Continuing

Chapter 18 · Equilibria in Aqueous Solutions – Solubility Product

We are now going to consider compounds that are only slightly soluble or "insoluble" in aqueous solutions. Quotation marks are used since nearly all compounds are soluble in water to some extent.

Rule of thumb used by some (but don't worry about it): If a compound dissolves in water to give 0.020 moles/L in solution, it is considered to be soluble. But there is a large gray area where substances are considered slightly soluble.

To work with slightly soluble compounds, a special equilibrium constant is used: the SOLUBILITY PRODUCT.

Consider AgCl:

This compound appears on the chart on back of exam envelope called SOLUBILITY PRODUCTS. So we know it is "insoluble" or rather slightly soluble.

In aqueous solution

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

$$K_c = K_{sp} = [Ag^+][Cl^-] = 1.8 \times 10^{-10} \quad \text{at } 25°C$$

(K_{sp}: solubility product)

Examples of solubility product expressions:

1. $Al(OH)_3(s) \rightleftharpoons Al^{3+}(aq) + 3\,OH^-(aq)$

$$K_{sp} = [Al^{3+}][OH^-]^3 = 1.9 \times 10^{-33}$$

2. $Bi_2S_3(s) \rightleftharpoons 2\,Bi^{3+}(aq) + 3\,S^{-2}(aq)$

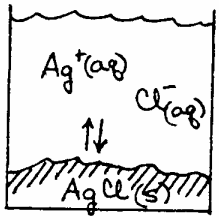
$$K_{sp} = [Bi^{3+}]^2[S^{-2}]^3 = 1.6 \times 10^{-72}$$

In general, $M_n X_y(s) \rightleftharpoons n M^{y+}(aq) + y X^{n-}(aq)$

$$K_{sp} = [M^{y+}]^n [X^{n-}]^y$$

Note: as the K_{sp} value gets smaller, the solid becomes <u>less</u> soluble
as the K_{sp} value gets larger, the solid becomes <u>more</u> soluble.

What does the solubility expression mean? It allows us to calculate the concentrations of the ions at equilibrium with the parent solid in aqueous solution at 25°C, provided we know the K_{sp} value.



when the system is at equilibrium
solid $\rightleftharpoons$ ions
eg $AgCl(s) \rightleftharpoons Ag^+(aq) + Cl^-(aq)$
and $K_{sp} = 1.8 \times 10^{-10} = [Ag^+][Cl^-]$
the solution is called SATURATED!!

How is K_{sp} determined for solids? The solid is put in water at 25°C and stirred until solid dissolves as much as it can forming a saturated solution. The molar solubility of the solid is measured + K_{sp} is calculated. So, what is molar solubility?

molar solubility: the number of moles of a compound that dissolve to give one liter of saturated solution.

Example: The molar solubility, s, of barium sulfate ($BaSO_4$) is 1.05×10^{-5} M. What is K_{sp} of $BaSO_4$?

$$BaSO_4(s) \rightleftharpoons Ba^{2+}(aq) + SO_4^{2-}(aq)$$

if $s = 1.05 \times 10^{-5}$ moles dissolves in 1L soln $\Rightarrow$ $1.05 \times 10^{-5} \frac{\text{moles}}{\text{L}}$ (s) $\quad 1.05 \times 10^{-5} \frac{\text{moles}}{\text{L}}$ (s)

$$\therefore K_{sp} = [Ba^{2+}][SO_4^{2-}] = s^2 = (1.05 \times 10^{-5})^2 = 1.1 \times 10^{-10}$$

where s = molar solubility

Example: One liter of a saturated solution of barium phosphate ($Ba_3(PO_4)_2$, MW = 601.8 g/mol) contains 3.94×10^{-4} g of $Ba_3(PO_4)_2$. Calculate the K_{sp} for $Ba_3(PO_4)_2$.

Plan: (1) calculate s, molar solubility
(2) write the K_{sp} expression in terms of s
(3) solve for K_{sp}.

