16.4: Quantitative Aspects of Acid-Base Equilibria

> ◖◗ **Learning Objectives**
>
> - To use K_a and K_b values to calculate the percent ionization and the pH of a solution of an acid or a base.

This section presents a quantitative approach to analyzing acid–base equilibriums. You will learn how to determine the values of K_a and K_b, how to use K_a or K_b to calculate the percent ionization and the pH of an aqueous solution of an acid or a base, and how to calculate the equilibrium constant for the reaction of an acid with a base from the K_a and K_b of the reactants.

Determining K_a and K_b

The ionization constants K_a and K_b are equilibrium constants that are calculated from experimentally measured concentrations, just like the equilibrium constants discussed in Chapter 15. Before proceeding further, it is important to understand exactly what is meant when we describe the concentration of an aqueous solution of a weak acid or a weak base. Suppose, for example, we have a bottle labeled 1.0 M acetic acid or 1.0 M ammonia. As you learned in Chapter 8, such a solution is usually prepared by dissolving 1.0 mol of acetic acid or ammonia in water and adding enough water to give a final volume of exactly 1.0 L. If, however, we were to list the actual concentrations of all the species present in either solution, we would find that *none* of the values is exactly 1.0 M because a weak acid such as acetic acid or a weak base such as ammonia always reacts with water to some extent. The extent of the reaction depends on the K_a or the K_b, the concentration of the acid or the base, and the temperature. Consequently, only the *total concentration* of both the ionized and unionized species is equal to 1.0 M.

The *analytical concentration* (*C*) is defined as the *total* concentration of all forms of an acid or a base that are present in solution, regardless of their state of protonation. Thus a "1.0 M" solution of acetic acid has an analytical concentration of 1.0 M, which is the sum of the *actual* concentrations of unionized acetic acid (CH_3CO_2H) and the ionized form ($CH_3CO_2^-$):

$$C_{CH_3CO_2H} = [CH_3CO_2H] + [CH_3CO_2^-] \tag{16.4.1}$$

As we shall see shortly, if we know the analytical concentration and the K_a, we can calculate the actual values of $[CH_3CO_2H]$ and $[CH_3CO_2^-]$.

The equilibrium equations for the reaction of acetic acid and ammonia with water are as follows:

$$K_a = \frac{[H^+][CH_3CO_2^-]}{[CH_3CO_2H]} \tag{16.4.2}$$

$$K_b = \frac{[NH_4^+][OH^-]}{[NH_3]} \tag{16.4.3}$$

where K_a and K_b are the ionization constants for acetic acid and ammonia, respectively. In addition to the analytical concentration of the acid (or the base), we must have a way to measure the concentration of at least *one* of the species in the equilibrium constant expression to determine the K_a (or the K_b). There are two common ways to obtain the concentrations: (1) measure the electrical conductivity of the solution, which is related to the total concentration of ions present, and (2) measure the pH of the solution, which gives $[H^+]$ or $[OH^-]$.

Example 6 and Example 7 illustrate the procedure for determining K_a for a weak acid and K_b for a weak base. In both cases, we will follow the procedure developed in Chapter 15: the analytical concentration of the acid or the base is the *initial* concentration, and the stoichiometry of the reaction with water determines the *change* in concentrations. The *final* concentrations of all species are calculated from the initial concentrations and the changes in the concentrations. Inserting the final concentrations into the equilibrium constant expression enables us to calculate the K_a or the K_b.

Example 16.4.1

Electrical conductivity measurements indicate that 0.42% of the acetic acid molecules in a 1.00 M solution are ionized at 25°C. Calculate K_a and pK_a for acetic acid at this temperature.

Given: analytical concentration and percent ionization

Asked for: K_a and pK_a

Strategy:

A Write the balanced equilibrium equation for the reaction and derive the equilibrium constant expression.

B Use the data given and the stoichiometry of the reaction to construct a table showing the initial concentrations, the changes in concentrations, and the final concentrations for all species in the equilibrium constant expression.

C Substitute the final concentrations into the equilibrium constant expression and calculate the K_a. Take the negative logarithm of K_a to obtain the pK_a.

Solution:

A The balanced equilibrium equation for the dissociation of acetic acid is as follows:

$$CH_3CO_2H_{(aq)} \rightleftharpoons H^+_{(aq)} + CH3CO^-_{2(aq)} \tag{16.4.1}$$
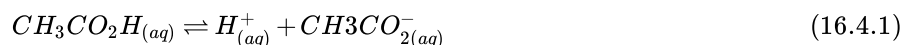
and the equilibrium constant expression is as follows:

$$K_a = \frac{[H^+][CH_3CO_2^-]}{[CH_3CO_2H]} \tag{16.4.2}$$

B To calculate the K_a, we need to know the equilibrium concentrations of CH_3CO_2H, $CH_3CO_2^-$, and H^+. The most direct way to do this is to construct a table that lists the initial concentrations and the changes in concentrations that occur during the reaction to give the final concentrations, using the procedure introduced in Chapter 15. The initial concentration of unionized acetic acid ($[CH_3CO_2H]_i$) is the analytical concentration, 1.00 M, and the initial acetate concentration ($[CH_3CO_2^-]_i$) is zero. The initial concentration of H^+ is not zero, however; $[H^+]_i$ is 1.00×10^{-7} M due to the autoionization of water. The measured percent ionization tells us that 0.42% of the acetic acid molecules are ionized at equilibrium. Consequently, the change in the concentration of acetic acid is $\Delta[CH_3CO_2H] = -(4.2 \times 10^{-3})(1.00$ M$) = -0.0042$ M. Conversely, the change in the acetate concentration is $\Delta[CH_3CO_2^-] = +0.0042$ M because every 1 mol of acetic acid that ionizes gives 1 mol of acetate. Because one proton is produced for each acetate ion formed, $\Delta[H^+] = +0.0042$ M as well. These results are summarized in the following table.

