Q: Will a precipitate form when 10.00 mL of 0.10 M lead nitrate are mixed with 40.00 mL of 0.010 M hydrochloric acid?

\[ \text{Pb(NO}_3\text{)}_2(aq) + 2 \text{HCl}(aq) \leftrightarrow \text{PbCl}_2(s) + 2 \text{HNO}_3(aq) \]

\[ \text{Pb}^{2+}(aq) + 2 \text{Cl}^-(aq) \leftrightarrow \text{PbCl}_2(s) \]

Imagine complete precipitation.

\[ \text{PbCl}_2(s) \leftrightarrow \text{Pb}^{2+}(aq) + 2 \text{Cl}^-(aq) \]

\[ K_{sp} = 1.6 \times 10^{-5} \]

Then see if there are enough ions to saturate the solution.
\[ Q = \left[ \text{Pb}^{2+} \right]_{\text{exp}} \left[ \text{Cl}^{-} \right]_{\text{exp}}^2 \]

\[ = \frac{1.00 \text{ mmol Pb}^{2+}}{50.00 \text{ mL}} \left( \frac{0.40 \text{ mmol Cl}^{-}}{50.00 \text{ mL}} \right)^2 \]

\[ = 1.3 \times 10^{-6} \]

\[ Q < K_{sp} \]

Probably, all the \text{PbCl}_2 will remain in solution.
Most of the shortcomings of the Ksp model that I have discussed would tend to make the salt more soluble than the model would suggest. However, there are other effects which are less obvious.

Making a precipitate by mixing two solutions is a bit different from dissolving the salt in water.

1) the ions may not be mixed in the same ratio as they occur in the salt

2) the spectator ions may affect solubility

3) the solution may not be ideal (some ions may interact with water more strongly than others)

\[
\begin{align*}
\text{Pb}^{2+} + \text{H}_2\text{O} &\rightarrow \text{Pb(OH)}^+ + \text{H}^+ \\
\sum \text{Pb}^{2+} &= 5 \\
\sum \text{Cl}^- &= 25
\end{align*}
\]

\[
\text{HCl} \rightarrow \text{H}^+ + \text{Cl}^-
\]

\[
\text{Pb(NO}_3\text{)}_2
\]

\[
\text{no fixed ratio of [Pb}^{2+} \text{] to [Cl}^- \text{]}
\]

Salt more soluble in more polar solution

\[
\text{H}^+ \text{ suppresses hydrolisis}
\]
Q: What are the concentrations of all ions in solution after 10.00 mL of 2.0 M lead nitrate is mixed with 100.00 mL of 2.0 M HCl?

\[ Q = \left( \frac{20.0 \text{ mmol}}{110.0 \text{ mL}} \right) \left( \frac{200 \text{ mmol}}{110.0 \text{ mL}} \right)^2 \]

\[ Q = 0.60 \]

\[ Q > K_{sp} \quad \text{ppt will result} \]

After ppt is complete:

\[ [\text{NO}_3^-] = 4.0 \text{ M} \left( \frac{10.0 \text{ mmol}}{110.0 \text{ mL}} \right) = 0.36 \text{ M} \]

\[ [\text{H}^+] = 2.0 \text{ M} \left( \frac{100.0 \text{ mmol}}{110.0 \text{ mL}} \right) = 1.8 \text{ M} \]
\[ \begin{align*}
\text{PbCl}_2 & \quad \text{n Pb}^{2+} \\
\text{c} & \quad 20 \text{ mmol} \\
\text{c} & \quad -20 \text{ mmol} \\
\text{e} & \quad 0 \\
\Sigma \text{Cl}^- & \quad \frac{160}{110 \text{ mL}} \\
\Sigma \text{Cl}^- & \quad 1.45 \text{ M} = 1.4 \text{ M}
\end{align*} \]

Use \( K_{sp} \) to find \( [\text{Pb}^{2+}] \)

\[
1.6 \times 10^{-5} = [\text{Pb}^{2+}] \left( \frac{1.45}{1.64} \right)^2
\]

\[
[\text{Pb}^{2+}] = 7.6 \times 10^{-6} \text{ M}
\]
Parts per million

Q: Can hard water that is 250 ppm in calcium ions be made 1 ppm in fluoride?

\[
\text{CaF}_2 \rightleftharpoons \text{Ca}^{2+} + 2\text{F}^-
\]

\[K_{sp} = 3.9 \times 10^{-11} \text{ for CaF}_2\]

\[
\frac{2.50 \text{ g Ca}^{2+}}{10^6 \text{ g H}_2\text{O}} \times \frac{10^3 \text{ g H}_2\text{O}}{1 \text{ L}} \times \frac{1 \text{ mO Ca}^{2+}}{40.1 \text{ g Ca}^{2+}}
\]

\[\left[\text{Ca}^{2+}\right] = 6.23 \times 10^{-3} \text{ M}\]

\[
\frac{1 \text{ g F}^-}{10^6 \text{ g H}_2\text{O}} \times \frac{10^3 \text{ g H}_2\text{O}}{1 \text{ L}} \times \frac{1 \text{ mO F}^-}{19.4 \text{ g F}^-}
\]

\[\left[\text{F}^-\right] = 5.26 \times 10^{-5} \text{ M}\]

\[Q = (6.23 \times 10^{-3})^2 (5.26 \times 10^{-5})\]

\[Q = 1.7 \times 10^{-4}\]

might be a problem
Most metal hydroxides are not soluble in water, but they do dissolve in acid solutions.

