

# **Chapter 34**

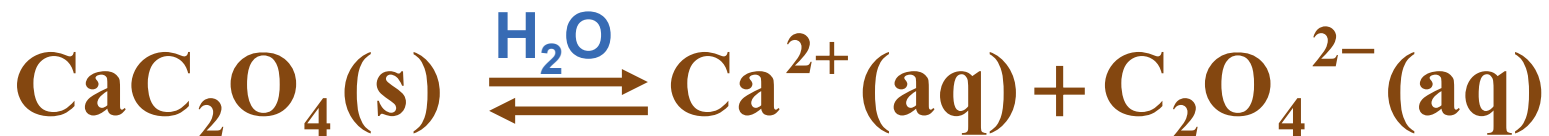
## **Solubility and Complex-ion Equilibria**

# Solubility Equilibria

- Many natural processes depend on the precipitation or dissolving of a **slightly soluble salt**. **Insoluble does not mean 100% insoluble.**
  - 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**.

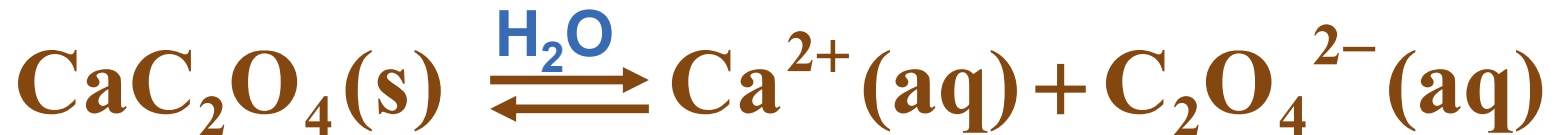
# 34.1 The Solubility Product Constant

- 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.**
- **Insoluble salts will have extremely small quantities of salt dissolve in water and a equilibrium will be established when the salt reaches its saturation point; exchange solid to ions in solution.**
  - For the salt calcium oxalate,  $\text{CaC}_2\text{O}_4$ , you have the following equilibrium.



# The Solubility Product Constant

- 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 and represented by a constant that is temp dependent.**
  - The equilibrium constant for this process is called the **solubility product constant,  $K_{sp}$ .**



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

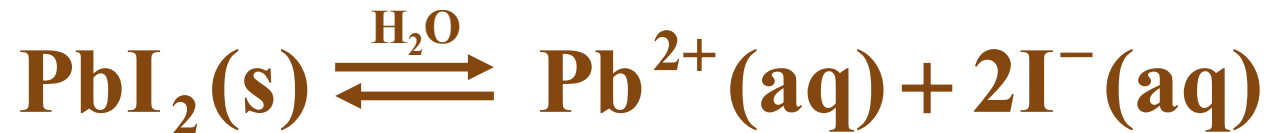
$K_{sp}$  basically relationship of amount of ions in solution at saturation point; once product of concentration of ions =  $K_{sp}$ , ppt occurs

# The Solubility Product Constant

- In general, the **solubility product constant**,  $K_{sp}$ , is the equilibrium constant for the solubility equilibrium of a slightly soluble (or nearly insoluble) ionic compound. It is a constant that relates to amount of substance that is dissolve in solution at saturation point not amount in flask (only amount dissolved)
  - It equals the **product of the equilibrium concentrations** of the ions in the compound. Solids activity of 1.
  - Each concentration is **raised to a power** equal to the number of such ions in the formula of the compound.

# The Solubility Product Constant

- For example, lead iodide,  $\text{PbI}_2$ , is another slightly soluble salt (insoluble salt). Its equilibrium is:



- The expression for the solubility product constant is:

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

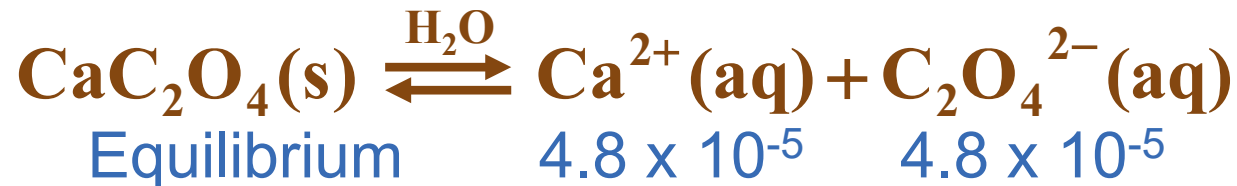
# Calculating $K_{sp}$ from the Solubility

- A 1.0-L sample of a saturated calcium oxalate solution,  $\text{CaC}_2\text{O}_4$ , contains 0.0061-g of the salt at  $25^\circ\text{C}$ . Calculate the  $K_{sp}$  for this salt at  $25^\circ\text{C}$ .
  - We must first convert the solubility of calcium oxalate from 0.0061 g/liter to moles per liter. Note to calculate the  $K_{sp}$  must have data on a saturated solution, if below saturation point can't determine  $K_{sp}$ .

