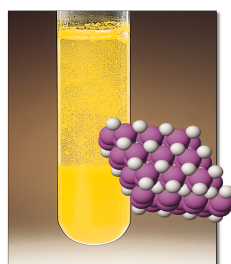


PRECIPITATION REACTIONS

Chapter 15



Chemistry 223
Professor Michael Russell



MAR Last update: 4/29/24

MAR

Flashback - Aqueous Salts!

SOLUBLE COMPOUNDS

Almost all salts of Na⁺, K⁺, NH₄⁺

Salts of nitrate, NO₃⁻,
chlorate, ClO₃⁻,
perchlorate, ClO₄⁻,
acetate, CH₃CO₂⁻

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

EXCEPTIONS

Almost all salts of Cl⁻, Br⁻, I⁻

Halides of Ag⁺, Hg₂²⁺, Pb²⁺

Compounds containing F⁻

Fluorides of Mg²⁺, Ca²⁺, Sr²⁺, Ba²⁺, Pb²⁺

Salts of sulfate, SO₄²⁻

Sulfates of Ca²⁺, Sr²⁺, Ba²⁺, Pb²⁺

INSOLUBLE COMPOUNDS

Most salts of carbonate, CO₃²⁻,
phosphate, PO₄³⁻,
oxalate, C₂O₄²⁻,
chromate, CrO₄²⁻

EXCEPTIONS

Salts of NH₄⁺ and the alkali metal cations

Most metal sulfides, S²⁻

Most metal hydroxides and oxides

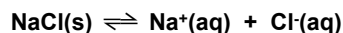
Ba(NO₃)₂(aq)?
soluble

BaCl₂(aq)?
soluble

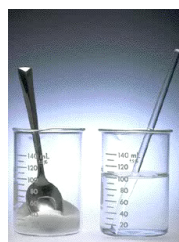
BaSO₄(aq)?
insoluble, BaSO₄(s)

Solubility of a Salt

Consider NaCl dissolving in water:

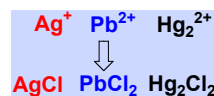


Solubility of NaCl exceeded when solid precipitate does not dissolve



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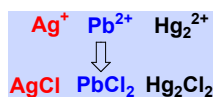
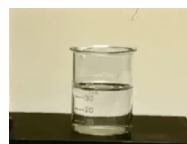
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Analysis of Silver Group

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.

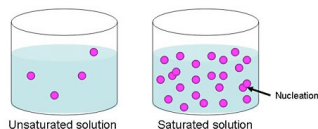


Analysis of Silver Group

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

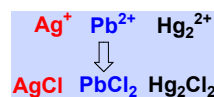


When equilibrium has been established, no more AgCl dissolves and the solution is **SATURATED**.



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Analysis of Silver Group

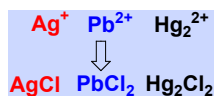


When solution is **SATURATED**, expt. shows that [Ag⁺] = 1.67 x 10⁻⁵ M.

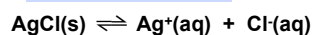
This is equivalent to the **SOLUBILITY** of AgCl.

What is [Cl⁻]?

This is also equivalent to the AgCl solubility, so [Cl⁻] = 1.67 x 10⁻⁵ M



Analysis of Silver Group



Saturated solution has

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

Use this to calculate K_c

$$\begin{aligned} K_c &= [\text{Ag}^+][\text{Cl}^-] \\ &= (1.67 \times 10^{-5})(1.67 \times 10^{-5}) \\ &= 2.79 \times 10^{-10} \end{aligned}$$

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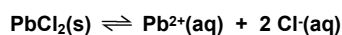
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Some Common, Slightly Soluble Compounds and Their K_{sp} Values*

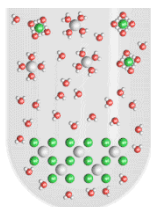
Formula	Name	K_{sp} (25 °C)	Common Names/Uses
CaCO ₃	Calcium carbonate	3.4×10^{-9}	Calcite, Iceland spar
MnCO ₃	Manganese(II) carbonate	2.3×10^{-11}	Rhodochrosite (forms rose-colored crystals)
FeCO ₃	Iron(II) carbonate	3.1×10^{-11}	Siderite
CaF ₂	Calcium fluoride	5.3×10^{-11}	Fluorite (source of HF and 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.

