8.4 Calculations Involving Acidic Solutions

In Section 8.2, we considered fundamental definitions relevant to acid–base solutions. Now we can describe the equilibria in these systems in a more quantitative way.

When we deal with acid–base equilibria, we must focus on the solution components and their chemistry. For example, what entities are present in a 1.0 mol/L solution of HCl(aq)? Since hydrochloric acid is a strong acid, we assume that it is completely ionized. Thus, although the label on the bottle says 1.0 mol/L HCl(aq), the solution contains virtually no HCl(aq) molecules. Typically, container labels indicate the substance(s) used to make the solution but do not necessarily describe the solution components after ionization. Thus a 1.0 mol/L HCl(aq) solution contains mostly water, a significant amount of H^+(aq) ions and Cl^-(aq) ions, and only a very tiny amount of dissolved HCl(aq) molecules. This solution also contains OH^-(aq) ions, but in a highly acidic solution, OH^-(aq) ions are present only in very tiny concentrations and are considered to be minor entities. In solving acid–base problems, the importance of writing the major entities in the solution as the first step is often the key to solving these problems successfully.

LEARNING TIP

Problem-Solving Strategy for Acid–Base Problems

Think chemistry. Focus on the solution components and their reactions. It will almost always be possible to choose one reaction that is the most important.

Be systematic. Acid–base problems require a step-by-step approach.

Be flexible. Although all acid–base problems are similar in many ways, important differences do occur. Treat each problem as a unique challenge. Do not try to force a given problem into matching any you have solved before. Look for both the similarities and the differences.

Be patient. The complete solution to a complicated problem cannot be seen immediately in all its detail. Pick the problem apart into its workable steps.

Be confident. Look within the problem for the solution, and let the problem guide you. Assume that you can think it out. Do not rely on memorizing solutions to problems. In fact, memorizing solutions is usually detrimental because you tend to try to force a new problem to be the same as one you have seen before. Understand and think; don't just memorize.

To illustrate the main ideas involved, let us calculate the pH of 1.0 mol/L HCl(aq). We first list the major entities: H^+ (aq), Cl^-(aq), and H_2O(l). When analyzing the acid–base characteristics of aqueous solutions, we consider the contributions of H^+(aq) and OH^-(aq) ions from the autoionization of water and external sources (dissolved acids and bases) separately. Since we want to calculate the pH, we will focus on those major entities that can produce H^+(aq) ions. Obviously, we must consider H^+(aq) from the ionization of HCl(aq). We know that HCl(aq) makes a significant contribution of H^+(aq) ions since it is a strong acid and therefore ionizes completely. However, we must also determine whether the autoionization of water is a significant source of H^+(aq) ions as well.

In pure water at 25 °C, $[H^+(aq)]$ is 1.0×10^{-7} mol/L. According to Le Châtelier's principle, in the acidic solution the H^+(aq) ions from the ionized HCl(aq) will drive the autoionization of water equilibrium to the left. Thus, the concentration of H^+(aq) produced by the autoionization of water will be even less than 1.0×10^{-7} mol/L. This is a negligible quantity compared with the 1.0 mol/L H^+(aq) contributed by the ionization of HCl(aq). Therefore, for this solution, we do not include the H^+(aq) ions produced by the autoionization of water in the calculation of pH; we only use the $[H^+(aq)]$ produced by the ionization of HCl(aq). Since HCl(aq) is a strong acid,

$$[H^+(aq)] = 1.0 \text{ mol/L}$$

$$\text{pH} = -\log[H^+]$$

$$= -\log(1.0)$$

$$\text{pH} = 0$$

Remember that, when analyzing equilibrium problems for solutions of acids and bases, all ions must be accounted for—hydrogen ions, hydroxide ions, conjugate bases, and conjugate acids—because these entities may all have an effect on the acid–base characteristics of the solution.

Calculations Involving Solutions of Strong Acids

Recall that a strong acid ionizes almost completely in water. Therefore, when solving problems involving strong acids, we can assume that the concentration of hydrogen ions in the solution is equal to the given concentration of the acid in the solution.

Tutorial 1 Determining $[H^+(aq)]$, $[OH^-(aq)]$, pH, and pOH

In this tutorial, you will learn how to calculate the $[H^+(aq)]$, $[OH^-(aq)]$, pH, and pOH of a solution of a strong acid, given the concentration of the acidic solution.

Sample Problem 1: Calculating $[H^+(aq)]$, $[OH^-(aq)]$, pH, and pOH from Solution Concentration

A scientist dilutes a commercial solution of nitric acid, $HNO_3(aq)$, by adding water. The final solution has 0.25 mol $HNO_3(l)$ in a total volume of 1.00 L. Determine the concentration of hydrogen ions and hydroxide ions, and the pH and pOH of the final solution at SATP.

Given: 0.25 mol HNO_3 (aq) in 1.00 L solution

Required: $[H^+(aq)]$ and $[OH^-(aq)]$

Solution:

Step 1. Calculate the amount concentration of the solution.

Since the solution that the scientist prepared has 0.25 mol nitric acid in a total volume of 1.00 L, the amount concentration is 0.25 mol/L $HNO_3(aq)$, or

$[HNO_3(aq)] = 0.25$ mol/L

Step 2. Determine the concentration of hydrogen ions in solution.

Nitric acid is a strong acid that ionizes 100 % in water, according to the equation

$$HNO_3(aq) \rightarrow H^+(aq) + NO_3^-(aq)$$

Therefore, every molecule of HNO_3 produces 1 hydrogen ion. You can therefore write

$[H^+(aq)] = [HNO_3(aq)]$

Step 3. Identify the major entities in solution.

The main entities in solution are $H^+(aq)$, $NO_3^-(aq)$, and $H_2O(l)$.

Step 4. Identify the major source(s) of hydrogen ions.

Since $HNO_3(aq)$ is a strong acid, you may ignore the $H^+(aq)$ ions contributed by the autoionization of water. Therefore, the only significant source of $H^+(aq)$ in solution is the ionization of $HNO_3(aq)$.

