# Solubility of Oxalic Acid

Oxalic acid, $H_2C_2O_4$, is a diprotic weak acid ($pK_{a1} = 1.252$, $pK_{a2} = 4.266$) found in the leaves of the rhubarb plant. Although the stalks of rhubarb are edible, the leaves are toxic. For many years this toxicity was believed to be due to oxalic acid's acidity. More recent work, however, suggests that its toxicity is due to its ability to form the insoluble calcium salt, CaC_2O_4 ($K_{sp} = 1.3 \times 10^{-8}$), which crystallizes in the renal tubes and leads to kidney failure. The pH of urine is around 5, but calculating the molar solubility of CaC_2O_4 at this pH is not easy because at this pH oxalate is present as both $HC_2O_4^-$ and $C_2O_4^{2-}$; instead, let's establish some limits by calculating its molar solubility at buffered pH levels of 7.00 and 3.00. For each pH, write the reaction that governs the solubility of CaC_2O_4, determine the reaction's equilibrium constant, and then solve for molar solubility.

Solubility at a pH of 7.00

Given its pK_a values, at a pH of 7, the only important form of oxalic acid in solution is $C_2O_4^{2-}$; thus, the solubility reaction is

$$CaC_2O_4(s) \rightleftharpoons Ca^{2+}(aq) + C_2O_4^{2-}(aq)$$
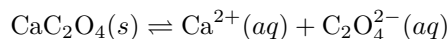
for which the equilibrium constant is K_{sp}. Using an ICE table to organize information

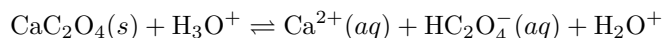| $CaC_2O_4(s)$	$\rightleftharpoons$	Ca^{2+} (aq)	+	$C_2O_4^{2-}$ (aq)
—		0		0
—		+x		+x
—		x		x

we find that

$$K_{sp} = [Ca^{2+}][C_2O_4^{2-}] = x^2 = 1.3 \times 10^{-8}$$
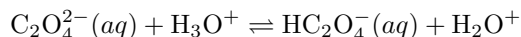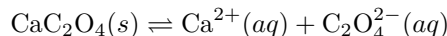
$$x = 1.14 \times 10^{-4} \text{ M}$$

The molar solubility of Ca_2O_4 is the same as the concentration of Ca^{2+}, or 1.14×10^{-4} M

Solubility at a pH of 3.00

At a pH of 3.00, the predominate form of oxalate in solution is $HC_2O_4^{2-}$ and the solubility reaction is

$$CaC_2O_4(s) + H_3O^+ \rightleftharpoons Ca^{2+}(aq) + HC_2O_4^-(aq) + H_2O^+$$

This reaction is the sum of the following two reactions

$$CaC_2O_4(s) \rightleftharpoons Ca^{2+}(aq) + C_2O_4^{2-}(aq)$$

$$C_2O_4^{2-}(aq) + H_3O^+ \rightleftharpoons HC_2O_4^-(aq) + H_2O^+$$

The equilibrium constant for the first reaction is, of course, K_{sp}. The equilibrium constant for the second reaction is, perhaps, less obvious. If you look at the reaction in reverse, you will see that it is the K_a reaction for $HC_2O_4^-$; thus, the equilibrium constant for the second reaction is $(K_{a2})^{-1}$. When adding together reactions, the equilibrium constant for the new reaction is the product of the individual equilibrium constants; thus

$$K = K_{sp} \times (K_{a2})^{-1} = (1.3 \times 10^{-8}) \times (5.42 \times 10^{-5})^{-1} = 2.40 \times 10^{-4}$$

Now we can solve for the molar solubility using an ICE table

$CaC_2O_4\,(s)$	+	$H_3O^+\,(aq)$	$\rightleftharpoons$	$Ca^{2+}\,(aq)$	+	$HC_2O_4^-$	+	$H_2O\,(l)$
—		0.001		0		0		—
—		0.001		+x		+x		—
—		0.001		x		x		—

Note that the solution is buffered to a pH of 3.00, so the concentration of H_3O^+ does not change. Substituting into the equilibrium constant expression and solving

$$K = \frac{[Ca^{2+}][HC_2O_4^-]}{[H_3O^+]} = \frac{(x)(x)}{0.001} = 2.40 \times 10^{-5}$$

$$x = 4.90 \times 10^{-4} \text{ M}$$

The molar solubility of CaC_2O_4 is the same as the concentration of Ca^{2+}, or $x = 4.90 \times 10^{-4}$ M. As expected, CaC_2O_4 is more soluble in acidic solutions.