

Solubility and Complex-ion Equilibria

Contents and Concepts

Solubility Equilibria

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Complex-Ion Equilibria

5. Complex-Ion Formation
6. Complex Ions and Solubility

An Application of Solubility Equilibria

7. Qualitative Analysis of Metal Ions

Learning Objectives

Solubility Equilibria

1. The Solubility Product Constant

- a. Define the *solubility product constant*, K_{sp} .
- b. Write solubility product expressions.
- c. Define *molar solubility*.
- d. Calculate K_{sp} from the solubility (simple example).
- e. Calculate K_{sp} from the solubility (more complicated example).
- f. Calculate the solubility from K_{sp} .

2. Solubility and the Common-Ion Effect

- a. Explain how the solubility of a salt is affected by another salt that has the same cation or anion. (*common ion*)
- b. Calculate the solubility of a slightly soluble salt in a solution of a common ion.

3. Precipitation Calculations

- a. Define *ion product*.
- b. State the criterion for precipitation.
- c. Predict whether precipitation will occur, given ion concentrations.
- d. Predict whether precipitation will occur, given solution volumes and concentrations.
- e. Define *fractional precipitation*.
- f. Explain how two ions can be separated using fractional precipitation.

4. Effect of pH on Solubility

- a. Explain the qualitative effect of pH on solubility of a slightly soluble salt.
- b. Determine the qualitative effect of pH on solubility.
- c. Explain the basis for the sulfide scheme to separate a mixture of metal ions.

Complex-Ion Equilibria

5. Complex-Ion Formation

- a. Define *complex ion* and *ligand*.
- b. Define *formation constant* or *stability constant*, K_f and *dissociation constant*, K_d .
- c. Calculate the concentration of a metal ion in equilibrium with a complex ion.
- d. Define *amphoteric hydroxide*.

6. Complex Ions and Solubility

- a. Predict whether a precipitate will form in the presence of the complex ion.
- b. Calculate the solubility of a slightly soluble ionic compound in a solution of the complex ion.

An Application of Solubility Equilibria

7. Qualitative Analysis of Metal Ions

- a. Define *qualitative analysis*.
- b. Describe the main outline of the sulfide scheme for qualitative analysis.

- To deal quantitatively with an equilibrium, you must know the equilibrium constant.
- We will look at the equilibria of slightly soluble (or nearly insoluble) ionic compounds and show how you can determine their equilibrium constants.
- Once you find these values for various ionic compounds, you can use them to answer questions about solubility or precipitation.

Solubility Equilibria

- Many natural processes depend on the precipitation or dissolving of a **slightly soluble salt**.
 - In the next section, we look at the **equilibria** of slightly soluble, or nearly insoluble, ionic compounds.
 - Their equilibrium constants can be used to answer questions regarding **solubility** and **precipitation**.

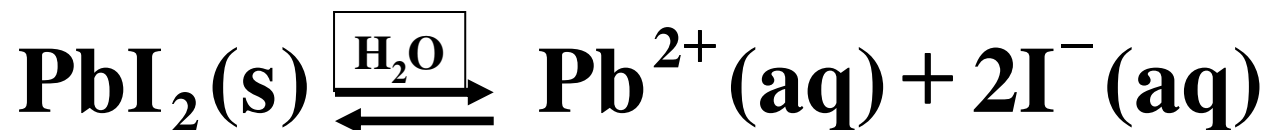
- When an ionic compound is insoluble or slightly soluble, an equilibrium is established:



- The equilibrium constant for this type of reaction is called the **solubility-product constant, K_{sp}** .
- For the above reaction,
 - $K_{\text{sp}} = [\text{M}^+][\text{X}^-]$

The Solubility Product Constant

- In general, the **solubility product constant** is the equilibrium constant for the solubility equilibrium of a slightly soluble (or nearly insoluble) ionic compound.
 - It equals the **product of the equilibrium concentrations** of the ions in the compound.
 - Each concentration is **raised to a power** equal to the number of such ions in the formula of the compound.
 - For example, lead iodide, PbI_2 , is another slightly soluble salt. Its equilibrium is:



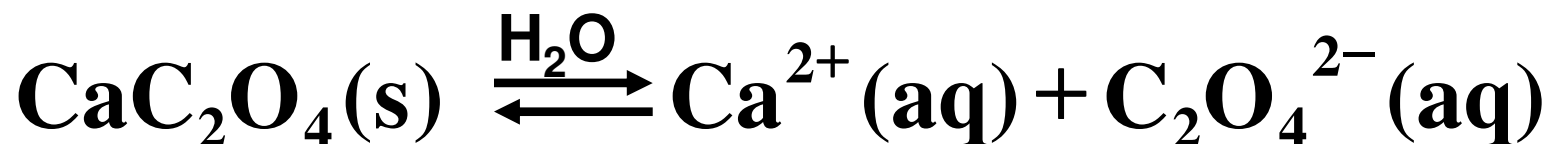
- The expression for the solubility product constant is:

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



$$K_{sp} = [\text{Ag}^{+}][\text{Cl}^{-}]$$

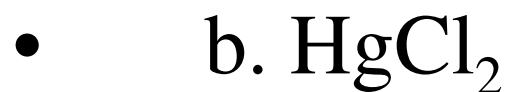
- When an excess of a slightly soluble ionic compound is mixed with water, **an equilibrium is established between the solid and the ions in the saturated solution.**
 - For the salt calcium oxalate, CaC_2O_4 , you have the following equilibrium.



- The equilibrium constant for this process is called the **solubility product constant.**

$$K_{\text{sp}} = [\text{Ca}^{2+}][\text{C}_2\text{O}_4^{2-}]$$

- Write the solubility-product expression for the following salts:



- $K_{\text{sp}} = [\text{Hg}_2^{2+}][\text{Cl}^-]^2$



- $K_{\text{sp}} = [\text{Hg}^{2+}][\text{Cl}^-]^2$

- Exactly 0.133 mg of AgBr will dissolve in 1.00 L of water. What is the value of K_{sp} for AgBr?

Solubility equilibrium:



Solubility-product constant expression:

$$K_{sp} = [\text{Ag}^+][\text{Br}^-]$$

The solubility is given as 0.133 mg/1.00 L, but K_{sp} uses molarity:

$$\frac{0.133 \times 10^{-3} \text{ g}}{1.00 \text{ L}} \times \frac{1 \text{ mol}}{187.772 \text{ g}} = 7.083 \times 10^{-7} \text{ M}$$

	$\text{AgBr}(s) \rightleftharpoons$	$\text{Ag}^+(aq)$ +	$\text{Br}^-(aq)$
Initial		0	0
Change		+ x	+ x
Equilibrium		x	x

$$[\text{Ag}^+] = [\text{Br}^-] = x = 7.083 \times 10^{-7} \text{ M}$$

$$K_{\text{sp}} = (7.083 \times 10^{-7})^2$$

$$K_{\text{sp}} = 5.02 \times 10^{-13}$$

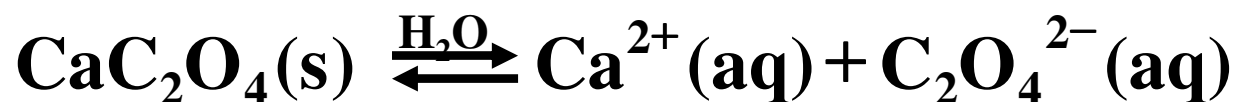
Calculating K_{sp} from the Solubility

- A 1.0-L sample of a saturated calcium oxalate solution, CaC_2O_4 , contains 0.0061-g of the salt at 25 °C. Calculate the K_{sp} for this salt at 25 °C.
 - We must first convert the solubility of calcium oxalate from 0.0061 g/liter to moles per liter.

$$\begin{aligned} M \text{ CaC}_2\text{O}_4 &= (0.0061 \text{ g CaC}_2\text{O}_4 / \text{L}) \times \frac{1 \text{ mol CaC}_2\text{O}_4}{128 \text{ g CaC}_2\text{O}_4} \\ &= 4.8 \times 10^{-5} \text{ mol CaC}_2\text{O}_4 / \text{L} \end{aligned}$$

Calculating K_{sp} from the Solubility

- A 1.0-L sample of a saturated calcium oxalate solution, CaC_2O_4 , contains 0.0061-g of the salt at 25 °C. Calculate the K_{sp} for this salt at 25 °C.
 - When 4.8×10^{-5} mol of solid dissolve it forms 4.8×10^{-5} mol of each ion.



Starting
Change
Equilibrium

0	0
$+4.8 \times 10^{-5}$	$+4.8 \times 10^{-5}$
4.8×10^{-5}	4.8×10^{-5}

- You can now substitute into the equilibrium-constant expression.

