Solubility of Calcium Carbonate

The solubility of salts of weak acids is very pH dependent. The most important example of the pH dependence of solubility is for CaCO$_3$, which is the major component of sea shells, limestone, and marble. The pH dependence of the solubility can be explained because when CaCO$_3$ dissolves:

$$\text{CaCO}_3(s) \rightleftharpoons \text{Ca}^{2+} + \text{CO}_3^{2-}$$

some of the carbonate hydrolyses to produce HCO$_3$:\n
$$\text{CO}_3^{2-} + \text{H}_2\text{O} \rightleftharpoons \text{HCO}_3^- + \text{OH}^-$$

The hydrolysis decreases the concentration of CO$_3^{2-}$, which pulls the solubility equilibrium to the right making CaCO$_3$ more soluble. In this supplement we will calculate the solubility of calcium carbonate at a given pH taking hydrolysis into account. This problem is an example of a general procedure that can be applied to any 1:1 salt of a monoprotic weak acid and under many circumstances for the salts of weak polyprotic acids.

Example problem:

Calculate the solubility of CaCO$_3$ at pH 6.5. The $K_{sp}$ of calcium carbonate is 5.0x10$^{-9}$:

$$\text{CaCO}_3(s) \rightleftharpoons \text{Ca}^{2+} + \text{CO}_3^{2-} \quad K_{sp} = [\text{Ca}^{2+}] [\text{CO}_3^{2-}] \quad (1)$$

If you don't take into account the hydrolysis of the carbonate ion the solubility $S$ is

$$S = [\text{Ca}^{2+}] = [\text{CO}_3^{2-}] = \sqrt{K_{sp}} \quad \text{neglecting hydrolysis of CO}_3^{2-} \quad (2)$$

The estimated solubility would be 7.1x10$^{-5}$M. We need to take into account the hydrolysis of the carbonate ion with $K_2 = 4.8 \times 10^{-11}$:

$$\text{HCO}_3^- \rightleftharpoons \text{H}^+ + \text{CO}_3^{2-} \quad K_2 = \frac{[\text{H}^+][\text{CO}_3^{2-}]}{[\text{HCO}_3^-]} \quad (3)$$

since the carbonate ion is a weak base. The solubility of CaCO$_3$ will still be equal to the Ca$^{2+}$ ion concentration, but we must consider that the carbonate ion from the CaCO$_3$ dissolution will take two forms, CO$_3^{2-}$ and HCO$_3$:\n
$$S = [\text{Ca}^{2+}] = [\text{CO}_3^{2-}] + [\text{HCO}_3^{2-}] \quad (4)$$

However, for the hydrogen carbonate ion, we can solve Eq. 3 for [HCO$_3^{2-}$]:

$$[\text{HCO}_3^{2-}] = \frac{[\text{H}^+][\text{CO}_3^{2-}]}{K_2} \quad (5)$$

and substitute into the solubility, Eq 4:

$$[\text{Ca}^{2+}] = [\text{CO}_3^{2-}] + \frac{[\text{H}^+][\text{CO}_3^{2-}]}{K_2} \quad (6)$$

We can now factor the [CO$_3^{2-}$] from each term on the right of Eq. 6:
\[ [\text{Ca}^{2+}] = [\text{CO}_3^{2-}] \left( 1 + \frac{[\text{H}^+]}{K_2} \right) \]  

(7)

Now multiply both sides of Eq 7 by \([\text{Ca}^{2+}]\):

\[ [\text{Ca}^{2+}]^2 = [\text{Ca}^{2+}] [\text{CO}_3^{2-}] \left( 1 + \frac{[\text{H}^+]}{K_2} \right) \]  

(8)

and substitute \(K_{sp}\) for \([\text{Ca}^{2+}] [\text{CO}_3^{2-}]\):

\[ [\text{Ca}^{2+}]^2 = K_{sp} \left( 1 + \frac{[\text{H}^+]}{K_2} \right) \]  

(9)

Finally we can also note that since the solubility \(S = [\text{Ca}^{2+}]\):

\[ S^2 = [\text{Ca}^{2+}]^2 = K_{sp} \left( 1 + \frac{[\text{H}^+]}{K_2} \right) \]  

(10)

And taking the square root of both sides gives the solubility as a function of the pH:

\[ S = [\text{Ca}^{2+}] = \sqrt{K_{sp} \left( 1 + \frac{[\text{H}^+]}{K_2} \right)} \]  

(11)

At a pH of 6.5, \([\text{H}^+] = 3.2 \times 10^{-7}\) M and

\[ S = [\text{Ca}^{2+}] = \sqrt{5.0 \times 10^{-9} \left( 1 + \frac{3.2 \times 10^{-7}}{4.8 \times 10^{11}} \right)} = 5.8 \times 10^{-3} \text{ M} \]  

(12)

Which is 80 times more soluble than the value we calculated neglecting hydrolysis!

Even though we derived Eq. 11 for calcium carbonate, the equation applies to all 1:1 salts of a weak acid. (For polyprotic acids we have also assumed that only two species are important at the given pH; for example for CaCO_3 we only considered CO_3^{2-} and HCO_3^- and neglected any H_2CO_3.) So another example is the solubility of FeS:

\[ \text{FeS (s)} \rightleftharpoons \text{Fe}^{2+} + \text{S}^{2-} \]  

\( K_{sp} = 4.2 \times 10^{-17} \)  

(13)

with \( \text{HS}^{-} \rightleftharpoons \text{H}^{+} + \text{S}^{2-} \)  

\( K_2 = 3.0 \times 10^{-13} \)  

(14)

So for example at pH = 8:

\[ S = [\text{Fe}^{2+}] = \sqrt{4.2 \times 10^{-17} \left( 1 + \frac{1.0 \times 10^{-5}}{3.0 \times 10^{-13}} \right)} = 1.2 \times 10^{-6} \text{ M} \]  

(15)

Neglecting hydrolysis we would have gotten \( S = [\text{Fe}^{2+}] = \sqrt{K_{sp}} = 6 \times 10^{-9} \text{ M} \) or a factor of 200 error.