

SOLUBILITY AND SIMULTANEOUS EQUILIBRIA

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Small marine organisms called corals extract calcium ions and carbonate ions from sea water and precipitate calcium carbonate to form their shells. Over time, these small shells become the major structural feature of coral reefs, such as the one shown here. The equilibria involved in the solubility of metal salts constitute the major focus of this chapter. (*Scott Tuason/Image Quest Marine*)



CHAPTER OUTLINE

17.1 An insoluble salt is in equilibrium with the solution around it

17.2 Solubility equilibria of metal oxides and sulfides involve reaction with water

17.3 Metal ions can be separated by selective precipitation

17.4 Complex ions participate in equilibria in aqueous solutions

17.5 Complex ion formation increases the solubility of a salt

THIS CHAPTER IN CONTEXT

In the preceding chapters you learned how the principles of equilibrium can be applied to aqueous solutions of acids and bases. In this chapter we extend these principles to aqueous reactions that involve the formation and dissolving of precipitates (a topic we introduced in Chapter 4). Many such reactions are common in the world around us. For example, groundwater rich in carbon dioxide dissolves deposits of calcium carbonate, producing vast underground caverns, and as the remaining calcium-containing solution gradually evaporates, stalactites and stalagmites form. Within living organisms, precipitation reactions form the hard calcium carbonate shells of clams, oysters, and coral as well as the unwanted calcium oxalate and calcium phosphate deposits we call kidney stones. Also, dilute acids in our mouths promote the dissolving of tooth enamel, which is composed of a mineral made up of calcium phosphate and calcium hydroxide.

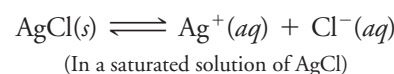
In this chapter you will learn how we can calculate the solubilities of “insoluble” salts in water and in other solutions, and how the formation of substances called complex ions can affect solubilities. The concepts we develop here can tell us when precipitates will form and when they will dissolve, and we can use these in a practical lab setting in the separation of metal ions for chemical analysis.

17.1

AN INSOLUBLE SALT IS IN EQUILIBRIUM WITH THE SOLUTION AROUND IT

The equilibrium constant for an “insoluble” salt is called the solubility product constant, K_{sp}

None of the salts we described in Chapter 4 as being insoluble are *totally* insoluble. For example, the solubility rules tell us that AgCl is “insoluble,” but if some solid AgCl is placed in water, a very small amount does dissolve. Once the solution has become saturated, the following equilibrium is established between the undissolved AgCl and its ions in the solution.



This is a heterogeneous equilibrium because it involves a solid reactant (AgCl) in equilibrium with ions in aqueous solution. Using the procedure developed in Section 14.4 (page 579), we write the equilibrium law as follows, omitting the solid from the mass action expression.

$$[\text{Ag}^+][\text{Cl}^-] = K_{sp} \quad (17.1)$$

The equilibrium constant, K_{sp} , is called the **solubility product constant** (because the system is a *solubility* equilibrium and the constant equals a *product* of ion concentrations).

It's important that you understand the distinction between solubility and solubility product. The *solubility* of a salt is the amount of the salt that dissolves in a given amount of solvent to give a saturated solution. The *solubility product* is the product of the molar concentrations of the ions in the saturated solution, raised to appropriate powers (see below).

The solubilities of salts change with temperature, so a value of K_{sp} applies only at the temperature at which it was determined. Some typical K_{sp} values are in Table 17.1 and in Appendix C.

In solubility equilibria, the reaction quotient is called the ion product

In preceding chapters we described the value of the mass action expression as the reaction quotient, Q . For simple solubility equilibria like those discussed in this section, the mass action expression is a product of ion concentrations raised to appropriate powers, so Q is often called the **ion product** of the salt. Thus, for AgCl,

$$\text{Ion product} = [\text{Ag}^+][\text{Cl}^-] = Q$$

At any dilution of a salt throughout the range of possibilities for an *unsaturated* solution, there will be varying values for the ion concentrations and, therefore, for Q . However, Q acquires a constant value, K_{sp} , in a *saturated* solution. When a solution is less than saturated, the value of Q is less than K_{sp} . Thus, we can use the numerical value of Q for a given solution as a test for saturation by comparing it to the value of K_{sp} .

Many salts produce more than one of a given ion per formula unit when they dissociate, and this introduces exponents into the ion product expression. For example, when silver chromate, Ag_2CrO_4 , precipitates (Figure 17.1), it enters into the following solubility equilibrium.



The equilibrium law is obtained following the procedure we developed in Chapter 14, using coefficients as exponents in the mass action expression.

Recall that when salts dissolve, they dissociate essentially completely, so the equilibrium is between the solid and the ions that are in the solution.

TOOLS

Solubility product constant, K_{sp}

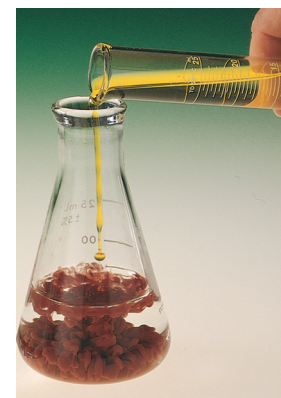


FIG. 17.1 Silver chromate.

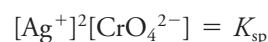
When sodium chromate is added to a solution of silver nitrate, deep red “insoluble” silver chromate, Ag_2CrO_4 , precipitates. (Michael Watson.)

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TABLE 17.1 Solubility Product Constants

Type	Salt	Ions of Salt	K_{sp} (25 °C)
Halides	CaF ₂	\rightleftharpoons Ca ²⁺ + 2F ⁻	3.9×10^{-11}
	AgCl	\rightleftharpoons Ag ⁺ + Cl ⁻	1.8×10^{-10}
	AgBr	\rightleftharpoons Ag ⁺ + Br ⁻	5.0×10^{-13}
	AgI	\rightleftharpoons Ag ⁺ + I ⁻	8.3×10^{-17}
	PbF ₂	\rightleftharpoons Pb ²⁺ + 2F ⁻	3.6×10^{-8}
	PbCl ₂	\rightleftharpoons Pb ²⁺ + 2Cl ⁻	1.7×10^{-5}
	PbBr ₂	\rightleftharpoons Pb ²⁺ + 2Br ⁻	2.1×10^{-6}
	PbI ₂	\rightleftharpoons Pb ²⁺ + 2I ⁻	7.9×10^{-9}
Hydroxides	Al(OH) ₃	\rightleftharpoons Al ³⁺ + 3OH ⁻	3×10^{-34} ^(a)
	Ca(OH) ₂	\rightleftharpoons Ca ²⁺ + 2OH ⁻	6.5×10^{-6}
	Fe(OH) ₂	\rightleftharpoons Fe ²⁺ + 2OH ⁻	7.9×10^{-16}
	Fe(OH) ₃	\rightleftharpoons Fe ³⁺ + 3OH ⁻	1.6×10^{-39}
	Mg(OH) ₂	\rightleftharpoons Mg ²⁺ + 2OH ⁻	7.1×10^{-12}
	Zn(OH) ₂	\rightleftharpoons Zn ²⁺ + 2OH ⁻	3.0×10^{-16} ^(b)
Carbonates	Ag ₂ CO ₃	\rightleftharpoons 2Ag ⁺ + CO ₃ ²⁻	8.1×10^{-12}
	MgCO ₃	\rightleftharpoons Mg ²⁺ + CO ₃ ²⁻	3.5×10^{-8}
	CaCO ₃	\rightleftharpoons Ca ²⁺ + CO ₃ ²⁻	4.5×10^{-9} ^(c)
	SrCO ₃	\rightleftharpoons Sr ²⁺ + CO ₃ ²⁻	9.3×10^{-10}
	BaCO ₃	\rightleftharpoons Ba ²⁺ + CO ₃ ²⁻	5.0×10^{-9}
	CoCO ₃	\rightleftharpoons Co ²⁺ + CO ₃ ²⁻	1.0×10^{-10}
	NiCO ₃	\rightleftharpoons Ni ²⁺ + CO ₃ ²⁻	1.3×10^{-7}
	ZnCO ₃	\rightleftharpoons Zn ²⁺ + CO ₃ ²⁻	1.0×10^{-10}
Chromates	Ag ₂ CrO ₄	\rightleftharpoons 2Ag ⁺ + CrO ₄ ²⁻	1.2×10^{-12}
	PbCrO ₄	\rightleftharpoons Pb ²⁺ + CrO ₄ ²⁻	1.8×10^{-14} ^(d)
Sulfates	CaSO ₄	\rightleftharpoons Ca ²⁺ + SO ₄ ²⁻	2.4×10^{-5}
	SrSO ₄	\rightleftharpoons Sr ²⁺ + SO ₄ ²⁻	3.2×10^{-7}
	BaSO ₄	\rightleftharpoons Ba ²⁺ + SO ₄ ²⁻	1.1×10^{-10}
	PbSO ₄	\rightleftharpoons Pb ²⁺ + SO ₄ ²⁻	6.3×10^{-7}
Oxalates	CaC ₂ O ₄	\rightleftharpoons Ca ²⁺ + C ₂ O ₄ ²⁻	2.3×10^{-9}
	MgC ₂ O ₄	\rightleftharpoons Mg ²⁺ + C ₂ O ₄ ²⁻	8.6×10^{-5}
	BaC ₂ O ₄	\rightleftharpoons Ba ²⁺ + C ₂ O ₄ ²⁻	1.2×10^{-7}
	FeC ₂ O ₄	\rightleftharpoons Fe ²⁺ + C ₂ O ₄ ²⁻	2.1×10^{-7}
	PbC ₂ O ₄	\rightleftharpoons Pb ²⁺ + C ₂ O ₄ ²⁻	2.7×10^{-11}

^(a)Alpha form. ^(b)Amorphous form. ^(c)Calcite form. ^(d)At 10 °C.



Thus, the ion product contains the ion concentrations raised to powers equal to the number of ions released per formula unit. This means that to obtain the correct ion product expression you have to know the formulas of the ions that make up the salt. In other words, you have to realize that Ag₂CrO₄ is composed of Ag⁺ and the polyatomic anion CrO₄²⁻. If necessary, review the list of polyatomic ions in Table 2.8 on page 69.

Practice Exercise 1: Write the equation for the equilibrium involved in the solubility of barium phosphate, Ba₃(PO₄)₂, and write the equilibrium law corresponding to K_{sp} . (Hint: Remember that it's a heterogeneous equilibrium.)

Practice Exercise 2: What are the ion product expressions for the following salts? (a) barium oxalate, (b) silver sulfate

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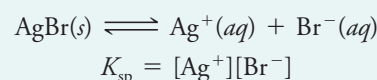
 K_{sp} can be determined from molar solubilities

One way to determine the value of K_{sp} for a salt is to measure its solubility—how much of the salt is required to give a saturated solution in a specified amount of solution. It is useful to express this as the **molar solubility**, which equals *the number of moles of salt dissolved in one liter of its saturated solution*. The molar solubility can be used to calculate the K_{sp} under the assumption that all of the salt that dissolves is 100% dissociated into the ions implied in the salt's formula.¹


EXAMPLE 17.1
 Calculating K_{sp} from Solubility Data

Silver bromide, AgBr, is the light-sensitive compound used in nearly all photographic film. The solubility of AgBr in water was measured to be $1.3 \times 10^{-4} \text{ g L}^{-1}$ at 25 °C. Calculate K_{sp} for AgBr at that temperature.

ANALYSIS: As usual, we begin with the chemical equation for the equilibrium, from which we construct the equilibrium law (here, the expression for K_{sp}).



To calculate K_{sp} , we need the concentrations of the ions expressed in moles per liter. We can obtain these from the molar solubility—the number of moles of AgBr dissolved per liter. Therefore, the first step will be to change $1.3 \times 10^{-4} \text{ g L}^{-1}$ to moles per liter.

For problems dealing with solubility, the concentration table is an especially useful tool. In setting up the table, it is helpful if we imagine the formation of the saturated solution to occur stepwise. First, we will look at the composition of the solvent into which the salt will be placed. Does it contain any of the ions involved in the equilibrium? If it doesn't, the initial concentrations will be set equal to zero. However, if the solvent contains a solute that is a source of one of the ions in the equilibrium, we will use its concentration as the initial concentration of that ion.

When the salt dissolves, the concentrations of the ions increase, so the entries in the “change” row will be positive and will have values determined by the formula of the salt. We will obtain these from the molar solubility.

The entries in the last row, which are the equilibrium values, are obtained by adding the initial concentrations to the changes. Once we have the equilibrium ion concentrations, we substitute them into the ion product expression to calculate K_{sp} .

SOLUTION: First, we calculate the number of moles of AgBr dissolved per liter.

$$\text{Molar solubility} = \frac{1.3 \times 10^{-4} \text{ g AgBr}}{1.00 \text{ L soln}} \times \frac{1.00 \text{ mol AgBr}}{187.77 \text{ g AgBr}} = 6.9 \times 10^{-7} \text{ mol L}^{-1}$$

Now we can begin to set up the concentration table, which is shown on the next page. Notice first that there are no entries in the “reactant” column. This is because AgBr is a solid and doesn't appear in the mass action expression.

Initial Concentrations In the first row, under the formulas of the ions, we enter the initial concentrations of Ag^+ and Br^- . Remember, these are the concentrations of the ions present in the solvent before any of the AgBr dissolves. In this case the solvent is pure water. Neither Ag^+ nor Br^- are present in pure water, so we set the initial concentrations equal to zero.

¹ This assumption works reasonably well for slightly soluble salts made up of singly charged ions, like silver bromide. For simplicity, and to illustrate the nature of calculations involving solubility equilibria, we will work on the assumption that all salts behave as though they are 100% dissociated. This is not entirely true, especially for salts of multiply charged ions, so the accuracy of our calculations is limited. We discussed the reasons for the incomplete dissociation of salts in Section 12.9.

Changes in Concentrations In the “change” row, we enter data on how the concentrations of the $\text{Ag}^+(aq)$ and $\text{Br}^-(aq)$ change when the AgBr dissolves. Because dissolving the salt always increases these concentrations, these entries are always positive. They are also related to each other by the stoichiometry of the dissociation reaction. Thus, when AgBr dissolves, Ag^+ and Br^- ions are released in a 1:1 ratio. So, when 6.9×10^{-7} mol of AgBr dissolves (per liter), 6.9×10^{-7} mol of Ag^+ ion and 6.9×10^{-7} mol of Br^- ion go into solution. The concentrations of these species thus *change* (increase) by those amounts.

Equilibrium Concentrations As usual, we obtain the equilibrium values by adding the “initial concentrations” to the “changes.”

There are no entries in the column under $\text{AgBr}(s)$ because this substance does not appear in the K_{sp} expression.

	$\text{AgBr}(s)$	\rightleftharpoons	$\text{Ag}^+(aq)$	+	$\text{Br}^-(aq)$
Initial concentrations (M)	No entries in this column		0		0
Changes in concentrations when AgBr dissolves (M)			$+6.9 \times 10^{-7}$		$+6.9 \times 10^{-7}$
Equilibrium concentrations (M)			6.9×10^{-7}		6.9×10^{-7}

We now substitute the equilibrium ion concentrations into the K_{sp} expression.

The K_{sp} we calculated from the solubility data here differs by only 4% from the value in Table 17.1.

$$\begin{aligned} K_{sp} &= [\text{Ag}^+][\text{Br}^-] \\ &= (6.9 \times 10^{-7})(6.9 \times 10^{-7}) \\ &= 4.8 \times 10^{-13} \end{aligned}$$

The K_{sp} of AgBr is thus calculated to be 4.8×10^{-13} at 25 °C.

