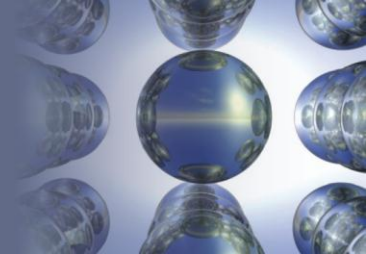


## Chapter 16

### *Solubility and Complex Ion Equilibria*

# Chapter 16

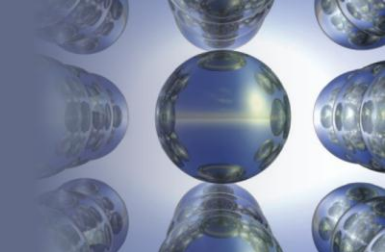
## *Table of Contents*



- (16.1) Solubility equilibria and the solubility product
- (16.2) Precipitation and qualitative analysis
- (16.3) Equilibria involving complex ions

## Section 16.1

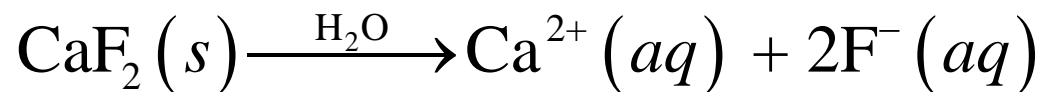
# *Solubility Equilibria and the Solubility Product*



## Equilibria

- When a typical ionic solid dissolves in water, it separates into cations and anions

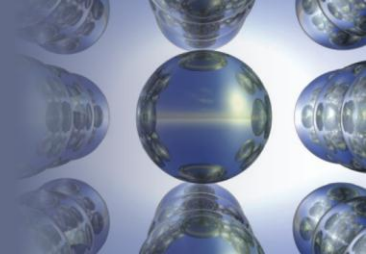
- Example



- Ions formed -  $\text{Ca}^{2+}$  and  $\text{F}^-$
- In this reaction, when solid salt is first added, no ions are present
- As dissolution proceeds, the ionic concentration increases

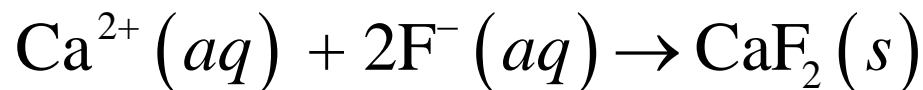
# Section 16.1

## *Solubility Equilibria and the Solubility Product*

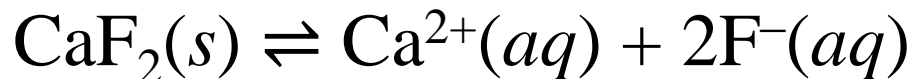


### Equilibria (Continued)

- The dissolution reaction and its reverse occurs, simultaneously



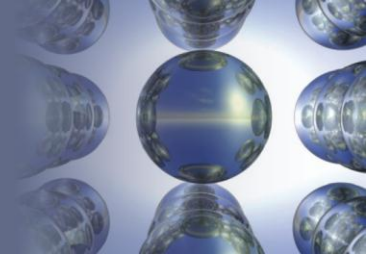
- Ultimately, the solution attains a state of saturation (dynamic equilibrium)



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

# Section 16.1

## *Solubility Equilibria and the Solubility Product*

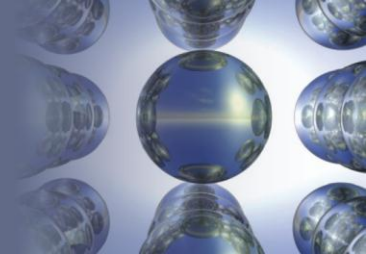


### Solubility Equilibria

- **Solubility product constant** ( $K_{sp}$ )
  - Equilibrium expression constant that represents the dissolution of an ionic solid in water
  - Known as **solubility product**
- Solubility equilibrium is unaffected by:
  - Excess solid formed
  - Size of particles present

# Section 16.1

## *Solubility Equilibria and the Solubility Product*

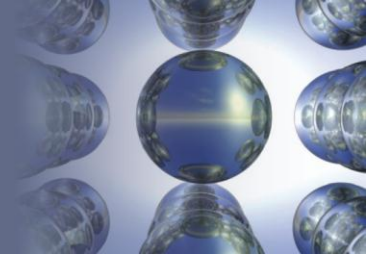


### Solubility Equilibria (Continued)

- Differences between the solubility of a given solid and its solubility product
  - Solubility is an equilibrium position
  - Solubility product is an equilibrium constant
    - Has only one value for a given solid at a given temperature

## Section 16.1

### *Solubility Equilibria and the Solubility Product*

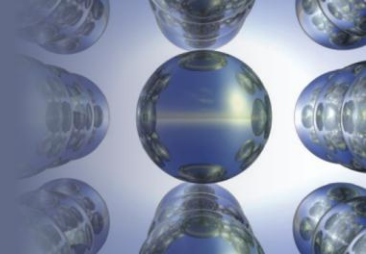


#### Interactive Example 16.2 - Calculating $K_{sp}$ from Solubility II

- Calculate the  $K_{sp}$  value for bismuth sulfide ( $\text{Bi}_2\text{S}_3$ ), which has a solubility of  $1.0 \times 10^{-15}$  mol/L at  $25^\circ \text{C}$

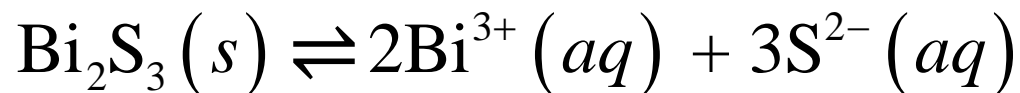
## Section 16.1

# *Solubility Equilibria and the Solubility Product*



### Interactive Example 16.2 - Solution

- The system initially contains  $\text{H}_2\text{O}$  and solid  $\text{Bi}_2\text{S}_3$ , which dissolves as follows:



$$K_{\text{sp}} = [\text{Bi}^{3+}]^2 [\text{S}^{2-}]^3$$

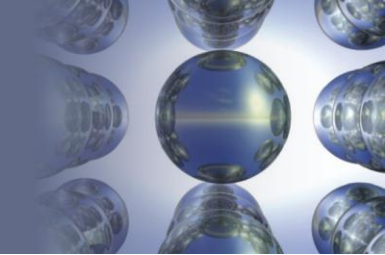
- Since no  $\text{Bi}^{3+}$  and  $\text{S}^{2-}$  ions were present in the solution before  $\text{Bi}_2\text{S}_3$  dissolved,

$$[\text{Bi}^{3+}]_0 = [\text{S}^{2-}]_0 = 0$$



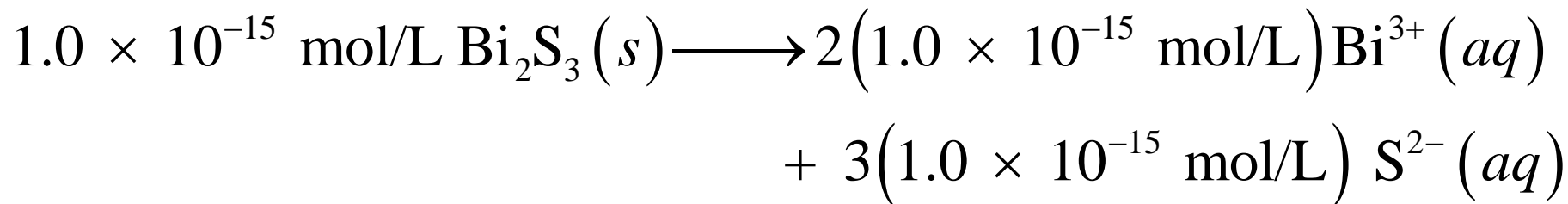
## Section 16.1

# *Solubility Equilibria and the Solubility Product*



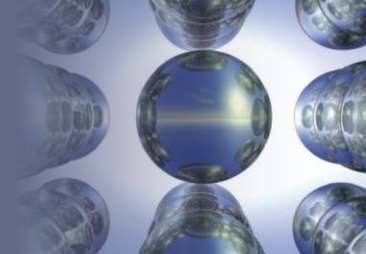
### Interactive Example 16.2 - Solution (Continued 1)

