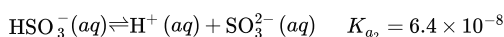
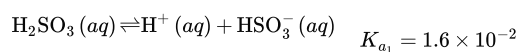




16.10: Polyprotic Acids

In Section 16.5, we stated that some acids, called polyprotic acids, contain two or more ionizable protons. Recall that sulfurous acid (H_2SO_3) is a diprotic acid containing two ionizable protons and that phosphoric acid (H_3PO_4) is a triprotic acid containing three ionizable protons. Typically, a **polyprotic acid** ionizes in successive steps, each with its own K_a . For example, sulfurous acid ionizes in two steps:

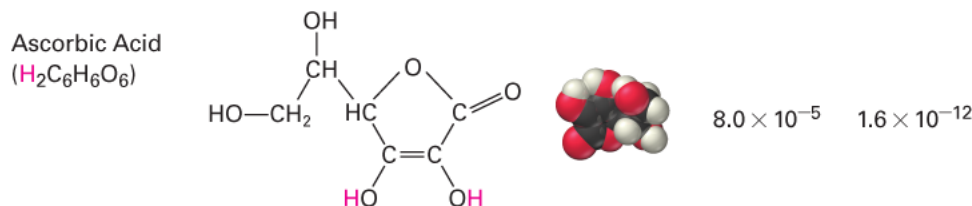
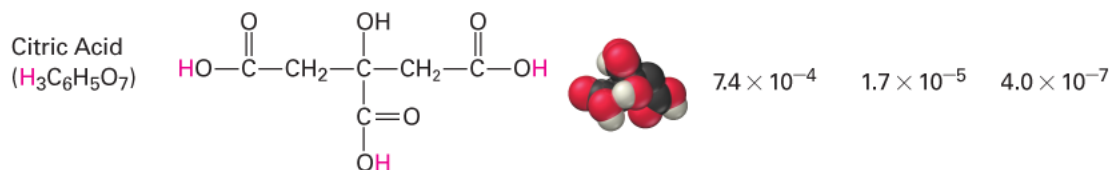


K_{a_1} is the acid ionization constant for the first step, and K_{a_2} is the acid ionization constant for the second step. Notice that K_{a_2} is smaller than K_{a_1} . This is true for all polyprotic acids and makes sense because the first proton separates from a neutral molecule, while the second must separate from an anion. The negatively charged anion holds the positively charged proton more tightly, making the proton more difficult to remove and resulting in a smaller value of K_a .

Table 16.10 lists some common polyprotic acids and their acid ionization constants. Notice that in all cases, the value of K_a for each step becomes successively smaller. The value of K_{a_1} for sulfuric acid is listed as strong because sulfuric acid is strong in the first step and weak in the second.

Table 16.10 Common Polyprotic Acids and Ionization Constants

Name (Formula)	Structure	Space-filling model	K_{a_1}	K_{a_2}	K_{a_3}
Sulfuric Acid (H_2SO_4)			Strong	1.2×10^{-2}	
Oxalic Acid ($\text{H}_2\text{C}_2\text{O}_4$)			6.0×10^{-2}	6.1×10^{-5}	
Sulfurous Acid (H_2SO_3)			1.6×10^{-2}	6.4×10^{-8}	
Phosphoric Acid (H_3PO_4)			7.5×10^{-3}	6.2×10^{-8}	4.2×10^{-13}



Finding the pH of Polyprotic Acid Solutions

Finding the pH of a polyprotic acid solution is less difficult than we might first imagine because, for most polyprotic acids, K_{a1} is much larger than K_{a2} (or K_{a3} for triprotic acids). Therefore, the amount of H_3O^+ formed by the first ionization step is much larger than that formed by the second or third ionization step. In addition, the formation of H_3O^+ in the first step inhibits the formation of additional H_3O^+ in the second step (because of Le Châtelier's principle). Consequently, we treat most polyprotic acid solutions as if the first step were the only one that contributes to the H_3O^+ concentration, as demonstrated in [Example 16.17](#). A major exception is a dilute solution of sulfuric acid, which we examine in [Example 16.18](#).

Example 16.17 Finding the pH of a Polyprotic Acid Solution

Find the pH of a 0.100 M ascorbic acid ($\text{H}_2\text{C}_6\text{H}_6\text{O}_6$) solution.

SOLUTION

To find the pH, you must find the equilibrium concentration of H_3O^+ . Treat the problem as a weak acid pH problem with a single ionizable proton. The second proton contributes a negligible amount to the concentration of H_3O^+ and can be ignored. Follow the procedure from [Example 16.6](#), shown in condensed form here. Use K_{a1} for ascorbic acid from [Table 16.10](#).

Confirm that the x is *small* approximation is valid by calculating the ratio of x to the number it was subtracted from in the approximation. The ratio should be less than 0.05 (or 5%).

Calculate the pH from the H_3O^+ concentration.