Step 5. Determine $[H^+(aq)]$.

Since HNO_3 ionizes completely, then

$[H^+(aq)] = 0.25$ mol/L

Step 6. Calculate the pH of the solution from $[H^+(aq)]$.

$$\begin{aligned} \text{pH} &= -\log[H^+(aq)] \\ &= -\log(0.25 \text{ mol/L}) \\ \text{pH} &= 0.60 \end{aligned}$$

Step 7. Use the K_w equation to calculate $[OH^-(aq)]$. Rearrange the equation so that the term you need is on the left side, then substitute in the known values.

$$\begin{aligned} K_w &= [H^+(aq)][OH^-(aq)] \\ [OH^-(aq)] &= \frac{K_w}{[H^+(aq)]} \\ &= \frac{1.0 \times 10^{-14}}{0.25} \text{ mol/L} \\ [OH^-(aq)] &= 4.0 \times 10^{-14} \text{ mol/L} \end{aligned}$$

Step 8. Use $[OH^-(aq)]$ to calculate the pOH of the solution.

$$\begin{aligned} \text{pOH} &= -\log[OH^-(aq)] \\ &= -\log(4.0 \times 10^{-14}) \\ \text{pOH} &= 13.40 \end{aligned}$$

Statement: For a 0.25 mol/L solution of $HNO_3(aq)$, the concentration of hydrogen ions is 0.25 mol/L, the concentration of hydroxide ions is 4.0×10^{-14} mol/L, pH is 0.60, and pOH is 13.40.

Practice

1. A hydrochloric acid solution has a concentration of 0.0700 mol/L. Calculate $[OH^-(aq)]$. K/U [ans: 1.43×10^{-13} mol/L].
2. A 2.00 L hydrobromic acid solution, HBr(aq), contains 0.070 mol of acid. Calculate the pH and pOH of the solution. K/U [ans: pH = 1.46; pOH = 12.54]

Calculations Involving Solutions of Weak Acids

When strong acids dissolve in water, virtually all of the acid molecules ionize into anions and hydrogen ions. However, weak acids do not completely ionize in water. Therefore, in a solution of a weak acid, there is a relatively large concentration of non-ionized acid molecules and much smaller concentrations of anions and hydrogen ions. Nevertheless, you may calculate the pH of a weak acid solution if you know the K_a value of the weak acid.

Percentage Ionization of Weak Acids

Before we calculate the pH of a weak acid solution, we will calculate the percentage ionization of a weak acid when it is dissolved in water. Consider the ionization of the generic weak acid, HA, in water. Since HA is a weak acid, only a small fraction of the molecules will ionize to form dissolved hydrogen ions and $A^-(aq)$ ions. If 0.10 mol of HA is added to 1.00 L of water, most of the HA molecules will remain non-ionized. Scientists commonly refer to the **percentage ionization** of weak acids, which is defined as follows:

percentage ionization the percentage of a solute that ionizes when it dissolves in a solvent

$$\text{percentage ionization} = \frac{\text{concentration of ionized acid}}{\text{initial concentration of acid}} \times 100\ \%$$

WEB LINK

For the general weak acid ionization reaction

$$HA(aq) \rightleftharpoons H^+(aq) + A^-(aq)$$

we may write the following equation:

$$\text{percentage ionization} = \frac{[H^+(aq)]}{[HA(aq)]} \times 100\ \%$$

and therefore

$$[H^+(aq)] = \frac{\text{percentage ionization}}{100\ \%} \times [HA(aq)]$$

where [HA(aq)] is the initial concentration of the acid.

Chemical analysis indicates that most weak acids ionize much less than 50 %. One common weak acid, ethanoic acid, $HC_2H_3O_2(aq)$, has a percentage ionization of about 1.3 % in aqueous solution at SATP. CAREER LINK

$$HC_2H_3O_2(aq) \overset{1.3\ \%}{\rightleftharpoons} H^+(aq) + C_2H_3O_2^-(aq)$$

In other words, in a 0.10 mol/L solution of ethanoic acid, only 1.3 % of the $HC_2H_3O_2(aq)$ molecules ionize to form hydrogen ions and ethanoate ions.

$$[H^+(aq)] = \frac{1.3}{100} \times 0.10\ \text{mol/L}$$

$$[H^+(aq)] = 1.3 \times 10^{-3}\ \text{mol/L}$$

Figure 1 Methanoic acid, also called formic acid, is one of the substances produced by ants that make their bite so painful.

Tutorial 2 Percentage Ionization and K_a of a Weak Acid

If you know the pH of a weak acid solution, you can calculate the percentage ionization of the acid. In this tutorial, you will calculate first the percentage ionization of a weak acid in solution, and then the K_a value of an acid.

Sample Problem 1: Calculating Percentage Ionization from pH

A chemist prepares a 0.10 mol/L solution of methanoic acid, $HCHO_2(aq)$, an acid produced by some ant species to protect themselves **(Figure 1**). The pH of the solution is 2.38. Determine the percentage ionization of the acid in the solution.

Given: pH = 2.38

Required: percentage ionization of methanoic acid

Solution:

Step 1. Calculate the $H^+(aq)$ concentration from the pH.

$$\begin{aligned}[H^+(aq)] &= 10^{-\text{pH}} \\ &= 10^{-2.38} \\ [H^+(aq)] &= 4.169 \times 10^{-3}\ \text{mol/L}\end{aligned}$$

Step 2. Calculate the percentage ionization of the acid in solution.

$$\frac{\text{percentage ionization}}{100} = \frac{[H^+(aq)]}{[HA(aq)]}$$

$$\text{percentage ionization} = \frac{[H^+(aq)]}{[HA(aq)]} \times 100\ \%$$

$$= \frac{4.169 \times 10^{-3}}{0.10} \times 100\%$$

$$\text{percentage ionization} = 4.2\ \%$$

Statement: Methanoic acid ionizes 4.2 %.

