Ch16 – Aqueous Ionic Equilibrium Solubility and Complex Ion Equilibria
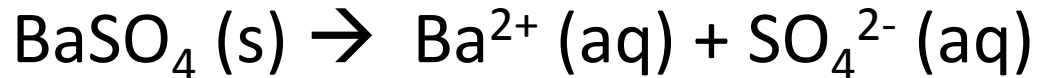

Lead (II) iodide precipitates when potassium iodide is mixed with lead (II) nitrate

Modified Dr. Cheng-Yu Lai

Solubility-product constant K_{sp}

The Equilibrium Constant for the equilibrium established between a solid solute and its ion in a saturated solutiion.

$$BaSO_4 (s) \rightarrow Ba^{2+} (aq) + SO_4^{2-} (aq)$$

- When writing the equilibrium constant expression for the dissolution of $BaSO_4$, *we remember that the concentration of a solid is constant*.
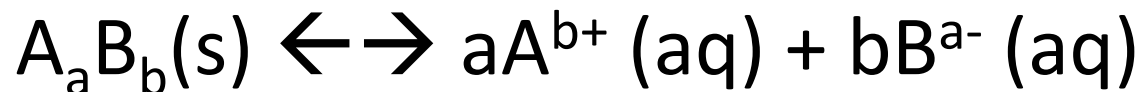
The equilibrium expression is therefore:

$$K = [Ba^{2+}][SO_4^{2-}]/[BaSO_4(s)]$$

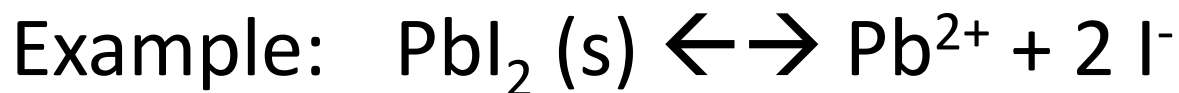since *the concentration of a solid is constant*, we could get new K'= k x[$BaSO_4(s)$]= Ksp

the solubility-product constant.

Ksp = [Ba^{2+}][SO$_4^{2-}$] Ksp, the **solubility-product constant**.

The Solubility Expression

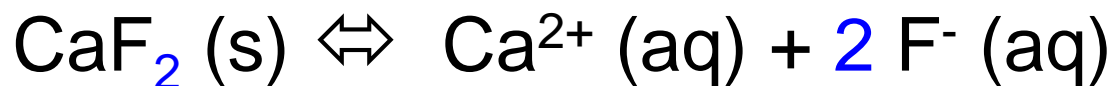$A_aB_b(s) \longleftrightarrow aA^{b+}(aq) + bB^{a-}(aq)$

$$K_{sp} = [A^{b+}]^a [B^{a-}]^b$$

Example: $PbI_2(s) \longleftrightarrow Pb^{2+} + 2\,I^-$

$K_{sp} = [Pb^{2+}][I^-]^2$
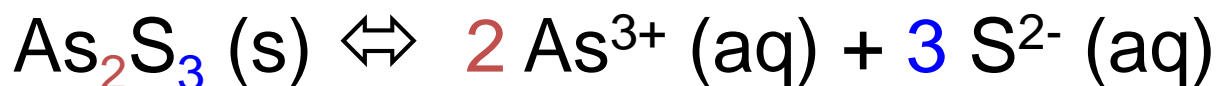
❖ The greater the ksp the more soluble the solid is in H_2O.

The Solubility Equilibrium Equation And K_{sp}

CaF_2 (s) $\Leftrightarrow$ Ca^{2+} (aq) + 2 F^- (aq)

$K_{sp} = [Ca^{2+}][F^-]^2$ $\qquad K_{sp} = 5.3 \times 10^{-9}$

As_2S_3 (s) $\Leftrightarrow$ 2 As^{3+} (aq) + 3 S^{2-} (aq)

$K_{sp} = [As^{3+}]^2[S^{2-}]^3$

* Remember, solids are not in equilibrium expressions!

K$_{sp}$ Values for Some Salts at 25°C

Name	Formula	K$_{sp}$
Barium carbonate	$BaCO_3$	2.6×10^{-9}
Barium chromate	$BaCrO_4$	1.2×10^{-10}
Barium sulfate	$BaSO_4$	1.1×10^{-10}
Calcium carbonate	$CaCO_3$	5.0×10^{-9}
Calcium oxalate	CaC_2O_4	2.3×10^{-9}
Calcium sulfate	$CaSO_4$	7.1×10^{-5}
Copper(I) iodide	CuI	1.3×10^{-12}
Copper(II) iodate	$Cu(IO_3)_2$	6.9×10^{-8}
Copper(II) sulfide	CuS	6.0×10^{-37}
Iron(II) hydroxide	$Fe(OH)_2$	4.9×10^{-17}
Iron(II) sulfide	FeS	6.0×10^{-19}
Iron(III) hydroxide	$Fe(OH)_3$	2.6×10^{-39}
Lead(II) bromide	$PbBr_2$	6.6×10^{-6}
Lead(II) chloride	$PbCl_2$	1.2×10^{-5}
Lead(II) iodate	$Pb(IO_3)_2$	3.7×10^{-13}
Lead(II) iodide	PbI_2	8.5×10^{-9}
Lead(II) sulfate	$PbSO_4$	1.8×10^{-8}

