Solubility Equilibria

Aqueous Salt Solutions & Solubility

CHM 101

- Ionic compounds were considered soluble or insoluble
- Soluble compounds dissociated fully in water
- Basic stoichiometry rules were used

CHM 112

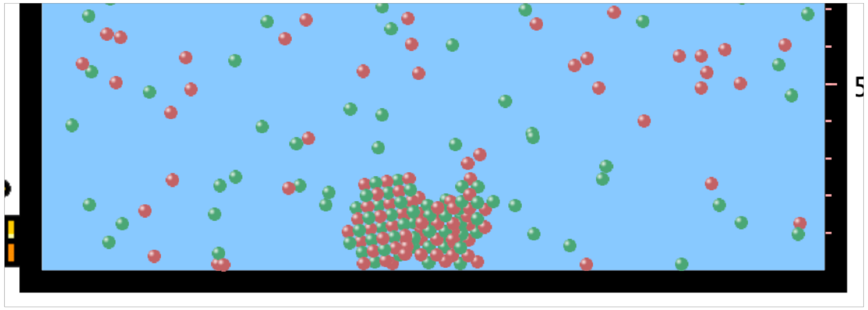
- Most ionic compounds are "slightly" soluble – they do dissolve a little, but not very much
- A small amount of dissolved & dissociated material is present with the bulk undissolved
- Ions are constantly moving between the dissolved and undissolved states – **EQUILIBRIUM!**
- Solubility constant is K_{sp} (solubility product constant)
- Discussed in terms of Molar Solubility –
    - moles solute/ 1L saturated solution

CHM 101 Solubility Rules for ions

Soluble	Ammonium (NH_4^+) Hydrogen (H^+) Alkali metals (group 1A) Nitrate (NO_3^-) Perchlorate (ClO_4^-) Acetate (CH_3COO^-)	Always soluble
Usually Soluble	Halides (F^-, Cl^-, Br^-, & I^-)	Exceptions (insoluble if with): Pb^{2+}, Hg_2^{2+}, Ag^+
	Sulfate (SO_4^{2-})	Pb^{2+}, Hg_2^{2+}, Ag^+, Ba^{2+}, Ca^{2+}, Sr^{2+}
Sparingly Soluble (Insoluble)	Sulfide (S^{2-}) Hydroxide (OH^-) Oxide (O^{2-}) Carbonate (CO_3^{2-}) Phosphate (PO_4^{3-})	Exceptions: soluble if with any of the cations listed in the always soluble box

Solubility Product Constant (K_{sp})

A slightly soluble ionic material is placed in water.



- The solubility is low so most will not dissolve
- What does dissolve will dissociate into ions

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

- The solid is in equilibrium with the dissolved ions
- The equilibrium expression is:

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

- Note that the $PbCl_2(s)$ is not included in the equilibrium expression. Why?

Solubility Product Constant (K_{sp})

- K_{sp} is an approximation used to estimate solubility
- Measures the extent to which a substance will dissolve in water
- Larger K_{sp} = higher solubility
- Amount of solid material present does not alter K_{sp}
    - Solids are not included in equilibrium expressions!

