Solubility and pH

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 quite 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 oxalate's ability to form the insoluble calcium salt, CaC_2O_4 ($K_{sp} = 1.3\times10^{-8}$), 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, 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 of $CaC_2O_4(s)$ at pH of 7

The solubility of CaC_2O_4 is expected to have some pH dependency because the oxalate ion, $C_2O_4^{2-}$, is a weak base. With pK_a values of 1.252 and 4.266, we expect to find only $C_2O_4^{2-}$ at pH levels greater than 5.3; thus, at a pH of 7, the solubility reaction is

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

for which the equilibrium constant is the K_{sp} expression. Using an ICE table to organize information, we find that

	$CaC_2O_4(s)$	⇆	$Ca^{2+}(aq)$	+	$C_2O_4^{2-}(aq)$
I	—		0		0
C	—		$+X$		$+X$
E	—		X		X

$$K_{sp} = [Ca^{2+}][C_2O_4^{2-}] = 1.3\times10^{-8} = X^2$$

$$X = 1.14\times10^{-4}\ \text{M}$$

The molar solubility of CaC_2O_4 is the same as the concentration of Ca^{2+}, or 1.1×10^{-4} M.

Solubility of $CaC_2O_4(s)$ at pH of 3

At a pH of 3, the oxalate ion is no longer the predominate form of oxalate ion in solution. Instead, the predominate form is monohydrogen oxalate, $HC_2O_4^-$. The solubility reaction, therefore, is

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

The equilibrium constant expression for this reaction is

$$K_{eq} = \frac{[Ca^{2+}][HC_2O_4^{2-}]}{[H_3O^+]}$$

the value for which is not provided. To find the value for this equilibrium constant, we seek two or more reactions, with known equilibrium constants, that we can combine to give the desired reaction. The following two reactions, when added together, give the desired reaction

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

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

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

$$K_{eq} = K_{sp} \times (K_{a2})^{-1} = (1.3\times10^{-8}) \times (5.42\times10^{-5})^{-1} = 2.40\times10^{-4}$$

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

	$CaC_2O_4(s)$	+	$H_3O^+(aq)$	$\leftrightarrows$	$Ca^{2+}(aq)$	+	$HC_2O_4^-(aq)$	+	$H_2O(l)$
I	—		0.001		0		0		—
C	—		0.001		$+X$		$+X$		—
E	—		0.001		X		X		—

Note that the solution is buffered to a pH of 3 so the concentration of H_3O^+ does not change. Continuing, we find that

$$K_{eq} = \frac{[Ca^{2+}][HC_2O_4^-]}{[H_3O^+]} = \frac{(X)(X)}{0.001} = 2.40\times10^{-4}$$

$$X = 4.90\times10^{-4}\ M$$

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