Sample Problem 2: Calculating K_a from Percentage Ionization

A chemistry student prepares a solution of ethanoic acid, $HC_2H_3O_2(aq)$, with a concentration of 0.1000 mol/L. If the percentage ionization of ethanoic acid is 1.3 %, what is the acid ionization constant, K_a, for ethanoic acid?

Given: concentration of solution, $c_{HC_2H_3O_2} = 0.1000$ mol/L; percentage ionization = 1.3 %

Required: K_a for ethanoic acid

Solution:

Step 1. Write the ionization equation for ethanoic acid. Use that to write the equation for K_a.

$$HC_2H_3O_2(aq) \rightleftharpoons H^+(aq) + C_2H_3O_2^-(aq)$$

$$K_a = \frac{[H^+(aq)][C_2H_3O_2^-(aq)]}{[HC_2H_3O_2(aq)]}$$

Step 2. Use the percentage ionization equation to determine how much of the acid ionizes.

You are told that the percentage ionization of ethanoic acid in solution is 1.3 % and the concentration of the initial solution is 0.1000 mol/L. Therefore, the decrease in concentration of ethanoic acid molecules at equilibrium will be

$$(0.1000\ \text{mol/L})\left(\frac{1.3}{100}\right) = 0.0013\ \text{mol/L}$$

According to the balanced ionization equation, the mole ratio is 1:1:1. Therefore, you know that the concentrations of $H^+(aq)$ and $C_2H_3O_2^-(aq)$ each increase by 0.0013 mol/L.

Step 3. Organize the information above in an ICE table (**Table 1**) in which x represents the change in $[HC_2H_3O_2(aq)]$ that occurs as the reaction reaches equilibrium.

Table 1 ICE Table for the Ionization of Ethanoic Acid

	$HC_2H_3O_2(aq)$	$\rightleftharpoons$	$H^+(aq)$	+	$C_2H_3O_2^-(aq)$
I	0.1000		0		0
C	–0.0013		+0.0013		+0.0013
E	0.0987		0.0013		0.0013

Step 4. Substitute the equilibrium concentrations into the K_a equation and solve for K_a.

$$K_a = \frac{[H^+(aq)][C_2H_3O_2^-(aq)]}{[HC_2H_3O_2(aq)]}$$

$$= \frac{(0.0013)(0.0013)}{(0.0987)}$$

$$K_a = 1.7 \times 10^{-5}$$

Statement: The acid ionization constant, K_a, for ethanoic acid is 1.7×10^{-5}.

Practice

1. Calculate the percentage ionization of a 0.050 mol/L solution of propanoic acid, $HC_3H_5O_2(aq)$, with a pH of 2.78. K/U [ans: 3.3 %]
2. A 0.100 mol/L solution of hydrofluoric acid, HF(aq), has a percentage ionization of 7.8 %. Calculate the K_a for hydrofluoric acid. K/U [ans: 6.6×10^{-4}]

Calculating the pH of Weak Acid Solutions

A weak acid ionizing in water behaves much like any equilibrium reaction system. Remembering this, we will proceed carefully and systematically to calculate the pH of a weak acid solution. Although some of the procedures we develop here may seem unnecessary, they will be helpful as the problems become more complicated.

Figure 2 Hydrofluoric acid used to be widely used for etching glass. However, because of the health risks posed by its corrosiveness, it is being replaced by other, safer compounds.

Tutorial 3 Calculating the pH of a Weak Acid Solution

This tutorial shows two different methods for calculating the pH of a weak acid solution, given the value of the acid ionization constant.

Sample Problem 1: Calculating the pH of a Weak Acid Solution from K_a

The standard value for the K_a of hydrofluoric acid, HF(aq), is 6.6×10^{-4}. Calculate the pH of a 1.00 mol/L solution of hydrofluoric acid (**Figure 2**).

Given: $K_a = 6.6 \times 10^{-4}$; concentration, [HF(aq)] = 1.00 mol/L

Required: pH

Solution:

Step 1. Identify the major entities in the solution.

From its small K_a value, you know that hydrofluoric acid is a weak acid and will ionize only slightly. Thus, the major entities in solution are HF(aq) and $H_2O(aq)$.

Step 2. Decide which of the major entities produces $H^+(aq)$ ions.

Both HF(aq) and $H_2O(aq)$ can do so:

$$HF(aq) \rightleftharpoons H^+(aq) + F^-(aq)$$

$$H_2O(l) \rightleftharpoons H^+(aq) + OH^-(aq)$$

Step 3. Identify the major source(s) of $H^+(aq)$ ions.

By comparing the K_a for HF(aq) with the K_w for $H_2O(l)$, you can see that hydrofluoric acid is a much stronger acid than water. Thus you may ignore the insignificant contribution of $H^+(aq)$ made by the autoionization of water. Therefore, it is the ionization of HF(aq) that will determine the equilibrium concentration of $H^+(aq)$ and hence the pH.

Step 4. Write the equilibrium constant equation for the reaction that is the primary source of $H^+(aq)$ ions.

$$K_a = \frac{[H^+(aq)][F^-(aq)]}{[HF(aq)]}$$

$$6.6 \times 10^{-4} = \frac{[H^+(aq)][F^-(aq)]}{[HF(aq)]}$$

Step 5. Determine the changes in concentration that occur as the reaction reaches equilibrium, using an ICE table.

Before any HF(aq) molecules ionize, the concentration of HF(aq) is 1.00 mol/L, and the concentrations of $H^+(aq)$ and $F^-(aq)$ are both 0 mol/L. Ignore $H^+(aq)$ ions produced by the autoionization of water. As the reaction progresses toward equilibrium, HF(aq) molecules will ionize to produce $H^+(aq)$ and $F^-(aq)$ ions in a 1:1 molar ratio. Thus, at equilibrium, $[H^+(aq)] = [F^-(aq)]$.

Let x represent the change in [HF(aq)] that occurs as the reaction reaches equilibrium. Your ICE table should be similar to **Table 2**.

