Solubility Equilibria

Chemistry by Chang and Goldsby Covering this material after equilibria works better than doing it after acids and bases. Jump ahead to chapter 16 section 6. 16.06 Solubility Equilibria ~~16.07 Separation of Ions by Fractional Precipitation~~ 16.08 Common Ion Effect and Solubility 16.09 pH and Solubility 16.10 Complex Ion Equilibria and Solubility 16.11 ~~Qualitative Analysis~~	I have posted a condensed version of Chang's Chapter 16 Solubility Sections on the classroom webpage that you can use with this summary.

16.6 Solubility Equilibria

Go over AP04 C04 Metathesis Precipitate Reactions in your binder to refresh your understanding of net ionic, ionic, and molecular reactions for the formation of a precipitate.

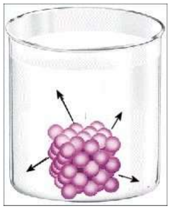
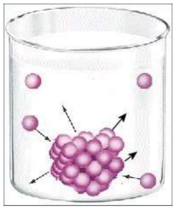
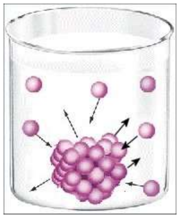
Solubility rules for the AP Exam: "All sodium, potassium, ammonium and nitrate salts are soluble."

Insoluble substances are the focus of this unit.

While called insoluble, even the most insoluble substances have some solute dissolve.

1. When placed in water, particles of compounds dissolve in the solvent (water).
2. Dissolution continues even as some dissolved solute particles reattach to the solid solute.
3. An equilibrium is reached when the rate of dissolving equals the rate of undissolving (precipitation).

While the solute appears to stop dissolving on the macroscopic scale, on the microscopic scale the dissolving and "undissolving" processes continue.

		
Salt is put into solvent and starts to dissolve. 4 particles dissolving 0 precipitating Equilibrium is not established. $Q < K_{sp}$	***Salt is still dissolving but some ions are precipitating.*** 4 particles dissolving 2 precipitating Equilibrium is not established. $Q < K_{sp}$	***Rate dissolving equals rate precipitating. (Saturated)*** 4 particles dissolving 4 precipitating Equilibrium is established. $Q = K_{sp}$

A saturated solution has a maximum solute concentration, *s*, for a given temperature.

Adding more solid, no matter how much, will not increase the concentration of the solution.
The extra solid has more surface area to dissolve, but also it has more surface area to precipitate.

Evaporating the solution that has a precipitate equilibrium does not make the solution more concentrated.
As the solvent evaporates, the "extra" solute precipitates.

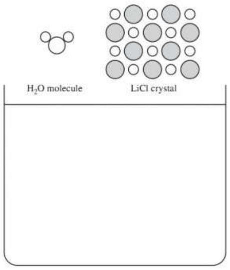
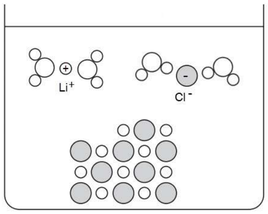
Solubility equilibria reactions can be of two types: molecular or ionic.

Molecular substances that don't ionize with water[1]: $X(s) \leftrightarrows X(aq)$

Ionic substances that ionize with water: $XY(s) \leftrightarrows X^{+}(aq) + Y^{-}(aq)$

If the cation and anion charges of the ionic compound are not equal, you will have to deal with the stoichiometry of the ions in solution. These will be the more difficult problems on the exam.

With the emphasis of drawings on the AP Chemistry exam, it is worth reviewing the process of the dissolution of an ionic compound on the atomic/ionic level including the involvement of water in the solution process.

This would be a typical question: Use the drawing on the right to show the interactions of the components of LiCl(*aq*) by drawing the different particles present in solution. Base the particles in your drawing on the particles shown above the beaker. Include only one formula unit of LiCl and no more than ten molecules of water. Identify the ions (symbols and charges) and arrangement and orientation of the particles in the solution.	
The drawing to the right would have received full credit. Separate the ions **and** select the correct ion size for each ion. In this example lithium ions are smaller than chloride ions. When surrounding the ions with water molecules, the negative portion of the water molecules, the oxygen atoms, must be oriented toward the lithium cation and the positive portion of the water molecules, the hydrogen atoms, must be oriented toward the chloride anion. You must use at least two water molecules to cloak the charge of each ion. In reality, there would be more than two water molecules around each ion.	

