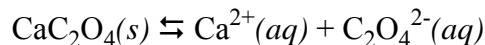


Solubility and Complexation Worksheet – Answer Key

Solubility of $\text{CaC}_2\text{O}_4(s)$ at pH of 7

The solubility of CaC_2O_4 is expected to have some pH dependency because the oxalate ion, $\text{C}_2\text{O}_4^{2-}$, is a weak base. With pK_a values of 1.252 and 4.266, we expect to find only $\text{C}_2\text{O}_4^{2-}$ at pH levels greater than 5.3; thus, at a pH of 7, the solubility reaction is



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

	$\text{CaC}_2\text{O}_4(s)$	\rightleftharpoons	$\text{Ca}^{2+}(aq)$	+	$\text{C}_2\text{O}_4^{2-}(aq)$
I	-		0		0
C	-		+X		+X
E	-		X		X

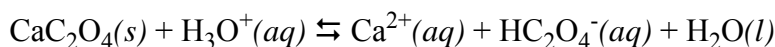
$$K_{\text{sp}} = [\text{Ca}^{2+}][\text{C}_2\text{O}_4^{2-}] = 1.3 \times 10^{-8} = X^2$$

$$X = 1.14 \times 10^{-4} \text{ M}$$

The molar solubility of CaC_2O_4 is the same as the concentration of Ca^{2+} , which is $1.1 \times 10^{-4} \text{ M}$.

Solubility of $\text{CaC}_2\text{O}_4(s)$ at pH of 3

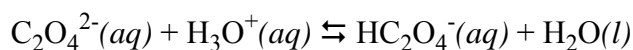
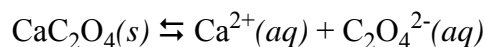
At a pH of 3, the oxalate ion is no longer the predominate form of oxalate ion in solution. Instead, the predominate form is monohydrogen oxalate, HC_2O_4^- . The solubility reaction, therefore, is



The equilibrium constant expression for this reaction is

$$K_{\text{eq}} = \frac{[\text{Ca}^{2+}][\text{HC}_2\text{O}_4^-]}{[\text{H}_3\text{O}^+]}$$

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 can be combined to give the desired reaction. The following two reactions, when added together, give the desired reaction



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 $(K_{\text{a}2})^{-1}$. When adding together reactions, the equilibrium constant for the new reaction is the product of the individual equilibrium constants; thus

$$K_{\text{eq}} = K_{\text{sp}} \times (K_{\text{a}2})^{-1} = (1.3 \times 10^{-8}) \times (5.42 \times 10^{-5})^{-1} = 2.40 \times 10^{-4}$$

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

	$\text{CaC}_2\text{O}_4(s)$	+	$\text{H}_3\text{O}^+(aq)$	\rightleftharpoons	$\text{Ca}^{2+}(aq)$	+	$\text{HC}_2\text{O}_4^-(aq)$	+	$\text{H}_2\text{O}(l)$
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

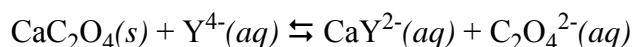
$$K_{\text{eq}} = \frac{[\text{Ca}^{2+}][\text{HC}_2\text{O}_4^-]}{[\text{H}_3\text{O}^+]} = \frac{(X)(X)}{0.001} = 2.40 \times 10^{-4}$$

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

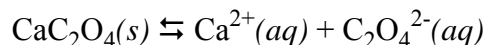
The molar solubility of CaC_2O_4 is the same as the concentration of Ca^{2+} , which is $4.90 \times 10^{-4} \text{ M}$. As expected, CaC_2O_4 is slightly more soluble in acidic solutions.

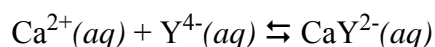
Solubility of $\text{CaC}_2\text{O}_4(s)$ in the presence of EDTA

In the presence of EDTA, the solubility reaction for CaC_2O_4 is



The equilibrium constant for this reaction, K_{eq} is found by combining the K_{sp} reaction for CaC_2O_4 and the K_1 reaction for the formation of the calcium-EDTA complex; thus





$$K_{\text{eq}} = K_{\text{sp}} \times K_1 = (1.38 \times 10^{-8}) \times (4.90 \times 10^{10}) = 637$$

Now we can solve for the molar solubility using an ICE table to organize information. Because the equilibrium constant is larger than 1, we first let the reaction proceed to completion and then let it relax back to equilibrium; thus

	$\text{CaC}_2\text{O}_4(\text{s})$	+	$\text{Y}^{4-}(\text{aq})$	\rightleftharpoons	$\text{CaY}^{2-}(\text{aq})$	+	$\text{C}_2\text{O}_4^{2-}(\text{aq})$
I	-		0.05		0		0
C	-		-0.05		+0.05		+0.05
I	-		0		0.05		0.05
C	-		+X		-X		-X
E	-		X		0.05 - X		0.05 - X

Substituting into the K_{eq} expression gives

$$K_{\text{eq}} = \frac{[\text{CaY}^{2-}][\text{C}_2\text{O}_4^{2-}]}{[\text{Y}^{4-}]} = \frac{(0.05 - X)(0.05 - X)}{X} = 637$$

To simplify the problem, let's assume that $0.05 - X \approx 0.05$

$$\frac{(0.05)(0.05)}{X} = 637$$

$$X = 3.92 \times 10^{-6}$$

Clearly the assumption is okay (the error is less than 0.01%). The molar solubility of CaC_2O_4 is equal to the concentration of dissolved calcium, which in this case is the concentration of CaY^{2-} ; thus, the molar solubility is $0.05 - X$, or 0.05 M. Given a total solution volume of 100 mL, this represents 0.005 mol or 0.64 g. This represents 64% of the initial 1.00 g of CaC_2O_4 .