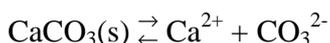
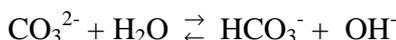


### Solubility of Calcium Carbonate

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



some of the carbonate hydrolyses to produce  $\text{HCO}_3^-$ :



The hydrolysis decreases the concentration of  $\text{CO}_3^{2-}$ , which pulls the solubility equilibrium to the right making  $\text{CaCO}_3$  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  $\text{CaCO}_3$  at pH 6.5. The  $K_{\text{sp}}$  of calcium carbonate is  $5.0 \times 10^{-9}$ :



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

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

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



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

$$S = [\text{Ca}^{2+}] = [\text{CO}_3^{2-}] + [\text{HCO}_3^-] \quad (4)$$

However, for the hydrogencarbonate ion, we can solve Eq. 3 for  $[\text{HCO}_3^-]$ :

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

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  $[\text{CO}_3^{2-}]$  from each term on the right of Eq. 6:

$$[\text{Ca}^{2+}] = [\text{CO}_3^{2-}] \left( 1 + \frac{[\text{H}^+]}{K_2} \right) \quad (7)$$

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

$$[\text{Ca}^{2+}]^2 = [\text{Ca}^{2+}] [\text{CO}_3^{2-}] \left( 1 + \frac{[\text{H}^+]}{K_2} \right) \quad (8)$$

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

$$[\text{Ca}^{2+}]^2 = K_{sp} \left( 1 + \frac{[\text{H}^+]}{K_2} \right) \quad (9)$$

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

$$S^2 = [\text{Ca}^{2+}]^2 = K_{sp} \left( 1 + \frac{[\text{H}^+]}{K_2} \right) \quad (10)$$

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

$$S = [\text{Ca}^{2+}] = \sqrt{K_{sp} \left( 1 + \frac{[\text{H}^+]}{K_2} \right)} \quad (11)$$

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

$$S = [\text{Ca}^{2+}] = \sqrt{5.0 \times 10^{-9} \left( 1 + \frac{3.2 \times 10^{-7}}{4.8 \times 10^{-11}} \right)} = 5.8 \times 10^{-3} \text{ M} \quad (12)$$

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  $\text{CaCO}_3$  we only considered  $\text{CO}_3^{2-}$  and  $\text{HCO}_3^-$  and neglected any  $\text{H}_2\text{CO}_3$ .) So another example is the solubility of  $\text{FeS}$ :



So for example at pH = 8:

$$S = [\text{Fe}^{2+}] = \sqrt{4.2 \times 10^{-17} \left( 1 + \frac{1.0 \times 10^{-8}}{3.0 \times 10^{-13}} \right)} = 1.2 \times 10^{-6} \text{ M} \quad (15)$$

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.