

SOLUBILITY EQUILIBRIA (The Solubility-Product Constant, K_{sp})

We've got good news and we've got bad news... Which do you want first?

The good news: Solubility equilibrium is really simple.

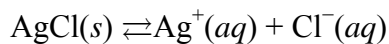
The bad news: You know all those solubility rules that state a substance is *insoluble*? They are actually a little bit soluble after all. Only the future attorneys among you read the fine print. Soluble is often defined as "greater than 3 grams dissolving in 100 mL of water". So, there is a lot of wiggle room for solubility up to 3 grams! This type of equilibria deals with that wiggle room. Apologies for "lying" to you.

If you can actually *see* that a salt is insoluble, usually evidenced by solid "stuff" sitting on the bottom of the container, then the solution is actually *saturated*. Saturated solutions of salts present due to a chemical reaction taking place present yet another type of chemical equilibria.

- Slightly soluble salts establish a dynamic equilibrium with the hydrated cations and anions in solution. Examine the formation of $\text{AgCl}(s)$ as a solution of $\text{AgNO}_3(aq)$ is squirted into a solution of $\text{NaCl}(aq)$.

- When the solid is first added to water, no ions are initially present.
- As dissolution proceeds, the concentration of ions increases until equilibrium is established. This occurs when the solution is saturated.
- The equilibrium constant, the K_{sp} , is no more than the product of the ions in solution. (Remember, solids do not appear in equilibrium expressions.)

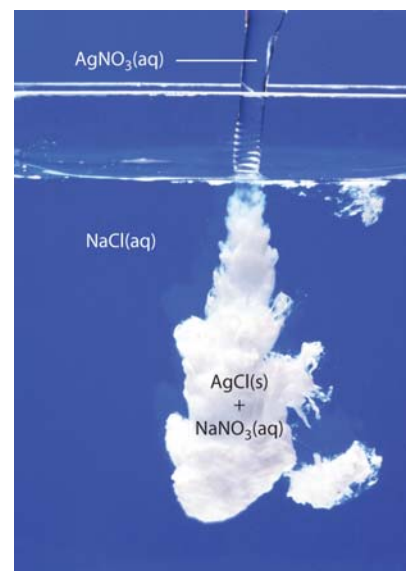
- For a saturated solution of AgCl , the equation would be:



- The solubility product expression for the $\text{AgCl}(s)$ precipitate would be:

$$K_{sp} = [\text{Ag}^+][\text{Cl}^-]$$

- The $\text{AgCl}(s)$ does not appear in the equilibrium expression since solids are left out. Why? *Because*, the concentration of the solid remains relatively constant.

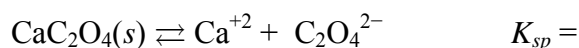
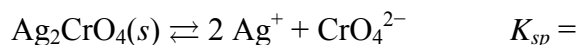


A table of K_{sp} values follows on the next page.

Solubility Product Constants, K_{sp} , at 25°C

Substance	Formula	K_{sp}	Substance	Formula	K_{sp}
Aluminum hydroxide	Al(OH) ₃	4.6×10^{-33}	Lead(II) sulfide	PbS	2.5×10^{-27}
Barium chromate	BaCrO ₄	1.2×10^{-10}	Magnesium arsenate	Mg ₃ (AsO ₄) ₂	2×10^{-20}
Barium fluoride	BaF ₂	1.0×10^{-6}	Magnesium carbonate	MgCO ₃	1.0×10^{-5}
Barium sulfate	BaSO ₄	1.1×10^{-10}	Magnesium hydroxide	Mg(OH) ₂	1.8×10^{-11}
Cadmium oxalate	CdC ₂ O ₄	1.5×10^{-8}	Magnesium oxalate	MgC ₂ O ₄	8.5×10^{-5}
Cadmium sulfide	CdS	8×10^{-27}	Manganese(II) sulfide	MnS	2.5×10^{-10}
Calcium carbonate	CaCO ₃	3.8×10^{-9}	Mercury(I) chloride	Hg ₂ Cl ₂	1.3×10^{-18}
Calcium fluoride	CaF ₂	3.4×10^{-11}	Mercury(II) sulfide	HgS	1.6×10^{-52}
Calcium oxalate	CaC ₂ O ₄	2.3×10^{-9}	Nickel(II) hydroxide	Ni(OH) ₂	2.0×10^{-15}
Calcium phosphate	Ca ₃ (PO ₄) ₂	1×10^{-26}	Nickel(II) sulfide	NiS	3×10^{-19}
Calcium sulfate	CaSO ₄	2.4×10^{-5}	Silver acetate	AgC ₂ H ₃ O ₂	2.0×10^{-3}
Cobalt(II) sulfide	CoS	4×10^{-21}	Silver bromide	AgBr	5.0×10^{-13}
Copper(II) hydroxide	Cu(OH) ₂	2.6×10^{-19}	Silver chloride	AgCl	1.8×10^{-10}
Copper(II) sulfide	CuS	6×10^{-36}	Silver chromate	Ag ₂ CrO ₄	1.1×10^{-12}
Iron(II) hydroxide	Fe(OH) ₂	8×10^{-16}	Silver iodide	AgI	8.3×10^{-17}
Iron(II) sulfide	FeS	6×10^{-18}	Silver sulfide	Ag ₂ S	6×10^{-50}
Iron(III) hydroxide	Fe(OH) ₃	2.5×10^{-39}	Strontium carbonate	SrCO ₃	9.3×10^{-10}
Lead(II) arsenate	Pb ₃ (AsO ₄) ₂	4×10^{-36}	Strontium chromate	SrCrO ₄	3.5×10^{-5}
Lead(II) chloride	PbCl ₂	1.6×10^{-5}	Strontium sulfate	SrSO ₄	2.5×10^{-7}
Lead(II) chromate	PbCrO ₄	1.8×10^{-14}	Zinc hydroxide	Zn(OH) ₂	2.1×10^{-16}
Lead(II) iodide	PbI ₂	6.5×10^{-9}	Zinc sulfide	ZnS	1.1×10^{-21}
Lead(II) sulfate	PbSO ₄	1.7×10^{-8}			

