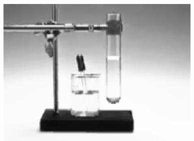
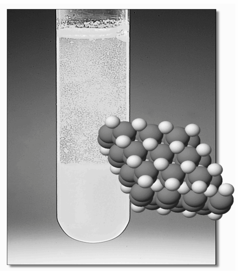
PRECIPITATION REACTIONS
Chapter 15





Chemistry 223
Professor Michael Russell

MAR *Last update: 4/29/24*

Flashback - Aqueous Salts!

SOLUBLE COMPOUNDS	EXCEPTIONS
Almost all salts of Na^+, K^+, NH_4^+	
Salts of nitrate, NO_3^-; chlorate, ClO_3^-; perchlorate, ClO_4^-; acetate, $CH_3CO_2^-$	
Almost all salts of Cl^-, Br^-, I^-	Halides of Ag^+, Hg_2^{2+}, Pb^{2+}
Compounds containing F^-	Fluorides of Mg^{2+}, Ca^{2+}, Sr^{2+}, Ba^{2+}, Pb^{2+}
Salts of sulfate, SO_4^{2-}	Sulfates of Ca^{2+}, Sr^{2+}, Ba^{2+}, Pb^{2+}

INSOLUBLE COMPOUNDS	EXCEPTIONS
Most salts of carbonate, CO_3^{2-}; phosphate, PO_4^{3-}; oxalate, $C_2O_4^{2-}$; chromate, CrO_4^{2-}	Salts of NH_4^+ and the alkali metal cations
Most metal sulfides, S^{2-}	
Most metal hydroxides and oxides	

If one ion from the "Soluble Compd." list is present in a compound, the compound is water soluble.

$Ba(NO_3)_2(aq)$?
soluble

$BaCl_2(aq)$?
soluble

$BaSO_4(aq)$?
insoluble, $BaSO_4(s)$

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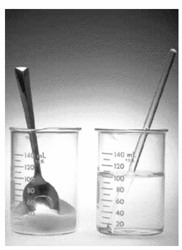
Solubility of a Salt

Consider NaCl dissolving in water:

$NaCl(s) \rightleftharpoons Na^+(aq) + Cl^-(aq)$

Solubility **of NaCl exceeded when solid precipitate does not dissolve**



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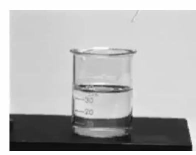
Analysis of Silver Group

Ag^+ Pb^{2+} Hg_2^{2+}
⇩
AgCl $PbCl_2$ Hg_2Cl_2

All salts formed in this experiment are said to be INSOLUBLE

They form when mixing moderately concentrated solutions of the metal ion with chloride ions.



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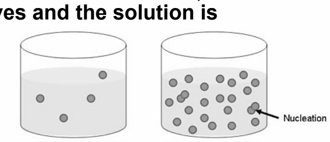
Analysis of Silver Group

Ag^+ Pb^{2+} Hg_2^{2+}
⇩
AgCl $PbCl_2$ Hg_2Cl_2

Although all salts formed in this experiment are said to be insoluble, they do dissolve to some SLIGHT extent.

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

When equilibrium has been established, no more AgCl dissolves and the solution is SATURATED.



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Analysis of Silver Group

Ag^+ Pb^{2+} Hg_2^{2+}
⇩
AgCl $PbCl_2$ Hg_2Cl_2

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

When solution is SATURATED, expt. shows that $[Ag^+] = 1.67 \times 10^{-5}$ M.

This is equivalent to the **SOLUBILITY** of AgCl.

What is $[Cl^-]$?

This is also equivalent to the AgCl solubility, so **$[Cl^-] = 1.67 \times 10^{-5}$ M**

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Analysis of Silver Group

Ag^{+} Pb^{2+} Hg_2^{2+}

⇩

AgCl $PbCl_2$ Hg_2Cl_2

$AgCl(s) \rightleftharpoons Ag^{+}(aq) + Cl^{-}(aq)$

Saturated solution has

$[Ag^{+}] = [Cl^{-}] = 1.67 \times 10^{-5}$ M

Use this to calculate K_c

$K_c = [Ag^{+}][Cl^{-}]$

$= (1.67 \times 10^{-5})(1.67 \times 10^{-5})$

$= 2.79 \times 10^{-10}$

This type of K_c is the product of "solubilities", we call it

K_{sp} = solubility product constant

See: Solubility Guide

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Some Common, Slightly Soluble Compounds and Their K_{sp} Values*