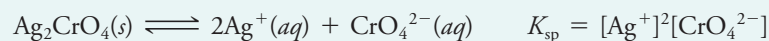
IS THE ANSWER REASONABLE? We’ve divided 1.3×10^{-4} by a number that’s approximately 200, which would give a value of about 6.5×10^{-7} , so our molar solubility seems reasonable. (Also, we know AgBr has a very low solubility in water, so we expect the molar solubility to be very small.) The reasoning involved in the change row also makes sense; the number of moles of ions formed per liter must each equal the number of moles of AgBr that dissolve. Finally, if we round 6.9×10^{-7} to 7×10^{-7} and square it, we obtain $49 \times 10^{-14} = 4.9 \times 10^{-13}$. Our answer of 4.8×10^{-13} seems to be okay.

EXAMPLE 17.2

Calculating K_{sp} from Molar Solubility Data

The molar solubility of silver chromate, Ag_2CrO_4 , in water is 6.7×10^{-5} mol L^{-1} at 25 °C. What is K_{sp} for Ag_2CrO_4 ?

ANALYSIS: We begin with the equilibrium equation and K_{sp} expression.



Once again, we use the concentration table as our tool for analyzing the concentrations.

The solute is pure water, so neither Ag^+ nor CrO_4^{2-} are present before the salt dissolves; their initial concentrations are zero. For the “change” row, we have to be careful to take into account the formula of the salt. In a liter of water, when 6.7×10^{-5} mol of Ag_2CrO_4 dissolves, we obtain 6.7×10^{-5} mol of CrO_4^{2-} and $2 \times (6.7 \times 10^{-5}$ mol) of Ag^+ . With this information, we can fill in the “initial” and “change” rows.

SOLUTION: As usual, we add the values in the “initial” and “change” rows to obtain the equilibrium concentrations of the ions.

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	$\text{Ag}_2\text{CrO}_4(s)$	\rightleftharpoons	$2\text{Ag}^+(aq)$	+	$\text{CrO}_4^{2-}(aq)$
Initial concentrations (M)			0		0
Changes in concentrations when Ag_2CrO_4 dissolves (M)			$+ [2 \times (6.7 \times 10^{-5})]$ $= +1.3 \times 10^{-4}$		$+6.7 \times 10^{-5}$
Equilibrium concentrations (M)			1.3×10^{-4}		6.7×10^{-5}

Substituting the equilibrium concentrations into the mass action expression for K_{sp} gives

$$\begin{aligned} K_{\text{sp}} &= (1.3 \times 10^{-4})^2(6.7 \times 10^{-5}) \\ &= 1.1 \times 10^{-12} \end{aligned}$$

So the K_{sp} of Ag_2CrO_4 at 25 °C is calculated to be 1.1×10^{-12} .

IS THE ANSWER REASONABLE? The critical step in solving the problem correctly is placing the correct quantities in the “initial” and “change” rows. The Ag_2CrO_4 is dissolved in water, so the initial concentrations of the ions must be zero; these entries are okay. For the “changes,” it’s important to remember that the quantities are related to each other by the coefficients in the chemical equation. That means the change for Ag^+ must be twice as large as the change for CrO_4^{2-} . Studying the table, we see that we’ve done this correctly. We can also see that we’ve added the “change” to the “initial” values correctly, and that we’ve performed the proper arithmetic in evaluating the mass action expression.

Practice Exercise 3: The solubility of thallium(I) iodide, TlI, in water at 20 °C is $5.9 \times 10^{-3} \text{ g L}^{-1}$. Using this fact, calculate K_{sp} for TlI on the assumption that it is 100% dissociated in the solution. (Hint: What is the molar solubility of TlI?)

Practice Exercise 4: One liter of water is able to dissolve $2.15 \times 10^{-3} \text{ mol}$ of PbF_2 at 25 °C. Calculate the value of K_{sp} for PbF_2 .

Now let’s introduce a complication. Let’s suppose that the aqueous system into which we’re dissolving a slightly soluble salt is not pure water, but instead is a solution of a solute that provides one of the ions of the salt.

EXAMPLE 17.3

Calculating K_{sp} from Molar Solubility Data

The molar solubility of PbCl_2 in a 0.10 M NaCl solution is $1.7 \times 10^{-3} \text{ mol L}^{-1}$ at 25 °C. Calculate the K_{sp} for PbCl_2 .

ANALYSIS: Again, we start by writing the equation for the equilibrium and the K_{sp} expression.



In this problem, the PbCl_2 is being dissolved not in pure water but in 0.10 M NaCl , which contains 0.10 M Cl^- . (It also contains 0.10 M Na^+ , but that’s not important here because Na^+ doesn’t affect the equilibrium and so doesn’t appear in the K_{sp} expression.) The initial concentration of Pb^{2+} is zero because none is in solution to begin with. The *initial* concentration of Cl^- , however, is 0.10 M .

For the change row, we note that when 1.7×10^{-3} mole of PbCl_2 dissolves per liter, the Pb^{2+} concentration increases by $1.7 \times 10^{-3} M$ and the Cl^- concentration increases by $2 \times (1.7 \times 10^{-3} M)$. With these data we build the concentration table and evaluate the ion product to obtain K_{sp} .

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SOLUTION: Here is the completed concentration table based on the analysis above.

	$\text{PbCl}_2(s) \rightleftharpoons \text{Pb}^{2+}(aq)$	$+ 2\text{Cl}^-(aq)$
Initial concentrations (M)	0	0.10 (because the solvent is 0.10 M NaCl)
Changes in concentrations when PbCl_2 dissolves (M)	$+1.7 \times 10^{-3}$	$+ [2 \times (1.7 \times 10^{-3})] = +3.4 \times 10^{-3}$
Equilibrium concentrations (M)	1.7×10^{-3}	$0.10 + 0.0034 = 0.10$ (rounded correctly)

Substituting the equilibrium concentrations into the K_{sp} expression gives

$$\begin{aligned} K_{\text{sp}} &= (1.7 \times 10^{-3})(0.10)^2 \\ &= 1.7 \times 10^{-5} \end{aligned}$$

The K_{sp} of PbCl_2 is calculated to be 1.7×10^{-5} at 25 °C.

IS THE ANSWER REASONABLE? The solvent here is 0.10 M NaCl, so we have Cl^- in the mixture before any PbCl_2 dissolves. We check the “initial” row to be sure we’ve entered 0.10 M under Cl^- , and we have. Next, we check to be sure we’ve taken the stoichiometry of the equilibrium equation into account when placing values into the “change” row. We’ve done this correctly, too, because the change for Cl^- is twice the change for Pb^{2+} . Finally, we can check to be sure we’ve performed the correct arithmetic on the equilibrium concentrations. We have, so our answer should be correct.

Practice Exercise 5: The molar solubility of Ag_2SO_4 in a solution containing 28.4 g Na_2SO_4 per liter is $4.3 \times 10^{-3} M$. What is K_{sp} for Ag_2SO_4 ? (Hint: What is the molarity of the Na_2SO_4 solution?)

Practice Exercise 6: At 25 °C, the molar solubility of CoCO_3 in a 0.10 M Na_2CO_3 solution is $1.0 \times 10^{-9} \text{ mol L}^{-1}$. Calculate the value of K_{sp} for CoCO_3 .

Practice Exercise 7: The molar solubility of PbF_2 in a 0.10 M $\text{Pb}(\text{NO}_3)_2$ solution at 25 °C is $3.1 \times 10^{-4} \text{ mol L}^{-1}$. Calculate the value of K_{sp} for PbF_2 .

Molar solubility can be calculated from K_{sp}

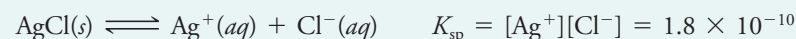
Besides calculating K_{sp} from solubility information, we can also compute solubilities from values of K_{sp} . The following examples illustrate the calculations.²

EXAMPLE 17.4

Calculating Molar Solubility from K_{sp}

What is the molar solubility of AgCl in pure water at 25 °C?

ANALYSIS: To solve this problem, we need the chemical equation, the equilibrium law, and the value of K_{sp} for AgCl (which we obtain from Table 17.1). The relevant equations are



²As noted earlier, these calculations ignore the fact that the salt that dissolves is not truly 100% dissociated into the ions implied in the salt’s formula. This is particularly a problem with the salts of multiply charged ions, so the solubilities of such salts, when calculated from their K_{sp} values, must be taken as rough estimates. In fact, many calculations involving K_{sp} give values that are merely estimates.

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Now we can build a concentration table. First, we see that the solvent is pure water, so neither Ag^+ nor Cl^- ion is present in solution at the start; their *initial* concentrations are zero.

Next, we turn to the “change” row. If we knew what the changes were, we could calculate the equilibrium concentrations and figure out the molar solubility. But we don’t know the changes, so we will have to find them algebraically. To do this, *we will define our unknown x as the molar solubility of the salt*—the number of moles of AgCl that dissolves in one liter. Because 1 mol of AgCl yields 1 mol Ag^+ and 1 mol Cl^- , the concentration of each of these ions increases by x (their changes are each $+x$).

SOLUTION: Our concentration table is as follows.

	$\text{AgCl}(s)$	\rightleftharpoons	$\text{Ag}^+(aq)$	+	$\text{Cl}^-(aq)$
Initial concentrations (M)			0		0
Changes in concentrations when AgCl dissolves (M)			$+x$		$+x$
Equilibrium concentrations (M)			x		x

We make the substitutions into the K_{sp} expression, using equilibrium quantities from the last row of the table:

$$(x)(x) = 1.8 \times 10^{-10}$$

$$x = 1.3 \times 10^{-5}$$

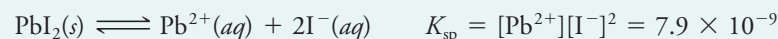
The calculated molar solubility of AgCl in water at 25°C is $1.3 \times 10^{-5} \text{ mol L}^{-1}$.

IS THE ANSWER REASONABLE? The solvent is water, so the initial concentrations are zero. If x is the molar solubility, then the changes in the concentrations of Ag^+ and Cl^- when the salt dissolves must also be equal to x . We can also check the algebra, which we’ve done correctly, so the answer seems to be okay.

By defining x as the molar solubility, the coefficients of x in the “change” row are the same as the coefficients of Ag^+ and Cl^- in the equation for the equilibrium.

Calculate the molar solubility of lead iodide in water from its K_{sp} at 25°C .

ANALYSIS: First, we need the formula for lead iodide, which is PbI_2 (obtained from the rules of nomenclature in Chapter 2). To set up the problem, we begin with the equation for the equilibrium and the K_{sp} expression. We obtain K_{sp} from Table 17.1.



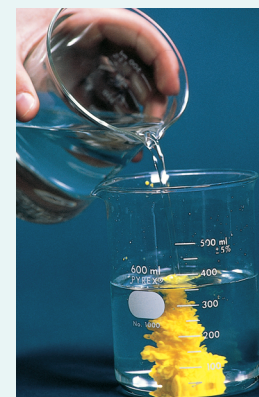
The solvent is water, so the initial concentrations of the ions are zero. As before, we will define x as the molar solubility of the salt. By doing this, the coefficients of x in the “change” row will be identical to the coefficients of the ions in the chemical equation. This assures us that the changes in the concentrations are in the correct mole ratio.

SOLUTION: Here is the concentration table.

	$\text{PbI}_2(s)$	\rightleftharpoons	$\text{Pb}^{2+}(aq)$	+	$2\text{I}^-(aq)$
Initial concentrations (M)			0		0
Changes in concentrations when PbI_2 dissolves (M)			$+x$		$+2x$
Equilibrium concentrations (M)			x		$2x$

EXAMPLE 17.5

Calculating Molar Solubility from K_{sp}



A precipitate of yellow PbI_2 forms when the two colorless solutions, one with sodium iodide and the other of lead(II) nitrate, are mixed. (Lawrence Migdale/Photo Researchers.)

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Substituting equilibrium quantities into the K_{sp} expression gives

$$\begin{aligned}K_{sp} &= (x)(2x)^2 = 4x^3 = 7.9 \times 10^{-9} \\x^3 &= 2.0 \times 10^{-9} \\x &= 1.3 \times 10^{-3}\end{aligned}$$

Thus, the molar solubility of PbI_2 is calculated to be $1.3 \times 10^{-3} \text{ mol L}^{-1}$.

IS THE ANSWER REASONABLE? We check the entries in the table. The solvent is water, so the initial concentrations are equal to zero. By setting x equal to the moles per liter of PbI_2 that dissolves (i.e., the molar solubility), the coefficients of x in the “change” row have to be the same as the coefficients of Pb^{2+} and Cl^- in the chemical equation. The entries in the “change” row are okay. In performing the algebra, notice that when we square $2x$, we get $4x^2$. Multiplying $4x^2$ by x gives $4x^3$. After that, the rest is straightforward.

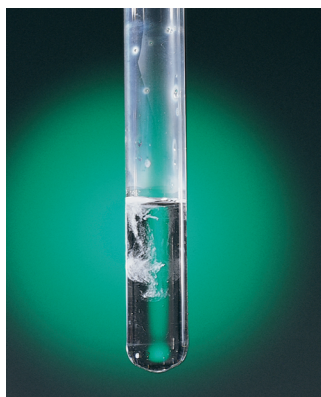


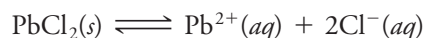
FIG. 17.2 The common ion effect. The test tube shown here initially held a saturated solution of NaCl , where the equilibrium $\text{NaCl}(s) \rightleftharpoons \text{Na}^+(aq) + \text{Cl}^-(aq)$ had been established. Addition of a few drops of concentrated HCl , containing a high concentration of the common ion Cl^- , forced the equilibrium to shift to the left. This caused some white crystals of solid NaCl to precipitate. (Michael Watson.)

Practice Exercise 8: Calculate the molar solubility of Ag_3PO_4 in water. Its $K_{sp} = 2.8 \times 10^{-18}$. (Hint: Review the algebra in the preceding example.)

Practice Exercise 9: What is the calculated molar solubility in water at 25°C of (a) AgBr and (b) Ag_2CO_3 ?

A salt is less soluble if the solvent already contains an ion of the salt

Suppose that we stir some lead chloride (a compound having a low solubility) with water long enough to establish the following equilibrium.



If we now add a concentrated solution of a soluble lead compound, such as $\text{Pb}(\text{NO}_3)_2$, the increased concentration of Pb^{2+} in the PbCl_2 solution will drive the position of equilibrium to the left, causing some PbCl_2 to precipitate. The phenomenon is simply an application of Le Châtelier’s principle, the net result being that PbCl_2 is less soluble in a solution that contains Pb^{2+} from another source than it is in pure water. The same effect is produced if a concentrated solution of a soluble chloride salt such as NaCl is added to the saturated PbCl_2 solution. The added Cl^- will drive the equilibrium to the left, reducing the amount of dissolved PbCl_2 .

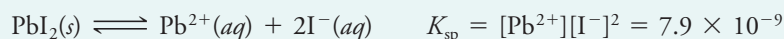
The phenomenon described above is an example of the *common ion effect*, which we described in Chapter 16. In this case, Pb^{2+} is the common ion when we add $\text{Pb}(\text{NO}_3)_2$ and Cl^- is the common ion when we add NaCl . Figure 17.2 shows how even a relatively soluble salt, NaCl , can be forced out of its saturated solution simply by adding concentrated hydrochloric acid, which serves as a source of the common ion, Cl^- . The common ion effect can dramatically lower the solubility of a salt, as the next example demonstrates.

EXAMPLE 17.6

Calculations Involving the Common Ion Effect

What is the molar solubility of PbI_2 in a 0.10 M NaI solution?

ANALYSIS: We begin with the chemical equation for the equilibrium, the appropriate K_{sp} expression, and the value of K_{sp} obtained from Table 17.1.



As usual, our tool to analyze what happens is the concentration table. As before, we imagine that we are adding the PbI_2 to a solvent into which it dissolves. This time, however, the solvent isn’t water; it’s a solution of NaI , which contains one of the ions of the salt PbI_2 . Therefore, our initial concentrations will not both be zero. The solvent doesn’t contain any lead compound,

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so the initial concentration of Pb^{2+} is equal to zero, but the solvent does contain 0.10 M NaI , which is completely dissociated and yields 0.10 M Na^+ and 0.10 M I^- . The initial concentration of I^- is therefore 0.10 M . These are the values we place in the “initial” row.