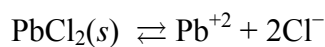
Write the K_{sp} expression for each of the following reactions and find its value in the table above.



❖ DETERMINING K_{sp} FROM EXPERIMENTAL MEASUREMENTS

- In practice, K_{sp} values are determined by careful laboratory measurements using various spectroscopic methods.
 - Remember STOICHIOMETRY? Surely, you've made peace with the concept by now...

Example: Lead(II) chloride dissolves to a slight extent in water according to the equation below.



Calculate the K_{sp} if the lead ion concentration has been found to be $1.62 \times 10^{-2}M$.

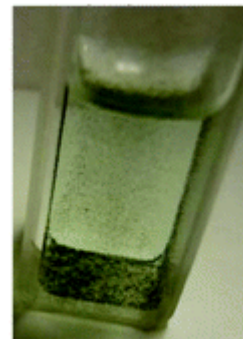
If lead's concentration is x , then chloride's concentration is $2x$. So . . .

$$K_{sp} = (1.62 \times 10^{-2})(3.24 \times 10^{-2})^2 = 1.70 \times 10^{-5}$$

Exercise 1

Calculating K_{sp} from Solubility I

Copper(I) bromide has a measured solubility of 2.0×10^{-4} mol/L at 25°C . Calculate its K_{sp} value.



[CuBr]

$$K_{sp} = 4.0 \times 10^{-8}$$

Exercise 2

Calculating K_{sp} from Solubility II

Calculate the K_{sp} value for bismuth sulfide (Bi_2S_3), which has a solubility of 1.0×10^{-15} mol/L at 25°C .



Precipitation of bismuth sulfide.

Sulfide is a very basic anion and really exists in water as HS^- . We will not consider this complication.

$$K_{sp} = 1.1 \times 10^{-73}$$

ESTIMATING SALT SOLUBILITY FROM K_{sp}

- ❖ Relative solubilities can be deduced by comparing values of K_{sp} BUT, BE CAREFUL!
- ❖ These comparisons can only be made for salts having the same ION:ION ratio.
- ❖ Please don't forget solubility changes with temperature! Some substances become less soluble in cold water while others increase in solubility! Aragonite is an example.

Example: The K_{sp} for CaCO_3 is 3.8×10^{-9} @ 25°C . Calculate the solubility of calcium carbonate in pure water in (a) moles per liter & (b) grams per liter:

Exercise 3

Calculating Solubility from K_{sp}

The K_{sp} value for copper(II) iodate, $\text{Cu}(\text{IO}_3)_2$, is 1.4×10^{-7} at 25°C . Calculate its solubility at 25°C .

$$= 3.3 \times 10^{-3} \text{ mol/L}$$

Exercise 4

Solubility and Common Ions

Calculate the solubility of solid CaF_2 ($K_{sp} = 4.0 \times 10^{-11}$) in a 0.025 M NaF solution.

$$= 6.4 \times 10^{-8} \text{ mol/L}$$

K_{sp} AND THE REACTION QUOTIENT, Q

With some knowledge of the reaction quotient, we can decide

- whether a precipitate (ppt) will form AND
- what concentrations of ions are required to begin the precipitation of an insoluble salt.