Now three important terms:

(1) Molar solubility or solubility, *s* :

s is the number of moles of the solute in its original, unionized formula that will dissolve in a liter of solution. Molar solubility is a fixed value in pure water for a given temperature, but molar solubility varies if extra common cations or anions are added to the solution. While molar solubility is a useful value that gives some indication of solubility, molar solubility of a compound is only valid for adding the solute to pure water.

(2) Solubility-product constant, K_{sp}:

K_{sp} is the constant for equilibrium expression for dissolving the solute.
Solubility-product constant, K_{sp}, is a constant for solution at a given temperature, no matter what is added to the solution.

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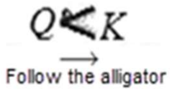
[1] Molecular substances are not usually seen in solubility equilibria problems. More commonly you will see ionic substances dissociating in solution.

The equilibrium expression for dissolving substances would always have a solid as a reactant so the denominator of the equilibrium expression will always be 1, as solids are not included in the expression. Thus, the name “solubility product constant” as there is no division by a reactant.

Molecular substance:	$X(s) \leftrightarrows X(aq)$	$K_{sp} = [X]$
Ionic substances:	$XY(s) \leftrightarrows X^+(aq) + Y^-(aq)$	$K_{sp} = [X][Y]$
	$X_2Y_3(s) \leftrightarrows 2\ X^+(aq) + 3\ Y^-(aq)$	$K_{sp} = [X]^2[Y]^3$

(3) Solubility product quotient, or ion product[2], *Q*

Q is the calculated product of the concentrations of the ions given in a solution using the equation of the solubility-product constant equation. If the solubility product, *Q*, is not equal to the solubility-product constant, K_{sp}, the system will react to approach the solubility-product constant, K_{sp}.



(a) If $Q < K_{sp}$ the ion concentrations will increase by **dissolving the solute →**.

When $Q < K_{sp}$ then $XY(s) \rightarrow [X\uparrow][Y\uparrow]$ until $Q = K_{sp}$

(b) If $Q > K_{sp}$ the ion concentrations will decrease **by forming a precipitate ←**.

When $Q > K_{sp}$ then $XY(s) \leftarrow [X\downarrow][Y\downarrow]]$ until $Q = K_{sp}$

Relationship between molar solubility, *s*, and solubility product, K_{sp}

The relationship is dependent on the ionic formula:

For $AB \leftrightarrows A^+ + B^-$	$K_{sp} = s^2$	
For $A_2B \leftrightarrows 2\ A^+ + B^{2-}$	$K_{sp} = [2s]^2[s]$	$K_{sp} = 4s^3$
For $AB_2 \leftrightarrows A^{2+} + 2\ B^-$	$K_{sp} = [s][2s]^2$	$K_{sp} = 4s^3$
For $A_3B \leftrightarrows 3A^+ + B^{3-}$	$K_{sp} = [3s]^3[s]$	$K_{sp} = 27s^4$
For $AB_3 \leftrightarrows A^{3+} + 3\ B^-$	$K_{sp} = [s][3s]^3$	$K_{sp} = 27s^4$
For $A_2B_3 \leftrightarrows 2\ A^{3+} + 3\ B^{2-}$	$K_{sp} = [2s]^2[3s]^3$	$K_{sp} = 108s^5$

Rather than memorizing these formulas, you should understand the relationship because they can easily be determined algebraically.

A large K_{sp} indicates a soluble substance.
A small K_{sp} indicates a low solubility.

CAVEAT! When comparing K_{sp} values of ionic compounds, the ion stoichiometry must be taken into account. You can only directly compare the K_{sp} values of substances with similar ion ratios.

e.g. You can compare the solubility of AgI and AgCl

AgI	$K_{sp} = 8 \times 10^{-13}$	molar solubility in pure water is $9 \times 10^{-7}\ M$
AgCl	$K_{sp} = 2 \times 10^{-10}$	molar solubility in pure water is $1 \times 10^{-5}\ M$

Silver chloride is more soluble than silver iodide.

