Sample Problem

#### Predicting the Acidity or Basicity of Salts

##### Problem

Predict the acid/base property of an aqueous solution of each of the following salts. If you predict that the solution is not neutral, write the equation for the reaction that causes the solution to be acidic or basic.

- (a) sodium phosphate,  $\text{Na}_3\text{PO}_4$  (commonly called trisodium phosphate, TSP, used in detergents and dishwashing compounds)
- (b) ammonium nitrate,  $\text{NH}_4\text{NO}_3$  (used as a fertilizer)
- (c) sodium chloride,  $\text{NaCl}$ , (used to de-ice winter roads)
- (d) ammonium hydrogen carbonate,  $\text{NH}_4\text{HCO}_3$  (used in baked foods as a leavening agent)

##### What Is Required?

Predict whether each aqueous solution is acidic, basic, or neutral. Write equations that represent the solutions that are acidic or basic.

##### What Is Given?

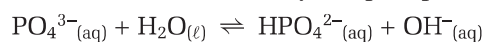
The formula of each salt is given.

##### Plan Your Strategy

Determine whether the cation is from a strong or weak base, and whether the anion is from a strong or weak acid. Ions derived from weak bases or weak acids react with water and affect the pH of the solution. If both ions react with water, compare the equilibrium constants ( $K_a$  and  $K_b$ ) to determine which reaction goes farthest to completion.

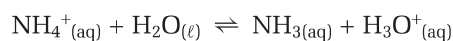
##### Act On Your Strategy

- (a) Sodium phosphate,  $\text{Na}_3\text{PO}_4$ , is the salt of a strong base ( $\text{NaOH}$ ) and a weak acid ( $\text{HPO}_4^{2-}$ ). Only the phosphate ions react with water.



The solution is basic.

- (b) Ammonium nitrate,  $\text{NH}_4\text{NO}_3$ , is the salt of a weak base ( $\text{NH}_3_{(\text{aq})}$ ) and a strong acid ( $\text{HNO}_3$ ). Only the ammonium ions react with water.



The solution is acidic.

- (c) Sodium chloride,  $\text{NaCl}$ , is the salt of a strong base ( $\text{NaOH}$ ) and a strong acid ( $\text{HCl}_{(\text{aq})}$ ). Neither ion reacts with water, so the solution is neutral.



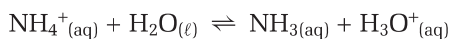
CHEM

FACT

If you cannot brush your teeth after a sweet snack, try chewing sugar-free gum. Chewing gum stimulates the production of saliva, which is usually weakly alkaline. The saliva helps to neutralize acids on your teeth. Eating cheese for dessert also helps to neutralize acid, because cheese is basic.

Continued ...

- (d) Ammonium hydrogen carbonate,  $\text{NH}_4\text{HCO}_3$ , is the salt of a weak base ( $\text{NH}_3(\text{aq})$ ) and a weak acid ( $\text{H}_2\text{CO}_3(\text{aq})$ ). Both ions react with water.



The equilibrium that lies farther to the right has the greater influence on the pH of the solution. The equilibrium constants you need are  $K_a$  for  $\text{NH}_4^+$  and  $K_b$  for  $\text{HCO}_3^-$ . Each ion is the conjugate of a compound for which the appropriate constant is given in tables.

From Appendix E,  $K_b$  for  $\text{NH}_3(\text{aq})$  is  $1.8 \times 10^{-5}$ . Using  $K_a K_b = K_w$ ,

$$\begin{aligned} K_a \text{ for } \text{NH}_4^+ &= \frac{1.0 \times 10^{-14}}{1.8 \times 10^{-5}} \\ &= 5.6 \times 10^{-10} \end{aligned}$$

Similarly, from Appendix E,  $K_a$  for  $\text{H}_2\text{CO}_3 = 4.5 \times 10^{-7}$ .

$$\begin{aligned} K_b \text{ for } \text{HCO}_3^- &= \frac{1.0 \times 10^{-14}}{4.5 \times 10^{-7}} \\ &= 2.2 \times 10^{-8} \end{aligned}$$

Because  $K_b$  for the hydrogen carbonate reaction is larger than  $K_a$  for the ammonium ion reaction, the solution is basic.

### Check Your Solution

The equations that represent the reactions with water support the prediction that  $\text{NH}_4\text{NO}_3$  dissolves to form an acidic solution and  $\text{Na}_3\text{PO}_4$  dissolves to form a basic solution. Calcium chloride is the salt of a strong base-strong acid, so neither ion reacts with water and the solution is neutral. Both ions in ammonium hydrogen carbonate react with water. Because  $K_b$  for  $\text{HCO}_3^-$  is greater than  $K_a$  for  $\text{NH}_4^+$ , the salt dissolves to form a weakly basic solution.

### Practice Problems

- Predict whether an aqueous solution of each salt is neutral, acidic, or basic.
 

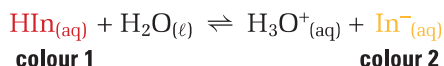
|          |                                |
|----------|--------------------------------|
| (a) NaCN | (c) $\text{Mg}(\text{NO}_3)_2$ |
| (b) LiF  | (d) $\text{NH}_4\text{I}$      |
- Is the solution of each salt acidic, basic, or neutral? For solutions that are not neutral, write equations that support your predictions.
 

|                               |                            |
|-------------------------------|----------------------------|
| (a) $\text{NH}_4\text{BrO}_4$ | (c) NaOBr                  |
| (b) $\text{NaBrO}_4$          | (d) $\text{NH}_4\text{Br}$ |
- $K_a$  for benzoic acid,  $\text{C}_6\text{H}_5\text{COOH}$ , is  $6.3 \times 10^{-5}$ .  $K_a$  for phenol,  $\text{C}_6\text{H}_5\text{OH}$ , is  $1.3 \times 10^{-10}$ . Which is the stronger base,  $\text{C}_6\text{H}_5\text{COO}^-(\text{aq})$  or  $\text{C}_6\text{H}_5\text{O}^-(\text{aq})$ ? Explain your answer.
- Sodium hydrogen sulfite,  $\text{NaHSO}_3$ , is a preservative that is used to prevent the discolouration of dried fruit. In aqueous solution, the hydrogen sulfite ion can act as either an acid or a base. Predict whether  $\text{NaHSO}_3$  dissolves to form an acidic solution or a basic solution. (Refer to Appendix E for ionization data.)

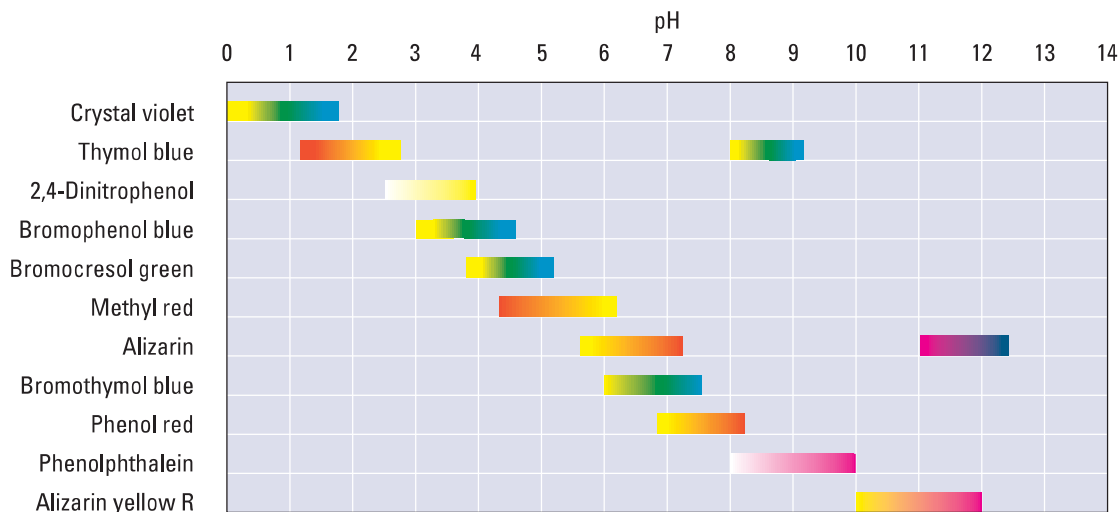
## Calculating pH at Equivalence

In an acid-base titration, you carefully measure the volumes of acid and base that react. Then, knowing the concentration of either the acid or the base, and the stoichiometric relationship between them, you calculate the concentration of the other reactant. The **equivalence point** in the titration occurs when just enough acid and base have been mixed for a complete reaction to occur, with no excess of either reactant. As you learned in Chapter 8, you can find the equivalence point from a graph that shows pH versus volume of one solution added to the other solution. To determine the equivalence point experimentally, you need to measure the pH. Because pH meters are expensive, and the glass electrodes are fragile, titrations are often performed using an acid-base indicator.

An acid-base indicator is usually a weak, monoprotic organic acid. The indicator is in equilibrium between the undissociated acid, which is one colour, and its conjugate base, which is a different colour.



For example, one indicator, called methyl red, is red when the pH is below 4.2, and yellow when the pH is above 6.2. The point in a titration at which an indicator changes colour is called the **end-point**. The colour change occurs over a range of about 2 pH units, but the pH of a solution changes rapidly near the equivalence point. Often a single drop of base causes the shift from colour 1 to colour 2. For methyl red, the end-point occurs over the pH range 4.2 to 6.2. Therefore, this indicator is used when an acid-base titration results in a moderately acidic solution at equivalence. Figure 9.3 shows the colours and end-points of various indicators.



**Figure 9.3** A range of indicators are available with different end-points are available. Thymol blue and alizarin are *diprotic*. They change colour over two different ranges.

To choose the appropriate indicator for a particular titration, you must know the approximate pH of the solution at equivalence. As you learned in Chapter 8, an acid-base titration curve provides this information. What if you do not have a titration curve? You can calculate the pH at equivalence using what you know about salts.



For example, suppose that you are titrating a strong acid solution against a weak base. At the equivalence point, the flask contains an aqueous solution of the salt that is formed by the reaction. The solution of a salt of a weak base and a strong acid is acidic, so methyl red may be an appropriate indicator. The pH at equivalence in a titration is the same as the pH of an aqueous solution of the salt formed.

### Sample Problem

#### Calculating pH at Equivalence

##### Problem

$2.0 \times 10^1$  mL of 0.20 mol/L  $\text{NH}_{3(\text{aq})}$  is titrated against 0.20 mol/L  $\text{HCl}_{(\text{aq})}$ . Calculate the pH at equivalence. Use Figure 9.3 to select an appropriate indicator.

##### What Is Required?

You need to calculate the pH at equivalence. As well, you need to find an indicator that changes colour at a pH that is close to the same pH at equivalence.

##### What Is Given?

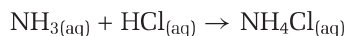
You know that 20 mL of 0.20 mol/L  $\text{NH}_{3(\text{aq})}$  base reacts with 0.20 mol/L  $\text{HCl}_{(\text{aq})}$ . Tables of  $K_a$  and  $K_b$  values are in Appendix E. Figure 9.3 shows the pH ranges and colour changes for various indicators.

##### Plan Your Strategy

- Step 1** Write the balanced chemical equation for the reaction
- Step 2** Calculate the amount (in mol) of  $\text{NH}_{3(\text{aq})}$ , using its volume and concentration. Then, determine the amount (in mol) of  $\text{HCl}_{(\text{aq})}$  that is needed to react with all the  $\text{NH}_{3(\text{aq})}$ .
- Step 3** Find the volume of  $\text{HCl}_{(\text{aq})}$ , based on the amount and concentration of  $\text{HCl}_{(\text{aq})}$ .
- Step 4** Calculate the concentration of the salt formed, based on the amount (in mol) and the total volume of the solution. Decide which ion reacts with water. Write the equation that represents the reaction.
- Step 5** Determine the equilibrium constant for the ion that is involved in the reaction. Then divide the  $[\text{NH}_4^+]$  by  $K_a$  to determine whether the change in concentration of the ammonium ion can be ignored.
- Step 6** Set up an ICE table for the ion that is involved in the reaction with water. Let  $x$  represent the change in the concentration of the ion that reacts.
- Step 7** Write the equilibrium expression. Substitute the equilibrium concentrations into the expression, and solve for  $x$ .
- Step 8** Use the value of  $x$  to determine the  $[\text{H}_3\text{O}^+]$ . Then calculate the pH of the solution. Using Figure 9.3, choose an indicator that changes colour in a range that includes the pH of the solution.

### Act on Your Strategy

**Step 1** The following chemical equation represents the reaction.



**Step 2** Amount (in mol) of  $\text{NH}_3(\text{aq}) = 0.20 \text{ mol/L} \times 0.020 \text{ L}$   
 $= 4.0 \times 10^{-3} \text{ mol}$

$\text{NH}_3(\text{aq})$  and  $\text{HCl}(\text{aq})$  react in a 1:1 ratio. Therefore,  $4.0 \times 10^{-3} \text{ mol}$  of  $\text{HCl}(\text{aq})$  is needed.

**Step 3** Amount (in mol)  $\text{HCl}(\text{aq}) = 4.0 \times 10^{-3} \text{ mol}$   
 $= 0.20 \text{ mol/L} \times \text{Volume HCl}(\text{aq}) \text{ (in L)}$

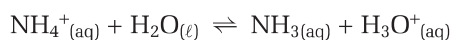
$$\text{Volume HCl}(\text{aq}) = \frac{4.0 \times 10^{-3} \text{ mol}}{0.20 \text{ mol/L}} \\ = 0.020 \text{ L}$$

**Step 4** From the chemical equation, the amount of  $\text{NH}_4\text{Cl}$  that is formed is equal to the amount of acid or base that reacts. Therefore,  $4.0 \times 10^{-3} \text{ mol}$  of ammonium chloride is formed.

$$\text{Total volume of solution} = 0.020 \text{ L} + 0.020 \text{ L} \\ = 0.040 \text{ L}$$

$$[\text{NH}_4\text{Cl}] = \frac{4.0 \times 10^{-3} \text{ mol}}{4.0 \times 10^{-2} \text{ L}} \\ = 0.10 \text{ mol/L}$$

The salt forms  $\text{NH}_4^+(\text{aq})$  and  $\text{Cl}^-(\text{aq})$  in solution.  $\text{NH}_4^+(\text{aq})$  is the conjugate acid of a weak base, so it reacts with water.  $\text{Cl}^-(\text{aq})$  is the conjugate base of a strong acid, so it does not react with water. The pH of the solution is therefore determined by the extent of the following reaction.