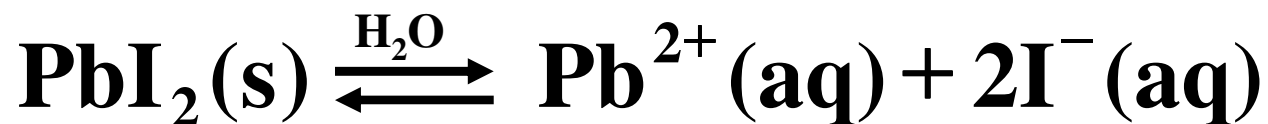
$$K_{sp} = [\text{Ca}^{2+}][\text{C}_2\text{O}_4^{2-}]$$

$$K_{sp} = (4.8 \times 10^{-5})(4.8 \times 10^{-5})$$

$$K_{sp} = 2.3 \times 10^{-9}$$

Calculating K_{sp} from the Solubility

- By experiment, it is found that 1.2×10^{-3} mol of lead(II) iodide, PbI_2 , dissolves in 1.0 L of water at 25 °C. What is the K_{sp} at this temperature?
 - Note that in this example, you find that 1.2×10^{-3} mol of the solid dissolves to give 1.2×10^{-3} mol Pb^{2+} and **2 x** (1.2×10^{-3}) mol of I^- .



Starting
Change
Equilibrium

0	0
$+1.2 \times 10^{-3}$	$+2 \times (1.2 \times 10^{-3})$
1.2×10^{-3}	$2 \times (1.2 \times 10^{-3})$

- Substituting into the equilibrium-constant expression:

$$\mathbf{K_{sp} = [Pb^{2+}][I^{-}]^2}$$

$$\mathbf{K_{sp} = (1.2 \times 10^{-3})(2 \times (1.2 \times 10^{-3}))^2}$$

$$\mathbf{K_{sp} = 6.9 \times 10^{-9}}$$

- Table 17.1 lists the solubility product constants for various ionic compounds.
- If the solubility product constant is known, the solubility of the compound can be calculated.

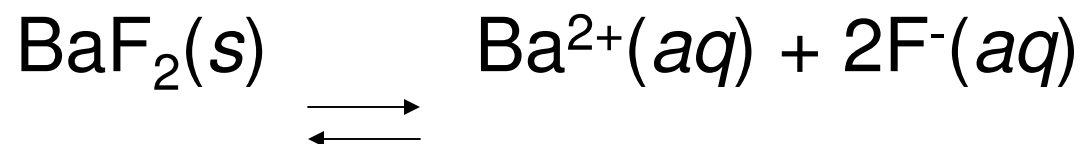
TABLE 17.1

Solubility Product Constants, K_{sp} , at 25°C

Substance	Formula	K_{sp}	Substance	Formula	K_{sp}
Aluminum hydroxide	$\text{Al}(\text{OH})_3$	4.6×10^{-33}	Lead(II) sulfide	PbS	2.5×10^{-27}
Barium chromate	BaCrO_4	1.2×10^{-10}	Magnesium arsenate	$\text{Mg}_3(\text{AsO}_4)_2$	2×10^{-20}
Barium fluoride	BaF_2	1.0×10^{-6}	Magnesium carbonate	MgCO_3	1.0×10^{-5}
Barium sulfate	BaSO_4	1.1×10^{-10}	Magnesium hydroxide	$\text{Mg}(\text{OH})_2$	1.8×10^{-11}
Cadmium oxalate	CdC_2O_4	1.5×10^{-8}	Magnesium oxalate	MgC_2O_4	8.5×10^{-5}
Cadmium sulfide	CdS	8×10^{-27}	Manganese(II) sulfide	MnS	2.5×10^{-10}
Calcium carbonate	CaCO_3	3.8×10^{-9}	Mercury(I) chloride	Hg_2Cl_2	1.3×10^{-18}
Calcium fluoride	CaF_2	3.4×10^{-11}	Mercury(II) sulfide	HgS	1.6×10^{-52}
Calcium oxalate	CaC_2O_4	2.3×10^{-9}	Nickel(II) hydroxide	$\text{Ni}(\text{OH})_2$	2.0×10^{-15}
Calcium phosphate	$\text{Ca}_3(\text{PO}_4)_2$	1×10^{-26}	Nickel(II) sulfide	NiS	3×10^{-19}
Calcium sulfate	CaSO_4	2.4×10^{-5}	Silver acetate	$\text{AgC}_2\text{H}_3\text{O}_2$	2.0×10^{-3}
Cobalt(II) sulfide	CoS	4×10^{-21}	Silver bromide	AgBr	5.0×10^{-13}
Copper(II) hydroxide	$\text{Cu}(\text{OH})_2$	2.6×10^{-19}	Silver chloride	AgCl	1.8×10^{-10}
Copper(II) sulfide	CuS	6×10^{-36}	Silver chromate	Ag_2CrO_4	1.1×10^{-12}
Iron(II) hydroxide	$\text{Fe}(\text{OH})_2$	8×10^{-16}	Silver iodide	AgI	8.3×10^{-17}
Iron(II) sulfide	FeS	6×10^{-18}	Silver sulfide	Ag_2S	6×10^{-50}
Iron(III) hydroxide	$\text{Fe}(\text{OH})_3$	2.5×10^{-39}	Strontium carbonate	SrCO_3	9.3×10^{-10}
Lead(II) arsenate	$\text{Pb}_3(\text{AsO}_4)_2$	4×10^{-36}	Strontium chromate	SrCrO_4	3.5×10^{-5}
Lead(II) chloride	PbCl_2	1.6×10^{-5}	Strontium sulfate	SrSO_4	2.5×10^{-7}
Lead(II) chromate	PbCrO_4	1.8×10^{-14}	Zinc hydroxide	$\text{Zn}(\text{OH})_2$	2.1×10^{-16}
Lead(II) iodide	PbI_2	6.5×10^{-9}	Zinc sulfide	ZnS	1.1×10^{-21}
Lead(II) sulfate	PbSO_4	1.7×10^{-8}			

- An experimenter finds that the solubility of barium fluoride is 1.1 g in 1.00 L of water at 25°C. What is the value of K_{sp} for barium fluoride, BaF_2 , at this temperature?

Solubility equilibrium:



Solubility-product constant expression:

$$K_{sp} = [Ba^{2+}][F^{-}]^2$$

The solubility is given as 1.1 g/1.00 L, but K_{sp} uses molarity:

$$x = \frac{1.1 \text{ g}}{1.00 \text{ L}} \times \frac{1 \text{ mol}}{175.32 \text{ g}} = 6.27 \times 10^{-3} \text{ M}$$

	$\text{BaF}_2(s) \rightleftharpoons$	$\text{Ba}^{2+}(aq)$	$2\text{F}^{-}(aq)$
Initial		0	0
Change		$+x$	$+2x$
Equilibrium		x	$2x$

m

$$[\text{Ba}^{2+}] = x = 6.27 \times 10^{-3} \text{ M}$$

$$[\text{F}^{-}] = 2x = 2(6.27 \times 10^{-3}) = 1.25 \times 10^{-2} \text{ M}$$

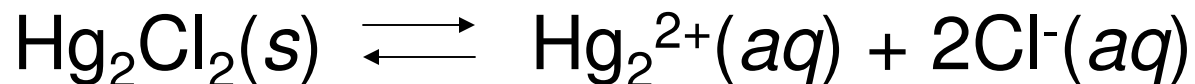
$$K_{\text{sp}} = (6.27 \times 10^{-3})(1.25 \times 10^{-2})^2$$

$$K_{\text{sp}} = 9.8 \times 10^{-7}$$

- When K_{sp} is known, we can find the molar solubility.

- Calomel, whose chemical name is mercury(I) chloride, Hg_2Cl_2 , was once used in medicine (as a laxative and diuretic). It has a K_{sp} equal to 1.3×10^{-18} . What is the solubility of Hg_2Cl_2 in grams per liter?

Solubility equilibrium:



Solubility-product constant expression:

$$K_{\text{sp}} = [\text{Hg}_2^{2+}][\text{Cl}^-]^2$$

	$\text{Hg}_2\text{Cl}_2(s) \rightleftharpoons$	$\text{Hg}_2^{2+}(aq) +$	$2\text{Cl}^-(aq)$
Initial		0	0
Change		$+x$	$+2x$
Equilibrium		x	$2x$

$$K_{\text{sp}} = x(2x)^2$$

$$K_{\text{sp}} = x(4x^2)$$

$$K_{\text{sp}} = 4x^3$$

$$1.3 \times 10^{-18} = 4x^3$$

$$x^3 = 3.25 \times 10^{-19}$$

$$x = 6.88 \times 10^{-7} \text{ M}$$

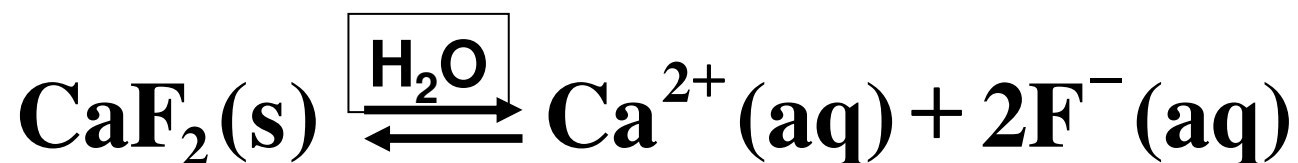
The molar solubility is $6.9 \times 10^{-7} M$, but we also need the solubility in g/L:

$$\frac{6.88 \times 10^{-7} \text{ mol}}{\text{L}} \times \frac{472.086 \text{ g}}{1 \text{ mol}} = 3.2 \times 10^{-4} \text{ g/L}$$

$= 0.32 \text{ mg/L}$

Calculating the Solubility from K_{sp}

- The mineral fluorite is calcium fluoride, CaF_2 .
Calculate the solubility (in grams per liter) of calcium fluoride in water from the K_{sp} (3.4×10^{-11})
 - Let x be the molar solubility of CaF_2 .