Next, we let x be the molar solubility of PbI_2 . When x mol of PbI_2 dissolves per liter, the concentration of Pb^{2+} changes by $+x$ and that of I^- changes by twice as much, or $+2x$. Finally, the equilibrium concentrations are obtained by summing the initial concentrations and the changes.

SOLUTION: Here is the concentration table.

	$\text{PbI}_2(\text{s})$	\rightleftharpoons	$\text{Pb}^{2+}(\text{aq})$	+	$2\text{I}^-(\text{aq})$
Initial concentrations (M)			0		0.10
Changes in concentrations when PbI_2 dissolves (M)			$+x$		$+2x$
Equilibrium concentrations (M)			x		$0.10 + 2x$

Substituting equilibrium values into the K_{sp} expression gives

$$K_{\text{sp}} = (x)(0.10 + 2x)^2 = 7.9 \times 10^{-9}$$

Just a brief inspection reveals that solving this expression for x will be difficult if we cannot simplify the math. Fortunately, a simplification is possible, because the small value of K_{sp} for PbI_2 tells us that the salt has a very low solubility. This means very little of the salt will dissolve, so x (or even $2x$) will be quite small. Let's assume that $2x$ will be much smaller than 0.10 . If this is so, then

$$0.10 + 2x \approx 0.10 \quad (\text{assuming } 2x \text{ is negligible compared to } 0.10)$$

Substituting 0.10 M for the I^- concentration gives

$$\begin{aligned} K_{\text{sp}} &= (x)(0.10)^2 = 7.9 \times 10^{-9} \\ x &= \frac{7.9 \times 10^{-9}}{(0.10)^2} \\ &= 7.9 \times 10^{-7}\text{ M} \end{aligned}$$

Thus, the molar solubility of PbI_2 in 0.10 M NaI solution is calculated to be $7.9 \times 10^{-7}\text{ M}$.

IS THE ANSWER REASONABLE? Check the entries in the table. The initial concentrations come from the solvent, which contains no Pb^{2+} but does contain 0.10 M I^- . By letting x equal the molar solubility, the coefficients of x in the “change” row equal the coefficients in the equation for the equilibrium. *We should also check to see if our simplifying assumption is valid.* Notice that $2x$, which equals 1.6×10^{-6} , is indeed vastly smaller than 0.10 , just as we anticipated. (If we add 1.6×10^{-6} to 0.10 and round correctly, we obtain 0.10 .)

Practice Exercise 10: Calculate the molar solubility of AgI in 0.20 M CaI_2 solution. Compare the answer to the calculated molar solubility of AgI in pure water. (Hint: What is the I^- concentration in 0.20 M CaI_2 ?)

Practice Exercise 11: Calculate the molar solubility of $\text{Fe}(\text{OH})_3$ in a solution where the OH^- concentration is initially 0.050 M . Assume the dissociation of $\text{Fe}(\text{OH})_3$ is 100%.

A Mistake to Avoid

The most common mistake that students make with problems like Example 17.6 is to use the coefficient of an ion in the solubility equilibrium at the wrong moment in the calculation. The coefficient of I^- in the PbI_2 equilibrium is 2. The mistake is to use this 2 to double the *initial* concentration of I^- . However, the *initial* concentration of I^- was

■ READ THESE TWO PARAGRAPHS!

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provided not by PbI_2 but by NaI . When 0.10 mol of NaI dissociates, it gives 0.10 mol of I^- , not 2×0.10 mol. *The coefficients in the equation for the equilibrium are only used to obtain the quantities in the “change” row.*

To avoid mistakes, it is useful to always view the formation of the final solution as a two-step process. You begin with a solvent into which the “insoluble solid” will be placed. In some problems, the solvent may be pure water, in which case the initial concentrations of the ions will be zero. In other problems, like Example 17.6, the solvent will be a *solution* that contains a common ion. When this is so, first decide what the concentration of the common ion is and enter that value into the “initial concentration” row of the table. Next, imagine that the solid is added to the solvent and a little of it dissolves. *The amount that dissolves is what gives the values in the “change” row.* These entries must be in the same ratio as the coefficients in the equilibrium, which is accomplished if we let x be the molar solubility of the salt. Then the coefficients of x will be the same as the coefficients of the ions in the chemical equation for the equilibrium.

In Example 17.5 (page 699) we found that the molar solubility of PbI_2 in *pure* water is $1.3 \times 10^{-3} M$. In water that contains 0.10 M NaI (Example 17.6), the solubility of PbI_2 is $7.9 \times 10^{-7} M$, well over a thousand times smaller. As we said, the common ion effect can cause huge reductions in the solubilities of sparingly soluble compounds by shifting the equilibrium toward the formation of the solid.

We can use K_{sp} to determine if a precipitate will form in a solution

If we know the anticipated concentrations of the ions of a salt in a solution, we can use the value of K_{sp} for the salt to predict whether or not a precipitate should form. This is because the computed value for Q (the ion product) can tell us whether a solution is unsaturated, saturated, or supersaturated. *For a precipitate of a salt to form, the solution must be supersaturated.*

If the solution is unsaturated, its ion concentrations are less than required for saturation, Q is less than K_{sp} , and no precipitate should form. For a saturated solution, we have Q equal to K_{sp} , and no precipitate will form. (If a precipitate were to form, the solution would become unsaturated and the precipitate would redissolve.) If the solution is supersaturated, the ion concentrations exceed those required for saturation and Q is larger than K_{sp} . Only in this last instance should we expect a precipitate to form. This can be summarized as follows.

TOOLS
Ion product, Q , of a salt



Precipitate will form	$Q > K_{\text{sp}}$	(supersaturated)
No precipitate will form	$Q = K_{\text{sp}}$	(saturated)
	$Q < K_{\text{sp}}$	(unsaturated)

Let's look at some sample calculations.

EXAMPLE 17.7

Predicting whether a Precipitate Will Form

Suppose we wish to prepare 0.500 L of a solution containing 0.0075 mol of NaCl and 0.075 mol of $\text{Pb}(\text{NO}_3)_2$. Knowing from the solubility rules that the chloride of Pb^{2+} is “insoluble,” we are concerned that a precipitate of PbCl_2 might form. Will it?

ANALYSIS: Our tool for answering this question is the criteria described above, which tell us a precipitate will only form if the computed Q for the solution is larger than K_{sp} . Therefore, our first task is to compute the value of the ion product (Q) appropriate for PbCl_2 *using the concentrations of the ions in the solution to be prepared.* This means we need the correct form of the ion product, which we can obtain by writing the solubility equilibrium and the K_{sp} expression that applies to a saturated solution of PbCl_2 .

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From Table 17.1, $K_{\text{sp}} = 1.7 \times 10^{-5}$. Also, we have to convert moles to molarity, because these are the quantities that we have to substitute into the ion product expression.

SOLUTION: The planned solution would have the following molar concentrations.

$$[\text{Pb}^{2+}] = \frac{0.075 \text{ mol}}{0.500 \text{ L}} = 0.15 \text{ M} \quad [\text{Cl}^{-}] = \frac{0.0075 \text{ mol}}{0.500 \text{ L}} = 0.015 \text{ M}$$

We use these values to compute the ion product for PbCl_2 in the solution.

$$Q = [\text{Pb}^{2+}][\text{Cl}^{-}]^2 = (0.15)(0.015)^2 = 3.4 \times 10^{-5}$$

This value of Q is larger than the K_{sp} of PbCl_2 , 1.7×10^{-5} , which means that a precipitate of PbCl_2 is likely to form if we attempt to prepare this solution.

IS THE ANSWER REASONABLE? We can double-check that the molarities of the ions in the planned solution are correct. Then, we check the calculation of Q . All seems to be in order, so our answer is correct.

It is usually difficult to prevent the extra salt from precipitating out of a supersaturated solution. (Sodium acetate is a notable exception. Supersaturated solutions of this salt are easily made.)

Practice Exercise 12: Will a precipitate of CaSO_4 form in a solution if the Ca^{2+} concentration is 0.0025 M and the SO_4^{2-} concentration is 0.030 M ? (Hint: What is the form of the ion product for CaSO_4 ?)

Practice Exercise 13: Will a precipitate form in a solution containing $3.4 \times 10^{-4} \text{ M}$ CrO_4^{2-} and $4.8 \times 10^{-5} \text{ M}$ Ag^{+} ?

EXAMPLE 17.8

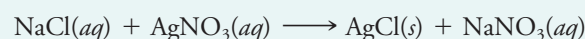
Predicting whether a Precipitate Will Form

What possible precipitate might form by mixing 50.0 mL of $1.0 \times 10^{-4} \text{ M}$ NaCl with 50.0 mL of $1.0 \times 10^{-6} \text{ M}$ AgNO_3 ? Will it form? (Assume the volumes are additive.)

ANALYSIS: In this problem we are being asked, in effect, whether a metathesis reaction will occur between NaCl and AgNO_3 . We should be able to use the solubility rules in Chapter 4 as a tool to predict whether this *might* occur. If the solubility rules suggest a precipitate, we can then calculate the ion product for the compound using the concentrations of the ions in the final solution. If this ion product exceeds K_{sp} for the salt, then a precipitate is expected.

To calculate Q correctly requires that we use the concentrations of the ions *after the solutions have been mixed*. Therefore, before computing the ion product, we must first take into account the fact that mixing the solutions dilutes each of the solutes. Dilution problems were covered in Chapter 4, where you learned that the tool for working such calculations is Equation 4.6 (page 158).

SOLUTION: Let's begin by writing the equation for the potential metathesis reaction between NaCl and AgNO_3 . Our tool is the solubility rules (page 147), which helps us determine whether each product is soluble or insoluble.



The solubility rules indicate that we expect a precipitate of AgCl . But are the concentrations of Ag^{+} and Cl^{-} actually high enough?

In the original solutions, the $1.0 \times 10^{-6} \text{ M}$ AgNO_3 contains $1.0 \times 10^{-6} \text{ M}$ Ag^{+} and the $1.0 \times 10^{-4} \text{ M}$ NaCl contains $1.0 \times 10^{-4} \text{ M}$ Cl^{-} . What are the concentrations of these ions after dilution? To determine these we use the equation that applies to all dilution problems involving molarity (Equation 4.6, page 158).

$$V_{\text{dil}} \cdot M_{\text{dil}} = V_{\text{conc}} \cdot M_{\text{conc}} \quad (\text{Equation 4.6})$$

To obtain the solution to this problem we must bring together tools from two different chapters.

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Solving for M_{dil} gives

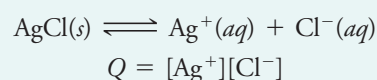
$$M_{\text{dil}} = \frac{V_{\text{conc}} M_{\text{conc}}}{V_{\text{dil}}}$$

The initial volumes of the more concentrated solutions are 50.0 mL and when the two solutions are combined, the final total volume is 100 mL. Therefore,

$$[\text{Ag}^+]_{\text{final}} = \frac{(50.0 \text{ mL})(1.0 \times 10^{-6} M)}{100.0 \text{ mL}} = 5.0 \times 10^{-7} M$$

$$[\text{Cl}^-]_{\text{final}} = \frac{(50.0 \text{ mL})(1.0 \times 10^{-4} M)}{100.0 \text{ mL}} = 5.0 \times 10^{-5} M$$

Now we use these to calculate Q for AgCl, which we can obtain from the dissociation reaction of the salt.



Substituting the concentrations computed above gives

$$Q = (5.0 \times 10^{-7})(5.0 \times 10^{-5}) = 2.5 \times 10^{-11}$$

In Table 17.1, the K_{sp} for AgCl is given as 1.8×10^{-10} . Notice that Q is *smaller* than K_{sp} , which means that the final solution is unsaturated in AgCl and a precipitate will *not* form.

IS THE ANSWER REASONABLE? There are several things we should check here. They include writing the equation for the metathesis, calculating the concentrations of the ions after dilution (we've doubled the volume, so the concentrations are halved), and setting up the correct ion product. All appear to be correct, so the answer should be okay.

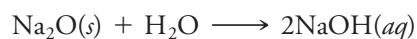
Practice Exercise 14: What precipitate might be expected if we pour together 100.0 mL of $1.0 \times 10^{-3} M$ $\text{Pb}(\text{NO}_3)_2$ and 100.0 mL of $2.0 \times 10^{-3} M$ MgSO_4 ? Will some form? (Assume that the volumes are additive.) (Hint: What tools will you need to solve the problem?)

Practice Exercise 15: What precipitate might be expected if we pour together 50.0 mL of $0.10 M$ $\text{Pb}(\text{NO}_3)_2$ and 20.0 mL of $0.040 M$ NaCl ? Will some form? (Assume that the volumes are additive.)

17.2 SOLUBILITY EQUILIBRIA OF METAL OXIDES AND SULFIDES INVOLVE REACTION WITH WATER

Aqueous equilibria involving insoluble oxides and sulfides are more complex than those we've considered so far because of reactions of the anions with the solvent, water.

When a metal oxide dissolves in water, it does so by reacting with water instead of by a simple dissociation of ions that remain otherwise unchanged. Sodium oxide, for example, consists of Na^+ and O^{2-} ions, and it readily dissolves in water. The solution, however, does not contain the oxide ion, O^{2-} . Instead, the hydroxide ion forms. The equation for the reaction is



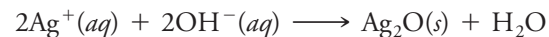
This actually involves the reaction of oxide ions with water as the crystals of Na_2O break up.



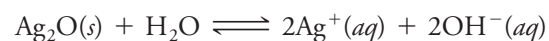
The oxide ion is simply too powerful a base to exist in water at any concentration worthy of experimental note. We can understand why from the extraordinarily high (estimated) value of K_{b} for O^{2-} , 1×10^{22} . Thus there is no way to supply *oxide ions* to an aqueous solution in order to form an insoluble metal oxide directly. Oxide ions react with water, instead, to generate the hydroxide ion. When an insoluble metal *oxide* instead of an insoluble metal

17.2 Solubility Equilibria of Metal Oxides and Sulfides Involve Reaction with Water 705

hydroxide does precipitate from a solution, it forms because the specific metal ion is able to react with OH^- , extract O^{2-} , and leave H^+ (or H_2O) in the solution. The silver ion, for example, precipitates as brown silver oxide, Ag_2O , when OH^- is added to aqueous silver salts (Figure 17.3).



The reverse of this reaction, written as an equilibrium, corresponds to the solubility equilibrium for Ag_2O .

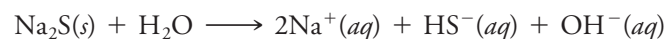


Metal sulfides behave like oxides in their solubility equilibria

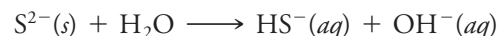
When we shift from oxygen to sulfur in Group VIA and consider metal sulfides, we find many similarities to oxides. One is that the sulfide ion, S^{2-} , like the oxide ion, is such a strong Brønsted base that it does not exist in any ordinary aqueous solution. The sulfide ion has not been detected in an aqueous solution even in the presence of 8 M NaOH where one might think that the reaction



could generate some detectable S^{2-} . An 8 M NaOH solution is at a concentration well outside the bounds of the “ordinary.” Thus, Na_2S , like Na_2O , dissolves in water *by reacting with it*, not by releasing an otherwise unchanged divalent anion, S^{2-} .



As with Na_2O , water reacts with the sulfide ion as the crystals break apart and the ions enter the solution.



The sulfides of most metals have quite low solubilities in water. Simply bubbling hydrogen sulfide gas into an aqueous solution of any one of a number of metal ions— Cu^{2+} , Pb^{2+} , and Ni^{2+} , for example—causes their sulfides to precipitate. Many of these have distinctive colors (Figure 17.4) that can be used to help identify which metal ion is in solution.