**Step 5** From Appendix E,  $K_b$  for  $\text{NH}_3(\text{aq})$  is  $1.8 \times 10^{-5}$ .

$K_a$  for the conjugate acid,  $\text{NH}_4^+(\text{aq})$ , can be calculated using the relationship  $K_a K_b = K_w$ .

$$K_a = \frac{K_w}{K_b} = \frac{1.0 \times 10^{-14}}{1.8 \times 10^{-5}} \\ = 5.6 \times 10^{-10}$$

$$\frac{[\text{NH}_4^+]}{K_a} = \frac{0.10}{5.6 \times 10^{-10}} \\ = 1.8 \times 10^8$$

This is well above 500, so the change in  $[\text{NH}_4^+]$ ,  $x$ , can be ignored.

**Step 6**

| Concentration (mol/L) | $\text{NH}_4^+(\text{aq})$ | + | $\text{H}_2\text{O}(\ell)$ | $\rightleftharpoons$ | $\text{NH}_3(\text{aq})$ | + | $\text{H}_3\text{O}^+(\text{aq})$ |
|-----------------------|----------------------------|---|----------------------------|----------------------|--------------------------|---|-----------------------------------|
| Initial               | 0.10                       |   | —                          |                      | 0                        |   | ~0                                |
| Change                | $-x$                       |   | —                          |                      | $+x$                     |   | $+x$                              |
| Equilibrium           | $0.10-x$<br>(~0.10)        |   | —                          |                      | $x$                      |   | $x$                               |

Continued ...

**Step 7** 
$$K_a = \frac{[\text{NH}_3][\text{H}_3\text{O}^+]}{[\text{NH}_4^+]}$$

$$5.6 \times 10^{-10} = \frac{(x)(x)}{0.10}$$

$$x = \sqrt{5.6 \times 10^{-11}} \quad (\text{only the positive value makes sense})$$

$$= \pm 7.5 \times 10^{-6} \text{ mol/L}$$

**Step 8**  $x = [\text{H}_3\text{O}^+]$

$$= 7.5 \times 10^{-6} \text{ mol/L}$$

$$\text{pH} = -\log[\text{H}_3\text{O}^+]$$

$$= -\log 7.5 \times 10^{-6}$$

$$= 5.13$$

Methyl red, which changes colour over pH 4.2 to 6.2, is a good choice for an indicator. If methyl red was not available, bromocresol green, which changes colour in the pH range 3.8–5.2, could be used.

### Check Your Solution

The titration forms an aqueous solution of a salt derived from a weak base and a strong acid. The solution should be acidic, which is supported by the calculation of the pH.

### PROBLEM TIP

When you are determining the concentration of ions in solution, remember to use the final volume of the solution. In Practice Problem 6, for example, the final volume of the solution is 50 mL because 20 mL of base is added to 30 mL of acid. You can assume that the total volume is the sum of the reactant volumes, because the reactant solutions are dilute.

### Practice Problems

- After titrating sodium hydroxide with hydrofluoric acid, a chemist determined that the reaction had formed an aqueous solution of 0.020 mol/L sodium fluoride. Determine the pH of the solution.
- Part way through a titration,  $2.0 \times 10^1$  mL of 0.10 mol/L sodium hydroxide has been added to  $3.0 \times 10^1$  mL of 0.10 mol/L hydrochloric acid. What is the pH of the solution?
- 0.025 mol/L benzoic acid,  $\text{C}_6\text{H}_5\text{COOH}$ , is titrated with 0.025 mol/L sodium hydroxide solution. Calculate the pH at equivalence.
- 50.0 mL of 0.10 mol/L hydrobromic acid is titrated with 0.10 mol/L aqueous ammonia. Determine the pH at equivalence.

### Section Summary

In this section, you learned why solutions of different salts have different pH values. You learned how to analyze the composition of a salt to predict whether the salt forms an acidic, basic, or neutral solution. Finally, you learned how to apply your understanding of the properties of salts to calculate the pH at the equivalence point of a titration. You used the pH to determine a suitable indicator for the titration. In section 9.2, you will further investigate the equilibria of solutions and learn how to predict the solubility of ionic compounds in solution.

## Section Review

- K/U** Sodium carbonate and sodium hydrogen carbonate both dissolve to form basic solutions. Comparing solutions with the same concentration, which of these salts forms the more basic solution? Explain.
- K/U** Determine whether or not each ion reacts with water. If the ion does react, write the chemical equation for the reaction. Then predict whether the ion forms an acidic solution or a basic solution.  
(a)  $\text{Br}^-$       (b)  $\text{CH}_3\text{NH}_3^+$       (c)  $\text{ClO}_4^-$       (d)  $\text{OCl}^-$
- K/U** Predict whether sodium dihydrogen citrate,  $\text{NaH}_2\text{C}_6\text{H}_5\text{O}_7$ , dissolves to form an acidic or a basic solution. (Refer to Appendix E)
- I** A chemist measures the pH of aqueous solutions of  $\text{Ca}(\text{OH})_2$ ,  $\text{CaF}_2$ ,  $\text{NH}_4\text{NO}_3$ ,  $\text{KNO}_3$ , and  $\text{HNO}_3$ . Each solution has the same concentration. Arrange the solutions from most basic to most acidic.
- I** A student uses a transfer pipette to put 25.00 mL of 0.100 mol/L acetic acid into an Erlenmeyer flask. Then the student adds sodium hydroxide from a burette to the flask, and records the following readings of volume and pH.

| volume (mL) | 0.00 | 6.00 | 10.00 | 12.00 | 14.00 | 14.40 | 14.60 | 14.80 | 15.20 | 15.40 | 16.00 |
|-------------|------|------|-------|-------|-------|-------|-------|-------|-------|-------|-------|
| pH          | 2.8  | 4.2  | 5.1   | 5.5   | 6.2   | 6.5   | 6.8   | 7.6   | 9.8   | 10.5  | 11.4  |

- Draw a graph that shows the results. Plot pH on the vertical axis and the volume of base added on the horizontal axis. Use spreadsheet software if available.
  - From your graph, what is the pH at the equivalence point?
  - Determine the initial concentration of the sodium hydroxide.
  - Use Figure 9.3 to suggest a suitable indicator for this titration.
- C** Congo red is an indicator that changes colour in the pH range 3.0 to 5.0. Suppose that you are titrating an aqueous sodium hydroxide solution with nitric acid added from a burette. Is congo red a suitable indicator? If so, explain why. If not, will the end-point occur before or after the equivalence point? Explain your answer.
  - K/U** If you were titrating a strong base with a weak acid, which of these indicators might be suitable: bromphenol blue, bromthymol blue, or phenolphthalein? (Refer to Figure 9.3.)
  - I** 0.10 mol/L hydrochloric acid is titrated with 0.10 mol/L methylamine,  $\text{CH}_3\text{NH}_2$ . Calculate the pH at the equivalence point.
  - MC** Sodium phosphate,  $\text{Na}_3\text{PO}_4$ , is sold at hardware stores as TSP (trisodium phosphate). Crystals of  $\text{Na}_3\text{PO}_4$  are dissolved in water to make an effective cleaning solution. TSP can be used, for example, to prepare a surface before painting.  
    - Explain why TSP is an effective cleaning solution.
    - Suggest safety precautions you should take when using TSP.
    - Explain why you should never mix a solution of TSP with other household cleaning products.

## 9.2

## Solubility Equilibria

Section Preview/  
Specific Expectations

In this section, you will

- **perform** an experiment to determine the solubility product constant ( $K_{sp}$ ) for calcium hydroxide
- **solve** equilibrium problems that involve concentrations of reactants and products, and  $K_{sp}$
- **calculate** the molar solubility of a pure substance in water or in a solution of a common ion, given  $K_{sp}$
- **communicate** your understanding of the following term: *solubility product constant* ( $K_{sp}$ )



**Figure 9.4** Barium sulfate,  $\text{BaSO}_4$ , is a sparingly soluble ionic compound that is used to enhance X-ray imaging.

In Chapter 7, you learned that a saturated solution containing undissolved solute is an example of a system at equilibrium. Recall from your previous chemistry course that the solubility of a solute is the amount of solute that will dissolve in a given volume of solvent at a certain temperature. In other words, the solubility of a solute indicates how much of that solute is present in a solution at equilibrium. Data tables often express solubility as (g solute)/(100 mL solvent). Molar solubility, on the other hand, is always expressed in terms of (mol solute/L solvent).

The solubility of ionic solids in water covers a wide range of values. Knowing the concentration of ions in aqueous solution is important in medicine and in chemical analysis. In this section, you will continue to study equilibrium. You will examine the solubility equilibria of ionic compounds in water.

## Solubility as an Equilibrium Process

In Chapter 7, you learned that three factors—change in enthalpy ( $\Delta H$ ), change in entropy ( $\Delta S$ ), and temperature ( $T$ )—determine whether or not a change is favoured. The same three factors are important for determining how much of a salt will dissolve in a certain volume of water. These factors are combined in the following equation, where  $\Delta G$  is the change in free energy of the system.

$$\Delta G = \Delta H - T\Delta S$$

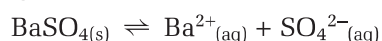
As you know from Chapter 7, a change is favoured when  $\Delta G$  is negative. When a salt dissolves, the entropy of the system always increases, because ions in solution are more disordered than ions in a solid crystal. An increase in entropy favours the formation of a solution because the term  $-T\Delta S$  is negative. Most solids dissolve to a greater extent at higher solution temperatures, because the term  $-T\Delta S$  becomes more negative.

Explaining the overall enthalpy change for a dissolving salt is more complicated because it involves a number of energy changes. Cations must be separated from anions, which requires energy. Water molecules then surround each ion in solution, which releases energy. If the overall enthalpy change is negative, the formation of a solution is favoured. If the enthalpy increases, the formation of a solution is not favoured because  $\Delta G$  is less negative.

## Heterogeneous Equilibrium: A Solubility System

Consider barium sulfate, a sparingly soluble salt. X-ray technicians give patients a barium sulfate suspension to drink before taking an X-ray of the large intestine. A suspension of barium sulfate is opaque to X-rays, which helps to define this part of the body. (See Figure 9.4.)

When you add barium sulfate crystals to water, barium ions and sulfate ions leave the surface of the solid and enter the solution. Initially, the concentration of these ions is very low. Thus, the forward change, dissolving, occurs at a greater rate than the reverse change:



As more ions enter the solution, the rate of the reverse change, recrystallisation, increases. Eventually, the rate of recrystallisation becomes equal to the rate of dissolving. As you know, when the forward rate and the backward rate of a process are equal, the system is at equilibrium. Because the reactants and the products are in different phases, the reaction is said to have reached heterogeneous equilibrium. For solubility systems of sparingly soluble ionic compounds, *equilibrium exists between the solid ionic compound and its dissociated ions in solution.*

## The Solubility Product Constant

When excess solid is present in a saturated solution, you can write the equilibrium constant expression for the dissolution of the solid in the same way that you wrote the equilibrium constant expression for a homogeneous equilibrium in Chapter 7. For example, the equilibrium constant expression for barium sulfate is written as follows:

$$K = \frac{[\text{Ba}^{2+}_{(\text{aq})}][\text{SO}_4^{2-}_{(\text{aq})}]}{[\text{BaSO}_{4(\text{s})}]}$$

The concentration of a solid, however, is itself a constant at a constant temperature. Therefore, you can combine the term for the concentration of the solid with the equilibrium constant to arrive at a new constant:

$$K[\text{BaSO}_{4(\text{s})}] = [\text{Ba}^{2+}_{(\text{aq})}][\text{SO}_4^{2-}_{(\text{aq})}]$$

$$K_{\text{sp}} = [\text{Ba}^{2+}_{(\text{aq})}][\text{SO}_4^{2-}_{(\text{aq})}]$$

The new constant is called the **solubility product constant,  $K_{\text{sp}}$** . The following Sample Problem shows how to write expressions for  $K_{\text{sp}}$ .

### Sample Problem

#### Writing Solubility Product Expressions

##### Problem

Write the solubility product expression for each compound.

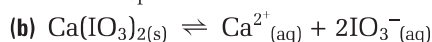
- (a) barium carbonate                      (b) calcium iodate  
(c) copper(II) phosphate

##### Solution

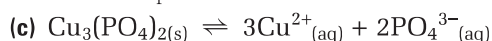
First write a balanced equation for the equilibrium between excess solid and dissolved ions in a saturated aqueous solution. Then use the balanced equation to write the expression for  $K_{\text{sp}}$ .



$$K_{\text{sp}} = [\text{Ba}^{2+}][\text{CO}_3^{2-}]$$



$$K_{\text{sp}} = [\text{Ca}^{2+}][\text{IO}_3^{-}]^2$$



$$K_{\text{sp}} = [\text{Cu}^{2+}]^3[\text{PO}_4^{3-}]^2$$

##### Check Your Solution

The  $K_{\text{sp}}$  expressions are based on balanced equations for saturated solutions of slightly soluble ionic compounds. The exponents in the  $K_{\text{sp}}$  expressions match the corresponding coefficients in the chemical equation. The coefficient 1 is not written, following chemical convention.

#### PROBLEM TIP

Ion concentration terms in solubility product expressions are usually written without their phases, as you see here.