- Thus, the equilibrium concentrations of these ions will be determined by the amount of salt that dissolves to reach equilibrium, which in this case is  $1.0 \times 10^{-15}$  mol/L
- Since each  $\text{Bi}_2\text{S}_3$  unit contains  $2\text{Bi}^{3+}$  and  $3\text{S}^{2-}$  ions,



## Section 16.1

# *Solubility Equilibria and the Solubility Product*



### Interactive Example 16.2 - Solution (Continued 2)

- The equilibrium concentrations are

$$[\text{Bi}^{3+}] = [\text{Bi}^{3+}]_0 + \text{change} = 0 + 2.0 \times 10^{-15} \text{ mol/L}$$

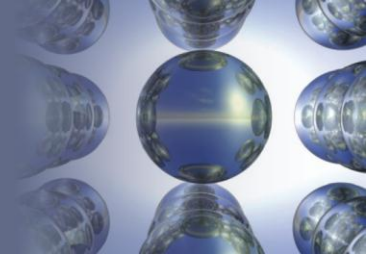
$$[\text{S}^{2-}] = [\text{S}^{2-}]_0 + \text{change} = 0 + 3.0 \times 10^{-15} \text{ mol/L}$$

- Therefore,

$$K_{\text{sp}} = [\text{Bi}^{3+}]^2 [\text{S}^{2-}]^3 = (2.0 \times 10^{-15})^2 (3.0 \times 10^{-15})^3 = 1.1 \times 10^{-73}$$

## Section 16.1

# *Solubility Equilibria and the Solubility Product*



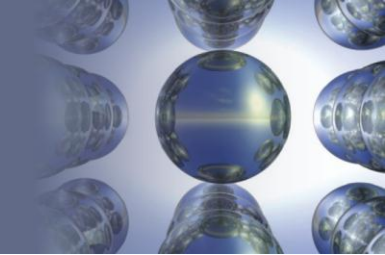
### Exercise

- Approximately 0.14 g nickel(II) hydroxide,  $\text{Ni}(\text{OH})_2$  (s), dissolves per liter of water at  $20^\circ \text{C}$ 
  - Calculate  $K_{\text{sp}}$  for  $\text{Ni}(\text{OH})_2$  (s) at this temperature

$$K_{\text{sp}} = 1.4 \times 10^{-8}$$

## Section 16.1

### *Solubility Equilibria and the Solubility Product*



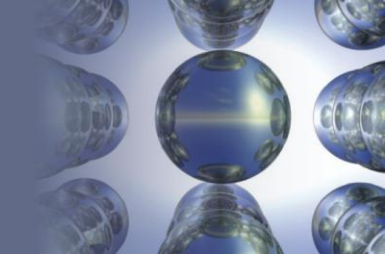
#### Interactive Example 16.3 - Calculating Solubility from

$K_{sp}$

- The  $K_{sp}$  value for copper(II) iodate,  $\text{Cu}(\text{IO}_3)_2$ , is  $1.4 \times 10^{-7}$  at  $25^\circ \text{C}$ 
  - Calculate its solubility at  $25^\circ \text{C}$

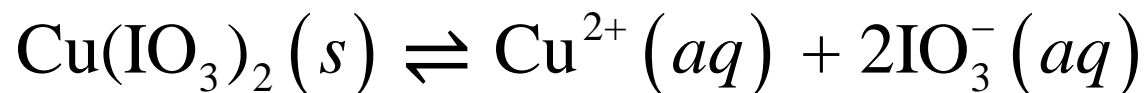
## Section 16.1

# *Solubility Equilibria and the Solubility Product*



### Interactive Example 16.3 - Solution

- The system initially contains H<sub>2</sub>O and solid Cu(IO<sub>3</sub>)<sub>2</sub>, which dissolves according to the following equilibrium

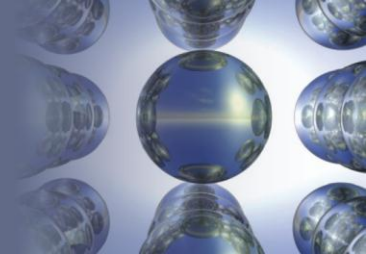


$$K_{\text{sp}} = [\text{Cu}^{2+}][\text{IO}_3^-]^2$$

- To find the solubility of Cu(IO<sub>3</sub>)<sub>2</sub>, we must find the equilibrium concentrations of the Cu<sup>2+</sup> and IO<sub>3</sub><sup>-</sup> ions

## Section 16.1

# *Solubility Equilibria and the Solubility Product*



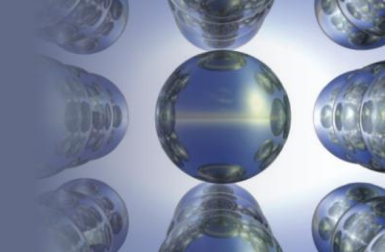
### Interactive Example 16.3 - Solution (Continued 1)

- We do this in the usual way by specifying the initial concentrations (before any solid has dissolved) and then defining the change required to reach equilibrium
- Since in this case we do not know the solubility, we will assume that  $x$  mol/L of the solid dissolves to reach equilibrium
- The 1:2 stoichiometry of the salt means that



# Section 16.1

## *Solubility Equilibria and the Solubility Product*



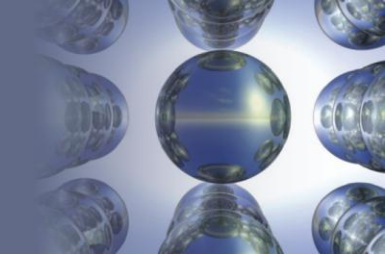
### Interactive Example 16.3 - Solution (Continued 2)

- The concentrations are as follows:

Initial Concentration (mol/L) [before any $\text{Cu}(\text{IO}_3)_2$ dissolves]		Equilibrium Concentration (mol/L)
$[\text{Cu}^{2+}]_0 = 0$ $[\text{IO}_3^-]_0 = 0$	$\xrightarrow[\text{to reach equilibrium}]{x \text{ mol/L dissolves}}$	$[\text{Cu}^{2+}] = x$ $[\text{IO}_3^-] = 2x$

## Section 16.1

# *Solubility Equilibria and the Solubility Product*



### Interactive Example 16.3 - Solution (Continued 3)

- Substituting the equilibrium concentrations into the expression for  $K_{sp}$  gives

$$1.4 \times 10^{-7} = K_{sp} = [\text{Cu}^{2+}][\text{IO}_3^-]^2 = (x)(2x)^2 = 4x^3$$