Starting
Change
Equilibrium

0	0
+x	+2x
x	2x

- You substitute into the equilibrium-constant equation

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

$$(\text{x})(2\text{x})^2 = 3.4 \times 10^{-11}$$

$$4\text{x}^3 = 3.4 \times 10^{-11}$$

- You now solve for x.

$$\text{x} = \sqrt[3]{\frac{3.4 \times 10^{-11}}{4}} = 2.0 \times 10^{-4}$$

- Convert to g/L (CaF_2 78.1 g/mol).

$$\begin{aligned}\text{solubility} &= 2.0 \times 10^{-4} \text{ mol/L} \times \frac{78.1 \text{ g CaF}_2}{1 \text{ mol CaF}_2} \\ &= 1.6 \times 10^{-2} \text{ g CaF}_2 / \text{L}\end{aligned}$$

Do Examples 18.2-4

See problems 18.22,23,34,25,26,29

Quick Quiz

- 1. The solubility product constant for CaCO_3 is 3.8×10^{-9} . Calculate the mass of calcium carbonate that will dissolve in 1 liter of water.
- 2. The solubility product constant for $\text{Fe}(\text{OH})_3$ is 2.5×10^{-39} . Calculate the moles of iron that will dissolve in 1 liter of water.

Lead compounds have been used as paint pigments, but because the lead(II) ion is toxic, the use of lead paints in homes is now prohibited. Which of the following lead(II) compounds would yield the greatest number of lead(II) ions when added to the same quantity of water (assuming that some undissolved solid always remains): PbCrO_4 , PbSO_4 , or PbS ?

- We can begin by identifying the value of K_{sp} for each compound:
 - PbCrO_4 1.8×10^{-14}
 - PbSO_4 1.7×10^{-8}
 - PbS 2.5×10^{-27}
- Each salt produces two ions, so each has the same expression for the solubility-product constant: $K_{\text{sp}} = x^2$.
- The solubility will be largest for PbSO_4 .

Solubility and the Common-Ion Effect

- In this section we will look at calculating solubilities **in the presence of other ions.**
 - The importance of the K_{sp} becomes apparent when you consider the solubility of one salt in the solution of another **having the same cation.**
 - For example, suppose you wish to know the solubility of calcium oxalate in a solution of calcium chloride.
 - Each salt contributes the same cation (Ca^{2+})
 - The effect is to make calcium oxalate **less soluble than it would be in pure water.**

- What effect does the presence of a common ion have on solubility?
- Given: $\text{MX}(s) \rightleftharpoons \text{M}^+(aq) + \text{X}^-(aq)$
- Qualitatively, we can use Le Châtelier's principle to predict that the reaction will shift in the reverse direction when M^+ or X^- is added, reducing the solubility.
- In the next problem, we will explore this situation quantitatively.

- What is the molar solubility of silver chloride in 1.0 L of solution that contains 2.0×10^{-2} mol of HCl?

First, using Table 17.1, we find that the K_{sp} for AgCl at 25 °C is 1.8×10^{-10} .

Next, we construct the ICE chart with the initial $[Cl^-] = 0.020 \text{ M}$. We then solve for x , the molar solubility.

	$\text{AgCl}(s) \rightleftharpoons$	$\text{Ag}^+(aq) +$	$\text{Cl}^-(aq)$
Initial		0	0.020
Change		$+x$	$+x$
Equilibrium		x	$0.020 + x$

$$K_{\text{sp}} = [\text{Ag}^+][\text{Cl}^-]$$

$$1.8 \times 10^{-10} = x(0.020 + x)$$

We make the following simplifying assumption:
 $0.020 + x \approx 0.020$.

$$1.8 \times 10^{-10} = 0.020x$$

The molar solubility is given by x :

$$x = 9.0 \times 10^{-9} M$$

- Let's compare this result to the solubility of AgCl in water:

- $K_{sp} = x^2$

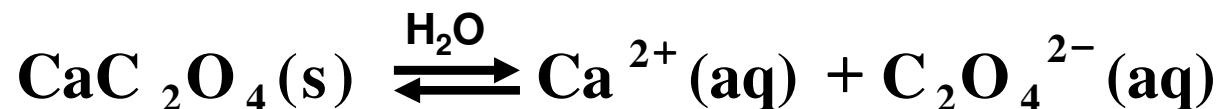
- $1.8 \times 10^{-10} = x^2$

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

- The solubility was reduced by a factor of about 1400!

A Problem To Consider

- What is the molar solubility of calcium oxalate in 0.15 M calcium chloride? The K_{sp} for calcium oxalate is 2.3×10^{-9} .
 - Note that before the calcium oxalate dissolves, there is already 0.15 M Ca^{2+} in the solution.



Starting
Change
Equilibrium

0.15	0
+x	+x
0.15+x	x

- You substitute into the equilibrium-constant equation

$$[\text{Ca}^{2+}][\text{C}_2\text{O}_4^{2-}] = K_{\text{sp}}$$

$$(0.15 + x)(x) = 2.3 \times 10^{-9}$$

- Now rearrange this equation to give

$$x = \frac{2.3 \times 10^{-9}}{0.15 + x} \cong \frac{2.3 \times 10^{-9}}{0.15}$$

- We expect x to be negligible compared to 0.15.

- Now rearrange this equation to give

$$x = \frac{2.3 \times 10^{-9}}{0.15 + x} \cong \frac{2.3 \times 10^{-9}}{0.15}$$

$$x = 1.5 \times 10^{-8}$$

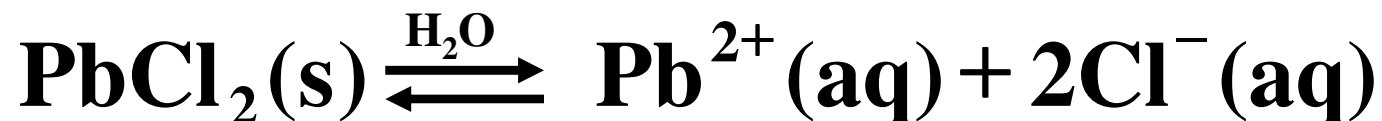
- Therefore, the molar solubility of calcium oxalate in 0.15 M CaCl_2 is 1.5×10^{-8} M.
- In pure water, the molarity was 4.8×10^{-5} M, which is over **3000 times greater**.

Precipitation Calculations

- Precipitation is merely another way of looking at solubility equilibrium.
 - Rather than considering how much of a substance will dissolve, we ask:
 - **Will precipitation occur for a given starting ion concentration?**

Criteria for Precipitation

- To determine whether an equilibrium system will go in the forward or reverse direction requires that we evaluate the **reaction quotient, Q_c** .
 - To predict the direction of reaction, you compare Q_c with K_c (Chapter 15).
 - The reaction quotient has the same form as the K_{sp} expression, but the concentrations of products are starting values.
 - Consider the following equilibrium.



- When a problem gives the amounts and concentrations of two samples that are then mixed, the first step in solving the problem is to calculate the new initial concentrations.
 - Exactly 0.400 L of 0.50 M Pb^{2+} and 1.60 L of $2.50 \times 10^{-2} M$ Cl^- are mixed together to form 2.00 L of solution.
 - Calculate Q_c and predict whether PbCl_2 will precipitate. K_{sp} for PbCl_2 is 1.6×10^{-5} .

$$[\text{Pb}^{2+}] = \frac{(0.500 \text{ M})(0.400 \text{ L})}{(2.00 \text{ L})} = 0.100 \text{ M}$$

$$[\text{Cl}^{-}] = \frac{(2.50 \times 10^{-2} \text{ M})(1.60 \text{ L})}{(2.00 \text{ L})} = 0.0200 \text{ M}$$

- $\text{PbCl}_2(s) \rightleftharpoons \text{Pb}^{2+}(aq) + 2\text{Cl}^{-}(aq)$
- $K_{\text{sp}} = [\text{Pb}^{2+}] [\text{Cl}^{-}]^2 = 1.6 \times 10^{-8}$
- $Q_{\text{c}} = (0.100)(0.0200)^2 = 4.00 \times 10^{-5}$

$$K_{\text{sp}} < Q_{\text{c}}$$

- A precipitate will form.