(1) molar solubility $= \frac{\text{moles } Ba_3(PO_4)_2}{\text{liter soln}} = \frac{(3.94 \times 10^{-4} \text{ g} / 601.8 \text{ g/mol})}{1 \text{ liter}} = 6.55 \times 10^{-7} \text{ M}$

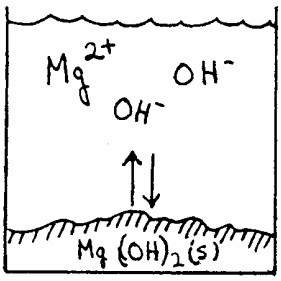
(2) $Ba_3(PO_4)_2(s) \rightleftharpoons 3\,Ba^{2+}(aq) + 2\,PO_4^{3-}(aq)$

if s is molar solubility, then at equilibrium $\Rightarrow$ $3s$ $2s$

$\therefore K_{sp} = [Ba^{2+}]^3[PO_4^{3-}]^2 = (3s)^3(2s)^2 = 27s^3 \times 4s^2 = 108\,s^5$

(3) $K_{sp} = 108\,(6.55 \times 10^{-7})^5 = (108)(1.21 \times 10^{-31}) = 1.30 \times 10^{-29}$

Example: Given a saturated solution of $Mg(OH)_2$ ($K_{sp} = 1.5 \times 10^{-11}$)
(a) What is the molar solubility of $Mg(OH)_2$? What is solubility (g/100mL)?
(b) What are the concentrations of Mg^{2+} and OH^- and the pH in saturated solution?



for every 1 mole of $(OH)_2(s)$ that dissolves, we get 1 mole of Mg^{2+} ions and 2 moles of OH^- ions.

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

if s = number of moles of $Mg(OH)_2$ that dissolve in 1 liter (molar solubility) $\Rightarrow$ s $2s$

(a) $K_{sp} = 1.5 \times 10^{-11} = [Mg^{2+}][OH^-]^2 = (s)(2s)^2 = 4s^3$

$\therefore s^3 = \frac{1.5 \times 10^{-11}}{4} = 3.75 \times 10^{-12}$

molar solubility, $s = \sqrt[3]{3.75 \times 10^{-12}} = (3.75 \times 10^{-12})^{\frac{1}{3}} = 1.55 \times 10^{-4}$ M

Note: to take the third root on calculator (or any root)

I	II	III
enter 3.75×10^{-12}	enter 3.75×10^{-12}	enter 3.75×10^{-12}
push $\sqrt[x]{y}$ or inv y^x	push y^x	push log
enter 3	enter $\frac{1}{3}=0.333$	push ÷, 3, =
push =	push =	push inv log

$$\therefore \text{solubility}\left(\frac{g}{100mL}\right) = \frac{1.55\times10^{-4}\ \text{moles}}{1\ \text{liter}} \times \frac{58\ g}{1\ \text{mole}} \times \frac{0.1\,L}{(100mL)} = 8.9\times10^{-4}\frac{g}{100mL}$$

(do not divide by 100)

OR we can reason:

we know, 1.55×10^{-4} moles of $Mg(OH)_2$ are dissolved in 1 liter solution

$\therefore 1.55\times10^{-5}$ moles of $Mg(OH)_2$ are dissolved in 100 mL (=0.1L) soln

and $?g = 1.55\times10^{-5}\ \text{moles} \times 58\ g/mol = 8.9\times10^{-4}\ g$

$$\therefore \text{solubility}\left(g/100mL\right) = 8.9\times10^{-4}\ g/100mL$$

(b) molar solubility = $s = [Mg^{2+}] = 1.55\times10^{-4}\ M$

$2s = [OH^-] = 3.1\times10^{-4}\ M$

$pOH = 3.51$

$pH = 14 - 3.51 = 10.49$

Common Ion Effect

In the calculations we have done so far, a solid has dissolved in water until an equilibrium is reached between the solid and its dissolved ions. What happens to the equilibrium if we add more of one of the ions?

Consider a saturated solution of magnesium fluoride: $MgF_{2(s)} \rightleftarrows Mg^{2+}_{(aq)} + 2F^-_{(aq)}$

$$K_{sp} = [Mg^{2+}][F^-]^2$$

What happens if more Mg^{2+} ions or more F^- ions are added?

The equilibrium shifts to the reactant side. The concentrations of ions, due to the dissolution of MgF_2, decreases; MgF_2 becomes less soluble and precipitates out until equilibrium is reached.

Example: Calculate the moles of MgF_2 that will dissolve in 1.00 L of (a) pure water (b) 0.010 M $Mg(NO_3)_2$ and (c) 0.010 M NaF.
Note: we are calculating molar solubility. K_{sp} $MgF_2 = 6.4 \times 10^{-9}$

(a) pure water: $MgF_2(s) \rightleftarrows Mg^{2+}(aq) + 2F^-(aq)$
let x = molar solubility: $x \quad 2x$

$K_{sp} = 6.4\times10^{-9} = [Mg^{2+}][F^-]^2 = (x)(2x)^2 = 4x^3$
$\therefore x = 1.2\times10^{-3}$ M = moles of MgF_2 required to make 1 L saturated solr

