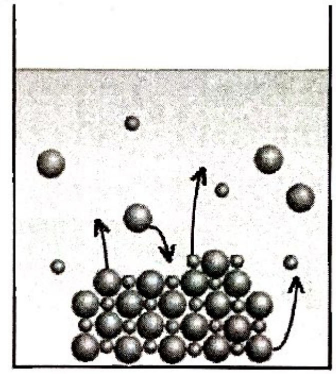
Solubility Equilibria: Dissolve All Your Troubles Away!

Up until now, we've pretended that compounds fall into one of two categories: 100% soluble or 100% insoluble. Actually, an equilibrium can exist between a partially soluble substance and its solution.



Solubility Product Constant (Ksp)

Equilibrium expression for dissolving a solid into ions

Like all K values, K_{sp} is constant at a constant temperature.

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

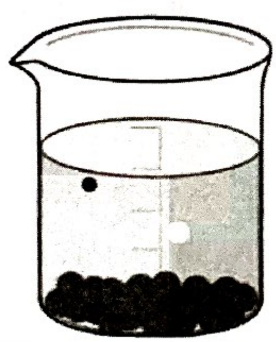
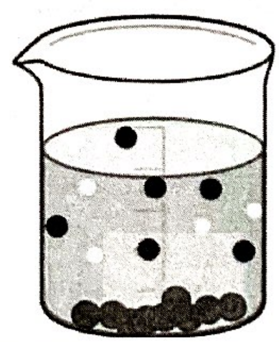
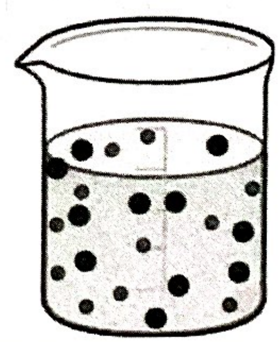
When the rate at which a solid dissolves into ions is equal to the rate at which ions precipitate back to solid, the system has reached equilibrium.

Let's Practice! Write the *Ksp* expression for each of the following dissolutions:

Salt	Dissociation reaction	K_{sp} Expression
K_2CO_3	$K_2CO_3(s) \rightleftarrows 2K^{+}(aq) + CO_3^{2-}(aq)$	$K_{sp} = [K^{+}]^2[CO_3^{2-}]$
Al_2S_3	$Al_2S_3(s) \rightleftarrows 2Al^{3+}(aq) + 3S^{2-}(aq)$	$K_{sp} = [Al^{3+}]^2[S^{2-}]^3$

Wait a sec, K_{sp} only has products! But why?

Dissolution always starts w/ a single, solid reactant, and solids aren't included in an equilibrium constant expression

Small K_{sp} ($K << 1$)	Larger K_{sp}	100% Soluble
• Only a small amount of solid dissociates into ions • Lower solubility	• More solid dissociates into ions • Higher solubility	• All solid dissociates into ions • Dissolves to completion
		

There are three types of 100% soluble ions that you have to memorize:

Always soluble: alkali metal cations, NH_4^{+} (ammonium), NO_3^{-} (nitrate)

K_{sp} Calculations

__Example__: When silver sulfide dissolves in pure water, $[S^{2-}] = 3.4 \times 10^{-17}$ mol/L at 25°C. Calculate its K_{sp} value.

$$Ag_2S_{(s)} \rightleftharpoons 2Ag^+_{(aq)} + S^{2-}_{(aq)}$$

Ag^+: 0, +2x, 2x $= (2)(3.4E-17) = 6.8E-17$

S^{2-}: 0, +x, $x = 3.4E-17$

$$K_{sp} = [Ag^+]^2[S^{2-}] = (6.8E-17)^2(3.4E-17) = \boxed{1.6 \times 10^{-49}}$$

OR: $[Ag^+]^2[S^{2-}] = (2x)^2 x = 4x^3 = 4(3.4E-17)^3 =$ ↑

Now you try!

1. What is the K_{sp} value of silver phosphate at 25°C, if $[PO_4^{3-}] = 1.8 \times 10^{-18}$ M when dissolved in pure water?

$$Ag_3PO_{4(s)} \rightleftharpoons 3Ag^+_{(aq)} + PO^{3-}_{4(aq)}$$

Ag^+: 0, +3x, 3x

PO_4^{3-}: 0, +x, $x = 1.8E-18$

$$K_{sp} = [Ag^+]^3[PO_4^{3-}] = (3x)^3 x = 27x^4 = 27(1.8E-18)^4 = \boxed{2.8 \times 10^{-70}}$$

2. What is the concentration of chloride ions that will form in a solution of $PbCl_2$ in pure water? The K_{sp} of lead (II) chloride at 25°C is 1.17×10^{-5}.

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

Pb^{2+}: +x

Cl^-: +2x

$$K_{sp} = [Pb^{2+}][Cl^-]^2 = x(2x)^2 = 4x^3 = 1.17E-5$$

$$\Rightarrow x = \sqrt[3]{\frac{1.17E-5}{4}} = \left(\frac{1.17E-5}{4}\right)^{1/3} = 0.0143$$

$$[Cl^-] = 2x = 2(0.0143) = \boxed{0.0286\,M}$$

But wait! The "_X_" term, for dissociation, always refers to the amount of _Solid_ that will dissolve (since the stoichiometric coefficient of the salt will always be _1_ in the dissociation reaction). This term has a special name!

<u>Solubility</u> "S" (aka <u>Molar Solubility</u>) = "x" in your K_{sp} RICE Table

How much of a _Solid_ will dissolve per _1.0_ L of solution (Units: M = mol/L)

Solubility is an equilibrium position and therefore _Can_ change (for example, if you change the number of ions in solution, this will shift the equilibrium position and thus, the solubility).

- Larger molar solubility values suggest _more_ dissociation into ions and <u>greater</u> solubility.
- Smaller molar solubility values suggest _less_ dissociation into ions and <u>lower</u> solubility.

Now we can answer problems using the same math we used on the previous page. The terminology will be different, but the calculations are the same! Let's try some:

3. The molar solubility of barium fluoride is at 25°C is 2.45×10^{-5} (= x, M). Calculate K_{sp}.

$$BaF_{2(s)} \rightleftharpoons Ba^{2+}_{(aq)} + 2F^-_{(aq)}$$

$+x$ $\quad$ $+2x$

$$K_{sp} = [Ba^{2+}][F^-]^2 = x(2x)^2 = 4x^3 = 4(2.45E-5)^3$$

$$= \boxed{5.88 \times 10^{-14}}$$

4. Calculate the molar solubility of nickel (II) carbonate, which has a K_{sp} of 1.4×10^{-7} at 25°C.

$$NiCO_{3(s)} \rightleftharpoons Ni^{2+}_{(aq)} + CO^{2-}_{3(aq)}$$

$+x$ $\quad$ $+x$

$$K_{sp} = [Ni^{2+}][CO_3^{2-}] = x^2 = 1.4E-7$$

$$x = \sqrt{1.4E-7} = \boxed{3.7 \times 10^{-4}\ M}$$