Formula	Name	K_{sp} (25 °C)	Common Names/Uses
$CaCO_3$	Calcium carbonate	3.4×10^{-9}	Calcite, Iceland spar
$MnCO_3$	Manganese(II) carbonate	2.3×10^{-11}	Rhodochrosite (forms rose-colored crystals)
$FeCO_3$	Iron(II) carbonate	3.1×10^{-11}	Siderite
CaF_2	Calcium fluoride	5.3×10^{-11}	Fluorite (source of HF and other inorganic fluorides)
AgCl	Silver chloride	1.8×10^{-10}	Chlorargyrite
AgBr	Silver bromide	5.4×10^{-13}	Used in photographic film
$CaSO_4$	Calcium sulfate	4.9×10^{-5}	Hydrated form is commonly called gypsum
$BaSO_4$	Barium sulfate	1.1×10^{-10}	Barite (used in "drilling mud" and as a component of paints)
$SrSO_4$	Strontium sulfate	3.4×10^{-7}	Celestite
$Ca(OH)_2$	Calcium hydroxide	5.5×10^{-5}	Slaked lime

*The values reported in this table were taken from *Lange's Handbook of Chemistry*, 15th Edition, McGraw Hill Publishers, New York, NY (1999). Additional K_{sp} values are given in Appendix J.

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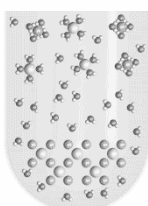
Lead(II) Chloride

$PbCl_2(s) \rightleftharpoons Pb^{2+}(aq) + 2\ Cl^{-}(aq)$

$K_{sp} = 1.9 \times 10^{-5}$



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Solubility of Lead(II) Iodide

Consider PbI_2 dissolving in water

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

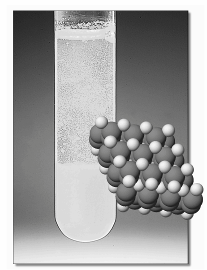
Calculate K_{sp} if solubility = 0.00130 M

Solution

Solubility refers to how many moles of *solid dissolve per L*

1. Solubility = $[Pb^{2+}]$
   $= 1.30 \times 10^{-3}$ M

$[I^{-}] = 2 \times [Pb^{2+}] = 2.60 \times 10^{-3}$ M



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

Calculate K_{sp} if solubility = 0.00130 M

Solution

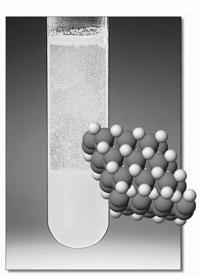
1. Solubility = $[Pb^{2+}]$
   $= 1.30 \times 10^{-3}$ M

$[I^{-}] = 2 \times [Pb^{2+}] = 2.60 \times 10^{-3}$ M

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

$= [Pb^{2+}]\{2 \cdot [Pb^{2+}]\}^2$

$= 4[Pb^{2+}]^3$



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Solubility of Lead(II) Iodide

Consider PbI_2 dissolving in water

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

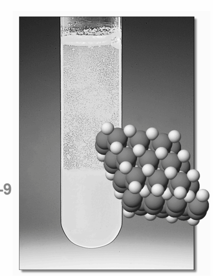
Calculate K_{sp} if solubility = 0.00130 M

Solution

2. $K_{sp} = 4[Pb^{2+}]^3 = 4(\text{solubility})^3$

$K_{sp} = 4(1.30 \times 10^{-3})^3 = 8.79 \times 10^{-9}$

Notice that solubility of PbI_2 (x) and K_{sp} related here by: $K_{sp} = 4x^3$



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Solubility and K_{sp} Relations

# cations	*# anions*	*K_{sp} and solubility (x)*	*Examples*
1	1	$K_{sp} = x^2$ $x = (K_{sp})^{1/2}$	NaCl, SrO, $KClO_3$
1	2	$K_{sp} = 4x^3$ $x = (K_{sp}/4)^{1/3}$	PbI_2, $Mg(OH)_2$
2	1	$K_{sp} = 4x^3$ $x = (K_{sp}/4)^{1/3}$	Na_2O, $(NH_4)_2SO_3$
3	1	$K_{sp} = 27x^4$ $x = (K_{sp}/27)^{1/4}$	Li_3P, $(NH_4)_3PO_4$
1	3	$K_{sp} = 27x^4$ $x = (K_{sp}/27)^{1/4}$	$AlBr_3$, $Cr(NO_3)_3$
2	3	$K_{sp} = 108x^5$ $x = (K_{sp}/108)^{1/5}$	Fe_2O_3, $Al_2(SO_4)_3$
3	2	$K_{sp} = 108x^5$ $x = (K_{sp}/108)^{1/5}$	Ti_3As_2, $Mg_3(PO_4)_2$

