SOLUBILITY PRODUCT CALCULATIONS – IDEAL BEHAVIOR

1. Calculate the approximate solubility of AgCl in pure water.

$$K_{sp} = 1.6 \times 10^{-10} = [Ag^+][Cl^-]$$

$$s = [Ag^+] \quad \text{and} \quad [Ag^+] = [Cl^-]$$

$$s = \sqrt{K_{sp}} = 1.3 \times 10^{-5} M$$

2. Approximate the solubility of PbI$_2$ in pure water.

$$K_{sp} = 1.4 \times 10^{-8} = [Pb^{2+}][I^-]^2$$

$$s = [Pb^{2+}]$$

$$[I^-] = 2[Pb^{2+}]$$

$$K_{sp} = [Pb^{2+}]\left(2[Pb^{2+}]\right)^2 = 4[Pb^{2+}]^3$$

$$s = \sqrt[3]{\frac{K_{sp}}{4}} = 1.52 \times 10^{-3} M$$

3. Approximate the solubility of PbI$_2$ in 0.01 M KI.

$$K_{sp} = 1.4 \times 10^{-8} = [Pb^{2+}][I^-]^2$$

$$s = [Pb^{2+}]$$

$$[I^-] = C_{KI} + 2[Pb^{2+}]$$

$(2[Pb^{2+}] < C_{KI}$ but by about 9% [prove it] so keeping the assumption is personal choice)

$$K_{sp} = [Pb^{2+}]\left(C_{KI} + 2[Pb^{2+}]\right)^2$$

$$s = [Pb^{2+}] = 1.33 \times 10^{-4} M$$

4. a. What volume of 1.0 M KI must be added to 100 mL of a solution which is 0.10 M $Pb(NO_3)_2$ and 0.05 M $AgNO_3$ to just start the precipitation of the first metal ion?

   b. What volume of 1.0 M KI must be added to the solution to just start the precipitation of the second cation?

   c. What is the concentration of the first cation to precipitate when the second cation just starts to precipitate?

a. $K_{sp, PbI_2} = 1.4 \times 10^{-8}$ $K_{sp, AgI} = 1.5 \times 10^{-16}$

$[I^-]$ to just start ppt'n:

for Ag^+: $[I^-] = \dfrac{K_{sp}}{[Ag^+]} = \dfrac{1.5 \times 10^{-16}}{0.05} = 3.0 \times 10^{-15} M$

$V_{KI} = \dfrac{3.0 \times 10^{-15} M \times 100 \text{ mL}}{1.0 M} = 3.0 \times 10^{-13} \text{ mL}$ (wow, not much!)

for Pb^{2+}: $[I^-] = \sqrt{\dfrac{K_{sp}}{[Pb^{2+}]}} = \sqrt{\dfrac{1.4 \times 10^{-8}}{0.10}} = 3.7 \times 10^{-4} M$

so, Ag^+ ppts first.

b. Need to calculate the volume necessary to consume 100 mL of 0.05 M Ag^+ first, then the volume necessary to raise the $[I^-]$ to $3.7 \times 10^{-4} M$.

$n_{Ag^+} = 100 \text{mL} \times 0.05 M = 5 \text{ mmol } Ag^+ \ (= n_{I^-})$

$V_{KI, \text{so far}} = \dfrac{5 \text{ mmol } I^-}{1.0 M} = 5 \text{ mL}$

Now, calculate the amount of KI necessary to raise the $[I^-]$ to $3.7 \times 10^{-4} M$.

$V_{KI} = \dfrac{105 \text{ mL} \times 3.7 \times 10^{-4} M}{1.0 M} = 0.039 \text{ mL}$

So, the total amount of KI necessary to just start ppt'ing PbI_2 is 5.04 mL.

c. $[Ag^+] = \dfrac{1.5 \times 10^{-16}}{3.7 \times 10^{-4} M} = 4.1 \times 10^{-13} M$

SOLUBILITY PRODUCT CALCULATIONS IN COMPLEX EQUILIBRIA

(In all calculations, assume ideal solution behavior)