To write the solubility equilibrium for an insoluble metal sulfide we have to take into account the reaction of the sulfide ion with water. For example, for CuS the equilibrium is best written as



This equation yields the ion product $[\text{Cu}^{2+}][\text{HS}^-][\text{OH}^-]$, and the solubility product constant for CuS is expressed by the equation.

$$K_{\text{sp}} = [\text{Cu}^{2+}][\text{HS}^-][\text{OH}^-]$$

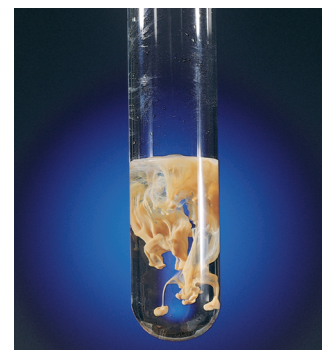


FIG. 17.3 Silver oxide.

A brown, mudlike precipitate of silver oxide forms as sodium hydroxide solution is added to a solution of silver nitrate. (Michael Watson.)

■ In the laboratory, the qualitative analysis of metal ions uses the precipitation of metal sulfides to separate some metal ions from others.

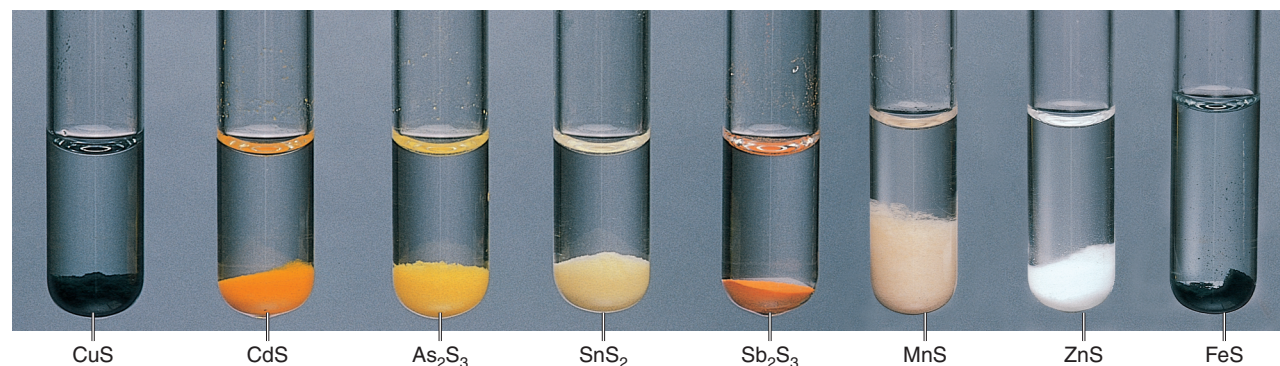


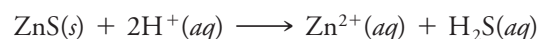
FIG. 17.4 The colors of some metal sulfides. (OPC, Inc.)

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Values of K_{sp} of this form for a number of metal sulfides are given in the last column in Table 17.2. Notice particularly how much the K_{sp} values vary—from 2×10^{-53} to 3×10^{-11} , a spread of a factor of 10^{42} .

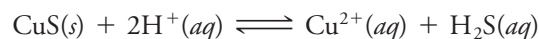
Acid-insoluble sulfides are so insoluble they don't dissolve in acid

Many metal sulfides are able to react with acid and thereby dissolve. An example is zinc sulfide.



However, some metal sulfides, referred to as the *acid-insoluble sulfides*, have K_{sp} values so low that they do not dissolve in acid. The cations in this group can be precipitated from the other cations simply by bubbling hydrogen sulfide into a sufficiently acidic solution that contains several metal ions.

When the solution is acidic, we have to treat the solubility equilibria differently. In acid, HS^- and OH^- would be neutralized, leaving their conjugate acids, H_2S and H_2O . Under these conditions, the equation for the solubility equilibrium becomes



Acid solubility product, K_{spa}

This changes the mass action expression for the solubility product equilibrium, which we will now call the **acid solubility product, K_{spa}** . The *a* in the subscript indicates that the medium is acidic.

$$K_{spa} = \frac{[\text{Cu}^{2+}][\text{H}_2\text{S}]}{[\text{H}^+]^2}$$

Table 17.2 also gives K_{spa} values for the metal sulfides. Notice that all K_{spa} values are 10^{21} larger than the K_{sp} values. Metal sulfides are clearly vastly more soluble in dilute acid than in water. Yet several—the acid-insoluble sulfides—are so insoluble that even the most soluble of them, SnS , barely dissolves, even in moderately concentrated acid. So there are two families of sulfides, the *acid-insoluble sulfides* and the acid-soluble ones, otherwise

TABLE 17.2 Metal Ions Separable by Selective Precipitation of Sulfides^a

Metal Ion	Sulfide	K_{spa}	K_{sp}
Acid-Insoluble Sulfides			
Hg^{2+}	HgS (black form)	2×10^{-32}	2×10^{-53}
Ag^+	Ag_2S	6×10^{-30}	6×10^{-51}
Cu^{2+}	CuS	6×10^{-16}	6×10^{-37}
Cd^{2+}	CdS	3×10^{-7}	3×10^{-28}
Pb^{2+}	PbS	3×10^{-7}	3×10^{-28}
Sn^{2+}	SnS	1×10^{-5}	1×10^{-26}
Base-Insoluble Sulfides (Acid-Soluble Sulfides)			
Zn^{2+}	$\alpha\text{-ZnS}$	3×10^{-4}	3×10^{-25}
	$\beta\text{-ZnS}$	3×10^{-2}	3×10^{-23}
Co^{2+}	CoS	5×10^{-1}	5×10^{-22}
Ni^{2+}	NiS	4×10^1	4×10^{-20}
Fe^{2+}	FeS	6×10^2	6×10^{-19}
Mn^{2+}	MnS (pink form)	3×10^{10}	3×10^{-11}
	MnS (green form)	3×10^7	3×10^{-14}

^aData are for 25 °C. See R.J. Meyers, *J. Chem. Ed.*, vol. 63, 1986, p. 689.

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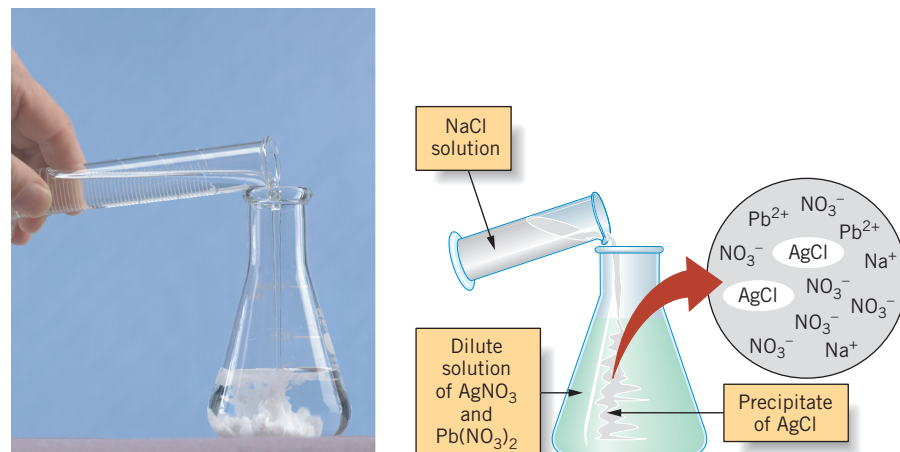


FIG. 17.5 Selective precipitation. When dilute sodium chloride is added to a solution containing both Ag^+ ions and Pb^{2+} ions (both dissolved as their nitrate salts), the less soluble AgCl precipitates before the more soluble PbCl_2 . Precipitation of the AgCl is nearly complete before any PbCl_2 begins to form. (Andy Washnik.)

known as the *base-insoluble sulfides*. As we discuss in the next section, the differing solubilities of their sulfides in acid provide a means of separating the two classes of metal ions from each other.

17.3 METAL IONS CAN BE SEPARATED BY SELECTIVE PRECIPITATION

Selective precipitation means causing one metal ion to precipitate while holding another in solution. Often this is possible because of large differences in the solubilities of salts that we would generally consider to be insoluble. For example, the K_{sp} values for AgCl and PbCl_2 are 1.8×10^{-10} and 1.7×10^{-5} , respectively, which gives them molar solubilities in water of $1.3 \times 10^{-5} M$ for AgCl and $1.6 \times 10^{-2} M$ for PbCl_2 . In terms of molar solubilities, lead chloride is approximately 1200 times more soluble in water than AgCl . If we had a solution containing both $0.10 M \text{Pb}^{2+}$ and $0.10 M \text{Ag}^+$ and began adding Cl^- , AgCl would precipitate first (Figure 17.5). In fact, we can calculate that before any PbCl_2 starts to precipitate, the concentration of Ag^+ will have been reduced to $1.4 \times 10^{-8} M$. Thus, nearly all the silver is removed from the solution without precipitating any of the lead, and the ions are effectively separated. All we need to do is find a way of adjusting the concentration of the Cl^- to achieve the separation.

Selective precipitation of metal sulfides is accomplished by controlling the pH

The large differences in K_{sp} values between the acid-insoluble and the base-insoluble metal sulfides make it possible to separate the corresponding cations from each other when they are in the same solution. The sulfides of the acid-insoluble cations are selectively precipitated by hydrogen sulfide from a solution kept at a pH that keeps the other cations in solution. A solution saturated in H_2S is used, for which the molarity of H_2S is $0.1 M$.

Let's work an example to show how we can calculate the pH needed to allow the selective precipitation of two metal cations as their sulfides. We will use Cu^{2+} and Ni^{2+} ions to represent a cation from each class.

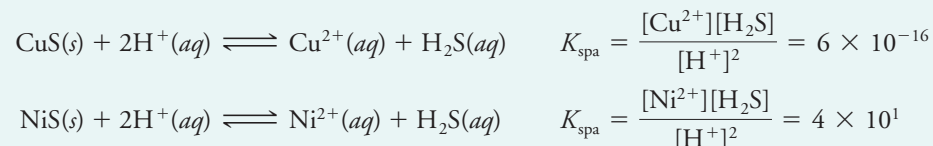
Over what range of hydrogen ion concentrations (and pH) is it possible to separate Cu^{2+} from Ni^{2+} when both metal ions are present in a solution at a concentration of $0.010 M$ and the solution is made saturated in H_2S (where $[\text{H}_2\text{S}] = 0.1 M$)?

ANALYSIS: We must work with the chemical equilibria for the metal sulfides and their associated equilibrium expressions (the equations for their K_{spa}).

EXAMPLE 17.9

Selective Precipitation of the Sulfides of Acid-Insoluble Cations from Base-Insoluble Cations

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The K_{spa} values (from Table 17.2) tell us that NiS is much more soluble in an acidic solution than CuS. Therefore, we want to make the H^+ concentration large enough to prevent NiS from precipitating, but small enough that CuS does precipitate.

The problem reduces to two questions. The first is, “What hydrogen ion concentration would be needed to keep the Cu^{2+} in solution?” (The answer to this question will give us the *upper limit* on $[\text{H}^+]$; we would really want a lower H^+ concentration so CuS *will* precipitate.) The second question is, “What is the hydrogen ion concentration just before NiS precipitates?” The answer to this will be the *lower limit* on $[\text{H}^+]$. At any lower H^+ concentration, NiS will precipitate, so we want an H^+ concentration equal to or larger than this value. Once we know these limits, we know that any hydrogen ion concentration in between them will permit CuS to precipitate but retain Ni^{2+} in solution.

SOLUTION: We will find the upper limit first. If CuS *does not precipitate*, the Cu^{2+} concentration will be the given value, $0.010 M$, so we substitute this along with the H_2S concentration ($0.1 M$) into the expression for K_{spa} .

$$K_{\text{spa}} = \frac{[\text{Cu}^{2+}][\text{H}_2\text{S}]}{[\text{H}^+]^2} = \frac{(0.010)(0.1)}{[\text{H}^+]^2} = 6 \times 10^{-16}$$

Now we solve for $[\text{H}^+]$.

$$[\text{H}^+]^2 = \frac{(0.010)(0.1)}{6 \times 10^{-16}} = 2 \times 10^{12}$$

$$[\text{H}^+] = 1 \times 10^6 M$$

If we could make $[\text{H}^+] = 1 \times 10^6 M$, we could prevent CuS from forming. However, it isn't possible to have 10^6 or a *million* moles of H^+ per liter! What the calculated $[\text{H}^+]$ tells us, therefore, is that *no matter how acidic the solution is, we cannot prevent CuS from precipitating when we saturate the solution with H_2S .* (You can now see why CuS is classed as an “acid-insoluble sulfide.”)

To obtain the lower limit, we calculate the $[\text{H}^+]$ required to give an equilibrium concentration of Ni^{2+} equal to $0.010 M$. If we keep the value of $[\text{H}^+]$ *equal to or larger* than this value, then NiS will be prevented from precipitating. The calculation is exactly like the one above. First, we substitute values into the K_{spa} expression.

$$K_{\text{spa}} = \frac{[\text{Ni}^{2+}][\text{H}_2\text{S}]}{[\text{H}^+]^2} = \frac{(0.010)(0.1)}{[\text{H}^+]^2} = 4 \times 10^1$$

Once again, we solve for $[\text{H}^+]$.

$$[\text{H}^+]^2 = \frac{(0.010)(0.1)}{4 \times 10^1}$$

$$[\text{H}^+] = 5 \times 10^{-3} M$$

$$\text{pH} = 2.3$$

If we maintain the pH of the solution of $0.010 M \text{Cu}^{2+}$ and $0.010 M \text{Ni}^{2+}$ at 2.3 or lower (more acidic), as we make the solution saturated in H_2S , virtually all the Cu^{2+} will precipitate as CuS, but all the Ni^{2+} will stay in solution.

IS THE ANSWER REASONABLE? The K_{spa} values certainly tell us that CuS is quite insoluble in acid and that NiS is a lot more soluble, so from that standpoint the results seem reasonable. There's not much more we can do to check the answer, other than to review the entire set of calculations.

17.3 Metal Ions Can Be Separated by Selective Precipitation 709

Practice Exercise 16: Suppose a solution contains 0.0050 M Co^{2+} and is saturated with H_2S (with $[\text{H}_2\text{S}] = 0.1\text{ M}$). Would CoS precipitate if the solution has a pH of 3.5? (Hint: What relationship do we use to determine whether a precipitate is going to form in a solution?)

Practice Exercise 17: Consider a solution containing Hg^{2+} and Fe^{2+} , both at molarities of 0.010 M . It is to be saturated with H_2S . Calculate the highest pH that this solution could have that would keep Fe^{2+} in solution while causing Hg^{2+} to precipitate as HgS .

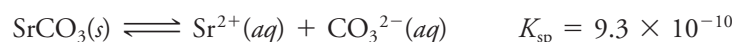
In actual lab work, separation of the acid-insoluble sulfides from the base-insoluble ones is performed with $[\text{H}^+] \approx 0.3\text{ M}$ which corresponds to a pH of about 0.5. This ensures that the base-insoluble sulfides will not precipitate. The calculation above also demonstrated why NiS can be classified as a “base-insoluble sulfide.” If the solution is *basic* when it is made saturated in H_2S , the pH will surely be larger than 2.3 and NiS will precipitate.

Selective precipitation can be applied to metal carbonates

The principles of selective precipitation by the control of pH apply to any system where the anion is that of a weak acid. The metal carbonates are examples, with many being quite insoluble in water (see Table 17.1). The dissociation of magnesium carbonate in water, for example, involves the following equilibrium and K_{sp} equations.