	$[\text{H}_2\text{C}_6\text{H}_6\text{O}_6]$	$[\text{H}_3\text{O}^+]$	$[\text{HC}_6\text{H}_6\text{O}_6^-]$
Initial	0.100	≈ 0.00	0.000
Change	$-x$	$+x$	$+x$
Equil	$0.100 - x$	x	x

$$\begin{aligned}
 K_{a_1} &= \frac{[\text{H}_3\text{O}^+][\text{HC}_6\text{H}_6\text{O}_6]}{[\text{H}_2\text{C}_6\text{H}_6\text{O}_6]} \\
 &= \frac{x^2}{0.100 - x} \quad (x \text{ is small}) \\
 8.0 \times 10^{-5} &= \frac{x^2}{0.100} \\
 x &= 2.8 \times 10^{-3} \\
 \frac{2.8 \times 10^{-3}}{0.100} \times 100\% &= 2.8\%
 \end{aligned}$$

The approximation is valid. Therefore,

$$\begin{aligned}
 [\text{H}_3\text{O}^+] &= 2.8 \times 10^{-3} \text{ M} \\
 \text{pH} &= -\log(2.8 \times 10^{-3}) = 2.55
 \end{aligned}$$

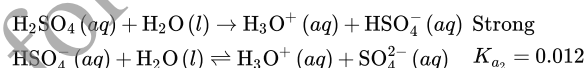
FOR PRACTICE 16.17 Find the pH of a 0.050 M H_2CO_3 solution.

Example 16.18 Finding the pH of a Dilute H_2SO_4 Solution

Find the pH of a 0.0100 M sulfuric acid (H_2SO_4) solution.

SOLUTION

Sulfuric acid is strong in its first ionization step and weak in its second. Begin by writing the equations for the two steps. As the concentration of an H_2SO_4 solution becomes smaller, the second ionization step becomes more significant because the percent ionization increases (as discussed in Section 16.7). Therefore, for a concentration of 0.0100 M, you can't neglect the H_3O^+ contribution from the second step, as you can for other polyprotic acids. You must calculate the H_3O^+ contributions from both steps.



The $[\text{H}_3\text{O}^+]$ that results from the first ionization step is 0.0100 M (because the first step is strong). To determine the $[\text{H}_3\text{O}^+]$ formed by the second step, prepare an ICE table for the second step in which the initial concentration of H_3O^+ is 0.0100 M. The initial concentration of HSO_4^- must also be 0.0100 M (due to the stoichiometry of the ionization reaction).

	$[\text{HSO}_4^-]$	$[\text{H}_3\text{O}^+]$	$[\text{SO}_4^{2-}]$
Initial	0.0100	≈ 0.0100	0.000
Change	$-x$	$+x$	$+x$
Equil	$0.0100 - x$	$0.0100 + x$	x

Substitute the expressions for the equilibrium concentrations (from the table in the previous step) into the expression for K_{a_2} . In this case, you cannot make the x is *small* approximation because the equilibrium constant (0.012) is *not small* relative to the initial concentration (0.0100).

Substitute the value of K_{a_2} and multiply out the expression to arrive at the standard quadratic form.

$$[\text{H}_3\text{O}^+][\text{SO}_4^{2-}]$$

$$\begin{aligned}
 K_{a_2} &= \frac{[\text{H}_3\text{O}^+][\text{SO}_4^{2-}]}{[\text{HSO}_4^-]} \\
 &= \frac{(0.0100 + x)x}{0.0100 - x} \\
 0.012 &= \frac{0.0100x + x^2}{0.0100 - x} \\
 0.012(0.0100 - x) &= 0.0100x + x^2 \\
 0.00012 - 0.012x &= 0.0100x + x^2 \\
 x^2 + 0.022x - 0.00012 &= 0
 \end{aligned}$$

Solve the quadratic equation using the quadratic formula.

$$\begin{aligned}
 x &= \frac{-b \pm \sqrt{b^2 - 4ac}}{2a} \\
 &= \frac{-(0.022) \pm \sqrt{(0.022)^2 - 4(1)(-0.00012)}}{2(1)} \\
 &= \frac{-0.022 \pm 0.031}{2} \\
 x &= -0.027 \text{ or } x = 0.0045
 \end{aligned}$$

Since x represents a concentration and since concentrations cannot be negative, we reject the negative root.

$$x = 0.0045$$

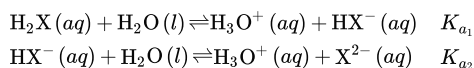
Determine the H_3O^+ concentration from the calculated value of x and calculate the pH. Notice that the second step produces almost half as much H_3O^+ as the first step—an amount that must not be neglected. This will always be the case with dilute H_2SO_4 solutions.

$$\begin{aligned}
 [\text{H}_3\text{O}^+] &= 0.0100 + x \\
 &= 0.0100 + 0.0045 \\
 &= 0.0145 \text{ M} \\
 \text{pH} &= -\log [\text{H}_3\text{O}^+] \\
 &= -\log (0.0145) \\
 &= 1.84
 \end{aligned}$$

FOR PRACTICE 16.18 Find the pH and $[\text{SO}_4^{2-}]$ of a 0.0075 M sulfuric acid solution.