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

# Calculating $K_{sp}$ from the Solubility

- When  $4.8 \times 10^{-5}$  mol of solid dissolve it forms  $4.8 \times 10^{-5}$  mol of each ion.



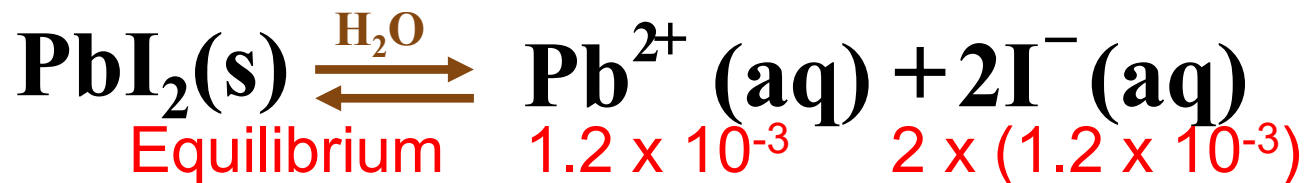
- You can now substitute into the equilibrium-constant expression.

$$\begin{aligned} K_{sp} &= [\text{Ca}^{2+}][\text{C}_2\text{O}_4^{2-}] \\ K_{sp} &= (4.8 \times 10^{-5})(4.8 \times 10^{-5}) \\ K_{sp} &= 2.3 \times 10^{-9} \end{aligned}$$



# Calculating $K_{sp}$ from the Solubility

- By experiment, it is found that  $1.2 \times 10^{-3}$  mol of lead(II) iodide,  $PbI_2$ , dissolves in 1.0 L of water at  $25^\circ C$  to reach saturation pt. What is the  $K_{sp}$  at this temperature?
  - The following table summarizes.



Note: if 2:1 ratio you double, etc.

# Calculating $K_{sp}$ from the Solubility

- Substituting into the equilibrium-constant expression:

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

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

$$K_{sp} = (1.2 \times 10^{-3})(2.4 \times 10^{-3})^2$$

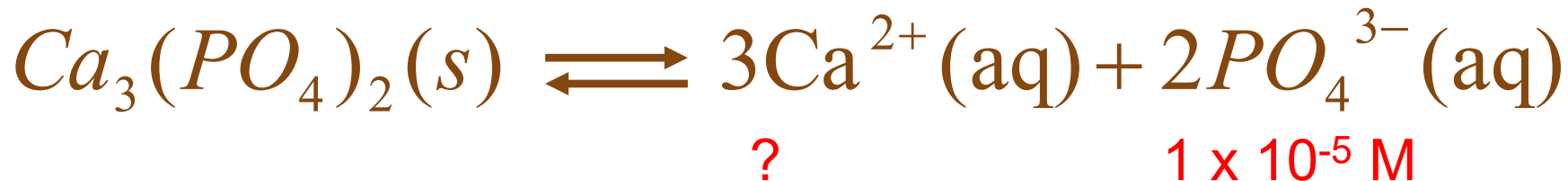
$$K_{sp} = 6.9 \times 10^{-9}$$

- note: conc of I is double due to 2:1 ratio.  
Also need to square due to the order of this elementary rxn.

**HW 40**

Sometimes you may want to determine the concentration of a species you need to reach the saturation point. Let's look at example.

What is the  $[Ca^{2+}]$  needed to form a saturated solution of  $Ca_3(PO_4)_2$  containing  $1 \times 10^{-5} M$  of phosphate ions?  $K_{sp} Ca_3(PO_4)_2 = 1 \times 10^{-33}$



note: didn't double phosphate; problem gave us total amount of phosphate; no mol:mol etc. Must read problem.

$$K_{sp} = 1 \times 10^{-33} = [Ca^{2+}]^3 [PO_4^{3-}]^2 = [Ca^{2+}]^3 [1 \times 10^{-5}]^2$$

$$\sqrt[3]{[Ca^{2+}]^3} = \frac{1 \times 10^{-33}}{[1 \times 10^{-5}]^2} = \sqrt[3]{1 \times 10^{-23}}$$