The same is true of other salts that contain anions that are weak bases.

\[ Cu(OH)_2 + 2H^+ \rightarrow 2H_2O + Cu^{2+} \]

\[ K_f = [Cu^{2+}][OH^-]^2 \]

\[ OH^- + H^+ \rightarrow H_2O \]

\( Cu(OH)_2 \rightleftharpoons Cu^{2+} + 2OH^- \)

Shift right in acid, \([OH^-]\) is lowered.
CaF_2 + 2H^+ \rightarrow Ca^{2+} + 2HF
CaCO_3 + 2H^+ \rightarrow Ca^{2+} + CO_2 + H_2O
AgCl + H^+ \rightarrow Ag^+ + HCl

AgCl + H^+ \rightarrow NR
Using the $K_{sp}$ model to predict changes in solubility
with changes in pH

$\text{Al(OH)}_3 \quad K_{sp} = 3.7 \times 10^{-15}$

a) water
b) in $\text{pH} = 8.00$ solution
   \[ \text{buffered} \]
c) in $\text{pH} = 3.00$ solution

\[ \text{Al (OH)}_3(s) \rightarrow \text{Al}^{3+} + 3\text{OH}^- \]
\[ s = 3.5 \]

2) $3.17 \times 10^{-15} = 5(3.5)^3 = 27.5$
   \[ s = 6.08 \times 10^{-4} \]
   \[ \Sigma \text{OH}^- = 3.24 \times 10^{-4} \quad p\text{OH} = 3.49 \]
   \[ \boxed{p\text{H} = 10.51} \]

b) $p\text{H} = 8.00 \quad p\text{OH} = 6.00$
   \[ 3.17 \times 10^{-15} = [\text{Al}^{3+}] \left(1.0 \times 10^{-6}\right)^3 \]
   \[ \Sigma [\text{Al}^{3+}] = 3.17 \times 10^{-3} \text{ M} \]

\[ \text{soluble} \]
c) buffered at pH = 3.06

pOH = 11.00

\[ [Al^{3+}] = \frac{3.7 \times 10^{-15}}{(1.0 \times 10^{-4})^3} \approx 3.7 \times 10^{-18} \]
Silver salts are more soluble in aqueous ammonia than in water.

Demo: Silver chloride dissolves in 6 M NH$_3$ but silver iodide does not.

Why?

\[ K_{\text{form}} = 1.7 \times 10^{-7} \]

\[ \text{Ag}^+ + 2\text{NH}_3 \leftrightarrow \text{Ag(NH}_3)_2^+ \]

Lewis <br> Acid <br> e$^-$ pair <br> acceptor

Lewis <br> base <br> e$^-$ pair <br> donors
Silver salts are more soluble in aqueous ammonia than in water.

Demo: Silver chloride dissolves in 6 M NH₃ but silver iodide does not. Why?

\[\begin{align*}
\text{AgCl} + 2\text{NH}_3 &\rightarrow \text{Ag(NH}_3)_2^+ + \text{Cl}^- \\
K &= K_{sp} \times K_{\text{form}} \\
&= 1.6 \times 10^{-10} \times 6.7 \times 10^{-7} \\
&= 2.7 \times 10^{-3}
\end{align*}\]

\[\begin{align*}
\text{AgCl} &\rightarrow \text{Ag}^+ + \text{Cl}^- \quad K = K_{sp} \\
\text{Ag}^+ + 2\text{NH}_3 &\rightarrow \text{Ag(NH}_3)_2^+ \\
K &= K_{\text{form}}
\end{align*}\]
\[ \text{AgCl} + 2\text{NH}_3 \rightarrow \text{Ag(NH}_3)_2^+ + \text{Cl}^- \]

\[ \sqrt{2.72 \times 10^{-3}} = \frac{5^2}{(6.25)^2} \]

\[ s = 0.28 \text{ mol/L} \]

2 mg AgCl dissolve in water

40.9 g AgCl dissolve in 6 M NH$_3$
For AgI

\[ \text{AgI} + 2\text{NH}_3 \rightarrow \text{Ag}^+ (\text{NH}_3)_2^- + \text{I}^- \]

\[ K = K_{sp} \times K_{form} = 2.6 \times 10^{-9} \]

\[ \sqrt{2.55 \times 10^{-9}} \approx \sqrt{\frac{5^4}{(6-35)^4}} \]

\[ S = 3.10 \times 10^{-4} \text{ mol/L} \]

2.9 mg AgI dissolve in 1 L H_2O

71 mg AgI dissolve in 1 L 6m NH_3