- We can use the reaction quotient, Q , to determine whether precipitation will occur.
- One form of kidney stones is calcium phosphate, $\text{Ca}_3(\text{PO}_4)_2$, which has a K_{sp} of 1.0×10^{-26} . A sample of urine contains $1.0 \times 10^{-3} \text{ M Ca}^{2+}$ and $1.0 \times 10^{-8} \text{ M PO}_4^{3-}$ ion.
- Calculate Q_c and predict whether $\text{Ca}_3(\text{PO}_4)_2$ will precipitate.



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

- $K_{\text{sp}} = 1.0 \times 10^{-26}$

- $Q_c = (1.0 \times 10^{-3})^3 (1.0 \times 10^{-8})^2$

- $Q_c = 1.0 \times 10^{-25}$

- $K_{\text{sp}} < Q_c$

- A precipitate will form.

- The Q_c expression is

$$Q_c = [\text{Pb}^{2+}]_i [\text{Cl}^-]_i^2$$

where initial concentration is denoted by i .

- If Q_c exceeds the K_{sp} , precipitation occurs.
- If Q_c is less than K_{sp} , more solute can dissolve.
- If Q_c equals the K_{sp} , the solution is saturated.

Predicting Whether Precipitation Will Occur

- The concentration of calcium ion in blood plasma is 0.0025 M. If the concentration of oxalate ion is 1.0×10^{-7} M, do you expect calcium oxalate to precipitate? K_{sp} for calcium oxalate is 2.3×10^{-9} .
 - The ion product quotient, Q_c , is:

$$Q_c = [\text{Ca}^{2+}]_i [\text{C}_2\text{O}_4^{2-}]_i$$

$$Q_c = (0.0025) \times (1.0 \times 10^{-7})$$

$$Q_c = 2.5 \times 10^{-10}$$

Do exercise 18.6

See problems 18.41 and 42

- This value is smaller than the K_{sp} , so **you do not expect precipitation to occur.**

$$Q_c = 2.5 \times 10^{-10} < K_{sp}$$

Fractional Precipitation

- **Fractional precipitation** is the technique of separating two or more ions from a solution by adding a reactant that precipitates first one ion, then another, and so forth. (page 744)
 - For example, when you slowly add potassium chromate, K_2CrO_4 , to a solution containing Ba^{2+} and Sr^{2+} , **barium chromate precipitates first.**

- **Fractional Precipitation**

- Fractional precipitation is the technique of separating two or more ions from a solution by adding a reactant that precipitates first one ion, then another ion, and so forth.
- The solubility of an insoluble salt can be manipulated by adding a species that reacts with either the cation or the anion.

- **Effect of pH on Solubility**

- When a salt contains the conjugate base of a weak acid, the pH will affect the solubility of the salt.

Fractional Precipitation

- 0.1 M Ba^{2+} and 0.1 M Sr^{2+}
- $[\text{Ba}^{2+}][\text{CrO}_4^{2-}] = K_{\text{sp}} = 1.2 \times 10^{-10}$

$$[\text{CrO}_4^{2-}] = 1.2 \times 10^{-9}$$

- $[\text{Sr}^{2+}][\text{CrO}_4^{2-}] = K_{\text{sp}} = 3.5 \times 10^{-5}$

$$[\text{CrO}_4^{2-}] = 3.5 \times 10^{-4}$$

Calculate the percent Ba^{2+} remaining when Sr^{2+} begins to Ppt

Fractional Precipitation

- **Fractional precipitation** is the technique of separating two or more ions from a solution by adding a reactant that precipitates first one ion, then another, and so forth.
 - After most of the Ba^{2+} ion has precipitated, strontium chromate begins to precipitate.
 - It is therefore possible to separate Ba^{2+} from Sr^{2+} by **fractional precipitation** using K_2CrO_4 .

- We will qualitatively explore the situation involving a generic salt, MX, where X is the conjugate base of a weak acid.



- As the acid concentration increases, X^- reacts with the H_3O^+ , forming HX and reducing the X^- concentration. As a result, more MX dissolves, increasing the solubility.

- Consider the two slightly soluble salts barium fluoride and silver bromide. Which of these would have its solubility more affected by the addition of strong acid? Would the solubility of that salt increase or decrease?

HF is a weak acid, while HBr is a strong acid.

BaF₂ is more soluble in an acidic solution.

AgBr is unaffected by an acidic solution.

If you add a dilute acidic solution to a mixture containing magnesium oxalate and calcium oxalate, which of the two compounds is more likely to dissolve?

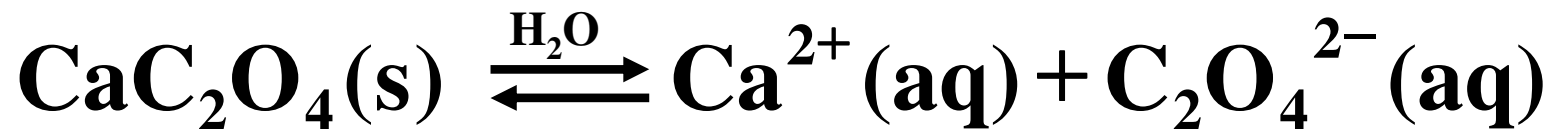
- K_{sp} for MgC_2O_4 is 8.5×10^{-5} .
- K_{sp} for BaC_2O_4 is 1.5×10^{-8} .
- MgC_2O_4 is more soluble.
- If a dilute acidic solution is added, it will increase the solubility of both salts. MgC_2O_4 is still more soluble.

- It is possible to use these differences to separate compounds.
- This is common practice when the goal is to separate sulfides from one another.
- The qualitative analysis scheme for the separation of metal ions uses sulfide solubility to separate Co^{2+} , Fe^{2+} , Mn^{2+} , Ni^{2+} , and Zn^{2+} (Analytical Group III).

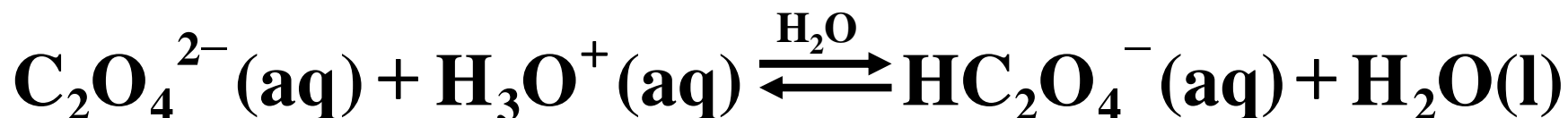
Effect of pH on Solubility

- Sometimes it is necessary to account for **other reactions** aqueous ions might undergo.
 - For example, if the anion is the **conjugate base of a weak acid**, it will react with H_3O^+ .
 - You should expect the solubility to be affected by pH.

- Consider the following equilibrium.



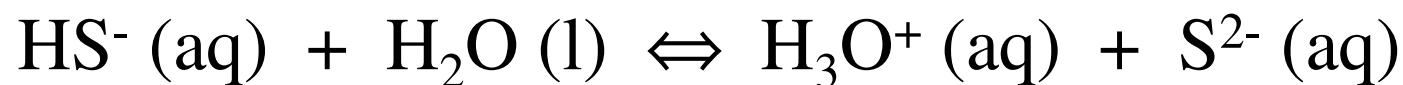
- Because the oxalate ion is conjugate to a weak acid (HC_2O_4^-), it will react with H_3O^+ .



- According to Le Chatelier's principle, as $\text{C}_2\text{O}_4^{2-}$ ion is removed by the reaction with H_3O^+ , more calcium oxalate dissolves.
- Therefore, you expect calcium oxalate to be **more soluble in acidic solution (low pH) than in pure water**.

Separation of Metal Ions by Sulfide Precipitation

- Many metal sulfides are insoluble in water but dissolve in acidic solution.
 - **Qualitative analysis** uses this change in solubility of the metal sulfides with pH to separate a mixture of metal ions.
 - By adjusting the pH in an aqueous solution of H_2S , you adjust the sulfide concentration to precipitate the least soluble metal sulfide first.
 - **Qualitative analysis** is covered in Section 17.7.