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[2] The AP curriculum uses solubility product while most texts use the term ion product.

If the ion ratios are not similar, the K_{sp} values cannot be simply compared. Instead, the solubility, s, must be calculated. For example: AgCl $K_{sp} = 1 \times 10^{-10}$ and Ag_2CO_3 $K_{sp} = 8 \times 10^{-12}$.
When comparing K_{sp} values it would seem that silver chloride is more soluble than silver carbonate.
However, when solving for the molar solubility of each compound the opposite is true.

AgCl € $Ag^+ + Cl^-$	$Ag_2CO_3 \leftrightarrows 2\,Ag^+ + CO_3^{2-}$
$K_{sp} = 1 \times 10^{-10}$ $K_{sp} = [Ag^+]\,[Cl^-]$ $1 \times 10^{-10} = [s]\,[s]$ $[s] = 1 \times 10^{-5}\ M$	$K_{sp} = 8 \times 10^{-12}$ $K_{sp} = [Ag^+]^2\,[CO_3^{2-}]$ $8 \times 10^{-12} = [2s]^2\,[s]$ $[s] = 1 \times 10^{-4}\ M$

Even though K_{sp} $Ag_2CO_3 <$ K_{sp} AgCl, the molar solubility comparison is: $[s]$ $Ag_2CO_3 > [s]$ AgCl,

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When working solubility problems use an RICE TABLE!

1. Calculate solubility-product constant, K_{sp}, from Molar Solubility, ***s***. The molar solubility is the initial amount of solid.

(a) The **solubility, *s*,** of $MgCO_3$ is 0.0067 *M*. Calculate the K_{sp} for magnesium carbonate.

Reaction	$MgCO_3(s)$	$\leftrightarrows$	$Mg^{2+}(aq)$	+	$CO_3^{2-}(aq)$
Initial	0.0067 mol		0 mol		0 mol
Change	-0.0067 mol		+0.0067 mol		+0.0067 mol m
Equilibrium	0 mol		0.0067 mol		0.0067 mol
In 1.00 liter solution [Equilibrium]			0.0067 *M*		0.0067 *M*

$K_{sp} = [Mg^{2+}]\,[CO_3^{2-}]$ $K_{sp} = [0.0067]\,[\ 0.0067]$ $K_{sp} = 4.5 \times 10^{-5}$

(b) The solubility of calcium sulfate is found to be 0.67 g/L in water. Calculate the K_{sp} for calcium sulfate. (molar mass=136.1 g/mol)

$$\frac{0.67\text{g } CaSO_4}{1\text{ L solution}} \times \frac{1\text{ mol } CaSO_4}{136.1\text{g } CaSO_4} = 0.0049\text{ mol } CaSO_4$$

Therefore, the molar solubility , ***s*** = 0.049 *M*
Put into an ICE chart showing this dissolving:

Reaction	$CaSO_4(s)$	$\leftrightarrows$	$Ca^{2+}(aq)$	+	$SO_4^{2-}(aq)$
Initial	0.0049 mol		0 mol		0 mol
Change	-0.0049 mol		+0.0049 mol		+0.0049 mol m
Equilibrium	0 mol		0.0049 mol		0.0049 mol
In 1.00 liter [Equilibrium]			0.0049 *M*		0.0049 *M*

The solubility product expression for $CaSO_4(s)$ is $K_{sp} = [Ca^{2+}]\,[CO_3^{2-}]$
$K_{sp} = [0.0049][\ 0.0049]$
$K_{sp} = 2.4 \times 10^{-5}$

2. Calculate Molar Solubility, *s*, from K_{sp}.

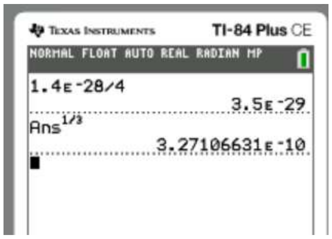
(a) Given that K_{sp} for tin(II) hydroxide $=1.4 \times 10^{-28}$. Calculate the molar solubility of tin(II) hydroxide.