(b) 0.010 M $Mg(NO_3)_2$: $MgF_2(s) \rightleftarrows Mg^{2+}(aq) + 2F^-(aq)$
let y = molar solubility: $y + 0.010 \quad 2y$

$K_{sp} = 6.4\times10^{-9} = [Mg^{2+}][F^-]^2 = (\cancel{x} + 0.010)(2y)^2 = (0.010)\,4y^2$ (Rule of Thumb)
$\therefore y = 4.0\times10^{-4}$ M = moles/L required to make saturated solution

(c) 0.010 M NaF: $MgF_2(s) \rightleftarrows Mg^{2+}(aq) + 2F^-aq$
let z = molar solubility: $z \quad 2z + 0.010$

$K_{sp} = 6.4\times10^{-9} = [Mg^{2+}][F^-]^2 = (z)(\cancel{2z} + 0.010)^2 = (z)(0.010)^2$ (Rule of Thumb)
$z = 6.4\times10^{-5}$ M = mol/L required to prepare saturated solution

Therefore in a solution with a common ion, the solubility of the compound decreases dramatically.

<u>More Uses of the Solubility Product</u> – Systems with <u>NO</u> solid present initially.

I When given a solution containing ions, it is useful to know if a precipitate will form.
To predict precipitation, we use Qsp (Reaction Quotient - Ch 17)
Consider $M_nX_y \rightleftarrows n\,M^{y+} + y\,X^{n-}$ $\quad Q_{sp} = [M^{y+}]^n[X^{n-}]^y$
where conc^n are NOT necessarily the equil. conc^n.

If $Q_{sp} = K_{sp}$ the system is at equilibrium
the ions are forming a precipitate just as fast as the solid is dissolving
the solution is <u>saturated</u>.

$Q_{sp} > K_{sp}$ the solution is <u>supersaturated</u> - the solubility is exceeded
a precipitate will form and will continue to form <u>until</u> the concentration of ions in the solution decrease to such a point that $Q_{sp} = K_{sp}$.
when the system is at equilibrium.

$Q_{sp} < K_{sp}$ the solution is <u>undersaturated</u>
no precipitation will occur.

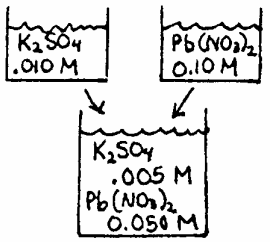
Example: If equal amounts of 0.010 M K_2SO_4 and 0.10 M $Pb(NO_3)_2$ solutions are mixed, will a precipitate form?

Step 1: What could the precipitate be?
The ions present are K^+ SO_4^{2-} Pb^{2+} and NO_3^-
Possible choices (switching partners): KNO_3? nope - is soluble
$PbSO_4$? yes
$K_{sp} = 1.8 \times 10^{-8}$

$\therefore PbSO_4$ may precipitate if $Q_{sp} > K_{sp}$

Step 2: Write the solubility product expression:
$K_{sp} = 1.8 \times 10^{-8} = [Pb^{2+}][SO_4^{2-}]$ at equilibrium

Step3: Calculate Q_{sp} for the final solution.



$Q_{sp} = [Pb^{2+}][SO_4^{2-}]$
$= (0.050\ M)(0.005\ M)$
$= 2.5 \times 10^{-4}$

Since equal volumes of the solutions are added together the concentration of each compound is halved in the final solution.

Step 4 : Compare Q_{sp} with K_{sp} :

in this case $Q_{sp} > K_{sp}$ ∴ the solution is supersaturated and a precipitate will form until the concentrations of the ions satisfy the solubility product expression.

Aside - for your interest : What are the concentrations of Pb^{2+} and SO_4^{2-} remaining in solution after the system reached equilibrium

since $Pb^{2+} + SO_4^{2-} \rightarrow PbSO_4$

	Pb^{2+}	SO_4^{2-}
$t=0$	0.05	0.005
$t=t_{eq}$	0.05-x	0.005-x

$$K_{sp} = 1.8 \times 10^{-8} = [Pb^{2+}][SO_4^{2-}]$$

$$= (0.05 - x)(0.005 - x)$$

$$1.8 \times 10^{-8} = x^2 - 0.055x + 2.5 \times 10^{-4}$$

$$0 = x^2 - 0.055x + 2.5 \times 10^{-4}$$ solve by quadratic

$$x = \cancel{0.05}\ ;\ 0.005$$

What does this mean? That at equilibrium, nearly all of the SO_4^{2-} ions have been removed from solution. ∴ $x = 0.004999\cdots$.