See: Solubility Guide

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Solubility and K_{sp} Relations

Example: **What is the solubility of copper(II) phosphate if $K_{sp} = 1.4*10^{-37}$?**

Answer: Formula = $Cu_3(PO_4)_2$

3 cations & 2 anions, so $K_{sp} = 108x^5$

$x = (1.4*10^{-37}/108)^{(1/5)}$ = **$1.7*10^{-8}$ M**

Example: **What is K_{sp} for magnesium carbonate if the solubility at 25 ˚C is $2.6*10^{-3}$ M?**

Answer: Formula = $MgCO_3$,

1 cation & 1 anion, so $K_{sp} = x^2$

$K_{sp} = (2.6*10^{-3})^2$ = **$6.8*10^{-6}$**

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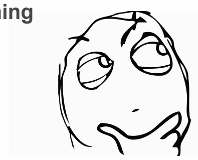
Precipitating an Insoluble Salt

$Hg_2Cl_2(s) \rightleftharpoons Hg_2^{2+}(aq) + 2\ Cl^-(aq)$

$K_{sp} = 1.1 \times 10^{-18} = [Hg_2^{2+}]\,[Cl^-]^2$

If $[Hg_2^{2+}]$ = 0.010 M, what $[Cl^-]$ is req'd to just begin the precipitation of Hg_2Cl_2?

That is, what is the maximum $[Cl^-]$ that can be in solution with 0.010 M Hg_2^{2+} without forming Hg_2Cl_2?



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Precipitating an Insoluble Salt

$Hg_2Cl_2(s) \rightleftharpoons Hg_2^{2+}(aq) + 2\ Cl^-(aq)$

$K_{sp} = 1.1 \times 10^{-18} = [Hg_2^{2+}]\,[Cl^-]^2$

Solution

$[Cl^-]$ that can exist when $[Hg_2^{2+}]$ = 0.010 M:

$$[Cl^-] = \sqrt{\frac{K_{sp}}{0.010}} = 1.0 \times 10^{-8}\ M$$

If this conc. of Cl^- is just exceeded, Hg_2Cl_2 begins to precipitate.

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Precipitating an Insoluble Salt

$Hg_2Cl_2(s) \rightleftharpoons Hg_2^{2+}(aq) + 2\ Cl^-(aq)$

$K_{sp} = 1.1 \times 10^{-18}$

Now raise $[Cl^-]$ to 1.0 M when $[Hg_2^{2+}]$ = 0.010 M. What is the value of $[Hg_2^{2+}]$ at this point?

Solution

$[Hg_2^{2+}] = K_{sp} / [Cl^-]^2$

$= K_{sp} / (1.0)^2 = 1.1 \times 10^{-18}$ M

The concentration of Hg_2^{2+} has been reduced by 10^{16}!

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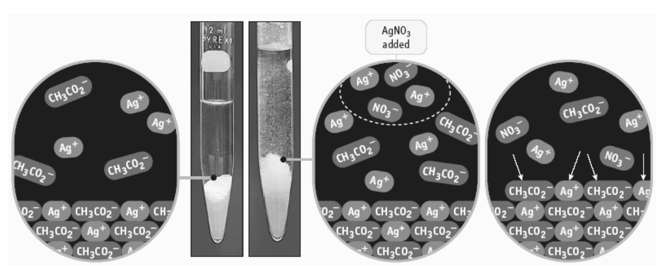
The Common Ion Effect

Adding an ion "common" to an equilibrium causes the equilibrium to shift back to reactant.



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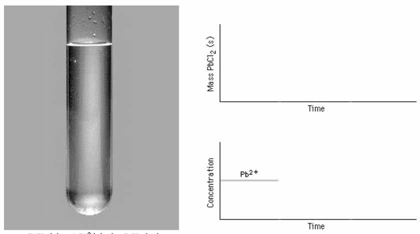
Common Ion Effect

Adding an Ion "Common" to an Equilibrium



$PbCl_2(s) \rightleftharpoons Pb^{2+}(aq) + 2\,Cl^-(aq)$

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The Common Ion Effect

Calculate the solubility of $BaSO_4$ in (a) pure water and (b) in 0.010 M $Ba(NO_3)_2$.

