AP* Chemistry
Solubility Equilibrium

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

We've got good news and we've got bad news…

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 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.

If you can actually see that a salt is insoluble, then the solution is actually saturated. Saturated solutions of salts present yet another type of chemical equilibria.

- Slightly soluble salts establish a dynamic equilibrium with the hydrated cations and anions in solution.
  - 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:

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

  - The solubility product expression would be:

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

  - The AgCl(s) does not appear in the equilibrium expression since solids are left out. Why? The concentration of the solid remains relatively constant.

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

Table 15.4 K_{sp} Values at 25°C for Common Ionic Solids

Ionic Solid	K_{sp} (at 25°C)	Ionic Solid	K_{sp} (at 25°C)	Ionic Solid	K_{sp} (at 25°C)
Fluorides		Hg_2CrO_4*	2×10^{-9}	$Co(OH)_2$	2.5×10^{-16}
BaF_2	2.4×10^{-5}	$BaCrO_4$	8.5×10^{-11}	$Ni(OH)_2$	1.6×10^{-16}
MgF_2	6.4×10^{-9}	Ag_2CrO_4	9.0×10^{-12}	$Zn(OH)_2$	4.5×10^{-17}
PbF_2	4×10^{-8}	$PbCrO_4$	2×10^{-16}	$Cu(OH)_2$	1.6×10^{-19}
SrF_2	7.9×10^{-10}			$Hg(OH)_2$	3×10^{-26}
CaF_2	4.0×10^{-11}	Carbonates		$Sn(OH)_2$	3×10^{-27}
		$NiCO_3$	1.4×10^{-7}	$Cr(OH)_3$	6.7×10^{-31}
Chlorides		$CaCO_3$	8.7×10^{-9}	$Al(OH)_3$	2×10^{-32}
$PbCl_2$	1.6×10^{-5}	$BaCO_3$	1.6×10^{-9}	$Fe(OH)_3$	4×10^{-38}
$AgCl$	1.6×10^{-10}	$SrCO_3$	7×10^{-10}	$Co(OH)_3$	2.5×10^{-43}
Hg_2Cl_2*	1.1×10^{-18}	$CuCO_3$	2.5×10^{-10}		
		$ZnCO_3$	2×10^{-10}	Sulfides	
Bromides		$MnCO_3$	8.8×10^{-11}	MnS	2.3×10^{-13}
$PbBr_2$	4.6×10^{-6}	$FeCO_3$	2.1×10^{-11}	FeS	3.7×10^{-19}
$AgBr$	5.0×10^{-13}	Ag_2CO_3	8.1×10^{-12}	NiS	3×10^{-21}
Hg_2Br_2*	1.3×10^{-22}	$CdCO_3$	5.2×10^{-12}	CoS	5×10^{-22}
		$PbCO_3$	1.5×10^{-15}	ZnS	2.5×10^{-22}
Iodides		$MgCO_3$	1×10^{-15}	SnS	1×10^{-26}
PbI_2	1.4×10^{-8}	Hg_2CO_3*	9.0×10^{-15}	CdS	1.0×10^{-28}
AgI	1.5×10^{-16}			PbS	7×10^{-29}
Hg_2I_2*	4.5×10^{-29}	Hydroxides		CuS	8.5×10^{-45}
		$Ba(OH)_2$	5.0×10^{-3}	Ag_2S	1.6×10^{-49}
Sulfates		$Sr(OH)_2$	3.2×10^{-4}	HgS	1.6×10^{-54}
$CaSO_4$	6.1×10^{-5}	$Ca(OH)_2$	1.3×10^{-6}		
Ag_2SO_4	1.2×10^{-5}	$AgOH$	2.0×10^{-8}	Phosphates	
$SrSO_4$	3.2×10^{-7}	$Mg(OH)_2$	8.9×10^{-12}	Ag_3PO_4	1.8×10^{-18}
$PbSO_4$	1.3×10^{-8}	$Mn(OH)_2$	2×10^{-13}	$Sr_3(PO_4)_2$	1×10^{-31}
$BaSO_4$	1.5×10^{-9}	$Cd(OH)_2$	5.9×10^{-15}	$Ca_3(PO_4)_2$	1.3×10^{-32}
		$Pb(OH)_2$	1.2×10^{-15}	$Ba_3(PO_4)_2$	6×10^{-39}
Chromates		$Fe(OH)_2$	1.8×10^{-15}	$Pb_3(PO_4)_2$	1×10^{-54}
$SrCrO_4$	3.6×10^{-5}				