$y^x$     $y^{1/3}$    or ^   or x sq rt y

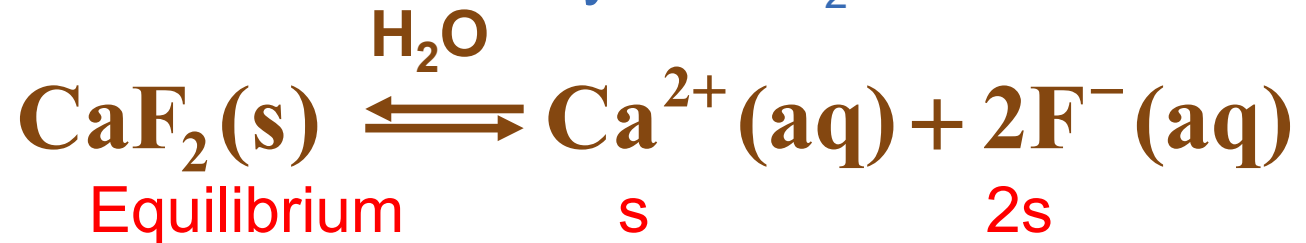
$$[Ca^{2+}] = 2 \times 10^{-8} M$$

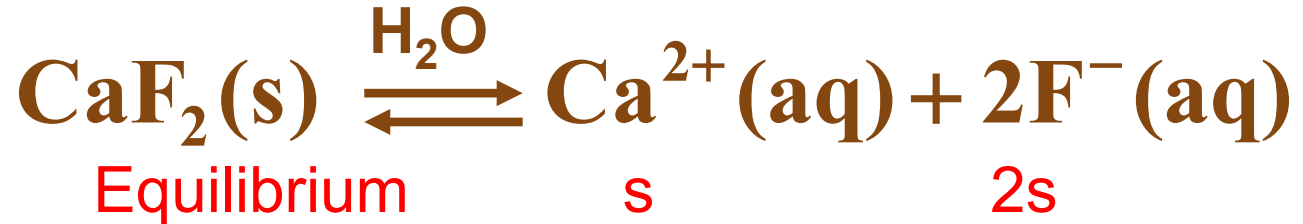
# Calculating $K_{sp}$ from the Solubility

- If the solubility product constant,  $K_{sp}$ , is known, the solubility of the compound can be calculated.
- The water solubility of an ionic compound is amount of compound that dissolves per unit volume of saturated solution; typically g/L. If the units on the solubility is mols/L called molar solubility.

# Calculating the Solubility from $K_{sp}$

- The mineral fluorite is calcium fluoride,  $\text{CaF}_2$ . Calculate the solubility (in grams per liter) of calcium fluoride in water from the  $K_{sp}$  ( $3.4 \times 10^{-11}$ )
  - Let  $s$  be the molar solubility of  $\text{CaF}_2$ .





- You substitute into the equilibrium-constant equation

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

$$3.4 \times 10^{-11} = (s)(2s)^2 = (s)(4s^2) = 4s^3$$

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

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

$$s^3 = \frac{3.4 \times 10^{-11}}{4}$$

$$s = \sqrt[3]{\frac{3.4 \times 10^{-11}}{4}} = 2.0 \times 10^{-4} \text{ M} = [\text{Ca}^{2+}] = [\text{CaF}_2]$$

note  $[\text{F}^-] = 2s = 4.0 \times 10^{-4} \text{ M}$

which equals the molar solubility of  $\text{CaF}_2$  but we want solubility.

# Calculating the Solubility from $K_{sp}$

- Convert to g/L ( $\text{CaF}_2$  78.1 g/mol).

$$\begin{aligned}\text{solubility} &= \frac{2.0 \times 10^{-4} \text{ mol CaF}_2}{L} \times \frac{78.1 \text{ g CaF}_2}{1 \text{ mol CaF}_2} \\ &= 1.6 \times 10^{-2} \text{ g CaF}_2 / L = 0.016 \text{ g CaF}_2 / L\end{aligned}$$

**HW 41**

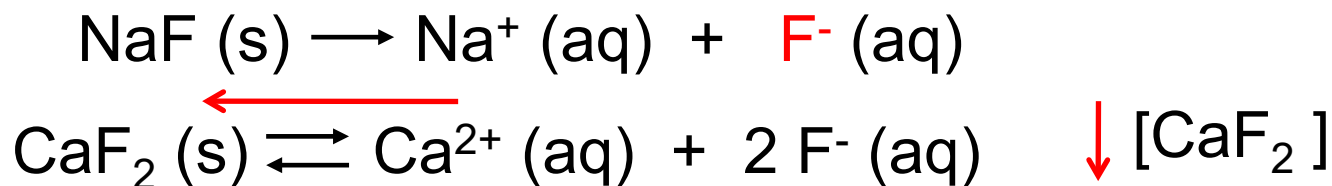


# 34.1.1 Solubility and the Common-Ion Effect

- In this section we will look at calculating solubilities **in the presence of other ions.**
- Common ion problem similar to buffer except involves insoluble and soluble salt.
  - 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 or anion.**
  - By having a common ion, the equil will shift to the left causing more to ppt out and decrease the solubility of the substance. We take advantage of this to get species to ppt out completely from a solution.