Name	Formula	K$_{sp}$
Lead(II) bromide	$PbBr_2$	6.6×10^{-6}
Lead(II) chloride	$PbCl_2$	1.2×10^{-5}
Lead(II) iodate	$Pb(IO_3)_2$	3.7×10^{-13}
Lead(II) iodide	PbI_2	8.5×10^{-9}
Lead(II) sulfate	$PbSO_4$	1.8×10^{-8}
Magnesium carbonate	$MgCO_3$	6.8×10^{-6}
Magnesium hydroxide	$Mg(OH)_2$	5.6×10^{-12}
Silver bromate	$AgBrO_3$	5.3×10^{-5}
Silver bromide	$AgBr$	5.4×10^{-13}
Silver carbonate	Ag_2CO_3	8.5×10^{-12}
Silver chloride	$AgCl$	1.8×10^{-10}
Silver chromate	Ag_2CrO_4	1.1×10^{-12}
Silver iodate	$AgIO_3$	3.2×10^{-8}
Silver iodide	AgI	8.5×10^{-17}
Strontium carbonate	$SrCO_3$	5.6×10^{-10}
Strontium fluoride	SrF_2	4.3×10^{-9}
Strontium sulfate	$SrSO_4$	3.4×10^{-7}
Zinc sulfide	ZnS	2.0×10^{-25}

Solubility and Ksp
Three important definitions:

1) solubility: quantity of a substance that dissolves to form a saturated solution

2) molar solubility: the number of moles of the solute that dissolves to form a liter of saturated solution

3) Ksp (solubility product): the equilibrium constant for the equilibrium between an ionic solid and its saturated solution

Example 16.9 Calculating K_{sp} from Molar Solubility

The molar solubility of Ag_2SO_4 in pure water is 1.2×10^{-5} M. Calculate K_{sp}.

Solution

Begin by writing the reaction by which solid Ag_2SO_4 dissolves into its constituent aqueous ions, then write the corresponding expression for K_{sp}.

$$Ag_2SO_4(s) \rightleftharpoons 2\ Ag^+(aq) + SO_4^{2-}(aq)$$

$$K_{sp} = [Ag^+]^2[SO_4^{2-}]$$

Use an ICE table to define $[Ag^+]$ and $[SO_4^{2-}]$ in terms of S, the amount of Ag_2SO_4 that dissolves.

$$Ag_2SO_4(s) \rightleftharpoons 2\ Ag^+(aq) + SO_4^{2-}(aq)$$

	$[Ag^+]$	$[SO_4^{2-}]$
Initial	0.00	0.00
Change	$+2S$	$+S$
Equil	$2S$	S

Substitute the expressions for $[Ag^+]$ and $[SO_4^{2-}]$ from the previous step into the expression for K_{sp}. Substitute the given value *of the molar solubility for S and calculate K_{sp}.*

$$
\begin{aligned}
K_{sp} &= [Ag^+]^2[SO_4^{2-}] \\
&= (2S)^2 S \\
&= 4S^3 \\
&= 4(1.2 \times 10^{-5})^3 \\
&= 6.9 \times 10^{-15}
\end{aligned}
$$

The **Molar Solubility** is the **molarity** required to **saturate** of fill the solution at any given temperature.

1. **The solubility (s) of $BaCO_3$ is 5.1×10^{-5} M @ 25^0 C. Calculate the solubility product or Ksp.**

$$BaCO_{3(s)} \rightleftharpoons Ba^{2+} + CO_3^{2-}$$

s   s   s
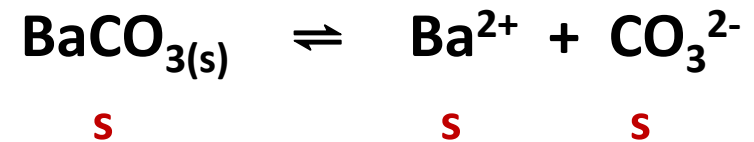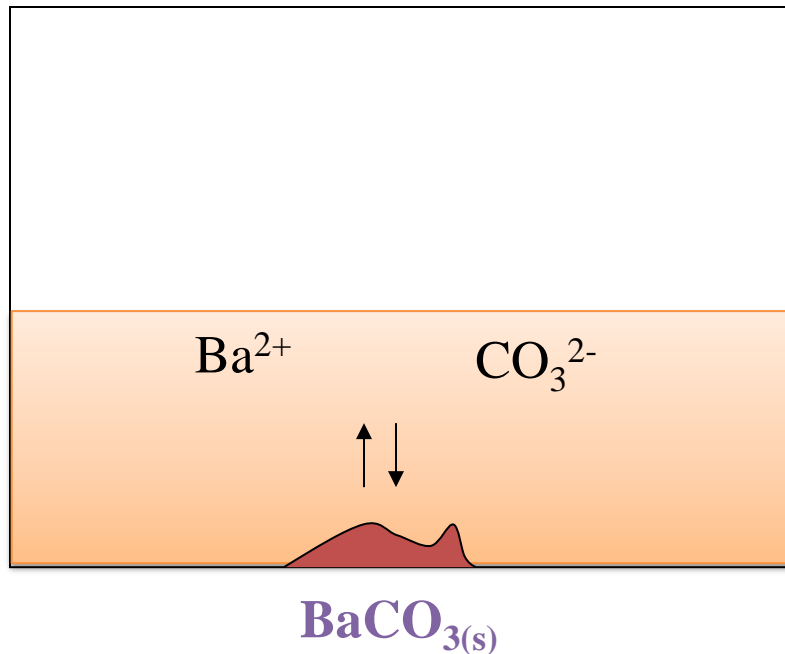
$$Ksp = [Ba^{2+}][CO_3^{2-}]$$