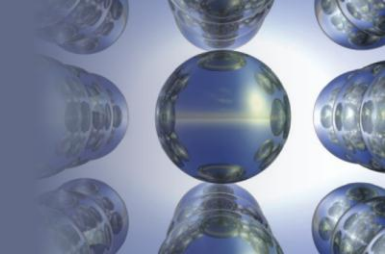
$$x = \sqrt[3]{3.5 \times 10^{-8}} = 3.3 \times 10^{-3} \text{ mol/L}$$

- Thus, the solubility of solid  $\text{Cu}(\text{IO}_3)_2$  is  $3.3 \times 10^{-3} \text{ mol/L}$



## Section 16.1

# *Solubility Equilibria and the Solubility Product*



### Exercise

- Calculate the solubility of each of the following compounds in moles per liter



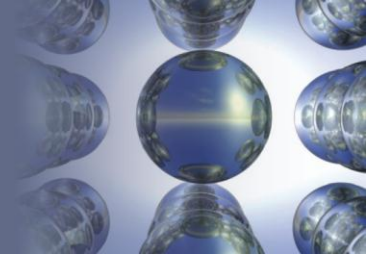
$$1.6 \times 10^{-5} \text{ mol/L}$$



$$9.3 \times 10^{-5} \text{ mol/L}$$

# Section 16.1

## *Solubility Equilibria and the Solubility Product*



### Relative Solubilities

- One must be careful in using  $K_{sp}$  values to predict the relative solubilities of a group of salts
- Possible cases
  - Salts being compared produce the same number of ions
    - $K_{sp}$  values cannot be compared to determine relative solubilities
  - Salts being compared produce varying number of ions
    - Cannot predict relative solubilities using  $K_{sp}$  values

## Section 16.1

# *Solubility Equilibria and the Solubility Product*

## Common Ion Effect

- The solubility of a solid becomes low when the solution already contains ions common to the solid

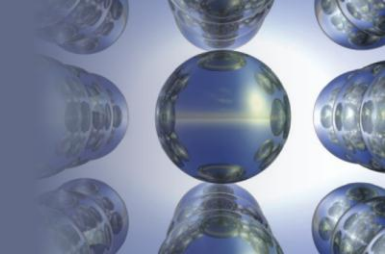
A potassium chromate solution being added to aqueous silver nitrate, forming silver chromate



Photo by Ken O'Donoghue © Cengage Learning

## Section 16.1

# *Solubility Equilibria and the Solubility Product*

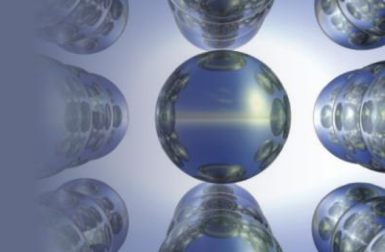


### Critical Thinking

- What if all you know about two salts is that the value of  $K_{sp}$  for salt A is greater than that of salt B?
  - Why can we not compare relative solubilities of the salts?
  - Use numbers to show how salt A could be more soluble than salt B, and how salt B could be more soluble than salt A

## Section 16.1

# *Solubility Equilibria and the Solubility Product*

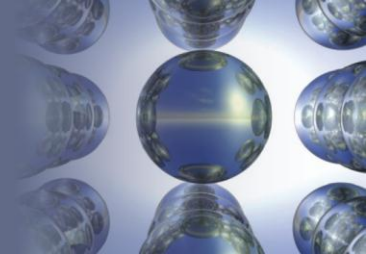


### Interactive Example 16.4 - Solubility and Common Ions

- Calculate the solubility of solid  $\text{CaF}_2$  ( $K_{\text{sp}} = 4.0 \times 10^{-11}$ ) in a 0.025-*M* NaF solution

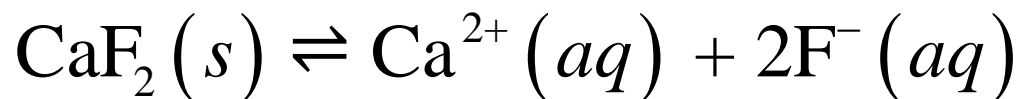
## Section 16.1

# *Solubility Equilibria and the Solubility Product*



### Interactive Example 16.4 - Solution

- Before any  $\text{CaF}_2$  dissolves, the solution contains the major species  $\text{Na}^+$ ,  $\text{F}^-$ , and  $\text{H}_2\text{O}$ 
  - The solubility equilibrium for  $\text{CaF}_2$  is



$$K_{\text{sp}} = 4.0 \times 10^{-11} = [\text{Ca}^{2+}][\text{F}^-]^2$$

# Section 16.1

## *Solubility Equilibria and the Solubility Product*

### Interactive Example 16.4 - Solution (Continued 1)

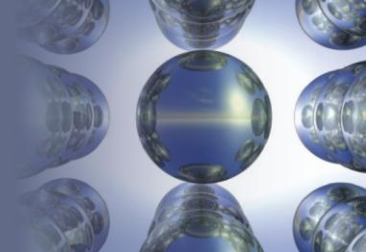
Initial Concentration (mol/L) (before any $\text{CaF}_2$ dissolves)		Equilibrium Concentration (mol/L)
$[\text{Ca}^{2+}]_0 = 0$ $[\text{F}^-]_0 = 0.025 \text{ M}$ ↗ From 0.025 M NaF	$x \text{ mol/L CaF}_2$ dissolves → to reach equilibrium	$[\text{Ca}^{2+}] = x$ $[\text{F}^-] = 0.025 + 2x$ ↗      ↗ From NaF    From $\text{CaF}_2$

- Substituting the equilibrium concentrations into the expression for  $K_{\text{sp}}$  gives

$$K_{\text{sp}} = 4.0 \times 10^{-11} = [\text{Ca}^{2+}][\text{F}^-]^2 = (x)(0.025 + 2x)^2$$

## Section 16.1

# *Solubility Equilibria and the Solubility Product*



### Interactive Example 16.4 - Solution (Continued 2)

- Assuming that  $2x$  is negligible compared with  $0.025$  (since  $K_{sp}$  is small) gives

$$4.0 \times 10^{-11} \approx (x)(0.025)^2$$

$$x \approx 6.4 \times 10^{-8}$$

- The approximation is valid (by the 5% rule)

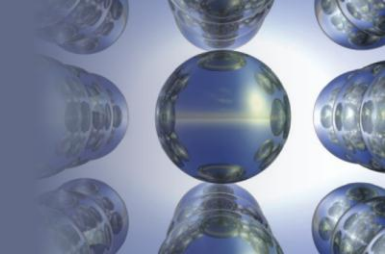
$$\text{Solubility} = x = 6.4 \times 10^{-8} \text{ mol/L}$$

- Thus  $6.4 \times 10^{-8}$  mole of solid  $\text{CaF}_2$  dissolves per liter of the  $0.025\text{-M}$  NaF solution



# Section 16.1

## *Solubility Equilibria and the Solubility Product*

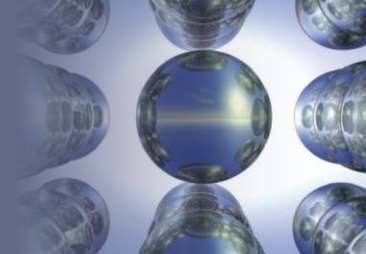


### pH and Solubility

- Increase in pH
  - Decreases solubility
  - Forces the equilibrium to the left
- Decrease in pH
  - Increases solubility
  - Equilibrium shifts to the right
  - If the anion  $X^-$  is an effective base, the salt  $MX$  will show increased solubility in an acidic solution