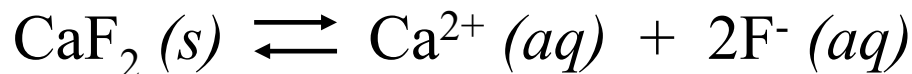
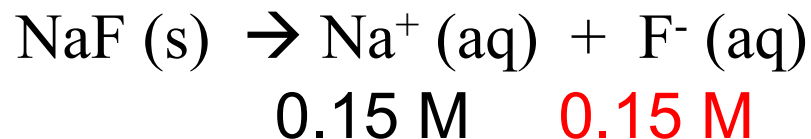
# Solubility and the Common-Ion Effect

- For example, suppose you wish to know the solubility of calcium fluoride in a solution of sodium fluoride (soluble salt).



- The salt contributes the fluoride to the system and shifts the equil causing the solubility of calcium fluoride to be less
- The effect is that calcium fluoride will be **less soluble than it would be in pure water.**

- What is the molar solubility of calcium fluoride in 0.15 M sodium fluoride? The  $K_{sp}$  for calcium fluoride is  $3.4 \times 10^{-11}$ .



	[Ca <sup>2+</sup> ]	[F <sup>-</sup> ]
Initial, [ ] <sub>o</sub>	0	0.15
Change, Δ[ ]	+s	+2s
Equilibrium, [ ] <sub>eq</sub>	s	0.15 + 2s

Note: don't double

**HW 42**

$$K_{sp} = [\text{Ca}^{2+}] [\text{F}^-]^2 = (s) (0.15 + \cancel{2s})^2 = 3.4 \times 10^{-11}$$

$$(s)(0.15)^2 = 3.4 \times 10^{-11}$$

$$s = \frac{3.4 \times 10^{-11}}{(0.15)^2} = 1.5 \times 10^{-9} \text{ M} = [\text{CaF}_2]$$

[CaF<sub>2</sub>] in pure H<sub>2</sub>O was 2.0 x 10<sup>-4</sup> M;  
100,000 times more soluble in water  
than in NaF

## 34.2 Precipitation

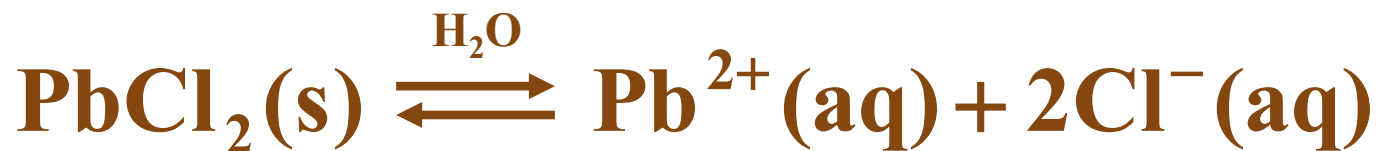
- Precipitation is merely another way of looking at solubility equilibrium.
  - Rather than considering how much of a substance will dissolve, we ask: **Will precipitation occur for a given starting ion concentration?**

# Criteria for Precipitation

- To determine whether an equilibrium system will go in the forward or reverse direction requires that we evaluate the **reaction quotient,  $Q$  (or  $IP$  or  $P$ ).**
  - To predict the direction of reaction, you compare  $Q$  with  $K_{sp}$ .
  - The reaction quotient has the same form as the  $K_{sp}$  expression, but the concentrations of products are starting values not necessarily saturated conc.

# Criteria for Precipitation

- Consider the following equilibrium.



$$K_{sp} = [\text{Pb}^{2+}]_{eq} [\text{Cl}^{-}]_{eq}^2$$

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

where initial concentration is denoted by *i*.

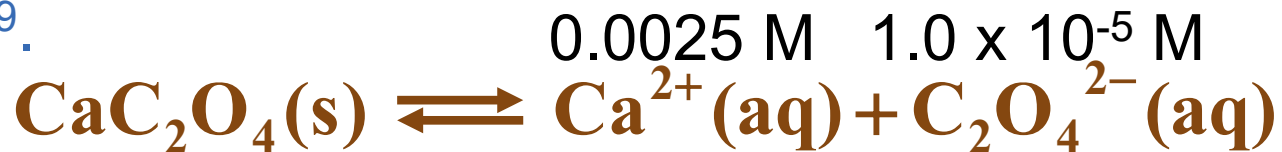
# Criteria for Precipitation

- If  $Q = K_{sp}$ , the solution is just saturated with ions and any additional solid will not dissolve in solution but instead will precipitate out.



- If  $Q < K_{sp}$ , the solution is unsaturated and more solid can be dissolved in the solution; no precipitate forms. Shift right increase  $Q$
- If  $Q > K_{sp}$ , the solution is supersaturated meaning the solution contains a higher concentration of ions than possible at equilibrium; a precipitate will form. Shift to left decrease  $Q$
- not really shifting but will give you where equil lies.