## Practice Problems

9. Write the balanced chemical equation that represents the dissociation of each compound in water. Then write the corresponding solubility product expression.
  - (a) copper(I) chloride
  - (b) barium fluoride
  - (c) silver sulfate
  - (d) calcium phosphate
10. Write a balanced dissolution equation and solubility product expression for silver carbonate,  $\text{Ag}_2\text{CO}_3$ .
11. Write a balanced dissolution equation and solubility product expression for magnesium ammonium phosphate,  $\text{MgNH}_4\text{PO}_4$ .
12. Iron(III) nitrate has a very low solubility.
  - (a) Write the solubility product expression for iron(III) nitrate.
  - (b) Do you expect the value of  $K_{\text{sp}}$  of iron(III) nitrate to be larger or smaller than the  $K_{\text{sp}}$  for aluminum hydroxide, which has a slightly higher solubility?



### CHEM

#### FACT

One compound that becomes *less* soluble at higher temperatures is calcium carbonate,  $\text{CaCO}_3$ . If you have an electric kettle, you have probably noticed a build-up of scale on the heating element. The scale is mostly calcium carbonate, which precipitates out of the water as it heats up.

You know intuitively that solubility depends on temperature. For most ionic compounds, more solute can dissolve in a solvent at higher temperatures. Chemists determine the solubility of an ionic compound by experiment, and then use the solubility data to determine  $K_{\text{sp}}$ . Like the equilibrium constant,  $K_{\text{sp}}$  is temperature-dependent. Therefore, different experiments must be carried out to determine  $K_{\text{sp}}$  at different temperatures.

Chemical reference books list the solubility of a wide variety of compounds. In the next Sample Problem, you will learn how to use measured solubilities to determine  $K_{\text{sp}}$ .

## Sample Problem

### Determining $K_{\text{sp}}$ from Measured Solubilities

#### Problem

A chemist finds that the solubility of silver carbonate,  $\text{Ag}_2\text{CO}_3$ , is  $1.3 \times 10^{-4}$  mol/L at  $25^\circ\text{C}$ . Calculate  $K_{\text{sp}}$  for silver carbonate.

#### What Is Required?

You need to find the value of  $K_{\text{sp}}$  for  $\text{Ag}_2\text{CO}_3$  at  $25^\circ\text{C}$ .

#### What Is Given?

You know the solubility of  $\text{Ag}_2\text{CO}_3$  at  $25^\circ\text{C}$ .

#### Plan Your Strategy

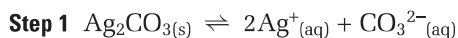
**Step 1** Write an equation for the dissolution of  $\text{Ag}_2\text{CO}_3$ .

**Step 2** Use the equation to write the solubility product expression.

**Step 3** Find the concentration (in mol/L) of each ion.

**Step 4** Substitute the concentrations into the solubility product expression, and calculate  $K_{\text{sp}}$ .

### Act on Your Strategy



**Step 2**  $K_{sp} = [\text{Ag}^+]^2[\text{CO}_3^{2-}]$

**Step 3**  $[\text{Ag}^+] = 2 \times [\text{Ag}_2\text{CO}_3]$   
 $= 2 \times 1.3 \times 10^{-4} \text{ mol/L}$   
 $= 2.6 \times 10^{-4} \text{ mol/L}$   
 $[\text{CO}_3^{2-}] = [\text{Ag}_2\text{CO}_3] = 3.2 \times 10^{-2} \text{ mol/L}$

**Step 4**  $K_{sp} = [\text{Ag}^+]^2[\text{CO}_3^{2-}]$   
 $= (2.6 \times 10^{-4})^2(1.3 \times 10^{-4})$   
 $= 8.8 \times 10^{-12}$

Based on the given solubility data,  $K_{sp}$  for silver carbonate is  $8.8 \times 10^{-12}$  at  $25^\circ\text{C}$ .

### Check Your Solution

The value of  $K_{sp}$  is less than the concentration of the salt, as expected. It has the correct number of significant digits.

Check that you wrote the balanced chemical equation and the corresponding  $K_{sp}$  equation correctly. Pay attention to molar relationships and to the exponent of each term in the  $K_{sp}$  equation.

## Practice Problems

13. The maximum solubility of silver cyanide,  $\text{AgCN}$ , is  $1.5 \times 10^{-8} \text{ mol/L}$  at  $25^\circ\text{C}$ . Calculate  $K_{sp}$  for silver cyanide.
14. A saturated solution of copper(II) phosphate,  $\text{Cu}_3(\text{PO}_4)_2$ , has a concentration of  $6.1 \times 10^{-7} \text{ g Cu}_3(\text{PO}_4)_2$  per  $1.00 \times 10^2 \text{ mL}$  of solution at  $25^\circ\text{C}$ . What is  $K_{sp}$  for  $\text{Cu}_3(\text{PO}_4)_2$  at  $25^\circ\text{C}$ ?
15. A saturated solution of  $\text{CaF}_2$  contains  $1.2 \times 10^{20}$  formula units of calcium fluoride per litre of solution. Calculate  $K_{sp}$  for  $\text{CaF}_2$ .
16. The concentration of mercury(I) iodide,  $\text{Hg}_2\text{I}_2$ , in a saturated solution at  $25^\circ\text{C}$  is  $1.5 \times 10^{-4} \text{ ppm}$ .
  - (a) Calculate  $K_{sp}$  for  $\text{Hg}_2\text{I}_2$ . The solubility equilibrium is written as follows:  
 $\text{Hg}_2\text{I}_2 \rightleftharpoons \text{Hg}_2^{2+} + 2\text{I}^-$
  - (b) State any assumptions that you made when you converted ppm to mol/L.

## Determining a Solubility Product Constant

In Investigation 9-A, you will collect solubility data and use these data to determine a  $K_{sp}$  for calcium hydroxide,  $\text{Ca}(\text{OH})_2$ . When you calculate  $K_{sp}$ , you assume that the dissolved ionic compound exists as independent hydrated ions that do not affect one another. This assumption simplifies the investigation, but it is not entirely accurate. Ions *do* interfere with one another. As a result, the value of  $K_{sp}$  that you calculate will be just an approximation.  $K_{sp}$  values that are calculated from data obtained from experiments such as Investigation 9-A are generally higher than the actual values.



## Determining $K_{sp}$ for Calcium Hydroxide

The value of  $K_{sp}$  for a basic compound, such as  $\text{Ca}(\text{OH})_2$ , can be determined by performing an acid-base titration.

### Question

What is the value of  $K_{sp}$  for  $\text{Ca}(\text{OH})_2$ ?

### Predictions

Look up the solubility of  $\text{Ca}(\text{OH})_2$  in a solubility table. Do you expect a large or a small value of  $K_{sp}$  for  $\text{Ca}(\text{OH})_2$ ?

### Materials

50 mL beaker  
white sheet of paper  
2 identical microscale pipettes  
wash bottle that contains distilled water  
phenolphthalein in dropping bottle  
glass stirring rod  
Petri dish or watch glass  
10 mL of recently filtered saturated solution of  $\text{Ca}(\text{OH})_2$   
10 mL of 0.050 mol/L HCl

### Safety Precautions



If you get acid or base on your skin, flush with plenty of cold water.

### Procedure

1. Read the Procedure, and prepare an appropriate data table. Remember to give your table a title.
2. Add exactly 10 drops of 0.050 mol/L HCl to a 50 mL beaker. To ensure uniform drop size, use the same type of pipette to dispense the acid and the base. Also, hold the pipette vertically when dispensing the solution. Always record the number of drops added.
3. Place the beaker on the white sheet of paper.
4. To transfer a small amount of indicator to the acid solution, place one drop of phenolphthalein solution on a watch glass. Touch the drop with the glass rod. Transfer this small amount of indicator to the HCl in the beaker.
5. Add saturated  $\text{Ca}(\text{OH})_2$  solution, drop by drop, to the HCl solution until the solution turns a permanent pale pink. Swirl the flask, particularly as the pink begins to appear. Record the number of drops of  $\text{Ca}(\text{OH})_2$  that you added. Conduct as many trials as you can.
6. Dispose of all solutions as directed by your teacher. Do not dispose of any chemicals down the drain.

### Analysis

1. Determine the average number of drops of  $\text{Ca}(\text{OH})_2$  solution that you needed to neutralize 10 drops of 0.050 mol/L HCl.
2. Write the balanced chemical equation for the dissociation of calcium hydroxide in water.
3. Write the balanced chemical equation that represents the neutralization of aqueous  $\text{Ca}(\text{OH})_2$  with  $\text{HCl}_{(aq)}$ .
4. Use the balanced chemical equation for the neutralization of HCl with  $\text{Ca}(\text{OH})_2$  to determine  $[\text{OH}^-]$  in mol/L. **Hint:** Why do you *not* need to know the volume of one drop?
5. From  $[\text{OH}^-]$ , determine  $[\text{Ca}^{2+}]$  in mol/L.

### Conclusion

6. Calculate  $K_{sp}$  for  $\text{Ca}(\text{OH})_2$ . If possible, look up the accepted value of  $K_{sp}$  for  $\text{Ca}(\text{OH})_2$ . Calculate your percent error.

## Using the Solubility Product Constant

You can use the value of  $K_{sp}$  for a compound to determine the concentration of its ions in a saturated solution. The following Sample Problem shows you how to do this. You will use an approach that is similar to the approach you used in section 7.2 to find equilibrium amounts using  $K_c$  for homogeneous equilibria.

Table 9.2 shows the values of  $K_{sp}$  for selected ionic compounds at 25°C. The compounds are organized from the largest  $K_{sp}$  to the smallest. You will find a more comprehensive table of  $K_{sp}$  values in Appendix E.

**Table 9.2** Values of  $K_{sp}$  for Some Ionic Compounds at 25°C

| Compound                                       | $K_{sp}$              |
|--|-----------------------|
| magnesium sulfate, $\text{MgSO}_4$             | $5.9 \times 10^{-3}$  |
| lead(II) chloride, $\text{PbCl}_2$             | $1.7 \times 10^{-5}$  |
| barium fluoride, $\text{BaF}_2$                | $1.5 \times 10^{-6}$  |
| cadmium carbonate, $\text{CdCO}_3$             | $1.8 \times 10^{-14}$ |
| copper(II) hydroxide, $\text{Cu}(\text{OH})_2$ | $2.2 \times 10^{-20}$ |
| silver sulfide, $\text{Ag}_2\text{S}$          | $8 \times 10^{-48}$   |

## CONCEPT CHECK

Suppose that two different salts,  $\text{AX}$  and  $\text{BY}_2$ , have the same  $K_{sp}$ . Are the salts equally soluble at the same temperature? Explain your answer.

### Sample Problem

#### Calculating Molar Solubility From $K_{sp}$

##### Problem

Lead(II) iodide,  $\text{PbI}_2$ , films are being investigated for their usefulness in X-ray imaging.  $\text{PbI}_2$  is also used for decorative work, such as mosaics, because of its attractive golden yellow colour. At 25°C,  $K_{sp}$  for  $\text{PbI}_2$  is  $9.8 \times 10^{-9}$ . What is the molar solubility of  $\text{PbI}_2$  in water at 25°C?

##### What Is Required?

You need to determine the solubility (in mol/L) of  $\text{PbI}_2$  at 25°C.

##### What Is Given?

At 25°C,  $K_{sp}$  for  $\text{PbI}_2$  is  $9.8 \times 10^{-9}$ .

##### Plan Your Strategy

**Step 1** Write the dissociation equilibrium equation.

**Step 2** Use the equilibrium equation to write an expression for  $K_{sp}$ .

**Step 3** Set up an ICE table. Let  $x$  represent molar solubility. Use the stoichiometry of the equilibrium equation to write expressions for the equilibrium concentrations of the ions.

**Step 4** Substitute your expressions into the expression for  $K_{sp}$ , and solve for  $x$ .

##### Act on Your Strategy

**Step 1**  $\text{PbI}_{2(s)} \rightleftharpoons \text{Pb}^{2+}_{(aq)} + 2\text{I}^{-}_{(aq)}$

**Step 2**  $K_{sp} = [\text{Pb}^{2+}][\text{I}^{-}]^2$

Continued ...

**Step 3**

| Concentration (mol/L) | $\text{PbI}_{2(s)}$ | $\rightleftharpoons$ | $\text{Pb}^{2+}_{(aq)}$ | + | $2\text{I}^{-}_{(aq)}$ |
|-----------------------|---------------------|----------------------|-------------------------|---|------------------------|
| Initial               | —                   |                      | 0                       |   | 0                      |
| Change                | —                   |                      | +x                      |   | +2x                    |
| Equilibrium           | —                   |                      | x                       |   | 2x                     |

**Step 4**  $K_{sp} = [\text{Pb}^{2+}][\text{I}^{-}]^2 = 9.8 \times 10^{-9}$

$$= x \times (2x)^2$$

$$= x \times 4x^2$$

$$= 4x^3$$

$$\therefore 4x^3 = 9.8 \times 10^{-9}$$

$$x = \sqrt[3]{\frac{9.8 \times 10^{-9}}{4}}$$

$$= 1.3 \times 10^{-3} \text{ mol/L}$$

The molar solubility of  $\text{PbI}_2$  in water is  $1.3 \times 10^{-3} \text{ mol/L}$ .

**Check Your Solution**

Recall that  $x = [\text{Pb}^{2+}]_{\text{eq}}$  and  $2x = [\text{I}^{-}]_{\text{eq}}$ . Substitute these values into the  $K_{sp}$  equation. You should get the given  $K_{sp}$ .