# Section 16.1

## *Solubility Equilibria and the Solubility Product*

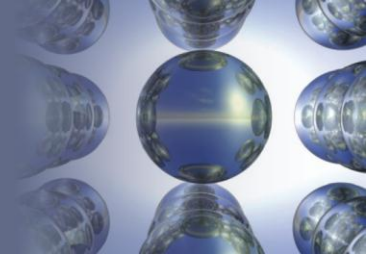


### pH and Solubility (Continued)

- Exception - AgCl has the same solubility in acid as in pure water
  - Cl<sup>-</sup> ion is a weak base
    - No HCl molecules are formed
  - Adding H<sup>+</sup> ions to a solution that contains Cl<sup>-</sup> ions does not affect:
    - Concentration of the Cl<sup>-</sup> ion
    - Solubility of the chloride salt

# Section 16.1

## *Solubility Equilibria and the Solubility Product*

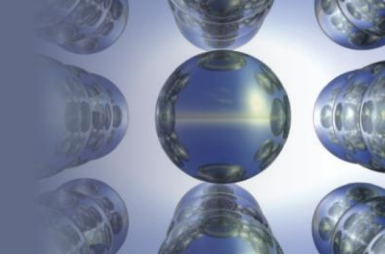


### Critical Thinking

- You and a friend are studying for a chemistry exam
  - What if your friend tells you that since acids are very reactive, all salts are more soluble in aqueous solutions of acids than in water?
  - How would you explain to your friend that this is not true?
  - Use a specific example to defend your answer

## Section 16.2

# *Precipitation and Qualitative Analysis*

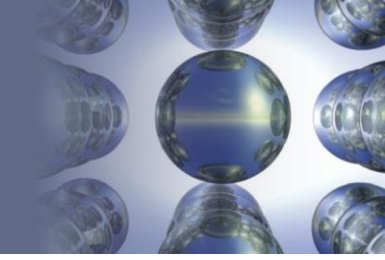


## Precipitation

- **Ion product ( $Q$ )**
  - Defined similar to the expression for  $K_{sp}$  for a given solid
  - Exception - Initial concentrations are used instead of equilibrium concentrations

## Section 16.2

# *Precipitation and Qualitative Analysis*

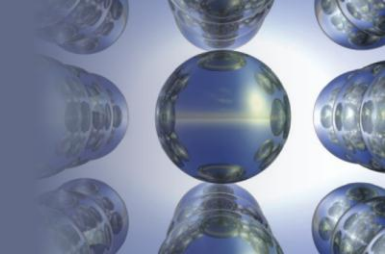


### Relationship between $Q$ and $K_{sp}$

- One can predict the possibility of precipitation by considering the relationship between  $Q$  and  $K_{sp}$ 
  - $Q > K_{sp}$ 
    - Precipitation occurs and will continue until the concentrations are reduced to the point that they satisfy  $K_{sp}$
  - $Q < K_{sp}$ 
    - No precipitation occurs

## Section 16.2

### *Precipitation and Qualitative Analysis*

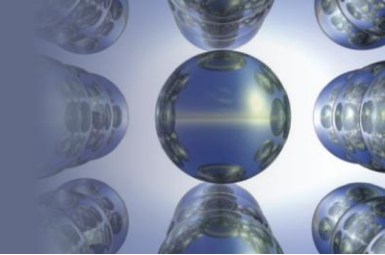


#### Interactive Example 16.5 - Determining Precipitation Conditions

- A solution is prepared by adding 750.0 mL of  $4.00 \times 10^{-3} \text{ M Ce(NO}_3)_3$  to 300.0 mL of  $2.00 \times 10^{-2} \text{ M KIO}_3$ 
  - Will  $\text{Ce(IO}_3)_3$  ( $K_{sp} = 1.9 \times 10^{-10}$ ) precipitate from this solution?

## Section 16.2

### *Precipitation and Qualitative Analysis*



#### Interactive Example 16.5 - Solution

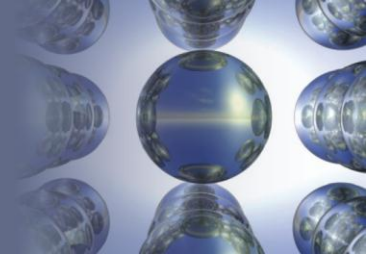
- First, we calculate  $[\text{Ce}^{3+}]_0$  and  $[\text{IO}_3^-]_0$  in the mixed solution before any reaction occurs:

$$[\text{Ce}^{3+}]_0 = \frac{(750.0 \text{ mL})(4.00 \times 10^{-3} \text{ mmol/mL})}{(750.0 + 300.0) \text{ mL}} = 2.86 \times 10^{-3} \text{ M}$$

$$[\text{IO}_3^-]_0 = \frac{(300.0 \text{ mL})(2.00 \times 10^{-2} \text{ mmol/mL})}{(750.0 + 300.0) \text{ mL}} = 5.71 \times 10^{-3} \text{ M}$$

## Section 16.2

# Precipitation and Qualitative Analysis



### Interactive Example 16.5 - Solution (Continued)

- The ion product for  $\text{Ce}(\text{IO}_3)_3$  is

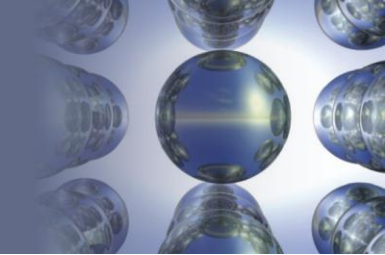
$$\begin{aligned} Q &= [\text{Ce}^{3+}]_0 [\text{IO}_3^-]_0^3 = (2.86 \times 10^{-3})(5.71 \times 10^{-3})^3 \\ &= 5.32 \times 10^{-10} \end{aligned}$$

- Since  $Q$  is greater than  $K_{\text{sp}}$ ,  $\text{Ce}(\text{IO}_3)_3$  will precipitate from the mixed solution



## Section 16.2

### *Precipitation and Qualitative Analysis*

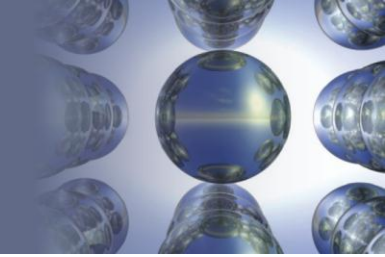


## Calculating Equilibrium Concentrations after Precipitation

- **Step 1 - Determine if the product is formed when the solutions are mixed**
  - Calculate the concentration of the ions in the mixed solution to determine  $Q$
- **Step 2 - Run the reaction to completion**
  - **Note - If a reaction virtually goes to completion when two solutions are mixed, it is necessary to conduct stoichiometric calculations prior to equilibrium calculations**