Table 2 ICE Table for the Ionization of Hydrofluoric Acid

	HF(aq)	$\rightleftharpoons$	**H^+(aq)**	+	**F^-(aq)**
I	1.00		0		0
C	$-x$		$+x$		$+x$
E	$1.00 - x$		x		x

Step 6. Substitute the equilibrium concentrations from the ICE table into the equilibrium constant equation:

$$K_a = \frac{[H^+(aq)][F^-(aq)]}{[HF(aq)]}$$

$$6.6 \times 10^{-4} = \frac{[H^+(aq)][F^-(aq)]}{[HF(aq)]}$$

$$= \frac{(x)(x)}{1.00 - x}$$

$$6.6 \times 10^{-4} = \frac{x^2}{1.00 - x}$$

Step 7. Solve the equilibrium constant equation.

First, determine if a simplifying assumption may be made to solve this equation. The hundred rule states that, if the concentration to which x is added or subtracted is at least 100 times the value of the equilibrium constant, the simplifying assumption will give an error of less than 5 %. In general, a difference of less than 5 % justifies the simplifying assumption. In this case, apply the hundred rule to determine whether x is small enough for us to assume that $1.00 - x \approx 1.00$, just as you did in similar equilibrium problems in Chapter 7:

$$\frac{[HF(aq)_{initial}]}{K_a} = \frac{1.00}{6.6 \times 10^{-4}}$$

$$\frac{[HF(aq)_{initial}]}{K_a} = 1515.2$$

Since the $\frac{[HF(aq)_{initial}]}{K_a}$ ratio is much greater than 100, you may assume that

$1.00 - x \approx 1.00$

Thus, the equilibrium equation we will use is

$$6.6 \times 10^{-4} \approx \frac{x^2}{1.00}$$

Step 8. Solve for x.

$$6.6 \times 10^{-4} \approx \frac{x^2}{1.00}$$

$$x^2 \approx (6.6 \times 10^{-4})(1.00)$$

$$x^2 \approx 6.6 \times 10^{-4}$$

$$x \approx \sqrt{6.6 \times 10^{-4}}$$

$$x \approx 2.6 \times 10^{-2}$$

Step 9. Use the 5 % rule to check your result.

This assumption was used in the denominator of the equilibrium equation used in Step 7. The procedure for doing this is the same as the procedure used in similar equilibrium problems in Chapter 7. To test the assumption, compare the calculated value of x to the initial concentration of the acid, [HF(aq)]. If x is less than or equal to 5 % of the initial concentration, you may be confident that the simplifying assumption made in Step 7 is valid.

$$\frac{x}{[\mathrm{HF(aq)}]} \times 100\ \% = \frac{2.6 \times 10^{-2}}{1.00} \times 100\ \%$$

$$\frac{x}{[\mathrm{HF(aq)}]} \times 100 = 2.6\ \%$$

Since 2.6 % < 5 %, the error in this result is acceptable.

Step 10. Use the ICE table and the value of x to determine the hydrogen ion concentration at equilibrium and then calculate pH.

Since $[\mathrm{H^+(aq)}] = x$ (from the ICE table)

and $x \approx 2.6 \times 10^{-2}$

$[\mathrm{H^+(aq)}] \approx 2.6 \times 10^{-2}$ mol/L

$$\mathrm{pH} = -\log[\mathrm{H^+(aq)}]$$

$$\mathrm{pH} \approx -\log(2.6 \times 10^{-2})$$

$$\mathrm{pH} \approx 1.59$$

Statement: The pH of the solution is 1.59.

Sample Problem 2: Calculating pH from K_a

The hypochlorite ion, $\mathrm{ClO^-(aq)}$, is a strong bleaching agent often found in household bleaches and disinfectants. It is also the active ingredient that forms when swimming pool water is treated with chlorine (**Figure 3**). In addition to its bleaching abilities, the hypochlorite ion has a relatively high affinity for hydrogen ions and forms weakly acidic hypochlorous acid, HClO(aq). Calculate the pH of a 0.100 mol/L solution of hypochlorous acid. (You will have to look up the value of K_a in Table 1, Appendix B5.)

Figure 3 This chlorine dispenser floats in a swimming pool and slowly releases chlorine. When the chlorine reacts with water it produces hypochlorous acid, HClO(aq). This weak acid kills bacteria and other micro-organisms.

Given: concentration, $c_{\mathrm{HClO}} = 0.100$ mol/L

Required: pH

Solution:

Step 1. Identify the major entities in solution at equilibrium.

Major entities are HClO(aq) and H_2O(aq).

Step 2. Look up the value of K_a.

$K_a = 3.5 \times 10^{-8}$

Step 3. Identify the primary source of hydrogen ions.

Although HClO(aq) and H_2O(l) can both produce $\mathrm{H^+(aq)}$, the K_a of hypochlorous acid (3.5×10^{-8}) is many orders of magnitude larger than K_w (1.0×10^{-14}). Therefore, assume that all of the $\mathrm{H^+(aq)}$ comes from hypochlorous acid.

Step 4. Write the equilibrium constant equation for the reaction that is the primary source of $H^+(aq)$ ions.

$$K_a = \frac{[H^+(aq)][ClO^-(aq)]}{[HClO(aq)]}$$

$$3.5 \times 10^{-8} = \frac{[H^+(aq)][ClO^-(aq)]}{[HClO(aq)]}$$

Step 5. Determine initial and equilibrium concentrations.

Set up an ICE table for the ionization of HClO(aq), letting x represent the change in [HClO(aq)] (**Table 3**).