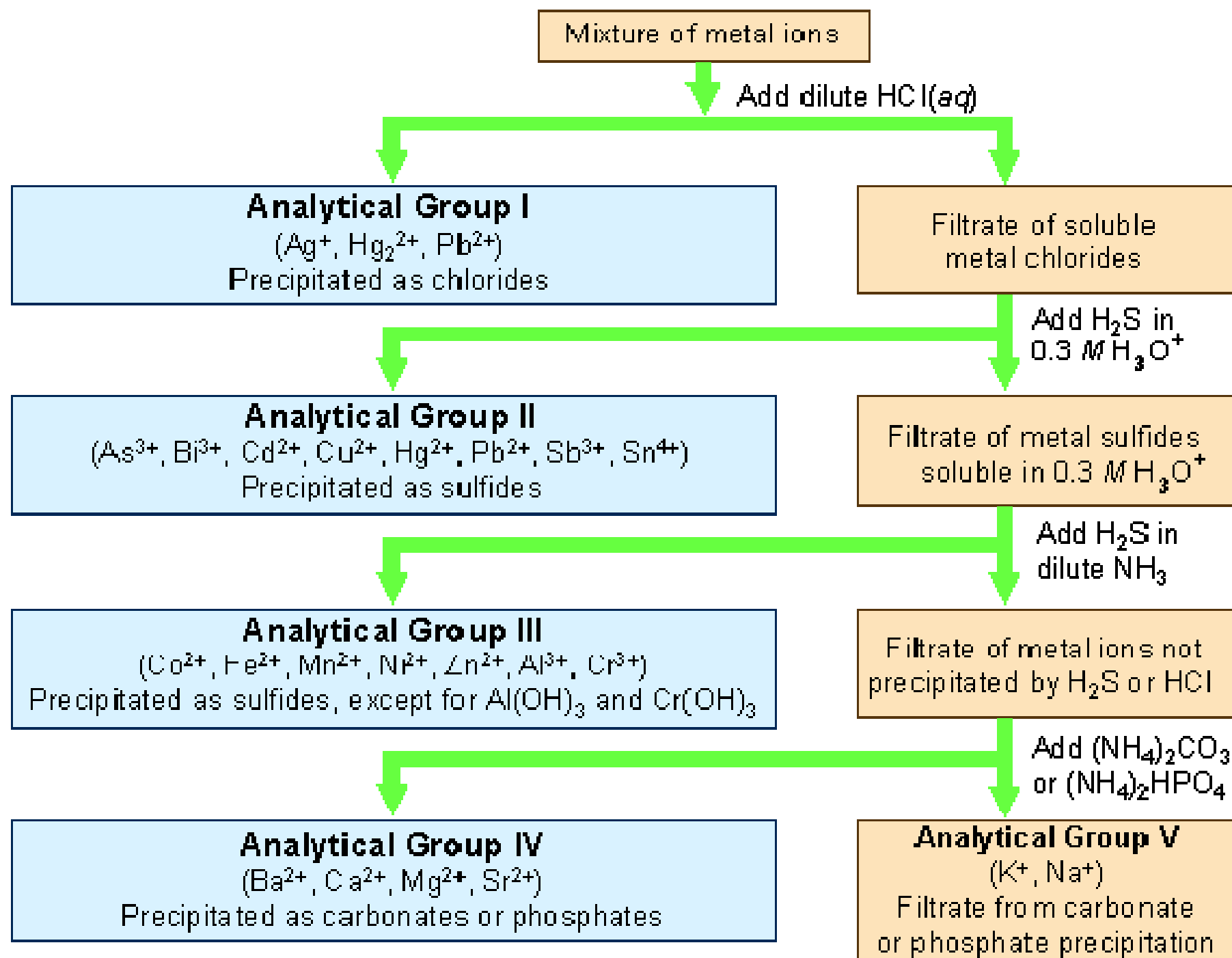


$$K_{a1} = \frac{[\text{HS}^-] [\text{H}_3\text{O}^+]}{[\text{H}_2\text{S}]} \quad K_{a2} = \frac{[\text{S}^{2-}] [\text{H}_3\text{O}^+]}{[\text{HS}^-]}$$

$$K_{a1} \times K_{a2} = \frac{[\text{H}_3\text{O}^+] [\text{HS}^-]}{[\text{H}_2\text{S}]} \times \frac{[\text{S}^{2-}] [\text{H}_3\text{O}^+]}{[\text{HS}^-]}$$

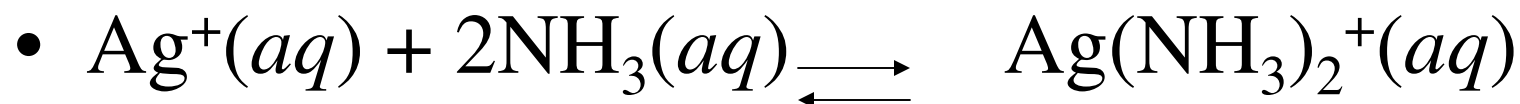
$$\frac{[\text{H}_3\text{O}^+]^2 [\text{S}^{2-}]}{[0.10]} = 1.3 \times 10^{-20}$$

$$[\text{H}_3\text{O}^+]^2 [\text{S}^{2-}] = 1.3 \times 10^{-21}$$

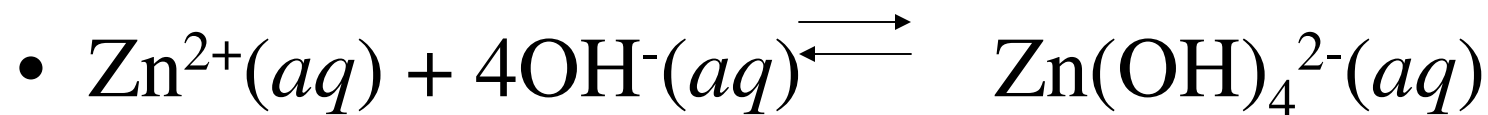


- **Complex-Ion Formation**
- Some cations form soluble complex ions.
Their formation increases the solubility of a salt containing those cations.

- Metal ions that form complex ions include Ag^+ , Cd^{2+} , Cu^{2+} , Fe^{2+} , Fe^{3+} , Ni^{2+} , and Zn^{2+} .
- Complexing agents, called ligands, are Lewis bases. They include CN^- , NH_3 , $\text{S}_2\text{O}_3^{2-}$, and OH^- .
- In each case, an equilibrium is established, called the complex-ion formation equilibrium.



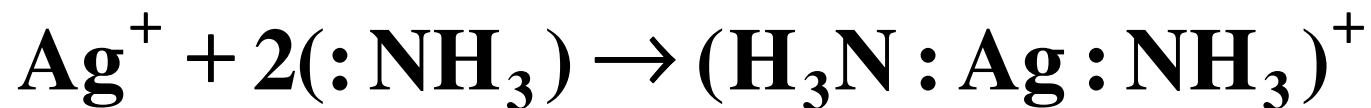
$$K_f = \frac{[\text{Ag}(\text{NH}_3)_2^+]}{[\text{Ag}^+][\text{NH}_3]^2}$$



$$K_f = \frac{[\text{Zn}(\text{OH})_4^{2-}]}{[\text{Zn}^{2+}][\text{OH}^-]^4}$$

Complex-Ion Equilibria

- Many **metal ions**, especially transition metals, form **coordinate covalent bonds** with molecules or anions having a lone pair of electrons.
 - This type of bond formation is essentially a Lewis acid-base reaction (Chapter 16).
 - For example, the silver ion, Ag^+ , can react with ammonia to form the $\text{Ag}(\text{NH}_3)_2^+$ ion.

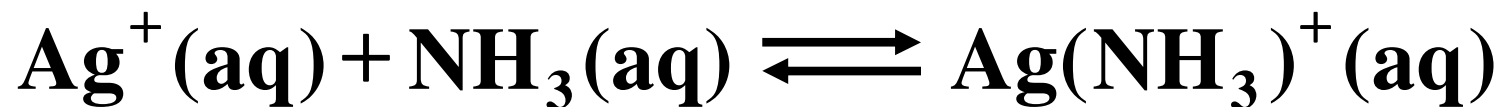


Complex-Ion Equilibria

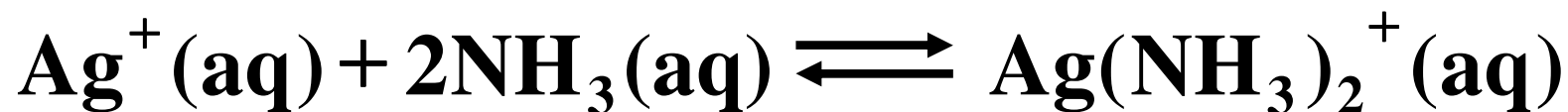
- A **complex ion** is an ion formed from a metal ion with a Lewis base attached to it by a coordinate covalent bond.
 - A **complex** is defined as a compound containing complex ions.
 - A **ligand** is a Lewis base (an electron pair donor) that bonds to a metal ion to form a complex ion.

Complex-Ion Formation

- The aqueous silver ion forms a complex ion with ammonia in steps.



- When you add these equations, you get the overall equation for the formation of $\text{Ag}(\text{NH}_3)_2^+$.



Complex-Ion Formation

- The **formation constant, K_f** , is the equilibrium constant for the formation of a complex ion from the aqueous metal ion and the ligands.
 - The formation constant for $\text{Ag}(\text{NH}_3)_2^+$ is:

$$K_f = \frac{[\text{Ag}(\text{NH}_3)_2^+]}{[\text{Ag}^+][\text{NH}_3]^2}$$

- The value of K_f for $\text{Ag}(\text{NH}_3)_2^+$ is 1.7×10^7 .