## Section 16.2

### *Precipitation and Qualitative Analysis*

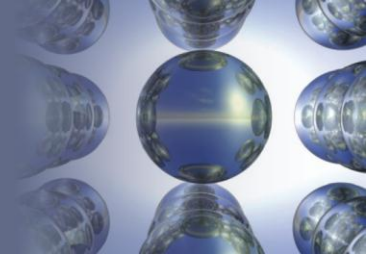


#### Calculating Equilibrium Concentrations after Precipitation Occurs (Continued)

- Step 3 - Allow the system to adjust to equilibrium and determine the concentrations of ions in the solution
- Step 4 - Substitute the expressions derived in step 3 to determine  $K_{sp}$

## Section 16.2

# Precipitation and Qualitative Analysis

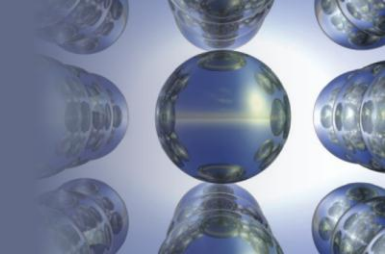


### Interactive Example 16.6 - Precipitation

- A solution is prepared by mixing 150.0 mL of  $1.00 \times 10^{-2} \text{ M}$   $\text{Mg}(\text{NO}_3)_2$  and 250.0 mL of  $1.00 \times 10^{-1} \text{ M}$   $\text{NaF}$ 
  - Calculate the concentrations of  $\text{Mg}^{2+}$  and  $\text{F}^-$  at equilibrium with solid  $\text{MgF}_2$  ( $K_{\text{sp}} = 6.4 \times 10^{-9}$ )

## Section 16.2

# Precipitation and Qualitative Analysis



### Interactive Example 16.6 - Solution

- First, determine whether solid  $\text{MgF}_2$  forms
  - To do this, we need to calculate the concentrations of  $\text{Mg}^{2+}$  and  $\text{F}^-$  in the mixed solution and find  $Q$

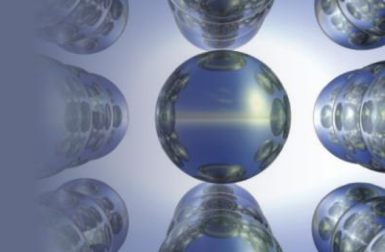
$$[\text{Mg}^{2+}]_0 = \frac{\text{mmol Mg}^{2+}}{\text{mL solution}} = \frac{(150.0 \text{ mL})(1.00 \times 10^{-2} \text{ M})}{400.0 \text{ mL}} = 3.75 \times 10^{-3} \text{ M}$$

$$[\text{F}^-]_0 = \frac{\text{mmol F}^-}{\text{mL solution}} = \frac{(250.0 \text{ mL})(1.00 \times 10^{-1} \text{ M})}{400.0 \text{ mL}} = 6.25 \times 10^{-2} \text{ M}$$

$$Q = [\text{Mg}^{2+}]_0 [\text{F}^-]_0^2 = (3.75 \times 10^{-3})(6.25 \times 10^{-2})^2 = 1.46 \times 10^{-5}$$

## Section 16.2

# Precipitation and Qualitative Analysis



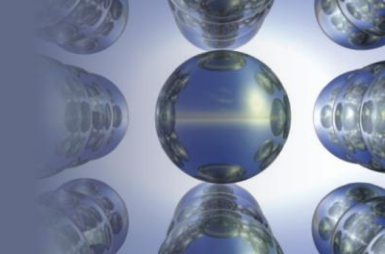
### Interactive Example 16.6 - Solution (Continued 1)

- Since  $Q$  is greater than  $K_{sp}$ , solid  $MgF_2$  will form
- The next step is to run the precipitation reaction to completion

	$Mg^{2+}$	+	$2F^{-}$	$\longrightarrow$	$MgF_2(s)$
Before reaction	$(150.0)(1.00 \times 10^{-2})$ $= 1.50 \text{ mmol}$		$(250.0)(1.00 \times 10^{-1})$ $= 25.0 \text{ mmol}$		
After reaction	$1.50 - 1.50 = 0$		$25.0 - 2(1.50)$ $= 22.0 \text{ mmol}$		

## Section 16.2

# Precipitation and Qualitative Analysis



### Interactive Example 16.6 - Solution (Continued 2)

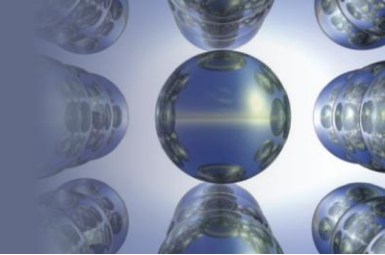
- Note that excess  $F^-$  remains after the precipitation reaction goes to completion
  - The concentration is

$$[F^-]_{\text{excess}} = \frac{22.0 \text{ mmol}}{400.0 \text{ mL}} = 5.50 \times 10^{-2} \text{ M}$$

- Although we have assumed that  $Mg^{2+}$  is completely consumed, we know that  $[Mg^{2+}]$  will not be zero at equilibrium

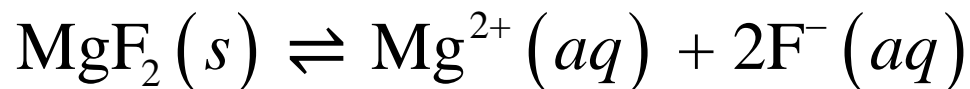
## Section 16.2

# Precipitation and Qualitative Analysis



### Interactive Example 16.6 - Solution (Continued 3)

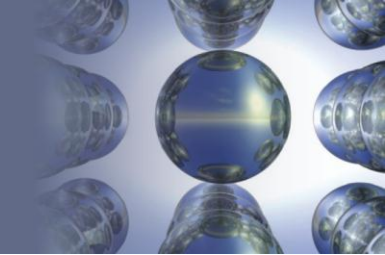
- We can compute the equilibrium  $[\text{Mg}^{2+}]$  by letting  $\text{MgF}_2$  redissolve to satisfy the expression for  $K_{\text{sp}}$
- How much  $\text{MgF}_2$  will dissolve in a  $5.50 \times 10^{-2}$ -M NaF solution?



$$K_{\text{sp}} = [\text{Mg}^{2+}][\text{F}^-]^2 = 6.4 \times 10^{-9}$$

## Section 16.2

# Precipitation and Qualitative Analysis



### Interactive Example 16.6 - Solution (Continued 4)

Initial Concentration (mol/L)		Equilibrium Concentration (mol/L)
$[Mg^{2+}]_0 = 0$ $[F^-]_0 = 5.50 \times 10^{-2}$	$\xrightarrow[x \text{ mol/L MgF}_2(s) \text{ dissolves}]{} \xrightarrow{\hspace{1cm}}$	$[Mg^{2+}] = x$ $[F^-] = 5.50 \times 10^{-2} + 2x$

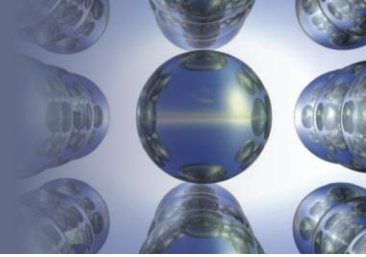
$$K_{sp} = 6.4 \times 10^{-9} = [Mg^{2+}][F^-]^2$$
$$= (x)(5.50 \times 10^{-2} + 2x)^2 \approx (x)(5.50 \times 10^{-2})^2$$

$$[Mg^{2+}] = x = 2.1 \times 10^{-6} M \quad [F^-] = 5.50 \times 10^{-2} M$$



## Section 16.2

# *Precipitation and Qualitative Analysis*

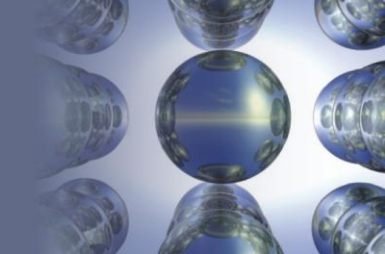


### Selective Precipitation

- Method used to separate mixtures of metal ions in aqueous solution
- Involves using a reagent whose anion forms a precipitate with only one or a few of the metal ions in the mixture