1. $Q < K_{sp}$, the system is not at equil. (*unsaturated*)
2. $Q = K_{sp}$, the system is at equil. (*saturated*)
3. $Q > K_{sp}$, the system is not at equil. (*supersaturated*)

Precipitates form when the solution is supersaturated!!!

Precipitation of insoluble salts

- Metal-bearing ores often contain the metal in the form of an insoluble salt, and, to complicate matters, the ores often contain several such metal salts.
- Dissolve the metal salts to obtain the metal ion, concentrate in some manner, and ppt. selectively only one type of metal ion as an insoluble salt.

Exercise 5

Determining Precipitation Conditions

A solution is prepared by adding 750.0 mL of $4.00 \times 10^{-3} M$ $Ce(NO_3)_3$ to 300.0 mL of $2.00 \times 10^{-2} M$ KIO_3 . Will $Ce(IO_3)_3$ ($K_{sp} = 1.9 \times 10^{-10}$) precipitate from this solution?

yes

Exercise 6

Precipitation

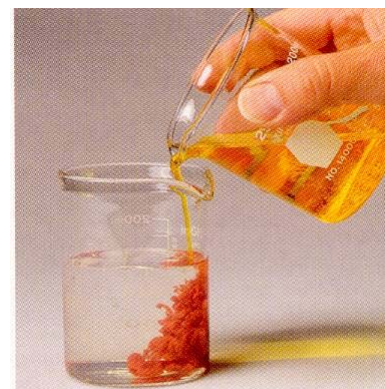
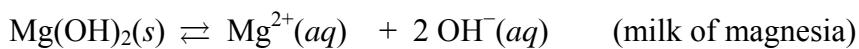
A solution is prepared by mixing 150.0 mL of $1.00 \times 10^{-2} M$ $Mg(NO_3)_2$ and 250.0 mL of $1.00 \times 10^{-1} M$ NaF. Calculate the concentrations of Mg^{2+} and F^- at equilibrium with solid MgF_2 ($K_{sp} = 6.4 \times 10^{-9}$).



$$[Mg^{2+}] = 2.1 \times 10^{-6} M$$
$$[F^-] = 5.50 \times 10^{-2} M$$

SOLUBILITY AND THE COMMON ION EFFECT

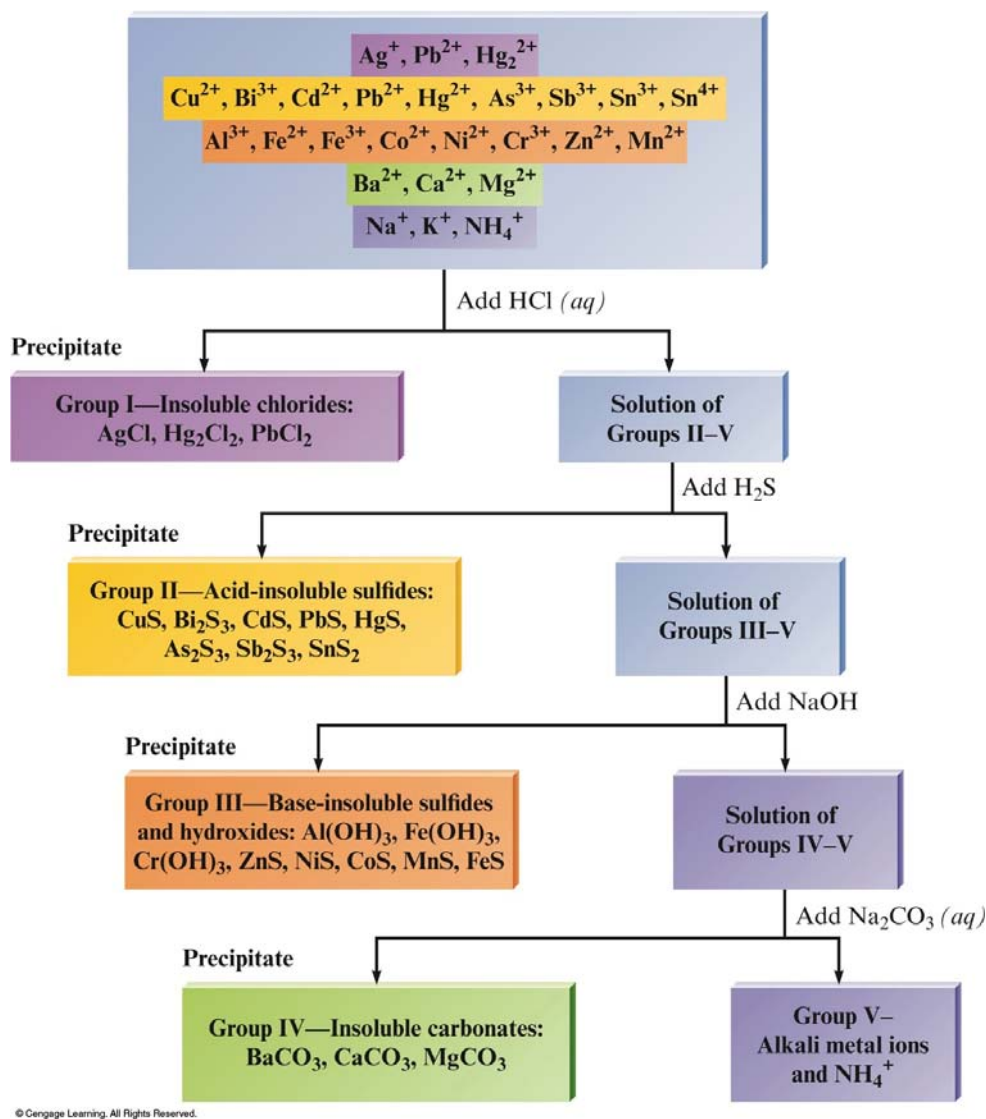
- Experiments show that the solubility of any salt is always less in the presence of a “common ion”.
- Why? LeChâtelier’s Principle, that’s why! Be reasonable and use approximations when you can.
- The pH can also affect solubility. Evaluate the equation to see which species reacts with the addition of acid or base.
- Would magnesium hydroxide be more soluble in an acid or a base? Why?