K_{sp} for $BaSO_4$ = 1.1×10^{-10} = $[Ba^{2+}]\,[SO_4^{2-}]$

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

Solution: (part a)

Solubility in pure water = $[Ba^{2+}] = [SO_4^{2-}] = x$

$K_{sp} = [Ba^{2+}]\,[SO_4^{2-}] = x^2$

$x = (K_{sp})^{1/2} = 1.0 \times 10^{-5}$ M

Note 1:1 ratio of cation to anion: $K_{sp} = x^2$

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The Common Ion Effect

Calculate the solubility of $BaSO_4$ in (a) pure water and (b) in 0.010 M $Ba(NO_3)_2$.

K_{sp} for $BaSO_4$ = 1.1×10^{-10} = $[Ba^{2+}]\,[SO_4^{2-}]$

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

Solution: (part b)

So... **Solubility in pure water = 1.0×10^{-5} mol/L.**

Now **dissolve $BaSO_4$ in water already containing 0.010 M Ba^{2+}.**

Which way will the "common ion" shift the equilibrium? ___ Will solubility of $BaSO_4$ be less than or greater than in pure water?___

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The Common Ion Effect

Calculate the solubility of $BaSO_4$ in (a) pure water and (b) in 0.010 M $Ba(NO_3)_2$.

K_{sp} for $BaSO_4$ = 1.1×10^{-10} = $[Ba^{2+}]\,[SO_4^{2-}]$

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

Solution: (part b)

	$[Ba^{2+}]$	$[SO_4^{2-}]$
initial		
change		
equilib.		

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The Common Ion Effect

Calculate the solubility of $BaSO_4$ in (a) pure water and (b) in 0.010 M $Ba(NO_3)_2$.

K_{sp} for $BaSO_4$ = 1.1×10^{-10} = $[Ba^{2+}]\,[SO_4^{2-}]$

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

Solution: (part b)

$K_{sp} = [Ba^{2+}]\,[SO_4^{2-}] = (0.010 + y)\,(y)$

Because $y < 1.0 \times 10^{-5}$ M (= x, the solubility in pure water), this means 0.010 + y is about equal to 0.010. Therefore,

$K_{sp} = 1.1 \times 10^{-10} = (0.010)(y)$

$y = 1.1 \times 10^{-8}$ M = solubility *in presence of added Ba^{2+} ion.*

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The Common Ion Effect

Calculate the solubility of $BaSO_4$ in (a) pure water and (b) in 0.010 M $Ba(NO_3)_2$.

K_{sp} for $BaSO_4$ = 1.1×10^{-10} = $[Ba^{2+}]\,[SO_4^{2-}]$

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

Solution:

Solubility in pure water = x = 1.0×10^{-5} M

Solubility in presence of added Ba^{2+}
= 1.1×10^{-8} M

Le Chatelier's Principle is followed!

See: Solubility Guide

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DISTRACTIONS!!!

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Separating Metal Ions
Cu^{2+}, Ag^{+}, Pb^{2+}

	K_{sp} Values
AgCl	1.8×10^{-10}
$PbCl_2$	1.7×10^{-5}
$PbCrO_4$	1.8×10^{-14}

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Separating Salts by Differences in K_{sp}

A solution contains 0.020 M Ag^+ and 0.020 M Pb^{2+}. Add CrO_4^{2-} to precipitate red Ag_2CrO_4 and yellow $PbCrO_4$. Which precipitates first?

K_{sp} for $Ag_2CrO_4 = 9.0 \times 10^{-12} = [Ag^+]^2 [CrO_4^{2-}]$

K_{sp} for $PbCrO_4 = 1.8 \times 10^{-14} = [Pb^{2+}] [CrO_4^{2-}]$

Solution

The substance whose K_{sp} is first exceeded precipitates first.

The ion requiring the lesser amount of CrO_4^{2-} ppts. first.

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Separating Salts by Differences in K_{sp}

A solution contains 0.020 M Ag^+ and 0.020 M Pb^{2+}. Add CrO_4^{2-} to precipitate red Ag_2CrO_4 and yellow $PbCrO_4$. Which precipitates first?