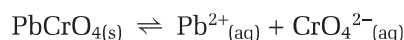
**Practice Problems**

- $K_{sp}$  for silver chloride,  $\text{AgCl}$ , is  $1.8 \times 10^{-10}$  at  $25^\circ\text{C}$ .
  - Calculate the molar solubility of  $\text{AgCl}$  in a saturated solution at  $25^\circ\text{C}$ .
  - How many formula units of  $\text{AgCl}$  are dissolved in 1.0 L of saturated silver chloride solution?
  - What is the percent (m/v) of  $\text{AgCl}$  in a saturated solution at  $25^\circ\text{C}$ ?
- Iron(III) hydroxide,  $\text{Fe}(\text{OH})_3$ , is an extremely insoluble compound.  $K_{sp}$  for  $\text{Fe}(\text{OH})_3$  is  $2.8 \times 10^{-39}$  at  $25^\circ\text{C}$ . Calculate the molar solubility of  $\text{Fe}(\text{OH})_3$  at  $25^\circ\text{C}$ .
- $K_{sp}$  for zinc iodate,  $\text{Zn}(\text{IO}_3)_2$ , is  $3.9 \times 10^{-6}$  at  $25^\circ\text{C}$ . Calculate the solubility (in mol/L and in g/L) of  $\text{Zn}(\text{IO}_3)_2$  in a saturated solution.
- What is the maximum number of formula units of zinc sulfide,  $\text{ZnS}$ , that can dissolve in 1.0 L of solution at  $25^\circ\text{C}$ ?  $K_{sp}$  for  $\text{ZnS}$  is  $2.0 \times 10^{-22}$ .

**The Common Ion Effect**

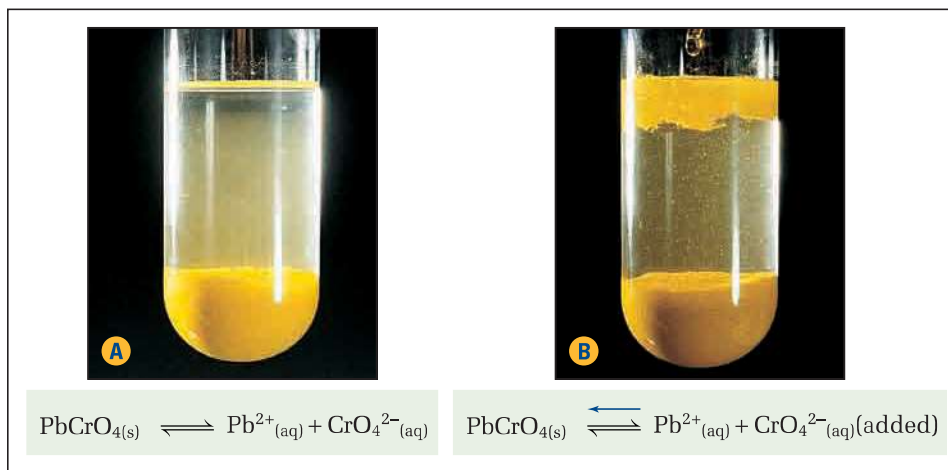
So far, you have considered solubility equilibria for pure substances dissolved in water. What happens to the solubility of an ionic compound when it is added to a solution that already contains one of its ions?

Consider a saturated solution of lead(II) chromate. See Figure 9.5(A) on the next page. The following equation represents this equilibrium.



A solution of a salt that contains chromate ions, such as sodium chromate,  $\text{Na}_2\text{CrO}_{4(\text{aq})}$ , is added to the mixture. More yellow lead(II) chromate precipitates out of solution, as shown in Figure 9.5(B).

As you learned in Chapter 8, this phenomenon is called the common ion effect. The observed result is predicted by Le Châtelier's principle. Adding a common ion to a solution increases the concentration of that ion in solution. As a result, equilibrium shifts away from the ion. In this example, adding chromate ions causes the equilibrium to shift to the left, and lead(II) chromate precipitates.



**Figure 9.5** Adding chromate ions to an equilibrium system of lead(II) chromate (A) causes the equilibrium position to shift to the left. As a result, more solid lead(II) chromate precipitates (B).

Analyzing the expression for the solubility product constant gives the same result.

$$K_{\text{sp}} = [\text{Pb}^{2+}][\text{CrO}_4^{2-}] = 2.3 \times 10^{-13} \text{ at } 25^\circ\text{C}$$

Since  $K_{\text{sp}}$  is a constant at a given temperature, an increase in the concentration of one ion must be accompanied by a decrease in the concentration of the other ion, achieved by the formation of a precipitate. This explains why solid lead(II) chromate precipitates out of solution.

The next Sample Problem shows how to predict the solubility of an ionic compound when a common ion is present in solution.

### Sample Problem

#### The Effect of a Common Ion on Solubility

##### Problem

The solubility of pure  $\text{PbCrO}_{4(\text{s})}$  in water is  $4.8 \times 10^{-7} \text{ mol/L}$ .

- Qualitatively predict how the solubility will change if  $\text{PbCrO}_{4(\text{s})}$  is added to a 0.10 mol/L solution of sodium chromate,  $\text{Na}_2\text{CrO}_4$ .
- $K_{\text{sp}}$  for  $\text{PbCrO}_{4(\text{s})}$  is  $2.3 \times 10^{-13}$ . Determine the solubility of  $\text{PbCrO}_{4(\text{s})}$  in a 0.10 mol/L solution of  $\text{Na}_2\text{CrO}_4$ .

##### What Is Required?

You need to predict, and then determine, the solubility of  $\text{PbCrO}_4$  (in mol/L) in a solution of  $\text{Na}_2\text{CrO}_4$ .

##### What Is Given?

You know  $K_{\text{sp}}$  for  $\text{PbCrO}_4$  and the concentration of the salt with the common ion.

*Continued ...*



**Plan Your Strategy**

(a) Use Le Châtelier's principle to make a prediction.

(b)

**Step 1** Write the equilibrium equation.

**Step 2** Use the equilibrium equation to write an expression for  $K_{sp}$ .

**Step 3** Set up an ICE table. Let  $x$  represent the concentration of chromate (the common ion) that is contributed by  $PbCrO_4$ . Initial conditions are based on the solution of  $Na_2CrO_4$ .

**Step 4** Solve for  $x$ , and check your prediction.

**Act on Your Strategy**

(a) Based on Le Châtelier's principle, the solubility of  $PbCrO_4$  in a solution that contains a common ion (chromate) will be less than the solubility of  $PbCrO_4$  in water.

(b)

**Step 1**  $PbCrO_{4(s)} \rightleftharpoons Pb^{2+}_{(aq)} + CrO_4^{2-}_{(aq)}$

**Step 2**  $K_{sp} = [Pb^{2+}][CrO_4^{2-}] = 2.3 \times 10^{-13}$

**Step 3**

| Concentration (mol/L) | $PbCrO_{4(s)}$ | $\rightleftharpoons$ | $Pb^{2+}_{(aq)}$ | + | $CrO_4^{2-}_{(aq)}$ |
|-----------------------|----------------|----------------------|------------------|---|---------------------|
| Initial               | —              |                      | 0                |   | 0.10                |
| Change                | —              |                      | +x               |   | +x                  |
| Equilibrium           | —              |                      | x                |   | 0.10 + x            |

**Step 4** Since  $K_{sp}$  is very small, you can assume that  $x$  is much smaller than 0.10. To check the validity of this assumption, determine whether or not 0.10 is more than 500 times greater than  $K_{sp}$ :

$$\begin{aligned}\frac{0.10}{K_{sp}} &= \frac{0.10}{2.3 \times 10^{-13}} \\ &= 4.3 \times 10^{11} > 500\end{aligned}$$

Therefore, in the  $(0.10 + x)$  term,  $x$  can be ignored. In other words,  $(0.10 + x)$  is approximately equal to 0.10. Therefore, you can simplify the equation as follows:

$$\begin{aligned}K_{sp} &= [Pb^{2+}][CrO_4^{2-}] = 2.3 \times 10^{-13} \\ &= (x)(0.10 + x) \\ &\approx (x)(0.10) \\ \therefore (x)(0.10) &\approx 2.3 \times 10^{-13} \\ x &\approx 2.3 \times 10^{-12} \text{ mol/L}\end{aligned}$$

The molar solubility of  $PbCrO_4$  in a solution of 0.10 mol/L  $Na_2CrO_4$  is  $2.3 \times 10^{-12}$  mol/L. Your prediction was correct. The solubility of  $PbCrO_4$  decreases in a solution of common ions.

**Check Your Solution**

The approximation in step 4 is reasonable. The solubility of  $x$  is much smaller than 0.10. To prove that the approximation works, substitute the calculated value of  $x$  into the initial expression for  $K_{sp}$ .

## Practice Problems

**Note:** Refer to Appendix E, as necessary.

21. Determine the molar solubility of AgCl
  - (a) in pure water
  - (b) in 0.15 mol/L NaCl
22. Determine the molar solubility of lead(II) iodide, PbI<sub>2</sub>, in 0.050 mol/L NaI.
23. Calculate the molar solubility of calcium sulfate, CaSO<sub>4</sub>,
  - (a) in pure water
  - (b) in 0.25 mol/L Na<sub>2</sub>SO<sub>4</sub>
24.  $K_{sp}$  for lead(II) chloride, PbCl<sub>2</sub>, is  $1.6 \times 10^{-5}$ . Calculate the molar solubility of PbCl<sub>2</sub>
  - (a) in pure water
  - (b) in 0.10 mol/L CaCl<sub>2</sub>



### Electronic Learning Partner

To learn more about solubility equilibria, go to the Chemistry 12 Electronic Learning Partner.

## Canadians in Chemistry



Dr. Joseph MacInnis has a medical degree, but he does not work in a clinic, a hospital, or a typical doctor's office. His office is the ocean, and he is an expert in deep-sea diving. He combines his medical expertise with his knowledge of the properties of gases to study the effects of deep-sea diving on humans.



MacInnis was born in Barrie, Ontario, in 1937. In 1963, after graduating from the University of Toronto's medical school, he received a fellowship to study diving medicine at the University of Pennsylvania. Diving medicine is a specialized field, dealing with the challenges that humans face when exposed to undersea environments.

For every 10 m below sea level that a diver descends under water, ambient pressure increases by one unit of atmospheric pressure. This increase in pressure, and its effect on heterogeneous equilibria

in the body, is one of the most profound challenges that a diver encounters. As a diver descends, and is subjected to increased pressure, gases such as nitrogen dissolve in the blood and tissues. In the equilibrium between dissolved nitrogen and gaseous nitrogen, increased pressure favours dissolved nitrogen, according to Le Châtelier's principle. As the diver ascends to the ocean surface and pressure decreases, equilibrium favours the nitrogen coming out of solution.

If a diver ascends too quickly, the lungs cannot remove the nitrogen fast enough. Gas bubbles form in the blood, causing decompression sickness. Decompression sickness is also known as "the bends," because one of its symptoms is an inability to bend the joints.

MacInnis was a consultant to the team that discovered the *Titanic*, and he was the first Canadian to explore the wreck. In 1991, MacInnis and his team used small submarines with pressurized hulls to film the wreck in IMAX format. The wreck is about 4000 m below sea level, but the pressure inside the submarines was kept similar to the pressure above the surface of the sea.

MacInnis is passionate about the environment, both below and above the sea. Since 1996, MacInnis has been Chair of the Friends of the Environment Foundation, a non-profit organization that funds projects that help to protect Canada's environment. In recognition of his accomplishments, MacInnis was made a member of the Order of Canada in 1976.



How do buffers in human blood maintain the blood's pH? In the Chemistry Course Challenge, you will learn about the buffer system in blood. How would you design an investigation to demonstrate how the system resists changes in pH?

## Buffers and the Common Ion Effect

In Chapter 8, you learned that buffers resist changes in pH when acids or bases are added. Buffers have many uses in a chemistry lab. For example, commercial buffers with certified pH values are available. Chemists in analytical laboratories use these acidic, basic, and neutral buffers to ensure the accuracy of their pH meters across the pH range.

Recall, from Chapter 8, that a buffer consists of a weak acid/conjugate base mixture or a weak base/conjugate acid mixture. One buffer that you examined previously contains acetic acid and sodium acetate. The common-ion effect applies to this buffer. The equilibrium of the acetic acid is affected by the common acetate ion from sodium acetate.

Since buffers are an example of the common-ion effect, the concentration of ions (hence the pH) of a buffer solution can be calculated using a method that is similar to the method you used to determine solubility in a common ion effect problem. You will use  $K_a$ , however, instead of  $K_{sp}$ . Also, buffers are in homogeneous equilibria, unlike saturated solubility systems, which are in heterogeneous equilibria. Therefore, you need to consider the initial concentration of the reactants. (The reactants are not solids, so their concentration is not constant.)

### Sample Problem

#### pH of a Buffer and the Common-Ion Effect

##### Problem

A buffer solution was made by mixing equal volumes of 0.20 mol/L solutions of acetic acid and sodium acetate at 25°C. What is the pH of the buffer solution?

##### What Is Required?

You need to determine the pH of the buffer solution.

##### What Is Given?

0.20 mol/L  $\text{CH}_3\text{COOH}$  and 0.20 mol/L  $\text{CH}_3\text{COONa}$  are mixed in equal volumes.  $K_a$  for  $\text{CH}_3\text{COOH}$  is  $1.8 \times 10^{-5}$ .