$CH_3CO_2H_{(aq)} \rightleftharpoons H^+_{(aq)} + CH_3CO^-_{2(aq)}$			(16.4.3)
	[CH₃CO₂H]	[H⁺]	[CH₃CO₂⁻]
initial	1.00	1.00×10^{-7}	0
change	−0.0042	+0.0042	+0.0042
final			

The final concentrations of all species are therefore as follows:

- $[CH_3CO_2H]_f = [CH_3CO_2H]_i + \Delta[CH_3CO_2H] = 1.00\ M + (-0.0042\ M) = 1.00\ M$
- $[CH_3CO_2^-]_f = [CH_3CO_2^-]_i + \Delta[CH_3CO_2^-] = 0\ M + (+0.0042\ M) = 0.0042\ M$
- $[H^+]_f = [H^+]_i + \Delta[H^+] = 1.00 \times 10^{-7}\ M + (+0.0042\ M) = 0.0042\ M$

**C** We can now calculate K_a by inserting the final concentrations into the equilibrium constant expression:

$$K_a = \frac{[H^+][CH_3CO_2^-]}{[CH_3CO_2H]} = \frac{(0.0042)(0.0042)}{1.00} = 1.8 \times 10^{-5} \tag{16.4.4}$$

The pK_a is the negative logarithm of K_a: pK_a = −log K_a = −log(1.8×10^{-5}) = 4.74.

Exercise

Picric acid is the common name for 2,4,6-trinitrophenol, a derivative of phenol (C_6H_5OH) in which three H atoms are replaced by nitro (–NO_2) groups. The presence of the nitro groups removes electron density from the phenyl ring, making picric acid a much stronger acid than phenol (pK_a = 9.99). The nitro groups also make picric acid potentially explosive, as you might expect based on

its chemical similarity to 2,4,6-trinitrotoluene, better known as TNT. A 0.20 M solution of picric acid is 73% ionized at 25°C. Calculate K_a and pK_a for picric acid.

picric acid   trinitrotoluene (TNT)
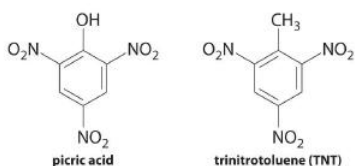
Answer: $K_a = 0.39$; $pK_a = 0.41$

Example 16.4.2

A 1.0 M aqueous solution of ammonia has a pH of 11.63 at 25°C. Calculate K_b and pK_b for ammonia.

Given: analytical concentration and pH

Asked for: K_b and pK_b

Strategy:

A Write the balanced equilibrium equation for the reaction and derive the equilibrium constant expression.

B Use the data given and the stoichiometry of the reaction to construct a table showing the initial concentrations, the changes in concentrations, and the final concentrations for all species in the equilibrium constant expression.

C Substitute the final concentrations into the equilibrium constant expression and calculate the K_b. Take the negative logarithm of K_b to obtain the pK_b.

Solution:

A The balanced equilibrium equation for the reaction of ammonia with water is as follows:

$$NH_{3(aq)} + H_2O_{(l)} \rightleftharpoons NH_{4(aq)}^+ + OH_{(aq)}^-$$
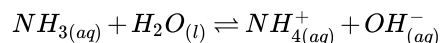
and the equilibrium constant expression is as follows:

$$K_b = \frac{[NH_4^+][OH^-]}{[NH_3]}$$

Remember that water does not appear in the equilibrium constant expression for K_b.

B To calculate K_b, we need to know the equilibrium concentrations of NH_3, NH_4^+, and OH^-. The initial concentration of NH_3 is the analytical concentration, 1.0 M, and the initial concentrations of NH_4^+ and OH^- are 0 M and 1.00×10^{-7} M, respectively. In this case, we are given the pH of the solution, which allows us to calculate the final concentration of one species (OH^-) directly, rather than the change in concentration. Recall that $pK_w = pH + pOH = 14.00$ at 25°C. Thus $pOH = 14.00 - pH = 14.00 - 11.63 = 2.37$, and $[OH^-]_f = 10^{-2.37} = 4.3 \times 10^{-3}$ M. Our data thus far are listed in the following table.

$NH_{3(aq)} \rightleftharpoons NH_{4(aq)}^+ + OH_{(aq)}^-$			(16.4.5)
	$[NH_3]$	$[NH_4^+]$	$[OH^-]$
initial	1.0	0	1.00×10^{-7}
change			
final			4.3×10^{-3}

The final $[OH^-]$ is much greater than the initial $[H^+]$, so the change in $[OH^-]$ is as follows:

$\Delta[OH^-] = (4.3 \times 10^{-3}$ M$) - (1.00 \times 10^{-7}$ M$) \approx 4.3 \times 10^{-3}$ M

The stoichiometry of the reaction tells us that 1 mol of NH_3 is converted to NH_4^+ for each 1 mol of OH^- formed, so

$\Delta[NH_4^+] = +4.3 \times 10^{-3}$ M and $\Delta[NH_3] = -4.3 \times 10^{-3}$ M

We can now insert these values for the changes in concentrations into the table, which enables us to complete the table.

$H_2O_{(l)} + NH3_{(aq)} \rightleftharpoons NH_{4(aq)}^+ + OH_{(aq)}^-$			(16.4.6)
	[NH$_3$]	[NH$_4^+$]	[OH$^-$]
initial	1.0	0	1.00×10^{-7}
change	-4.3×10^{-3}	$+4.3 \times 10^{-3}$	$+4.3 \times 10^{-3}$
final	1.0	4.3×10^{-3}	4.3×10^{-3}

**C** Inserting the final concentrations into the equilibrium constant expression gives K_b:

$$K_b = \frac{[NH_4^+][OH^-]}{[NH_3]} = \frac{(4.3 \times 10^{-3})^2}{1.0} = 1.8 \times 10^{-5}$$

and pK_b = −log K_b = 4.74.