For strontium carbonate, the equations are



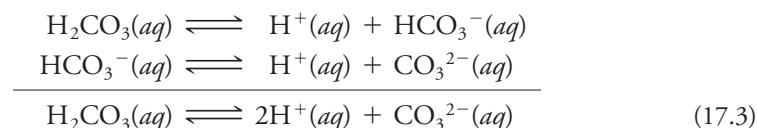
Would it be possible to separate the magnesium ion from the strontium ion by taking advantage of the difference in K_{sp} of their carbonates?

We can do so if we can control the carbonate ion concentration. Because the carbonate ion is a relatively strong Brønsted base, its control is available, indirectly, by adjusting the pH of the solution. This is because the hydrogen ion is one of the species in each of the following equilibria.³

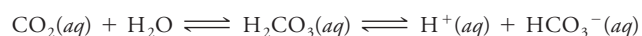


You can see that if we increase the hydrogen ion concentration, both equilibria will shift to the left, in accordance with Le Châtelier’s principle, and this will reduce the concentration of the carbonate ion. The value of $[\text{CO}_3^{2-}]$ thus decreases with decreasing pH. On the other hand, if we decrease the hydrogen ion concentration, making the solution more basic, we will cause the two equilibria to shift to the right. The concentration of the carbonate ion thus increases with increasing pH.

For the calculations ahead, it will be useful to combine the two hydrogen carbonate equilibria into one overall equation that relates the molar concentrations of carbonic acid, carbonate ion, and hydrogen ion. So we first add the two.



³The situation involving aqueous carbonic acid is complicated by the presence of dissolved CO_2 , which we could represent in an equation as $\text{CO}_2(aq)$. In fact, this is how most of the dissolved CO_2 exists, namely, as $\text{CO}_2(aq)$, not as $\text{H}_2\text{CO}_3(aq)$. But we may use $\text{H}_2\text{CO}_3(aq)$ as a surrogate or stand-in for $\text{CO}_2(aq)$, because the latter changes smoothly to the former on demand. The following two successive equilibria involving carbonic acid exist in a solution of aqueous CO_2 .



The value of K_{a_1} cited here for $\text{H}_2\text{CO}_3(aq)$ is really the product of the equilibrium constants of these two equilibria.

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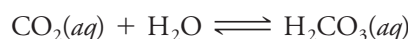
Recall from Chapter 14 that when we add two equilibria to get a third, the equilibrium constant of the latter is the product of the two equilibria that are combined. Thus, for Equation 17.3 the equilibrium constant, which we'll symbolize as K_a , is obtained as follows.

TOOLS
Combined K_a expression for
a diprotic acid

$$\begin{aligned} K_a &= K_{a_1} \times K_{a_2} = \frac{[\text{H}^+]^2[\text{CO}_3^{2-}]}{[\text{H}_2\text{CO}_3]} \\ &= (4.5 \times 10^{-7}) \times (4.7 \times 10^{-11}) \\ &= 2.1 \times 10^{-17} \end{aligned} \quad (17.4)$$

■ We can safely use Equation 17.4 *only* when two of the three concentrations are known.

With this K_a value we may now study how to find the pH range within which Mg^{2+} and Sr^{2+} can be separated by taking advantage of their difference in K_{sp} values. To perform such a separation we would saturate a solution with CO_2 , which provides H_2CO_3 through the rapidly established equilibrium



Thus, a solution that contains 0.030 M CO_2 has an effective H_2CO_3 concentration of 0.030 M.

EXAMPLE 17.10

Separation of Metal Ions by the
Selective Precipitation of Their
Carbonates

A solution contains magnesium nitrate and strontium nitrate, each at a concentration of 0.10 M. Carbon dioxide is to be bubbled in to make the solution saturated in $\text{CO}_2(aq)$, approximately 0.030 M. What pH range would make it possible for the carbonate of one cation to precipitate but not that of the other?

ANALYSIS: There are really two parts to this. First, what is the range in values of $[\text{CO}_3^{2-}]$ that allow one carbonate to precipitate but not the other? Second, given this range, what are the values of the solution's pH that produce this range in $[\text{CO}_3^{2-}]$ values?

To answer the first question, we will use the K_{sp} values of the two carbonate salts and their molar concentrations to find the CO_3^{2-} concentrations in their saturated solutions. To keep the more soluble carbonate from precipitating, the CO_3^{2-} concentration must be at or below that required for saturation. For the less soluble of the two, we must have a CO_3^{2-} concentration larger than in a saturated solution so that it will precipitate.

To answer the second question, we will use the combined K_a expression for H_2CO_3 to find the $[\text{H}^+]$ that gives the necessary CO_3^{2-} concentrations obtained in answering the first question. Having these $[\text{H}^+]$, it is then a simple matter to convert them to pH values.

SOLUTION: The range in $[\text{CO}_3^{2-}]$ values is obtained by using the K_{sp} values of the two carbonates.

$$K_{sp} = [\text{Mg}^{2+}][\text{CO}_3^{2-}] = 3.5 \times 10^{-8}$$

$$K_{sp} = [\text{Sr}^{2+}][\text{CO}_3^{2-}] = 9.3 \times 10^{-10}$$

On the basis of the K_{sp} values, we see that MgCO_3 is the more soluble of the two. Let's find the $[\text{CO}_3^{2-}]$ values required to give saturated solutions of these two salts.

For Magnesium Carbonate:

$$[\text{CO}_3^{2-}] = \frac{K_{sp}}{[\text{Mg}^{2+}]} = \frac{3.5 \times 10^{-8}}{0.10} = 3.5 \times 10^{-7} \text{ M}$$

For Strontium Carbonate:

$$[\text{CO}_3^{2-}] = \frac{K_{sp}}{[\text{Sr}^{2+}]} = \frac{9.3 \times 10^{-10}}{0.10} = 9.3 \times 10^{-9} \text{ M}$$

For separation, we have to keep the $[\text{CO}_3^{2-}]$ less than or equal to $3.5 \times 10^{-7} \text{ M}$ and larger than $9.3 \times 10^{-9} \text{ M}$.

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$$\begin{aligned}[\text{CO}_3^{2-}] &> 9.3 \times 10^{-9} M && \text{(to precipitate SrCO}_3\text{)} \\[\text{CO}_3^{2-}] &\leq 3.5 \times 10^{-7} M && \text{(to prevent MgCO}_3\text{ from precipitating)}\end{aligned}$$

The second phase of our calculation now asks what values of $[\text{H}^+]$ correspond to the calculated limits on $[\text{CO}_3^{2-}]$. For this we will use the K_a expression given by Equation 17.4. First we solve for the square of $[\text{H}^+]$, using the molarity of the dissolved CO_2 , $0.030 M$, as the value of $[\text{H}_2\text{CO}_3]$. This gives us

$$[\text{H}^+]^2 = K_a \times \frac{[\text{H}_2\text{CO}_3]}{[\text{CO}_3^{2-}]} = 2.1 \times 10^{-17} \times \frac{0.030}{[\text{CO}_3^{2-}]}$$

We will use this equation for each of the two boundary values of $[\text{CO}_3^{2-}]$ to calculate the corresponding two values of $[\text{H}^+]^2$. Once we have them, the steps to values of $[\text{H}^+]$ and pH are easy.

For Magnesium Carbonate: To prevent the precipitation of MgCO_3 , $[\text{CO}_3^{2-}]$ must be no higher than $3.5 \times 10^{-7} M$, so $[\text{H}^+]^2$ must not be less than

$$\begin{aligned}[\text{H}^+]^2 &= 2.1 \times 10^{-17} \times \frac{0.030}{3.5 \times 10^{-7}} = 1.8 \times 10^{-12} \\[\text{H}^+] &= 1.3 \times 10^{-6} M\end{aligned}$$

This corresponds to a pH of 5.89. At a higher (more basic) pH, magnesium carbonate precipitates. Thus, $\text{pH} \leq 5.89$ prevents precipitation of MgCO_3 .

For Strontium Carbonate: To have a saturated solution of SrCO_3 with $[\text{Sr}^{2+}] = 0.10 M$, the value of $[\text{CO}_3^{2-}]$ would be $9.3 \times 10^{-9} M$, as we calculated above. This corresponds to a value of $[\text{H}^+]^2$ found as follows.

$$\begin{aligned}[\text{H}^+]^2 &= 2.1 \times 10^{-17} \times \frac{0.030}{9.3 \times 10^{-9}} = 6.8 \times 10^{-11} \\[\text{H}^+] &= 8.2 \times 10^{-6} M \\ \text{pH} &= 5.09\end{aligned}$$

To cause SrCO_3 to precipitate, the $[\text{CO}_3^{2-}]$ would have to be higher than $9.3 \times 10^{-9} M$, and that would require that $[\text{H}^+]$ be *less than* $8.2 \times 10^{-6} M$. If $[\text{H}^+]$ were less than $8.2 \times 10^{-6} M$, the pH would have to be higher than 5.09. Thus, to cause SrCO_3 to precipitate from the given solution, $\text{pH} > 5.09$.

In summary, when the pH of the given solution is kept above 5.09 and less than or equal to 5.89, Sr^{2+} will precipitate as SrCO_3 but Mg^{2+} will remain dissolved.

IS THE ANSWER REASONABLE? The only way to be sure of the answer is to go back over the reasoning and the calculations. However, there is a sign that the answer is probably correct. Notice that the two K_{sp} values are not vastly different—they differ by just a factor of about 40. Therefore, it's not surprising that to achieve separation we would have to keep the pH within a rather narrow range (from 5.09 to 5.89).

Because $\text{CO}_2(\text{aq})$ can rapidly combine with water to give $\text{H}_2\text{CO}_3(\text{aq})$, the value of $[\text{H}_2\text{CO}_3]$ is taken to be that of $[\text{CO}_2(\text{aq})]$, namely, $0.030 M$.

Practice Exercise 18: The K_{sp} for barium oxalate, BaC_2O_4 , is 1.2×10^{-7} and for oxalic acid, $\text{H}_2\text{C}_2\text{O}_4$, $K_{a_1} = 5.6 \times 10^{-2}$ and $K_{a_2} = 5.4 \times 10^{-5}$. If a solution containing $0.10 M$ $\text{H}_2\text{C}_2\text{O}_4$ and $0.050 M$ BaCl_2 is prepared, what must the minimum H^+ concentration be in the solution to prevent the formation of a BaC_2O_4 precipitate? (Hint: Work with a combined K_a expression for $\text{H}_2\text{C}_2\text{O}_4$.)

Practice Exercise 19: A solution contains calcium nitrate and nickel nitrate, each at a concentration of $0.10 M$. Carbon dioxide is to be bubbled in to make its concentration equal $0.030 M$. What pH range would make it possible for the carbonate of one cation to precipitate but not that of the other?



FIG. 17.6 The complex ion of Cu^{2+} and water. A solution containing copper sulfate has a blue color because it contains the complex ion $\text{Cu}(\text{H}_2\text{O})_4^{2+}$. (Andy Washnik.)

Recall that a *Lewis base* is an electron pair donor in the formation of a coordinate covalent bond.

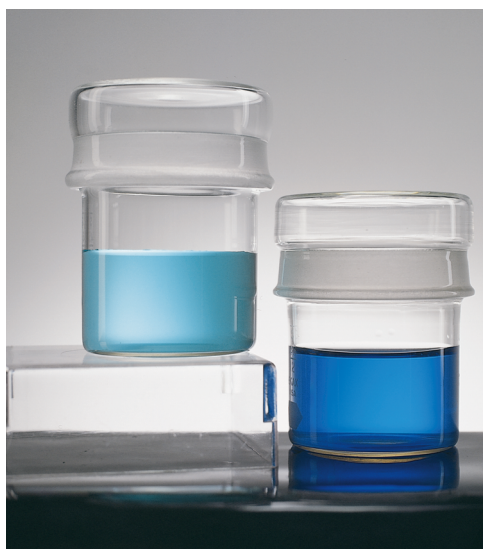


FIG. 17.7 The complex ion of Cu^{2+} and ammonia. Ammonia molecules displace water molecules from $\text{Cu}(\text{H}_2\text{O})_4^{2+}$ (left) to give the deep blue $\text{Cu}(\text{NH}_3)_4^{2+}$ ion (right). (Andy Washnik.)

17.4 COMPLEX IONS PARTICIPATE IN EQUILIBRIA IN AQUEOUS SOLUTIONS

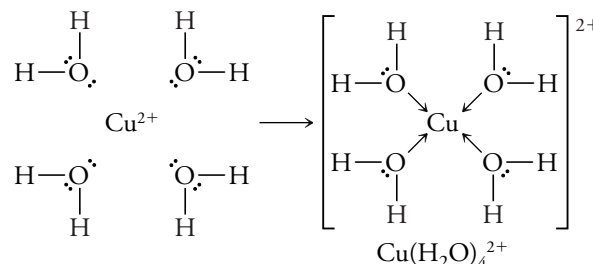
Metal ions can combine with anions or neutral molecules to form complex ions

In our previous discussions of metal-containing compounds, we left you with the impression that the only kinds of bonds in which metals are ever involved are ionic bonds. For some metals, like the alkali metals of Group IA, this is close enough to the truth to warrant no modifications. But for many other metal ions, especially those of the transition metals and the post-transition metals, it is not. This is because the ions of many of these metals are able to behave as Lewis acids (i.e., as electron pair acceptors in the formation of coordinate covalent bonds). Thus, by participating in Lewis acid–base reactions they become *covalently* bonded to other atoms. Copper(II) ion is a typical example.

In aqueous solutions of copper(II) salts, like CuSO_4 or $\text{Cu}(\text{NO}_3)_2$, the copper is not present as simple Cu^{2+} ions. Instead, each Cu^{2+} ion becomes bonded to four water molecules to give a pale blue ion with the formula $\text{Cu}(\text{H}_2\text{O})_4^{2+}$ (see Figure 17.6). We call this species a **complex ion** because it is composed of a number of simpler species (i.e., it is *complex*, not simple). The chemical equation for the formation of the $\text{Cu}(\text{H}_2\text{O})_4^{2+}$ ion is



which can be diagrammed using Lewis structures as follows.



As you can see in this analysis, the Cu^{2+} ion accepts pairs of electrons from the water molecules, so Cu^{2+} is a Lewis acid and the water molecules are each Lewis bases.

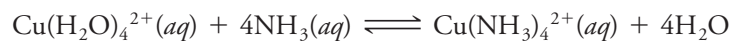
The number of complex ions formed by metals, especially the transition metals, is enormous, and the study of the properties, reactions, structures, and bonding in complex ions like $\text{Cu}(\text{H}_2\text{O})_4^{2+}$ has become an important specialty within chemistry. We will provide a more complete discussion of them in Chapter 21. For now, we will introduce you to some of the terminology that we use in describing these substances.

A Lewis base that attaches itself to a metal ion is called a **ligand** (from the Latin *ligare*, meaning “to bind”). Ligands can be neutral molecules with unshared pairs of electrons (like H_2O), or they can be anions (like Cl^- or OH^-). The atom in the ligand that actually provides the electron pair is called the **donor atom**, and the metal ion is the **acceptor**. The result of combining a metal ion with one or more ligands is a *complex ion*, or simply just a *complex*. The word “complex” avoids problems when the particle formed is electrically neutral, as sometimes happens. Compounds that contain complex ions are generally referred to as **coordination compounds** because the bonds in a complex ion can be viewed as coordinate covalent bonds. Sometimes the complex itself is called a *coordination complex*.