##### Plan Your Strategy

- Step 1** Determine the initial concentrations of  $\text{CH}_3\text{COOH}$  and  $\text{CH}_3\text{COO}^-$  in the buffer solution.
- Step 2** Write the reaction for the dissociation of  $\text{CH}_3\text{COOH}$ . Set up an ICE table, including the initial concentration of  $\text{CH}_3\text{COO}^-$  in the buffer.
- Step 3** Write the equation for  $K_a$ , and substitute equilibrium terms into the equation.
- Step 4** Solve the equation for  $x$ . Assume that  $x$  is small compared with the initial concentrations. Check the validity of this assumption when you find the value of  $x$ .
- Step 5**  $\text{pH} = -\log[\text{H}_3\text{O}^+]$

### Act on Your Strategy

**Step 1** When the solutions are mixed, the total volume is twice the volume of each component volume. Therefore, the concentration of each component is halved.

$$[\text{CH}_3\text{COOH}] = [\text{CH}_3\text{COO}^-] = 0.10 \text{ mol/L}$$

**Step 2**

| Concentration (mol/L) | $\text{CH}_3\text{COOH}_{(\text{aq})}$ | $+$ | $\text{H}_2\text{O}_{(\ell)}$ | $\rightleftharpoons$ | $\text{CH}_3\text{COO}^-_{(\text{aq})}$ | $+$ | $\text{H}_3\text{O}^+_{(\text{aq})}$ |
|-----------------------|--|-----|-------------------------------|----------------------|---|-----|--------------------------------------|
| Initial               | 0.10                                   |     | —                             |                      | 0.10                                    |     | ~0                                   |
| Change                | -x                                     |     | —                             |                      | +x                                      |     | +x                                   |
| Equilibrium           | 0.10-x                                 |     | —                             |                      | 0.10 + x                                |     | x                                    |

**Step 3**  $K_a = \frac{[\text{CH}_3\text{COO}^-][\text{H}_3\text{O}^+]}{[\text{CH}_3\text{COOH}]}$   
 $= \frac{(0.10 + x)(x)}{(0.10 - x)}$

**Step 4** Assume that  $(0.10 + x) \approx 0.10$  and  $(0.10 - x) \approx 0.10$ .

$$K_a \approx \frac{(0.10)(x)}{(0.10)} = 1.8 \times 10^{-5}$$

$$\therefore x = 1.8 \times 10^{-5} \text{ mol/L}$$

**Step 5**  $\text{pH} = -\log(1.8 \times 10^{-5})$   
 $= 4.74$

The pH of the buffer solution is 4.74.

### Check Your Solution

The value of  $x$  ( $1.8 \times 10^{-5}$ ) is negligible compared with the initial concentration of each component (0.10). A buffer that is made using a weak acid and its conjugate base should have a pH that is less than 7.

### PROBLEM TIP

You can check whether it is reasonable to ignore  $x$  by dividing 0.10 by  $K_a$ . The value is greater than 500, so the approximation is reasonable.

### Practice Problems

25. A buffer solution is made by mixing 250 mL of 0.200 mol/L aqueous ammonia and 400 mL of 0.150 mol/L ammonium chloride. Calculate the pH of the buffer solution.
26. A buffer solution is made by mixing 200 mL of 0.200 mol/L aqueous ammonia and 450 mL of 0.150 mol/L ammonium chloride. Calculate the pH of the buffer solution.
27. A buffer solution contains 0.200 mol/L nitrous acid,  $\text{HNO}_{2(\text{aq})}$ , and 0.140 mol/L potassium nitrite,  $\text{KNO}_{2(\text{aq})}$ . What is the pH of the buffer solution?
28. A buffer solution is prepared by dissolving 1.80 g of benzoic acid,  $\text{C}_6\text{H}_5\text{COOH}$ , and 1.95 g of sodium benzoate,  $\text{NaC}_6\text{H}_5\text{COO}$ , in 800 mL of water. Calculate the pH of the buffer solution.

## Section Summary

In this section, you determined the solubility product constant,  $K_{sp}$ , based on solubility data. You obtained your own solubility data and used these data to calculate a value for  $K_{sp}$ . You determined the molar solubility of ionic solutions in pure water and in solutions of common ions, based on their  $K_{sp}$  values. In section 9.3, you will further explore the implications of Le Châtelier's principle. You will use a reaction quotient,  $Q_{sp}$ , to predict whether a precipitate forms. As well, you will learn how selective precipitation can be used to identify ions in solution.

## Section Review

- 1 K/U** The values of  $K_{sp}$  for binary ionic compounds that contain either sodium, potassium, or ammonium cations are not listed in a  $K_{sp}$  table. State why.
- 2 K/U** A saturated solution of a slightly soluble ionic compound does not contain any of the solute in solid form. Is this system at equilibrium? Explain your answer briefly.
- 3 C** Does a larger value of  $K_{sp}$  necessarily mean a greater solubility? To illustrate your answer, calculate and compare the molar solubility of silver chloride,  $\text{AgCl}$  ( $K_{sp} = 1.8 \times 10^{-10}$ ), with silver chromate,  $\text{Ag}_2\text{CrO}_4$  ( $K_{sp} = 2.6 \times 10^{-12}$ ).
- 4 C** Explain why there is no simple relationship between  $K_{sp}$  for a given compound and the solubility of the compound in g/L.
- 5 I** The maximum solubility of barium fluoride,  $\text{BaF}_2$ , at  $25^\circ\text{C}$ , is 1.3 g/L.
  - (a)** Calculate  $K_{sp}$  for  $\text{BaF}_2$  at  $25^\circ\text{C}$ .
  - (b)** Calculate the solubility of  $\text{BaF}_2$  in formula units of  $\text{BaF}_2/\text{L}$ .
- 6 I** A chemist adds 20.0 g of sodium hydroxide,  $\text{NaOH}$ , to a 1.0 L solution of 1.0 mol/L acetic acid.
  - (a)** Explain why the resulting solution resists pH changes when an acid or a base is added.
  - (b)** Calculate the pH of the solution. Assume that there is no change in the volume of the solution when  $\text{NaOH}$  is added.
- 7 I** A buffer solution is prepared by adding 2.1 g of  $\text{NaF}$  to  $5.00 \times 10^2$  mL of 0.10 mol/L  $\text{HF}_{(\text{aq})}$ . Calculate the pH of the buffer solution. Assume that no change in volume results from the addition of  $\text{NaF}$  to the  $\text{HF}$  solution.
- 8 I** A solution of  $\text{BaCl}_2$  is added to a solution of  $\text{Na}_2\text{SO}_4$ .
  - (a)** What do you expect to observe? Include a balanced chemical equation in your answer.
  - (b)** Calculate the solubility (in mol/L and in g/L) of  $\text{BaSO}_4$  in pure water.
  - (c)** Calculate the solubility (in mol/L and in g/L) of  $\text{BaSO}_4$  in 0.085 mol/L  $\text{Na}_2\text{SO}_4$ .
- 9 C** Explain why the solubility of nickel(II) carbonate,  $\text{NiCO}_3$ , is unaffected by the addition of  $\text{NaCl}$  to a saturated solution of  $\text{NiCO}_3$ .

# Predicting the Formation of a Precipitate

## 9.3

In section 9.2, you worked with concentrations of ions in solutions at equilibrium. You used  $K_{sp}$  to determine the solubility of ionic substances in pure water and in solutions of common ions. The systems you worked with were saturated solutions that contained excess, undissolved solute.

How do you predict whether a given concentration of ions will result in the precipitation of an ionic compound? How can you tell if a solution is saturated? You substitute the concentrations of the ions into an expression that is identical to the solubility product expression. Because these concentrations may not be the same as the concentrations that the equilibrium system would have, however, the expression has a different name: the ion product.

### Comparing the Ion Product With the Solubility Product

The **ion product**,  $Q_{sp}$ , is an expression that is identical to the solubility product constant, but its value is calculated using concentrations that are not necessarily those at equilibrium. (The relationship between the expression for solubility product,  $K_{sp}$ , and the expression for the ion product,  $Q_{sp}$ , is analogous to the relationship between the equilibrium constant,  $K_c$ , and the reaction quotient,  $Q_c$ .)

For example, suppose that you slowly add an ionic compound, such as magnesium sulfate,  $MgSO_4$ , to water in a beaker. The following equation represents the dissociation.



Initially, all the magnesium sulfate dissolves. The solution is not at equilibrium as long as more solid can dissolve. As you add more solid, however, the solution reaches equilibrium. The solution is saturated, and no more salt will dissolve. If you continue to add magnesium sulfate to the water, you will see an increasing amount of solid in the beaker.

The ion product expression for magnesium sulfate is written as follows:

$$Q_{sp} = [Mg^{2+}][SO_4^{2-}]$$

You calculate  $Q_{sp}$  by substituting the concentration of each ion into the expression. If  $Q_{sp}$  is larger than  $K_{sp}$ , the product of the concentrations of the ions is greater than it would be at equilibrium. For the system to attain equilibrium, some of the ions must leave the solution by precipitation. Conversely, if  $Q_{sp}$  is less than  $K_{sp}$ , the product of the concentration of the ions is smaller than it is at equilibrium. Therefore, the solution is not yet saturated and more ions can be added to the solution without any precipitation. The relationship between  $Q_{sp}$  and  $K_{sp}$  for the dissociation of a slightly soluble ionic compound is summarized on the next page. Use the following general equation as a reference.



### Section Preview/ Specific Expectations

In this section, you will

- **predict** the formation of precipitates by using the solubility product constant
- **solve** equilibrium problems involving concentrations of reactants and products and  $K_{sp}$
- **communicate** your understanding of the following terms: *ion product ( $Q_{sp}$ )*, *fractional precipitation*, *qualitative analysis*, *quantitative analysis*



- |                   |   |
|-------------------|---|
| $Q_{sp} < K_{sp}$ | <ul style="list-style-type: none"> <li>The system attains equilibrium by moving to the right, favouring dissociation.</li> <li>More solid can dissolve.</li> </ul>                          |
| $Q_{sp} = K_{sp}$ | <ul style="list-style-type: none"> <li>The system is at equilibrium.</li> <li>No more solid can dissolve.</li> <li>No precipitate forms.</li> </ul>   |
| $Q_{sp} > K_{sp}$ | <ul style="list-style-type: none"> <li>The system attains equilibrium by moving to the left, favouring precipitation.</li> <li>A precipitate forms until equilibrium is reached.</li> </ul> |

## Using the Ion Product Expression

You can use the relationship between the ion product expression and the solubility product expression to predict whether a precipitate will form in a given system. One common system involves mixing solutions of two soluble ionic compounds, which react to form an ionic compound with a very low solubility. If  $Q_{sp} > K_{sp}$ , based on the initial concentrations of the ions in solution, the sparingly soluble compound will form a precipitate.

How do you know which ionic compounds are soluble and which are not? In your previous chemistry course, you learned a set of solubility guidelines. Table 9.3 summarizes these guidelines. Remember: the higher guideline takes precedence. (For instance, guideline 3 says that carbonates have very low solubility. Sodium carbonate is soluble, however, because guideline 1 says that ionic compounds containing sodium are soluble.) Chemists do not usually work with solubility products for soluble compounds. Thus, you will not find soluble ionic compounds listed in  $K_{sp}$  tables. If you see a compound in a  $K_{sp}$  table, you know that it has a low solubility relative to compounds such as sodium chloride.

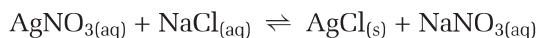
**Table 9.3** General Solubility Guidelines

| Guideline | Cations  | Anions  | Result              | Exceptions   |
|-----------|--|---|---------------------|--|
| 1         | $\text{Li}^+, \text{Na}^+, \text{K}^+, \text{Rb}^+, \text{Cs}^+, \text{NH}_4^+$                  | $\text{NO}_3^-, \text{CH}_3\text{COO}^-, \text{ClO}_3^-$                        | soluble             | $\text{Ca}(\text{ClO}_3)_2$ is insoluble.  |
| 2         | $\text{Ag}^+, \text{Pb}^{2+}, \text{Hg}^+$   | $\text{CO}_3^{2-}, \text{PO}_4^{3-}, \text{O}^{2-}, \text{S}^{2-}, \text{OH}^-$ | very low solubility | $\text{BaO}$ and $\text{Ba}(\text{OH})_2$ are soluble. Group 2 (IIA) sulfides tend to decompose. |
| 3         |  | $\text{Cl}^-, \text{Br}^-, \text{I}^-$  | soluble             |  |
| 4         | $\text{Ba}^{2+}, \text{Ca}^{2+}, \text{Sr}^{2+}$   |   | very low solubility |  |
| 5         | $\text{Mg}^{2+}, \text{Cu}^{2+}, \text{Zn}^{2+}, \text{Fe}^{2+}, \text{Fe}^{3+}, \text{Al}^{3+}$ | $\text{SO}_4^{2-}$  | soluble             |  |



**Figure 9.7** A chemist can test for the presence of chloride ions in a solution by adding silver nitrate solution. If a white precipitate of silver chloride forms, the test is positive for chloride.

For example, silver nitrate and sodium chloride are both soluble ionic compounds. When they are mixed in solution, however, they react to form silver chloride, as shown in Figure 9.7. The equation for the reaction is:



Silver chloride has a very low solubility. Therefore, a precipitate will form even if the initial concentration of chloride and silver ions is very small. The following Sample Problems show you how to decide whether a precipitate will form under a given set of conditions.

## Sample Problem

### Predicting Precipitation I

#### Problem

A common test for chloride ions in a solution involves adding  $\text{AgNO}_{3(\text{aq})}$  to the solution being tested. If chloride ions are present in sufficient quantity, the chemist will observe a white cloudiness that indicates the formation of a precipitate.  $K_{\text{sp}}$  for silver chloride is  $1.8 \times 10^{-10}$ .

A drop (0.050 mL) of 6.0 mol/L silver nitrate is added to 1.0 L of 0.10 mol/L sodium chloride. Does a precipitate of silver chloride form?

#### What Is Required?

Will silver chloride precipitate under the given conditions?

#### What Is Given?

You know the concentration and volume of the silver nitrate and sodium chloride solutions. For  $\text{AgNO}_3$ ,  $c = 6.0 \text{ mol/L}$  and  $V = 0.050 \text{ mL}$ . For  $\text{NaCl}$ ,  $c = 0.10 \text{ mol/L}$  and  $V = 1.0 \text{ L}$ . You also know  $K_{\text{sp}}$  for silver chloride.

#### Plan Your Strategy

- Step 1** Determine the concentrations of silver ions and chloride ions in the reaction mixture.
- Step 2** Substitute the ion concentrations into the ion product expression for silver chloride to determine  $Q_{\text{sp}}$ .
- Step 3** Compare  $Q_{\text{sp}}$  with  $K_{\text{sp}}$ , and predict whether or not a precipitate will form.