A potassium chromate solution being added to aqueous silver nitrate, forming silver chromate.

SOLUBILITY, ION SEPARATIONS, AND QUALITATIVE ANALYSIS

- ❖ This section will introduce you to the basic chemistry of various ions.
- ❖ It also illustrates how principles of chemical equilibria can be applied in the laboratory.
- ❖ **Objective:** Separate the following metal ions from an aqueous sample containing ions of silver, lead(II), cadmium(II) and nickel(II).



- From your knowledge of solubility rules, you know that chlorides of lead and silver will form precipitates while those of nickel and cadmium will not. Adding dilute HCl to sample will ppt. the lead and silver ions while the nickel and cadmium will stay in solution.
- Separate the lead and silver precipitates from the solution by filtration. Heating the solution causes some of the lead chloride to dissolve. Filtering the HOT sample will separate the lead (in the filtrate) from the silver (solid remaining in funnel with filter paper).
- Separating cadmium and nickel ions require precipitation with sulfur. Use the K_{sp} values to determine which ion will precipitate first as an aqueous solution of sulfide ion is added to the portion of the sample that still contains these ions. Which precipitates first?

Exercise 7

Selective Precipitation

A solution contains $1.0 \times 10^{-4} M \text{Cu}^+$ and $2.0 \times 10^{-3} M \text{Pb}^{2+}$. If a source of I^- is added gradually to this solution, will PbI_2 ($K_{sp} = 1.4 \times 10^{-8}$) or CuI ($K_{sp} = 5.3 \times 10^{-12}$) precipitate first? Specify the concentration of I^- necessary to begin precipitation of each salt.

CuI will precipitate first
Concentration in excess of $5.3 \times 10^{-8} M$ required

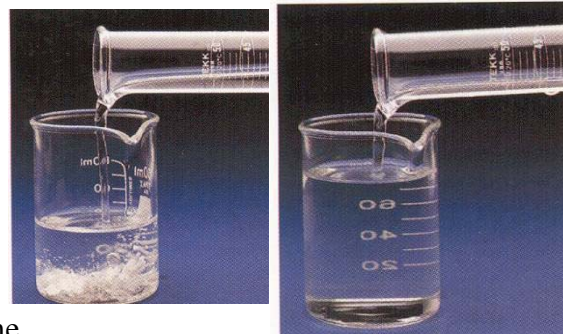
SOLUBILITY AND COMPLEX IONS

- The formation of complex ions can often dissolve otherwise insoluble salts.
- Often as the complex ion forms, the solubility equilibrium shifts to the right (away from the solid) and causes the insoluble salt to become more soluble.

Example: If sufficient aqueous ammonia is added to silver chloride, the latter can be dissolved as $[\text{Ag}(\text{NH}_3)_2]^+$ forms, which is soluble.

That is a significant improvement with regard to the solubility of $\text{AgCl}(s)$.

The equilibrium constant for dissolving silver chloride in ammonia is not large, but, if the concentration of ammonia is sufficiently high, the complex ion and chloride ion must also be high, and silver chloride will dissolve. Of course, this process is quite smelly!



(top) Aqueous ammonia is added to silver chloride (white). (bottom) Silver chloride, insoluble in water, dissolves to form $\text{Ag}(\text{NH}_3)_2^+(\text{aq})$ and $\text{Cl}^-(\text{aq})$.