$$Ksp = [s][s]$$

$$Ksp = s^2$$

$$Ksp = (5.1 \times 10^{-5})^2$$

$$Ksp = 2.6 \times 10^{-9}$$

Ba^{2+} CO_3^{2-}

$BaCO_{3(s)}$

Ask for solubility to Ksp

Calculating Molar Solubility

Calculate the molar solubility of Ag_2SO_4 in one liter of water. Ksp = 1.4×10^{-5}

$$Ag_2SO_4 \longleftrightarrow 2Ag^+ + SO_4^{2-}$$

	$2Ag^+$	SO_4^{2-}
Initial	0	0
Change	+2x	+x
Equilb	2x	x

Ksp = $[Ag^+]^2[SO_4^{2-}]$ = $(2x)^2(x)$ = 1.4×10^{-5}

X = 1.5×10^{-2} mol Ag_2SO_4 /L (molar solubility)

EXAMPLE 15.5

Consider the pesticide magnesium arsenate, $Mg_3(AsO_4)_2$. Its solubility is determined experimentally to be 1.6×10^{-3} g/100 g H_2O. What is the K_{sp} for $Mg_3(AsO_4)_2$? (Assume that the density of water is equal to the density of the solution.)

ANALYSIS

Information given:	solubility (1.6×10^{-3} g/100 g H_2O)
Information implied:	density of the solution = density of water MM $Mg_3(AsO_4)_2$
Asked for:	K_{sp}

STRATEGY

1. Assume 1.6×10^{-3} g/100 g $H_2O = 1.6 \times 10^{-3}$ g/100 mL of solution. Convert this solubility data to molar solubility (mol/L). Use the molar mass of $Mg_3(AsO_4)_2$.

2. Write a net ionic equation to represent dissolving $Mg_3(AsO_4)_2$.

3. Use stoichiometric ratios to relate $[Mg_3(AsO_4)_2]$ to $[Mg^{2+}]$ and $[AsO_4^{3-}]$.

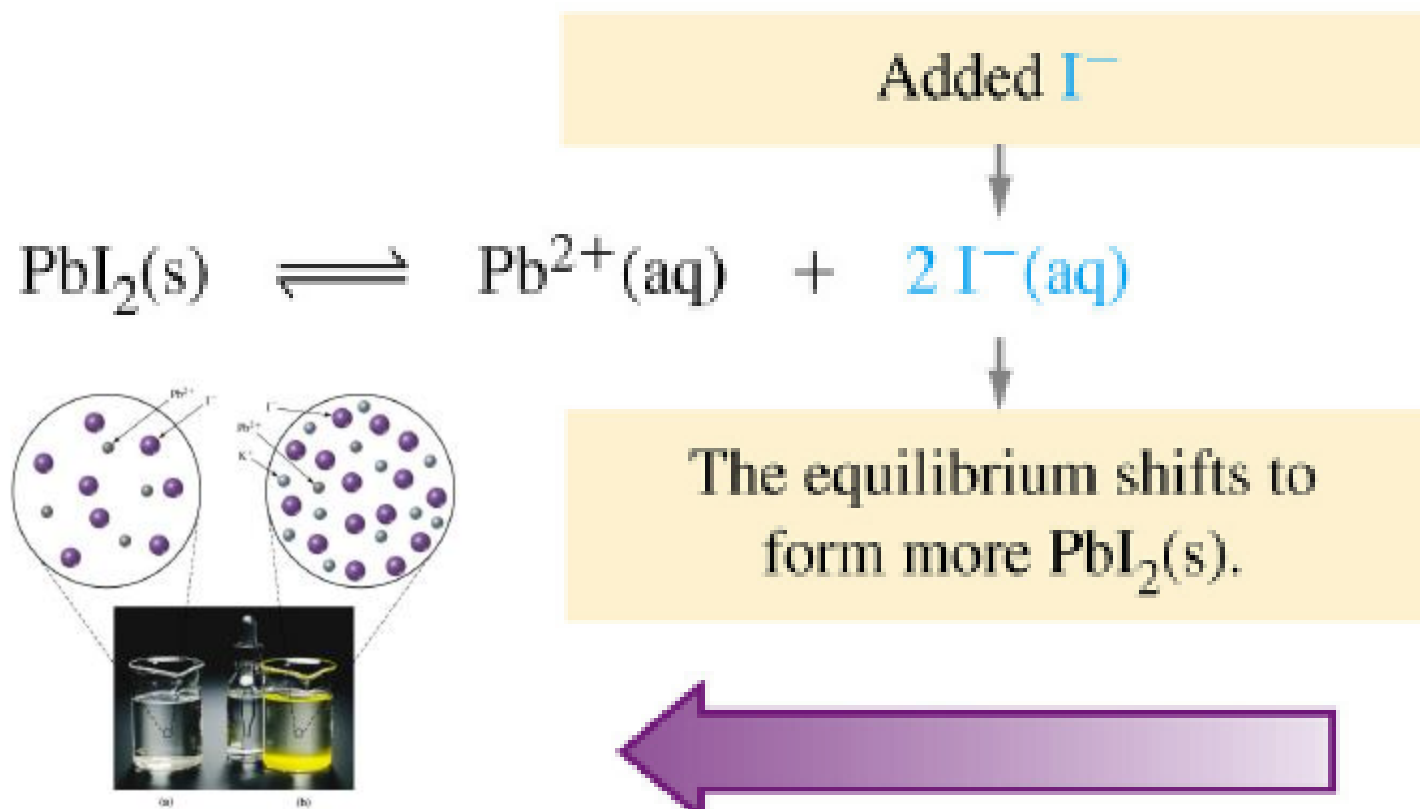4. Substitute into the K_{sp} expression and find K_{sp}.