The ICE chart for the dissolution of the tin(II) hydroxide is

Reaction	$Sn(OH)_2(s)$	$\leftrightarrows$	$Sn^{2+}(aq)$	+	$2\ OH^-(aq)$
Initial mol	s		0		0
Change mol	$-s$		$+s$		$+2s$
Equilibrium mol	0		$+s$		$+2s$

Putting the values at equilibrium in the solubility expression:

$$K_{sp} = [Sn^{2+}]\,[OH^-]^2$$
$$1.4 \times 10^{-28} = [s]\,[2s]^2$$
$$1.4 \times 10^{-28} = 4s^3$$
$$s = 3.3 \times 10^{-10}\ \text{moles/L}$$



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1.4E-28/4
                3.5E-29
Ans^(1/3)
        3.27106631E-10
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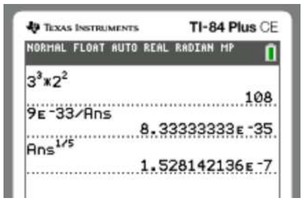
Molar solubility of $Sn(OH)_2$ $= 3.3 \times 10^{-10}\ M$

(b) Given that K_{sp} for zinc pho*sp*hate $= 9.0 \times 10^{-33}$. Calculate the molar solubility of zinc pho*sp*hate.

Reaction	$Zn_3(PO_4)_2(s)$	$\leftrightarrows$	$3\ Zn^{2+}(aq)$	+	$2\ PO_4^{3-}(aq)$
Initial mol	s		0		0
Change mol	$-s$		$+3s$		$+2s$
Equilibrium mol	0		$3s$		$2s$

In 1.00 liter

$$K_{sp} = [Zn^{2+}]^3[PO_4^{3-}]^2$$
$$9.0 \times 10^{-33} = [3s]^3[2s]^2$$
$$9.0 \times 10^{-33} = 108s^5$$



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3^3*2^2
                    108
9E-33/Ans
        8.333333333E-35
Ans^(1/5)
        1.528142136E-7
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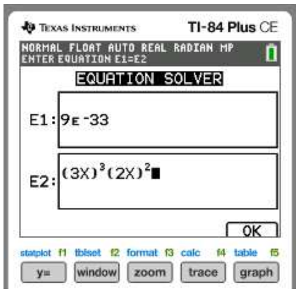
Molar solubility $Zn_3(PO_4)_2$ $s = 1.5 \times 10^{-7} M$

Or if you wanted to have SOLVER do all your algebra



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NORMAL FLOAT AUTO REAL RADIAN MP
ENTER EQUATION E1=E2
EQUATION SOLVER
E1:9E-33
E2:(3X)^3(2X)^2
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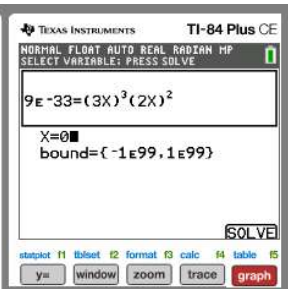

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NORMAL FLOAT AUTO REAL RADIAN MP
SELECT VARIABLE: PRESS SOLVE
9E-33=(3X)^3(2X)^2
  X=0
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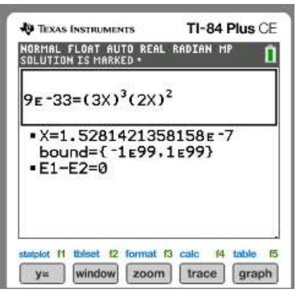

