

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

Solubility product for hydroxyl apatite

$$K_{sp} (\text{Ca}_5(\text{PO}_4)_3\text{OH}) = 1.0 \times 10^{-56}$$

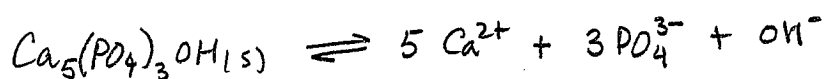
Acidity constants for H_3PO_4

$$K_{a1} = 7.5 \times 10^{-3}$$

$$K_{a2} = 6.2 \times 10^{-8}$$

$$K_{a3} = 4.8 \times 10^{-13}$$

$$K_{sp} = [\text{Ca}^{2+}]^5 [\text{OH}^-] [\text{PO}_4^{3-}]^3$$



Compute Q_{sp} and compare to K_{sp}

if $Q_{sp} > K_{sp}$, then soln. is super saturated and precipitation of hydroxylapatite will occur.

$$[\text{Ca}^{2+}] = 75 \frac{\text{mg}}{\text{L}} \times \frac{1 \text{ mol}}{40.1 \text{ g}} \times \frac{1 \text{ g}}{10^3 \text{ mg}} = 1.9 \times 10^{-3} \frac{\text{mol}}{\text{L}}$$

$$[\text{H}^+] = 10^{-7.25} = 5.6 \times 10^{-8} \frac{\text{mol}}{\text{L}}$$

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

$$[\text{PO}_4]_T = 0.12 \frac{\text{mg}}{\text{L}} \times \frac{1 \text{ mol}}{95 \text{ g}} \times \frac{1 \text{ g}}{10^3 \text{ mg}} = 1.3 \times 10^{-6} \frac{\text{mol}}{\text{L}}$$

$$[\text{PO}_4]_T = [\text{H}_3\text{PO}_4] + [\text{H}_2\text{PO}_4^-] + [\text{HPO}_4^{2-}] + [\text{PO}_4^{3-}]$$

$$[\text{PO}_4^{3-}]_T = 1.3 \times 10^{-6} \text{ mol L}^{-1}$$

$$[\text{PO}_4]_T = [\text{PO}_4^{3-}] + [\text{HPO}_4^{2-}] + [\text{H}_2\text{PO}_4^-] + [\text{H}_3\text{PO}_4]$$

let x represent $[\text{PO}_4^{3-}]$

and rearrange and substitute in for ^{other} species in terms of $[\text{H}^+]$ and K_a 's.

use K_{a3} expression for $\text{HPO}_4^{2-} \rightleftharpoons \text{H}^+ + \text{PO}_4^{3-}$

$$K_{a3} = \frac{[\text{H}^+][\text{PO}_4^{3-}]}{[\text{HPO}_4^{2-}]} = 4.8 \times 10^{-13}$$

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

and $[\text{HPO}_4^{2-}] = (1.2 \times 10^5) x$

use K_{a2} expression for $\text{H}_2\text{PO}_4^- \rightleftharpoons \text{H}^+ + \text{HPO}_4^{2-}$

$$K_{a2} = \frac{[\text{H}^+][\text{HPO}_4^{2-}]}{[\text{H}_2\text{PO}_4^-]} = 6.2 \times 10^{-8}$$

$$\begin{aligned} [\text{H}_2\text{PO}_4^-] &= \frac{[\text{H}^+][\text{HPO}_4^{2-}]}{6.2 \times 10^{-8}} = \frac{(5.6 \times 10^{-8})(1.2 \times 10^5 x)}{6.2 \times 10^{-8}} \\ &= 1.1 \times 10^5 x \end{aligned}$$

So $[\text{PO}_4]_T = x + 1.2 \times 10^5 x + 1.1 \times 10^5 x + \sim 0 = 1.3 \times 10^{-6} \text{ mol L}^{-1}$

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

$$\begin{aligned} Q_{sp} &= [\text{Ca}^{2+}]^5 [\text{PO}_4^{3-}]^3 [\text{OH}^-] \\ &= (1.9 \times 10^{-3})^5 (5.7 \times 10^{-12})^3 (1.8 \times 10^{-7}) \\ &= 8.3 \times 10^{-55} \end{aligned}$$

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

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

lake is supersaturated wrt $\text{Ca}_5(\text{PO}_4)_3\text{OH}$