Finding the Concentration of the Anions for a Weak Diprotic Acid Solution

In some cases, we may want to know the concentrations of the anions formed by a polyprotic acid. Consider the following generic polyprotic acid H_2X and its ionization steps:



In [Examples 16.17](#) and [16.18](#), we illustrated how to find the concentration of H_3O^+ for such a solution, which is equal to the concentration of HX^- . What if instead we needed to find the concentration of X^{2-} ? To find the concentration of X^{2-} , we use the concentration of HX^- and H_3O^+ (from the first ionization step) as the initial concentrations for the second ionization step. We then solve a second equilibrium problem using the second ionization equation and K_{a_2} , as demonstrated in [Example 16.19](#).

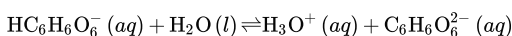
Example 16.19 Finding the Concentration of the Anions for a Weak Diprotic Acid Solution

Diprotic Acid Solution

Find the $[\text{C}_6\text{H}_6\text{O}_6^{2-}]$ of the 0.100 M ascorbic acid ($\text{H}_2\text{C}_6\text{H}_6\text{O}_6$) solution in [Example 16.17](#).

SOLUTION

To find the $[\text{C}_6\text{H}_6\text{O}_6^{2-}]$ use the concentrations of $[\text{HC}_6\text{H}_6\text{O}_6^-]$ and H_3O^+ produced by the first ionization step (as calculated in [Example 16.17](#)) as the initial concentrations for the second step. Because of the 1:1 stoichiometry, $[\text{HC}_6\text{H}_6\text{O}_6^-] = [\text{H}_3\text{O}^+]$. Then solve an equilibrium problem for the second step similar to that of [Example 16.6](#), shown in condensed form here. Use K_{a2} for ascorbic acid from [Table 16.10](#).



	$[\text{HC}_6\text{H}_6\text{O}_6^-]$	$[\text{H}_3\text{O}^+]$	$[\text{C}_6\text{H}_6\text{O}_6^{2-}]$
Initial	2.8×10^{-3}	2.8×10^{-3}	+0.000
Change	$-x$	$+x$	$+x$
Equil	$2.8 \times 10^{-3} - x$	$2.8 \times 10^{-3} + x$	x

$$\begin{aligned}
 K_{a2} &= \frac{[\text{H}_3\text{O}^+][\text{C}_6\text{H}_6\text{O}_6^{2-}]}{[\text{HC}_6\text{H}_6\text{O}_6^-]} \\
 &= \frac{(2.8 \times 10^{-3} + x)x}{2.8 \times 10^{-3} - x} \quad (x \text{ is small}) \\
 &= \frac{(2.8 \times 10^{-3})x}{2.8 \times 10^{-3}} \\
 x &= K_{a2} = 1.6 \times 10^{-12}
 \end{aligned}$$

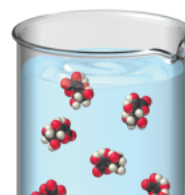
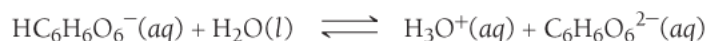
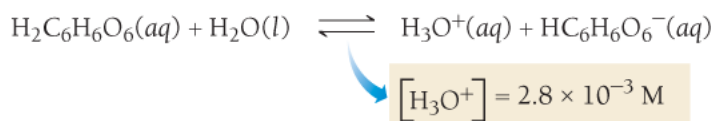
Since x is much smaller than 2.8×10^{-3} the x is small approximation is valid. Therefore,
 $[\text{C}_6\text{H}_6\text{O}_6^{2-}] = 1.6 \times 10^{-12} \text{ M}$


FOR PRACTICE 16.19 Find the $[\text{CO}_3^{2-}]$ of the 0.050 M carbonic acid (H_2CO_3) solution in [Practice 16.17](#).

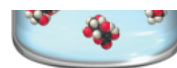
Notice from the results of [Example 16.19](#) that the concentration of X^{2-} for a weak diprotic acid H_2X is equal to K_{a2} . This general result applies to all diprotic acids in which the x is small approximation is valid. Notice also that the concentration of H_3O^+ produced by the second ionization step of a diprotic acid is very small compared to the concentration produced by the first step, as shown in [Figure 16.13](#).

Figure 16.13 Dissociation of a Polyprotic Acid

A 0.100 M $\text{H}_2\text{C}_6\text{H}_6\text{O}_6$ solution contains an H_3O^+ concentration of $2.8 \times 10^{-3} \text{ M}$ from the first step. The amount of H_3O^+ contributed by the second step is only $1.6 \times 10^{-12} \text{ M}$ which is insignificant compared to the amount produced by the first step.

Dissociation of a Polyprotic Acid


$$[\text{H}_3\text{O}^+] = 1.6 \times 10^{-12} \text{ M}$$



0.100 M $\text{H}_2\text{C}_6\text{H}_6\text{O}_6$

$$\text{Total } [\text{H}_3\text{O}^+] = 2.8 \times 10^{-3} \text{ M} + 1.6 \times 10^{-12} \text{ M}$$

$$= 2.8 \times 10^{-3} \text{ M}$$

Not for Distribution