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NORMAL FLOAT AUTO REAL RADIAN MP
SOLUTION IS MARKED ▪
9E-33=(3X)^3(2X)^2
▪X=1.5281421358158E-7
  bound={-1E99,1E99}
▪E1-E2=0
```

3. Predicting the Formation of Precipitates – Calculate the solubility product, *Q*

(a) The K_{sp} for calcium sulfate is $2.4 \times 10^{-5.}$ If 100. mL of 0.0040 *M* $CaCl_2$ and 400. mL of 0.0080 *M* K_2SO_4 are mixed, will a precipitate form?

From your solubility rules: all potassium compounds are soluble. So, calcium sulfate will be the only possible precipitate. Are the concentrations of the calcium ion and sulfate ion high enough to form a precipitate?

If $Q > K_{sp}$, ion concentration is greater than needed for a ppt: precipitate will form.
If $Q < K_{sp}$, ion concentration is lower than needed for a ppt: precipitate will not form.

First find the concentrations of the calcium ion and the sulfate ion.

$$\frac{0.0040\text{ mol }CaCl_2}{1\text{ L sol'n}} \times 0.100\text{ L sol'n} \times \frac{Ca^{2+}}{CaCl_2} = 0.00040\text{ mol }Ca^{2+} \qquad \frac{0.0080\text{ mol }K_2SO_4}{1\text{ L sol'n}} \times 0.400\text{ L sol'n} \times \frac{SO_4^{2-}}{K_2SO_4} = 0.0032\text{ mol }SO_4^{2-}$$

	$CaSO_4(s)$	⇆	$Ca^{2+}(aq)$	+	$SO_4^{2-}(aq)$
Solute mol			0.00040 mol		0.0032 mol
Solution total volume			(0.100 L + 0.400 L)		
[Solution]			0.00080 *M*		0.0064 *M*

Next find if the concentrations of these two ions in solution are high enough to form a precipitate

$Q = [Ca^{2+}][SO_4{}^{2-}]$
$Q = [0.0008\ M][0.0064]$
$Q = \mathbf{5.1 \times 10^{-6}}$

Given in the problem: $CaSO_4$ $K_{sp} = 2.4 \times 10^{-5}$

Q	<	K_{sp}
5.1×10^{-6}	<	2.4×10^{-5}
Concentrations are too low Therefore, no precipitate forms		

Chapter 16.7 Separation of Ions by Fractional Precipitation….

Classic analytical chemistry, but it is not part of AP Chemistry.

Chapter 16.8 Common Ion Effect and Solubility

Common ion:

A common is **ion** that is added which is the **same as one of the ions of the solute**.

For example, in a solution of AgCl at equilibrium

$$AgCl(s) \leftrightarrows Ag^+(aq) + Cl^-(aq)$$

Adding NaCl(s) to the solution would increase the [Cl$^-$] lowering the solubility of the AgCl and extra precipitate of AgCl(s) would form.

$$AgCl(s) \leftarrow Ag^+(aq) + Cl^-(aq) \uparrow$$

Adding AgNO$_3$(s) to the solution would increase the [Ag$^+$] lowering the solubility of the AgCl and a precipitate of AgCl(s) would form.

$$AgCl(s) \leftarrow Ag^+(aq) \uparrow + Cl^-(aq)$$

Adding NaNO$_3$(s) to the equilibrium will have no effect.

A common ion will decrease the molar solubility of the solute, *s*.
Other ions will not change the molar solubility.

This occurs because one of the concentrations of the ions in the solubility product expression is increased. This will increase the solubility product, Q.

If a solution is at equilibrium: $XY(s) \leftrightarrows X^+(aq) + Y^-(aq)$,

An increase in concentration of [$X^+\uparrow$] caused by the addition of X^+ ions from another soluble compound (XB) will increase $Q\uparrow$ resulting in a ← shift to decrease both the $X^+(aq)$ and $Y^-(aq)$ concentrations until the concentrations are such that the solubility product of ions in the equilibrium solution will be $Q = K_{sp.}$

The same would hold for adding $Y^-(aq)$ from a soluble compound AY.

To find the solubility in a solution with a common ion, the concentration of the common ion must be considered.

For example: The K_{sp} of AgCl is 1.6×10^{-10}. What is the solubility of silver chloride in a 0.10 M NaCl solution?

$$AgCl(s) \leftrightarrows Ag^+(aq) + Cl^-(aq) \qquad K_{sp} = 1.6 \times 10^{-10} \quad \text{molar solubility in water: } s = 1.2 \times 10^{-5}\ M$$

The NaCl's chloride ion (the common ion) increases [Cl$^-$] in the solubility expression.