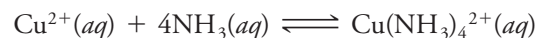
In an aqueous solution, the formation of a complex ion is really a reaction in which water molecules are replaced by other ligands. Thus, when NH_3 is added to a solution of copper ion, the water molecules in the $\text{Cu}(\text{H}_2\text{O})_4^{2+}$ ion are replaced, one after another, by molecules of NH_3 until the deeply blue complex $\text{Cu}(\text{NH}_3)_4^{2+}$ is formed (Figure 17.7). Each successive reaction is an equilibrium, so the entire chemical system involves many species and is quite complicated. Fortunately, when the ligand concentration is *large* relative to that of the metal ion, the concentrations of the intermediate complexes are very small and we can work only

17.4 Complex Ions Participate in Equilibria in Aqueous Solutions 713

with the *overall* reaction for the formation of the final complex. Our study of complex ion equilibria will be limited to these situations. The equilibrium equation for the formation of $\text{Cu}(\text{NH}_3)_4^{2+}$, therefore, can be written as though the complex forms in one step.



We will simplify this equation for the purposes of dealing quantitatively with the equilibria by omitting the water molecules. (It's safe to do this because the concentration of H_2O in aqueous solutions is taken to be effectively a constant and need not be included in mass action expressions.) In simplified form, we write the equilibrium above as follows:



We have two goals here: to study such equilibria themselves and to learn how they can be used to influence the solubilities of metal ion salts.

Formation constants reflect the stabilities of complex ions

When the chemical equation for the equilibrium is written so that the complex ion is the product, the equilibrium constant for the reaction is called the **formation constant**, K_{form} . The equilibrium law for the formation of $\text{Cu}(\text{NH}_3)_4^{2+}$ in the presence of excess NH_3 , for example, is

$$\frac{[\text{Cu}(\text{NH}_3)_4^{2+}]}{[\text{Cu}^{2+}][\text{NH}_3]^4} = K_{\text{form}}$$

Sometimes this equilibrium constant is called the **stability constant**. The larger its value, the greater is the concentration of the complex at equilibrium, and so the more stable is the complex.

Table 17.3 provides several more examples of complex ion equilibria and their associated equilibrium constants. (Additional examples are in Appendix C, Table C.6.) Notice that the most stable complex in the table, $\text{Co}(\text{NH}_3)_6^{3+}$, has, as you would expect, the largest value of K_{form} .

Instability constants are the inverse of formation constants

Some chemists prefer to describe the relative stabilities of complex ions differently. The *inverses* of formation constants are cited and are called **instability constants**, K_{inst} . This approach focuses attention on the *breakdown* of the complex, not its formation. Therefore,

According to Le Châtelier's principle, when the concentration of ammonia is high, the position of equilibrium in this reaction is shifted far to the right, so effectively all complex ions with water molecules are changed to those with ammonia molecules.



TABLE 17.3 Formation Constants and Instability Constants for Some Complex Ions

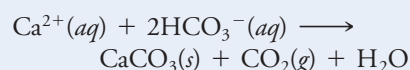
Ligand	Equilibrium	K_{form}	K_{inst}
NH ₃	$\text{Ag}^+ + 2\text{NH}_3 \rightleftharpoons \text{Ag}(\text{NH}_3)_2^+$	1.6×10^7	6.3×10^{-8}
	$\text{Co}^{2+} + 6\text{NH}_3 \rightleftharpoons \text{Co}(\text{NH}_3)_6^{2+}$	5.0×10^4	2.0×10^{-5}
	$\text{Co}^{3+} + 6\text{NH}_3 \rightleftharpoons \text{Co}(\text{NH}_3)_6^{3+}$	4.6×10^{33}	2.2×10^{-34}
	$\text{Cu}^{2+} + 4\text{NH}_3 \rightleftharpoons \text{Cu}(\text{NH}_3)_4^{2+}$	1.1×10^{13}	9.1×10^{-14}
	$\text{Hg}^{2+} + 4\text{NH}_3 \rightleftharpoons \text{Hg}(\text{NH}_3)_4^{2+}$	1.8×10^{19}	5.6×10^{-20}
F ⁻	$\text{Al}^{3+} + 6\text{F}^- \rightleftharpoons \text{AlF}_6^{3-}$	1×10^{20}	1×10^{-20}
	$\text{Sn}^{4+} + 6\text{F}^- \rightleftharpoons \text{SnF}_6^{2-}$	1×10^{25}	1×10^{-25}
Cl ⁻	$\text{Hg}^{2+} + 4\text{Cl}^- \rightleftharpoons \text{HgCl}_4^{2-}$	5.0×10^{15}	2.0×10^{-16}
Br ⁻	$\text{Hg}^{2+} + 4\text{Br}^- \rightleftharpoons \text{HgBr}_4^{2-}$	1.0×10^{21}	1.0×10^{-21}
I ⁻	$\text{Hg}^{2+} + 4\text{I}^- \rightleftharpoons \text{HgI}_4^{2-}$	1.9×10^{30}	5.3×10^{-31}
CN ⁻	$\text{Fe}^{2+} + 6\text{CN}^- \rightleftharpoons \text{Fe}(\text{CN})_6^{4-}$	1.0×10^{24}	1.0×10^{-24}
	$\text{Fe}^{3+} + 6\text{CN}^- \rightleftharpoons \text{Fe}(\text{CN})_6^{3-}$	1.0×10^{31}	1.0×10^{-31}

FACETS OF CHEMISTRY

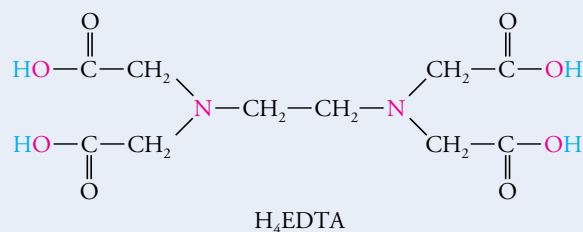
17.1

No More Soap Scum—Complex Ions and Solubility

A problem that has plagued homeowners with hard water—water that contains low concentrations of divalent cations, especially Ca^{2+} —is the formation of insoluble deposits of “soap scum” as well as “hard water spots” on surfaces such as shower tiles, shower curtains, and bathtubs. These deposits form when calcium ions interact with large anions in soap to form precipitates and also when hard water that contains bicarbonate ion evaporates, causing precipitation of calcium carbonate, CaCO_3 .

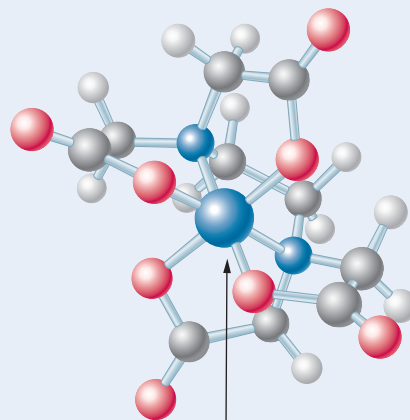


A variety of consumer products are sold that contain ingredients intended to prevent these precipitates from forming, and they accomplish this by forming complex ions with calcium ions, which has the effect of increasing the solubilities of the soap scum and calcium carbonate deposits. A principal ingredient in these products is an organic compound called *ethylenediaminetetraacetic acid* (mercifully abbreviated *EDTA*). The structure of the compound, which is also abbreviated as H_4EDTA to emphasize that it contains four acidic hydrogens which are part of carboxyl groups, is



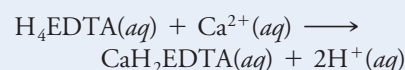
Acidic hydrogens are shown in blue, donor atoms are shown in red.

This molecule is an excellent complex-forming ligand; it contains a total of *six* donor atoms (in red) that can bind to a metal ion, enabling the ligand to wrap itself around the metal ion as illustrated below. (The usual colors are used to identify the various elements in the ligand.)



A metal ion surrounded octahedrally by all six donor atoms if H_4EDTA loses all of the acidic hydrogens.

One consumer product, called Clean Shower (Figure 1), contains H_4EDTA along with substances called surfactants. When the EDTA binds with calcium ions, it releases just two H^+ ions



The H^+ combine with anions of the soap to form neutral organic compounds called fatty acids that are usually not water-soluble. The surfactants in the product, however, enable the fatty acids to dissolve, preventing formation of precipitates. The Clean Shower product is sprayed on the wet walls after you take a shower, forming the products described above. The next

time you take a shower, the water washes away the soluble products, keeping soap scum from building up and keeping the shower walls clean.



FIG. 1 The product Clean Shower contains EDTA, which prevents the formation of soap scum and hard water spots in showers and on bathtubs. (*Andy Washnik.*)

Because we have added two equations to obtain a third equation, K_c for this expression is the product of K_{form} and K_{sp} . The values for K_{form} for $\text{Ag}(\text{NH}_3)_2^+$ and K_{sp} for AgBr are known, so by multiplying the two, we find the overall value of K_c for the silver bromide–ammonia system.

$$\begin{aligned} K_c &= (1.6 \times 10^7)(5.0 \times 10^{-13}) \\ &= 8.0 \times 10^{-6} \end{aligned}$$

This approach thus gives us a way to calculate the solubility of a sparingly soluble salt when a substance able to form a complex with the metal ion is put into its solution. The next example shows how this works.

▣ Recall that when equilibria are added, their equilibrium constants are multiplied.

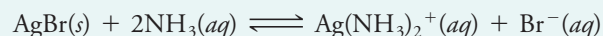
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EXAMPLE 17.11

Calculating the Solubility of a Slightly Soluble Salt in the Presence of a Ligand

How many moles of AgBr can dissolve in 1.0 L of 1.0 M NH₃?

ANALYSIS: A few preliminaries have to be done before we can take advantage of a concentration table. We need the overall equation and its associated equation for the equilibrium constant, which serve as our tools for dealing with these kinds of problems. The overall equilibrium is



The equation for K_c is

$$K_c = \frac{[\text{Ag}(\text{NH}_3)_2^+][\text{Br}^-]}{[\text{NH}_3]^2} = 8.0 \times 10^{-6} \quad (\text{as calculated earlier})$$

Now let's prepare the concentration table. To do this, we imagine we are adding solid AgBr to the ammonia solution.

Before any reaction takes place, the concentration of NH₃ is 1.0 M and the concentration of Ag(NH₃)₂⁺ is zero. The concentration of Br⁻ is also zero, because there is none of it in the ammonia solution.

If we define x as the molar solubility of the AgBr in the solution, then the concentrations of Ag(NH₃)₂⁺ and Br⁻ both increase by x and the concentration of ammonia decreases by $2x$ (because of the coefficient of NH₃ in the equation).

The equilibrium values are obtained as usual by adding the initial and change rows. However, another comment is in order here. Letting the concentration of Br⁻ equal that of Ag(NH₃)₂⁺ is valid because *and only because* K_{form} is such a large number. Essentially *all* Ag⁺ ions that do dissolve from the insoluble AgBr are changed to the complex ion. There are relatively few uncomplexed Ag⁺ ions in the solution, so the number of Ag(NH₃)₂⁺ and Br⁻ ions in the solution are very nearly the same.

SOLUTION: Here is the concentration table, built using the reasoning above.

	$\text{AgBr}(s) + 2\text{NH}_3(aq) \rightleftharpoons \text{Ag}(\text{NH}_3)_2^+(aq) + \text{Br}^-(aq)$		
Initial			
concentrations (M)	1.0	0	0
Changes in			
concentrations			
caused by NH ₃ (M)	-2x	+x	+x
Equilibrium			
concentrations (M)	(1.0 - 2x)	x	x

We've done all the hard work. Now all we need to do is substitute the values in the last row of the concentration table into the equation for K_c :

$$K_c = \frac{(x)(x)}{(1.0 - 2x)^2} = 8.0 \times 10^{-6}$$

This can be solved by taking the square root of both sides, which gives

$$\frac{x}{(1.0 - 2x)} = \sqrt{8.0 \times 10^{-6}} = 2.8 \times 10^{-3}$$

Solving for x and rounding to the correct number of significant figures gives

$$x = 2.8 \times 10^{-3}$$

Because we've defined x as the molar solubility of AgBr in the ammonia solution, we can say that 2.8×10^{-3} mol of AgBr dissolves in 1.0 L of 1.0 M NH₃. (This is not very much, of course, but in contrast, only 7.1×10^{-7} mol of AgBr dissolves in 1.0 L of pure water. Thus AgBr is nearly 4000 times more soluble in the 1.0 M NH₃ than in pure water.)

IS THE ANSWER REASONABLE? Everything depends on the reasoning used in preparing the concentration table, particularly letting $-2x$ represent the change in the concentration of NH_3 as a result of the presence of AgBr and the formation of the complex. Additionally, we can see that the maximum solubility of AgBr if all the NH_3 were complexed is 0.5 M while the minimum solubility if the NH_3 had no effect is the solubility of AgBr in distilled water ($7 \times 10^{-7}\text{ M}$). Our result is between these two limits, so the answer is reasonable.

Practice Exercise 20: Calculate the solubility of silver chloride in 0.10 M NH_3 and compare it with its solubility in pure water. Refer to Table 17.1 for the K_{sp} for AgCl . [Hint: Assume all the Ag^+ from the AgCl becomes incorporated into $\text{Ag}(\text{NH}_3)_2^+$.]

Practice Exercise 21: How many moles of NH_3 have to be added to 1.0 L of water to dissolve 0.20 mol of AgCl ? The complex ion $\text{Ag}(\text{NH}_3)_2^+$ forms.

SUMMARY

Solubility Equilibria for Salts. The mass action expression for a solubility equilibrium of a salt is called the **ion product**. It equals the product of the molar concentrations of its ions, each raised to a power equal to the subscript of the ion in the salt's formula. At a given temperature, the value of the ion product, Q , in a *saturated* solution of the salt equals a constant called the **solubility product constant**, or K_{sp} .

For solubility equilibria, the *common ion effect* is the ability of an ion of a soluble salt to suppress the solubility of a sparingly soluble compound that has the same (the "common") ion.

If soluble salts are mixed together in the same solution, a cation of one and an anion of another will precipitate if the ion product, Q , exceeds the solubility product constant of the salt formed from them.

Selective Precipitation. Metal sulfides are vastly more soluble in an acidic solution than in water. To express their solubility equilibria in acid, the **acid solubility constant** or K_{spa} is used.

Several metal sulfides have such low values of K_{spa} that they are insoluble even at low pH. These **acid-insoluble sulfides** can thus be selectively separated from the **base-insoluble sulfides** by making the solution both quite acidic as well as saturated in H_2S . By adjusting the pH, salts of other weak acids, like the carbonate salts, can also be selectively precipitated.

Complex Ions of Metals. **Coordination compounds** contain **complex ions** (also called **complexes** or **coordination complexes**), formed from a metal ion and a number of ligands. **Ligands** are Lewis bases and may be electrically neutral or negatively charged. Water and ammonia are common neutral ligands. The equilibrium constant for the formation of a complex in the presence of an excess of ligand is called the **formation constant**, K_{form} , of the complex. The larger the value of K_{form} , the more stable is the complex. Salts whose cations form stable complexes, like Ag^+ salts whose cation forms a stable complex with ammonia, $\text{Ag}(\text{NH}_3)_2^+$, are made more soluble when the ligand is present.



TOOLS FOR PROBLEM SOLVING

In this chapter you learned to apply the following concepts as tools in solving problems dealing with aspects of the solubility of salts. Study each tool carefully so that you know what each is used for. When faced with solving a problem, recall what each tool does and consider whether it will be helpful in finding a solution. This will aid you in selecting the tools you need.

Solubility product constant, K_{sp} (page 693) We use K_{sp} to calculate the molar solubility of a salt either in pure water or in a solution that contains a common ion. Comparing K_{sp} with the ion product of a potential precipitating salt permits us to decide whether a precipitate will form.

Molar solubility (page 695) This is used for calculating the value of K_{sp} for a salt. When calculating the solubility of a salt from K_{sp} , we let x represent the molar solubility in the concentration table.

Ion product, Q , of a salt (page 702) Compare Q with K_{sp} to determine whether a precipitate will form:

$$Q > K_{\text{sp}} \quad \text{a precipitate forms}$$

$$Q \leq K_{\text{sp}} \quad \text{a precipitate does not form}$$

Acid solubility product constant, K_{spa} (page 706) Use K_{spa} data to calculate the solubility of a metal sulfide at a given pH. We can use K_{spa} data for two or more metal sulfides to calculate the pH at which one will selectively precipitate from a solution saturated in H_2S .