The K_b and the pK_b for ammonia are almost exactly the same as the K_a and the pK_a for acetic acid at 25°C. In other words, ammonia is almost exactly as strong a base as acetic acid is an acid. Consequently, the extent of the ionization reaction in an aqueous solution of ammonia at a given concentration is the same as in an aqueous solution of acetic acid at the same concentration.

Exercise

The pH of a 0.050 M solution of pyridine (C$_6$H$_5$N) is 8.96 at 25°C. Calculate K_b and pK_b for pyridine.

pyridine
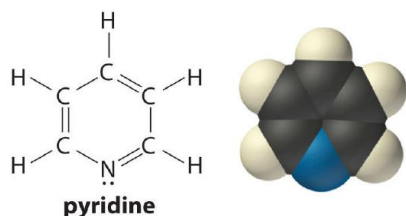
Answer: K_b = 1.7 × 10^{-9}; pK_b = 8.77

Calculating Percent Ionization from K_a or K_b

When carrying out a laboratory analysis, chemists frequently need to know the concentrations of all species in solution. Because the reactivity of a weak acid or a weak base is usually very different from the reactivity of its conjugate base or acid, we often need to know the percent ionization of a solution of an acid or a base to understand a chemical reaction. The percent ionization is defined as follows:

$$\text{percent ionization } of \text{ acid} = \frac{[H^+]}{C_{HA}} \times 100 \tag{16.4.4}$$

$$\text{percent ionization } of \text{ base} = \frac{[OH^-]}{C_B} \times 100 \tag{16.4.5}$$

One way to determine the concentrations of species in solutions of weak acids and bases is a variation of the tabular method we used previously to determine K_a and K_b values. As a demonstration, we will calculate the concentrations of all species and the percent ionization in a 0.150 M solution of formic acid at 25°C. The data in Table E1 show that formic acid (K_a = 1.8 × 10^{-4} at 25°C) is a slightly stronger acid than acetic acid. The equilibrium equation for the ionization of formic acid in water is as follows:

$$HCO_2H_{(aq)} \rightleftharpoons H_{(aq)}^+ + HCO_{2(aq)}^- \tag{16.4.6}$$
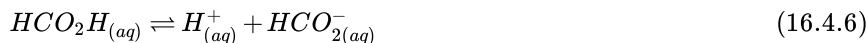
and the equilibrium constant expression for this reaction is as follows:

$$K_a = \frac{[H^+][HCO_2^-]}{[HCO_2H]} \tag{16.4.7}$$

We set the initial concentration of HCO_2H equal to 0.150 M, and that of HCO_2^- is 0 M. The initial concentration of H^+ is 1.00×10^{-7} M due to the autoionization of water. Because the equilibrium constant for the ionization reaction is small, the equilibrium will lie to the left, favoring the unionized form of the acid. Hence we can define x as the amount of formic acid that dissociates.

If the change in $[HCO_2H]$ is $-x$, then the change in $[H^+]$ and $[HCO_2^-]$ is $+x$. The final concentration of each species is the sum of its initial concentration and the change in concentration, as summarized in the following table.

$HCO_2H_{(aq)} \rightleftharpoons H^+_{(aq)} + HCO^-_{2(aq)}$			(16.4.7)
	[HCO$_2$H]	[H$^+$]	[HCO$_2^-$]
initial	0.150	1.00×10^{-7}	0
change	$-x$	$+x$	$+x$
final	$(0.150 - x)$	$(1.00 \times 10^{-7} + x)$	x

We can calculate x by substituting the final concentrations from the table into the equilibrium constant expression:

$$K_a = \frac{[H^+][HCO_2^-]}{[HCO_2H]} = \frac{(1.00 \times 10^{-7} + x)x}{0.150 - x} \tag{16.4.8}$$

Because the ionization constant K_a is small, x is likely to be small compared with the initial concentration of formic acid: $(0.150 - x)$ M ≈ 0.150 M. Moreover, $[H^+]$ due to the autoionization of water $(1.00 \times 10^{-7}$ M) is likely to be negligible compared with $[H^+]$ due to the dissociation of formic acid: $(1.00 \times 10^{-7} + x)$ M $\approx x$ M. Inserting these values into the equilibrium constant expression and solving for x,

$$K_a = \frac{x^2}{0.150} = 1.8 \times 10^{-4} \tag{16.4.9}$$

$$x = 5.2 \times 10^{-3} \tag{16.4.10}$$

We can now calculate the concentrations of the species present in a 0.150 M formic acid solution by inserting this value of x into the expressions in the last line of the table:

$$[HCO_2H] = (0.150 - x)\ M = 0.145\ M \tag{16.4.11}$$

$$[HCO_2] = x = 5.2 \times 10^{-3}\ M \tag{16.4.12}$$

$$[H^+] = (1.00 \times 10 - 7 + x)M = 5.2 \times 10^{-3} M \tag{16.4.13}$$

Thus the pH of the solution is $-\log(5.2 \times 10^{-3}) = 2.28$. We can also use these concentrations to calculate the fraction of the original acid that is ionized. In this case, the percent ionization is the ratio of $[H^+]$ (or [HCO$_2^-$]) to the analytical concentration, multiplied by 100 to give a percentage:

$$\text{percent ionization} = \frac{[H^+]}{C_{HA}} \times 100 = \frac{5.2 \times 10^{-3}\ M}{0.150} \times 100 = 3.5\% \tag{16.4.14}$$

Always check to make sure that any simplifying assumption was valid. As a general rule of thumb, approximations such as those used here are valid *only* if the quantity being neglected is no more than about 5% of the quantity to which it is being added or from which it is being subtracted. If the quantity that was neglected is much greater than about 5%, then the approximation is probably not valid, and you should go back and solve the problem using the quadratic formula. In the previous demonstration, both simplifying assumptions were justified: the percent ionization is only 3.5%, which is well below the approximately 5% limit, and the 1.00×10^{-7} M $[H^+]$ due to the autoionization of water is much, much less than the 5.2×10^{-3} M $[H^+]$ due to the ionization of formic acid.