- The concentration of calcium ion in blood plasma is 0.0025 M. If the concentration of oxalate ion is  $1.0 \times 10^{-5}$  M, do you expect calcium oxalate to precipitate?  $K_{sp}$  for calcium oxalate is  $2.3 \times 10^{-9}$ .



- The ion product quotient,  $Q_c$ , is:

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

$$Q = (0.0025) \times (1.0 \times 10^{-5})$$

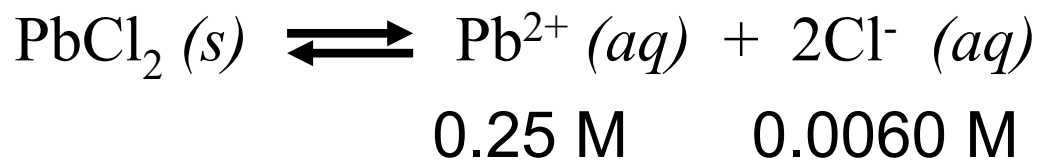
$$Q = 2.5 \times 10^{-8}$$

- This value is larger than the  $K_{sp}$ , so **you expect precipitation to occur past saturation point.**

$$Q = 2.5 \times 10^{-8} > K_{sp} = 2.3 \times 10^{-9}$$



- The concentration of lead ion is 0.25 M. If the concentration of chloride ion is 0.0060 M, do you expect lead chloride to precipitate?  $K_{sp}$  for lead chloride is  $1.7 \times 10^{-5}$ .



Note: did not double chloride concentration

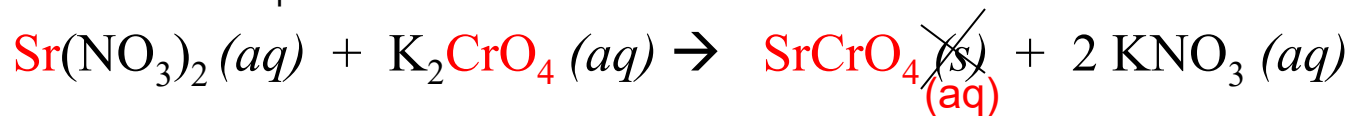
$$Q = [\text{Pb}^{2+}]_i [\text{Cl}^-]_i^2$$

$$Q = (0.25)(0.0060)^2$$

$$Q = 9.0 \times 10^{-6}$$

$Q < K_{sp} = 1.7 \times 10^{-5}$ , indicating that a no precipitate will form (below the saturation point).

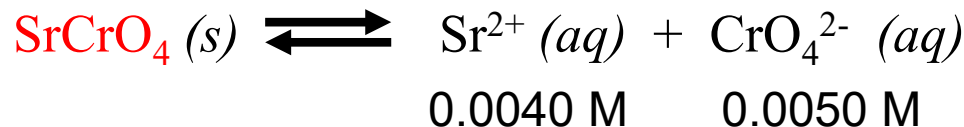
**example:** A student mixes 0.200 L of 0.0060 M  $\text{Sr}(\text{NO}_3)_2$  solution with 0.100 L of 0.015 M  $\text{K}_2\text{CrO}_4$  solution to give a final volume of 0.300L. Will a precipitate form under these conditions?  $K_{sp} \text{SrCrO}_4 = 3.6 \times 10^{-5}$



$$[\text{Sr}^{2+}] = \frac{(0.200 \text{ L})(0.0060 \text{ M})}{(0.300 \text{ L})} = 0.0040 \text{ M}$$

**HW 43**

$$[\text{CrO}_4^{2-}] = \frac{(0.100 \text{ L})(0.015 \text{ M})}{(0.300 \text{ L})} = 0.0050 \text{ M}$$



$$Q = [\text{Sr}^{2+}]_i [\text{CrO}_4^{2-}]_i = (0.0040)(0.0050)$$

$$= 2.0 \times 10^{-5}$$

we find that  $Q (2.0 \times 10^{-5}) < K_{sp} (3.6 \times 10^{-5})$  indicating that no precipitate will form (below saturation point)