#### Act on Your Strategy

- Step 1** Because the volume of the  $\text{AgNO}_3$  solution is much smaller than the volume of the  $\text{NaCl}$  solution, you can ignore it. In other words, assume that the final volume of the reaction mixture is 1.0 L.



$$\therefore [\text{Cl}^-] = [\text{NaCl}] = 0.10 \text{ mol/L}$$



$$\begin{aligned} [\text{Ag}^+] &= [\text{AgNO}_3] = \frac{c \times V_{\text{initial}}}{V_{\text{final}}} \\ &= \frac{(6.0 \text{ mol/L})(0.050 \text{ mL} \times 1.0 \times 10^{-3} \text{ L/mL})}{1.0 \text{ L}} \\ &= 3.0 \times 10^{-4} \text{ mol/L} \end{aligned}$$

$$\begin{aligned} \text{Step 2 } Q_{\text{sp}} &= [\text{Ag}^+][\text{Cl}^-] \\ &= (3.0 \times 10^{-4})(0.10) \\ &= 3.0 \times 10^{-5} \end{aligned}$$

- Step 3** Since  $Q_{\text{sp}} > K_{\text{sp}}$ ,  $\text{AgCl}$  will precipitate until  $Q_{\text{sp}} = 1.8 \times 10^{-10}$ .

#### Check Your Solution

The units are correct in the calculation of  $[\text{Ag}^+]$ . It seems reasonable that a precipitate formed, since  $K_{\text{sp}}$  for silver chloride is very small compared with the concentration of chloride ions and silver ions.

## Practice Problems

### PROBLEM TIP

For Practice Problems 31 and 32, you will need to look up values of  $K_{sp}$  in Appendix E.

29. A solution contains 0.15 mol/L of NaCl and 0.0034 mol/L  $Pb(NO_3)_2$ . Does a precipitate form? Include a balanced chemical equation for the formation of the possible precipitate.  $K_{sp}$  for  $PbCl_2$  is  $1.7 \times 10^{-5}$ .
30. One drop (0.050 mL) of 1.5 mol/L potassium chromate,  $K_2CrO_4$ , is added to 250 mL of 0.10 mol/L  $AgNO_3$ . Does a precipitate form? Include a balanced chemical equation for the formation of the possible precipitate.  $K_{sp}$  for  $Ag_2CrO_4$  is  $2.6 \times 10^{-12}$ .
31. A chemist adds 0.010 g of  $CaCl_2$  to  $5.0 \times 10^2$  mL of 0.0015 mol/L sodium carbonate,  $Na_2CO_3$ . Does a precipitate of calcium carbonate form? Include a balanced chemical equation for the formation of the possible precipitate.
32. 0.10 mg of magnesium chloride,  $MgCl_2$ , is added to  $2.5 \times 10^2$  mL of 0.0010 mol/L NaOH. Does a precipitate of magnesium hydroxide form? Include a balanced chemical equation for the formation of the possible precipitate.

The next Sample Problem shows how to predict whether or not a precipitate will form when two significant volumes of reactant are mixed together. You will need to use the solubility guidelines to decide whether or not an insoluble compound forms.

## Sample Problem

### Predicting Precipitation II

#### Problem

A chemist mixes 100.0 mL of 0.25 mol/L  $Ca(NO_3)_2$  with 200.0 mL of 0.070 mol/L NaF. Does a precipitate form?

#### What Is Given?

You know the initial concentration and volume of the calcium nitrate and sodium fluoride solutions. For  $Ca(NO_3)_2$ ,  $c = 0.25$  mol/L and  $V = 100.0$  mL. For NaF,  $c = 0.070$  mol/L and  $V = 200.0$  mL. As well, you have the solubility guidelines in Table 9.3.

#### Plan Your Strategy

- Step 1** Decide whether a compound with low solubility forms when calcium nitrate and sodium fluoride are mixed, using the solubility guidelines.
- Step 2** If an insoluble compound forms, write an equation that represents the reaction. Look up  $K_{sp}$  for the compound in Appendix E.
- Step 3** Determine the concentrations of the ions that make up the compound.
- Step 4** Substitute the concentrations of the ions into the ion product expression for the compound to determine  $Q_{sp}$ .
- Step 5** Compare  $Q_{sp}$  with  $K_{sp}$ , and predict whether or not a precipitate forms.

### Act on Your Strategy

**Step 1** According to the solubility guidelines, NaF and  $\text{Ca}(\text{NO}_3)_2$  are both soluble, because ionic compounds that contain sodium or nitrate ions are soluble. When you mix the solutions,  $\text{NaNO}_3$ , and  $\text{CaF}_2$  can also form.  $\text{NaNO}_3$  is soluble, but  $\text{CaF}_2$  is not, according to guideline 4.

**Step 2**  $\text{NaF}_{(\text{aq})} + \text{Ca}(\text{NO}_3)_{2(\text{aq})} \rightleftharpoons \text{NaNO}_{3(\text{aq})} + \text{CaF}_{2(\text{s})}$   
From Appendix E,  $K_{\text{sp}}$  for  $\text{CaF}_2$  is  $3.2 \times 10^{-11}$ .

**Step 3** When calculating the volume of the reaction mixture, assume that it is equal to the sum of the volumes of the solutions. This is a reasonable assumption, because both solutions are dilute.

$$\begin{aligned} [\text{Ca}^{2+}] &= [\text{Ca}(\text{NO}_3)_2] = \frac{c \times V_{\text{initial}}}{V_{\text{final}}} \\ &= \frac{(0.25 \text{ mol/L})(100.0 \text{ mL})}{(100.0 \text{ mL} + 200.0 \text{ mL})} \\ &= 8.3 \times 10^{-2} \text{ mol/L} \end{aligned}$$

$$\begin{aligned} [\text{F}^-] &= [\text{NaF}] = \frac{c \times V_{\text{initial}}}{V_{\text{final}}} \\ &= \frac{(0.070 \text{ mol/L})(200.0 \text{ mL})}{(100.0 \text{ mL} + 200.0 \text{ mL})} \\ &= 4.7 \times 10^{-2} \text{ mol/L} \end{aligned}$$

**Step 4**  $Q_{\text{sp}} = [\text{Ca}^{2+}][\text{F}^-]^2$   
 $= (8.3 \times 10^{-2})(4.7 \times 10^{-2})^2$   
 $= 1.8 \times 10^{-4}$

**Step 5** Since  $Q_{\text{sp}} > K_{\text{sp}}$ ,  $\text{CaF}_2$  precipitates until  $Q_{\text{sp}} = 3.2 \times 10^{-11}$ .

### Check Your Solution

The units in the calculation of the concentrations of the ions are correct. It seems reasonable that a precipitate formed, since  $K_{\text{sp}}$  for calcium fluoride is very small compared with the concentrations of the chloride ions and silver ions.

### Practice Problems

33.  $1.0 \times 10^2 \text{ mL}$  of  $1.0 \times 10^{-3} \text{ mol/L}$   $\text{Pb}(\text{NO}_3)_2$  is added to  $40 \text{ mL}$  of  $0.040 \text{ mol/L}$   $\text{NaCl}$ . Does a precipitate form? Include a balanced chemical equation for the formation of the possible precipitate.
34.  $2.3 \times 10^2 \text{ mL}$  of  $0.0015 \text{ mol/L}$   $\text{AgNO}_3$  is added to  $1.3 \times 10^2 \text{ mL}$  of  $0.010 \text{ mol/L}$  calcium acetate,  $\text{Ca}(\text{CH}_3\text{COO})_2$ . Does a precipitate form? Include a balanced chemical equation for the formation of the possible precipitate.  $K_{\text{sp}}$  for  $\text{AgCH}_3\text{COO}$  is  $2.0 \times 10^{-3}$ .
35.  $25 \text{ mL}$  of  $0.10 \text{ mol/L}$   $\text{NaOH}$  is added to  $5.0 \times 10^2 \text{ mL}$  of  $0.00010 \text{ mol/L}$  cobalt(II) chloride,  $\text{CoCl}_2$ . Does a precipitate form? Include a balanced chemical equation for the formation of the possible precipitate.
36.  $250 \text{ mL}$  of  $0.0011 \text{ mol/L}$   $\text{Al}_2(\text{SO}_4)_3$  is added to  $50 \text{ mL}$  of  $0.022 \text{ mol/L}$   $\text{BaCl}_2$ . Does a precipitate form? Include a balanced chemical equation for the formation of the possible precipitate.

## Analytical Applications of Precipitation Reactions

In the previous Sample Problems, you saw that combining solutions of soluble ionic compounds can cause the precipitation of a slightly soluble ionic compound. Analytical chemists use precipitation reactions to remove ions from solution or to identify ions in an unknown solution.

### Fractional Precipitation

Suppose a chemist has a solution that contains several similar ions. The chemist wants to remove some of these ions, while leaving other ions in solution. One way to do this is by **fractional precipitation**: a process in which ions are selectively precipitated from solution, leaving other ions.

For example, consider a solution that contains three halide ions:  $\text{Cl}^-$ ,  $\text{Br}^-$ , and  $\text{I}^-$ . Since these halides all come from the same group on the periodic table, they share many properties. When they are the anions in slightly soluble ionic compounds, however, they have different solubilities. (See Table 9.4.) Therefore, chemists can use fractional precipitation to separate them from solution.

**Table 9.4** Values of  $K_{\text{sp}}$  for Silver Halides

| Silver halide | $K_{\text{sp}}$       |
|---------------|-----------------------|
| AgCl          | $1.8 \times 10^{-10}$ |
| AgBr          | $3.3 \times 10^{-13}$ |
| AgI           | $1.5 \times 10^{-16}$ |

Out of the three compounds, silver chloride is the most soluble and silver iodide is the least soluble. (You can compare the solubilities of the compounds based on their solubility products because they are all the same type. Each formula unit contains two ions.)

To separate the halide ions, a chemist adds silver ions to the solution until most of the iodide ions precipitate out as AgI. The chemist stops adding silver ions before AgBr begins to precipitate. The chemist then removes the solid AgI by filtration or by using a centrifuge, as shown in Figure 9.8. To remove the bromide ions, the chemist repeats the process with the remaining solution. The chemist adds silver ions until most of the bromide ions precipitate out as AgBr, but stops adding ions before AgCl begins to precipitate. By filtering or centrifuging again, the chemist obtains a solution that contains only chloride ions.



**Figure 9.8** Chemists use a centrifuge to separate a precipitate from a solution. The centrifuge spins the samples quickly, and the resulting force pushes the precipitate to the bottom of the test tube. The solution can then be decanted.

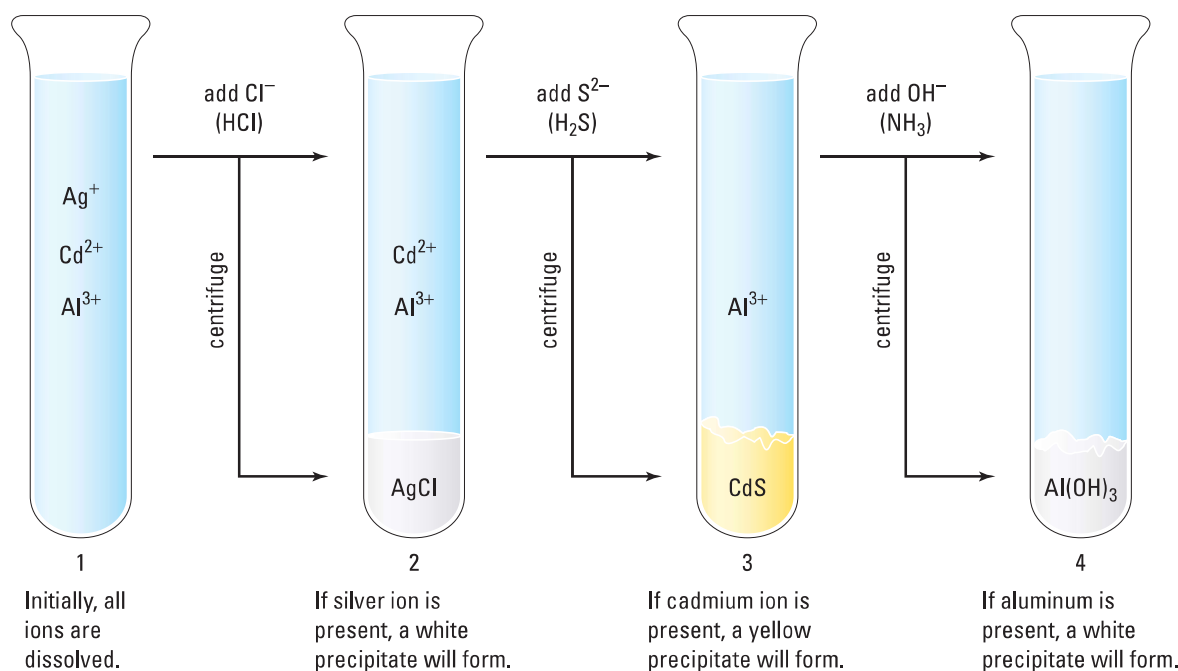
## Qualitative Analysis

As well as separating similar ions out of solution, chemists can also use their understanding of solubility and precipitation reactions to identify unknown ions in solution. **Qualitative analysis** is the branch of analytical chemistry that involves identifying elements, compounds, and ions in samples of unknown or uncertain composition. The other branch of analytical chemistry is **quantitative analysis**. In quantitative analysis, analytical chemists determine *how much* of a compound, element, or ion is in a sample.

One way to identify cations in solution is by selectively precipitating them out of solution. As you know, cations may form soluble or insoluble ionic compounds, depending on the anions that are present. For example, copper(II) chloride,  $\text{CuCl}_2$  is soluble in water. Copper(II) sulfide,  $\text{CuS}$ , is insoluble in an acidic solution. Knowing about the relative solubility of cations when combined with various anions helps chemists identify them.