1. Calculate the solubility of AgOH in pure water.

$$AgOH \; \rightleftharpoons \; Ag^+ + OH^- \qquad K_{sp} = 1.5 \times 10^{-8}$$

$$2\,H_2O \; \rightleftharpoons \; H_3O^+ + OH^- \qquad K_w = 1.0 \times 10^{-14}$$

$$s = [Ag^+]$$

$$[OH^-] = [Ag^+] + [H_3O^+]$$

Perhaps, since the solution will be slightly basic, [H₃O+] << [OH-]

$$K_{sp} = [Ag^+]^2$$

$$s = [Ag^+] = \sqrt{1.5 \times 10^{-8}} = 1.2 \times 10^{-4} \text{ M}$$

(Incidentally, with no assumptions: $[Ag^+] = \sqrt{\dfrac{K_{sp}^2}{K_{sp} + K_w}}$ (do the algebra) and since K_w is so small compared to K_{sp}, the same result as above is returned.)

2. Approximate the solubility of aluminum hydroxide in pure water.

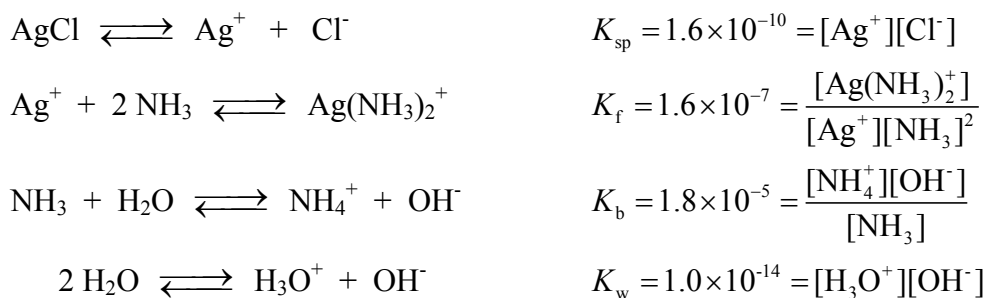$$Al(OH)_3 \; \rightleftharpoons \; Al^{3+} + 3\,OH^- \qquad K_{sp} = 3.7 \times 10^{-15}$$

$$2\,H_2O \; \rightleftharpoons \; H_3O^+ + OH^- \qquad K_w = 1.0 \times 10^{-14}$$
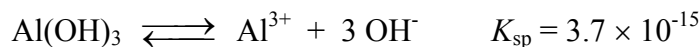
$$s = [Al^{3+}]$$

$$[OH^-] = 3[Al^{3+}] + [H_3O^+] \qquad\qquad \text{Try } [H_3O^+] << 3[Al^{3+}]$$

$$[Al^{3+}] = \sqrt[4]{\frac{K_{sp}}{27}} = \sqrt[4]{\frac{3.7 \times 10^{-15}}{27}} = 1.08 \times 10^{-4} \text{ M}$$

Good thing this works since the full solution is

$$3[Al^{3+}] = \sqrt[3]{\frac{K_{sp}}{[Al^{3+}]}} - \frac{K_w}{\sqrt[3]{\dfrac{K_{sp}}{[Al^{3+}]}}} \qquad [Ag^+] = 1.08 \times 10^{-4} \text{ M (solver)}$$

3. Calculate the solubility of AgCl in 0.5 M ammonia.

$AgCl \rightleftharpoons Ag^+ + Cl^-$ $\qquad$ $K_{sp} = 1.6 \times 10^{-10} = [Ag^+][Cl^-]$

$Ag^+ + 2\,NH_3 \rightleftharpoons Ag(NH_3)_2^+$ $\qquad$ $K_f = 1.6 \times 10^{-7} = \dfrac{[Ag(NH_3)_2^+]}{[Ag^+][NH_3]^2}$

$NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^-$ $\qquad$ $K_b = 1.8 \times 10^{-5} = \dfrac{[NH_4^+][OH^-]}{[NH_3]}$

$2\,H_2O \rightleftharpoons H_3O^+ + OH^-$ $\qquad$ $K_w = 1.0 \times 10^{-14} = [H_3O^+][OH^-]$

$s = [Cl^-] = [Ag^+] + [Ag(NH_3)_2^+]$

$C_{NH3} = [NH_3] + [NH_4^+] + 2[Ag(NH_3)_2^+]$

$[OH^-] = [NH_4^+] + [H_3O^+]$

Solution is basic so $[H_3O^+] \ll [NH_4^+]$

K_f = large so $[Ag^+] \ll [Ag(NH_3)_2^+]$

K_b = small so $[NH_4^+] \ll [NH_3]$

Put it all together:

$K_f K_{sp} = \dfrac{[Cl^-]^2}{(C_{NH_3} - 2[Cl^-])^2}$ $\quad$ so $\quad$ $\sqrt{K_f K_{sp}} = \dfrac{[Cl^-]}{C_{NH_3} - 2[Cl^-]}$ $\quad$ and $\quad$ $[Cl^-] = 0.023$ M

4. Approximate the solubility of calcium oxalate in pure water.

$CaOx \rightleftharpoons Ca^{2+} + Ox^{2-}$ $\qquad$ $K_{sp} = 1.8 \times 10^{-9} = [Ca^{2+}][Ox^{2-}]$

$Ox^{2-} + H_2O \rightleftharpoons HOx^- + OH^-$ $\qquad$ $K_{b1} = 1.89 \times 10^{-10} = \dfrac{[HOx^-][OH^-]}{[Ox^{2-}]}$

$HOx^- + H_2O \rightleftharpoons H_2Ox + OH^-$ $\qquad$ $K_{b2} = 1.85 \times 10^{-13} = \dfrac{[H_2Ox][OH^-]}{[HOx^-]}$

$2\,H_2O \rightleftharpoons H_3O^+ + OH^-$ $\qquad$ $K_w = 1.0 \times 10^{-14} = [H_3O^+][OH^-]$
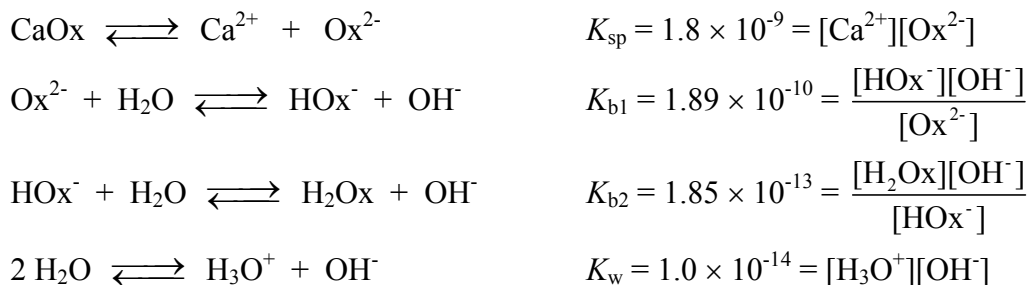
$s = [Ca^{2+}] = [Ox^{2-}] + [HOx^-] + [H_2Ox]$

$2[Ca^{2+}] + [H_3O^+] = 2[Ox^{2-}] + [HOx^-] + [OH^-]$

Assume $[H_3O^+]$ is vanishingly small: $2[Ca^{2+}] = 2[Ox^{2-}] + [HOx^-] + [OH^-]$

And $[HOx^-] = [OH^-]$

Assume $[H_2Ox]$ is vanishingly small: $[Ca^{2+}] = [Ox^{2-}] + [HOx^-]$

So: $[Ca^{2+}] = [Ox^{2-}] + [HOx^-] = \dfrac{K_{sp}}{[Ca^{2+}]} + \sqrt{K_{b1}[Ox^{2-}]} = \dfrac{K_{sp}}{[Ca^{2+}]} + \sqrt{\dfrac{K_{b1}K_{sp}}{[Ca^{2+}]}}$

$s = [Ca^{2+}] = 4.25 \times 10^{-5}$ M

5. Calculate the solubility of calcium oxalate in a solution buffered at pH 5.

$$CaOx \rightleftharpoons Ca^{2+} + Ox^{2-} \qquad\qquad K_{sp} = 1.8 \times 10^{-9} = [Ca^{2+}][Ox^{2-}]$$

$$Ox^{2-} + H_2O \rightleftharpoons HOx^- + OH^- \qquad K_{b1} = 1.89 \times 10^{-10} = \frac{[HOx^-][OH^-]}{[Ox^{2-}]}$$

$$HOx^- + H_2O \rightleftharpoons H_2Ox + OH^- \qquad K_{b2} = 1.85 \times 10^{-13} = \frac{[H_2Ox][OH^-]}{[HOx^-]}$$