## 34.2.1 Selective Precipitation

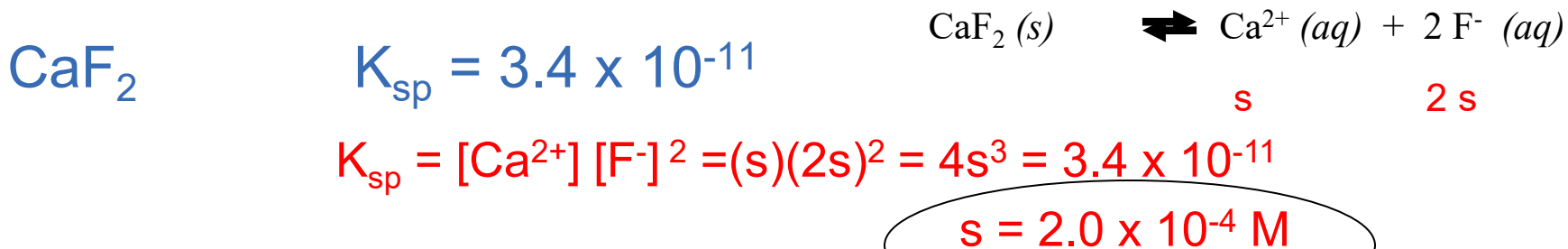
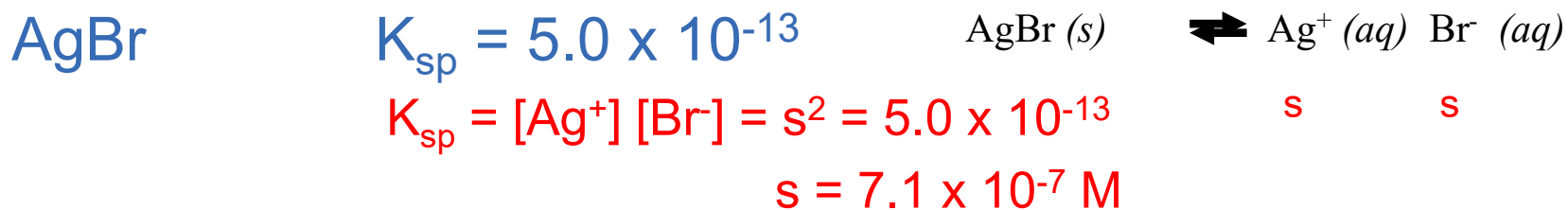
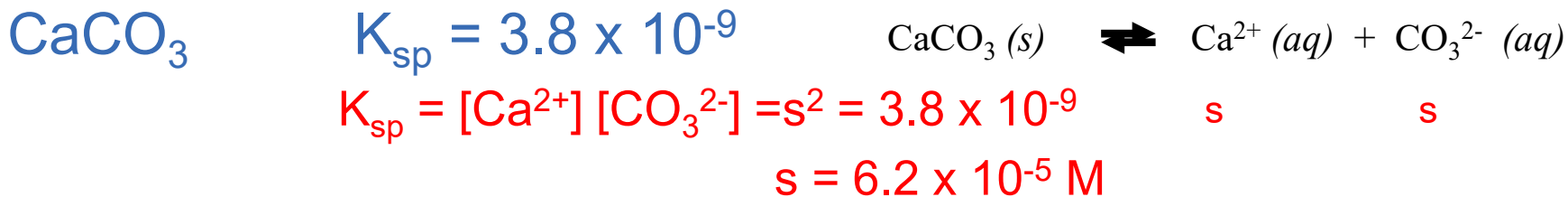
- **Selective precipitation** is the technique of separating two or more ions from a solution by adding a reactant that precipitates first one ion, then another, and so forth.
  - For example, when you slowly add potassium chromate,  $K_2CrO_4$ , to a solution containing  $Ba^{2+}$  and  $Sr^{2+}$ , **barium chromate precipitates first due to its lower solubility than  $SrCrO_4$ .**

# Selective Precipitation

- After most of the  $\text{Ba}^{2+}$  ion has precipitated, strontium chromate begins to precipitate.
- It is therefore possible to separate  $\text{Ba}^{2+}$  from  $\text{Sr}^{2+}$  by **selective precipitation** using  $\text{K}_2\text{CrO}_4$ .
- Take advantage in qual/quant type analysis.

## 34.1.2 Relative Solubility

Comparing solubilities: Which is most soluble in water?