* Contains Hg_2^{2+} ions. $K = [Hg_2^{2+}][X^-]^2$ for Hg_2X_2 salts, for example.

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

$CaF_2(s) \rightleftarrows Ca^{+2} + 2\ F^-$ K_{sp} =

$Ag_2SO_4(s) \rightleftarrows 2\ Ag^+ + SO_4^{2-}$ K_{sp} =

$Bi_2S_3(s) \rightleftarrows 2\ Bi^{+3} + 3\ S^{2-}$ K_{sp} =

❖ DETERMINING K_{sp} FROM EXPERIMENTAL MEASUREMENTS

- In practice, K_{sp} values are determined by careful laboratory measurements using various spectroscopic methods.
  - Remember STOICHIOMETRY!!

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

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

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**

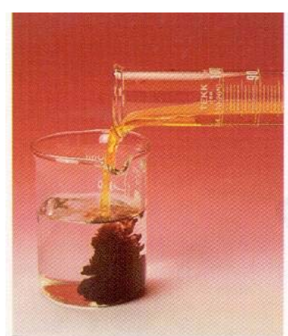
Copper(I) bromide has a measured solubility of 2.0×10^{-4} mol/L at 25°C. Calculate its K_{sp} value.

K_{sp} **= 4.0 × 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.

K_{sp} **= 1.1 × 10^{-73}**



Precipitation of bismuth sulfide.

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

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 other 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, $Cu(IO_3)_2$, is 1.4×10^{-7} at 25°C.
Calculate its solubility at 25°C.

$= 3.3 \times 10^{-3}$ 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.

$= 6.4 \times 10^{-8}$ 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. (*un*saturated)
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 4.00×10^{-3} M $Ce(NO_3)_3$ to 300.0 mL of 2.00×10^{-2} M KIO_3. Will $Ce(IO_3)_3$ ($K_{sp} = 1.9 \times 10^{-10}$) precipitate from this solution?

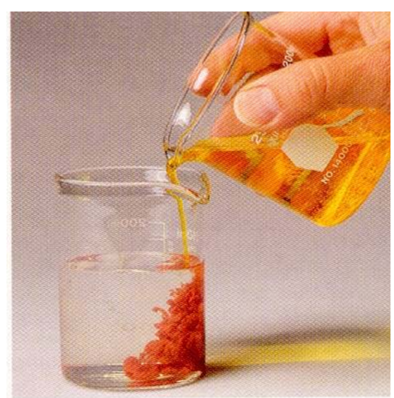
yes

Exercise 6 **Precipitation**

A solution is prepared by mixing 150.0 mL of 1.00×10^{-2} M $Mg(NO_3)_2$ and 250.0 mL of 1.00×10^{-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



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

- Experiments show that the solubility of any salt is always less in the presence of a "common ion".
- Why? LeChatelier'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?

$Mg(OH)_2(s) \rightleftarrows Mg^{2+}(aq) + 2\,OH^-(aq)$ (milk of magnesia)

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.