SOLUTION

1. Molar solubility	$\dfrac{1.6 \times 10^{-3} \text{ g}}{0.100 \text{ L}} \times \dfrac{1 \text{ mol}}{350.7 \text{ g}} = 4.6 \times 10^{-5} M$
2. Reaction	$Mg_3(AsO_4)_2(s) \rightleftharpoons 3Mg^{2+}(aq) + 2AsO_4^{3-}(aq)$
3. Stoichiometric ratios	1 mol $Mg_3(AsO_4)_2$ dissolved $\longrightarrow$ 3 mol Mg^{2+}; $[Mg^{2+}] = 3(4.6 \times 10^{-5}) = 1.4 \times 10^{-4}$ 1 mol $Mg_3(AsO_4)_2$ dissolved $\longrightarrow$ 2 mol AsO_4^{3-}; $[AsO_4^{3-}] = 2(4.6 \times 10^{-5}) = 9.2 \times 10^{-5}$
4. K_{sp}	$K_{sp} = [Mg^{2+}]^3[AsO_4^{3-}]^2 = (1.4 \times 10^{-4})^3(9.2 \times 10^{-5})^2 = 2.3 \times 10^{-20}$

The Common-Ion Effect and Le Châteliers Principle

Added I⁻

$$PbI_2(s) \rightleftharpoons Pb^{2+}(aq) + 2\,I^-(aq)$$

The equilibrium shifts to form more $PbI_2(s)$.

Common ion effect: "The solubility of one salt is reduced by the presence of another having a common ion"

Example 16.10 **Calculating Molar Solubility in the Presence of a Common Ion**

What is the Molar solubility of PbI_2 **if the** concentration of NaI is 0.10? $Ksp = 7.9 \times 10^{-9}$

So $[I-] = 0.10$ M

	$PbI_2(s)$	$Pb^{2+}(aq)$	$I^-(aq)$
R		1	2
I		0	0.10
C		x	2x
E		x	0.10 + 2x

$Ksp = [Pb^{2+}(aq)] [I^-(aq)]^2$
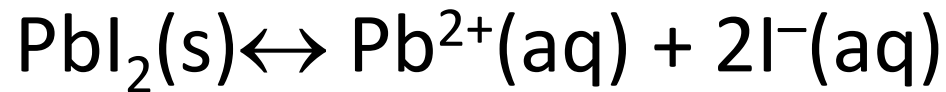
$Ksp = [x] [0.10 + 2x]^2 = 7.9 \times 10^{-9}$

x is small, thus we can ignore 2x in 0.10 + 2x

$Ksp = [x] [0.10]^2 = 7.9 \times 10^{-9}$, $x = 7.9 \times 10^{-7}$ M

Common ion Effect

Common ion: "The ion in a mixture of ionic substances that is common to the formulas of at least two." (PbI_2 + NaI)

$$PbI_2(s) \leftrightarrow Pb^{2+}(aq) + 2I^-(aq)$$

Ksp of PbI_2 = 7.9 x 10^{-9}, so the molar solubility is

$$7.9 \times 10^{-9} = (x)(2x)^2 = 4x^3$$

$$X = 1.3 \times 10^{-3}$$

Thus the solubility of the PbI_2 is reduced by the presence of the NaI.

Which is much greater than 7.9 x 10^{-7} when 0.10 M NaI is in solution (solubility becomes = 7.9 x 10^{-7} M)

pH and Solubility

- The presence of a common ion **decreases** the solubility.
- Insoluble bases dissolve in acidic solutions
- Insoluble acids dissolve in basic solutions

$$Mg(OH)_2\ (s) \rightleftharpoons Mg^{2+}\ (aq) + 2OH^-\ (aq)$$

$K_{sp} = [Mg^{2+}][OH^-]^2 = 1.2 \times 10^{-11}$

$K_{sp} = (s)(2s)^2 = 4s^3$

$4s^3 = 1.2 \times 10^{-11}$

$s = 1.4 \times 10^{-4}\ M$

$[OH^-] = 2s = 2.8 \times 10^{-4}\ M$

$pOH = 3.55\quad pH = 10.45$

At pH less than 10.45

Lower $[OH^-]$

$OH^-\ (aq) + H^+\ (aq) \longrightarrow H_2O\ (l)$

Increase solubility of $Mg(OH)_2$

At pH greater than 10.45

Raise $[OH^-]$

Decrease solubility of $Mg(OH)_2$

Determining Whether Precipitation Occurs

- Q_{sp} is the ion product reaction quotient and is based on initial conditions of the reaction.

- Q_{sp} can then be compared to K_{sp}.

