Example: A lake has a pH of 7.25 and is found to contain 0.12 ppm of total phosphate (as $\mathbf{PO_4^{3-}}$) and 75 ppm of $\mathbf{Ca^{2+}}$. Is the lake saturated with respect to hydroxylapatite?

Solubility product for hydroxyl apatite
K_{sp} $(\mathbf{Ca_5(PO_4)_3OH})$ = 1.0×10^{-56}

Acidity constants for $\mathbf{H_3PO_4}$
$K_{a1} = 7.5 \times 10^{-3}$
$K_{a2} = 6.2 \times 10^{-8}$
$K_{a3} = 4.8 \times 10^{-13}$

$$K_{sp} = [Ca^{2+}]^5 [OH^-] [PO_4^{3-}]^3$$

$$Ca_5(PO_4)_3OH_{(s)} \rightleftharpoons 5\,Ca^{2+} + 3\,PO_4^{3-} + OH^-$$

Compute Qsp and compare to Ksp

if Qsp > Ksp, then soln. is super saturated and precipitation of hydroxylapatite will occur.

$$[Ca^{2+}] = 75\,\frac{mg}{L} \times \frac{1\,mol}{40.\,g} \times \frac{1\,g}{10^3\,mg} = 1.9 \times 10^{-3}\,\frac{mol}{L}$$

$$[H^+] = 10^{-7.5} = 5.6 \times 10^{-8}\,\frac{mol}{L}$$

$$\text{and} \quad [OH^-] = K_w/[H^+] = 1.8 \times 10^{-7}\,\frac{mol}{L}$$

$$[PO_4]_T = 0.12\,\frac{mg}{L} \times \frac{1\,mol}{95\,g} \times \frac{1\,g}{10^3\,mg} = 1.3 \times 10^{-6}\,\frac{mol}{L}$$

$$[PO_4]_T = [H_3PO_4] + [H_2PO_4^-] + [HPO_4^{2-}] + [PO_4^{3-}]$$

$[PO_4^{3-}]_T = 1.3 \times 10^{-6}$ mol L^{-1}

$[PO_4]_T = [PO_4^{3-}] + [HPO_4^{2-}] + [H_2PO_4^-] + [H_3PO_4]$

let x represent $[PO_4^{3-}]$

and rearrange and substitute in for other species in terms of $[H^+]$ and Ka's.

use Ka_3 expression for $HPO_4^{2-} \rightleftharpoons H^+ + PO_4^{3-}$

$$Ka_3 = \frac{[H^+][PO_4^{3-}]}{[HPO_4^{2-}]} = 4.8 \times 10^{-13}$$

since pH = 7.25, $[H^+] = 5.6 \times 10^{-8}$

and $[HPO_4^{2-}] = (1.2 \times 10^5)\, x$

use Ka_2 expression for $H_2PO_4^- \rightleftharpoons H^+ + HPO_4^{2-}$

$$Ka_2 = \frac{[H^+][HPO_4^{2-}]}{[H_2PO_4^-]} = 6.2 \times 10^{-8}$$

$$[H_2PO_4^-] = \frac{[H^+][HPO_4^{2-}]}{6.2 \times 10^{-8}} = \frac{(5.6 \times 10^{-8})(1.2 \times 10^5 x)}{6.2 \times 10^{-8}}$$

$$= 1.1 \times 10^5\, x$$

So $[PO_4]_T = x + 1.2 \times 10^5 x + 1.1 \times 10^5 x + \sim 0 = 1.3 \times 10^{-6}$ mol L^{-1}

Solve for $x = 5.7 \times 10^{-12}$ mol L^{-1}

$$Q_{sp} = [Ca^{2+}]^5 \, [PO_4^{3-}]^3 \, [OH^-]$$

$$= (1.9 \times 10^{-3})^5 (5.7 \times 10^{-12})^3 (1.8 \times 10^{-7})$$

$$= 8.3 \times 10^{-55}$$

whereas $K_{sp} = 1.0 \times 10^{-56}$

Since $Q_{sp} > K_{sp}$

lake is supersaturated wrt $Ca_5(PO_4)_3OH$