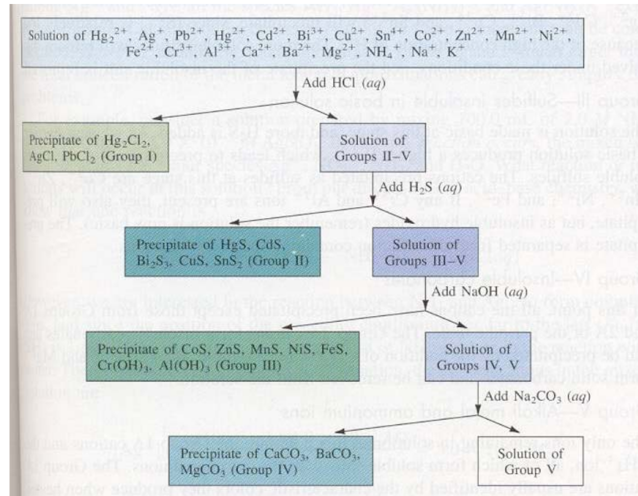


Figure 15.12
A schematic diagram of the classic method for separating the common cations by selective precipitation.

- ❖ ***Objective***: Separate the following metal ions from an aqueous sample containing ions of silver, lead, cadmium and nickel

  - ➢ 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?

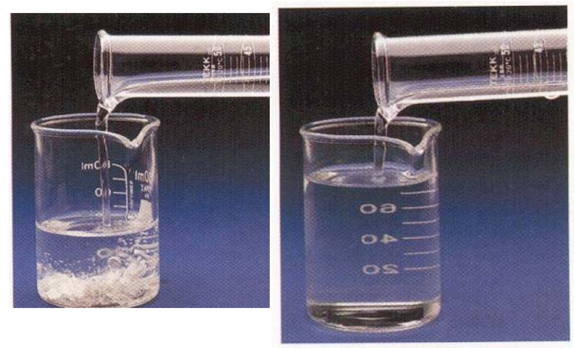
Exercise 7 **Selective Precipitation**

A solution contains 1.0×10^{-4} M Cu^+ and 2.0×10^{-3} M 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 5.3×10^{-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.



(top) Aqueous ammonia is added to silver chloride (white). (bottom) Silver chloride, insoluble in water, dissolves to form $Ag(NH_3)_2^+(aq)$ and $Cl^-(aq)$.

Example: If sufficient aqueous ammonia is added to silver chloride, the latter can be dissolved as $[Ag(NH_3)_2]^+$ forms.

$$AgCl\ (s) \rightleftarrows Ag^+\ (aq) + Cl^-\ (aq) \qquad K_{sp} = 1.8 \times 10^{-10}$$

$$Ag^+\ (aq) + 2\ NH_3\ (aq) \rightleftarrows [Ag(NH_3)_2]^+\ (aq) \qquad K_{\text{formation}} = 1.6 \times 10^7$$

Add these two equations together and determine the new K value.

$$\text{SUM: } AgCl\ (s) + 2\ NH_3\ (aq) \rightleftarrows [Ag(NH_3)_2]^+\ (aq) + + Cl^-\ (aq)$$

$$K = K_{sp} \times K_{\text{formation}} = 2.9 \times 10^{-3} = \frac{\{[Ag(NH_3)_2^+\}[Cl^-]}{[NH_3]^2}$$

That is a significant improvement with regard to the solubility of 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!

Exercise 8 **Complex Ions**

Calculate the concentrations of Ag^+, $Ag(S_2O_3)^-$, and $Ag(S_2O_3)_2^{3-}$ in a solution prepared by mixing 150.0 mL of 1.00×10^{-3} M $AgNO_3$ with 200.0 mL of 5.00 M $Na_2S_2O_3$. The stepwise formation equilibria are:

$$Ag^+ + S_2O_3^{2-} \rightleftarrows Ag(S_2O_3)^- \qquad K_1 = 7.4 \times 10^8$$

$$Ag(S_2O_3)^- + S_2O_3^{2-} \rightleftarrows Ag(S_2O_3)_2^{3-} \qquad K_2 = 3.9 \times 10^4$$

$[Ag^+] = 1.8 \times 10^{-18}$ M

$[Ag(S_2O_3)^-] = 3.8 \times 10\text{-}9$ M