K_{sp} for $Ag_2CrO_4 = 9.0 \times 10^{-12} = [Ag^+]^2 [CrO_4^{2-}]$

K_{sp} for $PbCrO_4 = 1.8 \times 10^{-14} = [Pb^{2+}] [CrO_4^{2-}]$

Solution - Calculate $[CrO_4^{2-}]$ required by each ion

$[CrO_4^{2-}]$ to ppt. $Ag_2CrO_4 = K_{sp} / [Ag^+]^2$

$= 9.0 \times 10^{-12} / (0.020)^2 = 2.3 \times 10^{-8}$ M

$[CrO_4^{2-}]$ to ppt. $PbCrO_4 = K_{sp} / [Pb^{2+}]$

$= 1.8 \times 10^{-14} / 0.020 = 9.0 \times 10^{-13}$ M

$PbCrO_4$ precipitates first.

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Separating Salts by Differences in K_{sp}

A solution contains 0.020 M Ag^+ and 0.020 M Pb^{2+}. Add CrO_4^{2-} to precipitate red Ag_2CrO_4 and yellow $PbCrO_4$. $PbCrO_4$ ppts. first.

K_{sp} $(Ag_2CrO_4) = 9.0 \times 10^{-12} = [Ag^+]^2 [CrO_4^{2-}]$

K_{sp} $(PbCrO_4) = 1.8 \times 10^{-14} = [Pb^{2+}] [CrO_4^{2-}]$

How much Pb^{2+} remains in solution when Ag^+ begins to precipitate (at 2.3×10^{-8} M)?

Solution

We know that $[CrO_4^{2-}] = 2.3 \times 10^{-8}$ M to begin to precipitate Ag_2CrO_4.

What is the Pb^{2+} conc. at this point?

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Separating Salts by Differences in K_{sp}

A solution contains 0.020 M Ag^+ and 0.020 M Pb^{2+}. Add CrO_4^{2-} to precipitate red Ag_2CrO_4 and yellow $PbCrO_4$.

K_{sp} $(Ag_2CrO_4) = 9.0 \times 10^{-12} = [Ag^+]^2 [CrO_4^{2-}]$

K_{sp} $(PbCrO_4) = 1.8 \times 10^{-14} = [Pb^{2+}] [CrO_4^{2-}]$

How much Pb^{2+} remains in solution when Ag^+ begins to precipitate (at 2.3×10^{-8} M)?

Solution

$[Pb^{2+}] = K_{sp} / [CrO_4^{2-}] = 1.8 \times 10^{-14} / 2.3 \times 10^{-8}$ M

$= 7.8 \times 10^{-7}$ M

Lead ion has dropped from 0.020 M to $< 10^{-6}$ M

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Formation Constants

Complex Ions are systems with Lewis bases connected around the (Lewis) acidic metal center.

Examples: **$Zn(NH_3)_4^{2+}$, $Ag(CN)_2^{-1}$**

Can write a Formation Constant, K_f

$Ag^+(aq) + 2\ CN^{-1}(aq) \rightleftharpoons Ag(CN)_2^{-1}(aq)$, *and*

$$K_f = \frac{[Ag(CN)_2^{-1}]}{[Ag^+][CN^{-1}]^2} = 5.6 * 10^{18}$$

K_f values usually quite large (product-favored) and product is *always* the complex ion

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Formation Constants (K_f) at 25 °C

Complex Ion	K_f
$Ag(CN)_2^-$	3.0×10^{20}
$Ag(NH_3)_2^+$	1.7×10^{7}
$Ag(S_2O_3)_2^{3-}$	4.7×10^{13}
AlF_6^{3-}	4×10^{19}
$Al(OH)_4^-$	3×10^{33}
$Be(OH)_4^{2-}$	4×10^{18}
CdI_4^{2-}	1×10^{6}
$Co(OH)_4^{2-}$	5×10^{9}
$Cr(OH)_4^-$	8.0×10^{29}
$Cu(NH_3)_4^{2+}$	5.6×10^{11}
$Fe(CN)_6^{4-}$	3×10^{35}
$Fe(CN)_6^{3-}$	4.0×10^{43}
$Hg(CN)_4^{2-}$	9.3×10^{38}
$Ni(NH_3)_6^{2+}$	2.0×10^{8}
$Pb(OH)_3^-$	8×10^{13}
$Sn(OH)_3^-$	3×10^{25}
$Zn(CN)_4^{2-}$	4.2×10^{19}
$Zn(NH_3)_4^{2+}$	7.8×10^{8}
$Zn(OH)_4^{2-}$	3×10^{15}