As a general rule, the [H$^+$] contribution due to the autoionization of water can be ignored as long as the product of the acid or the base ionization constant and the analytical concentration of the acid or the base is at least 10 times greater than the [H$^+$] or [OH$^-$] from the autoionization of water—that is, if

$$K_a C_{HA} \geq 10(1.00 \times 10^{-7}) = 1.0 \times 10^{-6} \tag{16.4.8}$$

or

$$K_b C_B \geq 10(1.00 \times 10^{-7}) = 1.0 \times 10^{-6} \tag{16.4.9}$$

By substituting the appropriate values for the formic acid solution into Equation 16.45, we see that the simplifying assumption is valid in this case:

$$K_a C_{HA} = (1.8 \times 10^{-4})(0.150) = 2.7 \times 10^{-5} > 1.0 \times 10^{-6} \tag{16.4.10}$$

Doing this simple calculation before solving this type of problem saves time and allows you to write simplified expressions for the final concentrations of the species present. In practice, it is necessary to include the [H$^+$] contribution due to the autoionization of water only for extremely dilute solutions of very weak acids or bases.

Example 8 illustrates how the procedure outlined previously can be used to calculate the pH of a solution of a weak base.

Example 16.4.3

Calculate the pH and percent ionization of a 0.225 M solution of ethylamine (CH$_3$CH$_2$NH$_2$), which is used in the synthesis of some dyes and medicines. The pK_b of ethylamine is 3.19 at 20°C.

Given: concentration and pK_b

Asked for: pH and percent ionization

Strategy:

A Write the balanced equilibrium equation for the reaction and the equilibrium constant expression. Calculate K_b from pK_b.

B Use Equation 16.4.8 to see whether you can ignore [H$^+$] due to the autoionization of water. Then use a tabular format to write expressions for the final concentrations of all species in solution. Substitute these values into the equilibrium equation and solve for [OH$^-$]. Use Equation 16.4.5 to calculate the percent ionization.

C Use the relationship K_w = [OH$^-$][H$^+$] to obtain [H$^+$]. Then calculate the pH of the solution.

Solution:

A We begin by writing the balanced equilibrium equation for the reaction:

$$CH_3CH_2NH_{2(aq)} + H_2O_{(l)} \rightleftharpoons CH_3CH_2NH_{3(aq)}^+ + OH_{(aq)}^-$$
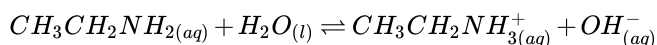
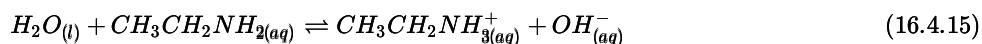The corresponding equilibrium constant expression is as follows:

$$K_b = \frac{[CH_3CH_2NH_3^+][OH^-]}{[CH_3CH_2NH_2]}]$$

From the pK_b, we have $K_b = 10 - 3.19 = 6.5 \times 10^{-4}$.

B To calculate the pH, we need to determine the H$^+$ concentration. Unfortunately, H$^+$ does not appear in either the chemical equation or the equilibrium constant expression. However, [H$^+$] and [OH$^-$] in an aqueous solution are related by K_w = [H$^+$][OH$^-$]. Hence if we can determine [OH$^-$], we can calculate [H$^+$] and then the pH. The initial concentration of CH$_3$CH$_2$NH$_2$ is 0.225 M, and the initial [OH$^-$] is 1.00 × 10^{-7} M. Because ethylamine is a weak base, the extent of the reaction will be small, and it makes sense to let x equal the amount of CH$_3$CH$_2$NH$_2$ that reacts with water. The change in [CH$_3$CH$_2$NH$_2$] is therefore −x, and the change in both [CH$_3$CH$_2$NH$_3$$^+$] and [OH$^-$] is +$x$. To see whether the autoionization of water can safely be ignored, we substitute K_b and C_B into Equation 16.4.10:

$$K_b C_B = (6.5 \times 10^{-4})(0.225) = 1.5 \times 10^{-4} > 1.0 \times 10^{-6}$$

Thus the simplifying assumption is valid, and we will not include [OH$^-$] due to the autoionization of water in our calculations.

$$H_2O_{(l)} + CH_3CH_2NH_{2(aq)} \rightleftharpoons CH_3CH_2NH_{3(aq)}^+ + OH_{(aq)}^- \tag{16.4.15}$$

	$[CH_3CH_2NH_2]$	$[CH_3CH_2NH_3{}^+]$	$[OH^-]$
initial	0.225	0	1.00×10^{-7}
change	$-x$	$+x$	$+x$
final	$(0.225 - x)$	x	x

Substituting the quantities from the last line of the table into the equilibrium constant expression,

$$K_b = \frac{[CH_3CH_2NH_3^+][OH^-]}{[CH_3CH_2NH_2]} = \frac{(x)(x)}{0.225 - x} = 6.5 \times 10^{-4}$$

As before, we assume the amount of $CH_3CH_2NH_2$ that ionizes is small compared with the initial concentration, so $[CH_3CH_2NH_2]_f$ = $0.225 - x \approx 0.225$. With this assumption, we can simplify the equilibrium equation and solve for x:

$$K_b = \frac{x^2}{0.225} = 6.5 \times 10^{-4}$$

$$x = 0.012 = [CH_3CH_2NH_3^+]_f = [OH^-]_f$$

The percent ionization is therefore

$$\text{percent ionization} = \frac{[OH^-]}{C_B} \times 100 = \frac{0.012 \ M}{0.225 \ M} \times 100 = 5.4\% \tag{16.4.16}$$

which is at the upper limit of the approximately 5% range that can be ignored. The final hydroxide concentration is thus 0.012 M.