## Section 16.2

# *Precipitation and Qualitative Analysis*

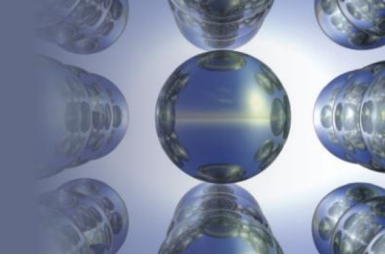


### Selective Precipitation - Example

- Consider a solution containing  $\text{Ba}^{2+}$  and  $\text{Ag}^+$  ions
  - NaCl is added to this solution
  - Result
    - AgCl precipitates as a white solid
    - $\text{BaCl}_2$  is soluble, so  $\text{Ba}^{2+}$  ions remain in the solution

## Section 16.2

### *Precipitation and Qualitative Analysis*

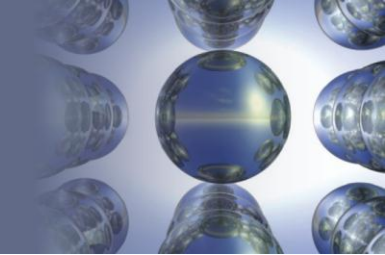


#### Example 16.7 - Selective Precipitation

- A solution contains  $1.0 \times 10^{-4} \text{ M Cu}^+$  and  $2.0 \times 10^{-3} \text{ M Pb}^{2+}$ 
  - If a source of  $\text{I}^-$  is added gradually to this solution, will  $\text{PbI}_2$  ( $K_{\text{sp}} = 1.4 \times 10^{-8}$ ) or  $\text{CuI}$  ( $K_{\text{sp}} = 5.3 \times 10^{-12}$ ) precipitate first?
  - Specify the concentration of  $\text{I}^-$  necessary to begin precipitation of each salt

## Section 16.2

# Precipitation and Qualitative Analysis



### Example 16.7 - Solution

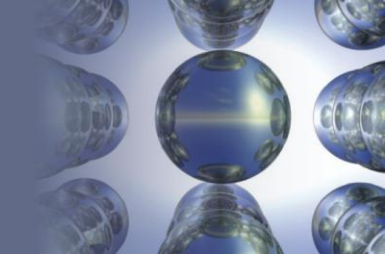
- For  $\text{PbI}_2$ , the  $K_{\text{sp}}$  expression is

$$1.4 \times 10^{-8} = K_{\text{sp}} = [\text{Pb}^{2+}][\text{I}^{-}]^2$$

- Since  $[\text{Pb}^{2+}]$  in this solution is known to be  $2.0 \times 10^{-3} \text{ M}$ , the greatest concentration of  $\text{I}^{-}$  that can be present without causing precipitation of  $\text{PbI}_2$  can be calculated from the  $K_{\text{sp}}$  expression

## Section 16.2

# Precipitation and Qualitative Analysis



### Example 16.7 - Solution (Continued 1)

$$1.4 \times 10^{-8} = [\text{Pb}^{2+}][\text{I}^{-}]^2 = (2.0 \times 10^{-3})[\text{I}^{-}]^2$$

$$[\text{I}^{-}] = 2.6 \times 10^{-3} \text{ M}$$

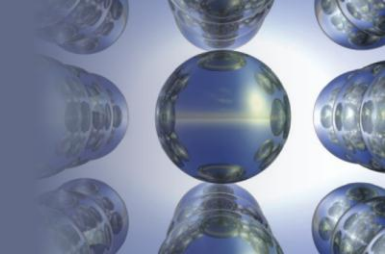
- Any  $\text{I}^{-}$  in excess of this concentration will cause solid  $\text{PbI}_2$  to form
- Similarly, for  $\text{CuI}$ , the  $K_{\text{sp}}$  expression is

$$5.3 \times 10^{-12} = K_{\text{sp}} = [\text{Cu}^{+}][\text{I}^{-}] = (1.0 \times 10^{-4})[\text{I}^{-}]$$

$$[\text{I}^{-}] = 5.3 \times 10^{-8} \text{ M}$$

## Section 16.2

# *Precipitation and Qualitative Analysis*

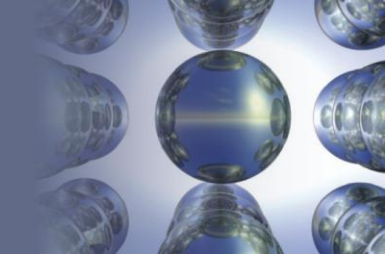


### Example 16.7 - Solution (Continued 2)

- A concentration of  $I^-$  in excess of  $5.3 \times 10^{-8} M$  will cause formation of solid  $CuI$
- As  $I^-$  is added to the mixed solution,  $CuI$  will precipitate first, since the  $[I^-]$  required is less
  - Therefore,  $Cu^+$  would be separated from  $Pb^{2+}$  using this reagent

## Section 16.2

# Precipitation and Qualitative Analysis



### Exercise

- A solution is  $1 \times 10^{-4} M$  in NaF, Na<sub>2</sub>S, and Na<sub>3</sub>PO<sub>4</sub>
  - What would be the order of precipitation as a source of Pb<sup>2+</sup> is added gradually to the solution?

- The relevant  $K_{sp}$  values are:

$$K_{sp}(\text{PbF}_2) = 4 \times 10^{-8}$$

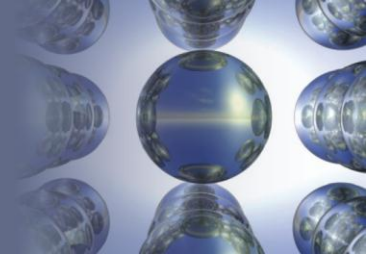
$$K_{sp}(\text{PbS}) = 7 \times 10^{-29}$$

$$K_{sp}[\text{Pb}_3(\text{PO}_4)_2] = 1 \times 10^{-54}$$

**PbS(s) will form first, followed by Pb<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub>(s), and PbF<sub>2</sub>(s) will form last**

## Section 16.2

# *Precipitation and Qualitative Analysis*



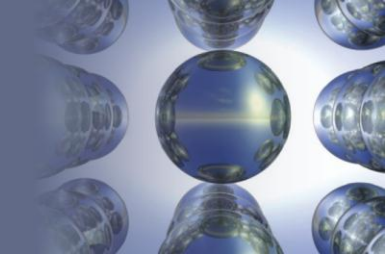
## Selective Precipitation of Metal Sulfide Salts

- Metal sulfide salts differ in solubilities
- Sulfide ion is used as a precipitating reagent to separate metal ions
  - Advantage - Sulfide ion is basic in nature
    - Its concentration can be controlled by regulating the pH of the solution