Lead(II) Chloride



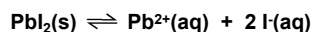
$$K_{sp} = 1.9 \times 10^{-5}$$



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Solubility of Lead(II) Iodide

Consider PbI_2 dissolving in water



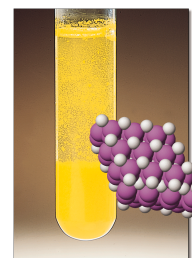
Calculate K_{sp} if solubility = 0.00130 M

Solution

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

$$\begin{aligned} 1. \quad \text{Solubility} &= [\text{Pb}^{2+}] \\ &= 1.30 \times 10^{-3} \text{ M} \end{aligned}$$

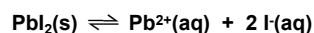
$$[\text{I}^-] = 2 \times [\text{Pb}^{2+}] = 2.60 \times 10^{-3} \text{ M}$$



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Solubility of Lead(II) Iodide

Consider PbI_2 dissolving in water



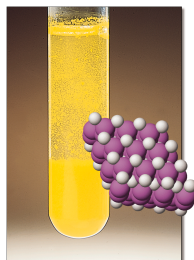
Calculate K_{sp} if solubility = 0.00130 M

Solution

$$\begin{aligned} 1. \quad \text{Solubility} &= [\text{Pb}^{2+}] \\ &= 1.30 \times 10^{-3} \text{ M} \end{aligned}$$

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

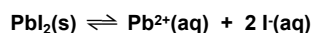
$$\begin{aligned} 2. \quad K_{sp} &= [\text{Pb}^{2+}][\text{I}^-]^2 \\ &= [\text{Pb}^{2+}][2 \cdot [\text{Pb}^{2+}]]^2 \\ &= 4 [\text{Pb}^{2+}]^3 \end{aligned}$$



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Solubility of Lead(II) Iodide

Consider PbI_2 dissolving in water



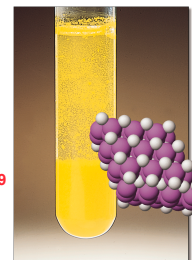
Calculate K_{sp} if solubility = 0.00130 M

Solution

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

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

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 ₂ O, (NH ₄) ₂ SO ₃
3	1	$K_{sp} = 27x^4$ $x = (K_{sp}/27)^{1/4}$	Li ₃ P, (NH ₄) ₃ PO 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 ₂ O ₃ , Al ₂ (SO ₄) ₃
3	2	$K_{sp} = 108x^5$ $x = (K_{sp}/108)^{1/5}$	Ti ₃ As 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 $K_{sp} = 1.4 \times 10^{-37}$?

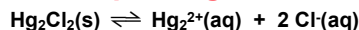
Answer: Formula = Cu₃(PO₄)₂
3 cations & 2 anions, so $K_{sp} = 108x^5$
 $x = (1.4 \times 10^{-37}/108)^{(1/5)} = 1.7 \times 10^{-8} \text{ M}$

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

Answer: Formula = MgCO₃,
1 cation & 1 anion, so $K_{sp} = x^2$
 $K_{sp} = (2.6 \times 10^{-3})^2 = 6.8 \times 10^{-6}$

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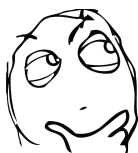
Precipitating an Insoluble Salt



$$K_{sp} = 1.1 \times 10^{-18} = [\text{Hg}_2^{2+}] [\text{Cl}^-]^2$$

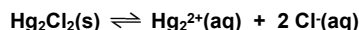
If $[\text{Hg}_2^{2+}] = 0.010 \text{ M}$, what $[\text{Cl}^-]$ is req'd to just begin the precipitation of Hg₂Cl₂?