C We can now determine the $[H^+]$ using the expression for K_w:

$$K_w = [OH^-][H^+]$$

$$1.01 \times 10^{-14} = (0.012 \ M)[H^+]$$

$$8.4 \times 10^{-13} \ M = [H^+]$$

The pH of the solution is $-\log(8.4 \times 10^{-13})$ = 12.08. Alternatively, we could have calculated pOH as $-\log(0.012)$ = 1.92 and determined the pH as follows:

$$pH + pOH = pK_w = 14.00$$

$$pH = 14.00 - 1.92 = 12.08$$

The two methods are equivalent.

Exercise

Aromatic amines, in which the nitrogen atom is bonded directly to a phenyl ring ($-C_6H_5$) tend to be much weaker bases than simple alkylamines. For example, aniline ($C_6H_5NH_2$) has a pK_b of 9.13 at 25°C. What is the pH of a 0.050 M solution of aniline?

Answer: 8.78

The previous examples illustrate a key difference between solutions of strong acids and bases and solutions of weak acids and bases. Because strong acids and bases ionize essentially completely in water, the percent ionization is always approximately 100%, regardless of the concentration. In contrast, the percent ionization in solutions of weak acids and bases is small and depends on the analytical concentration of the weak acid or base. As illustrated for benzoic acid in Figure 16.4.1, the percent ionization of a weak acid or a weak base actually *increases* as its analytical concentration decreases. The percent ionization also increases as the magnitude of K_a and K_b increases.
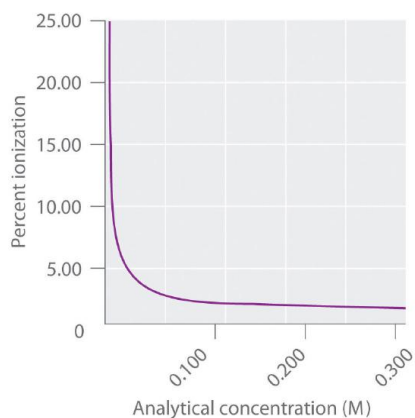
Figure 16.4.1 The Relationship between the Analytical Concentration of a Weak Acid and Percent **Ionization** As shown here for benzoic acid ($C_6H_5CO_2H$), the percent ionization decreases as the analytical concentration of a weak acid increases.

Unlike the K_a or the K_b, the percent ionization is not a constant for weak acids and bases but depends on *both* the K_a or the K_b *and* the analytical concentration. Consequently, the procedure in Example 8 must be used to calculate the percent ionization and pH for solutions of weak acids and bases. Example 9 and its corresponding exercise demonstrate that the combination of a dilute solution and a relatively large K_a or K_b can give a percent ionization much greater than 5%, making it necessary to use the quadratic equation to determine the concentrations of species in solution.

Note the Pattern

The percent ionization in a solution of a weak acid or a weak base *increases* as the analytical concentration *decreases* and as the K_a or the K_b *increases*.

Example 16.4.4

Benzoic acid ($C_6H_5CO_2H$) is used in the food industry as a preservative and medically as an antifungal agent. Its pK_a at 25°C is 4.20, making it a somewhat stronger acid than acetic acid. Calculate the percentage of benzoic acid molecules that are ionized in each solution.

1. a 0.0500 M solution
2. a 0.00500 M solution

Given: concentrations and pK_a
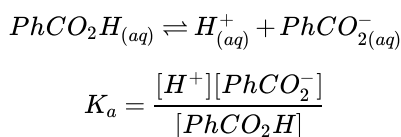
Asked for: percent ionization

Strategy:

A Write both the balanced equilibrium equation for the ionization reaction and the equilibrium equation (Equation 16.2.2). Use Equation 16.2.13 to calculate the K_a from the pK_a.

B For both the concentrated solution and the dilute solution, use a tabular format to write expressions for the final concentrations of all species in solution. Substitute these values into the equilibrium equation and solve for $[C_6H_5CO_2^-]_f$ for each solution.

C Use the values of $[C_6H_5CO_2^-]_f$ and Equation 16.4.4 to calculate the percent ionization.

Solution:

A If we abbreviate benzoic acid as $PhCO_2H$ where $Ph = -C_6H_5$, the balanced equilibrium equation for the ionization reaction and the equilibrium equation can be written as follows:

$$PhCO_2H_{(aq)} \rightleftharpoons H^+_{(aq)} + PhCO^-_{2(aq)}$$

$$K_a = \frac{[H^+][PhCO_2^-]}{[PhCO_2H]}$$

From the pK_a, we have $K_a = 10^{-4.20} = 6.3 \times 10^{-5}$.

1. **B** For the more concentrated solution, we set up our table of initial concentrations, changes in concentrations, and final concentrations:

$$PhCO_2H_{(aq)} \rightleftharpoons H^+_{(aq)} + PhCO^-_{2(aq)} \tag{16.4.17}$$

	[PhCO$_2$H]	[H$^+$]	[PhCO$_2$$^-$]
initial	0.0500	1.00×10^{-7}	0
change	$-x$	$+x$	$+x$
final	$(0.0500 - x)$	$(1.00 \times 10^{-7} + x)$	x

Inserting the expressions for the final concentrations into the equilibrium equation and making our usual assumptions, that [PhCO$_2$$^-$] and [H$^+$] are negligible due to the autoionization of water,

$$K_a = \frac{[H^+][PhCO_2^-]}{[PhCO_2H]} = \frac{(x)(x)}{0.0500 - x} = \frac{x^2}{0.0500} = 6.3 \times 10^{-5}$$

$$1.8 \times 10^{-3} = x$$

This value is less than 5% of 0.0500, so our simplifying assumption is justified, and [PhCO$_2$$^-$] at equilibrium is 1.8×10^{-3} M. We reach the same conclusion using C_{HA}: $K_a C_{HA} = (6.3 \times 10^{-5})(0.0500) = 3.2 \times 10^{-6} > 1.0 \times 10^{-6}$.