Let's solve for x

$$1.8 \times 10^{-8} = (0.05 - \overset{x}{0.005})(0.005 - x)$$ where x is very close to 0.005.

$$= (0.045)(0.005 - x)$$

$$0.005 - x = 4 \times 10^{-7}$$

$$x = 0.0049996$$

∴ concentrations still in solution: $[Pb^{2+}] = 0.045\ M$

$[SO_4^{2-}] = 4.0 \times 10^{-7}\ M$

Example:

(a) If equal amounts of 0.004 M $Pb(NO_3)_2$ and 0.004 M Na_2SO_4 are mixed will a precipitate form?

(b) if equal amounts of 0.004 M $Pb(NO_3)_2$ and 0.004 M KF are mixed will a precipitate form?

Step 1. What <u>could</u> the precipitate be?

(a) ions present: Pb^{2+} NO_3^- Na^+ SO_4^{2-}

possible choices (switch partners): $NaNO_3$ - nope - is soluble

$PbSO_4$ - yes

$K_{sp} = 1.8 \times 10^{-8}$

∴ if $Q_{sp} > K_{sp}$, a precipitate of $PbSO_4$ will form

(b) ions present: Pb^{2+} NO_3^- K^+ F^-

possible choices (switch partners): KNO_3 - nope - is soluble too

PbF_2 - yes

$K_{sp} = 3.7 \times 10^{-8}$

∴ if $Q_{sp} > K_{sp}$, a precipitate of PbF_2 will form.

Step 2. Write the solubility product expression.

(a) for $PbSO_4$ $K_{sp} = 1.8 \times 10^{-8} = [Pb^{2+}][SO_4^{2-}]$

(b) for PbF_2 $K_{sp} = 3.7 \times 10^{-8} = [Pb^{2+}][F^-]^2$

Step 3. Calculate Q_{sp} for final solution

(a) 0.004 M $Pb(NO_3)_2$ + 0.004 M Na_2SO_4 → 0.002 M $Pb(NO_3)_2$, 0.002 M Na_2SO_4

Note: since equal volumes are added together, the concentration of each is halved

$Q_{sp} = [Pb^{2+}][SO_4^{2-}]$

$= (0.002)^2$

$= 4 \times 10^{-6}$

$Q_{sp} > K_{sp}$ ∴ precipitation

(b) 0.004 M $Pb(NO_3)_2$ + 0.004 M KF → 0.002 M $Pb(NO_3)_2$, 0.002 M KF

$Q_{sp} = [Pb^{2+}][F^-]^2$

$= [0.002)(0.002)^2$

$= 8 \times 10^{-9}$

$Q_{sp} < K_{sp}$ ∴ no precipitation

In-Class Quiz

1. Write the solubility product expressions for
   (a) calcium hydroxide, $Ca(OH)_2$ (b) $Sr_3(PO_4)_2$, strontium phosphate

2. Write the above K_{sp} expressions in terms of s, the molar solubility

3. Calculate the molar solubility for $Sr_3(PO_4)_2$. $K_{sp} = 1.0 \times 10^{-31}$

4. If equal volumes of the following solutions are mixed, will a precipitate form?
   (a) 3.0×10^{-6} M $NiCl_2$ and 6.0×10^{-4} M Na_2CO_3 ($K_{sp\ NiCO_3} = 6.6 \times 10^{-9}$)
   (b) 2.0×10^{-2} M NaF and 2.0×10^{-3} M $MgCl_2$ ($K_{sp\ MgF_2} = 6.4 \times 10^{-9}$)

Answers:

1. (a) $K_{sp} = [Ca^{2+}][OH^-]^2$ (b) $K_{sp} = [Sr^{2+}]^3[PO_4^{3-}]^2$

2. (a) $Ca(OH)_2(s) \rightleftarrows Ca^{2+}(aq) + 2OH^-(aq)$ $K_{sp} = (s)(2s)^2 = 4s^3$
   s = molar solubility; Ca^{2+}: s; OH^-: 2s

   (b) $Sr_3(PO_4)_2(s) \rightleftarrows 3Sr^{2+}(aq) + 2PO_4^{3-}(aq)$ $K_{sp} = (3s)^3(2s)^2 = (27s^3)(4s^2) = 108\,s^5$
   s = molar solubility; Sr^{2+}: 3s; PO_4^{3-}: 2s

3. $K_{sp} = 1.0 \times 10^{-31} = 108\,s^5$ (see 2 b)
   $s^5 = 9.26 \times 10^{-34}$
   $s = 2.5 \times 10^{-7}$ M

4. (a) $Q_{sp} = [Ni^{2+}][CO_3^{2-}] = (1.5 \times 10^{-6}\ M)(3.0 \times 10^{-4}\ M) = 4.5 \times 10^{-10}$
   $Q_{sp} < K_{sp}$ $\therefore$ $NiCO_3$ does NOT precipitate

   (b) $Q_{sp} = [Mg^{2+}][F^-]^2 = (1.0 \times 10^{-3}\ M)(1.0 \times 10^{-2}\ M)^2 = 1.0 \times 10^{-7}$
   $Q_{sp} > K_{sp}$ $\therefore$ MgF_2 will precipitate.

