5.4: pH Calculations for Weak Acids

Learning Objectives

- Carry out equilibrium calculations for weak acid systems
- Determine the pH of a weak acid solution based on acid concentration and the acid ionization constant
- Calculate percent ionization for an acid

5.4.1: Acid Equilibrium Calculations

Acid equilibrium problems are one type of aqueous equilibrium reaction, and we can use the acid ionization constants (Ka) to quantitatively determine the concentrations of the acid, hydronium ions, and the conjugate base. Example $5.4.1$ demonstrates how an ICE table can be used for find equilibrium concentrations. To determine the pH of the solution at equilibrium we can use the equilibrium proton concentration, $[\mathrm{H_3O^+}]$, from the ICE table.

Example $5.4.1$: Equilibrium Concentrations in a Solution of a Weak Acid

Formic acid, HCO_2H, is the irritant that causes the body's reaction to ant stings.

The pain of an ant's sting is caused by formic acid. (credit: John Tann)

What is the concentration of hydronium ion and the pH in a 0.534-*M* solution of formic acid?

$$\mathrm{HCO_2H}(aq) + \mathrm{H_2O}(l) \rightleftharpoons \mathrm{H_3O^+}(aq) + \mathrm{HCO_2^-}(aq) \quad K_\mathrm{a} = 1.8 \times 10^{-4}$$

Solution

1. Determine x and equilibrium concentrations. The equilibrium expression is:

$$\mathrm{HCO_2H}(aq) + \mathrm{H_2O}(l) \rightleftharpoons \mathrm{H_3O^+}(aq) + \mathrm{HCO_2^-}(aq)$$

Because water is the solvent, it has a fixed activity equal to 1. Any small amount of water produced or used up during the reaction will not change water's role as the solvent, so the value of its activity remains equal to 1 throughout the reaction so we do not need to consider it when setting up the ICE table.

The table shows initial concentrations (concentrations before the acid ionizes), changes in concentration, and equilibrium concentrations follows (the data given in the problem appear in color):

	HCO_2H +	H_2O ⇌	H_3O^+
Initial concentration (*M*)	0.534	~0	0
Change (*M*)	−*x*	*x*	*x*
Equilibrium concentration (*M*)	0.534 + (−*x*)	0 + *x* = *x*	0 + *x* = *x*

2. Solve for x and the equilibrium concentrations. At equilibrium:

$$K_\mathrm{a} = 1.8 \times 10^{-4} = \frac{[\mathrm{H_3O^+}][\mathrm{HCO_2^-}]}{[\mathrm{HCO_2H}]}$$

$$= \frac{(x)(x)}{0.534 - x} = 1.8 \times 10^{-4}$$

Now solve for x. Because the initial concentration of acid is reasonably large and K_a is very small, we assume that $x << 0.534$, which *permits* us to simplify the denominator term as $(0.534 - x) = 0.534$. This gives:

$$K_{\mathrm{a}} = 1.8 \times 10^{-4} = \frac{x^2}{0.534}$$

Solve for x as follows:

$$\begin{aligned} x^2 &= 0.534 \times (1.8 \times 10^{-4}) \\ &= 9.6 \times 10^{-5} \\ x &= \sqrt{9.6 \times 10^{-5}} \\ &= 9.8 \times 10^{-3} \end{aligned}$$

To check the assumption that x is small compared to 0.534, we calculate:

$$\begin{aligned} \frac{x}{0.534} &= \frac{9.8 \times 10^{-3}}{0.534} \\ &= 1.8 \times 10^{-2} \ (1.8\% \text{ of } 0.534) \end{aligned}$$

x is less than 5% of the initial concentration; the assumption is valid.

We find the equilibrium concentration of hydronium ion in this formic acid solution from its initial concentration and the change in that concentration as indicated in the last line of the table:

$$\begin{aligned} [\mathrm{H_3O^+}] &= 0 + x = 0 + 9.8 \times 10^{-3}\ M. \\ &= 9.8 \times 10^{-3}\ M \end{aligned}$$

The pH of the solution can be found by taking the negative log of the $[\mathrm{H_3O^+}]$, so:

$$pH = -\log(9.8 \times 10^{-3}) = 2.01$$

Exercise 5.4.1: acetic acid

Only a small fraction of a weak acid ionizes in aqueous solution. What is the percent ionization of acetic acid in a 0.100-*M* solution of acetic acid, CH_3CO_2H?

$$\mathrm{CH_3CO_2H}(aq) + \mathrm{H_2O}(l) \rightleftharpoons \mathrm{H_3O^+}(aq) + \mathrm{CH_3CO_2^-}(aq) \quad K_{\mathrm{a}} = 1.8 \times 10^{-5}$$

Hint

Determine $[\mathrm{CH_3CO_2^-}]$ at equilibrium.) Recall that the percent ionization is the fraction of acetic acid that is ionized × 100, or $\frac{[\mathrm{CH_3CO_2^-}]}{[\mathrm{CH_3CO_2H}]_{\text{initial}}} \times 100$.

Answer

percent ionization = 1.3%

Some weak acids ionize to such an extent that the simplifying assumption that x is small relative to the initial concentration of the acid or base is inappropriate. As we solve for the equilibrium concentrations in such cases, we will see that we cannot neglect the change in the initial concentration of the acid or base, and we must solve the equilibrium equations by using the quadratic equation.