- To predict if a precipitation occurs:

  - Precipitation *should* occur if $Q_{sp} > K_{sp}$.

  - Precipitation *cannot* occur if $Q_{sp} < K_{sp}$.

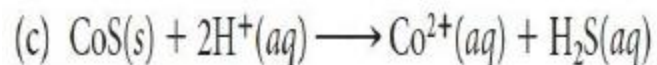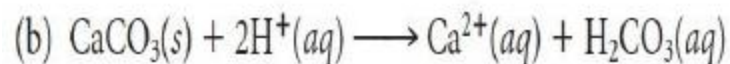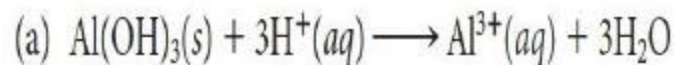 - A solution is *just saturated* if $Q_{sp} = K_{sp}$.

  Sometimes the concentrations of the ions are not high enough to produce a precipitate!

EXAMPLE 15.10

Write balanced equations to explain why each of the following precipitates dissolves in strong acid.

(a) $Al(OH)_3$ (b) $CaCO_3$ (c) CoS

SOLUTION

(a) $Al(OH)_3(s) + 3H^+(aq) \longrightarrow Al^{3+}(aq) + 3H_2O$

(b) $CaCO_3(s) + 2H^+(aq) \longrightarrow Ca^{2+}(aq) + H_2CO_3(aq)$

(c) $CoS(s) + 2H^+(aq) \longrightarrow Co^{2+}(aq) + H_2S(aq)$

Group 1 Cation Precipitates – lab exp

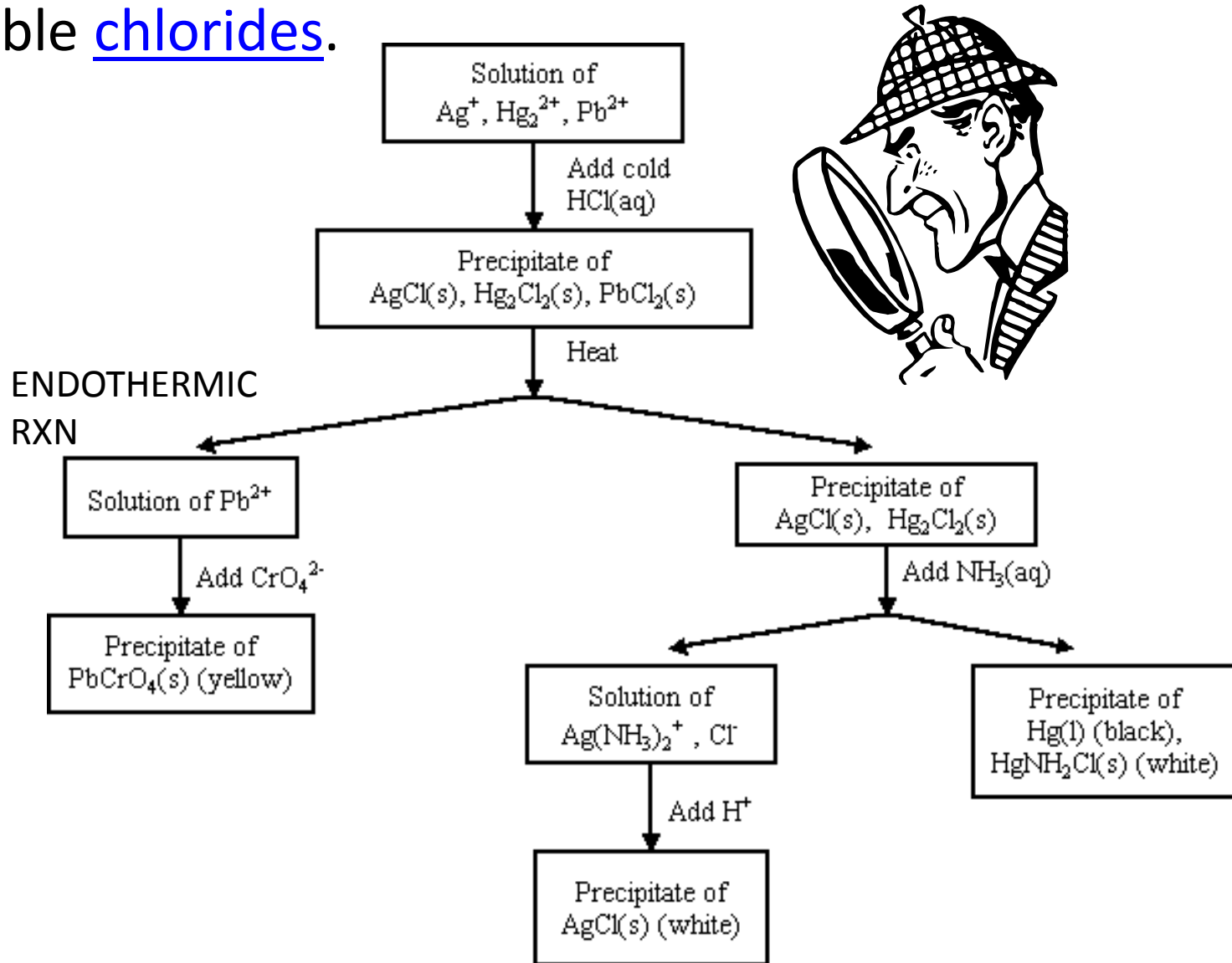*1st analytical group of cations* consists of ions that form insoluble [chlorides](#).