Table 3 ICE Table for the Ionization of Hypochlorous Acid

	HClO(aq)	$\rightleftharpoons$	**H^+(aq)**	+	**ClO^-(aq)**
I	0.100		0		0
C	$-x$		$+x$		$+x$
E	$0.100 - x$		x		x

Step 6. Substitute values from the ICE table into the equilibrium constant equation.

$$3.5 \times 10^{-8} = \frac{[H^+(aq)][ClO^-(aq)]}{[HClO(aq)]}$$

$$= \frac{(x)(x)}{0.100 - x}$$

$$3.5 \times 10^{-8} = \frac{x^2}{0.100 - x}$$

Step 7. Use the hundred rule to determine whether any simplifying assumptions may be made.

$$\frac{[HClO(aq)_{\text{initial}}]}{K_a} = \frac{0.100}{3.5 \times 10^{-8}}$$

$$\frac{[HClO(aq)_{\text{initial}}]}{K_a} = 2.9 \times 10^{6}$$

Since the $\frac{[HClO(aq)_{\text{initial}}]}{K_a}$ ratio is much greater than 100, assume that

$0.100 - x \approx 0.100$

Thus, the equilibrium equation you will use is

$$3.5 \times 10^{-8} \approx \frac{x^2}{0.100}$$

Step 8. Solve for x.

$$3.5 \times 10^{-8} \approx \frac{x^2}{0.100}$$

$$x^2 \approx (3.5 \times 10^{-8})(0.100)$$

$$x^2 \approx 3.5 \times 10^{-9}$$

$$x \approx \sqrt{3.5 \times 10^{-9}}$$

$$x \approx 5.9 \times 10^{-5}$$

Step 9. Use the 5 % rule to check your results.

$$\frac{x}{[HClO(aq)]} \times 100\ \% = \frac{5.9 \times 10^{-5}}{0.100} \times 100\ \%$$

$$\frac{x}{[HClO(aq)]} \times 100\ \% = 0.059\ \%$$

Since 0.059 % < 5 %, the error in this result is acceptable.

Step 10. Determine $[H^+(aq)]$ at equilibrium and calculate pH.

$$\text{Since } [H^+(aq)] = x \text{ (from the ICE table)}$$

$$\text{and } x \approx 5.9 \times 10^{-5}$$

$$[H^+(aq)] \approx 5.9 \times 10^{-5}$$

$$\text{pH} = -\log[H^+(aq)]$$

$$\approx -\log(5.9 \times 10^{-5})$$

$$\text{pH} \approx 4.23$$

Statement: The pH of a 0.100 mol/L hypochlorous acid solution, HClO(aq), is 4.23.

Practice

1. What is the pH of a 6.18×10^{-3} mol/L solution of hydrocyanic acid, HCN(aq)? (Look up the value of K_a for HCN(aq) in Table 1, Appendix B5.) K/U [ans: 5.7]
2. What is the pH of a 0.10 mol/L solution of nitrous acid, HNO_2(aq)? (Look up the value of K_a for HNO_2(aq) in Table 1, Appendix B5.) K/U [ans: 2.2]

You have now seen how to use the K_a values for weak acids to determine the pH of a solution. We can also reverse the calculations to determine K_a from pH.

Tutorial 4 Calculating the K_a of a Weak Acid Solution

In this tutorial, you will learn a problem-solving strategy to help you determine the acid ionization constant for a weak acid given the pH of the equilibrium solution.

Sample Problem 1: Calculating K_a from pH

A solution of hypochlorous acid, HClO(aq), has a concentration of 0.100 mol/L. If the pH of the solution is 4.23, calculate the K_a of hypochlorous acid.

Given: pH = 4.23; [HClO(aq)] = 0.100 mol/L

Required: K_a

Solution:

Step 1. Identify the source(s) of hydrogen ions. Assume that, while HClO(aq) is a weak acid, it is a much stronger acid than water and so all of the H^+(aq) in solution comes from the ionization of hypochlorous acid molecules, not water molecules. You will validate this assumption after calculating K_a.

Step 2. Write the ionization reaction equation and the equilibrium constant equation.

$$HClO(aq) \rightleftharpoons H^+(aq) + ClO^-(aq)$$

$$K_a = \frac{[H^+(aq)][ClO^-(aq)]}{[HClO(aq)]}$$

The reaction equation shows that for each mole of H^+(aq) produced, 1 mol of ClO^-(aq) is produced. Therefore, at equilibrium, $[H^+(aq)] = [ClO^-(aq)]$.

Step 3. Determine the concentration of the initial acid at equilibrium.

Since HClO(aq) is a weak acid, assume that only a small fraction of HClO(aq) molecules ionize. Therefore, assume that, at equilibrium,

$$[HClO(aq)] = 0.100 \text{ mol/L}$$

Step 4. Determine the $[H^+(aq)]$ at equilibrium using the known pH of the solution.

$$\text{pH} = 4.23$$

$$[H^+(aq)] = 10^{-\text{pH}}$$

$$= 10^{-4.23}$$

$$[H^+(aq)] = 5.9 \times 10^{-5} \text{ mol/L}$$

Step 5. Substitute the equilibrium concentrations into the acid ionization equation and solve for K_a.

$$K_a = \frac{[H^+(aq)][ClO^-(aq)]}{[HClO(aq)]}$$

$$= \frac{(5.9 \times 10^{-5})(5.9 \times 10^{-5})}{0.100}$$

$$K_a = 3.5 \times 10^{-8}$$

Step 6. Validate the assumption made in Step 1.

Since the calculated value of K_a (3.5×10^{-8}) is much larger than K_w (1.0×10^{-14}), our assumption that HClO(aq) is the main source of H^+(aq) is valid.

Step 7. Validate the assumption made in Step 3.

You assumed that at equilibrium,

$[HClO(aq)] = 0.100\ mol/L$

$$\frac{[HClO(aq)_{initial}]}{K_a} = \frac{0.100}{3.5 \times 10^{-8}}$$

$$\frac{[HClO(aq)_{initial}]}{K_a} = 2857143$$

Since the $\frac{[HClO(aq)_{initial}]}{K_a}$ ratio is much greater than 100, our assumption is valid.

Statement: The value of the acid ionization constant, K_a, of hypochlorous acid is 3.5×10^{-8}.