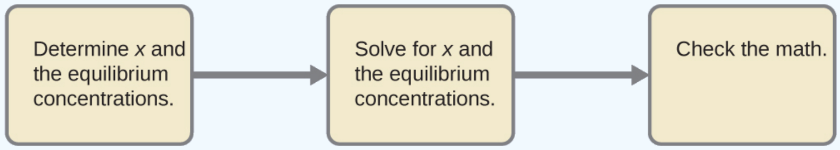
Example 5.4.2: Equilibrium Concentrations in a Solution of a Weak Acid

Sodium bisulfate, $NaHSO_4$, is used in some household cleansers because it contains the $\mathrm{HSO_4^-}$ ion, a weak acid. What is the pH of a 0.50-*M* solution of $\mathrm{HSO_4^-}$?

$$\mathrm{HSO_4^-}(aq) + \mathrm{H_2O}(l) \rightleftharpoons \mathrm{H_3O^+}(aq) + \mathrm{SO_4^{2-}}(aq) \quad K_{\mathrm{a}} = 1.2 \times 10^{-2}$$

Solution

We need to determine the equilibrium concentration of the hydronium ion that results from the ionization of HSO_4^- so that we can use $[H_3O^+]$ to determine the pH. As in the previous examples, we can approach the solution by the following steps:



1. Determine x and equilibrium concentrations. This table shows the changes and concentrations:

	HSO_4^-	$+ \; H_2O$	$\rightleftharpoons \; H_3O^+$	$+ \; SO_4^{2-}$
Initial concentration (*M*)	0.50		~0	0
Change (*M*)	−*x*		*x*	*x*
Equilibrium concentration (*M*)	0.50 + (−*x*) = 0.50 − *x*)		0 + *x* = *x*	0 + *x* = *x*

2. Solve for x and the concentrations.

As we begin solving for x, we will find this is more complicated than in previous examples. As we discuss these complications we should not lose track of the fact that it is still the purpose of this step to determine the value of x.

At equilibrium:

$$K_a = 1.2 \times 10^{-2} = \frac{[H_3O^+][SO_4^{2-}]}{[HSO_4^-]} = \frac{(x)(x)}{0.50 - x}$$

If we assume that *x* is small and approximate (0.50 − *x*) as 0.50, we find:

$$x = 7.7 \times 10^{-2}$$

When we check the assumption, we confirm:

$$\frac{x}{[HSO_4^-]_i} \overset{?}{\leq} 0.05$$

which for this system is

$$\frac{x}{0.50} = \frac{7.7 \times 10^{-2}}{0.50} = 0.15(15\%)$$

The value of x is not less than 5% of 0.50, so the assumption is not valid. We need the quadratic formula to find x.

The equation:

$$K_a = 1.2 \times 10^{-2} = \frac{(x)(x)}{0.50 - x}$$

gives

$$6.0 \times 10^{-3} - 1.2 \times 10^{-2} x = x^{2+}$$

or

$$x^{2+} + 1.2 \times 10^{-2} x - 6.0 \times 10^{-3} = 0$$

This equation can be solved using the quadratic formula. For an equation of the form

$$ax^{2+} + bx + c = 0,$$

x is given by the quadratic equation:

$$x = \frac{-b \pm \sqrt{b^{2+} - 4ac}}{2a}$$

In this problem, $a = 1$, $b = 1.2 \times 10^{-3}$, and $c = -6.0 \times 10^{-3}$.

Solving for x gives a negative root (which cannot be correct since concentration cannot be negative) and a positive root:

$$x = 7.2 \times 10^{-2}$$

Now determine the hydronium ion concentration and the pH:

$$\begin{aligned} [H_3O^+] &= 0 + x = 0 + 7.2 \times 10^{-2}\ M \\ &= 7.2 \times 10^{-2}\ M \end{aligned}$$

The pH of this solution is:

$$\mathrm{pH} = -\log[H_3O^+] = -\log 7.2 \times 10^{-2} = 1.14$$

5.4.2: Percent Ionization of Acids

Another measure of the strength of an acid is its *percent ionization*. The percent ionization of a weak acid is the ratio of the concentration of the ionized acid to the initial acid concentration, times 100:

$$\%\ \text{ionization} = \frac{[H_3O^+]_{eq}}{[HA]_0} \times 100\% \tag{5.4.1}$$

Because the ratio includes the initial concentration, the percent ionization for a solution of a given weak acid varies depending on the original concentration of the acid, and actually decreases with increasing acid concentration.

✓ Example 5.4.3: Calculation of Percent Ionization from pH

Calculate the percent ionization of a 0.125-*M* solution of nitrous acid (a weak acid), with a pH of 2.09.

Solution

The percent ionization for an acid is:

$$\frac{[H_3O^+]_{eq}}{[HNO_2]_0} \times 100$$

The chemical equation for the dissociation of the nitrous acid is:

$$HNO_2(aq) + H_2O(l) \rightleftharpoons NO_2^-(aq) + H_3O^+(aq).$$

Since $10^{-pH} = [H_3O^+]$, we find that $10^{-2.09} = 8.1 \times 10^{-3}\ M$, so that percent ionization (Equation 5.4.1) is:

$$\frac{8.1 \times 10^{-3}}{0.125} \times 100 = 6.5\%$$

Remember, the logarithm 2.09 indicates a hydronium ion concentration with only two significant figures.

? Exercise 5.4.3

Calculate the percent ionization of a 0.10 *M* solution of acetic acid with a pH of 2.89.

Answer

1.3% ionized

5.4.3: Summary

The strengths of Brønsted-Lowry acids in aqueous solutions can be determined by their acid ionization constants. Weak acids are only partially ionized in water. The pH of an acid solution can be determined using the concentration of the acid and the its acid ionization constant.

5.4.4: Key Equations

- $K_a = \frac{[H_3O^+][A^-]}{[HA]}$
- $\text{Percent ionization} = \frac{[H_3O^+]_{eq}}{[HA]_0} \times 100$

Glossary

acid ionization constant (K_a)

equilibrium constant for the ionization of a weak acid

percent ionization

ratio of the concentration of the ionized acid to the initial acid concentration, times 100