- The large value means that **the complex ion is quite stable.**
- When a large amount of NH_3 is added to a solution of Ag^+ , you expect most of the Ag^+ ion to react to form the complex ion.
- Table 17.2 lists formation constants of some complex ions.

- Formation constants are shown to the right.
- Note that all the values are quite large, which means that the equilibrium favors the complex ion.

TABLE 17.2

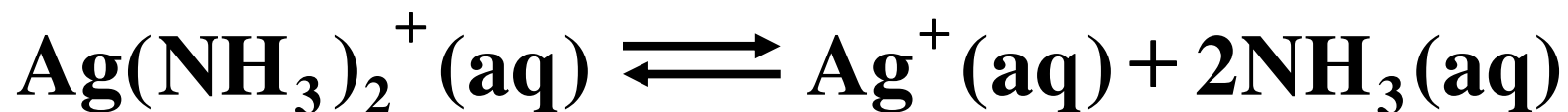
Formation Constants of Complex Ions at 25°C

Complex Ion	K_f
$\text{Ag}(\text{CN})_2^-$	5.6×10^{18}
$\text{Ag}(\text{NH}_3)_2^+$	1.7×10^7
$\text{Ag}(\text{S}_2\text{O}_3)_2^{3-}$	2.9×10^{13}
$\text{Cd}(\text{NH}_3)_4^{2+}$	1.0×10^7
$\text{Cu}(\text{CN})_2^-$	1.0×10^{16}
$\text{Cu}(\text{NH}_3)_4^{2+}$	4.8×10^{12}
$\text{Fe}(\text{CN})_6^{4-}$	1.0×10^{35}
$\text{Fe}(\text{CN})_6^{3-}$	9.1×10^{41}
$\text{Ni}(\text{CN})_4^{2-}$	1.0×10^{31}
$\text{Ni}(\text{NH}_3)_6^{2+}$	5.6×10^8
$\text{Zn}(\text{NH}_3)_4^{2+}$	2.9×10^9
$\text{Zn}(\text{OH})_4^{2-}$	2.8×10^{15}

Complex-Ion Formation

- The **dissociation constant, K_d** , is the reciprocal, or inverse, value of K_f .

— The equation for the dissociation of $\text{Ag}(\text{NH}_3)_2^+$ is



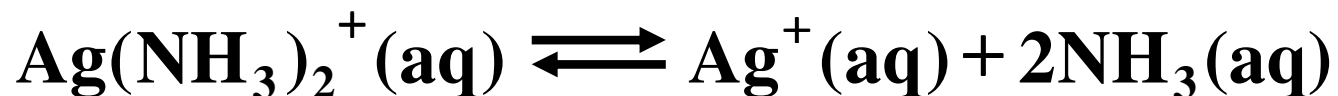
— The equilibrium constant equation is

$$K_d = \frac{1}{K_f} = \frac{[\text{Ag}^+][\text{NH}_3]^2}{[\text{Ag}(\text{NH}_3)_2^+]}$$

Equilibrium Calculations with K_f

- What is the concentration of $\text{Ag}^+(\text{aq})$ ion in 0.010 M AgNO_3 that is also 1.00 M NH_3 ? The K_f for $\text{Ag}(\text{NH}_3)_2^+$ is 1.7×10^7 .
 - In 1.0 L of solution, you initially have 0.010 mol $\text{Ag}^+(\text{aq})$ from AgNO_3 .
 - This reacts to give 0.010 mol $\text{Ag}(\text{NH}_3)_2^+$, leaving $(1.00 - (2 \times 0.010)) = 0.98$ mol NH_3 .
 - You now look at the dissociation of $\text{Ag}(\text{NH}_3)_2^+$.

—The following table summarizes.



Starting	0.010
Change	-x
Equilibrium	0.010-x

0	0.98
+x	+2x
x	0.98+2x

— The dissociation constant equation is:

$$\frac{[\text{Ag}^+][\text{NH}_3]^2}{[\text{Ag}(\text{NH}_3)_2^+]} = K_d = \frac{1}{K_f}$$

- Substituting into this equation gives:

$$\frac{(x)(0.98 + 2x)^2}{(0.010 - x)} = \frac{1}{1.7 \times 10^{-7}}$$

- If we assume x is small compared with 0.010 and 0.98, then

$$\frac{(x)(0.98)^2}{(0.010)} \cong 5.9 \times 10^{-8}$$

- and

$$x \cong 5.9 \times 10^{-8} \times (0.010) / (0.98)^2 = 6.1 \times 10^{-10}$$

- The silver ion concentration is **6.1 x 10⁻¹⁰ M**.

- Silver chloride usually does not precipitate in solutions of 1.00 M NH_3 . However, silver bromide has a smaller K_{sp} than silver chloride.
- Will silver bromide precipitate from a solution containing 0.010 M AgNO_3 , 0.010 M NaBr , and 1.00 M NH_3 ?
- Calculate the Q_c value and compare it with silver bromide's K_{sp} of 5.0×10^{-13} .

- We'll begin with the complex-ion formation, and then find the concentration of Ag^+ in solution. Finally, we'll find the value of Q_c for AgBr and compare it to K_{sp} .
- 1.00 L of solution contains 0.010 mol Ag^+ and 1.00 mol NH_3 .

	$\text{Ag}^+(aq) +$	$2\text{NH}_3(aq) \rightleftharpoons$	$\text{Ag}(\text{NH}_3)_2^+(aq)$
Initial	0.010	1.00	0
Change	-0.010	-2(0.010)	+0.010
Equilibrium	0	0.98	0.010

- $[\text{Ag}(\text{NH}_3)_2^+] = 0.0010 \text{ M}$; $[\text{NH}_3] = 0.998 \text{ M}$

	$\text{Ag}(\text{NH}_3)_2^+(aq)$		$+ 2\text{NH}_3(aq)$
Initial	0.010	$\text{Ag}^+(aq)$	0.980
Change	-x	$\xleftarrow{\hspace{1cm}} \xrightarrow{\hspace{1cm}}$ +x	+x
Equilibrium	$0.010 - x$	x	0.980

$$K_d = \frac{[\text{Ag}^+][\text{NH}_3]^2}{[\text{Ag}(\text{NH}_3)_2^+]} = \frac{1}{K_f} = \frac{1}{1.7 \times 10^7} = 5.9 \times 10^{-8}$$

$$5.9 \times 10^{-8} = \frac{x(0.980 + x)^2}{(0.010 - x)}$$

We can assume that $0.980 + x \approx 0.980$ and $0.010 - x \approx 0.010$.

$$5.9 \times 10^{-8} = \frac{x(0.980)^2}{0.010}$$

$$5.9 \times 10^{-8} = 96.0x$$

$$x = 6.1 \times 10^{-10} \text{ M}$$

- The assumptions are valid.
- $[\text{Ag}^+] = 6.1 \times 10^{-10} \text{ M}$

- Next we'll use the solubility equilibrium to find Q_c .

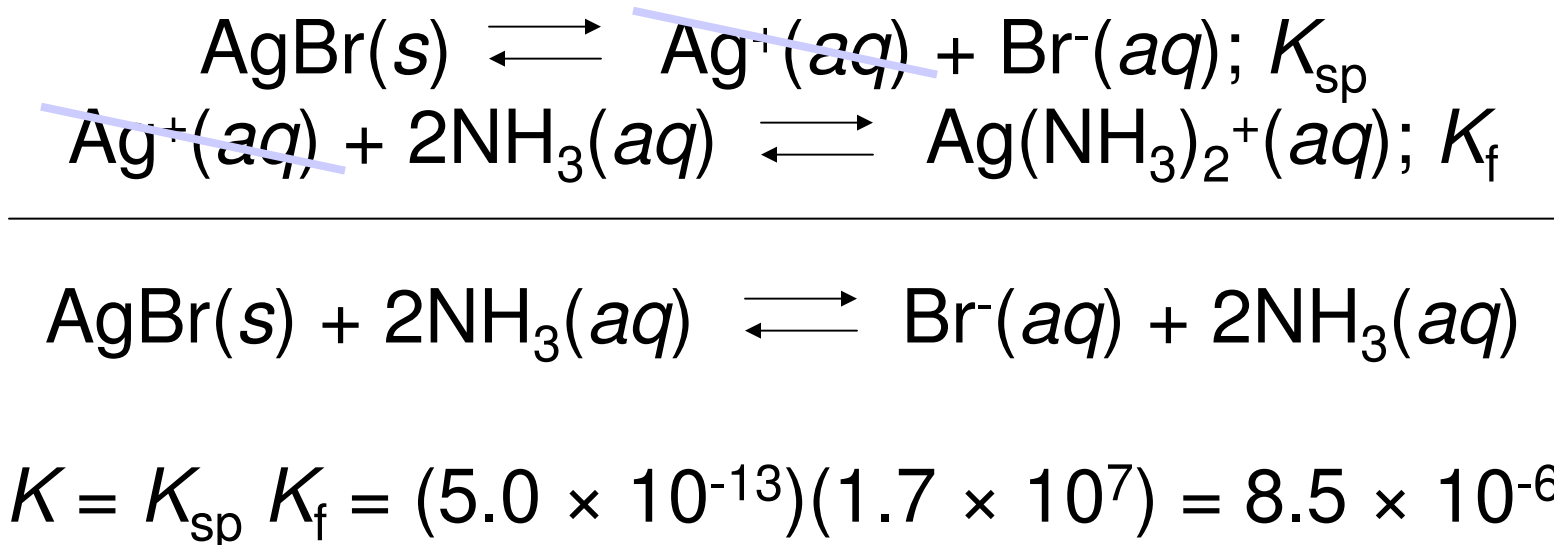
- $Q_c = [\text{Ag}^+] [\text{Br}^-]$
- $Q_c = (6.1 \times 10^{-10})(0.010)$
 - $Q_c = 6.1 \times 10^{-12}$
- $K_{\text{sp}} = 5.0 \times 10^{-13}$

$$\bullet K_{\text{sp}} < Q_c$$

- The precipitate forms.