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Combined K_a expression for a diprotic acid (page 710) Combining expressions for K_{a_1} and K_{a_2} for a diprotic acid, H_2A , yields the equation

$$\frac{[H^+]^2[A^{2-}]}{[H_2A]} = K_a = K_{a_1} \times K_{a_2}$$

This equation can be used if (and only if) we know two of the three quantities in the combined mass action expression. This is a useful tool when working problems involving selective precipitation of salts of diprotic acids where the concentration of the anion A^{2-} is controlled by adjusting the pH of the solution.

Formation constants (stability constants) of complexes (page 713) We can use K_{form} values to make judgments concerning the relative stabilities of complexes. Along with K_{sp} values, we can use formation constants of complexes to determine the solubility of a sparingly soluble salt in a solution containing a ligand that's able to form a complex with the cation of the salt.

QUESTIONS, PROBLEMS, AND EXERCISES

Answers to problems whose numbers are printed in color are given in Appendix B. More challenging problems are marked with asterisks. ILW = Interactive Learningware solution is available at www.wiley.com/college/brady. OH = an Office Hours video is available for this problem.

REVIEW QUESTIONS

Solubility Products

17.1 What is the difference between an *ion product* and an *ion product constant*?

17.2 Use the equilibrium below to demonstrate why the K_{sp} expression does not include the concentration of $Ba_3(PO_4)_2$ in the denominator.



17.3 What is the *common ion effect*? How does Le Châtelier's principle explain it? Use the solubility equilibrium for $AgCl$ to illustrate the common ion effect.

17.4 If sodium acetate is added to a solution of acetic acid, the pH increases. Explain how this is an example of the common ion effect.

17.5 With respect to K_{sp} , what conditions must be met if a precipitate is going to form in a solution?

17.6 What limits the accuracy and reliability of solubility calculations based on K_{sp} values?

Selective Precipitations

17.7 Potassium oxide is readily soluble in water, but the resulting solution contains essentially no oxide ion. Explain, using an equation, what happens to the oxide ion.

17.8 What chemical reaction takes place when solid sodium sulfide is dissolved in water? Write the chemical equation.

17.9 Consider cobalt(II) sulfide.

(a) Write its solubility equilibrium and K_{sp} equation for a saturated solution in water. (Remember, there is no free sulfide ion in the solution.)

(b) Write its solubility equilibrium and K_{spa} equation for a saturated solution in aqueous acid.

17.10 Use Le Châtelier's principle to explain how adjusting the pH enables the control of the concentration of $C_2O_4^{2-}$ in a solution of oxalic acid, $H_2C_2O_4$.

17.11 Suppose you wished to control the PO_4^{3-} concentration in a solution of phosphoric acid by controlling the pH of the solution. If you assume you know the H_3PO_4 concentration, what combined equation would be useful for that purpose?

Simultaneous and Complex Ion Equilibria

17.12 A solution of $MgBr_2$ can be changed to a solution of $MgCl_2$ by adding $AgCl(s)$ and stirring the mixture well. In terms of the equilibria involved, explain how this happens.

17.13 On the basis of Le Châtelier's principle, explain how the addition of solid NH_4Cl to a beaker containing solid $Mg(OH)_2$ in contact with water is able to cause the $Mg(OH)_2$ to dissolve. Write equations for *all* the chemical equilibria that exist in the solution after the addition of the NH_4Cl .

17.14 Using Le Châtelier's principle, explain how the addition of aqueous ammonia dissolves silver chloride. If HNO_3 is added after the $AgCl$ has dissolved in the NH_3 solution, it causes $AgCl$ to re-precipitate. Explain why.

17.15 For $PbCl_3^-$, $K_{\text{form}} = 2.5 \times 10^1$. If a solution containing this complex ion is diluted with water, $PbCl_2$ precipitates. Write the equations for the equilibria involved and use them together with Le Châtelier's principle to explain how this happens.

REVIEW PROBLEMS

Solubility Products

17.16 Write the K_{sp} expressions for each of the following compounds.

- | | | |
|----------------|----------------|----------------|
| (a) CaF_2 | (c) $PbSO_4$ | (e) PbI_2 |
| (b) Ag_2CO_3 | (d) $Fe(OH)_3$ | (f) $Cu(OH)_2$ |

17.17 Write the K_{sp} expressions for each of the following compounds.

- (a) AgI (c) PbCrO₄ (e) ZnCO₃
 (b) Ag₃PO₄ (d) Al(OH)₃ (f) Zn(OH)₂

Determining K_{sp}

17.18 In water, the solubility of lead(II) chloride is 0.016 *M*. Use that information to calculate the value of K_{sp} for PbCl₂.

OH 17.19 A student evaporated 100.0 mL of a saturated BaF₂ solution and found the solid BaF₂ she recovered weighed 0.132 g. From those data, calculate K_{sp} for BaF₂.

17.20 Barium sulfate is so insoluble that it can be swallowed without significant danger, even though Ba²⁺ is toxic. At 25 °C, 1.00 L of water dissolves only 0.00245 g of BaSO₄. Calculate K_{sp} for BaSO₄.

17.21 A student found that a maximum of 0.800 g silver acetate is able to dissolve in 100.0 mL of water. What is the molar solubility and the K_{sp} for the salt?

17.22 It was found that the molar solubility of BaSO₃ in 0.10 *M* BaCl₂ is 8.0×10^{-6} *M*. What is the value of K_{sp} for BaSO₃?

17.23 A student prepared a saturated solution of CaCrO₄ and found that when 156 mL of the solution was evaporated, 0.649 g of CaCrO₄ was left behind. What is the value of K_{sp} for the salt?

17.24 At 25 °C, the molar solubility of silver phosphate is 1.8×10^{-5} mol L⁻¹. Calculate K_{sp} for the salt.

17.25 The molar solubility of barium phosphate in water at 25 °C is 1.4×10^{-8} mol L⁻¹. What is the value of K_{sp} for the salt?

Using K_{sp} to Calculate Solubilities

17.26 What is the molar solubility of PbBr₂ in water?

17.27 What is the molar solubility of Ag₂CrO₄ in water?

17.28 Calculate the molar solubility of Ag₂CO₃ in water. (Ignore the reaction of the CO₃²⁻ ion with water.)

17.29 Calculate the molar solubility of PbF₂ in water.

17.30 At 25 °C, the value of K_{sp} for LiF is 1.7×10^{-3} , and that for BaF₂ is 1.7×10^{-6} . Which salt, LiF or BaF₂, has the larger molar solubility in water? Calculate the solubility of each in units of mol L⁻¹.

17.31 At 25 °C, the value of K_{sp} for AgCN is 2.2×10^{-16} and that for Zn(CN)₂ is 3×10^{-16} . In terms of grams per 100 mL of solution, which salt is the more soluble in water?

17.32 A salt whose formula is *MX* has a K_{sp} equal to 3.2×10^{-10} . Another sparingly soluble salt, *MX*₃, must have what value of K_{sp} if the molar solubilities of the two salts are to be identical?

17.33 A salt having a formula of the type *M*₂*X*₃ has $K_{sp} = 2.2 \times 10^{-20}$. Another salt, *M*₂*X*, has to have what K_{sp} value if *M*₂*X* has twice the molar solubility of *M*₂*X*₃?

17.34 Calcium sulfate is found in plaster. At 25 °C the value of K_{sp} for CaSO₄ is 2.4×10^{-5} . What is the calculated molar solubility of CaSO₄ in water?

17.35 Chalk is CaCO₃, and at 25 °C its $K_{sp} = 4.5 \times 10^{-9}$. What is the molar solubility of CaCO₃? How many grams of CaCO₃ dissolve in 100 mL of aqueous solution? (Ignore the reaction of CO₃²⁻ with water.)

Common Ion Effect

HW 17.36 Copper(I) chloride has $K_{sp} = 1.9 \times 10^{-7}$. Calculate the molar solubility of copper(I) chloride in (a) pure water, (b) 0.0200 *M* HCl solution, (c) 0.200 *M* HCl solution, and (d) 0.150 *M* CaCl₂ solution.

17.37 Gold(III) chloride has $K_{sp} = 3.2 \times 10^{-25}$. Calculate the molar solubility of gold(III) chloride in (a) pure water, (b) 0.010 *M* HCl solution, (c) 0.010 *M* MgCl₂ solution, and (d) 0.010 *M* Au(NO₃)₃ solution.

17.38 Calculate the molar solubility of Mg(OH)₂ in a solution that is basic with a pH of 12.50.

17.39 Calculate the molar solubility of Al(OH)₃ in a solution that is slightly basic with a pH of 9.50.

17.40 What is the highest concentration of Pb²⁺ that can exist in a solution of 0.10 *M* HCl?

17.41 Will lead(II) bromide be less soluble in 0.10 *M* Pb(C₂H₃O₂)₂ or in 0.10 *M* NaBr?

17.42 Calculate the molar solubility of Ag₂CrO₄ at 25 °C in (a) 0.200 *M* AgNO₃ and (b) 0.200 *M* Na₂CrO₄. For Ag₂CrO₄ at 25 °C, $K_{sp} = 1.2 \times 10^{-12}$.

17.43 What is the molar solubility of Mg(OH)₂ in (a) 0.20 *M* NaOH and (b) 0.20 *M* MgSO₄? For Mg(OH)₂, $K_{sp} = 7.1 \times 10^{-12}$.

17.44 How much will the percent ionization of the acetic acid change in 0.500 L of 0.10 *M* HC₂H₃O₂ if 0.050 mol of solid NaC₂H₃O₂ is added? (Assume no change in the volume of the solution.) How much will the pH change?

17.45 How much will the percent ionization of the acetic acid change in 0.500 L of 0.10 *M* HC₂H₃O₂ if 0.025 mol of gaseous HCl is dissolved in the solution? (Assume no change in volume.) How will the pH of the solution change?

***17.46** In an experiment 2.20 g of NaOH(*s*) is added to 250 mL of 0.10 *M* FeCl₂ solution. What mass of Fe(OH)₂ will be formed? What will the molar concentration of Fe²⁺ be in the final solution?

***17.47** Suppose that 1.75 g of NaOH(*s*) is added to 250 mL of 0.10 *M* NiCl₂ solution. What mass, in grams, of Ni(OH)₂ will be formed? What will be the pH of the final solution? For Ni(OH)₂, $K_{sp} = 6 \times 10^{-16}$.

17.48 What is the molar solubility of Fe(OH)₂ in a buffer that has a pH of 9.50?

17.49 What is the molar solubility of Ca(OH)₂ in (a) 0.10 *M* CaCl₂ and (b) 0.10 *M* NaOH?

Precipitation

17.50 Does a precipitate of PbCl₂ form when 0.0150 mol of Pb(NO₃)₂ and 0.0120 mol of NaCl are dissolved in 1.00 L of solution?

17.51 Silver acetate, AgC₂H₃O₂, has $K_{sp} = 2.3 \times 10^{-3}$. Does a precipitate form when 0.015 mol of AgNO₃ and 0.25 mol

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of $\text{Ca}(\text{C}_2\text{H}_3\text{O}_2)_2$ are dissolved in a total volume of 1.00 L of solution?

- ILW 17.52** Does a precipitate of PbBr_2 form if 50.0 mL of 0.0100 M $\text{Pb}(\text{NO}_3)_2$ is mixed with (a) 50.0 mL of 0.0100 M KBr and (b) 50.0 mL of 0.100 M NaBr ?

17.53 Would a precipitate of silver acetate form if 22.0 mL of 0.100 M AgNO_3 were added to 45.0 mL of 0.0260 M $\text{NaC}_2\text{H}_3\text{O}_2$? For $\text{AgC}_2\text{H}_3\text{O}_2$, $K_{\text{sp}} = 2.3 \times 10^{-3}$.

17.54 Both AgCl and AgI are very sparingly soluble salts, but the solubility of AgI is much less than that of AgCl , as can be seen by their K_{sp} values. Suppose that a solution contains both Cl^- and I^- with $[\text{Cl}^-] = 0.050 M$ and $[\text{I}^-] = 0.050 M$. If solid AgNO_3 is added to 1.00 L of this mixture (so that no appreciable change in volume occurs), what is the value of $[\text{I}^-]$ when AgCl first begins to precipitate?

17.55 Suppose that Na_2SO_4 is added gradually to 100.0 mL of a solution that contains both Ca^{2+} ion (0.15 M) and Sr^{2+} ion (0.15 M). (a) What will the Sr^{2+} concentration be (in mol L^{-1}) when CaSO_4 just begins to precipitate? (b) What percentage of the strontium ion has precipitated when CaSO_4 just begins to precipitate?

17.56 Suppose 50.0 mL each of 0.0100 M solutions of NaBr and $\text{Pb}(\text{NO}_3)_2$ are poured together. Does a precipitate form? If so, calculate the molar concentrations of the ions at equilibrium.

17.57 If a solution of 0.10 M Mn^{2+} and 0.10 M Cd^{2+} is gradually made basic, what will the concentration of Cd^{2+} be when $\text{Mn}(\text{OH})_2$ just begins to precipitate? Assume no change in the volume of the solution.

Selective Precipitation

- ILW 17.58** What value of $[\text{H}^+]$ and what pH permits the selective precipitation of the sulfide of just one of the two metal ions in a solution that has a concentration of 0.010 M Pb^{2+} and 0.010 M Co^{2+} ?

17.59 What pH would yield the maximum separation Mn^{2+} from Sn^{2+} in a solution that is 0.010 M in Mn^{2+} , 0.010 M in Sn^{2+} , and saturated in H_2S ? (Assume the green form of MnS in Table 17.2.)

17.60 What range of pH would permit the selective precipitation of Cu^{2+} as $\text{Cu}(\text{OH})_2$ from a solution that contains 0.10 M Cu^{2+} and 0.10 M Mn^{2+} ? For $\text{Mn}(\text{OH})_2$, $K_{\text{sp}} = 1.6 \times 10^{-13}$ and for $\text{Cu}(\text{OH})_2$, $K_{\text{sp}} = 4.8 \times 10^{-20}$.

17.61 Kidney stones often contain insoluble calcium oxalate, CaC_2O_4 , which has $K_{\text{sp}} = 2.3 \times 10^{-9}$. Calcium oxalate is considerably less soluble than magnesium oxalate, MgC_2O_4 , which has $K_{\text{sp}} = 8.6 \times 10^{-5}$. Suppose a solution contained both Ca^{2+} and Mg^{2+} at a concentration of 0.10 M . What pH would be required to achieve maximum separation of these ions by precipitation of CaC_2O_4 if the solution also contains oxalic acid, $\text{H}_2\text{C}_2\text{O}_4$ at a concentration of 0.10 M ? For $\text{H}_2\text{C}_2\text{O}_4$, $K_{\text{a}_1} = 5.6 \times 10^{-2}$ and $K_{\text{a}_2} = 5.4 \times 10^{-5}$.

Complex Ion Equilibria

17.62 Write the chemical equilibria and equilibrium laws that correspond to K_{form} for the following complexes:

- (a) CuCl_4^{2-}
 (b) AgI_2^-
 (c) $\text{Cr}(\text{NH}_3)_6^{3+}$

17.63 Write the chemical equilibria and equilibrium laws that correspond to K_{form} for the following complexes:

- (a) $\text{Ag}(\text{S}_2\text{O}_3)_2^{3-}$
 (b) $\text{Zn}(\text{NH}_3)_4^{2+}$
 (c) SnS_3^{2-}

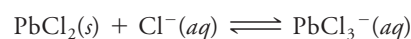
OH 17.64 Write equilibria that correspond to K_{form} for each of the following complex ions and write the equations for K_{form} .