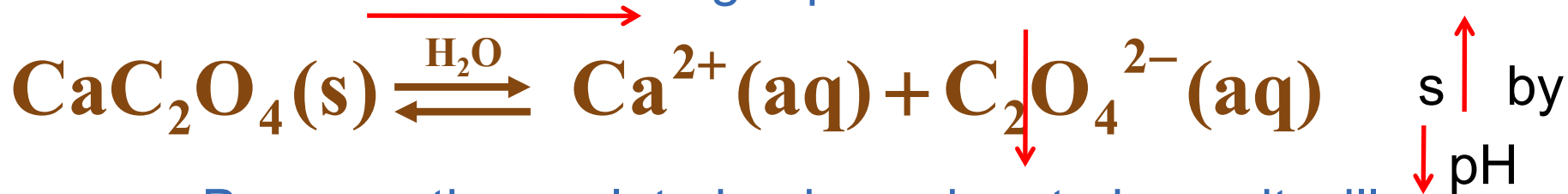


# Effect of pH on Solubility

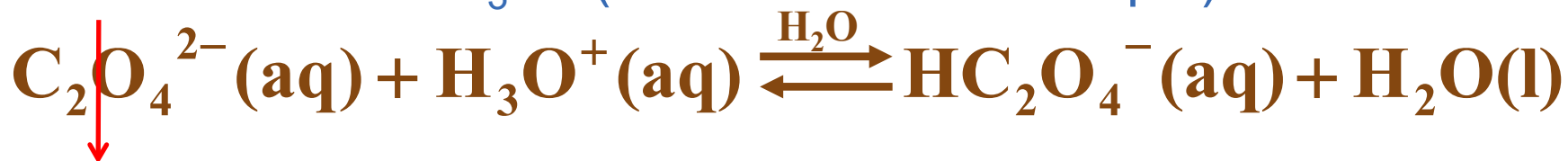
- Sometimes it is necessary to account for **other reactions** that aqueous ions might undergo.
  - For example, if the anion is the **conjugate base of a weak acid**, it will react with  $\text{H}_3\text{O}^+$ .
  - You should expect the solubility to be affected by pH. By adding and complexing out ions you can affect the pH of solution which could affect ppt reactions.

# Effect of pH on Solubility

- Consider the following equilibrium.



- Because the oxalate ion is conjugate base, it will react with  $\text{H}_3\text{O}^+$  (added acid to lower pH).



- According to Le Chatelier's principle, as  $\text{C}_2\text{O}_4^{2-}$  ion is removed by the reaction with  $\text{H}_3\text{O}^+$ , more calcium oxalate dissolves (increase solubility).
- Therefore, you expect calcium oxalate to be **more soluble in acidic solution (lower pH) than in pure water**. The acidity will react with the oxalate and shift the equil toward the right and allow more calcium oxalate to dissolve.

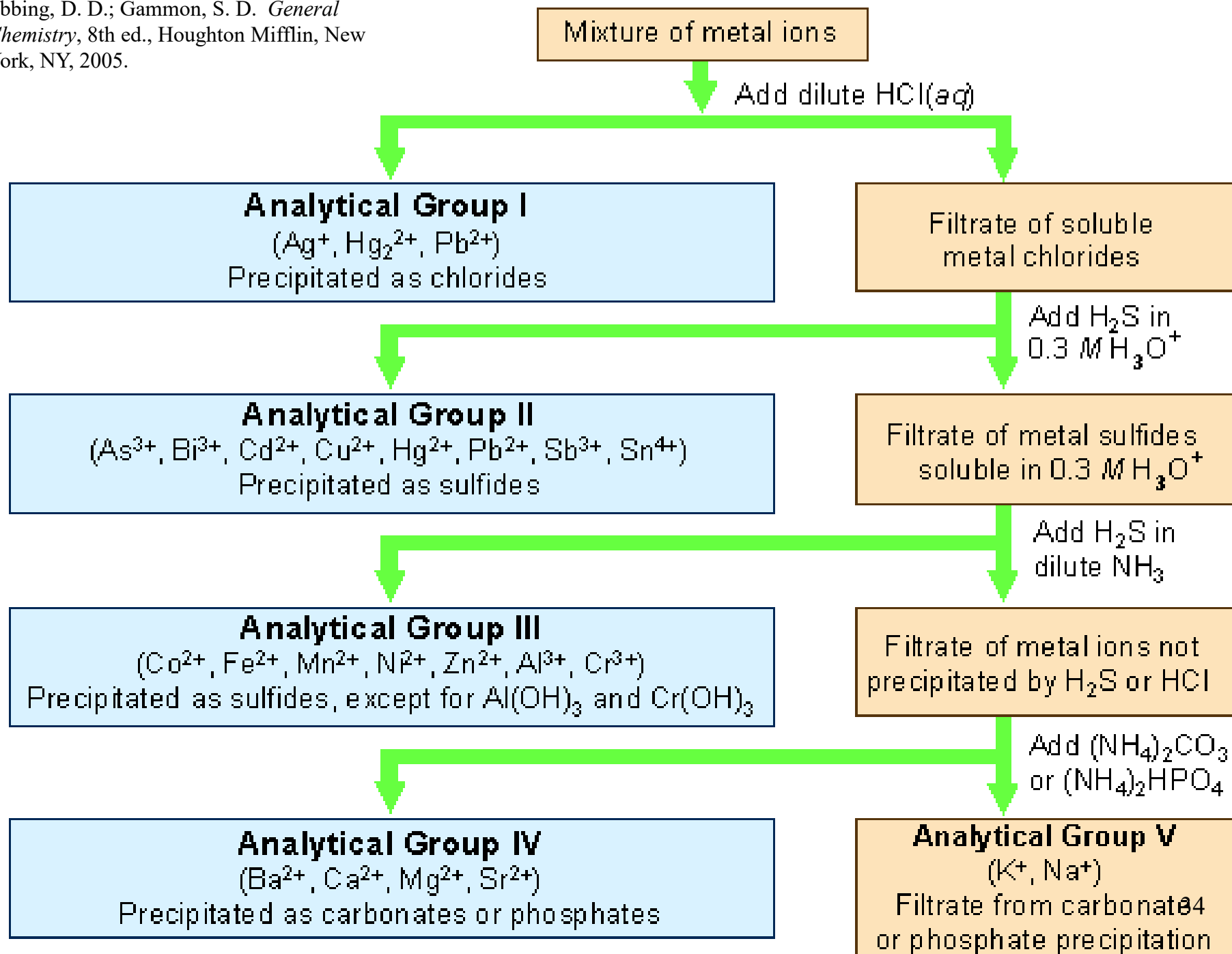
# Separation of Metal Ions by Sulfide Precipitation