$$2\,H_2O \rightleftharpoons H_3O^+ + OH^- \qquad\qquad K_w = 1.0 \times 10^{-14} = [H_3O^+][OH^-]$$

$$s = [Ca^{2+}] = [Ox^{2-}] + [HOx^-] + [H_2Ox]$$

The pH is known and fixed: $[OH-] = 10^{-9}$ M

$$[Ca^{2+}] = \frac{K_{sp}}{[Ca^{2+}]} + K_{b1}\frac{[Ox^{2-}]}{[OH^-]} + K_{b2}\frac{[HOx^-]}{[OH^-]}$$

$$[Ca^{2+}] = \frac{K_{sp}}{[Ca^{2+}]} + \frac{K_{sp}K_{b1}}{[Ca^{2+}][OH^-]} + K_{b1}K_{b2}\frac{[Ox^{2-}]}{[OH^-]^2}$$

$$[Ca^{2+}] = \frac{K_{sp}}{[Ca^{2+}]} + \frac{K_{sp}K_{b1}}{[Ca^{2+}][OH^-]} + \frac{K_{sp}K_{b1}K_{b2}}{[Ca^{2+}][OH^-]^2}$$

$$[Ca^{2+}] = \frac{1.8 \times 10^{-9}}{[Ca^{2+}]} + \frac{3.4 \times 10^{-10}}{[Ca^{2+}]} + \frac{6.3 \times 10^{-14}}{[Ca^{2+}]} = \frac{2.14 \times 10^{-9}}{[Ca^{2+}]}$$

$$[Ca^{2+}] = 4.6 \times 10^{-5}\ M$$

SOLUBILITY PRODUCT CALCULATIONS – NONIDEAL BEHAVIOR

1. What is approximate solubility of PbI_2 in pure water?

$$K_{sp} = 1.4 \times 10^{-8} = [Pb^{2+}][I^-]^2$$

$$s = [Pb^{2+}]$$

$$[I^-] = 2[Pb^{2+}]$$

$$K_{sp} = [Pb^{2+}]\left(2[Pb^{2+}]\right)^2 = 4[Pb^{2+}]^3$$

$$s = \sqrt[3]{\frac{K_{sp}}{4}} = 1.52 \times 10^{-3} M$$

2. Assuming no contribution to μ from the solubility of PbI_2, determine the apparent K_{sp} for PbI_2 at an ionic strength of 0.01 M.

at $\mu = 0.01$ M, $\gamma_{Pb^{2+}} = 0.665$ and $\gamma_{I^-} = 0.899$

$$K'_{sp} = \frac{K^\circ_{sp}}{\gamma_{Pb^{2+}}\gamma_{I^-}^2} = \frac{1.4 \times 10^{-8}}{0.665 \times 0.899^2} = 2.6 \times 10^{-8}$$

3. What is the calculated solubility of PbI_2 in 0.013 M KNO_3 (assuming no μ contribution from PbI_2)?

$$-\log\gamma_{Pb^{2+}} = \frac{0.5085(2)^2\sqrt{0.013}}{1+3.3(0.45)\sqrt{0.013}} = 0.198 \qquad \gamma_{Pb^{2+}} = 0.633$$

$$-\log\gamma_{I^-} = \frac{0.5085(-1)^2\sqrt{0.013}}{1+3.3(0.3)\sqrt{0.013}} = 0.0521 \qquad \gamma_{I^-} = 0.887$$

$$s = [Pb^{2+}]$$

$$[I^-] = 2[Pb^{2+}]$$

$$s = \sqrt[3]{\frac{K_{sp}}{4\gamma_{Pb^{2+}}\gamma_{I^-}^2}} = \sqrt[3]{\frac{1.4 \times 10^{-8}}{4(0.633)(0.887)^2}} = 1.9 \times 10^{-3} M$$

4. Assuming complete solution nonideality, determine the calculated solubility of PbI_2 in 0.013 M KNO_3 while also considering the ionic strength contribution from the dissolved PbI_2.

   Do the same problem as in (3) but add the concentration due to the lead and iodide ions into the ionic strength and recalculate. It will require at least 2 iterations for the solution to converge.