## Section 16.2

# *Precipitation and Qualitative Analysis*

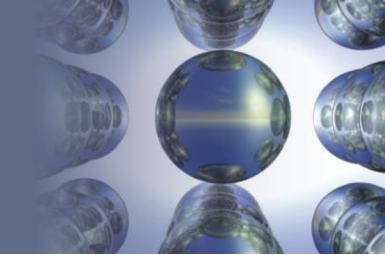


## Qualitative Analysis

- Involves separating common cations into five major groups based on solubilities
  - Individual ions are then identified from each of the groups
  - Group I - Insoluble chlorides
  - Group II - Sulfides insoluble in acid solution
  - Group III - Sulfides insoluble in basic solution
  - Group IV- Insoluble carbonates
  - Group V - Alkali metal and ammonium ions

## Section 16.2

### *Precipitation and Qualitative Analysis*

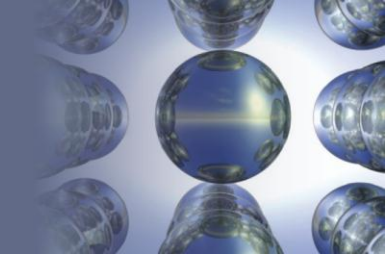


#### Group I - Insoluble Chlorides

- After adding dilute HCl to a solution that contains a mixture of common cations:
  - $\text{Ag}^+$ ,  $\text{Pb}^+$ , and  $\text{Hg}^{2+}$  precipitate as insoluble chlorides
  - Other chlorides are soluble and remain in the solution
- Group I precipitate is removed
  - The remaining ions are treated with sulfide ion

## Section 16.2

### *Precipitation and Qualitative Analysis*

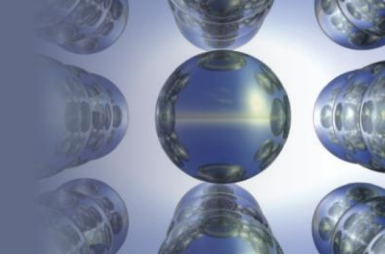


#### Group II - Sulfides Insoluble in Acid Solution

- The solution remains acidic after removing insoluble chlorides due to the presence of HCl
  - When  $\text{H}_2\text{S}$  is added to the solution:
    - Highly insoluble sulfides will precipitate due to the low concentration of  $\text{S}^{2-}$
    - Soluble sulfides will remain dissolved and the precipitate of the insoluble salt is removed

## Section 16.2

### *Precipitation and Qualitative Analysis*

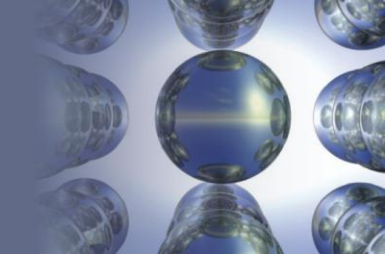


#### Group III - Sulfides Insoluble in Basic Solution

- The solution is basic at this stage
- More  $\text{H}_2\text{S}$  is added
- Cations that precipitate as sulfides include  $\text{Co}^{2+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Mn}^{2+}$ ,  $\text{Ni}^{2+}$ , and  $\text{Fe}^{2+}$ 
  - $\text{Cr}^{3+}$  and  $\text{Al}^{3+}$  ions precipitate as insoluble hydroxides
- Precipitate is separated from the solution

## Section 16.2

### *Precipitation and Qualitative Analysis*

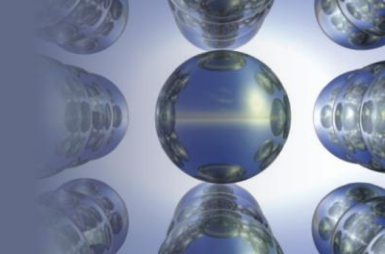


#### Group IV - Insoluble Carbonates

- All ions, except those from Groups 1A and 2A of the periodic table, have precipitated in this stage
- Group 2A cations form insoluble carbonates
  - Can be precipitated by the addition of  $\text{CO}_3^{2-}$  to the solution

## Section 16.2

### *Precipitation and Qualitative Analysis*

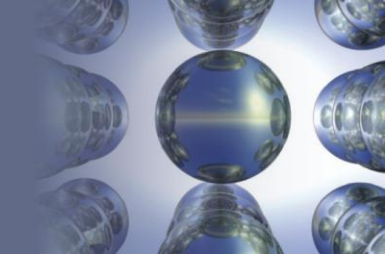


#### Group V - Alkali Metal and Ammonium Ions

- Ions remaining in the solution at this stage
  - Group 1A cations
  - $\text{NH}_4^+$  ion
- Ions form soluble salts with common anions

## Section 16.3

# *Equilibria Involving Complex Ions*

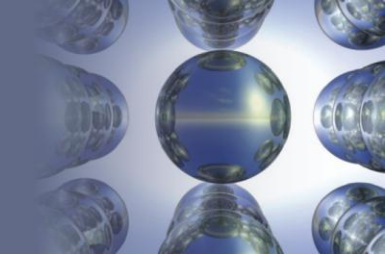


## Complex Ion Equilibria

- **Complex ion:** Charged species consisting of a metal ion surrounded by ligands
  - Ligand - Lewis base
    - Molecule or ion that has a lone pair that can be donated to an empty orbital on the metal ion to form a covalent bond
    - Coordination number - Number of ligands attached to a metal ion

## Section 16.3

### *Equilibria Involving Complex Ions*



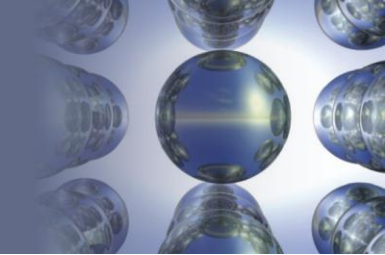
#### Formation (Stability) Constant

- Equilibrium constant for each step of the formation of a complex ion by the addition of an individual ligand to a metal ion or complex ion in aqueous solution
  - Usually, the total concentration of the ligand is larger than the total concentration of the metal ion



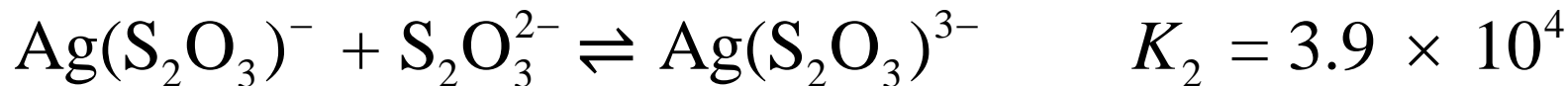
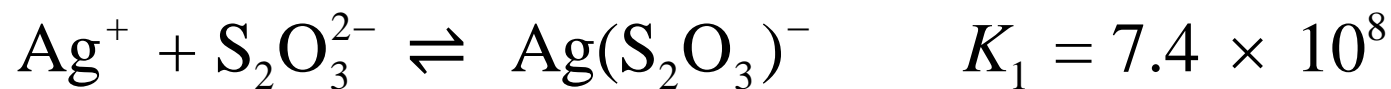
## Section 16.3

### *Equilibria Involving Complex Ions*



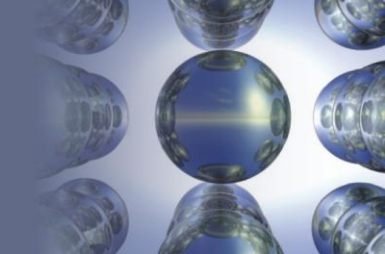
#### Interactive Example 16.8 - Complex Ions