II Example: (a) What concentration of Cu^{2+} is necessary to initiate precipitation from a solution containing 0.0015 M KOH? K_{sp} $Cu(OH)_2 = 1.6 \times 10^{-19}$
(Hint: precipitation is initiated at equilibrium!!) (This is #25 in Ch 20)

$$Cu(OH)_2(s) \rightleftarrows \underset{?}{Cu^{2+}(aq)} + \underset{0.0015\ M}{2OH^-(aq)}$$

do NOT double. The concentration of OH^- is what it is.

$$K_{sp} = 1.6 \times 10^{-19} = [Cu^{2+}][OH^-]^2 = [Cu^{2+}](0.0015\ M)^2$$
$$\therefore [Cu^{2+}] = 7.1 \times 10^{-14}\ M$$

(b) Suppose more solid $Cu(NO_3)_2$ was added until $[Cu^{2+}] = 0.0015$ M. What would be $[OH^-]$ in the solution? What is pH? (ignore effect of Cu^{2+} a weak acid)

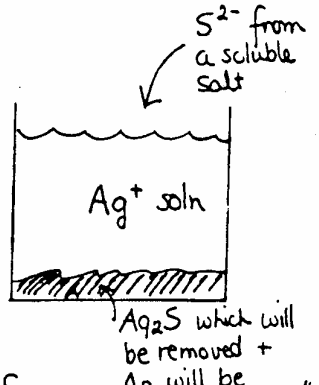
$$Cu(OH)_2(s) \rightleftarrows \underset{0.0015\ M}{Cu^{2+}(aq)} + \underset{?}{2OH^-(aq)}$$

$$K_{sp} = 1.6 \times 10^{-19} = [Cu^{2+}][OH^-]^2 = (0.0015\ M)[OH^-]^2$$
$$[OH^-]^2 = 1.07 \times 10^{-16}$$
$$[OH^-] = 1.0 \times 10^{-8}\ M;\ pOH = 8.00;\ pH = 6.00$$

Example: If silver ions are to be removed from solution by precipitation of Ag_2S, what final concentration of sulfide ions are required to reduce the Ag^+ concentration to 1.0×10^{-12} M? K_{sp} $Ag_2S = 1.0 \times 10^{-49}$

$$Ag_2S(s) \rightleftarrows \underset{1.0 \times 10^{-12}\ M}{2Ag^+(aq)} + \underset{?}{S^{2-}(aq)}$$

$$K_{sp} = 1.0 \times 10^{-49} = [Ag^+]^2[S^{2-}]$$
$$= (1.0 \times 10^{-12})^2 [S^{2-}]$$
$$\therefore [S^{2-}] = 1.0 \times 10^{-25}\ M$$



As more & more S^{2-} (from Na_2S) added, more & more Ag_2S precipitates out, but there is a tiny amount of S^{2-} and Ag^+ ions that are in solution at all times.

Fractional Precipitation (For Interest Only)

Fractional precipitation is the process whereby some ions are removed from solution while leaving other ions with similar properties still in solution.

Example: If solid NaCl is added slowly to a solution that is 0.010 M each in Cu^+, Ag^+ and Au^+, which salt precipitates first?

Cu^+	$K_{sp} = [Cu^+][Cl^-] = 1.9 \times 10^{-7}$	$CuCl(s) \rightleftharpoons Cu^+(aq) + Cl^-(aq)$
Ag^+	$K_{sp} = [Ag^+][Cl^-] = 1.8 \times 10^{-10}$	$AgCl(s) \rightleftharpoons Ag^+(aq) + Cl^-(aq)$
Au^+	$K_{sp} = [Au^+][Cl^-] = 2.0 \times 10^{-13}$	$AuCl(s) \rightleftharpoons Au^+(aq) + Cl^-(aq)$

We are adding Cl^- ions. In which system does $Q_{sp} > K_{sp}$ first?

ANSWER: The system with the smallest K_{sp} (with most insoluble salt)
∴ Au^+ precipitates out first as AuCl, then Ag^+, then Cu^+
as AgCl, as CuCl

Further calculations can be made :