Example five

Calculate the K_{SP} of $MgNH_4PO_4$ if you determine the solubility to be 0.52 g/l at pH 10.2

This looks pretty easy.

The molecular weight is 137.32 g/mol so you have 0.00379 moles.

The K_{SP} expression is

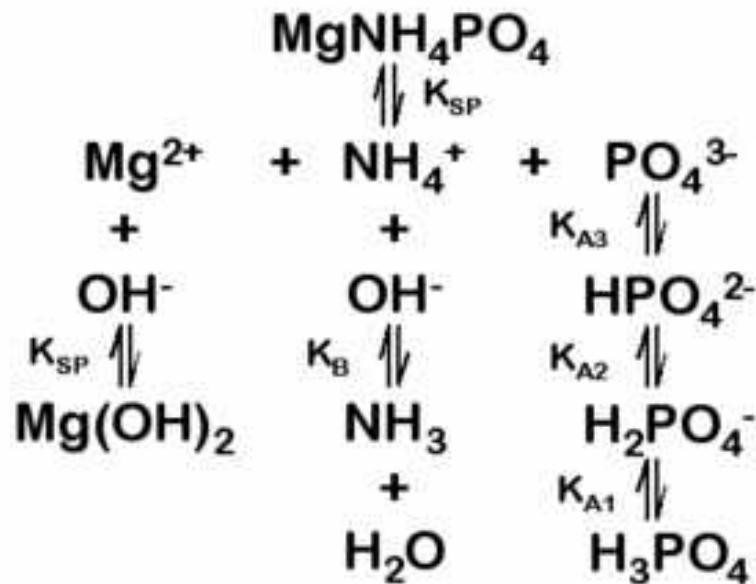$$K_{SP} = [Mg^{2+}][NH_4^+][PO_4^{3-}]$$

Example five

You might tend to solve for K_{SP} as

$$K_{SP} = (0.00379)^3$$

$$= 5.44 \times 10^{-8}$$

If you did this you would be **WRONG!**

We need to look at the equilibrium to appreciate what going on.

Example five

$$MgNH_4PO_4$$

$$\updownarrow K_{SP}$$

$$Mg^{2+} \;+\; NH_4^+ \;+\; PO_4^{3-}$$

$$+ \qquad\qquad + \qquad\qquad K_{A3} \updownarrow$$

$$OH^- \qquad\quad OH^- \qquad\quad HPO_4^{2-}$$

$$K_{SP} \updownarrow \qquad K_B \updownarrow \qquad\quad K_{A2} \updownarrow$$

$$Mg(OH)_2 \qquad NH_3 \qquad H_2PO_4^-$$

$$+ \qquad\qquad K_{A1} \updownarrow$$

$$H_2O \qquad\quad H_3PO_4$$

The H_3O^+ have been omitted from phosphate equilibria for clarity.

There's obviously more to this than we first thought!

Example five

As bad as things look, we still can take the same approach to solve this littel jewel.

To determine the K_{SP}, we'll need to cakulate the actual concentrations using other equilibrium expressions.

These are all $[H_3O^+]$ or $[OH^-]$ based.
Fortunately, we know the pH.

Example five

$$K_{SP\ Mg(OH)_2} = 1.2 \times 10^{11} = [Mg^{2+}][OH^-]^2$$

$$K_{B\ NH_4^+} = 1.78 \times 10^5 = \frac{[OH^-][NH_4^+]}{[NH_3]}$$

For phosphate

$$K_{A1} = 7.5 \times 10^{-3} = \frac{[H_3O^+][H_2PO_4^-]}{[H_3PO_4]}$$

$$K_{A2} = 6.0 \times 10^{-8} = \frac{[H_3O^+][HPO_4^{2-}]}{[H_2PO_4^-]}$$

$$K_{A3} = 4.8 \times 10^{13} = \frac{[H_3O^+][PO_4^{3-}]}{[HPO_4^{2-}]}$$

Example five

What do we already know?

$$[H_3O^+] = 3.98 \times 10^{11}$$
$$[OH^-] = 2.51 \times 10^4$$

We also have several mass balances

$$3.79 \times 10^3 = [NH_4^+] + [NH_3]$$
$$= [H_3PO_4] + [H_2PO_4^-] + [HPO_4^{2-}] + [PO_4^{3-}]$$

This actually works out to be three problems in one. We'll start with Mg^{2+}.

Example five

For Mg^{2+} we can see if we've exceeded the K_{SP} for $Mg(OH)_2$.

$K_{SP} = 1.2 \times 10^{11} = [Mg^{2+}][OH^-]^2$

$[Mg^{2+}] = K_{SP}/[OH^-]^2 = 4.7 \times 10^4$

We put 3.79×10^3 into the solution so some must have precipitated. The $[Mg^{2+}]$ is then based on the K_{SP} for $Mg(OH)_2$.

One down, two to go!

Example five

For ammonium, nothing will precipitate out of solution. However, some of it can be expected to be converted to ammonia.

$$K_{B \ NH_4^+} = 1.78 \times 10^{-5} = \frac{[OH^-][NH_4^+]}{[NH_3]}$$

$$\frac{K_B}{[OH^-]} = \frac{[NH_4^+]}{[NH_3]} = 0.11$$

Example five

Our mass balance for ammonia species is

$$3.79 \times 10^{-3} = [NH_4^+] + [NH_3]$$

Substituting for ammonia using: $\dfrac{[NH_4^+]}{0.11} = [NH_3]$

Gives us $[NH_4^+] + \dfrac{[NH_4^+]}{0.11} = 3.79 \times 10^{-3}$

$[NH_4^+] = 3.8 \times 10^{-4}$ M

Two down, one to go!

Example five

For phosphate, we need to determine which species exist at significant levels at pH 10.2

$$\frac{K_{A1}}{[H_3O^+]} = \frac{[H_2PO_4^-]}{[H_3PO_4]} = 1.88\times10^8$$

$$\frac{K_{A2}}{[H_3O^+]} = \frac{[HPO_4^{2-}]}{[H_2PO_4^-]} = 1.51\times10^3$$

$$\frac{K_{A3}}{[H_3O^+]} = \frac{[PO_4^{3-}]}{[HPO_4^{2-}]} = 0.012$$

It appears that most of our phosphate exists as HPO_4^{2-}

Example five

We can now solve for phosphate.

$[HPO_4^{2-}]$ = 3.79×10^{-3} M

$[PO_4^{3-}]$ = $0.012 [HPO_4^{2-}]$

= 4.6×10^{-5} M

K_{SP} $MgNH_4PO_4$

= $[Mg^{2+}][NH_4][PO_4]$

= $(4.7 \times 10^{-4})(3.8 \times 10^{-4})(4.6 \times 10^{-5})$

= 8.2×10^{-12}