Solution of
Ag^+, Hg_2^{2+}, Pb^{2+}

Add cold HCl(aq)

Precipitate of
AgCl(s), Hg_2Cl_2(s), $PbCl_2$(s)

Heat

ENDOTHERMIC RXN

Solution of Pb^{2+}

Add CrO_4^{2-}

Precipitate of
$PbCrO_4$(s) (yellow)

Precipitate of
AgCl(s), Hg_2Cl_2(s)

Add NH_3(aq)

Solution of
$Ag(NH_3)_2^+$, Cl^-

Add H^+

Precipitate of
AgCl(s) (white)

Precipitate of
Hg(l) (black),
$HgNH_2Cl$(s) (white)

TABLE 16.5 **Separation of Cations into Groups According to Their Precipitation Reactions with Various Reagents**

Group	Cation	Precipitating Reagents	Insoluble Compound	K_{sp}
1	Ag^+	HCl	AgCl	1.6×10^{-10}
	Hg_2^{2+}		Hg_2Cl_2	3.5×10^{-18}
	Pb^{2+}	↓	$PbCl_2$	2.4×10^{-4}
2	Bi^{3+}	H_2S	Bi_2S_3	1.6×10^{-72}
	Cd^{2+}	in acidic	CdS	8.0×10^{-28}
	Cu^{2+}	solutions	CuS	6.0×10^{-37}
	Hg^{2+}		HgS	4.0×10^{-54}
	Sn^{2+}	↓	SnS	1.0×10^{-26}
3	Al^{3+}	H_2S	$Al(OH)_3$	1.8×10^{-33}
	Co^{2+}	in basic	CoS	4.0×10^{-21}
	Cr^{3+}	solutions	$Cr(OH)_3$	3.0×10^{-29}
	Fe^{2+}		FeS	6.0×10^{-19}
	Mn^{2+}		MnS	3.0×10^{-14}
	Ni^{2+}		NiS	1.4×10^{-24}
	Zn^{2+}	↓	ZnS	3.0×10^{-23}
4	Ba^{2+}	Na_2CO_3	$BaCO_3$	8.1×10^{-9}
	Ca^{2+}		$CaCO_3$	8.7×10^{-9}
	Sr^{2+}	↓	$SrCO_3$	1.6×10^{-9}
5	K^+	No precipitating	None	
	Na^+	reagent	None	
	NH_4^+		None	

17.11

Example -Will a Precipitation Occur?

If 1.00 mg of Na_2CrO_4 is added to 225 ml of 0.00015 M $AgNO_3$, will a precipitate form?

$$Ag_2CrO_4 (s) \rightarrow 2Ag^+ + CrO_4^{2-}$$
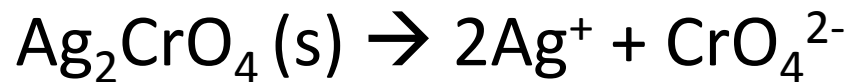
Determine the initial concentration of ions.

$$Ag^+ = 1.5 \times 10^{-4} \text{ M}$$

$CrO_4^{2-} = 1.00 \times 10^{-3}$ g / MM = 6.17×10^{-6} mol CrO_4^{2-}/ .225 L = 2.74×10^{-5} M

Example -Will a Precipitation Occur?

- Compare the initial concentration to the solubility product constant

Initial concentration of ions: $(Ag^+)^2 (CrO_4^{2-})$

$(1.5 \times 10^{-4})^2 (2.74 \times 10^{-5}$ M$)= 6.2 \times 10^{-13}$

Ag_2CrO_4 Ksp $= 1.1 \times 10^{-12}$

- No precipitation will occur because the initial concentration is less than the Ksp.

$$Q < Ksp$$

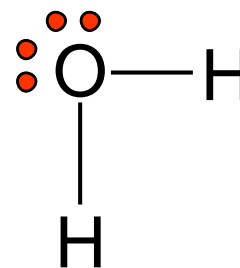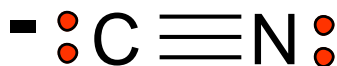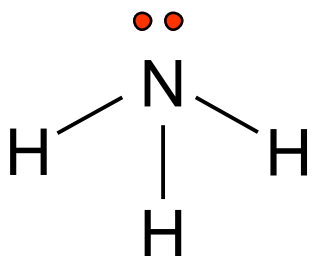# Complex Ions

A *Complex ion* is a charged species composed of:

   1. A metallic cation

   2. *Ligands* – Lewis bases that have a lone electron pair that can form a covalent bond with an empty orbital belonging to the metallic cation

NH_3, CN^-, and H_2O are Common Ligands
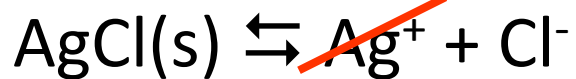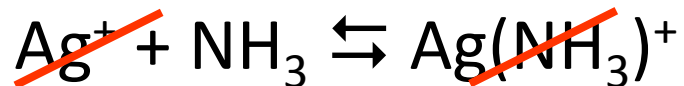
Coordination Number