Practice

1. A 0.050 mol/L solution of nicotinic acid, $HC_2H_6NO_2(aq)$, has a pH of 3.08. Calculate K_a for nicotinic acid. K/U [ans: 1.4×10^{-5}]
2. The pH of a 0.25 mol/L solution of benzoic acid, $HC_7H_5O_2(aq)$, is 2.40. Determine K_a for benzoic acid. K/U [ans: 6.3×10^{-5}]

Polyprotic Acids

The common strong acids are hydrochloric acid, $HCl(aq)$, nitric acid, $HNO_3(aq)$, and perchloric acid, $HClO_4(aq)$. An acid of this type is called a **monoprotic acid** because it has only one ionizable hydrogen atom. Hydrogen atoms that may ionize to form $H_3O^+(aq)$ ions are sometimes called "acidic hydrogens."

An acid that has more than one ionizable hydrogen atom is called a **polyprotic acid**. Sulfuric acid, $H_2SO_4(aq)$, and phosphoric acid, $H_3PO_4(aq)$, are examples of acids that are polyprotic. Sulfuric acid has 2 hydrogen atoms that may ionize to form $H_3O^+(aq)$ ions in water (**Figure 4**). Phosphoric acid has 3 such hydrogen atoms. We can describe these acids even more precisely using the terms "diprotic" (able to produce 2 hydronium ions) and "triprotic" (able to produce 3 hydronium ions). In the case of sulfuric acid, the first ionization reaction is strong. The single arrow in the following equation indicates that virtually every $H_2SO_4(aq)$ molecule ionizes into $H^+(aq)$ and $HSO_4^-(aq)$ and the reverse reaction is insignificant:

$$H_2SO_4(aq) \rightarrow H^+(aq) + HSO_4^-(aq)$$

The second ionization—that of the $HSO_4^-(aq)$ ion—is weak, however. This results in a much higher concentration of $HSO_4^-(aq)$ ions than $SO_4^{2-}(aq)$ ions in solution:

$$HSO_4^-(aq) \rightleftharpoons H^+(aq) + SO_4^{2-}(aq)$$

Note that both strong and weak acids may be polyprotic.

monoprotic acid an acid that possesses only one ionizable (acidic) hydrogen atom

polyprotic acid an acid that possesses more than one ionizable (acidic) hydrogen atom

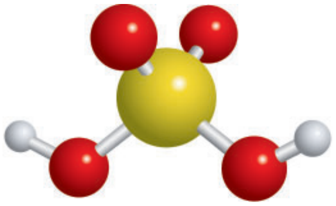

Figure 4 Sulfuric acid has 2 hydrogen atoms (represented as white spheres) that may be removed, one at a time, when the acid ionizes.

Ionization of Polyprotic Acids

Polyprotic acids do not ionize completely in one step. Ionizations occur in two or more steps and release only one hydrogen ion at a time. Each step in the ionization of a polyprotic acid has its own acid ionization constant. The K_a values for a polyprotic acid are numbered according to the reaction step they represent. K_{a1} is for the first ionization reaction step, K_{a2} is for the second ionization, and so on. The steps involved in the ionization of oxalic acid, $H_2C_2O_4(aq)$, a weak diprotic acid, are as follows:

- First ionization reaction

$$H_2C_2O_4(aq) \rightleftharpoons H^+(aq) + HC_2O_4^-(aq) \quad (K_{a1} = 5.4 \times 10^{-2})$$

$$K_{a1} = \frac{[H^+(aq)][HC_2O_4^-(aq)]}{[H_2C_2O_4(aq)]}$$

UNIT TASK BOOKMARK

Does your chosen consumer product include a polyprotic acid? If so, does this compound affect how the product reacts? The Unit Task is outlined on page 582.

- Second ionization reaction

$$HC_2O_4^-(aq) \rightleftharpoons H^+(aq) + C_2O_4^{2-}(aq) \quad (K_{a2} = 5.4 \times 10^{-5})$$

$$K_{a2} = \frac{[H^+(aq)][C_2O_4^{2-}(aq)]}{[HC_2O_4^-(aq)]}$$

Note that K_{a1} is significantly greater than K_{a2}. For most polyprotic acids the initial acid is the strongest and each subsequent acid gets weaker (**Table 4**).

Table 4 Acid Ionization Constants for Polyprotic Acids at SATP

Acid	Formula	K_{a1}	K_{a2}	K_{a3}
oxalic acid	$H_2C_2O_4(aq)$	5.4×10^{-2}	5.4×10^{-5}	–
ascorbic acid	$H_2C_6H_6O_6(aq)$	7.9×10^{-5}	1.6×10^{-12}	–
sulfuric acid	$H_2SO_4(aq)$	very large	1.0×10^{-2}	–
hydrosulfuric acid	$H_2S(aq)$	1.1×10^{-7}	1.3×10^{-13}	–
phosphoric acid	$H_3PO_4(aq)$	7.1×10^{-3}	6.3×10^{-8}	4.2×10^{-13}
arsenic acid	$H_3AsO_4(aq)$	5×10^{-3}	8×10^{-8}	4.0×10^{-12}
carbonic acid	$H_2CO_3(aq)$	4.4×10^{-7}	4.7×10^{-11}	–

Having multiple ionizations and different K_a values may make these problems appear to be more difficult to solve. If you break them down one step at a time, however, you will find that calculating the pH of a polyprotic acid is not much more challenging than calculating the pH of any other acid. When calculating the pH for a typical polyprotic acid, you usually only use the first reaction in the ionization sequence. This is because the percentage ionization of the second hydrogen ion is so small that its effect on the hydrogen ion concentration is insignificant.

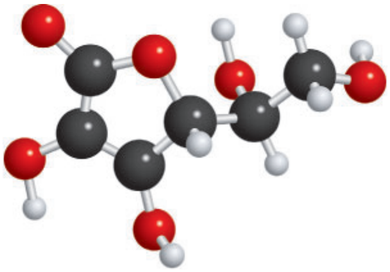

Figure 5 Ascorbic acid (vitamin C) helps maintain the elasticity of skin and promotes wound healing.

Tutorial 5 Calculating the pH of a Polyprotic Acid Solution

In this tutorial, you will learn how to calculate the pH of a polyprotic acid. Notice that only the first ionization reaction is a significant contributor to $[H^+(aq)]$.