TABLE 17.2 Solubility Products of Some Slightly Soluble Ionic Compounds at 25°C

Compound	K_{sp}	Compound	K_{sp}
Aluminum hydroxide [$Al(OH)_3$]	1.8×10^{-33}	Lead(II) chromate ($PbCrO_4$)	2.0×10^{-14}
Barium carbonate ($BaCO_3$)	8.1×10^{-9}	Lead(II) fluoride (PbF_2)	4.1×10^{-8}
Barium fluoride (BaF_2)	1.7×10^{-6}	Lead(II) iodide (PbI_2)	1.4×10^{-8}
Barium sulfate ($BaSO_4$)	1.1×10^{-10}	Lead(II) sulfide (PbS)	3.4×10^{-28}
Bismuth sulfide (Bi_2S_3)	1.6×10^{-72}	Magnesium carbonate ($MgCO_3$)	4.0×10^{-5}
Cadmium sulfide (CdS)	8.0×10^{-28}	Magnesium hydroxide [$Mg(OH)_2$]	1.2×10^{-11}
Calcium carbonate ($CaCO_3$)	8.7×10^{-9}	Manganese(II) sulfide (MnS)	3.0×10^{-14}
Calcium fluoride (CaF_2)	4.0×10^{-11}	Mercury(I) chloride (Hg_2Cl_2)	3.5×10^{-18}
Calcium hydroxide [$Ca(OH)_2$]	8.0×10^{-6}	Mercury(II) sulfide (HgS)	4.0×10^{-54}
Calcium phosphate [$Ca_3(PO_4)_2$]	1.2×10^{-26}	Nickel(II) sulfide (NiS)	1.4×10^{-24}
Chromium(III) hydroxide [$Cr(OH)_3$]	3.0×10^{-29}	Silver bromide ($AgBr$)	7.7×10^{-13}
Cobalt(II) sulfide (CoS)	4.0×10^{-21}	Silver carbonate (Ag_2CO_3)	8.1×10^{-12}
Copper(I) bromide ($CuBr$)	4.2×10^{-8}	Silver chloride ($AgCl$)	1.6×10^{-10}
Copper(I) iodide (CuI)	5.1×10^{-12}	Silver iodide (AgI)	8.3×10^{-17}
Copper(II) hydroxide [$Cu(OH)_2$]	2.2×10^{-20}	Silver sulfate (Ag_2SO_4)	1.4×10^{-5}
Copper(II) sulfide (CuS)	6.0×10^{-37}	Silver sulfide (Ag_2S)	6.0×10^{-51}
Iron(II) hydroxide [$Fe(OH)_2$]	1.6×10^{-14}	Strontium carbonate ($SrCO_3$)	1.6×10^{-9}
Iron(III) hydroxide [$Fe(OH)_3$]	1.1×10^{-36}	Strontium sulfate ($SrSO_4$)	3.8×10^{-7}
Iron(II) sulfide (FeS)	6.0×10^{-19}	Tin(II) sulfide (SnS)	1.0×10^{-26}
Lead(II) carbonate ($PbCO_3$)	3.3×10^{-14}	Zinc hydroxide [$Zn(OH)_2$]	1.8×10^{-14}
Lead(II) chloride ($PbCl_2$)	2.4×10^{-4}	Zinc sulfide (ZnS)	3.0×10^{-23}

Calculating K_{sp} from Solubility

The molar solubility of CaF_2 at 35˚C is 1.24×10^{-3} M.
(a) What is the solubility of CaF_2 in g/L? A: 0.968g/L

(b) What is K_{sp} at this temperature? A: 7.63×10^{-9}

Calculating Solubility from K_{sp}

The K_{sp} for LaF_3 is 2.0×10^{-19}.

(a) What is the molar solubility of LaF_3 in water? A: 9.3×10^{-6}M

(b) What is the solubility in g/L? A: 1.8×10^{-3}g/L

Comparing Molar Solubilities vs. K_{sp}

Compound	K_{sp}	Molar Solubility
$BaSO_4$	1.1×10^{-20}	1.0×10^{-5} M
$Mg_3(AsO_4)_2$	2.0×10^{-20}	5.0×10^{-5} M

Molar Solubility Comparison:

$Mg_3(AsO_4)_2$ molar solubility is 5X greater than $BaSO_4$

K_{sp} Comparison

$BaSO_4$ has a K_{sp} that is 10^9 X greater than $Mg_3(AsO_4)_2$

Be careful using K_{sp} directly to compare solubilities

- Number of ions present also matters
- Can only directly compare K_{sp} if # ions produced is identical

Factors Affecting Solubility:

Common-Ion Effect

- One of the ions in the compound is also part of another compound present in the solution

pH

- Presence of hydroxide (OH^-) or hydronium ions (H_3O^+)

Complexation

- Formation of coordinate bonds with solvent or other molecules present in solution

Common-Ion Effect

The extent of ionization of a weak electrolyte is <u>decreased</u> by the addition of a strong electrolyte that has an <u>ion in common</u> with the weak electrolyte.

Equilibrium process – presence of ions shifts process back to reactants.

Ex: A solution is made with 1.0M $CaCl_2$ and 2.0M $Ca(OH)_2$

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

$\longleftarrow$

Add extra Ca^{2+} from $CaCl_2$

Shift equilibrium

Will affect pH if solution is acidic or basic - in this case shift toward products decreases concentration of OH^- in solution.

Common-Ion Calculations

1. Calculate the pH of a solution containing 0.085M nitrous acid (HNO_2; $K_a = 4.5 \times 10^{-4}$) and 0.10M potassium nitrite (KNO_2).

A: pH = 3.42

2. The K_{sp} of $Mn(OH)_2$ is $1.6x10^{-13}$. Calculate the molar solubility of $Mn(OH)_2$ in:

a.) water A: $3.4x10^{-5}$M

b.) A solution that contains 0.020M NaOH A: $4.0x10^{-10}$M

c.) Compare the solubility of $Mn(OH)_2$ in these solutions

A: 85,000 times more soluble in water

3.) How much is the solubility of lead (II) chloride changed in the presence of 0.85M NaCl? $K_{sp} = 1.6x10^{-5}$

More than 700X less soluble than in water