- 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  $\text{H}_2\text{S}$ , you adjust the sulfide concentration to precipitate the least soluble metal sulfide first.
  - Typically do some qual experiment similar in lab.



# 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.**
  - Next slide shows a figure that summarizes how metal ions in an aqueous solution are separated into five analytical groups.

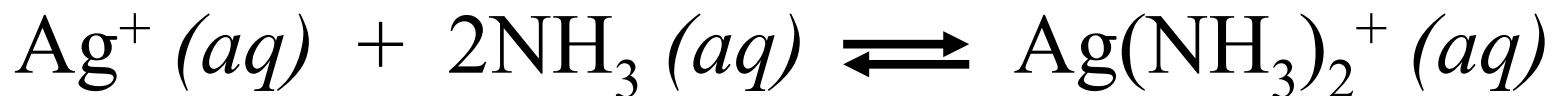


## 34.3 Complex-Ion Equilibria

- 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 (accepts share pair electrons)-base (makes available share pair electrons) reaction.

# Complex-Ion Equilibria

- For example, the silver ion,  $\text{Ag}^+$ , can react with ammonia to form the  $\text{Ag}(\text{NH}_3)_2^+$  ion.

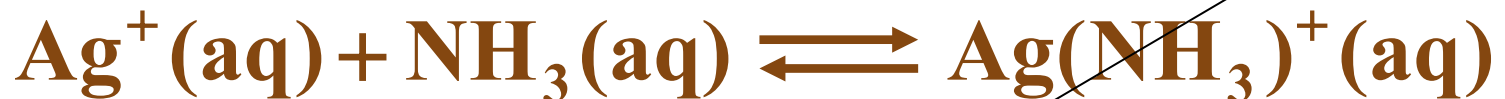


# Complex-Ion Equilibria

- A **complex ion** is an ion formed from a metal ion with a Lewis base attached to it by a coordinate covalent bond.  $\text{Ag}(\text{NH}_3)_2^+$ 
  - A **complex** is defined as a compound containing complex ions.  $\text{Ag}(\text{NH}_3)_2\text{Cl}$
  - A **ligand** is a Lewis base (makes electron pair available) that bonds to a metal ion to form a complex ion. Lewis Acid is the cation.  $:\text{NH}_3$

# 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  $1.7 \times 10^7$ .

# Complex-Ion Formation

- The large value means that **the complex ion is quite stable.**
- When a large amount of  $\text{NH}_3$  is added to a solution of  $\text{Ag}^+$ , you expect most of the  $\text{Ag}^+$  ion to react to form the complex ion (large  $K_f$  - equil lies far to right).
- Handle calculations same way as any other K



# 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 1.00 liters of solution that is 0.010 M  $\text{AgNO}_3$  and 1.00 M  $\text{NH}_3$ ? The  $K_f$  for  $\text{Ag}(\text{NH}_3)_2^+$  is  $1.7 \times 10^7$ .

1.) mols initially

$\text{AgNO}_3$  (1.00L) (0.010 mol/L) = 0.010 mol

$\text{NH}_3$  (1.00L) (1.00 mol/L) = 1.00 mol

2.) reaction



mol <sub>o</sub>	0.010	1.00	0	
$\Delta$ mol	-0.010	-0.020 (1:2)	+0.010	
mol <sub>rxn</sub>	0.000	0.98	+0.010	

3.) new conc

$$[\text{NH}_3] = \frac{0.98 \text{ mols}}{1.00 \text{ L}} = 0.98 \text{ M}$$

$$[\text{Ag}(\text{NH}_3)_2\text{NO}_3] = [\text{Ag}(\text{NH}_3)_2^+] = \frac{0.010 \text{ mols}}{1.00 \text{ L}} = 0.010 \text{ M}$$

4.) complex ion diss



Initial	0.010
Change	-x
Equilibrium	0.010-x

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

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

$$K_d = 5.9 \times 10^{-8} = \frac{[Ag^+][NH_3]^2}{[Ag(NH_3)_2^+]} = \frac{(x)(0.98 + 2x)^2}{(0.010 - x)}$$

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

$$x = 5.9 \times 10^{-8} \times \frac{(0.010)}{(0.98)^2} = 6.1 \times 10^{-10} M = [Ag^+]$$