Sample Problem 1: Calculating the pH of a Polyprotic Acid

Ascorbic acid (vitamin C) is essential in our diet (**Figure 5**). Calculate the pH of a 0.10 mol/L solution of ascorbic acid (vitamin C), $H_2C_6H_6O_6(aq)$. The K_a values for ascorbic acid are given in Table 4.

Given: $[H_2C_6H_6O_6(aq)] = 0.10$ mol/L; $K_{a1} = 7.9 \times 10^{-5}$; $K_{a2} = 1.6 \times 10^{-12}$

Required: pH of final solution; equilibrium concentrations of $H_2C_6H_6O_6(aq)$, $HC_6H_6O_6^-(aq)$, and $C_6H_6O_6^{2-}(aq)$

Solution:

Step 1. Identify the major entities in solution at equilibrium.

The major entities in solution are $H_2C_6H_6O_6(aq)$ and $H_2O(l)$.

Step 2. Identify the primary source of hydrogen ions.

Since K_{a2} is much smaller than K_{a1} and K_W, the first ionization reaction has the greatest effect on the pH of the solution.

$$H_2C_6H_6O_6(aq) \rightleftharpoons H^+(aq) + HC_6H_6O_6^-(aq) \quad K_{a1} = 7.9 \times 10^{-5}$$

Step 3. Write the equilibrium constant equation for the reaction that is the primary source of $H^+(aq)$ ions.

$$K_a = \frac{[H^+(aq)][HC_6H_6O_6{}^-(aq)]}{[H_2C_6H_6O_6(aq)]}$$

$$7.9 \times 10^{-5} = \frac{[H^+(aq)][HC_6H_6O_6{}^-(aq)]}{[H_2C_6H_6O_6(aq)]}$$

Step 4. Determine initial and equilibrium concentrations.

Set up an ICE table for the first ionization of $H_2C_6H_6O_6(aq)$, letting x represent the change in $[H_2C_6H_6O_6(aq)]$ (**Table 5**).

Table 5 ICE Table for the First Ionization of Ascorbic Acid

	$H_2C_6H_6O_6(aq)$ $\rightleftharpoons$	$HC_6H_6O_6{}^-(aq)$ +	$H^+(aq)$
I	0.10	0	0
C	$-x$	$+x$	$+x$
E	$0.10 - x$	x	x

Step 5. Substitute values from the ICE table into the equilibrium constant equation.

$$7.9 \times 10^{-5} = \frac{[H^+(aq)][HC_6H_6O_6{}^-(aq)]}{[H_2C_6H_6O_6(aq)]}$$

$$= \frac{(x)(x)}{0.10 - x}$$

$$7.9 \times 10^{-5} = \frac{x^2}{0.10 - x}$$

Step 6. Use the hundred rule to determine if any simplifying assumptions may be made.

$$\frac{[H_2C_6H_6O_6(aq)_{\text{initial}}]}{K_a} = \frac{0.10}{7.9 \times 10^{-5}}$$

$$\frac{[H_2C_6H_6O_6(aq)_{\text{initial}}]}{K_a} = 1.3 \times 10^3$$

Since the $\frac{[H_2C_6H_6O_6(aq)_{\text{initial}}]}{K_a}$ ratio is much greater than 100, assume that

$0.10 - x \approx 0.10$

Thus, the equilibrium equation that you will use is

$$7.9 \times 10^{-5} \approx \frac{x^2}{0.10}$$

Step 7. Solve for x.

$$7.9 \times 10^{-5} \approx \frac{x^2}{0.10}$$

$$x^2 \approx (7.9 \times 10^{-5})(0.10)$$

$$x^2 \approx 7.9 \times 10^{-6}$$

$$x \approx \sqrt{7.9 \times 10^{-6}}$$

$$x \approx 2.8 \times 10^{-3}$$

Step 8. Use the 5 % rule to check your results.

$$\frac{x}{[H_2C_6H_6O_6(aq)]} \times 100\ \% = \frac{2.8 \times 10^{-3}}{0.1} \times 100\ \%$$

$$\frac{x}{[H_2C_6H_6O_6(aq)]} \times 100\ \% = 2.8\ \%$$

Since 2.8 % < 5 %, the error in this result is acceptable.

Step 9. Determine $[H^+(aq)]$ at equilibrium and calculate pH.

Since $[H^+(aq)] = x$ (from the ICE table)

$$\begin{aligned} \text{and } x &\approx 2.8 \times 10^{-3}, \\ [H^+(aq)] &\approx 2.8 \times 10^{-3}\ \text{mol/L} \\ \text{pH} &= -\log[H^+(aq)] \\ &\approx -\log(2.8 \times 10^{-3}) \\ \text{pH} &\approx 2.55 \end{aligned}$$

Use the K_a values of ascorbic acid (from Table 4) to determine the equilibrium concentrations of $H_2C_6H_6O_6(aq)$, $HC_6H_6O_6^-(aq)$, and $C_6H_6O_6^{2-}(aq)$ in the equilibrium solution as follows:

First calculate the concentrations of $H_2C_6H_6O_6(aq)$ and $HC_6H_6O_6^-(aq)$ by substituting the value of x into the equilibrium concentration formulas for these entities in the ICE table.

$$\begin{aligned} [H_2C_6H_6O_6(aq)] &\approx 0.10\ \text{mol/L} - x \\ &\approx 0.10\ \text{mol/L} - 2.8 \times 10^{-3}\text{mol/L} \\ [H_2C_6H_6O_6(aq)] &\approx 0.097\ \text{mol/L} \\ [HC_6H_6O_6^-(aq)] &= x \\ [HC_6H_6O_6^-(aq)] &\approx 2.8 \times 10^{-3}\ \text{mol/L} \end{aligned}$$