That is, what is the maximum $[\text{Cl}^-]$ that can be in solution with 0.010 M Hg₂²⁺ without forming Hg₂Cl₂?



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Precipitating an Insoluble Salt



$$K_{sp} = 1.1 \times 10^{-18} = [\text{Hg}_2^{2+}] [\text{Cl}^-]^2$$

Solution

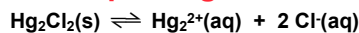
$[\text{Cl}^-]$ that can exist when $[\text{Hg}_2^{2+}] = 0.010 \text{ M}$:

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

If this conc. of Cl⁻ is just exceeded, Hg₂Cl₂ begins to precipitate.

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Precipitating an Insoluble Salt



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

Now raise $[\text{Cl}^-]$ to 1.0 M when $[\text{Hg}_2^{2+}] = 0.010 \text{ M}$. What is the value of $[\text{Hg}_2^{2+}]$ at this point?

Solution

$$[\text{Hg}_2^{2+}] = \frac{K_{sp}}{[\text{Cl}^-]^2}$$

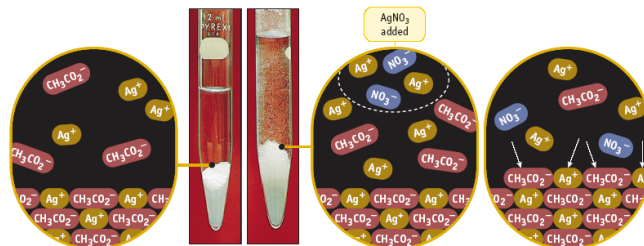
$$= \frac{K_{sp}}{(1.0)^2} = 1.1 \times 10^{-18} \text{ M}$$

The concentration of Hg₂²⁺ has been reduced by 10¹⁶!

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The Common Ion Effect

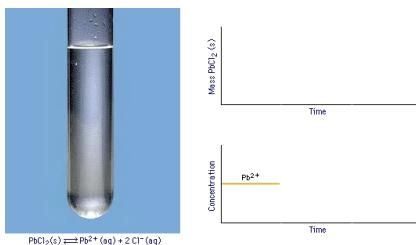
Adding an ion "common" to an equilibrium causes the equilibrium to shift back to reactant.



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Common Ion Effect

Adding an Ion "Common" to an Equilibrium

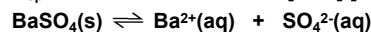


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The Common Ion Effect

Calculate the solubility of BaSO_4 in (a) pure water and (b) in $0.010 \text{ M Ba(NO}_3)_2$.

$$K_{\text{sp}} \text{ for BaSO}_4 = 1.1 \times 10^{-10} = [\text{Ba}^{2+}] [\text{SO}_4^{2-}]$$



Solution: (part a)

Solubility in pure water = $[\text{Ba}^{2+}] = [\text{SO}_4^{2-}] = x$

$$K_{\text{sp}} = [\text{Ba}^{2+}] [\text{SO}_4^{2-}] = x^2$$

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

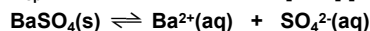
Note 1:1 ratio of cation to anion: $K_{\text{sp}} = x^2$

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The Common Ion Effect

Calculate the solubility of BaSO_4 in (a) pure water and (b) in $0.010 \text{ M Ba(NO}_3)_2$.

$$K_{\text{sp}} \text{ for BaSO}_4 = 1.1 \times 10^{-10} = [\text{Ba}^{2+}] [\text{SO}_4^{2-}]$$



Solution: (part b)

So... Solubility in pure water = $1.0 \times 10^{-5} \text{ mol/L}$.