- Calculate the molar solubility of AgBr in 1.0 M NH₃ at 25°C.

We will first combine the two equilibria and find the combined equilibrium constant.



- Now, we'll use the combined equilibrium to find the solubility of AgBr in 1.0 M NH₃.

	AgBr(s)	2NH ₃ (aq)	\rightleftharpoons Br ⁻	+ Ag(NH ₃) ₂ ⁺ (aq)
Initial	+	1.0	0	
Change		-2x	+x	+x
Equilibrium		1.0 - 2x	x	x

m

$$K = \frac{[\text{Br}^-][\text{Ag}(\text{NH}_3)_2^+]}{[\text{NH}_3]^2}$$

$$8.5 \times 10^{-6} = \frac{x^2}{(1.0 - 2x)^2}$$

- The right side of the equation is a perfect square.

$$2.9 \times 10^{-3} = \frac{x}{(1.0 - 2x)}$$

$$0.0029 - 0.0058x = x$$

$$0.0029 = 1.0058x$$

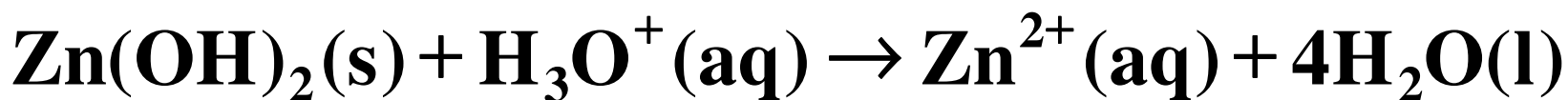
$$x = 2.9 \times 10^{-3}$$

- The molar solubility of AgBr in 1.0 M NH₃ is
 - $2.9 \times 10^{-3} \text{ M}$.

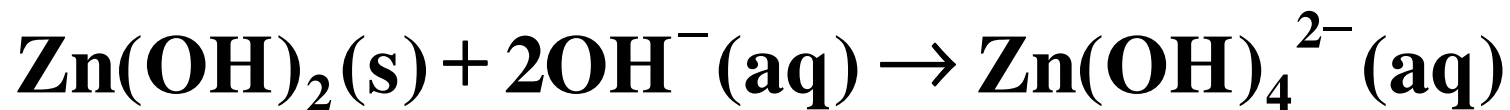
- The combination of solubility and complex-ion equilibria can be applied to separate metal ions.
- Cations can be separated into groups according to their precipitation properties.
- In each major step, one group of cations precipitates out. After separating the precipitate, the remaining solution is treated with the next reagent, precipitating the next group of cations.

Amphoteric Hydroxides

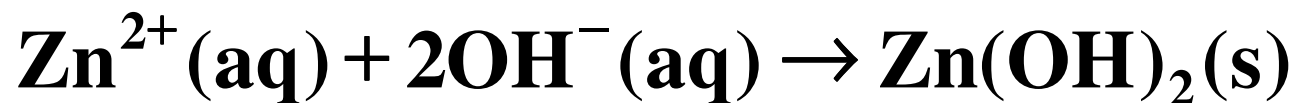
- An **amphoteric hydroxide** is a metal hydroxide that reacts with both acids and bases.
 - For example, zinc hydroxide, Zn(OH)_2 , reacts with a strong acid and the metal hydroxide dissolves.



- With a base however, Zn(OH)_2 reacts to form the complex ion Zn(OH)_4^{2-} .



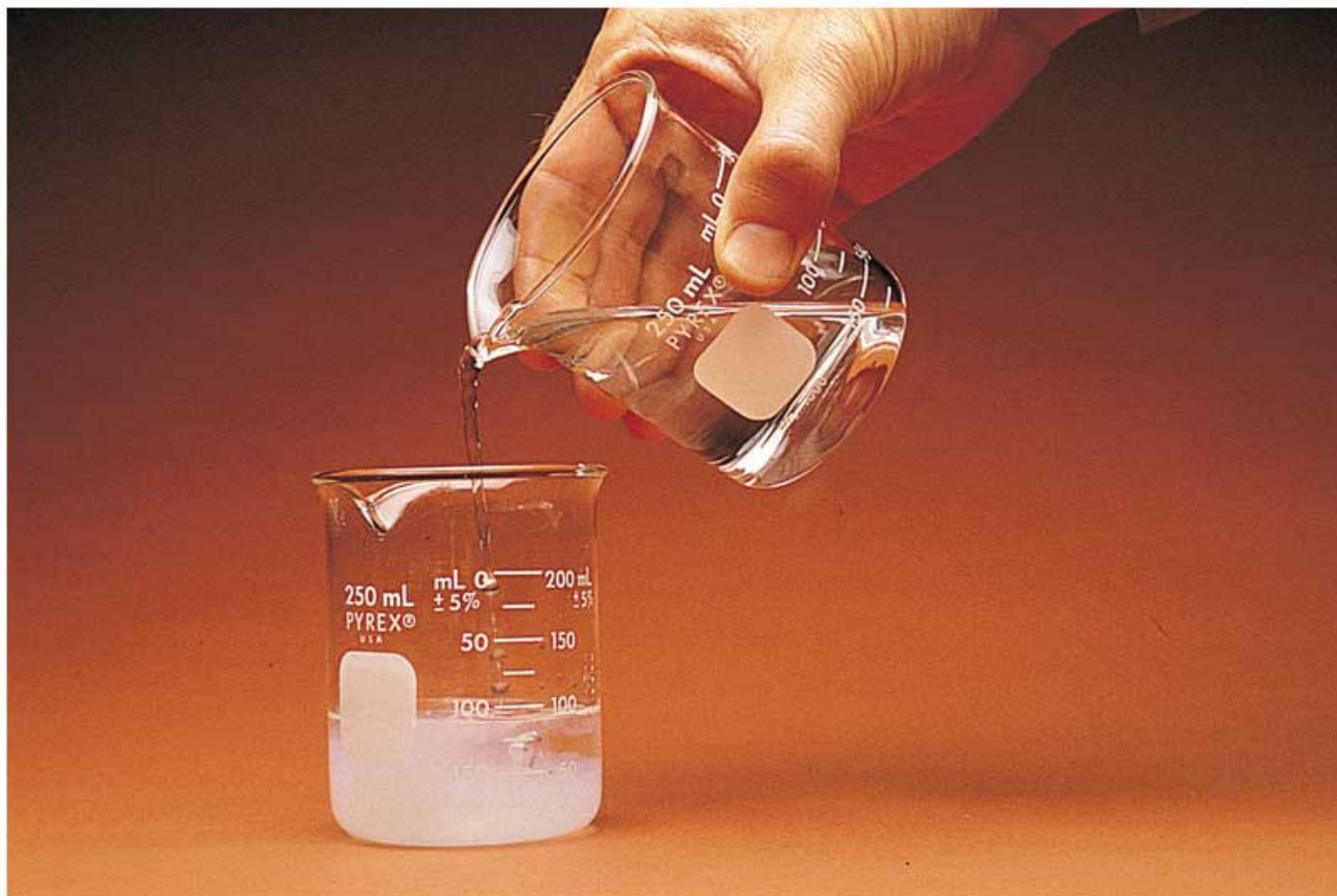
- When a strong base is slowly added to a solution of ZnCl_2 , a white precipitate of Zn(OH)_2 first forms.