Example:

$Ag^+(aq) + 2\ CN^{-1}(aq) \rightleftharpoons Ag(CN)_2^{-1}(aq)$

- **ions are reactants**
- **complex ion is product**
- **usually written as net ionic reactions**

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Formation Constants

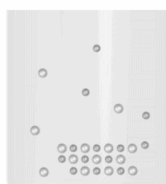
Complex Ions can be helpful when dissolving solids. *Ex:* **$AgCl(s)$ and $Ag(NH_3)_2^+(aq)$**

$AgCl(s) \rightleftharpoons Ag^+(aq) + Cl^-(aq)$ $\quad K_{sp}$

$Ag^+(aq) + 2\ NH_3(aq) \rightleftharpoons Ag(NH_3)_2^+(aq)$ $\quad K_f$

$AgCl_{(s)} + 2\ NH_3 \rightleftharpoons Ag(NH_3)_2^+ + Cl^-$

$K_{net} = K_{sp} * K_f$



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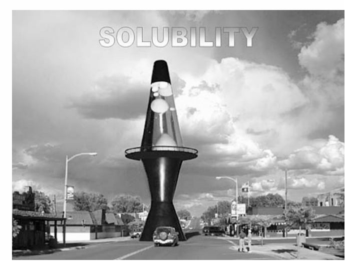
End of Chapter 15

See:

- *Chapter Fifteen Study Guide*
- *Chapter Fifteen Concept Guide*
- *Types of Equilibrium Constants*
- *Solubility Guide*
- *Important Equations (following this slide)*
- *End of Chapter Problems (following this slide)*



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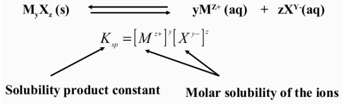
Important Equations, Constants, and Handouts from this Chapter:



- *know how to* **predict solubility** *using* **CH 221 solubility guide**

$Ag^+(aq) + 2\ CN^{-1}(aq) \rightleftharpoons Ag(CN)_2^{-1}(aq)$

$$K_f = \frac{[Ag(CN)_2^{-1}]}{[Ag^+][CN^{-1}]^2} = 5.6 * 10^{18}$$

Solubility: **Common ion effect, separating salts by differences in solubility**

Handouts:

- *Types of Equilibrium Constants*
- *Solubility Guide*

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End of Chapter Problems: ***Test Yourself***

1. Predict whether each of the following is insoluble or soluble in water: $(NH_4)_2CO_3$, $ZnSO_4$, NiS, $BaSO_4$
2. When 1.55 g of solid thallium(I) bromide is added to 1.00 L of water, the salt dissolves to a small extent: $TlBr(s) \rightleftharpoons Tl^+(aq) + Br^{-1}(aq)$ The thallium(I) and bromide ions in equilibrium with TlBr each have a concentration of 1.9×10^{-3} M. What is the value of K_{sp} for TlBr?
3. You add 0.979 g of $Pb(OH)_2$ to 1.00 L of pure water at 25 °C. The pH is 9.15. Estimate the value of K_{sp} for $Pb(OH)_2$.
4. Estimate the solubility of calcium fluoride, CaF_2, (a) in moles per liter and (b) in grams per liter of pure water. **$CaF_2(s) \rightleftharpoons Ca^{2+}(aq) + 2\ F^{-1}(aq)$** $K_{sp} = 5.3 \times 10^{-11}$
5. The K_{sp} value for radium sulfate, $RaSO_4$, is 3.7×10^{-11}. If 0.25 mg of radium sulfate is placed in 1.00×10^2 mL of water, does all of it dissolve? If not, how much dissolves? **$RaSO_4(s) \rightleftharpoons Ra^{2+}(aq) + SO_4^{-2}(aq)$**
6. Which compound is more soluble: $PbCl_2$ ($K_{sp} = 1.7 \times 10^{-5}$) or $PbBr_2$ ($K_{sp} = 6.6 \times 10^{-6}$)?

MAR

End of Chapter Problems: ***Answers***

1. $(NH_4)_2CO_3$ & $ZnSO_4$ (soluble), NiS & $BaSO_4$ (insoluble)
2. $K_{sp} = 3.6 \times 10^{-6}$
3. $K_{sp} = 1.4 \times 10^{-15}$
4. a) 2.4×10^{-4} M b) 0.018 g/L
5. 0.05 mg does not dissolve
6. $PbCl_2$

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