The concentration of $C_6H_6O_6^{2-}(aq)$ cannot be calculated using expressions derived from the first ionization reaction because $C_6H_6O_6^{2-}(aq)$ is not produced by this ionization reaction; it is produced in the second ionization reaction. You must use the second ionization constant equation and the value of K_{a2} to calculate this value. Thus,

$$K_{a2} = \frac{[H^+(aq)][C_6H_6O_6^{2-}(aq)]}{[HC_6H_6O_6^-(aq)]}$$

$$[C_6H_6O_6^{2-}(aq)] = \frac{[HC_6H_6O_6^-(aq)]K_{a2}}{[H^+(aq)]}$$

The value of K_{a2} may be found in Table 4: $K_{a2} = 1.6 \times 10^{-12}$

Substitute the values of $[H^+(aq)]$ and $[HC_6H_6O_6^-(aq)]$, calculated earlier, into this equation. Remember your assumption that the second ionization reaction is insignificant and so does not change these concentration values appreciably. Thus,

$$[C_6H_6O_6^{2-}(aq)] = \frac{(2.8 \times 10^{-3})(1.6 \times 10^{-12})}{2.8 \times 10^{-3}}$$

$$[C_6H_6O_6^{2-}(aq)] = 1.6 \times 10^{-12}\ \text{mol/L}$$

Notice that $[C_6H_6O_6^{2-}(aq)] = K_{a2}$.

Statement: The equilibrium concentrations of $H_2C_6H_6O_6(aq)$, $HC_6H_6O_6^-(aq)$, and $C_6H_6O_6^{2-}(aq)$ are, respectively, 0.097 mol/L, 2.8×10^{-3} mol/L, and 1.6×10^{-12} mol/L. Notice that the concentrations of the anions are very low, compared to the initial acid concentration.

Practice

1. Calculate the pH of 1.00 mol/L phosphoric acid, $H_3PO_4(aq)$. K/U [ans: 1.1]
2. Calculate the pH of 0.100 mol/L sodium bisulfate, $NaHSO_4(aq)$ K/U [ans: 1.50]

8.4 Review

Summary

- Percentage ionization is one way to describe the degree of ionization of a weak acid. The higher the percentage ionization, the stronger the acid.
- Polyprotic acids ionize one hydrogen ion at a time. Each step has a characteristic K_a value. Typically, for a polyprotic acid, $K_{a1} > K_{a2} > K_{a3}$

Questions

1. A lab technician prepares the following solutions. Calculate the $[H^+(aq)]$ and pH of each of the following solutions at SATP: K/U
   (a) a 0.0100 mol/L solution of hydrocyanic acid, $HCN(aq)$; $K_a = 6.2 \times 10^{-10}$
   (b) a 0.25 mol/L solution of hydrofluoric acid, $HF(aq)$; $K_a = 6.6 \times 10^{-4}$
   (c) a 0.0010 mol/L solution of lactic acid, $HC_3H_5O_3(aq)$; $K_a = 1.4 \times 10^{-4}$
   (d) a 0.150 mol/L solution of methanoic acid, $HCO_2H(aq)$, $K_a = 1.8 \times 10^{-4}$
2. The following solutions are required for an industrial process. Predict the percentage ionization of each acid. K/U
   (a) a 0.50 mol/L solution of propionic acid with a pH of 2.6
   (b) a 0.15 mol/L solution of peracetic acid with a pH of 4.5
   (c) a 0.01 mol/L solution of sorbic acid with a pH of 3.4
3. Determine the acid ionization constant, K_a, for each of the following weak acids: K/U
   (a) a 0.20 mol/L solution of ascorbic acid, $HC_6H_7O_6(aq)$, with a pH of 2.40
   (b) a 0.100 mol/L solution of nitrous acid, $HNO_2(aq)$, with a pH of 2.10
4. Calculate the percentage ionization of ethanoic acid, $HC_2H_3O_2(aq)$, in a 1.00 mol/L solution. $K_a = 1.8 \times 10^{-5}$ K/U
5. A textile artist plans to dye a skein of yarn. The dye recipe specifies adding 5 mL of 1.0 mol/L hydrochloric acid to 5 L of water, prior to adding the dye, some pickling salt, and the yarn. The artist does not have hydrochloric acid, but finds a bottle of vinegar. What volume of vinegar should she use to make her dye bath? (Assume that vinegar is 0.8 mol/L ethanoic acid, $HC_2H_3O_2(aq)$, and that this acid ionizes about 1.3 %.) T/I A
6. In a study of the effect of lactic acid on muscles, a biologist prepares a 0.100 mol/L solution of lactic acid, $HC_3H_5O_3(aq)$. The acid is 3.7 % ionized. What is the K_a for lactic acid? K/U A
7. Ascorbic acid, $H_2C_6H_6O_6(s)$, is an organic diprotic acid that is better known as vitamin C. A solution contains 0.091 mol of ascorbic acid in 1 L of solution. Determine the pH of this solution, given the following values: $K_1 = 6.7 \times 10^{-5}$; $K_2 = 2.5 \times 10^{-12}$ K/U
8. When a strong acid such as hydrochloric acid is spilled in the lab it must be neutralized before it is cleaned up. Would it be better to use sodium bicarbonate or sodium hydroxide to neutralize the spill? Explain your reasoning. C A
9. Benzoic acid is a commonly used food preservative. It inhibits the growth of many moulds and bacteria. K/U A
   (a) A solution of benzoic acid with a concentration of 8.3×10^{-3} mol/L has a pH of 3.14. Calculate the K_a value for benzoic acid.
   (b) Predict whether the pH of a non-carbonated fruit drink, containing benzoic acid at a concentration of 8.3×10^{-3} mol/L, would be greater or less than 3.14. Explain your reasoning.
10. Chloroacetic acid, $HC_2H_2O_2Cl(aq)$, is a weak acid commonly used in industry to synthesize the hormone epinephrine. It has a K_a of 1.36×10^{-3}. K/U C A
    (a) Determine the percent ionization of a 0.50 mol/L solution.
    (b) Research some of the medical uses of epinephrine, and the risks and benefits of its use. Present your findings in a format of your choice.

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