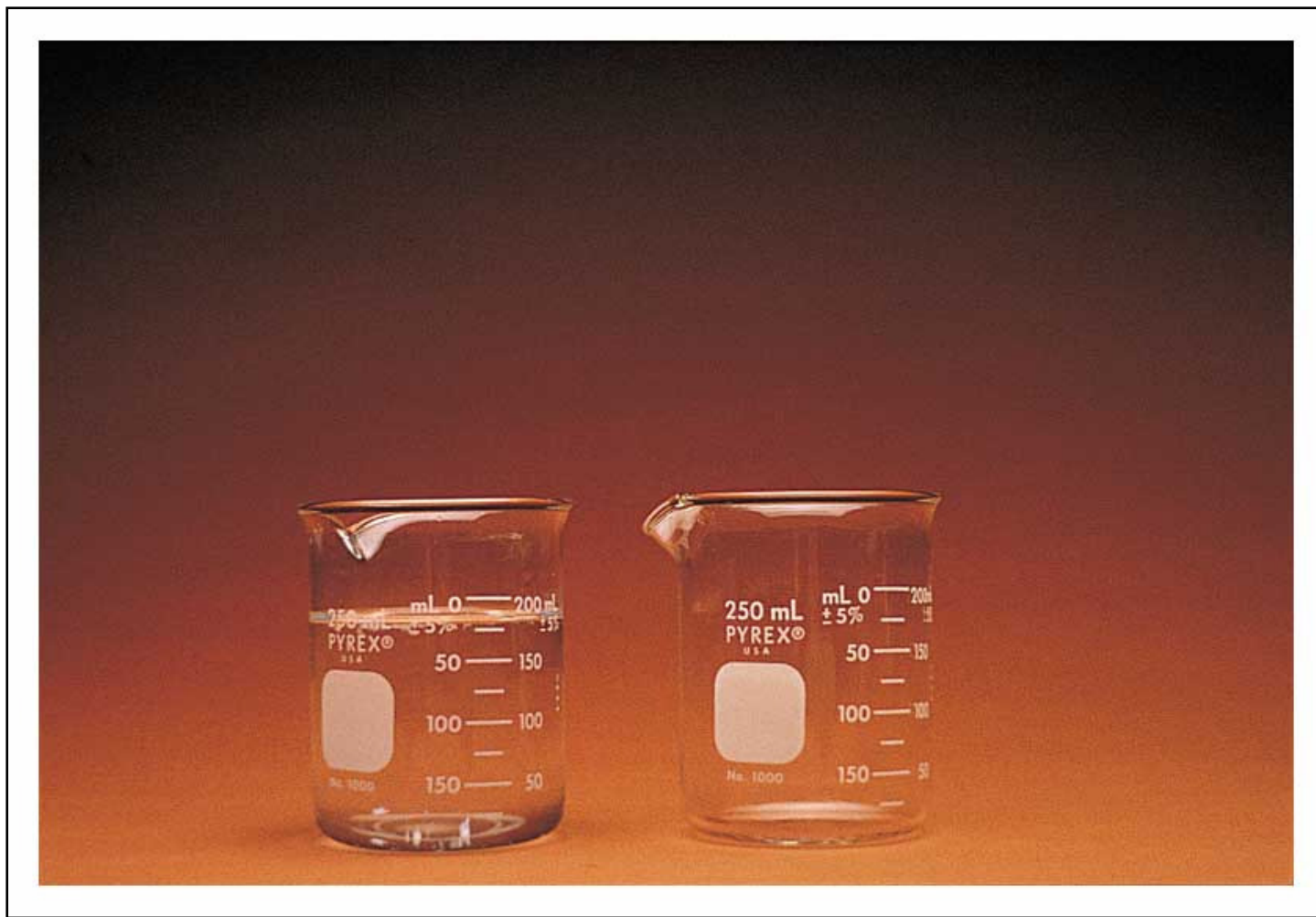


- But as more base is added, the white precipitate dissolves, forming the complex ion Zn(OH)_4^{2-} .

See Figure 17.

- Other common amphoteric hydroxides are those of aluminum, chromium(III), lead(II), tin(II), and tin(IV).





Do Exercises 18.9, 10, and 11

Look at Problems 18.57-62

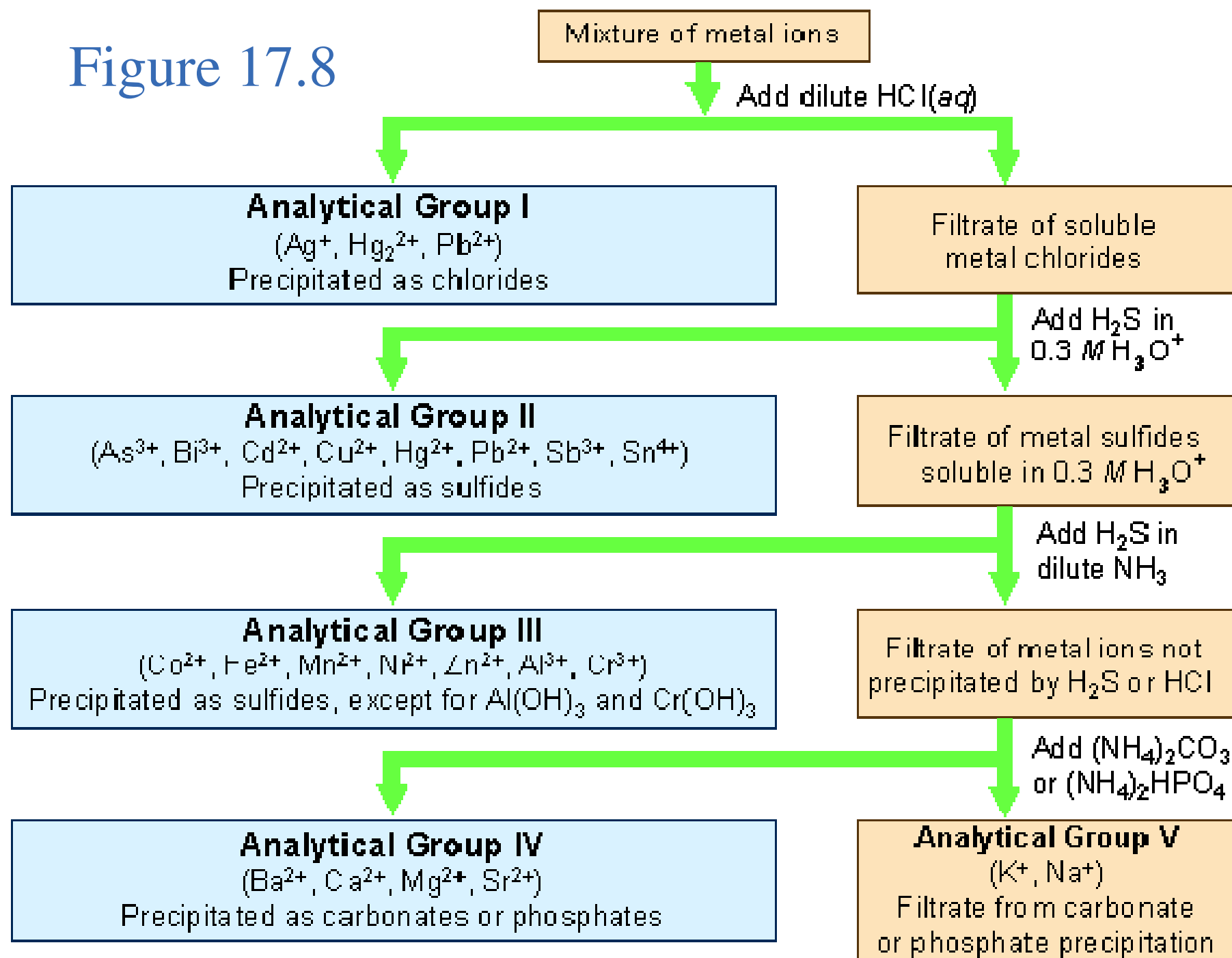
Figure 17.8: Demonstration of the amphoteric behavior of zinc hydroxide

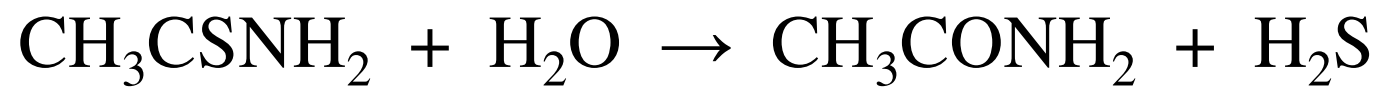


Qualitative Analysis

- **Qualitative analysis** involves the determination of the identity of substances present in a mixture.
 - In the qualitative analysis scheme for metal ions, a cation is usually detected by the **presence of a characteristic precipitate.**
 - Figure 18.8 summarizes how metal ions in an aqueous solution are separated into five analytical groups.

Figure 17.8





Operational Skills

- Writing solubility product expressions
- Calculating K_{sp} from the solubility, or vice versa.
- Calculating the solubility of a slightly soluble salt in a solution of a common ion.
- Predicting whether precipitation will occur
- Determining the qualitative effect of pH on solubility
- Calculating the concentration of a metal ion in equilibrium with a complex ion
- Predicting whether a precipitate will form in the presence of the complex ion
- Calculating the solubility of a slightly soluble ionic compound in a solution of the complex ion