C The percent ionized is the ratio of the concentration of PhCO$_2$$^-$ to the analytical concentration, multiplied by 100:

$$\text{percent ionized} = \frac{[PhCO_2^-]}{C_{PhCO_2H}} \times 100 = \frac{1.8 \times 10^{-30}}{0.0500} \times 100 = 3.6\%$$

Because only 3.6% of the benzoic acid molecules are ionized in a 0.0500 M solution, our simplifying assumptions are confirmed.

2. **B** For the more dilute solution, we proceed in exactly the same manner. Our table of concentrations is therefore as follows:

$$PhCO_2H_{(aq)} \rightleftharpoons H^+_{(aq)} + PhCO^-_{2(aq)} \tag{16.4.18}$$

	[PhCO$_2$H]	[H$^+$]	[PhCO$_2$$^-$]
initial	0.00500	1.00×10^{-7}	0
change	$-x$	$+x$	$+x$
final	$(0.00500 - x)$	$(1.00 \times 10^{-7} + x)$	x

Inserting the expressions for the final concentrations into the equilibrium equation and making our usual simplifying assumptions,

$$K_a = \frac{[H^+][PhCO_2^-]}{[PhCO_2H]} = \frac{(x)(x)}{0.00500 - x} = \frac{x^2}{0.00500} = 6.3 \times 10^{-5}$$

$$5.6 \times 10^{-4} = x$$

Unfortunately, this number is greater than 10% of 0.00500, so our assumption that the fraction of benzoic acid that is ionized in this solution could be neglected and that $(0.00500 - x) \approx x$ is not valid. Furthermore, we see that $K_a C_{HA} = (6.3 \times 10^{-5})(0.00500)$ = $3.2 \times 10^{-7} < 1.0 \times 10^{-6}$. Thus the relevant equation is as follows:

$$\frac{x^2}{0.00500 - x} = 6.3 \times 10^{-5}$$

which must be solved using the quadratic formula. Multiplying out the quantities,

$x^2 = (6.3 \times 10^{-5})(0.00500 - x) = (3.2 \times 10^{-7}) - (6.3 \times 10^{-5})x$

Rearranging the equation to fit the standard quadratic equation format,

$$x^2 + (6.3 \times 10^{-5})x - (3.2 \times 10^{-7}) = 0$$

This equation can be solved by using the quadratic formula:

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

$$x = \frac{-(6.3 \times 10^{-5}) \pm \sqrt{(6.3 \times 10^{-5})^2 - 4(1)(-3.2 \times 10^{-7})}}{2(1)}$$

$$x = \frac{-(6.3 \times 10^{-5}) \pm (1.1 \times 10^{-3})}{2} = 5.3 \times 10^{-4}$$

or

$$x = -5.9 \times 10^{-4}$$

Because a negative x value corresponds to a negative $[PhCO_2^-]$, which is not physically meaningful, we use the positive solution: $x = 5.3 \times 10^{-4}$. Thus $[PhCO_2^-] = 5.3 \times 10^{-4}$ M.

C The percent ionized is therefore

$$\text{percent ionized} = \frac{[PhCO_2^-]C_{PhCO_2H}}{\times}100 = \frac{5.3 \times 10^{-4}}{0.00500} \times 100 = 11\%$$

In the more dilute solution (C = 0.00500 M), 11% of the benzoic acid molecules are ionized versus only 3.6% in the more concentrated solution (C = 0.0500 M). Decreasing the analytical concentration by a factor of 10 results in an approximately threefold increase in the percentage of benzoic acid molecules that are ionized.

Exercise

Lactic acid ($CH_3CH(OH)CO_2H$) is a weak acid with a pK_a of 3.86 at 25°C. What percentage of the lactic acid is ionized in each solution?
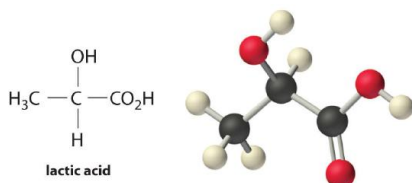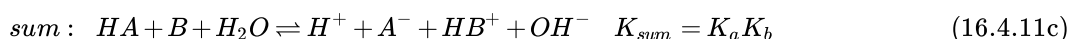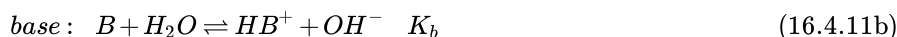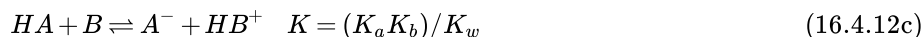

1. a 0.10 M solution
2. a 0.0020 M solution

Answer

1. 3.7%
2. 23%

Determining K_{eq} from K_a and K_b

In Section 16.2 , you learned how to use K_a and K_b values to qualitatively predict whether reactants or products are favored in an acid–base reaction. Tabulated values of K_a (or pK_a) and K_b (or pK_b), plus the K_w, enable us to quantitatively determine the direction and extent of reaction for a weak acid and a weak base by calculating K for the reaction. To illustrate how to do this, we begin by writing the dissociation equilibriums for a weak acid and a weak base and then summing them:

$$acid: \ \ HA \rightleftharpoons H^+ + A^- \quad K_a \tag{16.4.11a}$$

$$base: \ \ B + H_2O \rightleftharpoons HB^+ + OH^- \quad K_b \tag{16.4.11b}$$

$$sum: \ \ HA + B + H_2O \rightleftharpoons H^+ + A^- + HB^+ + OH^- \quad K_{sum} = K_a K_b \tag{16.4.11c}$$