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

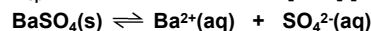
Which way will the "common ion" shift the equilibrium? ___ Will solubility of BaSO_4 be less than or greater than in pure water? ___

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The Common Ion Effect

Calculate the solubility of BaSO_4 in (a) pure water and (b) in $0.010 \text{ M Ba(NO}_3)_2$.

$$K_{\text{sp}} \text{ for BaSO}_4 = 1.1 \times 10^{-10} = [\text{Ba}^{2+}] [\text{SO}_4^{2-}]$$



Solution: (part b)

$$[\text{Ba}^{2+}] \quad [\text{SO}_4^{2-}]$$

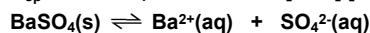
initial
change
equilib.

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The Common Ion Effect

Calculate the solubility of BaSO_4 in (a) pure water and (b) in $0.010 \text{ M Ba(NO}_3)_2$.

$$K_{\text{sp}} \text{ for BaSO}_4 = 1.1 \times 10^{-10} = [\text{Ba}^{2+}] [\text{SO}_4^{2-}]$$



Solution: (part b)

$$K_{\text{sp}} = [\text{Ba}^{2+}] [\text{SO}_4^{2-}] = (0.010 + y) (y)$$

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

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

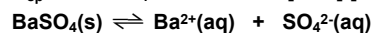
$y = 1.1 \times 10^{-8} \text{ M} = \text{solubility in presence of added Ba}^{2+} \text{ ion.}$

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The Common Ion Effect

Calculate the solubility of BaSO_4 in (a) pure water and (b) in $0.010 \text{ M Ba(NO}_3)_2$.

$$K_{\text{sp}} \text{ for BaSO}_4 = 1.1 \times 10^{-10} = [\text{Ba}^{2+}] [\text{SO}_4^{2-}]$$



Solution:

Solubility in pure water = $x = 1.0 \times 10^{-5} \text{ M}$

Solubility in presence of added Ba^{2+}
= $1.1 \times 10^{-8} \text{ M}$

Le Chatelier's Principle is followed!

See: [Solubility Guide](#)

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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?

$$K_{sp} \text{ for } \text{Ag}_2\text{CrO}_4 = 9.0 \times 10^{-12} = [\text{Ag}^+]^2 [\text{CrO}_4^{2-}]$$

$$K_{sp} \text{ for } \text{PbCrO}_4 = 1.8 \times 10^{-14} = [\text{Pb}^{2+}] [\text{CrO}_4^{2-}]$$

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?

$$K_{sp} \text{ for } \text{Ag}_2\text{CrO}_4 = 9.0 \times 10^{-12} = [\text{Ag}^+]^2 [\text{CrO}_4^{2-}]$$

$$K_{sp} \text{ for } \text{PbCrO}_4 = 1.8 \times 10^{-14} = [\text{Pb}^{2+}] [\text{CrO}_4^{2-}]$$

Solution - Calculate $[\text{CrO}_4^{2-}]$ required by each ion

$$[\text{CrO}_4^{2-}] \text{ to ppt. } \text{Ag}_2\text{CrO}_4 = K_{sp} / [\text{Ag}^+]^2$$

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

$$[\text{CrO}_4^{2-}] \text{ to ppt. } \text{PbCrO}_4 = K_{sp} / [\text{Pb}^{2+}]$$

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

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.

$$K_{sp} (\text{Ag}_2\text{CrO}_4) = 9.0 \times 10^{-12} = [\text{Ag}^+]^2 [\text{CrO}_4^{2-}]$$

$$K_{sp} (\text{PbCrO}_4) = 1.8 \times 10^{-14} = [\text{Pb}^{2+}] [\text{CrO}_4^{2-}]$$