❑ Coordination number refers to the number of ligands attached to the cation

❑ 2, 4, and 6 are the most common coordination numbers

Coordination number	Example(s)	
2	$Ag(NH_3)_2^+$	
4	$CoCl_4^{2-}$	$Cu(NH_3)_4^{2+}$
6	$Co(H_2O)_6^{2+}$	$Ni(NH_3)_6^{2+}$

Complex Ions and Solubility

$AgCl(s) \leftrightarrows \cancel{Ag^+} + Cl^-$ $K_{sp} = 1.6 \times 10^{-10}$

$\cancel{Ag^+} + NH_3 \leftrightarrows \cancel{Ag(NH_3)^+}$ $K_1 = 2.1 \times 10^3$

$\cancel{Ag(NH_3)^+} NH_3 \leftrightarrows Ag(NH_3)_2^+$ $K_2 = 8.2 \times 10^3$

$AgCl + 2NH_3 \leftrightarrows Ag(NH_3)_2^+ + Cl^-$ $K = K_{sp} \cdot K_1 \cdot K_2$
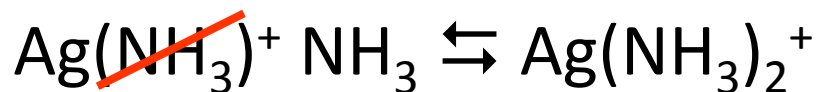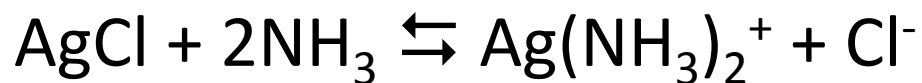
$$K = 2.8 \, x \, 10^{-3} = \frac{[Ag(NH_3)_2^+][Cl^-]}{[NH_3]^2}$$
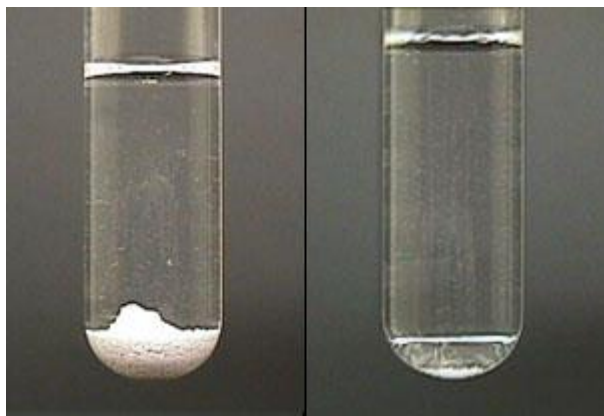
= **formation constant**

Formation Constants

TABLE 16.3 Formation Constants of Selected Complex Ions in Water at 25 °C

Complex Ion	K_f	Complex Ion	K_f
$Ag(CN)_2^-$	1×10^{21}	$Cu(NH_3)_4^{2+}$	1.7×10^{13}
$Ag(NH_3)_2^+$	1.7×10^7	$Fe(CN)_6^{4-}$	1.5×10^{35}
$Ag(S_2O_3)_2^{3-}$	2.8×10^{13}	$Fe(CN)_6^{3-}$	2×10^{43}
AlF_6^{3-}	7×10^{19}	$Hg(CN)_4^{2-}$	1.8×10^{41}
$Al(OH)_4^-$	3×10^{33}	$HgCl_4^{2-}$	1.1×10^{16}
$CdBr_4^{2-}$	5.5×10^3	HgI_4^{2-}	2×10^{30}
CdI_4^{2-}	2×10^6	$Ni(NH_3)_6^{2+}$	2.0×10^8
$Cd(CN)_4^{2-}$	3×10^{18}	$Pb(OH)_3^-$	8×10^{13}
$Co(NH_3)_6^{3+}$	2.3×10^{33}	$Sn(OH)_3^-$	3×10^{25}
$Co(OH)_4^{2-}$	5×10^9	$Zn(CN)_4^{2-}$	2.1×10^{19}
$Co(SCN)_4^{2-}$	1×10^3	$Zn(NH_3)_4^{2+}$	2.8×10^9
$Cr(OH)_4^-$	8.0×10^{29}	$Zn(OH)_4^{2-}$	2×10^{15}
$Cu(CN)_4^{2-}$	1.0×10^{25}		

Formation Constants for Complex Ions

- The very soluble silver complex ion removes Ag+ from the solution and shifts the equilibrium to the right increasing the solubility of AgCl.

$$AgBr + 2NH_3 \longleftrightarrow Ag(NH_3)^{2+} + Br^-$$
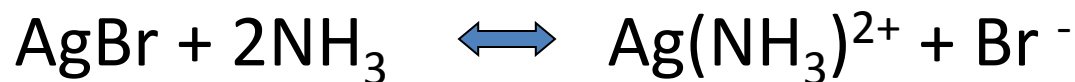
$$K = 8.0 \times 10^{-6} \longleftrightarrow = \frac{[Ag(NH_3)^{2+}][Br^-]}{[NH_3]}$$

$$K = k_{form} \times k_{sp} = (1.6 \times 10^7)(5.0 \times 10^{-13})$$
$$= 8.0 \times 10^{-6}$$

Example

- How many moles of AgBr can dissolve in 1 L of 1.0 M NH_3?