- (a) $\text{Co}(\text{NH}_3)_6^{3+}$ (b) HgI_4^{2-} (c) $\text{Fe}(\text{CN})_6^{4-}$

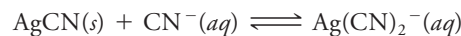
17.65 Write the equilibria that are associated with the equations for K_{form} for each of the following complex ions. Write also the equations for the K_{form} of each.

- (a) $\text{Hg}(\text{NH}_3)_4^{2+}$ (b) SnF_6^{2-} (c) $\text{Fe}(\text{CN})_6^{3-}$

17.66 For PbCl_3^- , $K_{\text{form}} = 2.5 \times 10^1$. Use this information plus the K_{sp} for PbCl_2 to calculate K_c for the reaction



17.67 The overall formation constant for $\text{Ag}(\text{CN})_2^-$ equals 5.3×10^{18} , and the K_{sp} for AgCN equals 1.2×10^{-16} . Calculate K_c for the reaction



17.68 How many grams of solid NaCN have to be added to 1.2 L of water to dissolve 0.11 mol of $\text{Fe}(\text{OH})_3$ in the form of $\text{Fe}(\text{CN})_6^{3-}$? Use data as needed from Tables 17.1 and 17.3. (For simplicity, ignore the reaction of CN^- ion with water.)

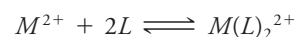
17.69 In photography, unexposed silver bromide is removed from film by soaking the film in a solution of sodium thiosulfate, $\text{Na}_2\text{S}_2\text{O}_3$. Silver ion forms a soluble complex with thiosulfate ion, $\text{S}_2\text{O}_3^{2-}$, that has the formula $\text{Ag}(\text{S}_2\text{O}_3)_2^{3-}$, and formation of the complex causes the AgBr in the film to dissolve. The $\text{Ag}(\text{S}_2\text{O}_3)_2^{3-}$ complex has $K_{\text{form}} = 2.0 \times 10^{13}$. How many grams of AgBr ($K_{\text{sp}} = 5.0 \times 10^{-13}$) will dissolve in 125 mL of 1.20 M $\text{Na}_2\text{S}_2\text{O}_3$ solution?

17.70 Silver iodide is very insoluble and can be difficult to remove from glass apparatus, but it forms a relatively stable complex ion, AgI_2^- ($K_{\text{form}} = 1 \times 10^{11}$), that makes AgI fairly soluble in a solution containing I^- . When a solution containing the AgI_2^- ion is diluted with water, AgI precipitates. Explain why this happens in terms of the equilibria that are involved. How many grams of AgI will dissolve in 100 mL of 1.0 M KI solution?

17.71 Silver forms a sparingly soluble cyanide salt, AgCN , for which $K_{\text{sp}} = 1.2 \times 10^{-16}$. It also forms a soluble cyanide complex, $\text{Ag}(\text{CN})_2^-$, for which $K_{\text{form}} = 5.3 \times 10^{18}$. How many grams of solid KCN must be added to 100 mL of water to dissolve 0.020 mol AgCN ? For simplicity, ignore the reaction of CN^- with water. Be sure to include all the cyanide that's added to the solution.

17.72 The formation constant for $\text{Ag}(\text{CN})_2^-$ equals 5.3×10^{18} . Use the data in Table 17.1 to determine the molar solubility of AgI in 0.010 M KCN solution.

17.73 Suppose that some divalent cation, M^{2+} , is able to form a complex ion with a ligand, L , by the following equation.



The cation also forms a sparingly soluble salt, $M\text{Cl}_2$. In which of the following circumstances would a given quantity of ligand be

more able to bring larger quantities of the salt into solution? Explain and justify the calculation involved.

- (a) $K_{\text{form}} = 1 \times 10^2$ and $K_{\text{sp}} = 1 \times 10^{-15}$
 (b) $K_{\text{form}} = 1 \times 10^{10}$ and $K_{\text{sp}} = 1 \times 10^{-20}$

17.74 The molar solubility of $\text{Zn}(\text{OH})_2$ in 1.0 *M* NH_3 is $5.7 \times 10^{-3} \text{ mol L}^{-1}$. Determine the value of the instability constant of the complex ion, $\text{Zn}(\text{NH}_3)_4^{2+}$. Ignore the reaction, $\text{NH}_3 + \text{H}_2\text{O} \rightleftharpoons \text{NH}_4^+ + \text{OH}^-$.

OH 17.75 Calculate the molar solubility of $\text{Cu}(\text{OH})_2$ in 2.0 *M* NH_3 . (For simplicity, ignore the reaction of NH_3 as a base.)

ADDITIONAL EXERCISES

***17.76** How many milliliters of 0.10 *M* HCl would have to be added to 100 mL of a saturated solution of PbCl_2 in contact with 50.0 g of solid PbCl_2 to reduce the Pb^{2+} concentration to 0.0050 *M*? (Don't forget to take into account the combined volumes of the two solutions.)

17.77 Magnesium hydroxide, $\text{Mg}(\text{OH})_2$, found in milk of magnesia, has a solubility of $7.05 \times 10^{-3} \text{ g L}^{-1}$ at 25 °C. Calculate K_{sp} for $\text{Mg}(\text{OH})_2$.

17.78 Does iron(II) sulfide dissolve in 8 *M* HCl ? Perform the calculations that prove your answer.

17.79 As noted earlier, milk of magnesia is an aqueous suspension of $\text{Mg}(\text{OH})_2$. If we assume that besides the $\text{Mg}(\text{OH})_2$ the only other component is water, use K_{sp} to estimate the pH of milk of magnesia.

***17.80** Suppose that 25.0 mL of 0.10 *M* HCl is added to 1.000 L of saturated $\text{Mg}(\text{OH})_2$ in contact with more than enough $\text{Mg}(\text{OH})_2(\text{s})$ to react with all the HCl . After reaction has ceased, what will the molar concentration of Mg^{2+} be? What will the pH of the solution be?

OH *17.81 Solid $\text{Mn}(\text{OH})_2$ is added to a solution of 0.100 *M* FeCl_2 . After reaction, what will be the molar concentrations of Mn^{2+} and Fe^{2+} in the solution? What will be the pH of the solution? For $\text{Mn}(\text{OH})_2$, $K_{\text{sp}} = 1.6 \times 10^{-13}$.

***17.82** Suppose that 50.0 mL of 0.12 *M* AgNO_3 is added to 50.0 mL of 0.048 *M* NaCl solution. (a) What mass of AgCl would form? (b) Calculate the final concentrations of all of the ions in the solution that is in contact with the precipitate. (c) What percentage of the Ag^+ ions have precipitated?

***17.83** A sample of hard water was found to have 278 ppm Ca^{2+} ion. Into 1.00 L of this water, 1.00 g of Na_2CO_3 was dissolved. What is the new concentration of Ca^{2+} in parts per million? (Assume that the addition of Na_2CO_3 does not change the volume, and assume that the density of the aqueous solutions involved are all 1.00 g mL^{-1} .)

***17.84** What value of $[\text{H}^+]$ and what pH would allow the selective separation of the carbonate of just one of the two metal ions in a solution that has a concentration of 0.010 *M* La^{3+} and 0.010 *M* Pb^{2+} ? For $\text{La}_2(\text{CO}_3)_3$, $K_{\text{sp}} = 4.0 \times 10^{-34}$; for PbCO_3 , $K_{\text{sp}} = 7.4 \times 10^{-14}$. A saturated solution of CO_2 in water has a concentration of H_2CO_3 equal to $3.3 \times 10^{-2} \text{ M}$.

***17.85** When solid NH_4Cl is added to a suspension of $\text{Mg}(\text{OH})_2(\text{s})$, some of the $\text{Mg}(\text{OH})_2$ dissolves.

- (a) Write equations for *all* the chemical equilibria that exist in the solution after the addition of the NH_4Cl .

(b) How many moles of NH_4Cl must be added to 1.0 L of a suspension of $\text{Mg}(\text{OH})_2$ to dissolve 0.10 mol of $\text{Mg}(\text{OH})_2$?

(c) What is the pH of the solution after the 0.10 mol of $\text{Mg}(\text{OH})_2$ has dissolved in the solution containing the NH_4Cl ?

***17.86** After solid CaCO_3 was added to a slightly basic solution, the pH was measured to be 8.50. What was the molar solubility of CaCO_3 in the solution?

17.87 In modern construction, walls and ceilings are constructed of "drywall," which consists of plaster sandwiched between sheets of heavy paper. Plaster is composed of calcium sulfate, $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$. Suppose you had a leak in a water pipe that was dripping water on a drywall ceiling 1/2 in. thick at a rate of 2.00 L per day. Use the K_{sp} of calcium sulfate to estimate how many days it would take to dissolve a hole 1.0 cm in diameter. Assume the density of the plaster is 0.97 g cm^{-3} .

17.88 What is the molar solubility of $\text{Fe}(\text{OH})_3$ in water? (Hint: Don't forget the self-ionization of water.)

***17.89** In Example 17.11 (page 716) we say, "There are relatively few uncomplexed Ag^+ ions in the solution." Calculate the molar concentration of Ag^+ ion actually left after the complex forms as described in Example 17.11.

***17.90** What are the concentrations of Pb^{2+} , Br^- , and I^- in an aqueous solution that's in contact with both PbI_2 and PbBr_2 ?

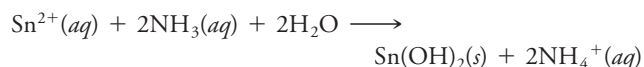
***17.91** Will a precipitate form in a solution made by dissolving 1.0 mol of AgNO_3 and 1.0 mol $\text{HC}_2\text{H}_3\text{O}_2$ in 1.0 L of solution? For $\text{AgC}_2\text{H}_3\text{O}_2$, $K_{\text{sp}} = 2.3 \times 10^{-3}$ and for $\text{HC}_2\text{H}_3\text{O}_2$, $K_{\text{a}} = 1.8 \times 10^{-5}$.

***17.92** How many grams of solid sodium acetate must be added to 0.200 L of a solution containing 0.200 *M* AgNO_3 and 0.10 *M* nitric acid to cause silver acetate to begin to precipitate? For $\text{HC}_2\text{H}_3\text{O}_2$, $K_{\text{a}} = 1.8 \times 10^{-5}$ and for $\text{AgC}_2\text{H}_3\text{O}_2$, $K_{\text{sp}} = 2.3 \times 10^{-3}$.

***17.93** How many grams of solid potassium fluoride must be added to 200 mL of a solution that contains 0.20 *M* AgNO_3 and 0.10 *M* acetic acid to cause silver acetate to begin to precipitate? For HF , $K_{\text{a}} = 6.8 \times 10^{-4}$; for $\text{HC}_2\text{H}_3\text{O}_2$, $K_{\text{a}} = 1.8 \times 10^{-5}$; for $\text{AgC}_2\text{H}_3\text{O}_2$, $K_{\text{sp}} = 2.3 \times 10^{-3}$.

***17.94** What is the molar solubility of $\text{Mg}(\text{OH})_2$ in 0.10 *M* NH_3 solution? Remember that NH_3 is a weak base.

***17.95** If 100 mL of 2.0 *M* NH_3 is added to 400 mL of a solution containing 0.10 *M* Mn^{2+} and 0.10 *M* Sn^{2+} , what minimum number of grams of HCl would have to be added to the mixture to prevent $\text{Mn}(\text{OH})_2$ from precipitating? For $\text{Mn}(\text{OH})_2$, $K_{\text{sp}} = 1.6 \times 10^{-13}$. Assume that virtually all the tin is precipitated as $\text{Sn}(\text{OH})_2$ by the reaction



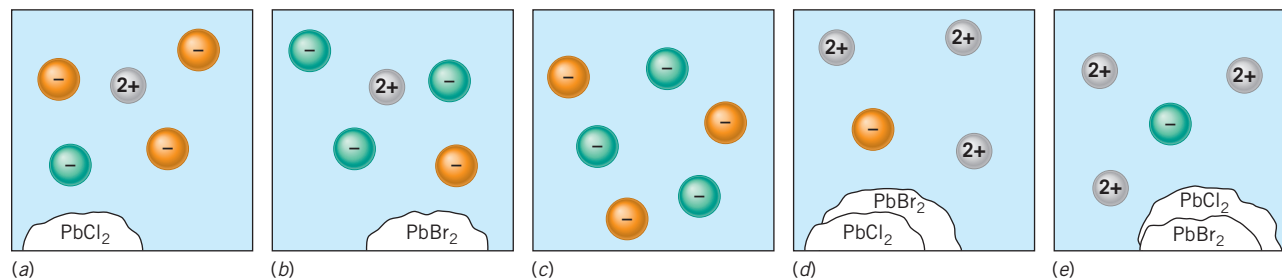
***17.96** What is the molar concentration of Cu^{2+} ion in a solution prepared by mixing 0.50 mol of NH_3 and 0.050 mol of CuSO_4 in 1.00 L of solution? For NH_3 , $K_{\text{b}} = 1.8 \times 10^{-5}$; for $\text{Cu}(\text{OH})_2$, $K_{\text{sp}} = 4.8 \times 10^{-20}$; and for $\text{Cu}(\text{NH}_3)_4^{2+}$, $K_{\text{form}} = 1.1 \times 10^{13}$.

***17.97** On the basis of the K_{sp} of $\text{Al}(\text{OH})_3$, what would be the pH of a mixture consisting of solid $\text{Al}(\text{OH})_3$ mixed with pure water? (Assume 100% dissociation of the aluminum hydroxide.)

17.98 You are given a sample containing $\text{NaCl}(\text{aq})$ and $\text{NaBr}(\text{aq})$, both with concentrations of 0.020 *M*. Some of the figures below

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represent a series of snapshots of what molecular level views of the sample would show as a 0.200 M $\text{Pb}(\text{NO}_3)_2(\text{aq})$ solution is slowly added. In these figures, Br^- is red-brown and Cl^- is green. Also, spectator ions are not shown, nor are ions whose concentrations are much less than the other ions. The K_{sp} constants for PbCl_2 and PbBr_2 are 1.7×10^{-5} and 2.1×10^{-6} , respectively.



EXERCISES IN CRITICAL THINKING

17.99 Consider mercury(II) sulfide, HgS , which has a solubility product of 2×10^{-53} . Suppose some solid HgS was added to 1.0 L of water. How many ions of Hg^{2+} and S^{2-} are present in the water when equilibrium is reached? If your answer is accurate, is there a true equilibrium between $\text{HgS}(s)$ and the ions in the solution? Explain your answer.

17.100 If aqueous ammonia is added gradually to a solution of copper sulfate, a pale blue precipitate forms that then dissolves to give a deep blue solution. Describe the chemical reactions that take place during these changes.

17.101 From a practical standpoint, can you effectively separate Pb^{2+} and Sr^{2+} ions by selective precipitation of their sulfates? Support your conclusions using calculations.

(1) Arrange the figures in a time sequence to show what happens as the lead nitrate solution is added, excluding any that do not “make sense.”

(2) Explain why you excluded any figures that did not belong in the observed time sequence.

17.102 A salt with the formula of MX_2 is slightly soluble in water. Estimate the minimum reliable mass you can determine on your laboratory balance. Use that estimate to determine the smallest value of the solubility product of MX_2 that could be determined by evaporating a liter of a solution that is saturated in MX_2 .

17.103 In older textbooks the solubility equilibrium for lead(II) sulfide was written as $\text{PbS}(s) \rightleftharpoons \text{Pb}^{2+}(\text{aq}) + \text{S}^{2-}(\text{aq})$ with $K_{\text{sp}} = 3.0 \times 10^{-28}$. Calculate the solubility of lead sulfide using K_{sp} (assuming no reaction of S^{2-} with water) and with K_{spa} . Is there a difference between the two answers? Discuss the results of your calculations.

17.104 Suppose two silver wires, one coated with silver chloride and the other coated with silver bromide, are placed in a beaker containing pure water. Over time, what if anything will happen to the compositions of the coatings on the two wires? Justify your answer.