The overall reaction has H_2O on the left and H^+ and OH^- on the right, which means it involves the autoionization of water ($H_2O \rightleftharpoons H^+ + OH^-$) in addition to the acid–base equilibrium in which we are interested. We can obtain an equation that includes only the acid–base equilibrium by simply adding the equation for the reverse of the autoionization of water ($H^+ + OH^- \rightleftharpoons H_2O$), for which $K = 1/K_w$, to the overall equilibrium in Equation 16.4.11 and canceling:

$$HA + B + H_2\cancel{O} \rightleftharpoons \cancel{H^+} + A^- + HB^+ + \cancel{OH^-} \quad K_{sum} = K_a K_b \tag{16.4.12a}$$

$$\cancel{H^+} + \cancel{OH^-} \rightleftharpoons H_2\cancel{O} \quad 1/K_w \tag{16.4.12b}$$

$$HA + B \rightleftharpoons A^- + HB^+ \quad K = (K_a K_b)/K_w \tag{16.4.12c}$$

Thus the equilibrium constant for the reaction of a weak acid with a weak base is the product of the ionization constants of the acid and the base divided by K_w. Example 10 illustrates how to calculate the equilibrium constant for the reaction of a weak acid with a weak base.

Example 16.4.5

Fish tend to spoil rapidly, even when refrigerated. The cause of the resulting "fishy" odor is a mixture of amines, particularly methylamine (CH_3NH_2), a volatile weak base (pK_b = 3.34). Fish is often served with a wedge of lemon because lemon juice contains citric acid, a triprotic acid with pK_a values of 3.13, 4.76, and 6.40 that can neutralize amines. Calculate the equilibrium constant for the reaction of excess citric acid with methylamine, assuming that only the first dissociation constant of citric acid is important.

CH$_2$CO$_2$H
|
HOCCO$_2$H
|
CH$_2$CO$_2$H

citric acid
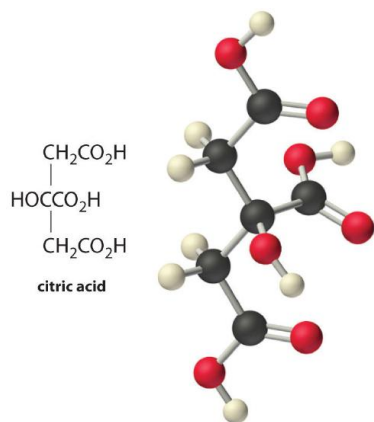
Given: pK_b for base and pK_a for acid

Asked for: K

Strategy:

A Write the balanced equilibrium equation and the equilibrium constant expression for the reaction.

B Convert pK_a and pK_b to K_a and K_b and then use Equation 16.4.12 to calculate K.

Solution:

A If we abbreviate citric acid as H$_3$citrate, the equilibrium equation for its reaction with methylamine is as follows:

$$CH_3NH_{2(aq)} + H_3citrate_{(aq)} \rightleftharpoons CH_3NH^+_{3(aq)} + H_2citrate^-_{(aq)}$$
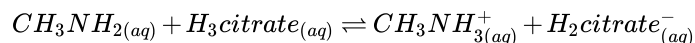
The equilibrium constant expression for this reaction is as follows:

$$K = \frac{[CH_3NH^+_3][H_2citrate^-]}{[CH_3NH_2][H_3citrate]}$$

B Equation 16.49 is $K = (K_a K_b)/K_w$. Converting pK_a and pK_b to K_a and K_b gives $K_a = 10^{-3.13} = 7.4 \times 10^{-4}$ for citric acid and $K_b = 10^{-3.34} = 4.6 \times 10^{-4}$ for methylamine. Substituting these values into the equilibrium equation,

$$K = \frac{K_a K_b}{K_w} = \frac{(7.4 \times 10^{-4})(4.6 \times 10^{-4})}{1.01 \times 10^{-14}} = 3.4 \times 10^7$$

The value of pK can also be calculated directly by taking the negative logarithm of both sides of Equation 16.49, which gives

\(pK = pK_a + pK_b − pK_w = 3.13 + 3.34 − 14.00 = −7.53 \notag \]

Thus $K = 10^{-(-7.53)} = 3.4 \times 10^7$, in agreement with the earlier value. In either case, the K values show that the reaction of citric acid with the volatile, foul-smelling methylamine lies very far to the right, favoring the formation of a much less volatile salt with no odor. This is one reason a little lemon juice helps make less-than-fresh fish more appetizing.

Exercise

Dilute aqueous ammonia solution, often used as a cleaning agent, is also effective as a deodorizing agent. To see why, calculate the equilibrium constant for the reaction of aqueous ammonia with butyric acid ($CH_3CH_2CH_2CO_2H$), a particularly foul-smelling substance associated with the odor of rancid butter and smelly socks. The pK_b of ammonia is 4.75, and the pK_a of butyric acid is 4.83.

Answer: 2.6×10^4

Summary

If the concentration of one or more of the species in a solution of an acid or a base is determined experimentally, K_a and K_b can be calculated, and K_a, pK_a, K_b, and pK_b can be used to quantitatively describe the composition of solutions of acids and bases. The concentrations of all species present in solution can be determined, as can the pH of the solution and the percentage of the acid or base that is ionized. The equilibrium constant for the reaction of a weak acid with a weak base can be calculated from K_a (or pK_a), K_b (or pK_b), and K_w.

Key Takeaway

- For a solution of a weak acid or a weak base, the percent ionization increases as the K_a or the K_b increases and as the analytical concentration decreases.

Key Equations

Percent ionization of acid

Equation 16.4.4: $= \dfrac{[H^+]}{C_{HA}} \times 100$

Percent ionization of base

Equation 16.4.5: $= \dfrac{[OH^-]}{C_B} \times 100$

Equilibrium constant for reaction of a weak acid with a weak base

Equation 16.4.12: $K = \dfrac{K_a K_b}{K_w}$

Conceptual Problems

1. Explain why the analytical concentration (C) of H_2SO_4 is equal to $[H_2SO_4] + [HSO_4^-] + [SO_4^{2-}]$.

2. Write an expression for the analytical concentration (C) of H_3PO_4 in terms of the concentrations of the species actually present in solution.