Using precipitation reactions to identify cations was once a common part of qualitative analyses. Today, chemists usually identify and quantify unknowns using instruments such as spectrophotometers. However, examining the identification of cations through precipitation reactions allows you to see how solubility equilibria can be manipulated. It also provides an opportunity to solve a chemical “mystery”—what is in the unknown solution?

To find out what cations are in a solution using precipitation reactions, chemists carry out reactions according to a *scheme* that incorporates tests for each component that may be present. One example of such a scheme is shown in Figure 9.9. This scheme shows how a chemist would analyze an unknown solution that may contain all, some, or none of the following ions: silver,  $\text{Ag}^+$ ; cadmium,  $\text{Cd}^{2+}$ ; and aluminium,  $\text{Al}^{3+}$ . The analysis uses selective, step by step precipitation.



**Figure 9.9** This diagram shows a scheme for identifying silver,  $\text{Ag}^+$ , cadmium,  $\text{Cd}^{2+}$ , and aluminium,  $\text{Al}^{3+}$ , ions. After each step, if a precipitate forms, it is separated by centrifugation. Then the solution is carefully poured into a new test tube and used in the next step.

Web LINK

[www.mcgrawhill.ca/links/chemistry12](http://www.mcgrawhill.ca/links/chemistry12)

Bauxite is the most abundant ore of aluminum. The first step in extracting aluminum from bauxite is called the *Bayer process*. The Bayer process involves a fractional precipitation of impurities, including iron(III) oxide and titanium dioxide. Search the Internet to find the history of the Bayer process and learn how it works. Present your findings as a poster. To start your search, go to the web site above and click on **Web Links**.



The scheme that is shown in Figure 9.9 is very simple. More complex qualitative analyses involve many more steps of isolation and identification, including some steps that are not precipitation reactions. For example, some ions, such as sodium,  $\text{Na}^+$ , and potassium,  $\text{K}^+$ , cannot be precipitated out of an aqueous solution, because the ionic compounds that contain them are always soluble. Instead, chemists identify these ions using a flame test. In the following ThoughtLab, you will simulate a qualitative analysis that includes a flame test.

## ThoughtLab A Qualitative Analysis

Suppose that you are an analytical chemist. You want to test an unknown solution that contains some or all of the following ions: silver,  $\text{Ag}^+$ ; arsenic,  $\text{As}^{3+}$ ; chromium,  $\text{Cr}^{3+}$ ; and sodium,  $\text{Na}^+$ . Your laboratory assistant has already performed some tests on known solutions of these ions and has made the following observations:

- $\text{As}^{3+}$  forms a precipitate when  $\text{H}_2\text{S}_{(\text{aq})}$  is added.  $\text{Cr}^{3+}$  and  $\text{Na}^+$  do not form a precipitate when  $\text{H}_2\text{S}_{(\text{aq})}$  is added.
- $\text{Ag}^+$  forms a precipitate when  $\text{HCl}_{(\text{aq})}$  is added. The other ions do not form a precipitate when  $\text{HCl}_{(\text{aq})}$  is added.
- $\text{Cr}^{3+}$  forms a precipitate when a solution of  $\text{NH}_3$  is added. (Making the solution basic has the same effect as adding  $\text{OH}^-$ .)  $\text{Ag}^+$  also forms a precipitate in a basic solution.
- $\text{Na}^+$  produces a bright yellow flame in a flame test.

### Procedure

1. Based on these observations, devise a step-by-step scheme for testing an unknown solution. The solution may contain all, some, or just one of the possible ions. Use Figure 9.9 to help you.
2. Decide which ions are in the unknown solution. (Remember, the solution may contain one, two, three, or all of the possible ions listed above.) Based on your scheme, write down the observations that you expect to make for this solution.

3. Exchange schemes and observations with a classmate. Do not tell your classmate which ions are in your unknown solution. Based on your classmate's scheme and observations, determine which ions are in your classmate's unknown solution.
4. Discuss your results with your classmate. Did you both succeed in identifying the ions in the unknown solution? If not, you or your classmate may need to modify your schemes or observations.

### Analysis

1. Explain how qualitative analysis depends on the different solubilities of ionic compounds.
2.  $\text{Hg}_2^{2+}$  forms an insoluble chloride,  $\text{Hg}_2\text{Cl}_2$ . If your unknown solution contained a mixture of all or some of the  $\text{Hg}_2^{2+}$ ,  $\text{Ag}^+$ ,  $\text{Cr}^{3+}$ , and  $\text{As}^{3+}$  ions, would the scheme you developed be sufficient to identify all the ions in the solution? Explain your answer.
3. If you were performing this analysis in a laboratory, what safety precautions would you need to take? Explain your answer.

## Section Summary

In Chapter 9, as in most of Unit 4, you learned about equilibrium reactions. In this section, you analyzed precipitation reactions. You mainly examined double-displacement reactions—reactions in which two soluble ionic compounds react to form a precipitate. You used the solubility product constant,  $K_{\text{sp}}$ , to predict whether or not a precipitate would form for given concentrations of ions. In Unit 5, you will learn about a class of reactions that will probably be new to you. You will see how these reactions interconvert chemical and electrical energy.

## Section Review

- 1 **K/U** Answer the following questions about the ion product.
  - (a) Under what circumstances would a chemist want to determine  $Q_{sp}$  for a system?
  - (b) How does  $Q_{sp}$  differ from  $K_{sp}$ ?
  - (c) Why are there no tabulated  $Q_{sp}$  values?
- 2 **I** A chemist adds 1.0 mg of NaI to 50 mL of a 0.010 mol/L solution of  $Pb(NO_3)_2$ . Does a precipitate form?  $K_{sp}$  for  $PbI_2$  is  $9.8 \times 10^{-9}$ .
- 3 **I** How many milligrams of  $Na_2SO_4$  will just begin to precipitate  $CaSO_4$  from  $5.0 \times 10^2$  mL of a 0.10 mol/L solution of  $CaCl_2$ ?  $K_{sp}$  for  $CaSO_4$  is  $2.4 \times 10^{-5}$ . **Hint:** How does  $Q_{sp}$  compare with  $K_{sp}$  at the point when precipitation just begins?
- 4 **I** How many drops of 0.0010 mol/L silver nitrate solution will just begin to precipitate AgCl from  $5.0 \times 10^4$  mL of a 0.90% (m/v) solution of NaCl? (Assume that one drop equals 0.050 mL.)  $K_{sp}$  for AgCl is  $1.8 \times 10^{-10}$ .
- 5 **I**  $K_{sp}$  for  $CaSO_4$  is  $2.4 \times 10^{-5}$ , and  $K_{sp}$  for  $SrSO_4$  is  $3.2 \times 10^{-7}$ . Suppose that you have a 1.0 L solution that is 0.20 mol/L in  $Ca^{2+}$  ions and 0.20 mol/L in  $Sr^{2+}$  ions. You slowly begin to add solid  $Na_2SO_4$ .
  - (a) Explain why  $SrSO_4$  precipitates first.
  - (b) How many milligrams of  $Al_2(SO_4)_3$  will just begin to precipitate  $SrSO_4$  from the solution?
- 6 **C** Consider a solution that contains  $Pb^{2+}$ ,  $Cu^{2+}$ , and  $Mg^{2+}$  cations, present as their (soluble) nitrate salts. How could you selectively precipitate these cations, given solutions of NaCl,  $Na_2S$ , and  $Na_3PO_4$ ? Present your answer as a flowchart, with a chemical equation accompanying each step.
- 7 **MC** To purify sodium chloride, NaCl, for use as table salt, HCl is added to a saturated solution of NaCl. Explain how this process works, using the concept of the ion product. What do you think is the next step in the process? Explain your answer.

### Reflecting on Chapter 9

Summarize this chapter in the format of your choice. Here are a few ideas to use as guidelines:

- Explain how to predict whether a solution of a specific salt will be acidic, basic, or neutral.
- Explain how to determine a substance's solubility product constant,  $K_{sp}$ , based on the molar solubility of the substance.
- Explain how to calculate the molar solubility of a pure substance in water or in a solution of a common ion, given  $K_{sp}$ .
- Describe how to use  $K_{sp}$  to predict the formation of a precipitate.
- Identify the effects of solubility equilibria in the human body.
- Describe how chemists use solubility equilibria to remove specific ions from solution and to identify ions in solution.

### Reviewing Key Terms

For each of the following terms, write a sentence that shows your understanding of its meaning.

equivalence point

end-point

solubility product constant ( $K_{sp}$ )

ion product ( $Q_{sp}$ )

fractional precipitation

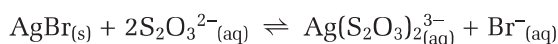
qualitative analysis

quantitative analysis

### Knowledge/Understanding

- Assume that the aqueous solutions in each pair have the same concentration. For each pair, identify which of the two solutions has the lower pH.
  - $\text{NH}_4\text{Cl}_{(\text{aq})}$  and  $\text{KHSO}_4_{(\text{aq})}$
  - $\text{H}_2\text{S}_{(\text{aq})}$  and  $\text{KHSO}_4_{(\text{aq})}$
  - $\text{NaHPO}_4_{(\text{aq})}$  and  $\text{CaBr}_2_{(\text{aq})}$
  - $\text{Al}(\text{NO}_3)_3_{(\text{aq})}$  and  $\text{Al}(\text{NO}_2)_2_{(\text{aq})}$
- Suppose that you have the following indicators available: bromphenol blue, methyl red, bromthymol blue, and phenolphthalein. Use Figure 9.3 to suggest an appropriate indicator for each of the following titrations. Do *not* do any calculations.
  - sulfuric acid with sodium hydroxide
  - formic acid with sodium hydroxide
  - pyridine with nitric acid
- There are many different acid-base indicators. State two ways in which they are all similar.
- What substance can be added to an aqueous solution of propanoic acid to prepare a buffer solution?
- Hydrochloric acid is slowly added to a solution of sodium hydroxide. How does the pH of the solution change?
- A solution of a certain salt is tested with litmus paper, and the litmus turns red. What does this tell you about the relative strengths of the acid and base from which the salt is derived?
- List the names and formulas of three salts that dissolve in water to form
  - an acidic solution
  - a basic solution
- When performing an acid-base titration, you should add only a few drops of indicator rather than a few millilitres. Explain why.
- Distinguish between the terms “solubility” and “solubility product constant.”
- Why do tables of  $K_{sp}$  values for compounds not include values for soluble compounds?
- Values of  $K_{sp}$  are given for a certain temperature. How do the  $K_{sp}$  values for most salts change if the temperature of the solution is increased?
- Write an equation for the dissociation of each compound in water. Then write the corresponding  $K_{sp}$  expression.
  - $\text{CuBr}$
  - $\text{CaCrO}_4$
  - $\text{Ni}(\text{OH})_2$
  - $\text{Mg}_3(\text{PO}_4)_2$
  - $\text{MgNH}_4\text{PO}_4$
- For a solubility system to reach equilibrium, some undissolved solid must be present. Explain why.
- Compare the solubility of magnesium hydroxide in a saturated solution of ammonium chloride with the solubility of magnesium hydroxide in pure water. Would you expect magnesium hydroxide to be more or less soluble, or to have the same solubility, in the ammonium chloride solution? Explain your answer.
- In aqueous solution, the dihydrogen phosphate,  $\text{H}_2\text{PO}_4^-$ , ion can act as either an acid or a base. When tested, a solution containing  $\text{H}_2\text{PO}_4^-$  was found to be acidic. Write the equation for the reaction that took place.

16. Why must  $Q_{sp}$  usually be much larger than  $K_{sp}$  before you can observe a precipitate forming?
17. Silver halide salts are used in black and white photography. During the developing process, excess silver halide is removed from the film by using a solution of sodium thiosulfate (commonly called “hypo”).



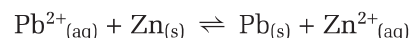
What is the effect on this equilibrium if a more concentrated solution of hypo is used?

## Inquiry

18. Suppose that you have an aqueous solution of copper iodide,  $\text{CuI}_2$ , which you must precipitate and filter before pouring the remaining liquid into a disposal beaker. You decide to use the common ion effect to precipitate the  $\text{CuI}_2$ . In the laboratory, you find stock solutions of  $\text{Cu}(\text{NO}_3)_2$  and  $\text{NaI}$  with the same concentrations. You want to use the smallest volume possible. Which stock solution will you choose to precipitate the  $\text{CuI}_2$ ? Explain your answer.
19. Which has the greater effect on the solubility of  $\text{PbI}_2$  in 1.0 L of a saturated solution: the addition of 0.10 mol of solid  $\text{Pb}(\text{NO}_3)_2$ , or the addition of 0.10 mol of solid  $\text{NaI}$ ? Justify your answer with calculations. Assume that you can ignore the volume change when solid  $\text{Pb}(\text{NO}_3)_2$  is added.
20. Lead(II) iodide and barium sulfate have almost the same value for  $K_{sp}$ . ( $K_{sp}$  for  $\text{PbI}_2$  is  $9.8 \times 10^{-9}$ , and  $K_{sp}$  for  $\text{BaSO}_4$  is  $1.1 \times 10^{-10}$ .) What is the ratio of  $\text{Pb}^{2+}{}_{(aq)}$  to  $\text{Ba}^{2+}{}_{(aq)}$  in saturated solutions of the salts?
21. Silver cyanide is used in aqueous solutions to plate a coating of silver on ornaments, jewellery, and silver cutlery. What is the concentration of  $\text{Ag}^+{}_{(aq)}$  in a saturated solution of  $\text{AgCN}$ ?
22. Water with a high chloride ion content is not safe to drink. The following process is used to test for the presence of  $\text{Cl}^-{}_{(aq)}$ : Dissolve 5.0 g of  $\text{AgNO}_3$  in 500 mL of distilled water. Add 10 drops of the solution to 10 mL of the water being tested, and look for a cloudy white precipitate.

What is the smallest concentration of  $\text{Cl}^-{}_{(aq)}$  in the test water that will cause the formation of a precipitate?