$AgBr + 2NH_3 \longleftrightarrow Ag(NH_3)^{2+} + Br^-$

	1.0	0	0
	-2x	+x	+x
	1.0-2x	x	x

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

X = 2.8×10^{-3}, 2.8×10^{-3} mol of AgBr dissolves in 1L of NH_3

Example 16.15 Complex Ion Equilibria

You mix a 200.0 mL sample of a solution that is 1.5×10^{-3} M in $Cu(NO_3)_2$ with a 250.0 mL sample of a solution that is 0.20 M in NH_3. After the solution reaches equilibrium, what concentration of $Cu^{2+}(aq)$ remains?

Solution

Write the balanced equation for the complex ion equilibrium that occurs and look up the value of K_f in Table 16.3. Since this is an equilibrium problem, you have to create an ICE table, which requires the initial concentrations of Cu^{2+} and NH_3. Calculate those concentrations from the given values.

TABLE 16.3 Formation Constants of Selected Complex Ions in Water at 25 °C

Complex Ion	K_f	Complex Ion	K_f
$Ag(CN)_2^-$	1×10^{21}	$Cu(NH_3)_4^{2+}$	1.7×10^{13}
$Ag(NH_3)_2^+$	1.7×10^7	$Fe(CN)_6^{4-}$	1.5×10^{35}
$Ag(S_2O_3)_2^{3-}$	2.8×10^{13}	$Fe(CN)_6^{3-}$	2×10^{43}
AlF_6^{3-}	7×10^{19}	$Hg(CN)_4^{2-}$	1.8×10^{41}
$Al(OH)_4^-$	3×10^{33}	$HgCl_4^{2-}$	1.1×10^{16}
$CdBr_4^{2-}$	5.5×10^3	HgI_4^{2-}	2×10^{30}
CdI_4^{2-}	2×10^6	$Ni(NH_3)_6^{2+}$	2.0×10^8
$Cd(CN)_4^{2-}$	3×10^{18}	$Pb(OH)_3^-$	8×10^{13}
$Co(NH_3)_6^{3+}$	2.3×10^{33}	$Sn(OH)_3^-$	3×10^{25}
$Co(OH)_4^{2-}$	5×10^9	$Zn(CN)_4^{2-}$	2.1×10^{19}
$Co(SCN)_4^{2-}$	1×10^3	$Zn(NH_3)_4^{2+}$	2.8×10^9
$Cr(OH)_4^-$	8.0×10^{29}	$Zn(OH)_4^{2-}$	2×10^{15}
$Cu(CN)_4^{2-}$	1.0×10^{25}		

Example 16.15 Complex Ion Equilibria

Continued

$$Cu^{2+}(aq) + 4 NH_3(aq) \rightleftharpoons Cu(NH_3)_4^{2+}(aq)$$
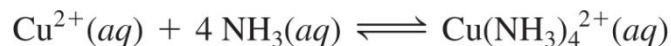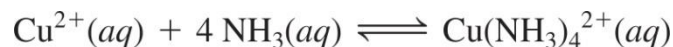
$$K_f = 1.7 \times 10^{13}$$

$$[Cu^{2+}]_{initial} = \frac{0.200 \, L \times \dfrac{1.5 \times 10^{-3} \, mol}{L}}{0.200 \, L + 0.250 \, L} = 6.7 \times 10^{-4} \, M$$

$$[NH_3]_{initial} = \frac{0.250 \, L \times \dfrac{0.20 \, mol}{1 \, L}}{0.200 \, L + 0.250 \, L} = 0.11 \, M$$

Construct an ICE table for the reaction and write down the initial concentrations of each species.

$$Cu^{2+}(aq) + 4 NH_3(aq) \rightleftharpoons Cu(NH_3)_4^{2+}(aq)$$

	$[Cu^{2+}]$	$[NH_3]$	$[Cu(NH_3)_4^{2+}]$
Initial	6.7×10^{-4}	0.11	0.0
Change			
Equil			

Example 16.15 Complex Ion Equilibria

Continued

Since the equilibrium constant is large and the concentration of ammonia is much larger than the concentration of Cu^{2+}, you can assume that the reaction will be driven to the right so that most of the Cu^{2+} is consumed. Unlike previous ICE tables, where you let x represent the change in concentration in going to equilibrium, here you let x represent the small amount of Cu^{2+} that remains when equilibrium is reached.

$$Cu^{2+}(aq) + 4\,NH_3(aq) \rightleftharpoons Cu(NH_3)_4{}^{2+}(aq)$$
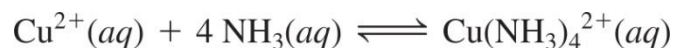
	$[Cu^{2+}]$	$[NH_3]$	$[Cu(NH_3)_4{}^{2+}]$
Initial	6.7×10^{-4}	0.11	0.0
Change	$\approx(-6.7 \times 10^{-4})$	$\approx 4(-6.7 \times 10^{-4})$	$\approx(+6.7 \times 10^{-4})$
Equil	x	0.11	6.7×10^{-4}

Substitute the expressions for the equilibrium concentrations into the expression for K_f and solve for x.

$$K_f = \frac{[Cu(NH_3)_4{}^{2+}]}{[Cu^{2+}][NH_3]^4}$$

$$= \frac{6.7 \times 10^{-4}}{x(0.11)^4}$$

$$x = \frac{6.7 \times 10^{-4}}{K_f(0.11)^4}$$

$$= \frac{6.7 \times 10^{-4}}{1.7 \times 10^{13}(0.11)^4}$$

$$= 2.7 \times 10^{-13}$$