SOLUBILITY OF A SLIGHTLY SOLUBLE SALT

One important example of heterogeneous equilibria is the solubility of a slightly soluble salt. The equilibrium expression for this is termed the **solubility product, K_{SP}**.

For example, the compound, $Mg(OH)_2$, has the following equilibrium.

$$Mg(OH)_2(s) \Leftrightarrow Mg^{2+}(aq) + 2OH^{-}(aq)$$

$$K_{SP} = [Mg^{2+}][OH^{-}]^2$$

Solubility values are for saturated solutions and thus are equilibrium values. Solubilities are generally provided in units of g/100 mL solution or in terms of molarity (termed **molar solubility**).

Example1:
Calculate the K_{SP} for $Mg(OH)_2$ if at 25°C the solubility is 9.3×10^{-4} g/100mL.

First, the **molar solubility** must be calculated.

$$\left(\frac{9.3x10^{-4}g\ Mg(OH)_2}{100\ mL}\right)\left(\frac{1mol\ Mg(OH)_2}{58.31g\ Mg(OH)_2}\right)\left(\frac{1000\ mL}{1L}\right) = 1.6x10^{-4}\,\tfrac{mol}{L}\ Mg(OH)_2$$

Second, an ICE chart and the solubility product equilibrium expression are set up.

	$Mg(OH)_2(s)$ ⇔	Mg^{2+}	+	$2OH^{-}$
I	X	0		0
C		+x		+2x
E		x		2x

$$K_{SP} = [Mg^{2+}][OH^-]^2$$
$$K_{SP} = (x)\,(2x)^2 = 4x^3$$

x = change and thus the amount of $Mg(OH)_2$ that has dissolved to form Mg^{2+} and OH^- ions.

Thus:

$$x = \text{molar solubility value} = 1.6 \text{ x } 10^{-4} \text{ mol/L}$$

$$K_{SP} = 4x^3 = 4*(1.6 \text{ x } 10^{-4} \text{ M})^3 = 1.6 \text{ x } 10^{-11} \text{ M}^3$$

The K_{SP} value for $Mg(OH)_2$ of $1.6 \text{ x } 10^{-11}$ agrees well with the text value of $1.8 \text{ x } 10^{-11}$. In a latter section, several reasons as to why the values may vary (within an order of magnitude) will be presented.

Example2:

Calculate the molar solubility of AgBr at 25°C. $K_{SP} = 5.4 \text{ x } 10^{-13}$.

	AgBr(s)	⇔	Ag^+	+	Br^-
I	X		0		0
C			+x		+x
E			x		x

$$K_{SP} = [Ag^+][Br^-]$$
$$5.4 \text{ x } 10^{-13} = x^2$$
$$x = 7.3 \text{ x } 10^{-7} \text{ M} = \text{molar solubility}$$

$\mathbf{K_{SP}}$ is a constant depending only upon temperature.
Molar solubility, however, can be affected by other solution factors. One key factor is the "**common ion effect**."

In Example 1, the molar solubility for $Mg(OH)_2$ was given as 1.6×10^{-4} M in pure water. What is the molar solubility of $Mg(OH)_2$ in 0.10M $Mg(NO_3)_2$? $K_{SP} = 1.8 \times 10^{-11}$

	$Mg(OH)_2(s)$ ⇔	Mg^{2+}	+	$2OH^-$
I	X	0.10M		0
C		+x		+2x
E		0.10 +x		2x

$$K_{SP} = [Mg^{2+}][OH^-]^2$$
$$1.8 \times 10^{-11} = (0.10 + x)\,(2x)^2$$
$$x = 6.7 \times 10^{-6}\ M$$

Much lower solubility.

The "common ion" Mg^{2+} decreases solubility. Does it make a difference if the common ion is the hydroxide?

What is the molar solubility of $Mg(OH)_2$ in a NaOH solution with a pH of 12.50?
pOH = 14.00 – 12.50 = 1.50 $[OH^-] = 10^{-1.50} = 3.2 \times 10^{-2}$M

	$Mg(OH)_2(s)$ ⇔	Mg^{2+}	+	$2OH^-$
I	X	0		3.2×10^{-2}M
C		+x		+2x
E		x		$3.2 \times 10^{-2} + 2x$

$$K_{SP} = [Mg^{2+}][OH^-]^2$$
$$1.8 \times 10^{-11} = (x)\,(3.2 \times 10^{-2} + 2x)^2$$
$$x = 1.8 \times 10^{-8}\ M$$

Even lower solubility.

Presence of either common ion shifts the equilibrium to the left so the solubility decreases.

The value calculated for the molar solubility using K_{SP} may vary significantly from the experimental value.

Reasons for variations include the following.

1. In calculations, molar concentrations are used. In actuality, the correct form is "activity" which involves other experimental factors including charge.

2. Complete dissociation of the ionic compound is assumed. This is not always true. For example, for $Mg(OH)_2$, the ions in solution may be Mg^{2+}, OH^-, $MgOH^+$, and $Mg(OH)_2$.

3. Some salts hydrolyze in water. This is especially true of sulfides. Instead of the reaction $ZnS(s) \Leftrightarrow Zn^{2+} + S^{2-}$
the reaction is $ZnS(s) + H_2O \Leftrightarrow Zn^{2+} + OH^- + HS^-$
In fact HS^- is the major species because S^{2-} is the conjugate base of a **very weak acid** so $S^2 + H_2O \Leftrightarrow OH^- + HS^-$
occurs to a significant extent.