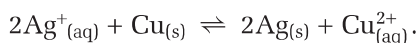
23. Design an experiment to determine  $K_{sp}$  for lead(II) chloride,  $\text{PbCl}_2$ , using the following reaction.



Assume that you have solid  $\text{PbCl}_2$ , a strip of zinc metal, filter paper, an electronic balance, and any other standard laboratory equipment.

- (a) Write the equation for the dissolution of  $\text{PbCl}_2$  and the corresponding  $K_{sp}$  equation.
- (b) Provide a step-by-step procedure, clearly indicating what needs to be measured and/or recorded.
- (c) Explain how you would use your empirical data to determine  $K_{sp}$  for  $\text{PbCl}_2$ .
24. Design an experiment to determine  $K_{sp}$  for lead(II) iodide,  $\text{PbI}_2$ , using the reaction below.
- $$\text{Pb}^{2+}{}_{(aq)} + \text{CrO}_4^{2-}{}_{(aq)} \rightleftharpoons \text{PbCrO}_{4(s)}$$
- Assume that you have solid  $\text{PbCl}_2$ , a 0.50 mol/L solution of  $\text{K}_2\text{CrO}_4$ , filter paper, an electronic balance, and any other standard laboratory equipment.
- (a) Write the equation for the dissolution of  $\text{PbI}_2$  and the corresponding  $K_{sp}$  equation.
- (b) Provide a step-by-step procedure, clearly indicating what needs to be measured and/or recorded.
- (c) Explain how you would use your empirical data to determine  $K_{sp}$  for  $\text{PbI}_2$ .
- (d) If  $K_{sp}$  for  $\text{PbI}_2$  is  $7.9 \times 10^{-9}$ , explain why the solubility of  $\text{PbCrO}_4$  can be ignored. ( $K_{sp}$  for  $\text{PbCrO}_4$  is  $1.8 \times 10^{-14}$ .)
25. A student titrated 25.0 mL of 0.280 mol/L hydrochloric acid with 0.360 mol/L sodium hydroxide solution. The end-point was observed after adding 18.80 mL of  $\text{NaOH}_{(aq)}$ . Some of the steps that were followed by the student are listed below:
1. A transfer pipette was rinsed with water. The pipette was then used to obtain 25.0 mL of hydrochloric acid, which was placed in an Erlenmeyer flask.
  2. About 50 mL of water was added to the Erlenmeyer flask.
  3. A few drops of phenolphthalein indicator were added to the Erlenmeyer flask.

4. A burette was rinsed with water, and then filled with the sodium hydroxide solution.
- Calculate the volume of  $\text{NaOH}_{(\text{aq})}$  that the student should have used to reach equivalence.
  - What was the percent error in the titration?
  - Which step(s) in the titration could account for the error?
26. Assume that you have a solution that is  $0.0010 \text{ mol/L}$  in  $\text{Cu}^+_{(\text{aq})}$  and  $0.0010 \text{ mol/L}$  in  $\text{Ag}^+_{(\text{aq})}$ . If you begin to add solid  $\text{NaCl}$  to the solution, which compound will precipitate first? Explain.
27. A sample of well water contains  $1.0 \times 10^{-3} \text{ mol/L}$  calcium sulfate and  $1.0 \times 10^{-4} \text{ mol/L}$  calcium carbonate ion. A chemist adds barium chloride to the sample. Which precipitate forms first, barium sulfate or barium carbonate?
28. Solutions that contain dissolved ions have been shown to conduct electricity.
- Design an experiment in which you use a sensitive conductivity meter to determine the  $K_{\text{sp}}$  of a slightly soluble compound.
  - How do you propose to calibrate the conductivity meter?
  - If your teacher approves of your experimental design, and if you have access to a conductivity meter, carry out your experiment to determine  $K_{\text{sp}}$  for  $\text{Ca}(\text{OH})_2$ .
29. A student performs an experiment to determine  $K_{\text{sp}}$  for silver acetate,  $\text{AgCH}_3\text{CO}_2$ , using the following reaction.



The student adds a strip of copper metal, with a known mass, to a saturated solution of  $\text{AgCH}_3\text{CO}_2$ . After the reaction, the copper strip is washed, dried, and re-weighed.

- Write the equilibrium equation that represents the equilibrium of  $\text{AgCH}_3\text{CO}_2$ . Also write the corresponding  $K_{\text{sp}}$  equation.
  - $K_{\text{sp}}$  for  $\text{AgCH}_3\text{CO}_2$  is  $2.0 \times 10^{-3}$ . A strip of copper metal, with an initial mass of  $23.4 \text{ g}$ , was placed in  $1.00 \times 10^2 \text{ mL}$  of saturated  $\text{AgCH}_3\text{CO}_2$  solution with no solid  $\text{AgCH}_3\text{CO}_2$  present. Calculate the expected mass of the copper strip after the reaction.
  - Why must the saturated  $\text{AgCH}_3\text{CO}_2$  solution be free of any solid  $\text{AgCH}_3\text{CO}_2$ ?
30. A  $0.150 \text{ mol/L}$  solution of acetic acid was titrated with  $25.0 \text{ mL}$  of  $0.250 \text{ mol/L}$  sodium hydroxide.
- Calculate the volume of acetic acid that was needed at the equivalence point.
  - What is the pH of the solution at equivalence?
  - Suggest a suitable indicator for this titration.
31. A buffer solution is prepared by adding  $30.0 \text{ g}$  of pure acetic acid to  $41.0 \text{ g}$  of sodium acetate in water, and then diluting the solution to  $1.00 \text{ L}$ . What is the pH of the buffer solution?

## Communication

- Are “insoluble” compounds really insoluble? Explain.
- Why is the concentration of a solid, undissolved compound not included in a  $K_{\text{sp}}$  expression?
- Is a supersaturated solution an example of an equilibrium system? Explain.
- When a solution of potassium iodide,  $\text{KI}$ , is added to a solution of lead (II) nitrate,  $\text{Pb}(\text{NO}_3)_2$ , a precipitate forms.
  - Write a chemical equation for the reaction. Indicate the physical state of each reactant and product.
  - How does the product of the concentration of the ions that make up the precipitate compare with the value of  $K_{\text{sp}}$  for the precipitate immediately before precipitation begins?
  - After the precipitate forms, how would you describe the solution with respect to the precipitated compound: unsaturated, saturated, or supersaturated?
- Explain “fractional precipitation” in your own words. On what principle is it based?
- How is the common ion effect an application of Le Châtelier’s principle? Illustrate your answer with an example, including diagrams and chemical equations.



## Making Connections

38. The concentration of calcium,  $\text{Ca}^{2+}$ , ions in a city's water supply is too high.

- (a) Explain, with the help of chemical equation(s), how to use solid sodium carbonate (washing soda or soda ash),  $\text{Na}_2\text{CO}_3$ , to reduce  $[\text{Ca}^{2+}]$  in the water.
- (b) What challenges would engineers need to overcome when implementing the system for reducing  $[\text{Ca}^{2+}]$ ?

## Answers to Practice Problems and Short Answers to Section Review Questions

**Practice Problems:** 1.(a) basic (b) basic (c) neutral (d) acidic

2.(a) acidic;  $\text{NH}_4^+(\text{aq}) + \text{H}_2\text{O}(\ell) \rightleftharpoons \text{NH}_3(\text{aq}) + \text{H}_3\text{O}^+(\text{aq})$  (b) neutral

(c) basic;  $\text{OBr}^-(\text{aq}) + \text{H}_2\text{O}(\ell) \rightleftharpoons \text{HOBr}(\text{aq}) + \text{OH}^-(\text{aq})$  (d) acidic;

$\text{NH}_4^+(\text{aq}) + \text{H}_2\text{O}(\ell) \rightleftharpoons \text{NH}_3(\text{aq}) + \text{H}_3\text{O}^+(\text{aq})$  3.  $\text{C}_6\text{H}_5\text{O}^-$  is the stronger base because  $K_a$  for its conjugate acid is smaller.

4. acidic 5. 7.74 6. 1.70 7. 8.15 8. 5.28

9.(a)  $\text{CuCl}(\text{s}) \rightleftharpoons \text{Cu}^+(\text{aq}) + \text{Cl}^-(\text{aq})$ ;  $K_{\text{sp}} = [\text{Cu}^+][\text{Cl}^-]$

(b)  $\text{BaF}_2(\text{s}) \rightleftharpoons \text{Ba}^{2+}(\text{aq}) + 2\text{F}^-(\text{aq})$ ;  $K_{\text{sp}} = [\text{Ba}^{2+}][\text{F}^-]^2$

(c)  $\text{Ag}_2\text{SO}_4(\text{s}) \rightleftharpoons 2\text{Ag}^+(\text{aq}) + \text{SO}_4^{2-}(\text{aq})$ ;  $K_{\text{sp}} = [\text{Ag}^+]^2[\text{SO}_4^{2-}]$

(d)  $\text{Ca}_3(\text{PO}_4)_2(\text{s}) \rightleftharpoons 3\text{Ca}^{2+}(\text{aq}) + 2\text{PO}_4^{3-}(\text{aq})$ ;  $K_{\text{sp}} = [\text{Ca}^{2+}]^3[\text{PO}_4^{3-}]^2$

10.  $\text{Ag}_2\text{CO}_3(\text{s}) \rightleftharpoons 2\text{Ag}^+(\text{aq}) + \text{CO}_3^{2-}(\text{aq})$ ;  $K_{\text{sp}} = [\text{Ag}^+]^2[\text{CO}_3^{2-}]$

11.  $\text{MgNH}_4\text{PO}_4(\text{s}) \rightleftharpoons \text{Mg}^{2+}(\text{aq}) + \text{NH}_4^+(\text{aq}) + \text{PO}_4^{3-}(\text{aq})$ ;

$K_{\text{sp}} = [\text{Mg}^{2+}][\text{NH}_4^+][\text{PO}_4^{3-}]$  12.(a)  $K_{\text{sp}} = [\text{Fe}^{3+}][\text{NO}_3^-]^3$

(b) smaller 13.  $2.2 \times 10^{-16}$  14.  $1.1 \times 10^{-37}$  15.  $3.2 \times 10^{-11}$

16.(a)  $4.8 \times 10^{-29}$  (b) 1 g solution = 1 mL solution

17.(a)  $1.3 \times 10^{-5}$  mol/L (b)  $7.8 \times 10^{18}$  formula units of  $\text{AgCl}/\text{L}$

(c)  $1.9 \times 10^{-4}\%$  (m/v) 18.  $1.0 \times 10^{-10}$  mol/L

19.  $9.9 \times 10^{-3}$  mol/L; 4.1 g/L

20.  $8.5 \times 10^{12}$  formula units of  $\text{ZnS}/\text{L}$  21.(a)  $1.33 \times 10^{-5}$  mol/L

(b)  $1.18 \times 10^{-9}$  mol/L 22.  $3.9 \times 10^{-6}$  mol/L

23.(a)  $7.02 \times 10^{-3}$  mol/L (b)  $1.97 \times 10^{-4}$  mol/L

24.(a)  $1.6 \times 10^{-2}$  mol/L (b)  $4.0 \times 10^{-4}$  mol/L 25. 9.18 26. 9.03

27. 310 28. 4.16

29.  $Q_{\text{sp}} = 7.5 \times 10^{-5} > K_{\text{sp}}$ , therefore a precipitate forms.

30.  $Q_{\text{sp}} = 3.0 \times 10^{-6} > K_{\text{sp}}$ , therefore a precipitate forms.

31.  $Q_{\text{sp}} = 2.7 \times 10^{-7} > K_{\text{sp}}$ , therefore a precipitate forms.

32.  $Q_{\text{sp}} = 4.2 \times 10^{-12} < K_{\text{sp}}$ , therefore no precipitate forms.

33.  $Q_{\text{sp}} = 8.6 \times 10^{-8} < K_{\text{sp}}$ , therefore no precipitate forms.

34.  $Q_{\text{sp}} = 6.9 \times 10^{-6} < K_{\text{sp}}$ , therefore no precipitate forms.

35.  $Q_{\text{sp}} = 2.2 \times 10^{-9} > K_{\text{sp}}$ , therefore a precipitate forms.

36.  $Q_{\text{sp}} = 1.0 \times 10^{-5} > K_{\text{sp}}$ , therefore a precipitate forms.

**Section Review: 9.1:** 1. sodium carbonate 2.(a) no reaction

(b)  $\text{CH}_3\text{NH}_3^+(\text{aq}) + \text{H}_2\text{O}(\ell) \rightleftharpoons \text{CH}_3\text{NH}_2(\text{aq}) + \text{H}_3\text{O}^+(\text{aq})$ ; acidic

(c) no reaction (d)  $\text{OCl}^-(\text{aq}) + \text{H}_2\text{O}(\ell) \rightleftharpoons \text{HOCl}(\text{aq}) + \text{OH}^-(\text{aq})$ ;

basic 3. acidic 4.  $\text{Ca}(\text{OH})_2$ ,  $\text{CaF}_2$ ,  $\text{KNO}_3$ ,  $\text{NH}_4\text{NO}_3$ ,  $\text{HNO}_3$

5.(b) 8.7 (c) 0.167 mol/L (d) phenolphthalein

7. phenolphthalein 8. 5.97 9.2: 5.(a)  $1.6 \times 10^{-6}$  (b)  $9.6 \times 10^{17}$

formula units of  $\text{BaF}_2/\text{L}$  6.(b) 4.74 7. 3.17

8.(b)  $1.0 \times 10^{-5}$  mol/L;  $2.4 \times 10^{-3}$  g/L (c)  $1.3 \times 10^{-9}$  mol/L;

$3.0 \times 10^{-7}$  g/L 9.3: 2.  $Q_{\text{sp}} = 1.7 \times 10^{-10} > K_{\text{sp}}$ , therefore no precipitate forms. 3. 17 mg 4. one drop 5.(b) 0.18 mg