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

Solution

We know that $[\text{CrO}_4^{2-}] = 2.3 \times 10^{-8} \text{ M}$ 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 .

$$K_{sp} (\text{Ag}_2\text{CrO}_4) = 9.0 \times 10^{-12} = [\text{Ag}^+]^2 [\text{CrO}_4^{2-}]$$

$$K_{sp} (\text{PbCrO}_4) = 1.8 \times 10^{-14} = [\text{Pb}^{2+}] [\text{CrO}_4^{2-}]$$

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

Solution

$$[\text{Pb}^{2+}] = K_{sp} / [\text{CrO}_4^{2-}] = 1.8 \times 10^{-14} / 2.3 \times 10^{-8} \text{ M}$$

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

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

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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

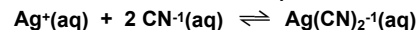
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Formation Constants (K_f) at 25 °C

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}
$Be(OH)_2^{2-}$	4×10^{18}
CdI_2^{2-}	1×10^6
$Co(OH)_2^{2-}$	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}
$Hg(CN)_2^{2-}$	9.3×10^{38}
$Ni(NH_3)_6^{2+}$	2.0×10^8
$Pb(OH)_2^{-}$	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
$Zn(OH)_2^{2-}$	3×10^{15}

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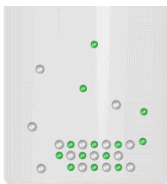
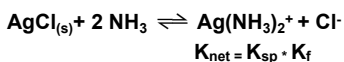
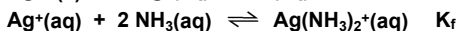
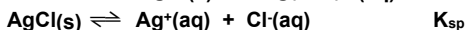
Example:



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

Formation Constants

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



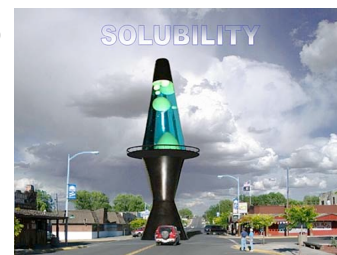
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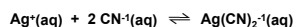
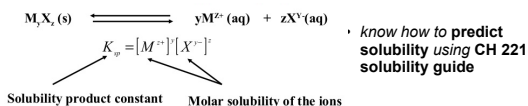
End of Chapter 15

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)



Important Equations, Constants, and Handouts from this Chapter:



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

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

- Predict whether each of the following is insoluble or soluble in water: $(NH_4)_2CO_3$, $ZnSO_4$, NiS , $BaSO_4$
- When 1.55 g of solid thallium(I) bromide is added to 1.00 L of water, the salt dissolves to a small extent: $TlBr(s) \rightleftharpoons Tl^+(aq) + Br^-(aq)$. 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 $TlBr$?
- 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 $Pb(OH)_2$.
- Estimate the solubility of calcium fluoride, CaF_2 , (a) in moles per liter and (b) in grams per liter of pure water. $CaF_2(s) \rightleftharpoons Ca^{2+}(aq) + 2 F^{-1}(aq)$ $K_{sp} = 5.3 \times 10^{-11}$
- 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? $RaSO_4(s) \rightleftharpoons Ra^{2+}(aq) + SO_4^{2-}(aq)$
- Which compound is more soluble: $PbCl_2$ ($K_{sp} = 1.7 \times 10^{-5}$) or $PbBr_2$ ($K_{sp} = 6.6 \times 10^{-6}$)?

End of Chapter Problems: *Answers*

1. $(\text{NH}_4)_2\text{CO}_3$ & ZnSO_4 (soluble), NiS & BaSO_4 (insoluble)
2. $K_{\text{sp}} = 3.6 \times 10^{-6}$
3. $K_{\text{sp}} = 1.4 \times 10^{-15}$
4. a) $2.4 \times 10^{-4} \text{ M}$ b) 0.018 g/L
5. 0.05 mg does not dissolve
6. PbCl_2

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