3. For relatively dilute solutions of a weak acid such as acetic acid (CH_3CO_2H), the concentration of undissociated acetic acid in solution is often assumed to be the same as the analytical concentration. Explain why this is a valid practice.

4. How does dilution affect the percent ionization of a weak acid or a weak base?

5. What is the relationship between the K_a of a weak acid and its percent ionization? Does a compound with a large pK_a value have a higher or a lower percent ionization than a compound with a small pK_a value (assuming the same analytical concentration in both cases)? Explain.

6. For a dilute solution of a weak acid (HA), show that the pH of the solution can be approximated using the following equation (where C_{HA} is the analytical concentration of the weak acid):

$$pH = -\log \sqrt{K_a C_{HA}} \qquad (16.4.19)$$

Under what conditions is this approximation valid?

Numerical Problems

1. The pK_a of NH_3 is estimated to be 35. Its conjugate base, the amide ion (NH_2^-), can be isolated as an alkali metal salt, such as sodium amide ($NaNH_2$). Calculate the pH of a solution prepared by adding 0.100 mol of sodium amide to 1.00 L of water. Does the pH differ appreciably from the pH of a NaOH solution of the same concentration? Why or why not?

2. Phenol is a topical anesthetic that has been used in throat lozenges to relieve sore throat pain. Describe in detail how you would prepare a 2.00 M solution of phenol (C_6H_5OH) in water; then write equations to show all the species present in the solution. What is the equilibrium constant expression for the reaction of phenol with water? Use the information in Table E1 and Table E2 to calculate the pH of the phenol solution.

3. Describe in detail how you would prepare a 1.50 M solution of methylamine in water; then write equations to show all the species present in the solution. What is the equilibrium constant expression for the reaction of methylamine with water? Use the information in Table E1 and Table E2 to calculate the pH of the solution.

4. A 0.200 M solution of diethylamine, a substance used in insecticides and fungicides, is only 3.9% ionized at 25°C. Write an equation showing the equilibrium reaction and then calculate the pK_b of diethylamine. What is the pK_a of its conjugate acid, the diethylammonium ion? What is the equilibrium constant expression for the reaction of diethylammonium chloride with water?

5. A 1.00 M solution of fluoroacetic acid (FCH_2CO_2H) is 5% dissociated in water. What is the equilibrium constant expression for the dissociation reaction? Calculate the concentration of each species in solution and then calculate the pK_a of FCH_2CO_2H.

6. The pK_a of 3-chlorobutanoic acid ($CH_3CHClCH_2CO_2H$) is 4.05. What percentage is dissociated in a 1.0 M solution? Do you expect the pK_a of butanoic acid to be greater than or less than the pK_a of 3-chlorobutanoic acid? Why?

7. The pK_a of the ethylammonium ion ($C_2H_5NH_3^+$) is 10.64. What percentage of ethylamine is ionized in a 1.00 M solution of ethylamine?

8. The pK_a of Cl_3CCO_2H is 0.64. What is the pH of a 0.580 M solution? What percentage of the Cl_3CCO_2H is dissociated?

9. The pH of a 0.150 M solution of aniline hydrochloride ($C_6H_5NH_3^+Cl^-$) is 2.70. What is the pK_b of the conjugate base, aniline ($C_6H_5NH_2$)? Do you expect the pK_b of $(CH_3)_2CHNH_2$ to be greater than or less than the pK_b of $C_6H_5NH_2$? Why?

10. What is the pH of a 0.620 M solution of $CH_3NH_3^+Br^-$ if the pK_b of CH_3NH_2 is 10.62?

11. The pK_b of 4-hydroxypyridine is 10.80 at 25°C. What is the pH of a 0.0250 M solution?
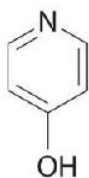
12. The pK_a values of formic acid and the methylammonium ion are 3.75 and 10.62, respectively. Calculate K for the following reaction:

$$HCO_{2(aq)}^- + CH_3NH_{3(aq)}^+ \rightleftharpoons HCO_2H_{(aq)} + CH_3NH_{2(aq)} \qquad (16.4.20)$$
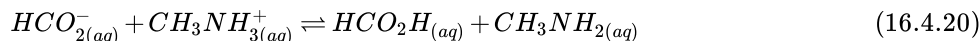
13. The pK_a values of butanoic acid and the ammonium ion are 4.82 and 9.24, respectively. Calculate K for the following reaction:

$$CH_3CH_2CH_2CO_{2(aq)}^- + NH_{4(aq)}^+ \rightleftharpoons CH_3CH_2CH_2CO_2H_{(aq)} + NH_{3(aq)} \qquad (16.4.21)$$
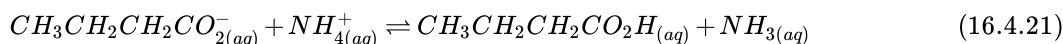
14. Use the information in Tables E1 and E2 to calculate the pH of a 0.0968 M solution of calcium formate.

15. Calculate the pH of a 0.24 M solution of sodium lactate. The pK_a of lactic acid is 3.86.

16. Use the information in Tables E1 and E2 to determine the pH of a solution prepared by dissolving 750.0 mg of methylammonium chloride ($CH_3NH_3^+Cl^-$) in enough water to make 150.0 mL of solution.

17. Use the information in Tables E1 and E2 to determine the pH of a solution prepared by dissolving 855 mg of sodium nitrite ($NaNO_2$) in enough water to make 100.0 mL of solution.

Answers

1.
2.
3.
4.
5.
6.
7.
8.

9. pK_b = 9.43; $(CH_3)_2CHNH_2$ will be a stronger base and have a lower pK_b; aniline is a weaker base because the lone pair on the nitrogen atom can be delocalized on the aromatic ring.

10.
11.
12.

13. 3.8×10^{-5}

14.
15.
16.

17. 8.18

Contributors

- Anonymous

Modified by Joshua B. Halpern