At equilibrium in water: $AgCl(s) \leftrightarrows Ag^+(aq) + Cl^-(aq)$
Reaction to extra Cl$^-$: $AgCl(s) \leftarrow Ag^+(aq) + \mathbf{Cl^-(aq)}$ Think Le Châtelier!

$K_{sp} = 1.6 \times 10^{-10} = [Ag^+][Cl^-]$
$1.6 \times 10^{-10} = [Ag^+][0.10]$
$[Ag^+] = 1.6 \times 10^{-9}\ M$ which is one ten thousandth the [Ag$^+$] in pure water

The molar solubility, s, of AgCl in 0.10 M NaCl(aq) is decreased from $1.2 \times 10^{-5}\ M$ to $1.6 \times 10^{-9}\ M$.

Chapter 16 Section 9 - pH and Solubility

pH is an indication of acidity in an aqueous solution.

A low pH (1-6) indicates an excess of H^+ ions
A high pH (8-14) indicates an excess of OH^- ions.

You will not be re*sp*onsible for calculations involving pH and solubility.
However, you should be aware of the consequences of low and high pH values on the solubility of certain ionic compounds.

Low pH's cause hydroxide precipitates to dissolve.

The solubility equilibria of OH^- precipitates will be significantly affected by low pH because the H^+ reacts with OH^- decreasing OH^- concentration by forming H_2O, and cause the precipitate to dissolve.

Low pH's cause carbonate precipitates to decompose.

In substances with carbonate anions such as $CaCO_3$ and $MgCO_3$, solubility equilibria are significantly affected by pH.

Calcium carbonate and magnesium carbonate are the major compounds in many rocks (limestone, dolomite, marble, chalk) and carbonates are used as a building material (concrete). Carbonates are an integral part of giant coral reefs and the tiniest seashells.

Calcium and magnesium carbonate are relatively insoluble in neutral water.
The solubility-product constant of calcium carbonate is 8.7×10^{-9}, a solubility of 0.00008 *M* and magnesium carbonate is even less soluble, $K_{sp}=1.2\times10^{-11}$ and $s = 0.000003\ M$. So, carbonates don't readily dissolve in water.

However, carbonates are not stable in acids. In low pH, acidic environments, the carbonate ion will decompose into carbon dioxide and water.

$$2\ H^+(aq) + CO_3^{2+}(aq) \rightarrow H_2O(l) + CO_2(g) \quad \text{(this actually takes place in two steps)}$$

The reaction favors products because the carbon dioxide gas can bubble out of solution.
Getting back to the calcium carbonate equilibria.

$$CaCO_3(s) \leftrightarrows Ca^{2+}(aq) + CO_3^{2-}(aq)$$

In an acid environment the carbonate ion decomposes into carbon dioxide and, as Le Châtelier's principle would indicate, a forward reaction → would occur to replace the decomposed carbonate ions and the solid calcium carbonate would dissolve.

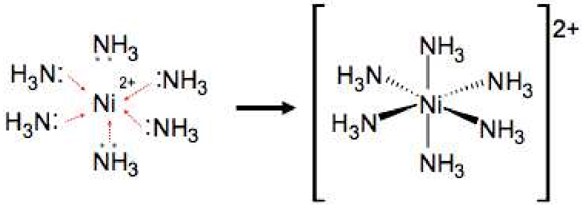
Chapter 16 Section 10 - Complex Ion Equilibria and Solubility

Complex Ions are not directly tested on the AP Chemistry exam, but complexes sometimes show up in reactions where you must apply AP Chem principles to the reactions.

Complexing agents or ligands, are substances rich in electrons, such as the ammonia molecule, $:NH_3$, the hydroxide ion, $:OH^-$, halide ions and even water molecules.

Ligands use their available pairs of electrons to bond to a metal cation.
These bonds are called coordinate covalent bonds.

In the case of the complex, $[Ni(NH_3)_6]^{2+}$, the unshared pairs of electrons of neutral ammonia molecules are attracted to the small 2+ ion of Ni and therefore form ligands.



A complex ion will be indicated by brackets.
Here are examples of complex ions:

$[Co(H_2O)_6]^{2+}$ $[CoCl_4]^{2-}$ $[Cu(NH_3)_4]^{2+}$

Complexing agents take small metal ions out of solution.

Complexing agents will shift the equilibrium of a precipitate by removing cations from the equilibrium system.

Chapter 16.11

Application of Solubility Product Principle to Qualitative Analysis are not part of AP and may be skipped.