- Calculate the concentrations of  $\text{Ag}^+$ ,  $\text{Ag}(\text{S}_2\text{O}_3)^-$ , and  $\text{Ag}(\text{S}_2\text{O}_3)_2^{3-}$  in a solution prepared by mixing 150.0 mL of  $1.00 \times 10^{-3} \text{ M}$   $\text{AgNO}_3$  with 200.0 mL of  $5.00 \text{ M}$   $\text{Na}_2\text{S}_2\text{O}_3$ 
  - The stepwise formation equilibria are as follows:



## Section 16.3

### *Equilibria Involving Complex Ions*



#### Interactive Example 16.8 - Solution

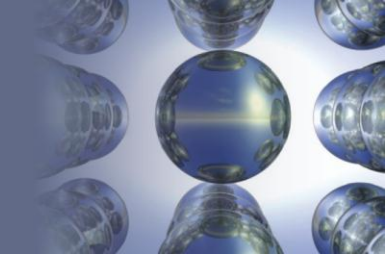
- The concentrations of the ligand and metal ion in the mixed solution before any reaction occurs are

$$\left[ \text{Ag}^+ \right]_0 = \frac{(150.0 \text{ mL})(1.00 \times 10^{-3} \text{ M})}{(150.0 \text{ mL} + 200.0 \text{ mL})} = 4.29 \times 10^{-4} \text{ M}$$

$$\left[ \text{S}_2\text{O}_3^{2-} \right]_0 = \frac{(200.0 \text{ mL})(5.00 \text{ M})}{(150.0 \text{ mL} + 200.0 \text{ mL})} = 2.86 \text{ M}$$

## Section 16.3

### *Equilibria Involving Complex Ions*



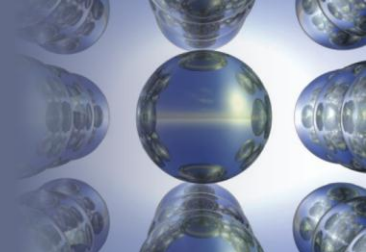
#### Interactive Example 16.8 - Solution (Continued 1)

- Since  $[S_2O_3^{2-}]_0 \gg [Ag^+]_0$ , and since  $K_1$  and  $K_2$  are large, both formation reactions can be assumed to go to completion, and the net reaction in the solution is as follows:

	$Ag^+$	+	$2S_2O_3^{2-}$	$\longrightarrow$	$Ag(S_2O_3)_2^{3-}$
Before reaction	$4.29 \times 10^{-4} M$		$2.86 M$		0
After reaction	$\sim 0$		$2.86 - 2(4.29 \times 10^{-4})$ $\approx 2.86 M$		$4.29 \times 10^{-4} M$

## Section 16.3

### *Equilibria Involving Complex Ions*



#### Interactive Example 16.8 - Solution (Continued 2)

- Note that  $\text{Ag}^+$  is limiting and that the amount of  $\text{S}_2\text{O}_3^{2-}$  consumed is negligible
  - Also note that since all these species are in the same solution, the molarities can be used to do the stoichiometry problem
- Of course, the concentration of  $\text{Ag}^+$  is not zero at equilibrium, and there is some  $\text{Ag}(\text{S}_2\text{O}_3)^-$  in the solution
  - To calculate the concentrations of these species, we must use the  $K_1$  and  $K_2$  expressions

## Section 16.3

### *Equilibria Involving Complex Ions*

#### Interactive Example 16.8 - Solution (Continued 3)

- We can calculate the concentration of  $\text{Ag}(\text{S}_2\text{O}_3)^-$  from  $K_2$

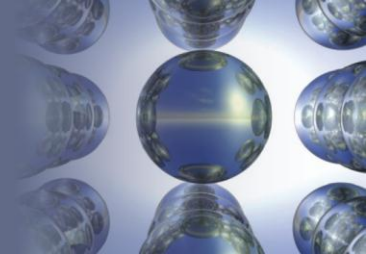
$$3.9 \times 10^4 = K_2 = \frac{[\text{Ag}(\text{S}_2\text{O}_3)_2^{3-}]}{[\text{Ag}(\text{S}_2\text{O}_3)^-][\text{S}_2\text{O}_3^{2-}]} = \frac{4.29 \times 10^{-4}}{[\text{Ag}(\text{S}_2\text{O}_3)^-](2.86)}$$

- We can calculate  $[\text{Ag}^+]$  from  $K_1$

$$7.4 \times 10^8 = K_1 = \frac{[\text{Ag}(\text{S}_2\text{O}_3)^-]}{[\text{Ag}^+][\text{S}_2\text{O}_3^{2-}]} = \frac{3.8 \times 10^{-9}}{[\text{Ag}^+](2.86)}$$

## Section 16.3

### *Equilibria Involving Complex Ions*



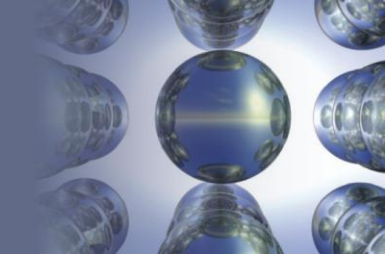
#### Interactive Example 16.8 - Solution (Continued 4)

$$[\text{Ag}^+] = 1.8 \times 10^{-18} \text{ M}$$

- These results show that  $[\text{Ag}(\text{S}_2\text{O}_3)_2^{3-}] \gg [\text{Ag}(\text{S}_2\text{O}_3)^-] \gg [\text{Ag}^+]$ 
  - Thus, the assumption is valid that essentially all the original  $\text{Ag}^+$  is converted to  $\text{Ag}(\text{S}_2\text{O}_3)_2^{3-}$  at equilibrium

## Section 16.3

### *Equilibria Involving Complex Ions*

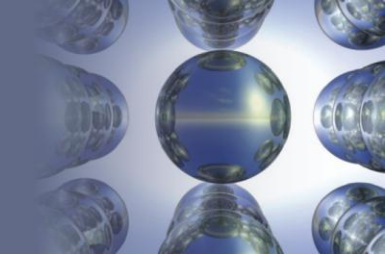


#### Complex Ions and Solubility

- Ionic solids that are nearly water-insoluble must be dissolved somehow in aqueous solutions
  - Example - When the various qualitative analysis groups are precipitated out, the precipitates must be redissolved to separate the ions within each group

## Section 16.3

### *Equilibria Involving Complex Ions*



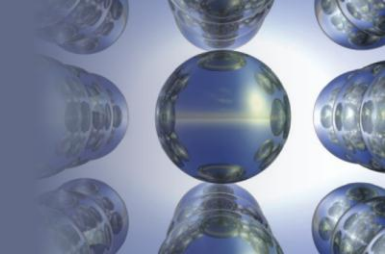
#### Strategies for Dissolving a Water-Insoluble Ionic Solid

- If the anion of the solid is a good base, the solubility is greatly increased by acidifying the solution
- When the anion is not sufficiently basic, the ionic solid can be dissolved in a solution containing a ligand that forms stable complex ions with its cation



## Section 16.3

### *Equilibria Involving Complex Ions*



## Strategies for Dissolving a Water-Insoluble Ionic Solid (Continued)

- Some insoluble solids have to go through a combination of reactions to be dissolved
- The solubility of many salts increases with temperature
  - Simple heating is enough to make a salt sufficiently soluble