4. pH affects the solubility of many compounds. For example,
$CaCO_3(s) + H_3O^+ \rightarrow HCO_3^- + Ca^{2+} + H_2O$

5. Complex ions form in some cases.
$AgCl(s) \Leftrightarrow Ag^+ + Cl^-$
$Ag^+ + 2Cl^- \Leftrightarrow AgCl^{2-}$

Complex Ion Formation

Example: AgCl is very soluble in ammonia because a complex ion is formed.

$$AgCl(s) \Leftrightarrow Ag^{+} + Cl^{-} \qquad K_{SP} = [Ag^{+}][Br^{-}]$$

$$Ag^{+} + 2NH_3 \Leftrightarrow Ag(NH_3)_2^{+} \qquad K_f = \frac{\left[Ag(NH_3)_2^{+}\right]}{\left[Ag^{+}\right]\left[NH_3\right]^2}$$

Net: $AgCl(s) + 2NH_3 \Leftrightarrow Ag(NH_3)_2^{+} + Cl^{-}$

When the two equilibrium reactions are added together, the new equilibrium constant for the net reaction is determined by calculating the product of the two separate K values.

$$K_{NET} = K_{SP} * K_f = \left(\left[\mathbf{Ag^{+}}\right]\left[\mathbf{Cl^{-}}\right]\right)\frac{\left[\mathbf{Ag(NH_3)_2^{+}}\right]}{\left[\mathbf{Ag^{+}}\right]\left[\mathbf{NH_3}\right]^{2}}$$

$$K_{NET} = K_{SP} * K_f = \frac{\left[\mathbf{Cl^{-}}\right]\left[\mathbf{Ag(NH_3)_2^{+}}\right]}{\left[\mathbf{NH_3}\right]^{2}}$$

$$K_{NET} = K_{SP} * K_f = \left(1.8x10^{-10}\right)\left(1.7x10^{7}\right) = 3.1x10^{-3}$$

Now use the new K value to detemine the solubility of AgCl in 0.50M NH_3.

	$AgCl(s)$ +	$2NH_3$ $\Leftrightarrow$	$Ag(NH_3)_2^{+}$ +	Cl^{-}
I	X	0.50 M	0	0
C		–2x	+x	+x
E		0.50-2x	x	x

$$K_{NET} = \frac{[\mathbf{Cl^-}][\mathbf{Ag(NH_3)_2^+}]}{[NH_3]^2}$$

$$3.1x10^{-3} = \frac{(x)(x)}{(0.50 - 2x)^2}$$

$x = 2.5 \text{ x } 10^{-2}M$

So the molar solubility of AgCl is $2.5 \text{ x } 10^{-2}M$ versus $1.3 \text{ x } 10^{-5}M$ in pure water.

Using Q_{SP} to predict whether or not a precipitate will form.

If $Q_{SP} = K_{SP}$ the solution is saturated and in equilibrium.
If $Q_{SP} > K_{SP}$ a precipitate will form (R<–P).
If $Q_{SP} < K_{SP}$ still soluble so no precipitate.

Example:
The pH of a hard water sample have a magnesium ion concentration of 2.5×10^{-4} M is adjusted to 10.80. Will the magnesium ion precipitate as $Mg(OH)_2$?
$K_{SP} = 1.8 \times 10^{-11}$ for $Mg(OH)_2$

To check, determine the $Q_{SP.}$
$[Mg^{2+}] = 2.5 \times 10^{-4}$ M
$[OH^-] = 10^{-3.20} = 6.3 \times 10^{-4}$ M since pOH = 14.00 – pH

$Q_{SP} = [Mg^{2+}][OH^-]^2 = (2.5 \times 10^{-4} \text{ M})(6.3 \times 10^{-4} \text{ M})^2$
$Q_{SP} = 1.0 \times 10^{-10}$

$Q_{SP} > K_{SP}$
1.0×10^{-10} 1.8×10^{-11}

Precipitate will form.

Once known that a precipitate will form, determine how much precipitate will form in a 250 mL sample of the water.

	$Mg(OH)_2(s)$ ⇔	Mg^{2+}	+	$2OH^-$
I	X	2.5×10^{-4} M		6.3×10^{-4} M
C		$-x$		$-2x$
E		$2.5 \times 10^{-4} - x$		$6.3 \times 10^{-4} - 2x$

$$K_{SP} = [Mg^{2+}][OH^{-}]^2$$
$$1.8 \times 10^{-11} = (2.5 \times 10^{-4} - x)(6.3 \times 10^{-4} - 2x)^2$$

$x = 1.25 \times 10^{-4}$ M
This is amount that reacts to form precipitate

In a 250 mL sample, the amount in grams can now be calculated.

$$(0.250\text{L})\left(\frac{1.25\text{x}10^{-4}\text{mol Mg(OH)}_2}{\text{L}}\right) = 3.1\text{x}10^{-5}\text{mol Mg(OH)}_2$$

$$\left(3.1\text{x}10^{-5}\text{mol Mg(OH)}_2\right)\left(\frac{58.31\text{g Mg(OH)}_2}{\text{mol}}\right) = 0.0018\text{g Mg(OH)}_2$$